CORRELATION OF EXCESS VOLUME OF OIL STOCKS

A Thesis
Submitted to the College of Engineering of
Al-Nahrain University in Partial Fulfillment of the
Requirements for the Degree of Master of
Science in Chemical Engineering

by

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(B.Sc. in Chemical Engineering 2001)

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November 2004

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Abstract

Binary mixtures of three, selected Iraqi crude oils had been subjected to density measurements at temperatures 15, 25, 30 ^0C and precise data had been acquired on the volumetric behavior of these systems. The results are reported in terms of equations for excess specific volumes of the mixtures. The crude oil types used were of good varity, they ranged from light crude with API value of 44.3 (khana) to medium crude (Basrah) of API 31.4 reaching the heavy crude (Shark Baghdad) of API 24.2.

Temperatures in the range of 15-30 ^0C have a minor effect on excess volume of crude binary mixtures thus, low decrease of expansion or low increase of shrinkage is observed by increasing the temperature.

Mixture of crudes with aromatic oil-stocks shows positive excess volume. This expansion effect is greatest for the lowest boiling point spike as in the case of toluene. While, the presence of methyl groups in aromatic rings results in a lower positive excess volume. The API gravity of crude oil has predominated effect on the expansion of aromatic spiked crude oils. Those, khana crude, as a typical light type gives the maximum positive excess volumes of 2.68 when spiked with toluene. While the spiked heavy crude, shark Baghdad resulted in the lowest excess value of 0.7.

Spiking of the considered Iraqi crudes with either kerosene or gas oil resulted in negative excess volume. This shrinkage is greatest for the lowest-boiling spike as in the case of kerosene. The gravity of crude oil has an effect on excess volume when the crude was spiked with petroleum fraction. Those, shark Baghdad as typical heavy type resulted in minimum negative excess

volume of -4.81 and -3.29, when it was spiked with the petroleum fraction (Kerosene and Gas Oil respectively), while the spiked light crude and Khana gave maximum negative excess volume of -7.56 and -6.38 respectively.

Density prediction was calculated using a generalized Costald-equation of state through –Hankinson-Brobst-Thomson (HBT) technique for binary crude oil mixtures studied. The over all average absolute percent error for 54 data point is 0.874.

A generalized density-temperature-composition correlation for undefined liquid petroleum fractions was developed to represent the data at temperatures 15-30 ^{0}C over a range of weight percent (0-100), as follows:

$$\rho_{mix} = \rho_{15}\left[A_o + \frac{A_1(\rho_{15}X)}{(t-288)} + \frac{A_2(\rho_{15}X)^{A_3}}{(t-288)^{A_4}}\right]$$

Detailed analysis shows that the proposed correlation fits the 384 data point, with an over all absolute error of 0.305 %.

Excess volume was calculated using the proposed density prediction equation. The equation was subjected to 384 data point and gave satisfactory results with an average absolute error of 3.8%.

CONTENETS

Chapter One: Introduction

Chapter Two: Literature Survey

Chapter Three: Experimental Work

Chapter Four: Results and Discussion

Chapter Five: Conclusion and Recommendations

NOMENCLATURE

Nomenclature

A_i, a_i, b_i, c_i = constants

A, b, c, d, e, f, g, h, j, k =constants

API = American Petroleum Institute Gravity, ^{o}API

C = concentration of spike

CI = correlation index

G = gravity difference (crude spike -), ^{o}API

K, K_o, K_P = experimental constants

K_w = Watson characterization factor

MABP = mole average boiling point, K

M_w = molecular weight, gm/g. mole

P = pressure, N/m^2

P_c = critical pressure, N/m^2

P_r = reduced pressure, N/m^2

P_s = saturation pressure, N/m^2

SG = specific gravity 15^{o}C

T, t = temperature, ^{o}C

T_b = normal boiling point, K

T_c = critical temperature, K

T_{ci} = critical temperature of component i, K

T_{cm} = mixture critical temperature

V_c = critical volume, cm^3/g. mole

V^* = characterization volume, cm^3/g. mole

VCF = volume correlation factor

V^E = excess volume, cm^3/kg

$V_R^{(O)}$ = corresponding states function for normal fluid

$V_R^{(\delta)}$ = corresponding states deviation function

x = mass fraction of reference component

Z = compressibility factor

Greek Letters

α = Correlation coefficient of thermal expansion m^3/kg

ρ = Density, kg/m^3

ρ_{15} = Density at 15 °C, kg/m^3

ϕ = Volume fraction

α, β, γ = constants

ω = a centric factor

ω_{SRK} = a centric factor from Soave equation of state

Δv = specific volume change for petroleum fractions

ΔV = specific volume change for hydrocarbon fractions

ΔV^R = Relative excess volume of oil blend, m^3/kg

σ = standard deviation between experimental and fitted value

Subscript

cal = calculated value

exp = experimental value

mix, m = mixture

i, j = components

Superscript

E = Excess

id = ideal

(o) = simple fluid

Chapter One 1

Introduction

The appearance and characteristics of crude oils vary widely from oil field to oil field and even from wells in the same oil field. Knowledge of the physical and chemical properties of oils is necessary for the marketing requirements, reefing and further processes [1].

As a part of the conservation effort of the pipeline industry, the causes of losses in transit are being investigated continuously. Such an investigation of the volume loss experienced in systems handling the light components blended into a common crude oil stream indicated that the losses did not result entirely from increased evaporation but were caused partly by a phenomenon associated with the blending of the lighter crude oils components and the heavier types. When a lighter product such as butane or natural gasoline is mixed with crude oil, the resulting volume is less than the sum of the individual component volumes. This loss or shrinkage is only an "apparent loss" on a volume basis for here is, of course, no loss of weight as a result of the mixing operation [2].

In fact such blending is encouraged because it reduces viscosity and pump suction difficulties. Different grades of crude oils from different sources are usually mixed and handled in the same pipelines to the consumer or to the refiner [3].

In the blending of petroleum components having different physical properties, excess volumes occur because the components do not form ideal solutions. In an ideal solution, the total solution volume is equal to the sum of the volumes of the components. In order for a solution to approach ideality, the molecules of the materials blended together must be similar in size, shape, and properties. If the nature of the components differs appreciably, then deviation from ideal behavior may be expected. This deviation may be either positive or negative; that is, the total volume may increase or decrease when the components are blended.

The blending of oil stocks results in volume changes, caused by the non-ideal behavior of oil systems as compared with the calculated ideal volume. Since the oil industry uses volume measurement in its balances, the apparent discrepancies in material may cause financial complications, which in some cases have led to litigation [4].

Crude oil and its products are sold usually on a basis of volume delivered corrected to $60F\,(15.5\,^{0}C)$ by means of standard tables of volume corrections [5]. Weight is important in determining freight rates, cargoes, and the power required in pumping. Gravity is not of much direct significance, but the test is so simple and so widely used that it assumes importance as a means of judging many other properties and in controlling plant operations.

Density is a property, which has the greatest influence on the value of crude oil and its products and together with viscosity active roles in selling, transportation and other industrial applications [6].

Density is temperature-dependent; in most cases a fluid becomes less dense as the temperature rises [1]. The variation of density with temperature is a property of great technical importance, since most petroleum products are sold by volume and specific gravity which are usually determined at the prevailing temperatures rather than at the standard $15.6\,^{0}C$ [7].

Prediction of the true volume of an oil blend is important to the refiners since small change can have considerable economic significance when products are measured in thousands of barrels.

The excess properties are due to the molecular interactions. Excess thermodynamic property (excess volume) is an important thermodynamic property in process design calculation, and accurate prediction of this property is required.

A mixture of crude oils, with hydrocarbons form non-ideal systems for which excess volumes may be positive or negative, according to the nature of the species [8].

Generally observed that the addition of light paraffinic oil stocks to crude produces negative excess volumes. That means shrinkage occurs relative to the calculated ideal volume.

The excess volume behavior of oil mixtures is important. Only a small amount of database has been published, especially on mixtures of oil stocks with pure hydrocarbons. However, no or little studies were published on mixtures of different types of crude oils.

The current project was carried out to evaluate the volumetric behavior of blends of a typical Iraqi lighter crude oil with a heavier type. Further aim of the work was to investigate the effect of API gravity of crude oils on excess volume of these mixtures.

Research was done to develop appropriate equations to predict the densities and then evaluate excess volumes of the blended crude at different compositions and temperatures.

Another objective of this study was to search a computer program to evaluate the developed mathematical methods. In addition the application of the generalized Costald equation of state for density prediction of oil-stock mixtures was tested.

Chapter Two 2

Literature Survey

2.1 Crude Oils

2.1.1 Classification

Petroleum is considered as the most important energy sources in the world. It is the basic raw material for refineries and petrochemical industries [1].

Crude oil or petroleum is defined as a naturally occurring mixture, consisting predominantly of hydrocarbons and of sulphur, nitrogen and oxygen as derivatives of hydrocarbons.

Physically, crude oils can vary from liquid, mobile, straw-colored liquid containing a large proportion of easily distillable material to highly viscous, semi-solid black substances from which lower amount of fractions can be isolated by distillation before the onset of the thermal decomposition. Densities generally lie in the range 0.79 to 0.95 g/cm^3, and viscosities vary widely, from about 0.7cp to more than 42000cp [1].

The chemical compositions of crude oils are surprisingly uniform even though their physical characteristics vary widely. The hydrocarbons present in crude petroleum are classified into three general types: paraffins, naphthenes, and aromatics. In addition there are fourth type olefins that are formed during processing by the dehydrogenation of paraffins and naphthenes [9]. In this way, the differences between crude oils could be explained by the relative amounts of each series, paraffins, naphenes and aromatics present in a given oil, and the extent to which individual members of a series appear in the crude. This view has been corroborated by modern studies.

Crude oils are classified usually as paraffin base, naphthene base, asphalt base, or mixed base. There are some crude oils in the Far East which have up to 80% aromatic content, and these are known as aromatic- base oils. The U. S. Bureau of Mines [7, 10] had developed a system which classifies the crude according to two key fractions obtained in distillation: No. 1 from 250 to 275°C at atmospheric pressure and No. 2 from 275 to 300°C at 40 mmHg pressure. The gravity of these two fractions is used to classify crude oils into types as shown in table 2.1. The paraffinic and asphaltic, classifications in common use are based on the properties of the residuum left from non destructive distillation and are more descriptive to the refiner because they convey the nature of the products to be expected and the processing necessary.

Table 2.1: Classification of crude oils according to API [11]

Base	**Key fractions , ^{0}API**	
	No. 1	No. 2
Paraffin	**=> 40**	**=> 30**
paraffin Intermediate	**=> 40**	**20 – 30**
Intermediate Paraffin	**33 – 40**	**=> 30**
Intermediate	**33 – 40**	**20 – 30**
Intermediate, naphthene	**33 – 40**	**=> 20**
Naphthene, intermediate	**=> 33**	20-30
Naphthene	**=> 33**	**=> 20**

No attempt is made by the refiner to analyze for the pure components contained in the crude oil. Relatively simple analytical tests are run on the crude and the results of these are used with empirical correlations to evaluate the crude oils as feed-stocks for the particular refinery. Each crude is compared with the other feed-stocks available and based upon the product realization, is assigned a value.

2.1.2 Properties

Crude oils are usually characterized by there properties, which are measured by standard methods such as ASTM and IP. The more specified properties of crude oils are described as follows [11]:

Gravity, API

The density of petroleum oils is expressed in terms of API gravity rather than specific gravity; it is related to specific gravity in such a fashion that an increase in API gravity corresponds to a decrease in specific gravity. The units of API gravity are °API and can be calculated from specific gravity as follows:

$$API = \frac{(141.5)}{SP.gr} - 131.5 \tag{2-1}$$

In the above equation, specific gravity and API gravity refer to the weight per unit volume at 60°F. Crude oil gravity may range from less than 20°API for typical heavy types to over 40°API for light crudes. The most crude oils fall in the 20 to 45°API range [11].

Characterization Factors

There are several correlations between yield and the aromaticity and paraffinicity of crude oils but, the two most widely used are the UOP or "Watson characterization factor" (K_w) and the U. S. Bureau of Mines "correlation index" (Cl) [11].

$K_w = (T_B)^{1/3} / G$ (2-2)

$Cl = (87{,}552/T_B) + 473.7G - 456.8$ (2-3)

Where:
TB = mean average boiling point, ^oR.
G = specific gravity at 60°F.

The Watson characterization factor ranges from less than 10 for highly aromatic materials to almost 15 for highly paraffinic compounds. Crude oils show a narrower range of K_w and vary from 10.5 for highly naphthenic crude to 12.9 for paraffinic base crude.

The correlation index is useful in evaluating individual fractions from crude oils. The Cl scale is based upon straight-chain paraffins have a Cl value of 0 and benzene having a Cl value of 100. The Cl values are not quantitative, but the lower the Cl value the greater the concentrations of paraffin hydrocarbons in the fraction, and the higher the Cl value the greater the concentrations of naphthenes and aromatics [11].

Distillation properties

The distillation of petroleum fraction is carried out according to standard method (i.e. ASTM or IP) in a procedure of evaluating the percentage distillate with the corresponding temperature. The results are usually plotted as distillation curves. The distillation curves give information about initial boiling point temperature, final boiling point temperature and the temperature of any particulate cut, such as 10%, 20%, etc.

The ASTM-distillation is carried out in a simple apparatus which gives a general idea of the distillation range yields and little information about the composition of the fraction [11].

The boiling range distribution of the crude gives an indication of the quantities of the various products present. The most useful type of distillation is known as a true boiling point (TBP) distillation and generally refers to a distillation performed in equipment that accomplishes a reasonable degree of fractionation. A more detailed procedure for correlation of ASTM and TBP distillations is given in the "API" Technical Data Book-Petroleum Refining [11].

Distillation curve is of value in assessing the suitability of petroleum fractions for various applications, particularly in respect to volatility. Such information is also needed for the design and control of distillation columns. It is also useful, usually in conjunction with some other physical property such as density, in characterizing petroleum fractions to permit prediction of other properties [1].

Sulfur Content

Sulfur content and API gravity are two properties which have had the greatest influence on the value of crude oil. The sulfur content is expressed as percent sulfur by weight and varies from less than 0.1% to greater than 5.0 %. Crude with greater than 0.5% sulfur generally require more extensive processing than those with lower sulfur content [11]. Although the term "sour" crude initially had reference to those crude containing dissolved hydrogen sulfide independent of total sulfur content .There is no sharp dividing line between sour and sweet crude, but 0.5% sulfur content is frequently used as the criterion.

Viscosity

An adequate knowledge of the viscosity plays very important role in a variety of interesting engineering problems involving fluid flow and momentum transfer [11]. Viscosity and viscosity-temperature relationship is considered as important property when dealing with fuel oils during pumping, storage and atomization at burning.

The viscosity of the liquid can be described as its internal friction, the resistance it offers to motion, either of a foreign body through it or of it against a foreign body. It can be measured by timing the flow of a given volume of the liquid through a properly calibrated tube of capillary size. The result of kinematic viscosity, expressed usually in centistokes [1].

Viscosity depends on temperature, it decreases as temperature increases; the temperature must therefore always be specified in starting the viscosity of a material [1].

Pour and cloud point

The pour point of the crude oil, in ^{o}F, is a rough indicator of the relative paraffinicity and aromaticity of the crude. The lower the pour point the lower the paraffin content and the greater the content of aromatics [11].

Cloud point is the temperature at which the incipient crystallization of wax in the oil results in an opcity or cloud, without necessarily complete solidification. This temperature will be higher than that of the pour points, since the fuel does not fail to pour until some of the wax crystals have coalesced. The purpose of quoting the cloud point is to indicate a temperature at which the blockage of fine filters may occur owing to the accumulation of waxy deposits.

Water and sediment

Sediments are the insoluble remaining after extraction by toluene. These insoluble residues are contaminants such as sand, dirt, and rust scale, and are not derived from the fuel. Such a definition and test method are suitable for clear distillate fuels, but are not applicable for residual fuels [1].

These determine the possible life of the oil during storage. Unsatisfactory blending or the presence of unstable, oxidizable, sediments that cause clogging of filters or nozzles and corrode storage tanks and pipe lines. Cracked oils are particularly bad in this respect. Oxidation and corrosion inhibitors are sometimes added to reduce these troubles. When oils of different origins are mixed, an asphaltic sludge may be deposited, in such a case the oils are said to be incompatible [1].

Of all the possible contaminants in marine fuel is water. Normally the actual level is very low, since every effort is made by the supplier to deliver fuel as dry as possible, (0.1-0.2 per cent by volume is typical). The ingress of water can come from a number of sources which include tank condensation, heating coil leakage, as steam is the usual heating medium, and also tank leakage [1].

If the salt content of the crude, when expressed as NaCl, is greater than 10 lb /1,000 bbl, it is generally necessary to desalt the crude before processing. The salt causes severe corrosion problems and plugging problems. If residue are processed catalytically, desalting is desirable at even lower salt contents of the crude [11].

Metals content of crude oils can vary from a few parts per million to more than 1,000 ppm and in spite of their relatively low concentrations are of considerable importance [12]. Minor quantities of some of these metals (nickel, vanadium, and copper) can severely affect the activities of catalysts and result in a lower-value product distribution. Vanadium concentrations above 2 ppm in fuel oils can lead to severe corrosion to boilers and furnaces tubes and deterioration of refractory linings and stacks [11].

The metallic constituents of crude are concentrated in the residues during the distillation. Some of the organometallic compounds are actually volatilized at refinery distillation temperatures and appear in the higher-boiling distillates [13].

Carbon residue is determined by distillation to a coke residue in the absence of air. The carbon residue is roughly related to the asphalt content of the crude and to the quantity of the lubricating oil fraction that can be recovered. In most cases the lower the carbon residue the more valuable the crude. This is expressed in terms of the weight percent carbon residue by either the Ramsbottom (RCR) or Conradson (CCR) according to ASTM test procedures (D- 524 and D-189) [11].

2.2 Blending

Crude oils from different fields are usually mixed for marketing properties. Commonly blending processes are also used on a large scope as a complementary stage in refinery processes.

Increased operating flexibility and profits result when refinery operations produce basic intermediate streams that can be blended to produce a variety of on-specification finished products [11]. The objective of product blending is to allocate the available blending components in such a way as to meet product demands and specifications at the least cost and to produce incremental products which maximize overall profit. The volumes of products sold, even by a medium-sized refiner, are so large that savings of a fraction of a cent per gallon will produce a substantial increase in profit over the period of one year.

Today's trend is to use computer-controlled in-line blending for blending gasoline and other high-volume products. Inventories of blending stocks, together with cost and physical property data are maintained in the computer. The computer uses, when a certain volume of a given quality product is specified.

Blending components to meet all critical specifications most economically is a trial-and-error procedure and, because of the large number of variables, it is possible to have a number of equivalent solutions that give the same total overall cost or profit.

The refiner and supplier blend oils for two reasons; first, to meet certain specifications and second, to make the oil easier to handle. The user may blend the oils in his storage tank for two reasons also; first, to change some of the oil characteristic, such as lowering the pour point, the carbon content, or the viscosity, usually, when trouble has occurred, and second, to decrease the total sediment and water percent [1].

Prediction of the true volume of an oil blend is important to the refiners since small changes can have considerable economic signification when products are measured in thousands of barrels. Several investigators have presented charts and equations for estimating these volumetric contractions [14].

2.3 Oil-Stocks Density

2.3.1 Introduction

The densities of petroleum liquids under given conditions of temperature and pressure are required in engineering calculations in the petroleum industry. Thus, in the calculations of the pressure drop in pipelines, and in determining bubble tower diameter, knowledge of densities is essential [15].

Density and specific gravity are extensively used in connection with petroleum products, but engineers and technicians generally, prefer the "API gravity", which they frequently term simply the "gravity". API gravity is usually reported as part of a crude oil or product analysis, and hence no short-cut methods of estimation are needed [7].

In mixing heavy oils, no significance in total arithmetic volume of the two components occurs, and the specific gravity of the mixtures is exactly what would be expected from the properties used in the mixtures. However, the API gravity of the mixtures does not behave as an additive function because API gravity is not a liner function of specific gravity [16].

Although a number of graphical and mathematical methods have been published to suggest ways to estimate the density of crude oil and its fractions when no experimental data are available, most of them suffer various shortcomings [17].

Data on density at specified temperatures are required daily in a variety of chemical engineering computations. Some of these computations involve: fluid flow, heat and mass transfer, pumping mixing, estimates of other properties, and interconvsions of volumetric and mass flow rates [17].

2.3.2 Standard Techniques for Calculating Oil-Stocks Density

Calculation of oil-stock density under varying temperature and pressure is fundamental to all custody transfer operations. There are several standard techniques for estimating the density of oil-stocks, as follows:

I. API Standard 2540 [18]

Crude oil density can be calculated at any temperature from a single density measurement at any other temperature. The basis is the correlation coefficient of thermal expansion as a function of density at $15^o C$. The coefficient α for crude oil is given as:

$$\alpha_T = \frac{K_O + K_1 \rho_{15}}{\rho_{15}^2} \tag{2-4}$$

Where, $K_O = 613.9723$, in the metric measurement system.

The volume correlation factor (VCF) is then given by:

$$VCF = Exp\left[-\alpha(T-15) - 0.8\alpha^2 (T-15)^2\right] \tag{2-5}$$

Where, T is the temperature $\left({}^{o}C\right)$, whose correlation is to be made.

To determine the density from an input density at a temperature other than $15^{o}C$ requires an iterative process assuming a value for the density at $\mathbf{15^{o}C}$, calculating the VCF and comparing the density calculated from this with the input value.

The accuracy of the standard is given by the following statement:

VCF precision at 95 percent confidence level

Temperature, ${}^{O}F$	100	150	200	250
Precision,%	± 0.05	± 0.05	± 0.25	± 0.35

II IP Petroleum Measurement Manual Part X, Section I, Table 3 [19]

Compressibility of a crude can be evaluated from the relationship:

$$C^{*} = Exp\left(\begin{array}{l} 1.38315 + 0.00343804T - 3.02909\ln\left(\rho_{15}/1000\right) \\ -0.0161654T\ln\left(\rho_{15}/1000\right) \end{array}\right) \qquad (2\text{-}6)$$

Where, C^{*} is compressibility (x10^{5}/bar)

The range of applicability is given as 0 to 35 bar.

II. IP Tables 53 and 54 [20]

Densities of oils at any temperature can be calculated from a single input value at any temperature. The section for densities between 500 and 600 Kg/m^{3} is still of interest for LPG mixtures although, beyond this the new API 2540 is now the standard.

The range 500 and 600 Kg/m^3 is based upon tables and graphs produced by the Natural Gasoline Association of America. No convenient arithmetic formulation was made. Accuracy of experimental work on pure components was thought to have been accurate to 0.015% above $0^0 F$ to 0.03% below $0 F$. No conclusion on the accuracy of the tables for use with mixtures is possible.

IV API "Shrinkage" Procedure [21]

Reduction in volume can be calculated for light hydrocarbon mixtures blended with oils. Shrinkage is calculated by:

$$S = 0.00214 C^{-0.0704} G^{1.76} \tag{2-7}$$

Where, $S =$ Shrinkage factor, as vol. % of spike.

$G =$ Specific Gravity

$C =$ Concentration

2.3.3 Hankinson-Brobst-Thomson (HBT) Technique

Hankinson et. al. [22] obtained a fine tuned version of the Costal correlation that predicts the density for 40 "LNG-Like" mixtures with an average absolute percent error of 0.078. The five parameter (critical temperature, critical pressure, acentric factor, characteristic volume and molecular weight) correlated as a function of crude oil density at 15°C.

This correlation related the saturated molar volume of a liquid, V_s, to a characteristic volume, V^*, the reduced temperature, T_r, and a modified a centric factor, ω_{SRK}, for each stream component as shown in the following equations:

$$V_S \big/ V^* = V_R^{(0)}\left(1-\omega_{SRK} V_R^{(\delta)}\right) \tag{2-8}$$

$$V_R^{(0)} = 1 + a\left(1-T_r\right)^{1/3} + b\left(1-T_r\right)^{2/3} + c\left(1-T_r\right) + d\left(1-T_r\right)^{4/3} \qquad 0.25 < Tr < 0.95 \tag{2-9}$$

$$V_R^{(\delta)} = \left(e + fT_r + gT_r^2 + hT_r^3\right) \big/ \left(T_r - 1.00001\right) \qquad 0.25 < Tr < 1.0 \tag{2-10}$$

The constants are:

a = -1.52816 b = 1.43907 C = -0.81446 d = 0.190454

e = -0.296123 f = 0.386914 g = -0.0427253 h = -0.0480645

Thomson et al. [23] have extended the HBT method to allow the calculation of compressed liquid volumes by generalizing the constants in Tail equations (13 and 14). Thus:

$$V = V_S\left(1 - C \cdot \log\left(\left(B+P\right) \big/ \left(B+P_S\right)\right)\right) \tag{2-11}$$

Where, $V_S =$ standard volume from equation 2-8

$$B = P_C\left(-1.0 + a\left(1-T_r\right)^{1/3} + b\left(1-T_r\right)^{2/3} + d\left(1-T_r\right) + e\left(1-T_r\right)^{4/3}\right) \tag{2-12}$$

$$e = Exp\left(f + g\omega_{SRK} + h\omega_{SRK}^{\ 2}\right) \tag{2-13}$$

And $C = j + k\omega_{SRK}$ (2-14)

The parameters a through k is given in table 2.2b.

Table 2.2b:- Parameter for Equations 2-12, 2-13 and 2-14

a = -9.070217	b = 62.45326	d = 135.1102	f = 4.79594
g = 0.250047	h = 1.14188	j = 0.0861488	k = 0.0344483

The saturation pressure, P_S, for either a pure compound or a mixture, may be obtained from a bubble point calculation or estimation from a generalized vapor pressure relationship. The generalized relationship presented by Hankinson et al. [24], is as follows:

$$Log\left(P_r\right) = P_r^{(0)} + \omega P_r^{(1)} \tag{2-15}$$

Where,

$$F = 35.0 - 36.0T_r - 96.736\log(T_r) + T_r^{\,6} \tag{2-16}$$

$$G = \log(T_r) + 0.03721754(F) \tag{2-17}$$

$$P_r^{(1)} = 4.86601(G) \tag{2-18}$$

$$P_r^{(0)} = 5.8031817\log(T_r) + 0.07608141 \tag{2-19}$$

The values of any mixtures properly (like density) obtained from a corresponding states correlation are sensitive to the calculated pseudo-critical constants of the mixture.

The set of mixing rules giving the minimum average absolute percent errors is given by Hankinson, Brobst and Thomson [23].

$$T_{cm} = \frac{\sum\sum x_i x_j V_{ij}^* T_{cij}}{V_m^*} \tag{2-20}$$

$$V_m^* = \frac{1}{4}\left\{\sum_i x_i V_i^* + 3\left(\sum_i x_i V_i^{*2/3}\right)\left(\sum_i x_i V_i^{*1/3}\right)\right\} \tag{2-21}$$

$$V_{ij}^* T_{cij} = \left(V_i^* T_{ci} V_j^* T_{cj}\right)^{1/2} \tag{2-22}$$

And $\omega_m = \sum_i x_i \omega_{SRK}$ (2-23)

Mixture critical pressure is calculated from:

$$P_{cm} = {(Z_{cm} R T_{cm})}/{V_m^*} \tag{2-24}$$

Where V_m^* comes from equation 2-21 and Z_{cm} from:

$$Z_{cm} = 0.291 - 0.08\omega_{SRK} \tag{2-25}$$

The Costald equation has been generalized to permit calculation of densities of crude oils and petroleum fractions and their binary and ternary mixtures using critical properties and molecular weight. The average absolute percent error when tested against 288 points was 6.1 percent [25].

J. Shanshool and E. T. Hashim tested the Hankinson-Brobst-Thomson techniques on different binary and ternary of crude oil and fraction. They obtained results of 888 spicks shown to be very acceptable [25].

2.3.4 Predicting the mixture Density

Teja [26] described an analytical method for calculating saturated liquid densities, and hence swelling factors, of CO_2-crude oil systems, which are of interest in enhanced oils recovery. The method uses an extension of Pitzer's three-parameter corresponding states principle based on two reference fluids chosen so that their properties are close to the key components of interest. The method gives extremely accurate predictions of the saturated liquid densities of LNG mixtures, when the critical properties and centric factors of the components are known.

The variation of density with temperature, or effectively, the thermal coefficient of expansion, is a property of great technical important, since most petroleum products are sold by volume and specific gravities are usually determined at the prevailing temperature rather than at the standard temperature 60 ^{o}F. Consequently, much work has been expended on the investigation of this function [7].

Orwoll and Flory [29] measured the values of the thermal expansion coefficients $\left(\alpha = \frac{1}{V}(\partial V / \partial T)_P\right)$ of n-hexane and n-heptane. The values of $((\partial V / \partial T)_P)$ thus found were fitted by the method of least squares to a polynomial equation, cubic in temperature, which was integrated to give the volume of the hydrocarbon as a function of temperature:

$$V = \int_{to}^{t} \left(A + Bt' + Ct'^2 + Dt'^3 \right) dt' + V_o \qquad (2\text{-}26)$$

Where: V_o is the volume of n-alkane at t_o.

Some of the equations obtained by Orwoll and Flory are detailed in table 2.3. In this table, densities are given by the polynomials in power of temperature. The estimated ranges of error in densities were ± 0.0002 g.cm^3.

Table 2.3: The densities of some n-alkanes as function of temperature

n-alkane	ρ, g.cm^{-3}	Temperature range, ^{o}C
n-C_6H_{14}	$\rho = 0.667 - 0.089*10^{-2}t - 0.086*10^{-6}t^2 - 0.652*10^{-8}t^3$	-15-89
n-C_8H_{18}	$\rho = 0.791 - 0.081*10^{-2}t - 0.001*10^{-6}t^2 - 0.313*10^{-8}t^3$	26-145
n-$C_{16}H_{34}$	$\rho = 0.787 - 0.070*10^{-2}t - 0.0185*10^{-6}t^2 - 0.134*10^{-8}t^3$	18-207
n-$C_{22}H_{46}$	$\rho = 0.809 - 0.068*10^{-2}t - 0.187*10^{-6}t^2 - 0.082*10^{-8}t^3$	44-201
n-$C_{36}H_{74}$	$\rho = 0.832 - 0.066*10^{-2}t - 0.338*10^{-6}t^2 - 0.094*10^{-8}t^3$	76-188

The thermal expansion coefficients given by Downer and Inkely [30] are derived from accurate density measurements at various temperatures ranging from 40 to 200 F. These measurements were carried out on the best available samples, using a Bingham-type pycnometer.

The thermal expansion coefficient is a measure of the rate of change of density with temperature. The greater the rate of change, the larger the coefficient of expansion.

Downer and Inkely [30] demonstrated that the change of the density with temperature has a linear relationship with a slope represents the coefficient of expansion.

For the purpose of transfer of bulk petroleum oils and products, bulk volumes and contractual densities are stated at a fixed reference or base temperature, which are 60 °F in countries dealing with the U.S.A. and 15 °C or 20 °C in a significant number of nations. Volumes metered at temperatures other than base value are adjusted to the base value by factors developed and tabulated in the petroleum measurement [31].

O'Donnell [32] found an equation which is explicitly solvable either for density at any temperature or density at a standard temperature, its implicit form is:

$$\rho^2 = A + kt \tag{2-27}$$

Where the A is an arbitrary constant. The constant k has the same value for all petroleum products about -0.0011 $g^2.m^{-6}.C^{-1}$.

If the standard temperature is taken as 15.5°C, the equation may be solving explicitly as follows:

$$\rho_t = \sqrt{\rho_{15.5}^2 + k(t - 15.5)} \tag{2-28}$$

The standard errors in specific volume for a linear relationship between several forms of the dependent variable, volume namely, v, (ln V, V^{-1}, V^{-2}, V^{-3}) and also several forms of the independent variable temperature namely, ln(t + 273), t, $(t + 273)^2$, and, $(t + 273)^3$, are tabulated [32], based on Jessup's data. The errors are expressed as errors in specific volume so that the different relationships may be compared on the same base.

Two other accurate correlations were predicted by O'Donnell [32], the first one is,

$$V^{-3} = A + k\sqrt{t + 273} \qquad (2\text{-}29)$$

, and has standard error of 0.0018 which is slightly better than the 0.0021 for V^{-2} and t. the other equation is:

$$V^{-3} = Ak(t + 273)^{0.57} \qquad (2\text{-}30)$$

Has standard error of only 0.0012. This is a remarkably low value. It is almost as low as a quadratic expression in t can do on the same power of volume.

Rice and Teja [28] stated that the liquid densities of the pure components are represented as functions of reduced temperature by an equation of the type:

$$\rho_R = a + b(1 - T_R)^{1/3} \qquad (2\text{-}31)$$

The values of the constants a and b are given in table 2.4 for hexane, hexadecane and n-propyl alcohol.

Table 2.4: Constants in equation 2-31

	a	b
Hexane	0.832722	9.02597
Hexadecane	-1.763718	5.962086
N-propyl alcohol	-0.354601	4.289542

Al-Najjar, et al. [33] demonstrated that the change of density of crude oil with temperature in the range of (15-50) °C had a linear relationship:

$$\rho = a + bt \qquad (2\text{-}32)$$

This equation was applicable, for samples of several crude oils and products, at varying gravities from light to heavy [33].

2.4 Volumetric Behavior of mixtures

2.4.1 Excess volume phenomenon

The change in volume on mixing liquids is not a recently observed phenomenon, but has been reported by a number of authors. Excess volume for non-hydrocarbon compounds, there are many volume-change data in the literature on blends of pure hydrocarbons, and blends of pure hydrocarbons and petroleum fractions [34].

The volumetric properties of binary mixtures of pure compounds have been extensively studied.

A mixture of typical hydrocarbons forms non-ideal system, for which excess volume may be positive or negative according to the nature of the species [8].

The phenomenon of volume shrinkage experienced in blending of petroleum components having different physical properties, volumetric shrinkage occurs because the components do not form ideal solution. An ideal solution, may be defined as one in which no specific forces of attraction exist between the components of the solution and no change occur in the phenomenon. Thus in an ideal solution, the total solution volume is equal to the sum of the volumes of the components and the other physical properties such as refractive index, fluidity, and vapor pressure can be calculated by taking the molar average of the components properties. For a solution to approach ideality, the molecules in the solution must be identical or very similar in size, shape and properties.

If the molecules are identical or very similar, then the environment of the molecules, and hence the forces acting upon the molecules, will be about the same in the solution and in the pure state. If the nature of the molecules of the component should differ appreciably, then deviations from ideal behavior are to be expected and can be observed.

Deviation from ideality as concerns the volume of the solution can be in either a positive or negative direction. That is, it can result in either an expansion or contraction of total volume upon mixing. Glasston [35] states that if a solution of two or more components exhibits positive deviation from Raoult’s law, the observed vapor pressure and volume would be greater than if the components had formed an ideal solution. Thus he attributes to the mean attractive forces between the molecules in the mixture being smaller than for the constituents separately.

Conversely, if a solution should exhibit negative deviation from Raoult’s law, usually there is a decrease in vapor pressure and volume on mixing. This is attributes to the mean attractive forces between the molecules in the mixture being greater than for the constituents separately [21].

In as much as petroleum components contain molecules of various sizes and weights, solution of two separates components are seldom ideal.

Consequently, it is to be expected there may be change in volume associated with mixing or blending of petroleum components of varying gravities and molecular structure.

Usually, in blends of light components and crude, this change in volume is negative in direction and results in shrinkage in total volume.

The excess thermodynamic properties (like excess volumes) of mixtures of crude are of considerable interest in the field of transportation.

Usually light crude oil blended into heavy crude to satisfy such specification for selling and transportation. Although these treatment have led to considerable insight into thermodynamic behavior of these mixtures. But these blending led to loss in volume [21].

The volumetric properties of binary mixtures of long-chain linear paraffinic hydrocarbons have been extensively studied. Generally they are shown to exhibit negative excess volumes, particularly when there is a large difference between the carbon-chain lengths of the components.

Thermodynamic-property relations already presented would suffice. However, liquid solutions are often more easily dealt with through properties that measure their deviations, not from ideal-gas behavior, but from ideal solution behavior. Thus the mathematical formalism of excess properties is analogous to that of the residual properties.

If M represented the molar value of an extensive thermodynamic property (for example, $V, U, H, S, G,$ etc.), then an excess property M^E is defined as the difference between the actual property value of a solution and the value it would have as an ideal solution at the same temperature, pressure, and composition [36]. Thus,

$$M^E = M - M^{id} \tag{2-33}$$

Where the superscript *id* denotes an ideal solution value.

In view of need for mixing crude/spike pair with more accurate weight values for each samples we used weight fraction rather than volume fraction. Volume fraction of spike ϕ_2 can readily be calculated by means of the following equation 2-34:

$$\phi_2 = \frac{x_2 \rho_1^o}{\rho_2^o + x_2 \rho_1^o - x_2 \rho_2^o} \qquad (2\text{-}34)$$

where:

x_2 = mass fraction of spike

ϕ_2 = volume fraction of spike

ρ_1^o = density of crude oil

ρ_2^o = density of spike

In view of need to establish quantitative expressions on a volumetric basis, these results were expressed in the form of excess specific volume, V^E according to the following equation:

$$V^E = V_{mix} - V_{ideal} \qquad (2\text{-}35)$$

Where V_{mix} is the actual specific volume, which is equal to $1/\rho_{mix}$ in cm^3/kg and ρ_{mix} is the measured density in kg/m^3.

The ideal volume, V^{id}, is given in terms of volume fractions of spike, ϕ_2, and the densities of the crude oil, ρ_1^o, and spike, ρ_2^o by equation 2-36:

$$V^{id} = \frac{1}{(1-\phi_2)\rho_1^o + \phi_2 \rho_2^o} \left(cm^3/kg\right) \qquad (2\text{-}36)$$

2.4.2 Mixture of Defined Composition:

The excess volume of pure component systems where discussed in details in the literature. Some results could be mentioned below to explain and describe the effect of chemical composition on the volumetric behavior, see also part 2-5-1.

van Der Vet [14] found a decrease in the total volume of 0.2 percent for blends of propane and butane.

Reamer,Sage and Lacey [37] determined the volumetric behavior of four mixtures of n-butane and decane experimentally at seven temperature from 100 to 460 F, and different pressure up to 10,000 psig. The results indicate that at the lower temperatures and higher pressures the system approaches the volumetric behavior of ideal solutions, but at the high temperatures and intermediate pressure the volume may differ from such behavior by more than 50%.

Goff, Farrington and Sage [38] determined the volumetric behavior of four mixtures of propene and 1-butene experimentally at temperature range (40-280) ^{o}F. For up to 10,000 psig. The results are presented in graphical and tabular form.

Winnick and Kong [39] measured the excess volumes for five binary polar liquid mixtures using pycnometers for density measurements. The results were compared with predictions made using a partition function developed earlier. Good comparisons are achieved if the arithmetic mean unlike diameter of interaction is adjusted with a single. The excess volumes predicted were, however, not generally in quantitative agreement. The densities of five binary liquid mixtures were measured at several mole fractions. Each mixture contained at least one polar liquid. The molar excess volumes were then calculated from the densities.

Kosanvich and Cullinan [40] developed a method for the characterization of transport properties of multi-component liquid systems by combining the concept of ultimate volume of pure liquids with known behavior of the self-diffusion coefficient and extending the results to liquid mixtures. Comparison of the prediction of the resulting model with available data for several binary, ternary, and quaternary liquid systems yields excellent agreement.

Hossein, K. [41] measured the excess volumes for mixtures of tetrachloroethylene with aliphatic ketones (methyl ethyl ketone, methyl propyl ketone, and diethyl ketone), and alicyclic ketones (cyclopentanone, and cyclohexanone) at 303.15 and 313.15 K. they shown that excess volumes has a positive temperature coefficient except for the system methyl propyl ketone with tetrachloroethylene. The observed excess volumes of these mixtures are due to the existence of specific interactions between the dipole of the ketones and tetrachloroethylene.

Nettem, Jyoti, et al. [42] measured the excess volumes of 1,1,2,2-tetrachloroethane with methyl ethyl ketone, diethyl ketone, and methyl propyl ketone between 303.15 and 313.15 K. He had shown that the excess volumes were negative over the entire composition range in all the mixtures at both the temperatures. The negative value of excess volumes is indicative of important interactions between unlike molecules. When a nonpolar molecule such as 1,1,2,2-tetrachloroethane is situated in an electric field set by the presence of a polar molecule, the ketone, a dipole is induced. The force between the permanent dipole of the ketone and the induced dipole of tetrachloroethane is always attractive. This leads to negative deviation in excess volume.

Nettem, A. et al [43] measured the excess volumes for six binary mixtures of 1,1,2,2-tetrachloroethane with 1-alkanols (1-propanol, 1-butanol, 1-pentanol, 1-hexanol, 1-heptanol, and 1-octanol). The results are examined in the light of depolymerization of alcohols, interstitial accommodation of chloroalkane in hydrogen-bounded alcohol aggregates, possible hydrogen-bounded interactions of the type Cl…H-O, between unlike molecules, and the influence of chain length of the alcohol on the aforesaid factors. They showed that the excess volumes were negative in mixtures rich in alcohols. The negative values of excess volumes decreases with the increase in the chain length of the alcohol. Further, the excess quantity tends to become positive as the concentration of chloroalkane increases. The results may be explained in terms of two opposing contributions; first, expansion in volume due to depolymerization of alcohol aggregrates, second, contraction in volume due to interstitial accommodation of chloroalkane in the aggregrates of alcohols and weak hydrogen-bond interactions of the type Cl…H-O between unlike molecules.

Jean-Pierro and Emmerich W. [44] measured the molar excess volumes as a function of mole fraction at 298.15, 308.15, and 318.15 K for binary liquid systems for the cyclic ethers were oxolane (tetrahydrofuran,C_4H_8O), oxane (tetrahydropyran, $C_5H_{10}O$), 1,3-dioxolane (1,3- $C_3H_6O_2$), and 1,4-dioxane (1,4- $C_4H_8O_2$); the n-alkanes were n-decane and n-tetradecane. All excess volumes are positive ($x_1 = 0.5$) for any mixture containing an m_c-membered cyclic diether is considerably larger than for the corresponding mixture (i.e., with the same n-alkane) involving an m_c-membered cyclic monoether. For given ether excess volume shows a pronounced increase with increasing chain length of the n-alkane.

Jagan and Geeta [45] measured the excess volumes for binary mixtures of 1,2-dichloroethane (CH_2ClCH_2Cl) with benzene, toluene, p-xylene, and quinoline at 298.15 and 308.15 K, and for mixtures of CH_2ClCH_2Cl with cyclohexane at 308.15 K. they shown that the value of excess volumes was positive for CH_2ClCH_2Cl-benzene, CH_2ClCH_2Cl-toluene, CH_2ClCH_2Cl-p-xylene, and CH_2ClCH_2Cl-cyclohexane, and negative for CH_2ClCH_2Cl-quinoline. The values of excess volumes for CH_2ClCH_2Cl-cyclohexane are found to be highly positive in comparison to those for the systems CH_2ClCH_2Cl-benzene, CH_2ClCH_2Cl-toluene, CH_2ClCH_2Cl-p-xylene, and CH_2ClCH_2Cl-cyclohexane.

David S. and Charies A. [46] measured the excess volumes for the benzene + 1,1,2-trichloroethylene system at 283.15 and 313.15 K and atmospheric pressure. They showed that the excess volumes were positive and decrease with increasing the temperature.

2.4.3 Oil-stock Blends

Cragoe and hill [14] have pointed out that an expansion of 0.36 percent may occur when mixing benzene and gasoline. Ylonen [15] reports an expansion of 0.5 percent on mixing benzene and kerosene.

Thiele and Kay [15] reported a contraction of 0.25 percent volume when blending light and heavy naphthas. While in the case of mixing light naphtha, heavy naphtha, gas oil, paraffin distillate and residue, which may represent the general contains of crude oil, shrinkage in volume with about 0.23% is occurred.

Loff [15] showed contractions of 0.3 percent for petroleum ether and kerosene mixtures, 0.64 percent for petroleum ether and Vaseline oil and 0.11 percent for gasoline and kerosene.

Other literature data indicate much larger volume changes for blends of light fractions, such as ethane, propane and butane, with the heavier petroleum components.

Reeves [47] correlates blending data for various hydrocarbon liquids, including ethane, propane, butane, decane, benzene, naphtha, kerosene, and crude oils. Volumetric contraction is presented in both tabular and graphical form and ranges as high as 30 percent variation from ideality in some cases.

A chart has been prepared by Reeves [47] for predicting the blending value of the lighter compound in mixture of petroleum fractions. Blending value was defined as the ratio of the partial specific volume to the actual specific volume or the apparent volume of this component. This blending value can be used when the mixture contains 15% or less of the lighter component.

Childress and Grove [34] demonstrated that, when a light product such as butane or natural gasoline are mixed with crude, the resulting volume is less than the sum of the individual component volumes.

From a study of the data, the API gravity of the components (or more accurately, the differences in gravity between the components) has been selected as the best particle index of the amount of shrinkage that would occur. It was realized, of course, that occasionally blends with the same gravity differential would experience different amounts of shrinkage as the result of the difference in characteristics of the various components.

The use of gravity as an index was further facilitated by the fact that is the most common and easily obtained characteristic of the components being handled in a crude-oil pipeline system.

Rossini [21] plotted the gravity difference between the light and heavy components, of different concentration levels of the light component, against the change in total volume expressed as a percentage of the volume of light component in curves, which percent the values of shrinkage from 1 to 15 percent of light component in the mixture.

S. J. Ashcroft [8] studied seven European, South American and African crude (Furzebrook, Statfjord, Forties, Cabinda, Cano-Limon, Bonny, and Sovene) combined with ten light hydrocarbon mixtures (Toluene, Cyclohexaine, n-heptaine, Petroleum fraction at different boiling temperature range, and Lucini fraction) for non ideal systems. He showed that mixtures of crude oils with toluene or cyclohexane have positive values of excess volumes, and thus exhibit expansion, cyclohexane being particularly effective. Paraffinic spikes usually produce negative excess volume values. The high-boiling paraffinic spikes can, with some crude oils, lead to small positive values of excess volume.

2.5 Prediction of excess volume

2.5.1 Mixture of Defined Composition:

A number of equations are available in the literature to calculate the value of excess volumes for different pure components mixtures when no experimental data are available.

Kumaran [48] measured molar volume of (benzene + n-hexane) at 298.15 and 323.15 K. the excess molar volumes are positive over the whole mole fraction range. The excess molar volumes for (benzene + n-hexane) are represented by the equation:

$$V^E = x(1-x)\left[1.612 - 0.09(1-2x) + 0.127(1-2x)^2 - 0.08(1-2x)^3\right] \qquad (2\text{-}37)$$

At 298.15 K with a standard deviation of 0.0005, and

$$V^E = x(1-x)\left[1.44 - 0.003(1-2x) + 0.073(1-2x)^2 - 0.05(1-2x)^3\right] \qquad (2\text{-}38)$$

At 323.15 K with a standard deviation of 0.0006

Cokele [49] measured the density of a mixture of 1,1,2,2,-tetrabromoethane and 1-Bromododecane at atmospheric pressure over the entire composition range and in the temperature range between 25 and 40 ^{0}C. The molar volume of a mixture calculated as the mole fraction weighted average of the pure component, molar volumes is within 0.14% of the correct value. The resulting equation for mixture molar volume is:

$$V^E = \left(114.86\frac{ml}{mole} + 0.0876t\frac{ml}{mol.^0C}\right) + \left(120.6\frac{ml}{mole} + 0.117t\frac{ml}{mol.^0C}\right)x \qquad (2\text{-}39)$$

Rex Goates et al. [50] measured the densities of binary mixtures of cyclohexane, n-hexane, n-heptane, n-octane, n-nonane, and n-decane at three temperatures of 283.15, 298.15, and 313.15 K. The excess volume increased regularly with increasing size of the alkyl group of the hydrocarbon. Results for the excess volumes were fitted by a least squares method to an equation of the type:

$$V^E = x(1-x)\sum a_i(1-2x)^i \qquad (2\text{-}40)$$

Subramanyam Reddy [51] measured the density of mixtures of (benzene + 2-ethoxyethanol) of 303.15 and 323.15 K over the entire composition range. The excess volumes were positive at small mass fraction but then become negative on the increase of x at each of the three temperatures, changing sign at $X \approx 0.5$, 0.32 and 0.2 at 303.15, 313.15 and 323.15 K respectively. The results for the excess volumes were fitted by equation 2-40.

Biron [14] proposed the following relation for calculating the change in molar volumes ΔV for hydrocarbon mixtures.

$$\Delta V = KN_1N_2 \tag{2-41}$$

N_1 and N_2 are mole fractions of the components and K is an experimental constant. This equation is valid for hydrocarbon systems where the molecular weights of the components are approximately equal. When the molecular weight ratio is greater than 1.5, K varies widely and is a function of the composition of the mixture.

Orwoll and Flory [29] observed and calculated the molar excess volumes for the system $n-C_6H_{14}+n-C_{16}H_{34}$ for temperatures between 20 and 60 ^{o}C, using the following equation:

$$V^E = V-(x_1v_1-x_2v_2) \tag{2-42}$$

Where:

$$V = \bar{v}\left(x_1v_1^*-x_2v_2^*\right) \tag{2-43}$$

Contraction of the volume when mixing occurs for all combinations of n-alkanes, resulted in negative excess volumes in all cases. The average difference and standard deviation are 0.09 and 0.11 cm^3 mol^{-1}, respectively.

Benson, Halpin and Treszcznowicz [52] reported that the excess volumes of (2-ethoxyethanol + n-heptane) is positive over the whole mole-fraction range and even larger in magnitude than V_m^E observed for mixtures of short alkanols, such as methanol or ethanol, with n-heptane. They fitted the data using the following formula:

$$V^E = x(1-x)\sum_{j=1}^{n} a_j x^{(j-1)/2} \tag{2-44}$$

Although equation 2-44 provides a satisfactory smoothing of the results over most of the mole-fraction range, it is suitable for calculating partial molar quantities at low values of x. for this purpose the polynomial:

$$V^E = \sum_{j=1}^{n} a_j x^j \qquad (2\text{-}45)$$

The results were fitted at low mass fraction (x < 0.1). Values of the coefficients a_j and the standard deviation σ obtained from least-squares analyses in which all points were weighted equally.

Kanbour and Madfai [53] measured the densities of mixtures of n-methyl pyrolidone (NMP) + benzene, and + toluene at various temperatures over the whole mole fraction range. Excess volumes of solution V^E and the apparent molar ϕ of benzene and toluene in NMP were calculated. Negative departure from ideality which increased with increase in temperature was observed. The minimum point in V^E was skewed toward the aromatic hydrocarbon regions. These results were interpreted as indicative of specific interaction between like as well as unlike molecules. Results for the excess volumes were fitted by least square computer program to a smoothing equation 2-40, where x represented the mass fraction of benzene or toluene. The data for each system could be fitted satisfactory with three parameters in the equation above. The best values for a_i coefficient obtained from the best fitting are given in table 2.5.

Table 2.5: Values of coefficients of excess volumes calculated by equation 2-40

Temperature ^oC	a_o	a_1	a_2
15	-1.93872	-1.68560	0.20514
25	-2.15249	-1.76507	-0.20181
35	-2.11272	-2.43832	0.46765
50	-2.42706	-2.53495	0.25747
70	-3.63456	-2.12093	-1.04715

Valero [54] measured the excess molar volumes of n-hexane +, 2,2-dimethylbutane +, cyclohexane +, n-hexadecane +, benzene +, and tetrachloromethane + 1,2-dichloroethane, at four temperatures ranging from 288.15 to 318.15 K and 298.15 to 328.15 K for n-hexadecane and 1,2-dichloroethane. The positive temperature coefficient are explained in terms of the conformational equilibrium in 1,2- dicloroethane. Then fit the data for each system, using equation 2-40, values for a_i coefficient obtained from the best fitting, and the standard deviation are given in table 2.6 for one system as example.

Table 2.6: Values of coefficient for excess volumes equation 2-40 for a system {(1-x) C_6H_{14} +x 1,2-$C_2H_{14}Cl_2$}, with standard deviation.

Temperature K	a_o	a_1	a_2	σ
288.15	2.626	-0.95	0.033	0.003
298.15	2.644	-1.018	0.056	0.006
308.15	2.763	-1.025	0.130	0.004
318.15	2.756	-1.018	0.0220	0.007

Awwad and Kanbour [55] masured the excess volumes of binary mixture of n-formylmorpholine with methanol +, ethanol +, n-propanol +, n-butanol +, and n-pentanol from density measurement at 298.15 K over the whole mole fraction range. The excess volume is negative and decreases markedly with molecule. The significant of these values is discussed in relation to supposed structural change in the mixtures.

Rao and Reddy [56] obtained the densities of the mixtures form excess volumes, V^E, using the relation:

$$\rho = \frac{x_1 M_1 + x_2 M_2}{x_1 v_1 + x_2 v_2 + V^E} \tag{2-46}$$

Density values were accurate to $\pm 0.05 Kg/m^3$.

Reduced volumes of the mixture for the pure components are calculated using the following equations:

$$\bar{v} = v \Big/ \left(x_1 v_1^* + x_2 v_2^*\right) \tag{2-47}$$

$$\bar{v_i} = \frac{v_i}{v_i^*} \qquad (i = 1, 2) \tag{2-48}$$

The molar volumes are obtained from measured density data.

Chhabra and Sridhar [57] predicted the volume of the mixture using the following formula,

$$V_{o,mix} = \sum_{i=1}^{n} x_i v_i \tag{2-49}$$

They used Hidebrand's fluidity theory to calculate the free volume for arrange of mixtures, and proposed the following mixing rule for V$_o$:

$$V_{o,mix} = \left(\frac{x_1^2}{V_{o.1}} + \frac{2x_1x_2}{V_{o.12}} + \frac{x_2^2}{V_{o.2}} \right)^{-1} \tag{2-50}$$

Where:

$$V_{o.12} = \left(\frac{V_{o.1}{}^{1/3} + V_{o.2}{}^{1/3}}{2} \right)^3 \tag{2-51}$$

2.5.2 Crude oils and fractions

It is generally observed that the addition of light paraffinic hydrocarbons to crude oil produces negative excess volumes; in other words "shrinkage" occurs relative to the calculated ideal volume. The effect is less pronounced as the molecular size of the added hydrocarbon increases.

Loffe [14] presented an equation for predicting the specific volume change (ΔV) in systems of petroleum fractions, as follows:

$$\Delta V = \boldsymbol{K_P P_1 P_2} \tag{2-52}$$

where P_1 and P_2 are weight percentages of the components and K_P is an experimental constant. When blending light materials, such as ethane, propane or butane with heavier petroleum fractions, Kp varies considerably with composition.

Inspection of the curve plotted by Reeves [14] indicates that the volume change is a function of the composition and the molecular weights of the components. Accordingly, it was assumed that the volumetric contraction could be expressed by the following empirical relation:

$$LogC = \alpha \log P + \beta \log M_1 + \gamma \log(M_2 - M_1) + K \tag{2-53}$$

Where C is volume percent contraction, P is the weight percent of high molecular weight component in the blend, M_1 and M_2 are the molecular weights of the lighter component and heavier component respectively. α, β and γ are experimental constants.

Volume changes of seven different blends of petroleum fractions at (60-70) ^{0}F with a total of 44 experimental points were used to determine the values of constants in equation 2-53.

The data were analyzed by the least square method where, it was assumed that the relation was a straight-line equation with a minimum deviation between the experimental points and the function.

The derived equation is shown below:

$$LogC = 0.6107\log P + \beta \log M_1 + 0.537\log(M_2 - M_1) + 4.418 \tag{2-54}$$

Equation 2-54 is valid for concentration (P) of 50% or less of the heavier component, while for higher concentrations take log(100-P) instate of log P the relation becomes:

$$LogC = 0.6107\log(100 - P) + \beta \log M_1 + 0.537\log(M_2 - M_1) + 4.41) \tag{2-55}$$

The parameter β in equation 2-55 becomes a larger negative number as the molecular weight of the fraction increases and goes through a minimum point (largest negative number) at a molecular weight corresponding to butane. With fraction heavier than butane the value of β increases. Conversely, it is constant at about -3.5 for materials with molecular weights of 100 or more.

Ashcroft et al. [8] carried out a series of experimental work to study the volumetric behavior of different types of world crude oils with different petroleum fractions or pure hydrocarbons. The results were reported in terms of an equation for percentage relative excess volume of the mixtures, from which excess specific volume can be calculated.

The density data obtained cover the entire composition range from 0 to 100 vol. % spikes. In view of the need to establish quantities expressions on a volumetric basis, these results were expressed in the form of a dimensionless quantity-the percentage relative excess volume, given by:

$$\Delta V^{R} = 100 * \left(\frac{V_{mix} - V_{ideal}}{V_{ideal}} \right) \tag{2-56}$$

The data were fitted for each crude/spike pair mostly by quadratic equations of equation 2-56 in terms of volume fraction of spike ϕ_2:

$$\Delta V^{R} = \phi_2 (1 - \phi_2)\left(A_O + A_1 (1 - 2\phi_2) + A_2 (1 - 2\phi_2)^2\right) \tag{2-57}$$

J. Shanshool and E. T. Hashim [58] were developed a new correlation for predicting shrinkage factors of paraffinic-spiked crude oil:

$$\boldsymbol{S = 8.6 \times 10^{-7} (100 - C) G^{2.64} \upsilon^{-0.14}} \tag{2-58}$$

This new equation is more accurate than other knows forms [4].

Chapter Three 3

Experimental Work

3.1 Materials

Three Iraqi crude oils (heavy, medium, and light) were chosen to provide as diverse range of oils as possible. The first was North Iraqi crude (Khana) as light type, the second was Middle Iraqi (Shrake Baghdad) as typical heavy crude, and the third from South Iraq crude (Basarh) having a medium density . They supplied as "stock tanks" crude by Al-Dura Refinery. The specifications of the three types of crude oils are listed in table 3.1.

Table 3.1: specifications of crude oils:

Specification	Khana	Basarh	Shark - Baghdad
SP.GR(15.6 ^0C/15.6 ^0C)	0.8110	0.8744	0.9137
Gravity(^{0}API)	42.98	30.32	23.36
Kin Viscosity cs,			
@ 10 ^0C	5.3	28.4	205.89
@ 21.1 ^0C	3.5	18.5	92
@ 37.8 ^0C	2.2	10.1	35.5
@ 50.0 ^0C	1.65	8.0	n.d
Sulphur content wt. %	0.56	2.8	3.95
H_2S wt. %	0.017	0.0003	4
Pour Point ^0C	-18	-30	-26.1
Reid vapour pressure(Psi)	0.62	0.51	4.6
Water and Sediment B.S. &W.Vol. %	Traces	0.15	1.2
Salt Content Wt. %	0.0009	0.0009	4.3
Carbon Residue Wt. %	0.78	5.66	n.d
Asphaltenes Wt. %	0.06	1.95	n.d
Ash Wt. %	0.0027	0.01	n.d

n.d: Not determined

Gas oil and Kerosene were used as petroleum fractions to study the excess volume phenomena of crude oils. These fractions were supplied by Al-Dura Refinery as stock tank. The Specific gravity and other specification of these cuts are given in table 3.2.

Table 3.2: Some properties of petroleum fractions

Properties	Gas oil	kerosene
Sp.gr(15.6/15.6 ^0C)	0.85	0.801
Boiling point ^0C	235-425	150-235
Flash point ^0C	54	38
Sulpher content wt. $\%$ (Max)	1.0	0.2
Cetane No. (Min)	53	-
Disel index (Min)	55	-
Ash Wt. $\%$	0.01	-
Calorific value kcal/kg est	10800	10900

Furthermore, Toluene and Xylene mixture are considered also as spikes for crude oils, which are supplied from (GCC-Gainland Chemical Company, and UCB-in Belgium) respectively. Table 3.3 shows the main specifications of Toluene and Xylene mixture.

Table 3.3: properties of aromatic spikes

properties	Toluene C_7H_8	Xylene $C_6H_4(CH_3)_2$
Density at 25 ^0C	0.8641	0.8677
Boiling point ^0C	110	137-144
Molecular weight	92.14	106.17
Flash point ^0C	4	29
Melting point ^0C	-93	-
Refractive index (nb^{20})	1.496	1.497
safety	2,3363D	2,3619C

3.2 Measurements

3.2.1 Blends

Mixing process was occurred by electrical mixer at room temperature (20-25^0C). Density measurement was made immediately, after preparing the mixtures to avoid deposit formation or vaporizing the light ends. All density measurements are carried out at atmospheric pressure.

The following mixtures were prepared in this study:

1. Three crude oil binary mixtures, over a range of weight percent (0-100) at temperatures 15, 25 and 30^0C.
2. Binary mixtures of crude oils with petroleum fractions (Gas oil and Kerosene), over a range of weight percent (0-100) at temperature 25^0C.
3. Binary mixtures of crude oils with spikes (toluene and xylene mixture), over a range of weight percent (0-100) at temperature 25^0C.

3.2.2 Determination of density

Density determination of different Iraqi crude oils, petroleum fractions, spikes and their blends were carried out using pyknometers having sizes 25cm^3, and 50cm^3 according to the standard method (IP 190) [58].

The calibration of the pyknometer was done by determining the density of distilled water, with a good degree of purity. Filling pyknometer with freshly-boiled distilled water, cooling to slightly below 15^{o}C, and firmly insert the stopper, taking care to avoid the inclusion of any air bubbles. Immersing the pyknometer to the neck in the constant-temperature bath.

Placing the reservoir cap firmly on the stopper and immersing the pyknometer to half way up the reservoir cap in a constant temperature bath. Maintaining the bath within ±0.1°C of the calibration temperature for not less than one hour. The samples weights are measured by sensitive digital plate balance type (kern 770) with readings of five decimal places.

The pyknometer was placed in a water path type (Julabo HC) which was capable of maintaining the temperature within ±0.1°C of the selected temperature. Thoroughly cleaning the pyknometer and stopper with a surfactant cleaning fluid (light naphtha, chromic acid), rinsing well with distilled water, then with acetone and dried. Ensuring that all traces of moisture are removed by drying with a current hot air passing slowly through the pyknometer and stopper capillary. Wiping the outside of the pyknometer and stopper with a clean, lint-free cloth. Normally pyknometer cleaned by using (light naphtha), and dried. All the density measurements were carried out at atmospheric pressure.

The density of crude oils, however are difficult to measure accurately owing to the presence of suspended material and ill-defined substances such as asphalternces. In spite of such differently the repeatability of crude oil density was $\pm 1 * 10^{-4}$ gm/cm^3.

Chapter Four 4

Result and Discussion

4.1 Excess volume of crude oil binary mixtures

The excess thermodynamic properties such as excess volumes of mixtures of crude oil are of considerable interest in the field of transportation. Usually light crude oil blended with medium and also with heavy crude oils to satisfy such specification for selling and transportation. Although these treatment have led to considerable insight into thermodynamic behavior of these mixtures. But these blending led mostly to loss in volume [21].

Measured densities and API gravities at 15, 25 and $30^{0}C$ for individual crude oils are listed in table 4.1. The crude oil types used were of good varity, they range from light crude with API value of 44.3 (Khana) to medium crude (Basrah) of API 31.4, reaching the heavy crude (Shark Baghdad) in which API is 24.2.

Table 4.1: Densities and API gravities of crude oils

Crude	Temperature ^{o}C	Density kg/m^3	Gravity ^{o}API
Khana	$15^{o}C$	**810.30**	**43**
	$25^{o}C$	**804.02**	**44.3**
	$30^{o}C$	**799.16**	**45.4**
Basrah	$15^{o}C$	**873.63**	**30.3**
	$25^{o}C$	**867.81**	**31.4**
	$30^{o}C$	**866.32**	**31.7**
Shark Baghdad	$15^{o}C$	**912.85**	**23.4**
	$25^{o}C$	**908.28**	**24.2**
	$30^{o}C$	**906.17**	**24.5**

Three binary mixtures of crude have been made. The volumetric behavior of the binary mixtures of crude oils with different gravities was evaluated. The effect of temperature was also considered in this investigation to get an idea about composition and temperature effect on the excess volume of oil-stocks.

The ideal volume was calculated by the linear expression in terms of mass fraction of blending component as follows [8].

$$V^{id} = \frac{\rho_2^o + x_2\left(\rho_1^o - \rho_2^o\right)}{\rho_1^o \rho_2^o}\left(cm^3 / kg\right) \tag{4-1}$$

Excess volume is defined by the equation:-

$$V^E = V_{mix} - V_{ideal} \tag{4-2}$$

Where V_{mix} is the actual specific volume, which is equal to $1/\rho_{mix}$ in cm^3 / kg and ρ_{mix} is the measured density in kg / m^3.

Excess volumes for binary crude mixtures are summarized in tables 4.2, 4.3, and 4.4:

Table 4.2: Excess volume of binary systems; of Khana with Basrah crude at 15, 25 and 30^{o}C

Khana X_2	Excess Volume	Temperature ^oC		
		15^oC	25^oC	30^oC
0.1	$V^E{}_{\text{exp}}$	-0.36	-1.53	-1.67
0.2	$V^E{}_{\text{exp}}$	-1.30	-2.23	-2.45
0.3	$V^E{}_{\text{exp}}$	-1.88	-2.75	-2.95
0.4	$V^E{}_{\text{exp}}$	-2.16	-3.05	-3.39
0.5	$V^E{}_{\text{exp}}$	-2.30	-3.22	-3.89
0.6	$V^E{}_{\text{exp}}$	-2.23	-3.16	-3.78
0.7	$V^E{}_{\text{exp}}$	-1.96	-2.89	-3.20
0.8	$V^E{}_{\text{exp}}$	-1.63	-2.55	-2.83
0.9	$V^E{}_{\text{exp}}$	-1.03	-1.83	-2.27

Table 4.3: Excess volume of binary systems; of Khana with Shark Baghdad crude at 15, 25 and 30^{o}C

Khana X_2	Excess Volume	Temperature ^oC		
		15^oC	25^oC	30^oC
0.1	$V^E{}_{\text{exp}}$	-0.34	-0.87	-1.66
0.2	$V^E{}_{\text{exp}}$	-0.78	-1.49	-2.36
0.3	$V^E{}_{\text{exp}}$	-1.22	-1.92	-2.92
0.4	$V^E{}_{\text{exp}}$	-1.73	-2.47	-3.31
0.5	$V^E{}_{\text{exp}}$	-2.12	-2.87	-3.80
0.6	$V^E{}_{\text{exp}}$	-2.04	-2.83	-3.72
0.7	$V^E{}_{\text{exp}}$	-1.78	-2.43	-3.16
0.8	$V^E{}_{\text{exp}}$	-1.22	-1.80	-2.64
0.9	$V^E{}_{\text{exp}}$	-0.63	-1.14	-1.95

Table 4.4: Excess volume of binary systems; of Basrah with Shark Baghdad crude at 15, 25 and 30^{o}C

Basrah X_2	Excess Volume	Temperature ^{o}C		
		15^{o}C	**25^{o}C**	**30^{o}C**
0.1	$V^{E}{}_{\exp}$	**-0.29**	**-1.10**	**-1.36**
0.2	$V^{E}{}_{\exp}$	**-0.57**	**-1.32**	**-1.75**
0.3	$V^{E}{}_{\exp}$	**-0.90**	**-1.60**	**-2.16**
0.4	$V^{E}{}_{\exp}$	**-1.45**	**-1.94**	**-2.62**
0.5	$V^{E}{}_{\exp}$	**-1.77**	**-2.16**	**-2.82**
0.6	$V^{E}{}_{\exp}$	**-1.59**	**-2.03**	**-2.70**
0.7	$V^{E}{}_{\exp}$	**-1.25**	**-1.83**	**-2.46**
0.8	$V^{E}{}_{\exp}$	**-0.84**	**-1.39**	**-2.08**
0.9	$V^{E}{}_{\exp}$	**-0.34**	**-0.86**	**-1.72**

If the data in the form of excess volumes are plotted against mass fraction of reference components, smooth curves are obtained as shown in Figures 4.1, 4.2 and 4.3.These curves pass through zero at 0 wt % and 100 wt % reference component, while the maximum excess volume occur at, or close to, mass fraction of 0.5, indicating that V^{E} at this point should be good indicator of the molecular interactions in the mixtures.

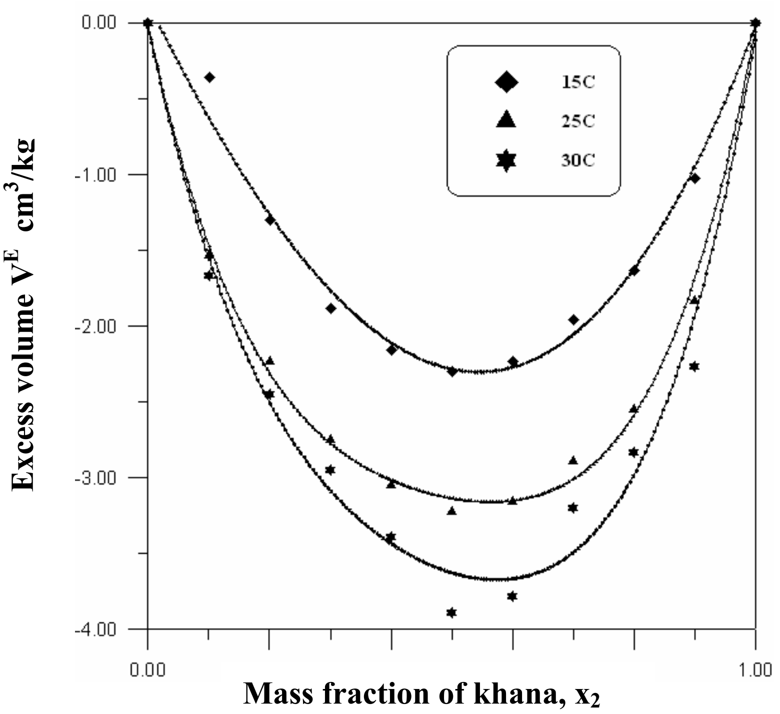

Figure 4.1: Excess volume V^E for Khana with Basrah crude oils

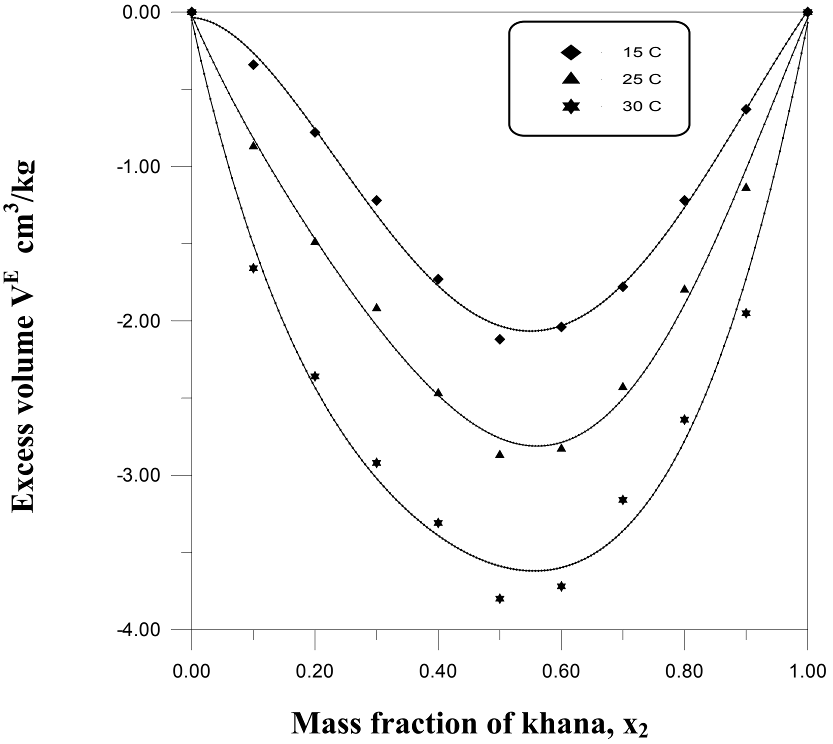

Figure 4.2: Excess volume V^E for Khana with shark Baghdad crude oils

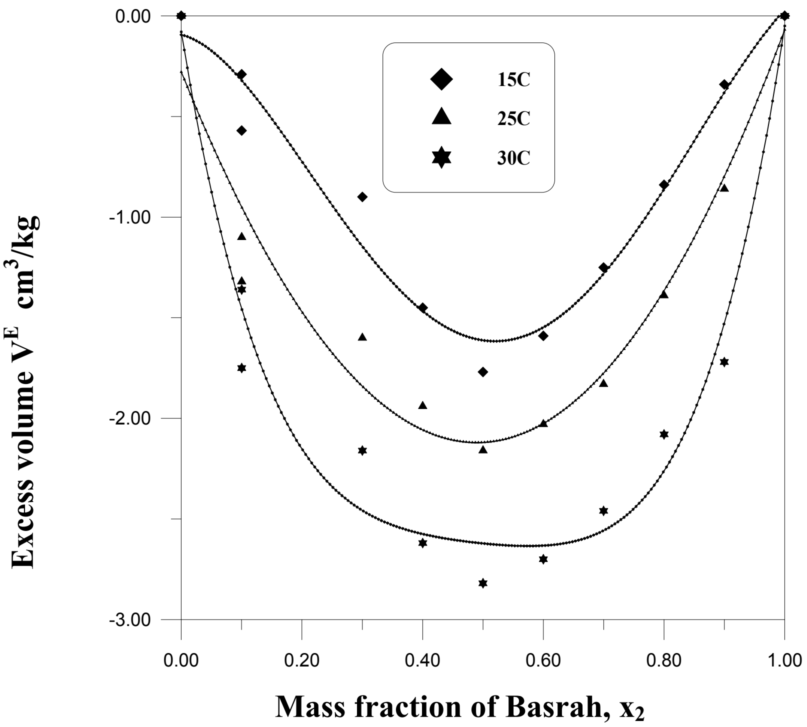

Figure 4.3: Excess volume V^E for shark Baghdad with Basrah crude oils

As shown in figures 4.1 to 4.3 the increase in temperature will decrease the value of V^E of binary crude oils. Negative V^E are obtained over the whole mass fraction range for binary crude oil mixtures at 288, 298, and 303K.

It is generally observed that the blending of light or medium with heavy crude oil results in volume "losses" caused by the non-ideal behavior of this system as compared with the calculated ideal volume. The lighter crude, khana which is considered as paraffinic type, resulted in more shrinkage.

Table 4.5: Excess volumes, in cm^3/kg at 288, 298, and 303 K for a mass fraction of 0.5

Binary mixture of crude-oil	Temperature		
	$V^E_{288\ K}$	$V^E_{298\ K}$	$V^E_{303\ K}$
Khana and Basrah	-2.30	-3.22	-3.89
Khana and shark Baghdad	-2.12	-2.87	-3.80
shark Baghdad and Basrah	-1.77	-2.16	-2.82

Furthermore it appears that the low aromatics crude lead to an increase the negative excess volume, as follows:

$-V^E_{\text{light/medium}} > -V^E_{\text{light/heavy}} > -V^E_{\text{medium/heavy}}$ at different temperatures. As show in Figures 4.4, 4.5 and 4.6.

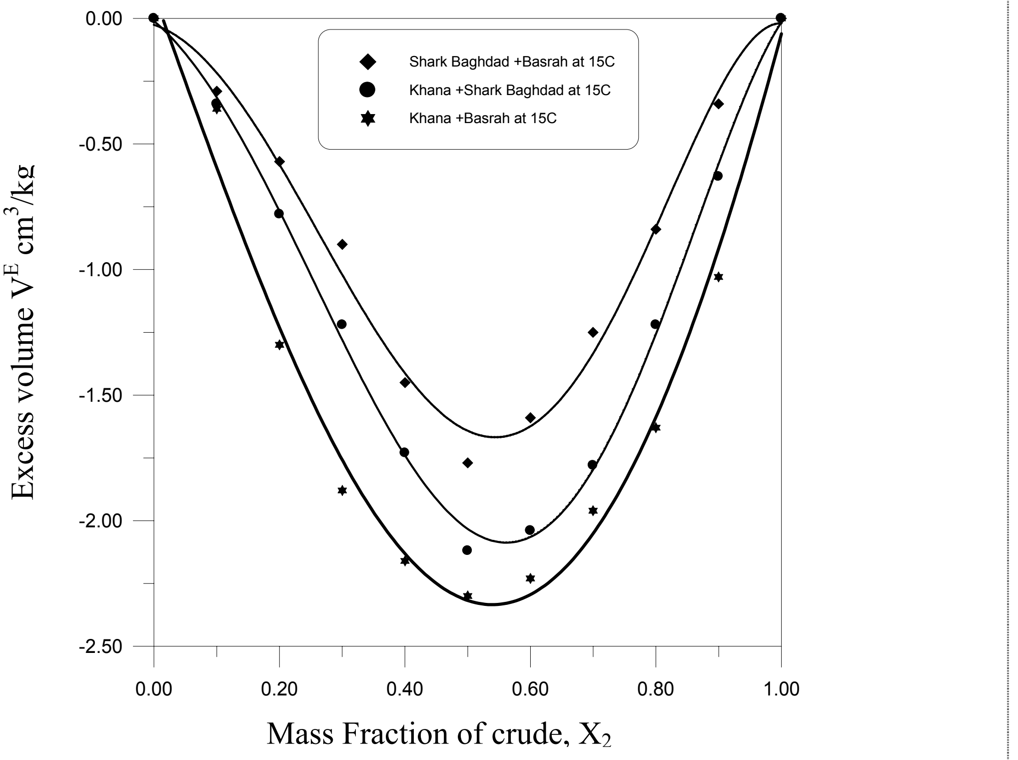

Figure 4.4: Excess volume V^E for Binary mixtures of crude oil at 288 k

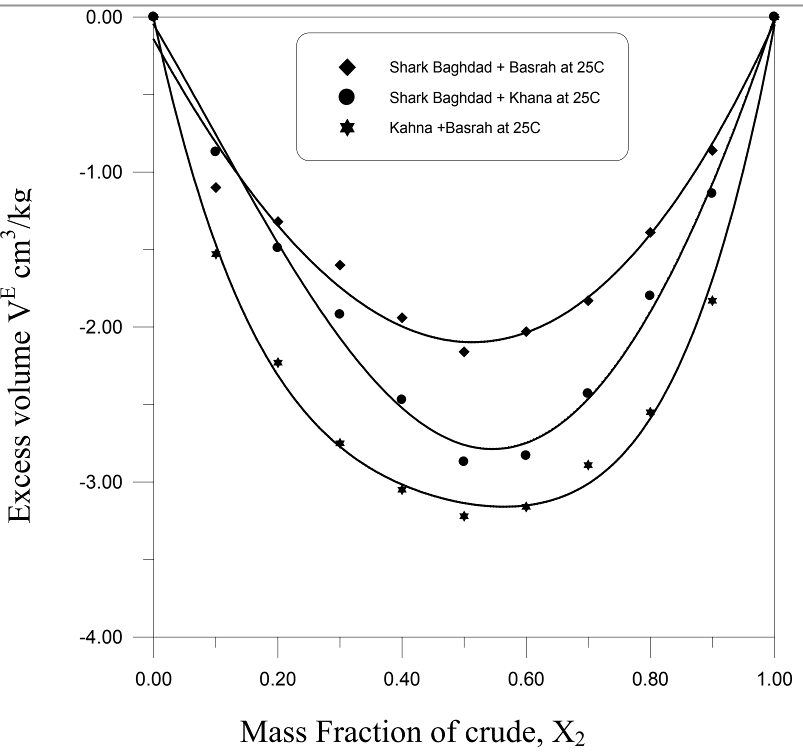

Figure 4.5: Excess volume V^E for Binary mixtures of crude oil at 298 k

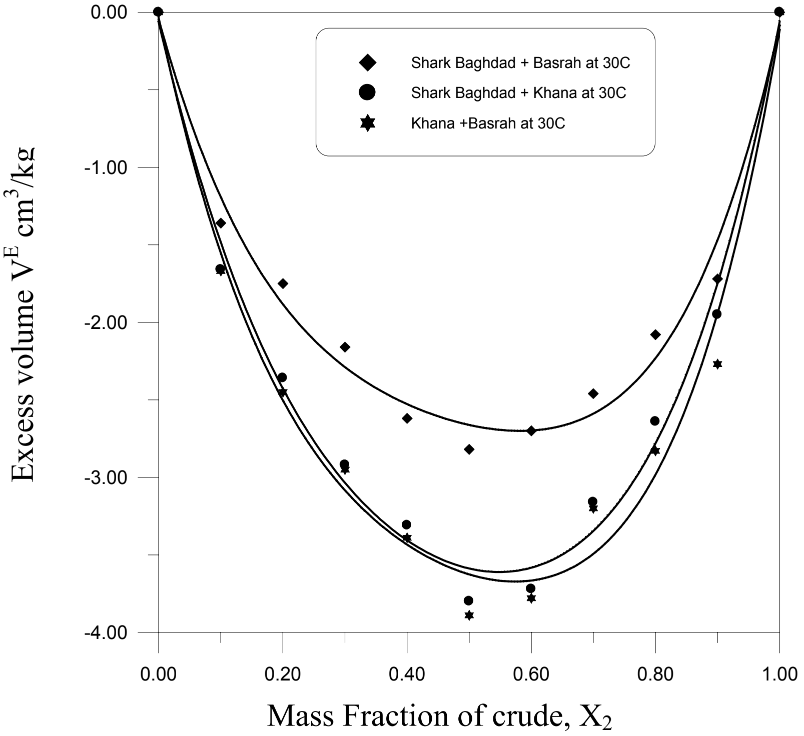

Figure 4.6: Excess volume V^E for Binary mixtures of crude oil at 303 k

4.2 Excess specific volume of crude/spike systems

The three Iraqi crude oils provide a diverse range of gravities, had been blended with a xylene mixture, toluene, kerosene and gas oil. The spiked crude oils have been subjected to density measurements to evaluate the volumetric behavior of these systems. The density data obtained cover the entire composition range from 0 to 100 wt % spike.

The gravities and boiling ranges of the spikes are given in table 4.6.

Table 4.6: Boiling ranges, densities and API gravities of spikes

spikes	Boiling rang, ^0C	Density,kg/m^3	Gravity, ^0API
Toluene	**110**	**864.08**	**32.17**
Xylene mixture	**137-144**	**867.70**	**31.43**
Kerosene	**150-235**	**781.31**	**49.45**
Gas oil	**235-425**	**831.76**	**38.47**

The density data obtained for each crude/spike pairs are reported in the form of excess specific volume V^E at a given mass fraction of spike X_2 as shown in tables 4.7, 4.8 and 4.9.

Table 4.7: Excess volumes V^E, for spiked Khana Crude at 25 ^{0}C

Khana with:				
X_2	**V^E (xylene)**	**V^E (Toluene)**	**V^E (gas oil)**	**V^E (kerosene)**
0.1	0.33	1.82	-2.38	-2.46
0.2	0.61	2.12	-4.35	-5.17
0.3	1.09	2.75	-5.79	-6.54
0.4	1.38	2.96	-6.80	-7.19
0.5	1.41	2.68	-6.38	-7.56
0.6	1.32	2.08	-5.16	-6.92
0.7	1.13	1.81	-4.30	-5.86
0.8	0.75	1.25	-3.21	-4.70
0.9	0.32	0.72	-1.91	-3.26

Table 4.8: Excess volumes V^E, for spiked Basrah Crude at 25 ^{0}C

Basrah with:				
X_2	**V^E (Xylene)**	**V^E (Toluene)**	**V^E (gas oil)**	**V^E (kerosene)**
0.1	0.15	0.05	-1.23	-1.73
0.2	0.25	0.14	-2.41	-3.77
0.3	0.6	0.60	-3.91	-4.75
0.4	0.7	1.01	-4.60	-5.85
0.5	0.8	1.14	-5.25	-6.15
0.6	0.72	1.10	-4.48	-6.18
0.7	0.61	0.96	-3.64	-5.35
0.8	0.4	0.62	-2.29	-3.89
0.9	0.1	0.20	-1.11	-2.40

Table 4.9: Excess volumes V^E, for spiked Shark Baghdad Crude at 25 ^{0}C

Shark Baghdad with:				
X_2	**V^E (xylene)**	**V^E (Toluene)**	**V^E (gas oil)**	**V^E (kerosene)**
0.1	**0.13**	**0.12**	**-1.33**	**-1.97**
0.2	**0.20**	**0.26**	**-2.25**	**-2.87**
0.3	**0.26**	**0.40**	**-2.73**	**-3.85**
0.4	**0.28**	**0.60**	**-3.25**	**-4.53**
0.5	**0.32**	**0.70**	**-3.29**	**-4.81**
0.6	**0.30**	**0.63**	**-2.95**	**-4.65**
0.7	**0.26**	**0.43**	**-2.51**	**-3.80**
0.8	**0.21**	**0.17**	**-2.14**	**-2.81**
0.9	**0.13**	**0.07**	**-1.17**	**-1.70**

If the data in form of specific excess volume are plotted against mass fraction spike, smooth curves are obtained as shown in figures 4.7, 4.8 and 4.9. These curves pass through zero at 0 wt % spike and 100 wt % spikes. The maximum occur at, or close to, mass fraction of 0.5, indicating that $\mathbf{V^E}$ at this point should be a good indicator of the interactions in these systems. Values of excess volume at mass fraction 0.5 of spikes are given in table 4.10

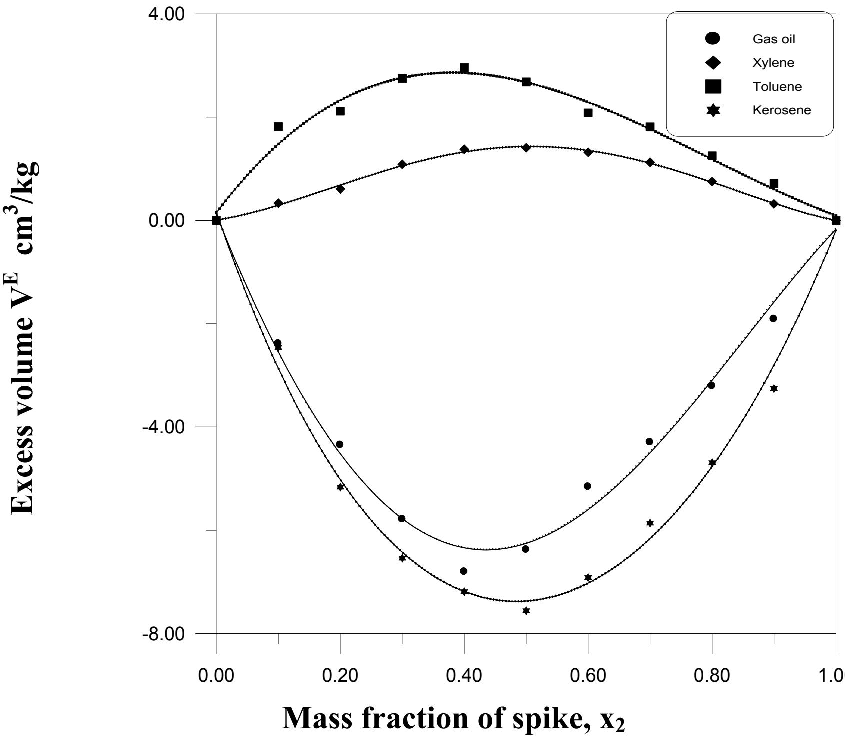

Figure 4.7: Excess volume V^E for spiked light crude (Khana) at $298k$

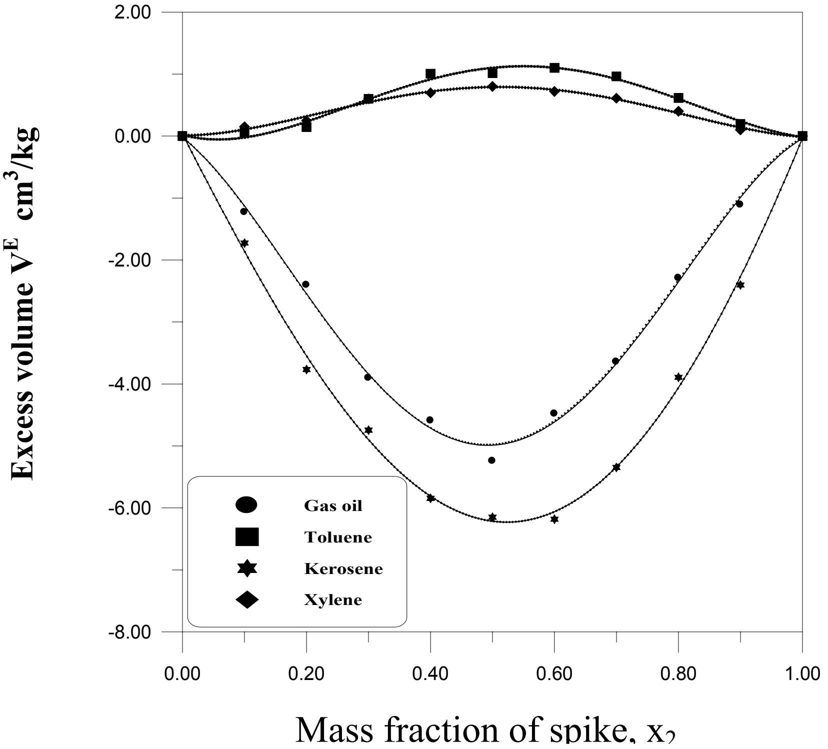

Figure 4.8: Excess volume V^E for spiked medium crude (Basrah) at $298k$

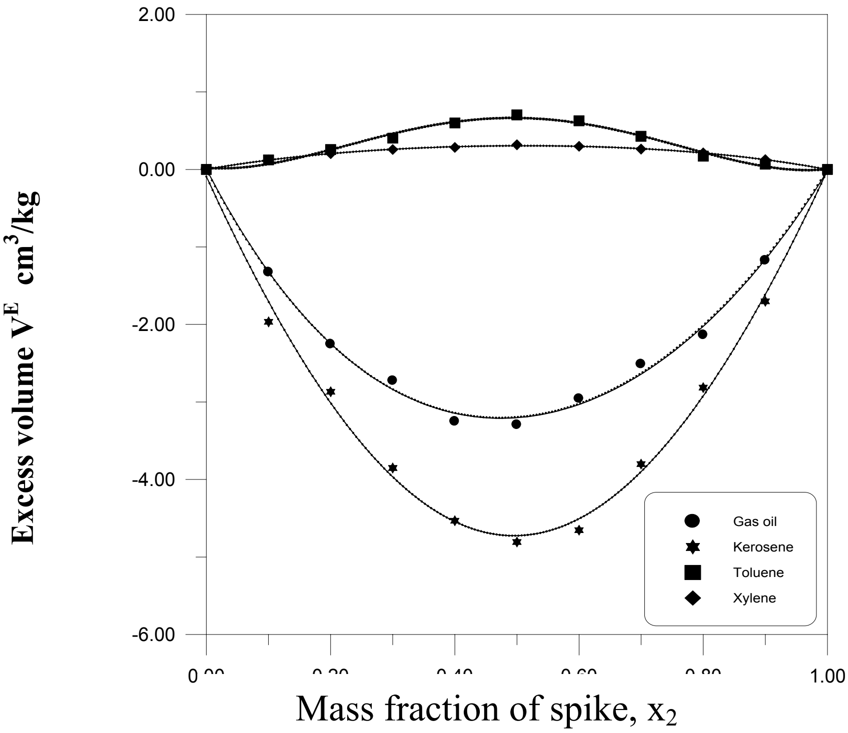

Figure 4.9: Excess volume V^E for spiked heavy crude (Shark Baghdad) at $298k$

Table 4.10: Excess volumes, in cm^3/kg at 298 K for a mass fraction of 0.5 Spike

Crude	$V^E_{298\ K}$ (Toluene)	$V^E_{298\ K}$ (Xylene)	$V^E_{298\ K}$ (Kerosene)	$V^E_{298\ K}$ (Gas oil)
Khana	2.68	1.41	-7.56	-6.38
Basrah	1.14	0.8	-6.15	-5.25
Shark Baghdad	0.70	0.32	-4.81	-3.29

The aromatic spikes, namely xylene mixture and toluene gives a positive V^E for all crude oils indicating that interactions between unlike molecules are weak and give rise to positive deviations. This expansion effect is greatest for the lowest boiling point spike, toluene.

The decrease in the positive excess volume of xylene mixture spiked crude compared with toluene spiked curve is also due to the effect of the additional methyl group in xylenes mixture. Figure 4.10 gives an example for the effect of introducing of methyl group on excess volume, in case of khana crude.

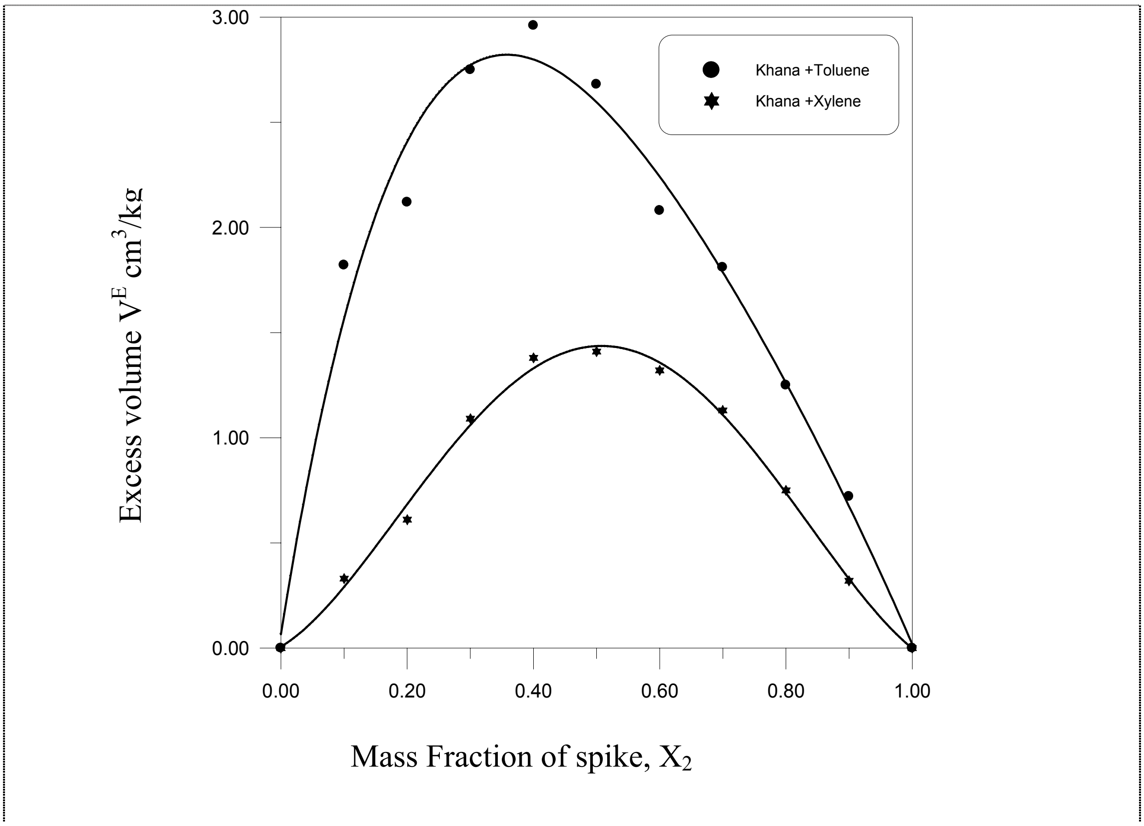

Figure 4.10: Excess volume V^E for Binary mixtures of Khana / aromatic spike at 298 k

As shown in figure 4.11 the API gravity of crude oil has predominate effect on the expansion of aromatic spiked crude oils. Those, khana crude, as a typical light type (44.3 API) gives the maximum positive excess volumes of 2.68 cm^3/kg when spiked with toluene. While the spiked heavy crude, shark Baghdad (24.2 API) resulted in the lowest excess value of 0.7 cm^3/kg.

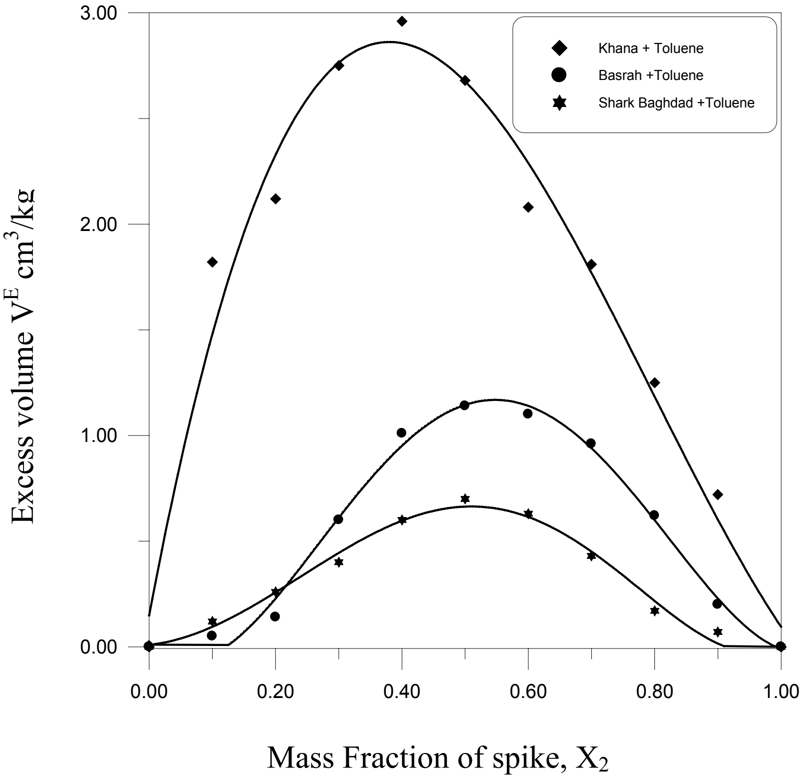

Figure 4.11: Excess volume V^E for Binary mixtures of crude oil/Toluene at 298 K

It is generally observed that the addition of middle petroleum fractions, such as kerosene and gas oil to the three types of crude oils of different API gravities produces negative excess volumes; in other words a small "shrinkage" occurs relative to the calculated ideal volume, as shown in table 4.12

This shrinkage effect is greatest for the lowest –boiling spike, i.e. in case of Khana/Kerosene.

$-V^E_{\text{Khana/kerosene}} > -V^E_{\text{Khana/ gas oil}}$, as shown in Figure 4.12:

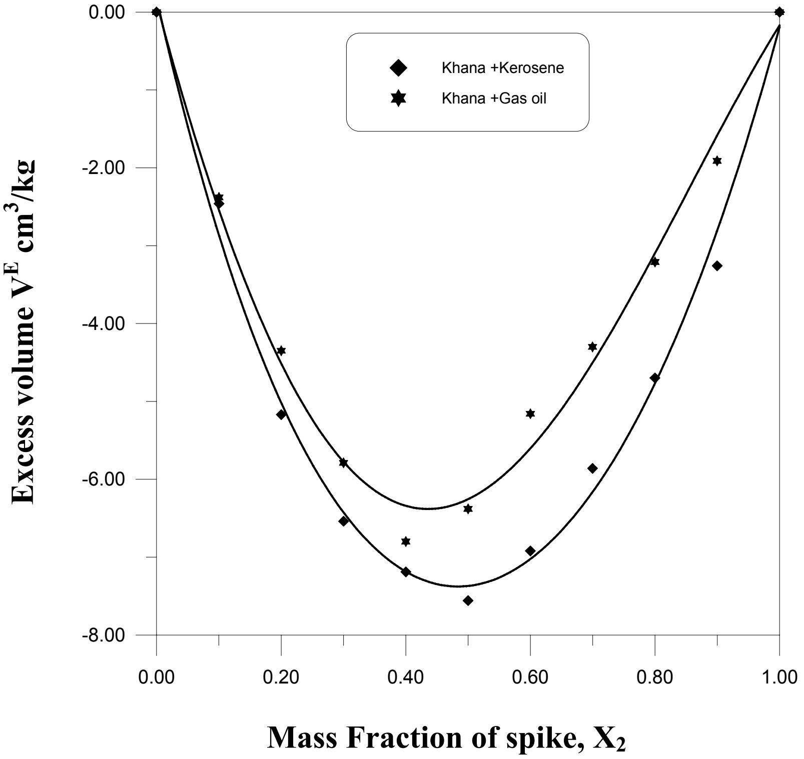

Figure 4.12: Excess volume V^E for Binary mixtures of spiked Khana/with middle distillates at 298 K

The same behavior was obtained when applying Basrah crude middle instead of Khana crude light, where the V^E is less negative than those of Khana, but higher negative than V^E obtained when shark Baghdad crude (heavy) is used. As show in Figures 4.13 and 4.14:

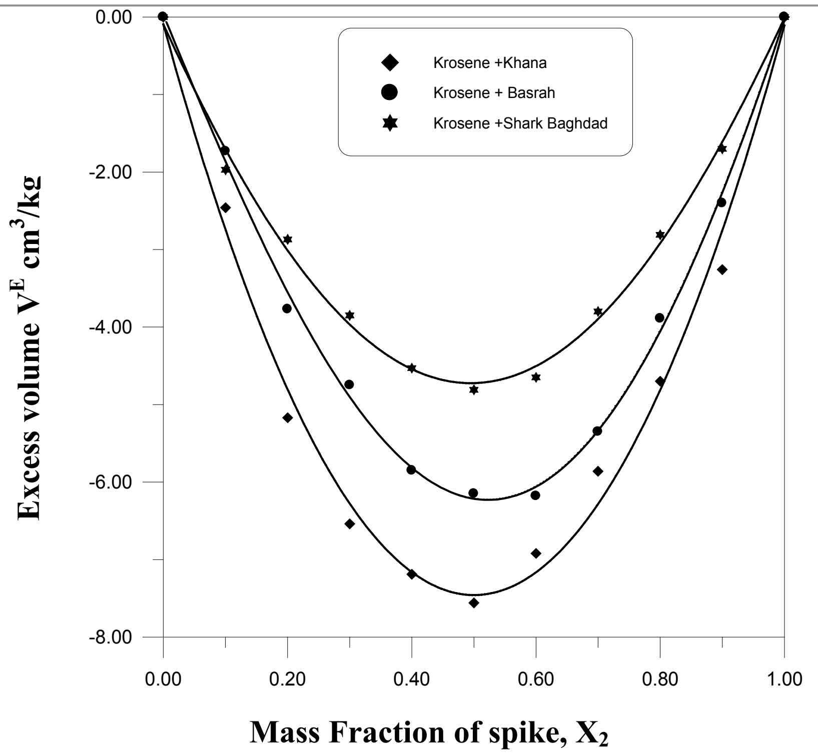

Figure 4.13: Excess volume V^E for Binary mixtures of Crude oil/Kerosene at 298 K

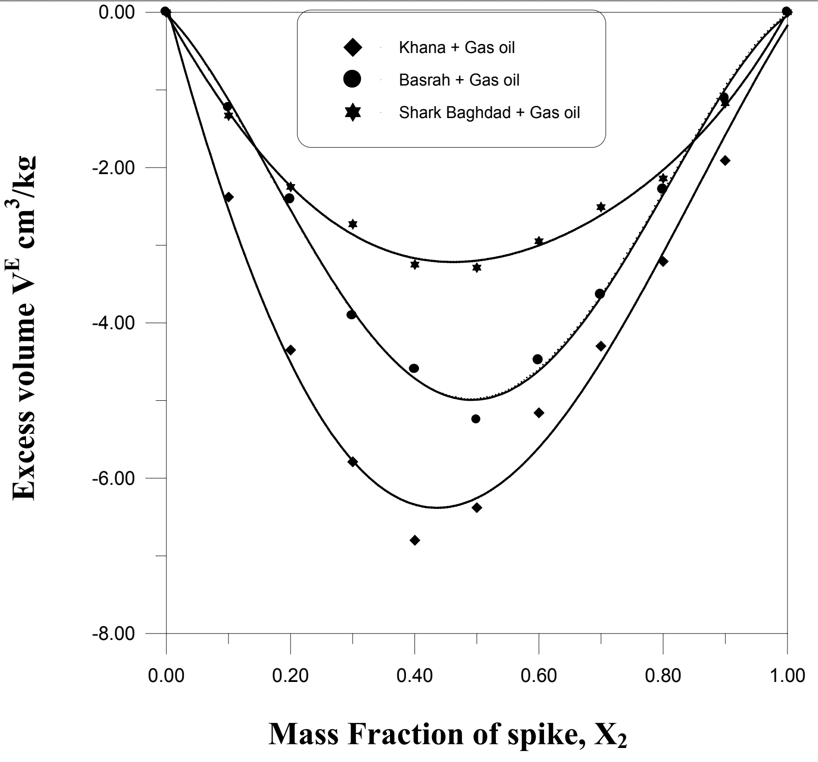

Figure 4.14: Excess volume V^E for Binary mixtures of Crude oil/Gas oil at 298 K

It can be concluded that the gravity of crude oil has an effect of excess volume when the crude was spiked with petroleum fraction. Those, shark Baghdad as typical heavy type (24.2 API) resulted in minimum negative excess volume of -4.81 and -3.29, when it was spiked with the petroleum fraction (Kerosene and Gas Oil respectively), while the spiked light crude, Khana (44.3 API) resulted in maximum negative excess volume of -7.56 and -6.38 respectively.

4.2 Density Correlation of Oil-Stocks

4.2.1 API Standard 2540

Several equations are available in literatures to describe the effect of temperature on oil density. The API standard 2540 is one of the common known method to calculate the crude oil density at any temperature [18].

Hankinson, et al [59] developed a correlation for the thermal expansion, using the following equation:

$$\alpha = \alpha_T + \beta \Delta t \qquad (4\text{-}3)$$

Where:

$\alpha_T = \alpha$ at the base temperature

$\beta =$ a function of α and is independent of temperature

The fundamental definition for the coefficient of thermal expansion α is:

$$\alpha = \frac{1}{v} \cdot \frac{dv}{dt} \qquad (4\text{-}4)$$

Where:

$v =$ Volume at any temperature

Combination of equation 4-3 and 4-4 give:

$$\frac{1}{v}\cdot\frac{dv}{dt}=\alpha_T+\beta\Delta t \tag{4-5}$$

$$\Delta t=t-T \tag{4-6}$$

Which can be rearranged and integrated between t and T to give:

$$\ln_c\frac{V}{V_T}=\alpha_T\Delta t+\frac{\beta}{2}\Delta t^2 \tag{4-7}$$

A study of the NBS data demonstrated that:

$$\beta=K\alpha_T^2 \tag{4-8}$$

Where K is the temperature independent constant, and the best value of K is to be found 1.6. Thus equation 4-7 becomes:

$$VCF=\frac{V_T}{V}=\frac{\rho}{\rho_T}=Exp\left[-\alpha_T\Delta t\left(1+0.8\alpha_T\Delta t\right)\right] \tag{4-9}$$

Where: $t=$any temperature

$T=$base temperature

Equation 4-9 is valid for a particular fluid of known thermal expansion coefficient.

The coefficients of thermal expansion at the base temperature for each group are related to the densities at the base temperature by:

$$\alpha_T=\frac{K_O+K_1\rho_T}{\rho_T^2} \tag{4-10}$$

The values of K_O and K_1 were established for each major group from a simultaneous nonlinear regression of all data pointed within that group. The results and accuracy indicators are presented in table 4.11.

Table 4.11: The constants of equation 4-10

Group	K_O, $^oF^{-1}$	K_1, $^oF^{-1}$	Percent standard deviation
Crude oils	**341.0957**	**0.00**	**0.0253**
Gasolines	**192.4571**	**0.2438**	**0.0266**
Jet fuels	**330.3010**	**0.00**	**0.0174**
Fuel oils	**103.8720**	**0.2701**	**0.0180**
Lubricating oils	**144.0427**	**0.1896**	**0.0197**

The above method is applicable only for single system. An improvement has been done to the above method in order to be applicable for different binary systems crude/crude, crude/fraction, crude/spike and fraction/spike mixtures.

The modified equation of VCF equation 4.11 was obtained by introducing equation 4-10 into equation 4-9.

$$VCF = \frac{V_{15}}{V_{mix}} = \frac{\rho_{mix}}{\rho_{15}} = Exp\left[-\left(K_o + K_1\rho_{15}/\rho_{15}^2\right)\left(1+0.8\left(K_o + K_1\rho_{15}/\rho_{15}^2\right)\right)\left(t-288\right)\right] \tag{4-11}$$

Where: ρ_{mix} = density at any temperature in Kg/m^3.

ρ_{15} = density at base temperature $288K$ ($15\,^0C$) in Kg/m^3

V_{mix} = volume of mixture at any temperature.

V_{15} = volume of mixture at base temperature.

t = any temperature in K.

K_0 and K_1: constants of equation 4-11.

The density of oil-stocks at any temperature was calculated using the density of oil-stocks at 288 $K\,(15^0 C)$ as an initial input to equation 4-11.

This improvement was done by calculating new values for the constants K_0 and K_1 for different temperatures and different mixtures calculated by statistical methods in which all points were weighed equally and summarized in table 4.12 for different crude oil mixtures.

Table 4.12: Smoothing coefficient equation 4-11 for the binary crude mixtures at 25, and 30 ^0C

Crude	Temp.	K0	K1
Khana and Shark Baghdad	**25°C**	**-0.016801**	**19.28907**
	30°C	**-0.038914**	**40.80131**
Basrah and Shark Baghdad	**25°C**	**-0.038042**	**38.59634**
	30°C	**-0.012887**	**17.20341**
Khana and Basrah	**25°C**	**-0.010115**	**13.714**
	30°C	**-0.050684**	**50.3595**

The experimental densities data of binary mixtures of the three crude types are listed in tables 4.13 to 4.15.

Table 4.13: density measurements of binary systems; of Khana with Shark Baghdad cruds at 15, 25 and 30^{o}C

Khana X_2	Density Kg/m^3	Temperature ^oC		
		15^oC	25^oC	30^oC
0.1	ρ_{exp}	901.71	897.35	895.52
0.2	ρ_{exp}	890.93	886.49	884.37
0.3	ρ_{exp}	880.40	875.74	873.39
0.4	ρ_{exp}	870.17	865.34	862.56
0.5	ρ_{exp}	860.09	855.07	852.06
0.6	ρ_{exp}	849.89	844.73	841.40
0.7	ρ_{exp}	839.81	834.38	830.68
0.8	ρ_{exp}	829.76	824.13	820.26
0.9	ρ_{exp}	819.93	814.11	809.98

Table 4.14: density measurements of binary systems; of Khana with Basrah cruds at 15, 25 and 30^{o}C

Khana X_2	Density Kg/m^3	Temperature ^oC		
		15^oC	25^oC	30^oC
0.1	ρ_{exp}	867.13	862.11	860.33
0.2	ρ_{exp}	861.15	855.89	853.78
0.3	ρ_{exp}	854.98	849.61	847.13
0.4	ρ_{exp}	848.70	843.28	840.53
0.5	ρ_{exp}	842.40	836.94	834.08
0.6	ρ_{exp}	836.05	830.55	827.31
0.7	ρ_{exp}	829.66	824.11	820.33
0.8	ρ_{exp}	823.32	817.72	813.61
0.9	ρ_{exp}	816.90	811.17	806.87

Table 4.15: density measurements of binary systems; of Basrah with Shark Baghdad cruds at 15, 25 and 30^{o}C

Basrah X_2	Density Kg/m^3	Temperature ^oC		
		15^oC	25^oC	30^oC
0.1	$\rho_{\exp}$	**909.01**	**904.96**	**903.12**
0.2	$\rho_{\exp}$	**905.19**	**900.95**	**899.32**
0.3	$\rho_{\exp}$	**901.45**	**897.03**	**895.56**
0.4	$\rho_{\exp}$	**897.91**	**893.19**	**891.87**
0.5	$\rho_{\exp}$	**894.22**	**889.29**	**888.01**
0.6	$\rho_{\exp}$	**890.17**	**885.14**	**883.93**
0.7	$\rho_{\exp}$	**886.01**	**880.98**	**879.80**
0.8	$\rho_{\exp}$	**881.85**	**876.68**	**875.59**
0.9	$\rho_{\exp}$	**877.73**	**872.35**	**871.45**

Further testing of the correlated equation 4-11 was carried out by using published experimental density data [25] for some oil-stokes as a binary mixtures. Those binary mixtures are:

1. Crude oils binary mixtures:

Five Iraqi crude oils; Jamboor (33.94 API), Basrah (30.49 API), Kirkuk (29.26 API), Byee-Hassin (25.77 API), and Baghdad (24.35 API) are applicable in equation 4-11 as a binary mixtures .The values of constants K_0 and K_1 are listed in table 4.16.

2. Crude spiked with petroleum fraction

The same Iraqi crude oils with addition Safyia (23.3 API) were mixed with four petroleum fractions; Light naphtha (85.4 API), Heavy naphtha (60.8 API), Kerosene (50.17 API), and Gas oil (41.44 API) are used in equation 4-11 as a binary mixtures .The values of constants K_0 and K_1 are listed in table 4.17.

3. Crude spiked with pure hydrocarbons:

The above six Iraqi crude oils were mixed with five pure hydrocarbons; Cyclohexane (50.82 API), Toluene (32.16 API), n-Hexadecane (51.75 API), n-Heptane (76.21 API), and n-Nonane (66.31 API) are used in equation 4-11 as a binary mixtures .The values of constants K_0 and K_1 are listed in table 4.18.

4. Binary mixtures of petroleum fraction:

The same four petroleum fractions are applicable in equation 4-11 as binary mixtures .The values of constants K_0 and K_1 are listed in table 4.19.

Table A.16: Smoothing coefficient equation 4-11 for the binary crude mixtures at 25, 30, 40 and 50^{0}C

Temperature ^{o}C					
Crudes		**25^{o}C**	**30^{o}C**	**40^{o}C**	**50^{o}C**
Jamboor and Basrah	K0	0.024801	-0.115638	-0.009687	-0.011457
	K1	-15.4026	19.34387	21.89687	-37.3576
Jamboor and Baghdad	K0	-0.01445	-0.070387	-0.02472	-0.016607
	K1	18.29125	-19.6730	34.70754	-32.7566
Basrah and Kirkuk	K0	0.005668	-0.092529	0.014017	-0.053308
	K1	0.099899	0.099786	0.099903	0.099835
Kirkuk and Byee-Hassin	K0	0.005668	-0.092529	0.014017	-0.053308
	K1	0.099899	0.099786	0.099903	0.099835
Kirkuk and Baghdad	K0	0.005687	-0.092261	0.013599	-0.053029
	K1	0.0999	0.099787	0.099904	0.099836

Table A.17: Smoothing coefficient equation 4-11 for the crude-fraction systems at 25^{o}C

Crude		Light naphtha	Heavy naphtha	Kerosene	Gas oil
Jamboor	K_o		-0.115686		
	K_1		-13.9734		
Basrah	K_o		-0.119781		
	K_1		-10.9231		
Kirkuk	K_o	-0.112365	-0.112685		
	K_1	-15.8811	-16.2127		
Byee-Hassin	K_o	-0.109306	-0.112163	-0.104077	-0.12212
	K_1	-18.8792	-16.5743	-23.8858	-7.53607
Baghdad	K_o	-0.112233	-0.114695		
	K_1	-16.4644	-14.664		
Safyia	K_o		-0.113943	-0.109977	-0.128507
	K_1		-15.2706	-19.2499	-2.1961

Table A.18: Smoothing coefficient equation 4-11 for the crude-spike systems at $25^o C$

Crude		Cyclohexane	Toluene	n-Heptane	n-Nonane	n-Hexadecane
Jamboor	K_o					-0.118026
	K_1					-11.9584
Basrah	K_o			-0.116651	-0.11723	
	K_1			-13.6654	-13.2102	
Kirkuk	K_o		0.172751	-0.112484		
	K_1		-268.085	-16.3072		
Byee-Hassin	K_o	-0.098031	-0.374412			-0.228074
	K_1	-29.519	208.3301			73.68964
Baghdad	K_o			-0.112211	-0.11241	-0.11638
	K_1			-16.7862	-16.8059	-13.1520
Safyia	K_o	-0.101891	0.077355			
	K_1	-26.0757	-185.273			

Table A.19: Smoothing coefficient equation 4-11 for binary combination system of petroleum fraction mixture at $25^o C$

Petroleum fraction pairs	K_o	K_1
LN & HN	-0.112708	-16.1852
LN & KER	-0.119447	-11.7596
HN & KER	-0.131996	-1.87539
KER & GO	-0.059223	53.87264

4.2.2 Prediction equation of Volume Correction Factor (VCF)

Although a number of graphical and mathematical methods had been published to suggest a way to estimate the density of crude oils and there fractions when no experimental data are available most of them suffer various shortcomings.

One of the objectives of the present work was to extend the application of density/volume prediction techniques to include different type of mixtures of different oil-stocks.

It was therefore suggested to find the final relationship between density, temperature and composition by introducing the mass fraction X of lighter density compound into equation 4-11 and modify it mathematically to become equation 4-12.

$$VCF = \left[A_o + \frac{A_1(\rho_{15} X)}{(t-288)} + \frac{A_2(\rho_{15} X)^{A_3}}{(t-288)^{A_4}} \right] \tag{4.12}$$

Where: $t =$ any temperature in K.

$T =$ base temperature equal to288 K.

$VCF =$ Volume Correction Factor.

As in equation 4-11:

$$VCF = \frac{V_{15}}{V_{mix}} = \frac{\rho_{mix}}{\rho_{15}}$$

Then

$$VCF = \frac{V_{15}}{V} = \frac{\rho}{\rho_{15}} = \left[A_o + \frac{A_1(\rho_{15} X)}{(t-288)} + \frac{A_2(\rho_{15} X)^{A_3}}{(t-288)^{A_4}} \right] \tag{4.13}$$

From equation 4-13 resulted equation 4-14:

$$\rho_{mix} = \rho_{15}.VCF \tag{4.14}$$

Combination of equation 4-14 and equation 4-12 can be developed to get the overall density predicating equation for oil mixtures in general, over a whole composition range and at various temperature for different mixtures, resulting equation 4-15:-

$$\rho_{mix} = \rho_{15}\left[A_o + \frac{A_1(\rho_{15}X)}{(t-288)} + \frac{A_2(\rho_{15}X)^{A_3}}{(t-288)^{A_4}} \right] \tag{4.15}$$

Where: X= mass fraction of lighter density compound.

A_0, to A_4= constants of equation 4-15.

Equation 4-15 contains four variables, density at $288K$, density at any temperature, composition, and the temperature, when three of them are known, then the four variables could be calculated. The density of oil-stocks at any temperature was calculated using the density of oil-stocks at 288 K (15^0C) as an initial input to equation 4-15. The following systems were considered for predicting the densities from which suitable results of excess volume could be obtained.

- Crude oil binary mixtures.
- Crude oil with pure component.
- Crude oil with petroleum fraction.
- Binary Petroleum fraction.

Values of the parameters ($A_0$to A4) in equation 4-15 were calculated by statistical methods in which all points were weighed equally. The values are summarized in table 4.23 for crude oil mixture.

Table 4.20: Smoothing coefficient equation 4-15 for the binary crude mixtures at 25, and 30 ^0C

Crude	Temp.	A0	A1	A2	A3	A4
Khana and Shrak Baghdad	25°C	0.652214	-0.000046	0.644328	0.001074	0.275453
	30°C	0.863596	-0.00015	0.866040	0.004321	0.706232
Basrah and Shrak Baghdad	25°C	0.833427	-0.000016	0.844074	-0.001636	0.712853
	30°C	0.851783	-0.000016	0.796547	-0.000099	0.636938
Khana and Basrah	25°C	0.62896	-0.000009	0.617443	-0.000672	0.226643
	30°C	0.850381	-0.000103	0.829409	0.000499	0.651785

Further testing of the proposed modified equation 4-15 was carried out by using published experimental density data [25] for some oil-stokes. Those binary mixtures are:

1. **Crude oils binary mixtures:**

Five Iraqi crude oils; Jamboor (33.94 API), Basrah (30.49 API), Kirkuk (29.26 API), Byee-Hassin (25.77 API), and Baghdad (24.35 API) are applicable in equation 4-15 as a binary mixtures .the values of constants are listed in table 4.21.

2. Crude spiked with petroleum fraction

The same Iraqi crude oils with addition Safyia (23.3 API) were mixed with four petroleum fractions; Light naphtha (85.4 API), Heavy naphtha (60.8 API), Kerosene (50.17 API), and Gas oil (41.44 API) are applied in equation 4-15 as a binary mixtures. The values of constants are listed in table 4.22.

3. Crude spiked with pure hydrocarbons:

The above six Iraqi crude oils were mixed with five pure hydrocarbons; Cyclohexane (50.82 API), Toluene (32.16 API), n-Hexadecane (51.75 API), n-Heptane (76.21 API), and n-Nonane (66.31 API) are applied in equation 4-15 as a binary mixtures. The values of constants are listed in table 4.23.

4. Binary mixtures of petroleum fraction:

The same four petroleum fractions are applicable in equation 4-15 as binary mixtures to calculate densities with average absolute percent error are listed in appendix A table A.36 to A.39. The values of constants are listed in table 4.24.

Table A.21: Smoothing coefficient equation 4-15 for the binary crude mixtures at 25, 30, 40 and 50 ^{0}C

Temperature ^{o}C					
Crudes		25^{o}C	30^{o}C	40^{o}C	50^{o}C
Jamboor and Basrah	A0	0.785611	0.643166	0.585502	0.572376
	A1	0.000003	0.000008	-0.000032	-0.000086
	A2	0.822731	0.455731	0.415101	0.523057
	A3	0.000302	0.000163	0.00025	0.000296
	A4	0.600447	0.102686	0.015945	0.075586
Jamboor and Baghdad	A0	0.755867	0.56575	0.86009	0.524011
	A1	-0.000019	-0.000043	-0.000164	-0.000266
	A2	0.678457	0.42134	0.17649	0.500146
	A3	0.000638	0.000919	0.007387	0.002262
	A4	0.455737	-0.001385	0.122678	0.031762
Basrah and Kirkuk	A0	0.522476	0.810517	0.791065	0.713995
	A1	-0.000005	-0.000005	-0.000017	-0.00004
	A2	0.0467457	0.881616	0.676005	0.389265
	A3	-0.000062	0.000229	0.000293	-0.000008
	A4	-0.004116	0.587977	0.392706	0.112564
Kirkuk and Byee-Hassin	A0	0.807149	0.609002	0.646602	0.556971
	A1	-0.000008	-0.00007	-0.000029	-0.000071
	A2	0.000192	0.544459	0.414708	0.550862
	A3	0.67547	0.000208	0.000522	0.000442
	A4	0.885641	0.132087	0.066369	0.078208
Kirkuk and Baghdad	A0	0.77499	0.576108	0.648632	0.545420
	A1	-0.000005	-0.00002	-0.000081	-0.000124
	A2	0.762079	0.501888	0.330322	0.524236
	A3	0.000175	0.000667	0.002057	0.001745
	A4	0.541666	0.071844	-0.001048	0.057987

Table A.22: Smoothing coefficient equation 4-15 for the crude-fraction systems at $25^{o}C$

Crude		Light naphtha	Heavy naphtha	Kerosene	Gas oil
Jamboor	A_o		0.767764		
	A_1		-0.000079		
	A_2		0.992947		
	A_3		0.0061		
	A_4		0.657139		
Basrah	A_o		0.732635		
	A_1		-0.000048		
	A_2		0.663345		
	A_3		0.00149		
	A_4		0.409910		
Kirkuk	A_o	0.571314	0.739903		
	A_1	-0.000156	-0.00006		
	A_2	0.431393	0.704282		
	A_3	0.002358	0.000785		
	A_4	0.011637	0.444519		
Byee-Hassin	A_o	0.722102	0.81406	0.731667	0.783692
	A_1	-0.000163	-0.000066	-0.00006	-0.000013
	A_2	0.786947	0.875694	0.631604	0.786073
	A_3	0.003515	0.0001197	0.000535	0.0004
	A_4	0.466439	0.688576	0.382054	0.572746
Baghdad	A_o	0.827688	0.82082		
	A_1	-0.000168	-0.000052		
	A_2	0.882651	0.890895		
	A_3	0.008317	-0.000497		
	A_4	0.737976	0.709975		
Safyia	A_o	0.803087	0.708265	0.63965	0.967155
	A_1	-0.00009	-0.00094	-0.00005	-0.000004
	A_2	0.931324	0.621332	0.396279	0.016069
	A_3	0.003405	0.004457	0.000024	0.00072
	A_4	0.693603	0.346047	0.048734	-0.218934

Table A.23: Smoothing coefficient equation 4-15 for the crude-spike systems at 25^{o}C

Crude		Cyclohexane	Toluene	n-Heptane	n-Nonane	n-Hexadecane
Jamboor	A_o					**0.733149**
	A_1					**-0.00002**
	A_2					**0.646096**
	A_3					**-0.000175**
	A_4					**0.395705**
Basrah	A_o			**0.810906**	**0.729332**	
	A_1			**-0.000055**	**-0.000061**	
	A_2			**0.953311**	**0.645476**	
	A_3			**-0.002052**	**0.001191**	
	A_4			**0.716007**	**0.391986**	
Kirkuk	A_o		**0.729462**	**0.773204**		
	A_1		**-0.000053**	**-0.000082**		
	A_2		**0.662536**	**0.749961**		
	A_3		**-0.000075**	**-0.000065**		
	A_4		**0.399122**	**0.530782**		
Byee-Hassin	A_o	**0.795534**	**0.835797**			**0.757058**
	A_1	**-0.000086**	**0.000187**			**0.000255**
	A_2	**0.903422**	**1.090625**			**0.778458**
	A_3	**0.002384**	**-0.000216**			**-0.002725**
	A_4	**0.661903**	**0.900173**			**0.552123**
Baghdad	A_o			**0.765303**	**0.887017**	**0.772358**
	A_1			**-0.000119**	**-0.000102**	**-0.000035**
	A_2			**0.787172**	**0.05121**	**0.813721**
	A_3			**0.002250**	**0.008614**	**-0.000148**
	A_4			**0.539710**	**-0.303074**	**0.564506**
Safyia	A_o		**0.817124**			
	A_1		**-0.000132**			
	A_2		**0.888509**			
	A_3		**0.000607**			
	A_4		**0.686977**			

Table A.24: Smoothing coefficient equation 4-15 for binary combination system of petroleum fraction mixture at 25^oC

Petroleum fraction pairs	A_o	A_1	A_2	A_3	A_4
LN & HN	**0.78585**	**-0.00005**	**0.91473**	**0.000305**	**0.652209**
LN & KER	**0.599420**	**-0.000052**	**0.726441**	**0.000194**	**0.269848**
HN & KER	**0.628224**	**-0.000005**	**0.399694**	**0.000202**	**0.000202**
KER & GO	**0.623981**	**-0.000046**	**0.421598**	**0.000174**	**0.057717**

Referring to API standard equation new equation new equation of state with introducing a parameter for the effect of the light substance composition was proposed to evaluate ρ. They were examined using random data, and they gave different R. The best equation (with maximum $R = 0.985$) was set to be the finally proposed one which is:

$$\rho_{mix} = \rho_{15}\left[-8.24 + \frac{-0.000082(\rho_{15}X)}{(t-288)} + \frac{9.27(\rho_{15}X)^{0.000165}}{(t-288)^{0.00194}}\right] \qquad \text{4-15*}$$

A set of random experimental data of crude oil only to equation above from which the constants A_o, A_1, A_3, and A_4 were obtained with an acceptable R of (0.985). These constants were examined against the remaining experimental data consist of crude, fraction, and pure component mixtures in order to evaluate the accuracy of the new correlation. They new correlation satisfies the experimental data\ with an average absolute present error of 0.305%. The new equation shows accurate results for range of temperature 15-50^{o}C.

It was also found that it is very important to introduce the effect of mass fraction in calculating the excess volume, which gives a priority to equation 4-15 over equation 4-11.

In order to get high applicability of equation 4-15*, effort was to achieve constants that fit all different types of binary mixtures of all systems; the constants obtained give a high acceptable accuracy method. The general constants are listed in table 4.25.

Table 4.25: constants parameters of equation 4-15*

A_0	A_1	A_2	A_3	A_4
-8.24	**-0.000082**	**9.27**	**0.000165**	**0.00194**

The modified method was subjected to experimental data, and the results obtained by using equation 4-15* at constant parameters as shown in table 4.25 were highly accurate to calculate the crude mixture densities, as shown in table 4.26 to 4.28. The overall average absolute present error is 0.185 for 54 data point.

Table 4.26: Comparisons between measured and predicted densities of binary systems; of Khana with Basrah cruds at 25 and 30^{o}C, ρ_{calc2} by equation 4-15* at constant parameter in table 4.25.

Khana	Density	Temperature		Av. Abs.
X_2	Kg/m^3	298 k (25 $^{\circ}C$)	303 k (30 $^{\circ}C$)	% error
0.1	$\rho_{\exp}$	862.11	860.33	
	ρ_{calc2}	862.59	856.50	0.25
0.2	$\rho_{\exp}$	855.89	853.78	
	ρ_{calc2}	856.94	851.09	0.22
0.3	$\rho_{\exp}$	849.61	847.13	
	ρ_{calc2}	850.73	845.12	0.18
0.4	$\rho_{\exp}$	843.28	840.53	
	ρ_{calc2}	844.26	838.89	0.16
0.5	$\rho_{\exp}$	836.94	834.08	
	ρ_{calc1}	837.72	832.57	0.14
0.6	ρ_{calc2}	830.55	827.31	
	ρ_{calc2}	831.07	826.14	0.10
0.7	$\rho_{\exp}$	824.11	820.33	
	ρ_{calc2}	824.36	819.65	0.06
0.8	$\rho_{\exp}$	817.72	813.61	
	ρ_{calc2}	817.70	813.20	0.03
0.9	$\rho_{\exp}$	811.17	806.87	
	ρ_{calc2}	810.94	806.65	0.03
Av. Abs. % error				
	ρ_{calc2}	0.072	0.186	

Table 4.27: Comparisons between measured and predicted densities of binary systems; of Shark Baghdad with Khana cruds at 25 and 30^{o}C, ρ_{calc2} by equation 4-15* at constant parameter in table 4.25.

Khana X_2	Density Kg/m^3	Temperature ^{o}C		Av. Abs. % error
		298 k (25^{o}C)	303 k (30^{o}C)	
0.1	ρ_{exp}	897.35	895.52	
	ρ_{calc2}	897.03	890.70	0.29
0.2	ρ_{exp}	886.49	884.51	
	ρ_{calc2}	886.58	880.55	0.22
0.3	ρ_{exp}	875.74	873.58	
	ρ_{calc2}	876.01	860.11	0.20
0.4	ρ_{exp}	865.34	862.78	
	ρ_{calc2}	865.60	870.25	0.16
0.5	ρ_{exp}	855.07	852.11	
	ρ_{calc2}	855.27	850.03	0.13
0.6	ρ_{exp}	844.73	841.44	
	ρ_{calc2}	844.79	839.80	0.10
0.7	ρ_{exp}	834.38	830.82	
	ρ_{calc2}	834.42	829.67	0.06
0.8	ρ_{exp}	824.13	820.26	
	ρ_{calc2}	824.07	819.55	0.05
0.9	ρ_{exp}	814.11	809.09	
	ρ_{calc2}	813.94	809.63	0.03
Av. Abs. % error	ρ_{HPT}	0.290615	0.752142	
	ρ_{calc2}	0.02	0.25	

Table 4.28: Comparisons between measured and predicted densities of binary systems; of Shark Baghdad with Basrah cruds at 25 and 30^{o}C, ρ_{calc2} by equation 4-15*at constant parameter in table 4.25.

Khana X_2	Density Kg/m^3	Temperature ^oC		Av. Abs. % error
		298 k (25 ^oC)	303 k (30 ^oC)	
0.1	$\rho_{\exp}$	904.96	903.12	
	ρ_{calc2}	904.29	897.92	0.32
0.2	$\rho_{\exp}$	900.95	899.32	
	ρ_{calc2}	900.77	894.65	0.27
0.3	$\rho_{\exp}$	897.03	895.56	
	ρ_{calc2}	896.94	891.06	0.26
0.4	$\rho_{\exp}$	893.19	891.87	
	ρ_{calc2}	893.15	887.51	0.25
0.5	$\rho_{\exp}$	889.29	888.01	
	ρ_{calc2}	889.14	883.74	0.25
0.6	$\rho_{\exp}$	885.14	883.93	
	ρ_{calc2}	884.71	879.55	0.27
0.7	$\rho_{\exp}$	880.98	879.80	
	ρ_{calc2}	880.16	875.23	0.31
0.8	$\rho_{\exp}$	876.67	875.59	
	ρ_{calc2}	875.59	870.88	0.33
0.9	$\rho_{\exp}$	872.35	871.45	
	ρ_{calc2}	871.03	866.55	0.36
Av. Abs. % error	ρ_{HPT}	0.715264	1.172389	
	ρ_{calc2}	0.06	0.52	

Further testing of the proposed modified equation 4-15* was carried out by using published experimental density data [25] for some oil-stokes. Those binary mixtures are:

1. Crude oils binary mixtures:

Five Iraqi crude oils; Jamboor (33.94 API), Basrah (30.49 API), Kirkuk (29.26 API), Byee-Hassin (25.77 API), and Baghdad (24.35 API) are applicable in equation 4-15* as a binary mixtures to calculate densities with average absolute percent error are listed in appendix A tables A.1 to A.5. The overall average absolute percent error is 0.168 for 100 data points.

5. Crude spiked with petroleum fraction

The same Iraqi crude oils with addition Safyia (23.3 API) were mixed with four petroleum fractions; Light naphtha (85.4 API), Heavy naphtha (60.8 API), Kerosene (50.17 API), and Gas oil (41.44 API) are applied in equation 4-15* as a binary mixtures to calculate densities with average absolute percent error are listed in appendix A table A.6 to A.18. The overall average absolute percent error is 0.286 for 78 data points.

6. Crude spiked with pure hydrocarbons:

The above six Iraqi crude oils were mixed with five pure hydrocarbons; Cyclohexane (50.82 API), Toluene (32.16 API), n-Hexadecane (51.75 API), n-Heptane (76.21 API), and n-Nonane (66.31 API) are applied in equation 4-15* as a binary mixtures to calculate densities with average absolute percent error are listed in appendix A table A.19 to A.31. The overall average absolute percent error is 0.43 for 78 data points.

7. Binary mixtures of petroleum fraction:

The same four petroleum fractions are applicable in equation 4-15 as binary mixtures to calculate densities with average absolute percent error are listed in appendix A table A.32 to A.35. The overall average absolute percent error is 0.475 for 20 data points.

The predicted densities using the proposed method are summarized and compared in table 4.29 for the considered oil-stock systems. It seen that the method presented in this study produces an overall average absolute error of 0.305% for all considered oil-stock systems (330 points). The maximum deviation in densities 0.475% was obtained for Crude/spike, probably due to those wide range densities.

Table 4.29: comparisons of error for density prediction by equation 4-15*

No.	Mixture type	No. of point	A.A% E	Detailed tables in appendix A
1	Crude+ Crude	100	0.168	A. 1 - A.5
2	Crude+fraction	78	0.286	A.6 - A.18
3	Crude+fraction	78	0.43	A.19 - A.31
4	Fraction+spike	20	0.475	A.32 - A.35
5	All systems	330	0.305	-

4.3.3 A Generalized Equation of State

Hankinson-Brobst- Thomson (HBT) recommended the Costald equation of state for liquid density calculations for various pure compounds and mixtures and claimed high accuracy for their procedures [18]. They presented various equations for estimating volumes or densities of liquids, which could be divided into two groups, those for saturated liquids, and for compressed liquids. The five parameters of equation 2-11 are based on critical pressure, critical temperature, a centric factor and characteristic volume, which must be correlated as function oil densities at $\mathbf{15^{o}C}$.

J. Shanshool and E. T. Hashim tested the Hankinson-Brobst-Thomson techniques on different binary crude oils and fractions. The results obtained shown to be very acceptable [25].

The modified HBT correlation equation 2-41 was used to predict the densities of binary mixtures for the three different origins of Iraqi crude oils. The calculated densities were also compared with those data obtained by the previously proposed equation 4-15*. The results are listed in tables 4.30, 4.31, and 4.32 for crude oils Khana ($API^{O} =$ 44.3)/ Basrah ($API^{O} =$31.4), Shark Baghdad ($API^{O} =$24.2)/ Khana, and Shark Baghdad/ Basrah respectively at $25^{o}C$ and $30^{o}C$. From which the accuracy of the proposed methods was much higher than the modified HBT correlation.

Table 4.30: Comparisons between measured and predicted densities of binary systems; of Khana with Basrah cruds at 25 and 30^{o}C, ρ_{calc2} by equation 4-15* .

Khana X_2	Density Kg/m^3	Temperature		Av. Abs. % error
		298 k (25 ^oC)	303 k (30 ^oC)	
0.1	$\rho_{\exp}$	862.11	860.33	
	ρ_{HPT}	855.23	849.80	1.02
	ρ_{calc2}	862.59	856.50	0.25
0.2	$\rho_{\exp}$	855.89	853.78	
	ρ_{HPT}	849.12	843.38	1.01
	ρ_{calc2}	856.94	851.09	0.22
0.3	$\rho_{\exp}$	849.61	847.13	
	ρ_{HPT}	842.84	836.78	1.02
	ρ_{calc2}	850.73	845.12	0.18
0.4	$\rho_{\exp}$	843.28	840.53	
	ρ_{HPT}	836.38	829.99	1.04
	ρ_{calc2}	844.26	838.89	0.16
0.5	$\rho_{\exp}$	836.94	834.08	
	ρ_{HPT}	829.74	822.98	1.1
	ρ_{calc1}	837.72	832.57	0.14
0.6	ρ_{calc2}	830.55	827.31	
	ρ_{HPT}	822.89	815.75	1.17
	ρ_{calc2}	831.07	826.14	0.10
0.7	$\rho_{\exp}$	824.11	820.33	
	ρ_{HPT}	815.82	808.28	1.25
	ρ_{calc2}	824.36	819.65	0.06
0.8	$\rho_{\exp}$	817.72	813.61	
	ρ_{HPT}	808.5274	800.54	1.38
	ρ_{calc2}	817.70	813.20	0.03
0.9	$\rho_{\exp}$	811.17	806.87	
	ρ_{HPT}	800.998	792.53	1.53
	ρ_{calc2}	810.94	806.65	0.03
Av. Abs. % error	ρ_{HPT}	0.930204	1.388811	
	ρ_{calc2}	0.072	0.186	

Table 4.31: Comparisons between measured and predicted densities of binary systems; of Shark Baghdad with Khana cruds at 25 and 30^{o}C, ρ_{calc2} by equation 4-15* .

Khana X_2	Density Kg/m^3	Temperature ^oC		Av. Abs. % error
		298 k (25^oC)	303 k (30^oC)	
0.1	ρ_{exp}	897.35	895.52	
	ρ_{HPT}	893.78	887.99	0.62
	ρ_{calc2}	897.03	890.70	0.29
0.2	ρ_{exp}	886.49	884.51	
	ρ_{HPT}	884.64	878.62	0.44
	ρ_{calc2}	886.58	880.55	0.22
0.3	ρ_{exp}	875.74	873.58	
	ρ_{HPT}	875.09	868.82	0.31
	ρ_{calc2}	876.01	860.11	0.20
0.4	ρ_{exp}	865.34	862.78	
	ρ_{HPT}	865.10	858.55	0.26
	ρ_{calc2}	865.60	870.25	0.16
0.5	ρ_{exp}	855.07	852.11	
	ρ_{HPT}	854.62	847.77	0.28
	ρ_{calc2}	855.27	850.03	0.13
0.6	ρ_{exp}	844.73	841.44	
	ρ_{HPT}	843.62	836.43	0.36
	ρ_{calc2}	844.79	839.80	0.10
0.7	ρ_{exp}	834.38	830.82	
	ρ_{HPT}	832.03	824.48	0.52
	ρ_{calc2}	834.42	829.67	0.06
0.8	ρ_{exp}	824.13	820.26	
	ρ_{HPT}	819.80	811.84	0.78
	ρ_{calc2}	824.07	819.55	0.05
0.9	ρ_{exp}	814.11	809.09	
	ρ_{HPT}	806.88	798.44	1.1
	ρ_{calc2}	813.94	809.63	0.03
Av. Abs. % error	ρ_{HPT}	0.290615	0.752142	
	ρ_{calc2}	0.02	0.25	

Table 4.32: Comparisons between measured and predicted densities of binary systems; of Shark Baghdad with Basrah cruds at 25 and 30°C, ρ_{calc2} by equation 4-15* .

Khana X_2	Density Kg/m^3	Temperature ^oC		Av. Abs. % error
		298 k (25 ^oC)	303 k (30 ^oC)	
0.1	$\rho_{\exp}$	904.96	903.12	
	ρ_{HPT}	898.76	893.23	0.89
	ρ_{calc2}	904.29	897.92	0.32
0.2	$\rho_{\exp}$	900.95	899.32	
	ρ_{HPT}	894.90	889.40	0.89
	ρ_{calc2}	900.77	894.65	0.27
0.3	$\rho_{\exp}$	897.03	895.56	
	ρ_{HPT}	890.96	885.51	0.9
	ρ_{calc2}	896.94	891.06	0.26
0.4	$\rho_{\exp}$	893.19	891.87	
	ρ_{HPT}	886.95	881.53	0.93
	ρ_{calc2}	893.15	887.51	0.25
0.5	$\rho_{\exp}$	889.29	888.01	
	ρ_{HPT}	882.86	877.49	0.95
	ρ_{calc2}	889.14	883.74	0.25
0.6	$\rho_{\exp}$	885.14	883.93	
	ρ_{HPT}	878.70	873.36	0.96
	ρ_{calc2}	884.71	879.55	0.27
0.7	$\rho_{\exp}$	880.98	879.80	
	ρ_{HPT}	874.45	869.16	0.98
	ρ_{calc2}	880.16	875.23	0.31
0.8	$\rho_{\exp}$	876.67	875.59	
	ρ_{HPT}	870.11	864.87	0.99
	ρ_{calc2}	875.59	870.88	0.33
0.9	$\rho_{\exp}$	872.35	871.45	
	ρ_{HPT}	886.569	860.50	0.2
	ρ_{calc2}	871.03	866.55	0.36
Av. Abs. % error	ρ_{HPT}	0.715264	1.172389	
	ρ_{calc2}	0.06	0.52	

This was to extend the use of equation 4-15* which become a general density estimation equation. A comparison between the general obtained equation and HBT is shown in table 4.33. The details of the results of the new generalized equation are shown in Appendix A.1 to A.5 for crude/crude system, A.6 to A.18 for crude/fraction system, A.19to A.31 for crude/pure component system, and A.32 to A.35 for binary petroleum fraction system.

Table 4.33: comparisons of error for density prediction by equations 4-15* and 2-11

No.	Mixture type	No. of point	A.A% E of Eq.(4-15)	A.A% E of Eq.(2-11)	Detailed tables in appendix A
1	Crude+ Crude	154	0.168	0.479	A. 1 - A.5
2	Crude+fraction	78	0.286	2.269	A.6 - A.18
3	Crude+fraction	78	0.43	0.33	A.19 - A.31
4	Fraction+spike	20	0.475	3.875	A.32 - A.35
5	All systems	384	0.305	1.49	-

4.4 Calculation of Excess volume

4.4.1 Correlation of excess volume

A number of correlations are available in the literature to calculate the value of excess volumes for different pure compounds mixtures; On the other hand there are little correlations available for estimating the V^E for oil-stock mixtures.

Several attempts were carried out to find the best equation which can represent the experimental data, at acceptable accuracy. A software computer program statistical was used to predict the suitable correlations.

From equation 4-2 where:

$$V^E = V_{mix.} - V^{id}$$

So that:

$$V^E = \frac{1}{\rho_{15} VCF} - V^{id} \tag{4.16}$$

Where:

$$V_{mix.} = \frac{1}{\rho_{15} VCF} \tag{4.17}$$

Where VCF is calculated using equation 4-12.

Equation 4.15 used to calculate the density of mixtures to obtain V_{mix}. From V_{mix} and V^{id} the excess volume V^E was obtained.

The predicted results using equation 4-16 for the considered Iraqi crude oils were in agreement with the experimental data, with high accuracy. Samples of the results of equation 4-16 are shown in tables 4.34 to 4.36 for crude oils Khana / Basrah, Khana / Shark Baghdad, and Basrah / Shark Baghdad, respectively.

Table 4.34: Comparisons between measured and predicted excess volume of binary systems; Khana / Basrah crudes at 25 and 30^{o}C, using equation 4-16

Khana X_2	Excess volume	Temperature		Av. Abs. % error
		$25^o C$	$30^o C$	
0.1	$V^E{}_{\exp}$	**-1.53**	**-1.67**	
	V^E_{calc1}	**-1.49**	**-1.57**	
	% error	**2.6**	**5.9**	**4.3**
0.2	$V^E{}_{\exp}$	**-2.23**	**-2.45**	
	V^E_{calc1}	**-2.29**	**-2.56**	
	% error	**2.4**	**4.4**	**3.4**
0.3	$V^E{}_{\exp}$	**-2.75**	**-2.95**	
	V^E_{calc1}	**-2.80**	**-3.16**	
	% error	**1.9**	**7.1**	**4.5**
0.4	$V^E{}_{\exp}$	**-3.05**	**-3.39**	
	V^E_{calc1}	**-3.06**	**-3.46**	
	% error	**0.1**	**1.9**	**1.0**
0.5	$V^E{}_{\exp}$	**-3.22**	**-3.89**	
	V^E_{calc1}	**-3.18**	**-3.61**	
	% error	**1.1**	**7.3**	**4.2**
0.6	$V^E{}_{\exp}$	**-3.16**	**-3.78**	
	V^E_{calc1}	**-3.11**	**-3.54**	
	% error	**1.6**	**6.3**	**4.0**
0.7	$V^E{}_{\exp}$	**-2.89**	**-3.20**	
	V^E_{calc1}	**-2.84**	**-3.27**	
	% error	**1.8**	**2.3**	**2.0**
0.8	$V^E{}_{\exp}$	**-2.55**	**-2.83**	
	V^E_{calc1}	**-2.52**	**-2.93**	
	% error	**1.4**	**3.8**	**2.6**

0.9	$V^{E}_{\exp}$	**-1.83**	**-2.27**	
	V^{E}_{calc1}	**-1.93**	**-2.32**	
	% error	**5.4**	**2.5**	**3.9**
Av. Abs. % error		**2.0**	**4.6**	

Table 4.35: Comparisons between measured and predicted excess volume of binary systems; Khana / Shrak Baghdad cruds at 25 and 30^{o}C, using equation 4-16

Khana X_2	**Excess volume**	**Temperature ^{o}C**		**Av. Abs. % error**
		$25^{o}C$	**$30^{o}C$**	
0.1	$V^{E}_{\exp}$	**-0.87**	**-1.66**	
	V^{E}_{calc1}	**-0.86**	**-1.66**	
	% error	**0.8**	**0.0**	**0.4**
0.2	$V^{E}_{\exp}$	**-1.49**	**-2.36**	
	V^{E}_{calc1}	**-1.48**	**-2.36**	
	% error	**0.9**	**0.2**	**0.55**
0.3	$V^{E}_{\exp}$	**-1.92**	**-2.92**	
	V^{E}_{calc1}	**-1.97**	**-2.88**	
	% error	**2.7**	**1.2**	**1.95**
0.4	$V^{E}_{\exp}$	**-2.47**	**-3.31**	
	V^{E}_{calc1}	**-2.49**	**-3.40**	
	% error	**0.8**	**2.6**	**1.7**
0.5	$V^{E}_{\exp}$	**-2.87**	**-3.80**	
	V^{E}_{calc1}	**-2.86**	**-3.76**	
	% error	**0.1**	**1.1**	**0.6**
0.6	$V^{E}_{\exp}$	**-2.83**	**-3.72**	
	V^{E}_{calc1}	**-2.74**	**-3.61**	
	% error	**3.2**	**2.8**	
0.7	$V^{E}_{\exp}$	**-2.43**	**-3.16**	
	V^{E}_{calc1}	**-2.44**	**-3.28**	
	% error	**0.3**	**4.0**	**0.35**
0.8	$V^{E}_{\exp}$	**-1.80**	**-2.64**	
	V^{E}_{calc1}	**-1.82**	**-2.62**	
	% error	**0.8**	**0.8**	

0.9	V^E_{exp}	**-1.14**	**-1.95**	
	V^E_{calc1}	**-1.17**	**-1.93**	
	% error	**2.2**	**0.7**	**1.45**
Av. Abs. % error		**1.3**	**1.5**	

Table A.36: Comparisons between measured and predicted excess volume of binary systems; Basrah / Shrak Baghdad cruds at 25 and 30^{o}C, using equation 4-16

Basrah X_2	**Excess volume**	**Temperature ^oC**		**Av. Abs. % error**
		25^oC	**30^oC**	
0.1	V^E_{exp}	**-1.10**	**-1.36**	
	V^E_{calc1}	**-1.14**	**-1.41**	
	% error	**4.2**	**4.0**	**4.1**
0.2	V^E_{exp}	**-1.32**	**-1.75**	
	V^E_{calc1}	**-1.25**	**-1.69**	
	% error	**5.2**	**3.3**	**4.25**
0.3	V^E_{exp}	**-1.60**	**-2.16**	
	V^E_{calc1}	**-1.49**	**-2.04**	
	% error	**6.7**	**5.6**	**6.15**
0.4	V^E_{exp}	**-1.94**	**-2.62**	
	V^E_{calc1}	**-2.00**	**-2.61**	
	% error	**2.9**	**0.5**	**1.7**
0.5	V^E_{exp}	**-2.16**	**-2.82**	
	V^E_{calc1}	**-2.29**	**-2.95**	
	% error	**6.2**	**4.7**	**5.45**
0.6	V^E_{exp}	**-2.03**	**-2.70**	
	V^E_{calc1}	**-2.09**	**-2.79**	
	% error	**3.3**	**3.3**	**3.3**
0.7	V^E_{exp}	**-1.83**	**-2.46**	
	V^E_{calc1}	**-1.73**	**-2.45**	
	% error	**5.1**	**0.3**	**2.7**

0.8	$V^{E}_{\exp}$	**-1.39**	**-2.08**	
	V^{E}_{calc1}	**-1.32**	**-2.06**	
	% error	**5.4**	**0.9**	**3.15**
0.9	$V^{E}_{\exp}$	**-0.86**	**-1.72**	
	V^{E}_{calc1}	**-0.90**	**-1.66**	
	% error	**4.6**	**3.5**	**4.05**
Av. Abs. % error		**4.8**	**2.9**	

The validity of the proposed, modified predicted equation 4-16 was tested by using published experimental density data for some oil stokes. Those were binary mixtures of Jamboor (33.94 API) with heavy naphtha and with Hexadecane and Heavy naphtha with Light naphtha [60]. The calculated excess volumes with the average absolute percent error are listed in tables 4.37 to 4.39, for the mentioned system respectively. These tables show excellent overall agreements.

Table 4.37: Comparisons between measured and predicted excess volume of Jamboor crude oil with Heavy naphtha at 25 ^{0}C, by equation 4-16

Heavy naphtha X_2	Excess volume (exp.R)	Excess volume (Cal.eq.1)	Abs. %error
0.0987	**-0.46**	**-0.46**	**0.4**
0.2732	**-0.97**	**-0.97**	**0.39**
0.4223	**-1.21**	**-1.25**	**2.9**
0.5215	**-1.30**	**-1.26**	**3.0**
0.6589	**-1.18**	**-1.18**	**0.06**
0.8625	**-0.52**	**-0.53**	**1.5**
Over all abs. % error			**1.4**

Table 4.38: comparisons between measured and predicted excess volume of Jamboor crude oil with n-Hexadecane at 25^0C, by equation 4-16

n-Hexadecane X_2	Excess volume (exp.R)	Excess volume (Cal.eq.1)	Abs. %error
0.0993	0.39	0.39	0.68
0.3288	0.93	0.96	2.8
0.4234	1.11	1.09	2.1
0.5011	1.16	1.14	1.9
0.6717	1.04	1.07	2.8
0.8534	0.85	0.84	0.97
Over all abs. % error			1.9

Table 4.39: comparisons between measured and predicted excess volume of Light naphtha with Heavy naphtha at 25 ^0C, by equation 4-16

Light naphtha X_2	Excess volume (exp.R)	Excess volume (Cal.eq.1)	Abs. %error
0.0614	-0.26	-0.262	0.65
0.2079	-0.59	-0.586	0.65
0.4814	-0.87	-0.866	0.51
0.7084	-0.68	-0.697	2.5
0.9022	-0.36	-0.35	2.9
Over all abs. % error			1.4

Further testing of the proposed modified equation 4-16 was carried out by using published experimental excess volume data [60] for some oil-stokes as a binary mixtures to calculate excess volumes. Those binary mixtures are:

1. **Crude oils binary mixtures:**

Five Iraqi crude oils; Jamboor (33.94 API), Basrah (30.49 API), Kirkuk (29.26 API), Byee-Hassin (25.77 API), and Baghdad (24.35 API) are applicable in equation 4-16 to calculate excess volume with average absolute percent error as a binary mixtures as shown in appendix A (table **A.36** to **A.40**). The overall average absolute percent error is 7.3 for 100 data points.

2. Crude spiked with petroleum fraction

The same Iraqi crude oils with addition Safyia (23.3 API) were mixed with four petroleum fractions; Light naphtha (85.4 API), Heavy naphtha (60.8 API), Kerosene (50.17 API), and Gas oil (41.44 API) are applied in equation 4-16 as a binary mixtures to calculate excess volume with average absolute percent error are listed in appendix A (table **A.41** to **A.53**). The overall average absolute percent error is 3.8 for 78 data points.

3. Crude spiked with pure hydrocarbons:

The above six Iraqi crude oils were mixed with five pure hydrocarbons; Cyclohexane (50.82 API), Toluene (32.16 API), n-Hexadecane (51.75 API), n-Heptane (76.21 API), and n-Nonane (66.31 API) are applied in equation 4-16 as a binary mixtures to calculate excess volume with average absolute percent error are listed in appendix A (table **A.54** to **A.66**). The overall average absolute percent error is 3.8 for 78 data points.

4. Binary mixtures of petroleum fraction:

The same four petroleum fractions are applicable in equation 4-16 as binary mixtures to calculate excess volume with average absolute percent error are listed in appendix A (table **A.67** to **A.70**). The overall average absolute percent error is 1.7 for 20 data points.

The predicted excess volumes using the proposed method are summarized and compared in table 4.40 for the considered oil-stock systems. It seen that the method presented in this study produces an overall average absolute error of 3.8% for all considered oil-stock systems (384 points). The maximum deviation in excess volume 5.1% was obtained for Crude/Crude mixtures, propably due to those wide range densities.

Table 4.40: comparisons of error for excess volume prediction, by equation 4-16

No.	Mixture type	No. of point	A.A% E	Detailed tables in appendix A
1	Crude+ Crude	154	5.1	A.36 - A.40 Tables 34 - 36
2	Crude+fraction	78	3.8	A.41 - A.53
3	Crude+spike	78	3.8	A.54 - A.66
4	Fraction+fraction	20	1.7	A.67 - A.70
5	All systems	384	3.6	-

4.4.2 Analyzing an existing Equation for calculated excess volume

Ashcruft S. J. et al. suggested a quartic equation 4-18 to calculate the excess volume of spiked crude oils [8].

$$V^E = X_2(1-X_2)(A_0 + A_1(1-2X_2) + A_2(1-2X_2)^2) \qquad (4.18)$$

where:

X_2 is the volume fraction of spike and A_i are constants.

Equation 4-18 was originally used to calculate the excess volume of binary mixtures for three world crudes spiked with different hydrocarbons or petroleum fractions [4].

Equation 4-18 was used firstly in the present project to estimate the excess volumes of binary mixtures of the three Iraqi crudes, which provided a diverse range of oils. The constants A_o, A_1 and A_2 were calculated by fitting the experimental data at $25^o C$ and $30^o C$, and the results are listed in table 4.41. the calculated excess volumes and their composition with experimental data are presented in tables 4.42, 4.43, and 4.44 for Khana ($API^O =$ 44.3)/ Basrah ($API^O = 31.4$), Shark Baghdad ($API^O = 24.2$)/ Khana, and Shark Baghdad/ Basrah respectively at $25^o C$ and $30^o C$. The maximum absolute average error between the experimental and calculated values is 5.57 for 54 data points.

Table 4.41: Smoothing coefficients of Equation 4-18 for the binary crude mixtures at 25, and 30 $^0 C$

Crudes	Temp.	A0	A1	A2
Khana and Shrak Baghdad	25°C	-11.0256	2.309541	1.390368
	30°C	-14.335	1.84739	-5.47883
Basrah and Shrak Baghdad	25°C	-8.14737	0.273707	-2.21542
	30°C	-10.6145	1.837453	-6.34515
Khana and Basrah	25°C	-12.5308	1.460716	-7.83654
	30°C	-14.4892	2.481609	-7.47622

Table 4.42: Comparisons between measured and predicted excess volume of binary systems; of Khana with Basrah cruds at 25 and 30^{o}C, by equation 4-18

Khana X_2	Excess volume	Temperature ^{o}C		Av. Abs. % error
		$25^{o}C$	$30^{o}C$	
0.1	$V^E{}_{\exp}$	**-1.53**	**-1.67**	
	V^E_{calc2}	**-1.47**	**-1.56**	
	% error	**3.7**	**6.6**	**5.15**
0.2	$V^E{}_{\exp}$	**-2.23**	**-2.45**	
	V^E_{calc2}	**-2.32**	**-2.51**	
	% error	**3.6**	**2.4**	**3.0**
0.3	$V^E{}_{\exp}$	**-2.75**	**-2.95**	
	V^E_{calc2}	**-2.77**	**-3.09**	
	% error	**0.8**	**4.5**	**2.65**
0.4	$V^E{}_{\exp}$	**-3.05**	**-3.39**	
	V^E_{calc2}	**-3.01**	**-3.43**	
	% error	**1.3**	**1.0**	**1.15**
0.5	$V^E{}_{\exp}$	**-3.22**	**-3.89**	
	V^E_{calc2}	**-3.13**	**-3.62**	
	% error	**2.7**	**7.0**	**1.7**
0.6	$V^E{}_{\exp}$	**-3.16**	**-3.78**	
	V^E_{calc2}	**-3.15**	**-3.67**	
	% error	**0.1**	**2.9**	**1.5**
0.7	$V^E{}_{\exp}$	**-2.89**	**-3.20**	
	V^E_{calc2}	**-3.02**	**-3.50**	
	% error	**4.2**	**9.5**	**6.85**
0.8	$V^E{}_{\exp}$	**-2.55**	**-2.83**	
	V^E_{calc2}	**-2.60**	**-2.99**	
	% error	**1.6**	**5.7**	**3.65**
0.9	$V^E{}_{\exp}$	**-1.83**	**-2.27**	
	V^E_{calc2}	**-1.68**	**-1.91**	
	% error	**7.9**	**15.6**	**11.75**
Av. Abs. % error		**2.9**	**6.1**	

Table 4.43: Comparisons between measured and predicted excess volume of binary systems; of Khana with Shark Baghdad cruds at 25 and 30^oC, by equation 4-18

Khana X_2	Excess volume	Temperature ^oC		Av. Abs. % error
		25^oC	30^oC	
0.1	$V^E_{\exp}$	-0.87	-1.66	
	V^E_{calc2}	-0.75	-1.47	
	% error	13.8	11.2	12.5
0.2	$V^E_{\exp}$	-1.49	-2.36	
	V^E_{calc2}	-1.46	-2.43	
	% error	1.9	3.2	5.1
0.3	$V^E_{\exp}$	-1.92	-2.92	
	V^E_{calc2}	-2.07	-3.04	
	% error	8.1	4.2	6.15
0.4	$V^E_{\exp}$	-2.47	-3.31	
	V^E_{calc2}	-2.52	-3.40	
	% error	2.1	2.7	2.4
0.5	$V^E_{\exp}$	-2.87	-3.80	
	V^E_{calc2}	-2.76	-3.58	
	% error	3.8	5.8	4.8
0.6	$V^E_{\exp}$	-2.83	-3.72	
	V^E_{calc2}	-2.74	-3.58	
	% error	3.1	3.6	3.35
0.7	$V^E_{\exp}$	-2.43	-3.16	
	V^E_{calc2}	-2.46	-3.35	
	% error	1.3	6.2	3.75
0.8	$V^E_{\exp}$	-1.80	-2.64	
	V^E_{calc2}	-1.91	-2.79	
	% error	5.8	5.4	5.6
0.9	$V^E_{\exp}$	-1.14	-1.95	
	V^E_{calc2}	-1.08	-1.74	
	% error	5.4	10.7	8.05
Av. Abs. % error		5.0	5.9	

Table 4.44: Comparisons between measured and predicted excess volume of binary systems; of Basrah with Shark Baghdad cruds at 25 and 30^{o}C, by equation 4-18

Khana X_2	Excess volume	Temperature ^oC		Av. Abs. % error
		25^oC	30^oC	
0.1	$V^E{}_{\exp}$	-1.10	-1.36	
	V^E_{calc2}	-0.84	-1.19	
	% error	23.3	12.3	17.8
0.2	$V^E{}_{\exp}$	-1.32	-1.75	
	V^E_{calc2}	-1.40	-1.89	
	% error	6.7	7.9	7.3
0.3	$V^E{}_{\exp}$	-1.60	-2.16	
	V^E_{calc2}	-1.76	-2.29	
	% error	10.0	6.0	8.0
0.4	$V^E{}_{\exp}$	-1.94	-2.62	
	V^E_{calc2}	-1.96	-2.52	
	% error	1.1	3.8	2.45
0.5	$V^E{}_{\exp}$	-2.16	-2.82	
	V^E_{calc2}	-2.04	-2.65	
	% error	5.6	5.8	5.7
0.6	$V^E{}_{\exp}$	-2.03	-2.70	
	V^E_{calc2}	-1.99	-2.70	
	% error	1.8	0.0	0.9
0.7	$V^E{}_{\exp}$	-1.83	-2.46	
	V^E_{calc2}	-1.81	-2.60	
	% error	0.9	5.5	3.2
0.8	$V^E{}_{\exp}$	-1.39	-2.08	
	V^E_{calc2}	-1.46	-2.24	
	% error	4.7	7.8	6.25
0.9	$V^E{}_{\exp}$	-0.86	-1.72	
	V^E_{calc2}	-0.88	-1.45	
	% error	2.3	15.7	9.0
Av. Abs. % error		6.3	7.2	

The predicted excess volumes using the proposed method are summarized and compared in table 4.45 for the considered oil-stock systems. It seen that the method presented in this study produces an overall average absolute error of 6 % for all considered oil-stock systems (384 points). The maximum deviation in excess volume 6.9% was obtained for Crude/Crude mixtures and also Crude/ fraction, propably due to those wide range densities.

Table 4.45: comparisons of error for excess volume prediction by equations 4-16 and 4-18

No.	Mixture type	No. of point	A.A% E of Eq.(4-16)	A.A% E Eq.(4-18)	Detailed tables in appendix A
1	Crude+ Crude	154	5.1	6.9	A.36 - A.40 Tables 34 – 36 Tables 42 - 44
2	Crude+fraction	78	3.8	6.9	A.41 - A.53
3	Crude+spike	78	3.8	5.5	A.54 - A.66
4	Fraction+fraction	20	1.7	3.7	A.67 - A.70
5	All systems	384	3.6	6	-

From table 4.45, it is clear that equation 4-16 is much better than 4-18, due to the higher accuracy of equation 4-16 over equation 4-18. Then equation 4-16 is the most applicable equation to calculate the excess volume for different binary systems crude/crude, crude/fraction, crude/spike and fraction/spike mixtures.

Conclusions and Recommendations

5.1 conclusions

From the results of the present work, the following conclusions are made.

1- It's generally observed that the blending of light and medium crudes with heavy crude oil results in volume "losses" caused by the non-ideal behavior of this system as compared with the calculated ideal volume. Temperature increase in the range $15-30^{o}C$ leads in some increase of the shrinkage of binary crude systems.

2- It's generally observed that the mixing of aromatic hydrocarbons with crude oils produces positive excess volume. This expansion effect is greatest for the lower boiling spike as in case of toluene. Paraffinic blends produce negative excess volume. This shrinkage effect is greatest for the lowest boiling point spikes as in case of kerosene.

3- The Costald equation of Hankinson-Brobst-Thomson can be used for density calculation for all the binary system with degree of accuracy 0.874% for 54 data points.

4- A correlation has been proposed to predict the density for all binary system of crude/crude, crude/fraction, crude/spike and binary fraction at constant parameter with acceptable accuracy. This correlation based on density at 288 K, temperature and mass fraction of spiked with degree of accuracy 0.305% for 384 data points. The predicted equation gives a higher accuracy than HBT equation.

5- A generalized correlation with different constant have been proposed, according to the nature of the species to predict the excess volume for all binary system of crude/crude, crude/fraction, crude/spike and binary fraction with acceptable accuracy. This correlation based on density at 288 K, temperature and mass fraction of spiked with degree of accuracy 3.83% for 384 data points compared with a well known equation (Ashcroft equation) which gives an accuracy of 5.474 for the same data points..

5.2 Recommendations

1- Studying the effect of blending ternary oil-stocks on the density and the volumetric behavior of the resultant mixture.

2- Future work can be carried out to find accurate correlations for excess volume of crude oil mixtures according to the nature of the species.

3- Modeling the effects of pressure in addition to the temperature, composition, API-gravity on the volumetric behavior of oil-stock mixtures.

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Appendix A

Table A.1: Comparisons between measured and predicted densities of binary systems; of Jamboor with Basrah cruds at 25, 30, 40, and 50 ^{o}C where ρ_{Cal2} is calculated by equation 4-15* at constant parameter.

Jamboor X_2	Density Kg/m^3	Temperature ^{o}C				Av. Abs. % error
		25 ^{o}C	30 ^{o}C	40 ^{o}C	50 ^{o}C	
0.106	$\rho_{\exp}$	869.12	865.79	858.43	851.70	
	ρ_{HBT}	869.31	865.77	858.69	851.58	0.017
	ρ_{Cal2}	871.26	865.13	857.30	852.11	0.126
0.307	$\rho_{\exp}$	865.59	862.29	854.72	847.86	
	ρ_{HBT}	865.35	861.80	854.69	847.55	0.031
	ρ_{Cal2}	867.78	862.09	854.62	849.59	0.123
0.500	$\rho_{\exp}$	862.12	858.88	851.10	844.10	
	ρ_{HBT}	861.58	858.02	850.88	843.71	0.059
	ρ_{Cal2}	863.67	858.40	851.28	846.41	0.133
0.694	$\rho_{\exp}$	858.54	855.34	847.34	840.20	
	ρ_{HBT}	875.81	854.24	847.07	839.88	0.553
	ρ_{Cal2}	859.28	854.42	847.65	842.93	0.139
0.912	$\rho_{\exp}$	854.45	851.29	843.05	835.77	
	ρ_{HBT}	853.62	850.03	842.83	835.61	0.073
	ρ_{Cal2}	854.17	849.76	843.37	838.82	0.154
Av. Abs.% error (HBT)		0.06	0.09	0.02	0.03	
Av. Abs.% error (Cal 2)		0.16	0.089	0.048	0.243	

Table A.2: Comparisons between measured and predicted densities of binary systems; of Jamboor with Baghdad cruds at 25, 30, 40, and 50 ^{o}C where ρ_{Cal2} is calculated by equation 4-15* at constant parameter.

Jambor X_2	Density Kg/m^3	Temperature ^{o}C				Av. Abs. % error
		$25^{o}C$	$30^{o}C$	$40^{o}C$	$50^{o}C$	
0.1521	$\rho_{\exp}$	897.30	893.95	887.00	879.98	
	ρ_{HBT}	896.50	893.07	886.18	879.28	0.09
	ρ_{Cal2}	898.33	892.11	884.13	878.81	0.194
0.2910	$\rho_{\exp}$	890.00	886.68	879.70	872.62	
	ρ_{HBT}	888.99	885.53	878.59	871.63	0.121
	ρ_{Cal2}	891.12	885.25	877.58	872.41	0.138
0.4909	$\rho_{\exp}$	879.52	876.26	868.99	861.94	
	ρ_{HBT}	878.33	874.82	867.81	860.77	0.143
	ρ_{Cal2}	880.29	874.91	867.66	862.69	0.120
0.6888	$\rho_{\exp}$	869.22	865.88	858.33	851.26	
	ρ_{HBT}	867.94	864.40	857.31	850.19	0.141
	ρ_{Cal2}	869.42	864.50	857.65	852.88	0.113
0.8723	$\rho_{\exp}$	859.57	856.21	848.35	841.17	
	ρ_{HBT}	858.46	854.88	847.72	840.53	0.109
	ρ_{Cal2}	859.24	854.74	848.26	843.66	0.129
Av. Abs.% error (HBT)		0.12	0.14	0.11	0.11	
Av. Abs.% error (Cal 2)		0.078	0.170	0.162	0.146	

Table A.3: Comparisons between measured and predicted densities of binary systems; of Basrah with Kirkuk cruds at 25, 30, 40, and 50 ^{o}C where ρ_{Cal2} is calculated by equation 4-15*at constant parameter.

Basrah X_2	Density Kg/m^3	Temperature ^{o}C				Av. Abs. % error
		$25^{o}C$	$30^{o}C$	$40^{o}C$	$50^{o}C$	
0.090	ρ_{exp}	895.13	891.38	884.34	877.62	
	ρ_{HBT}	894.39	890.95	884.05	877.13	0.055
	ρ_{Cal2}	895.58	889.24	881.17	875.82	0.213
0.301	ρ_{exp}	891.29	887.65	880.60	873.79	
	ρ_{HBT}	890.41	886.95	880.02	873.07	0.081
	ρ_{Cal2}	892.11	886.25	878.59	873.42	0.130
0.503	ρ_{exp}	887.59	884.03	876.97	870.05	
	ρ_{HBT}	886.71	883.24	876.28	869.30	0.088
	ρ_{Cal2}	887.87	882.48	875.19	870.19	0.107
0.962	ρ_{exp}	883.67	880.19	873.10	866.08	
	ρ_{HBT}	883.31	879.82	872.84	865.84	0.035
	ρ_{Cal2}	882.00	877.62	871.15	866.51	0.189
0.918	ρ_{exp}	879.86	876.45	869.27	862.17	
	ρ_{HBT}	879.26	875.76	868.75	861.72	0.065
	ρ_{Cal2}	878.54	874.07	867.55	862.90	0.176
Av. Abs.% error (HBT)		0.08	0.07	0.05	0.06	
Av. Abs.% error (Cal 2)		0.10	0.23	0.24	0.08	

Table A.4: Comparisons between measured and predicted densities of binary systems; of Kirkuk with Byee-Hassin cruds at 25, 30, 40, and $50^{o}C$ where ρ_{Cal2} is calculated by equation 4-15*at constant parameter.

Kirkuk X_2	Density Kg/m^3	Temperature ^{o}C				Av. Abs. % error
		$25^{o}C$	$30^{o}C$	$40^{o}C$	$50^{o}C$	
0.104	$\rho_{\exp}$	895.13	891.38	884.34	877.62	
	ρ_{HBT}	894.39	890.95	884.05	877.13	0.055
	ρ_{Cal2}	895.69	889.38	881.33	876.00	0.20
0.308	$\rho_{\exp}$	891.29	887.65	880.60	873.79	
	ρ_{HBT}	890.41	886.95	880.02	873.07	0.081
	ρ_{Cal2}	892.09	886.26	878.60	873.44	0.13
0.500	$\rho_{\exp}$	887.59	884.03	876.97	870.05	
	ρ_{HBT}	886.71	883.24	876.28	869.30	0.088
	ρ_{Cal2}	887.88	882.48	875.19	870.19	0.11
0.698	$\rho_{\exp}$	883.67	880.19	873.10	866.08	
	ρ_{HBT}	883.31	879.82	872.84	865.84	0.035
	ρ_{Cal2}	883.28	878.32	871.40	866.57	0.13
0.889	$\rho_{\exp}$	879.86	876.45	869.27	862.17	
	ρ_{HBT}	879.26	875.76	868.75	861.72	0.065
	ρ_{Cal2}	878.68	874.15	867.58	862.91	0.17
Av. Abs.% error (HBT)		0.08	0.07	0.05	0.06	
Av. Abs.% error (Cal 2)		0.07	0.21	0.23	0.08	

Table A.5: Comparisons between measured and predicted densities of binary systems; of Kirkuk with Baghdad cruds at 25, 30, 40, and 50 ^{o}C where ρ_{Cal2} is calculated by equation 4-15*at constant parameter.

Kirkuk X_2	**Density Kg/m^3**	**Temperature ^{o}C**				**Av. Abs. % error**
		25^{o}C	**30^{o}C**	**40^{o}C**	**50^{o}C**	
0.111	ρ_{exp}	**902.39**	**899.07**	**892.27**	**885.17**	
	ρ_{HBT}	**901.71**	**898.30**	**891.45**	**884.59**	**0.08**
	ρ_{Cal2}	**903.13**	**896.79**	**888.69**	**883.32**	**0.24**
0.303	ρ_{exp}	**897.33**	**894.07**	**887.37**	**880.30**	
	ρ_{HBT}	**896.32**	**892.88**	**886.00**	**879.09**	**0.134**
	ρ_{Cal2}	**898.20**	**892.31**	**884.60**	**879.40**	**0.18**
0.501	ρ_{exp}	**891.93**	**888.74**	**881.97**	**874.95**	
	ρ_{HBT}	**890.83**	**887.38**	**880.45**	**873.50**	**0.154**
	ρ_{Cal2}	**892.26**	**886.84**	**879.52**	**874.50**	**0.14**
0.709	ρ_{exp}	**886.25**	**882.95**	**876.08**	**869.06**	
	ρ_{HBT}	**885.21**	**881.73**	**874.76**	**867.77**	**0.139**
	ρ_{Cal2}	**885.74**	**880.80**	**873.88**	**869.04**	**0.14**
0.840	ρ_{exp}	**882.28**	**878.96**	**871.93**	**864.91**	
	ρ_{HBT}	**881.51**	**878.02**	**871.02**	**864.00**	**0.101**
	ρ_{Cal2}	**881.23**	**876.59**	**869.92**	**865.20**	**0.16**
Av. Abs.% error (HBT)		**0.10**	**0.12**	**0.13**	**0.12**	
Av. Abs.% error (Cal 2)		**0.08**	**0.24**	**0.29**	**0.08**	

Table A.6: Comparisons between measured and predicted densities of Jamboor crude oil with Heavy naphtha at 25 ^{0}C where ρ_{Cal2} is calculated by equation 4-15*at constant parameter.

Heavy naphtha X_2		Density kg/m^3 (exp.)	Density kg/m^3 (HBT)	Density kg/m^3 (Cal.2)
0.0987		839.65	831.33	841.57
	% error		1.0	0.23
0.2732		817.20	799.39	819.82
	% error		2.2	0.32
0.4223		798.83	775.01	801.53
	% error		3.0	0.34
0.5215		787.02	759.82	789.62
	% error		3.5	0.33
0.6589		771.07	739.84	773.56
	% error		4.0	0.32
0.8625		748.33	712.12	750.57
	% error		4.8	0.30
Av. Abs. %error			3.1	0.31

Table A.7: Comparisons between measured and predicted densities of Basrah crude oil with Heavy naphtha at 25 ^{0}C where ρ_{Cal2} is calculated by equation 4-15* at constant parameter.

Heavy naphtha X_2		Density kg/m^3 (exp.)	Density kg/m^3 (HBT)	Density kg/m^3 (Cal.2)
0.0943		856.24	848.80	858.51
	% error		0.9	0.27
0.2506		832.63	816.10	835.44
	% error		2.0	0.34
0.4760		800.78	775.02	803.46
	% error		3.2	0.33
0.5445		791.49	763.48	794.18
	% error		3.5	0.34
0.6402		778.73	747.95	781.28
	% error		4.0	0.33
0.9102		744.50	707.17	746.78
	% error		5.0	0.31
Av. Abs. %error			3.1	0.32

Table A.8: Comparisons between measured and predicted densities of Kirkuk crude oil with Heavy naphtha at 25 ^{0}C where ρ_{Cal2} is calculated by equation 4-15*at constant parameter.

Heavy naphtha X_2		Density kg/m^3 (exp.)	Density kg/m^3 (HBT)	Density kg/m^3 (Cal.2)
0.0902		862.83	854.68	863.97
	% error		0.9	0.13
0.2705		834.38	815.92	836.41
	% error		2.2	0.24
0.4234		811.41	786.91	813.60
	% error		3.0	0.27
0.5438		794.09	756.71	796.37
	% error		3.6	0.29
0.6802		775.27	743.06	777.45
	% error		4.2	0.28
0.9142		744.41	706.95	746.57
	% error		5.0	0.29
Av. Abs. %error			3.2	0.25

Table A.9: Comparisons between measured and predicted densities of Kirkuk crude oil with Light naphtha at 25 ^{0}C where ρ_{Cal2} is calculated by equation 4-15*at constant parameter.

Light naphtha X_2		Density kg/m^3 (exp.)	Density kg/m^3 (HBT)	Density kg/m^3 (Cal.2)
0.1036		848.77	845.96	847.57
	% error		0.3	0.14
0.3325		790.84	791.39	792.77
	% error		-0.1	0.24
0.4432		765.14	767.74	767.53
	% error		-0.4	0.31
0.5197		748.04	752.08	750.65
	% error		-0.5	0.35
0.6538		719.22	725.86	721.84
	% error		-0.9	0.36
0.9367		662.31	675.33	666.13
	% error		-2.0	0.58
Av. Abs. %error			0.7	0.33

Table A.10: Comparisons between measured and predicted densities of Byee-Hassin crude oil with Gas oil at 25 ^{0}C where ρ_{Cal2} is calculated by equation 4-15*at constant parameter.

Gas oil X_2		Density kg/m^3 (exp.)	Density kg/m^3 (HBT)	Density kg/m^3 (Cal.2)
0.1082		887.64	885.92	888.23
	% error		0.2	0.07
0.3122		870.34	865.96	871.16
	% error		0.5	0.09
0.4968		855.21	847.73	855.67
	% error		0.9	0.05
0.5567		850.38	841.79	850.69
	% error		1.0	0.04
0.7534		834.93	822.21	834.67
	% error		1.5	0.03
0.9345		821.16	804.13	820.34
	% error		2.1	0.10
Av. Abs. %error			1.0	0.06

Table A.11: Comparisons between measured and predicted densities of Byee-Hassin crude oil with Kerosene at 25 ^{0}C where ρ_{Cal2} is calculated by equation 4-15*at constant parameter.

Kerosene X_2		Density kg/m^3 (exp.)	Density kg/m^3 (HBT)	Density kg/m^3 (Cal.2)
0.0902		884.88	877.96	885.64
	% error		0.8	0.09
0.2654		862.03	844.89	863.77
	% error		2.0	0.20
0.4642		837.35	810.56	839.34
	% error		3.2	0.24
0.5279		829.68	800.12	831.71
	% error		3.2	0.24
0.6038		820.68	787.98	822.73
	% error		4.0	0.25
0.8336		794.55	853.03	796.57
	% error		5.2	0.25
Av. Abs. %error			3.1	0.21

Table A.12: Comparisons between measured and predicted densities of Byee-Hassin crude oil with Light naphtha at 25 ^{0}C where ρ_{Cal2} is calculated by equation 4-15*at constant parameter.

Light naphtha X_2		Density kg/m^3 (exp.)	Density kg/m^3 (HBT)	Density kg/m^3 (Cal.2)
0.1112		862.93	859.88	863.88
	% error		0.4	0.11
0.3786		789.24	791.57	792.03
	% error		-0.3	0.35
0.4534		770.44	774.34	773.66
	% error		0.5	0.42
0.5122		756.32	761.20	759.43
	% error		0.6	0.41
0.6234		730.23	737.30	733.62
	% error		1.0	0.46
0.7778		695.61	706.07	699.79
	% error		1.5	0.60
Av. Abs. %error			0.7	0.39

Table A.13: Comparisons between measured and predicted densities of Byee-Hassin crude oil with Heavy naphtha at 25 ^{0}C where ρ_{Cal2} is calculated by equation 4-15*at constant parameter.

Heavy naphtha X_2		Density kg/m^3 (exp.)	Density kg/m^3 (HBT)	Density kg/m^3 (Cal.2)
0.1281		872.76	861.58	873.85
	% error		1.3	0.12
0.2620		848.51	830.16	850.20
	% error		2.2	0.20
0.3786		828.60	805.30	830.44
	% error		2.8	0.22
0.4556		815.79	789.81	817.76
	% error		3.2	0.24
0.5583		799.21	770.08	801.27
	% error		3.6	0.26
0.8007		762.39	726.49	764.41
	% error		4.6	0.27
Av. Abs. %error			3.0	0.22

Table A.14: Comparisons between measured and predicted densities of Baghdad crude oil with Heavy naphtha at 25 ^{0}C ^{0}C where ρ_{Cal2} is calculated by equation 4-15*at constant parameter.

Heavy naphtha X_2		Density kg/m^3 (exp.)	Density kg/m^3 (HBT)	Density kg/m^3 (Cal.2)
0.1281		879.59	868.43	880.84
	% error		1.3	0.14
0.2620		854.18	835.68	855.96
	% error		2.2	0.21
0.3786		832.97	809.78	835.40
	% error		2.8	0.29
0.4775		815.81	789.18	817.74
	% error		3.3	0.24
0.5583		802.12	773.10	804.09
	% error		3.6	0.25
0.8007		763.24	728.20	765.34
	% error		4.6	0.27
Av. Abs. %error			2.9	0.23

Table A.15: Comparisons between measured and predicted densities of Baghdad crude oil with Light naphtha at 25 ^{0}C ^{0}C where ρ_{Cal2} is calculated by equation 4-15*at constant parameter.

Light naphtha X_2		Density kg/m^3 (exp.)	Density kg/m^3 (HBT)	Density kg/m^3 (Cal.2)
0.1029		873.53	869.42	874.43
	% error		0.5	0.10
0.3033		813.83	814.76	816.30
	% error		-0.1	0.30
0.4855		765.44	770.72	768.27
	% error		-0.7	0.37
0.5234		756.04	762.02	758.95
	% error		-0.8	0.38
0.6056		735.93	743.67	738.95
	% error		-1.1	0.41
0.8807		674.32	687.16	678.41
	% error		-1.9	0.61
Av. Abs. %error			0.8	0.36

Table A.16: Comparisons between measured and predicted densities of Safyia crude oil with Gas oil at 25 $^{0}C\ ^{0}C$ where ρ_{Cal2} is calculated by equation 4-15*at constant parameter.

Gas oil X_2		Density kg/m^3 (exp.)	Density kg/m^3 (HBT)	Density kg/m^3 (Cal.2)
0.0980		901.21	900.17	896.51
	% error		0.1	0.52
0.2956		881.26	877.83	876.87
	% error		0.4	0.50
0.3911		871.89	866.98	867.32
	% error		0.6	0.52
0.4855		862.81	856.23	858.01
	% error		0.8	0.56
0.5201		859.54	852.28	854.64
	% error		0.8	0.57
0.7345		839.74	827.82	834.19
	% error		1.4	0.66
Av. Abs. %error			0.7	0.55

Table A.17: Comparisons between measured and predicted densities of Safyia crude oil with Kerosene at 25 $^{0}C\ ^{0}C$ where ρ_{Cal2} is calculated by equation 4-15*at constant parameter.

Kerosene X_2		Density kg/m^3 (exp.)	Density kg/m^3 (HBT)	Density kg/m^3 (Cal.2)
0.1577		887.58	876.59	889.24
	% error		1.2	0.19
0.2275		877.27	862.33	879.23
	% error		1.7	0.22
0.4194		850.12	825.56	852.35
	% error		2.9	0.26
0.4821		841.60	814.19	843.84
	% error		3.3	0.27
0.5819		828.33	796.64	830.50
	% error		3.8	0.26
0.7846		802.49	762.81	804.59
	% error		4.9	0.26
Av. Abs. %error			3.6	0.24

Table A.18: Comparisons between measured and predicted densities of Safyia crude oil with Heavy naphtha at 25 ^{0}C ^{0}C where ρ_{Cal2} is calculated by equation 4-15*at constant parameter.

Heavy naphtha X_2		**Density kg/m^3 (exp.)**	**Density kg/m^3 (HBT)**	**Density kg/m^3 (Cal.2)**
0.2275		**865.86**	**848.17**	**867.56**
	% error		**2.0**	**0.20**
0.4194		**829.60**	**804.27**	**831.54**
	% error		**3.1**	**0.23**
0.5119		**813.06**	**784.80**	**815.02**
	% error		**3.5**	**0.24**
0.5819		**800.85**	**770.65**	**802.84**
	% error		**3.8**	**0.25**
0.6667		**786.33**	**754.11**	**788.40**
	% error		**4.1**	**0.26**
0.9144		**746.50**	**709.03**	**748.65**
	% error		**5.0**	**0.29**
Av. Abs. %error			**3.6**	**0.25**

Table A.19: Comparisons between measured and predicted densities of Jamboor crude oil with n-Hexadecane at 25^{0}C where ρ_{Cal2} is calculated by equation 4-15*at constant parameter.

n-Hexadecane X_2		**Density kg/m^3 (exp.)**	**Density kg/m^3 (HBT)**	**Density kg/m^3 (Cal.2)**
0.0993		**843.47**	**843.07**	**845.34**
	% error		**0.0**	**0.22**
0.3288		**822.99**	**823.35**	**825.34**
	% error		**0.0**	**0.29**
0.4234		**814.86**	**815.52**	**817.15**
	% error		**-0.1**	**0.28**
0.5011		**808.37**	**809.21**	**810.54**
	% error		**-0.1**	**0.27**
0.6717		**794.61**	**795.74**	**796.41**
	% error		**-0.1**	**0.23**
0.8534		**780.51**	**781.93**	**781.92**
	% error		**-0.2**	**0.23**
Av. Abs. %error			**0.1**	**0.24**

Table A.20: Comparisons between measured and predicted densities of Basrah crude oil with n-heptane at 25 ^{0}C where ρ_{Cal2} is calculated by equation 4-15*at constant parameter.

n-heptane X_2		Density kg/m^3 (exp.R)	Density kg/m^3 (HBT)	Density kg/m^3 (Cal.2)
0.0674		855.77	852.19	857.49
	% error		0.4	0.20
0.2538		815.17	808.33	818.53
	% error		0.8	0.41
0.4378		777.99	771.49	781.56
	% error		0.8	0.46
0.5011		765.85	759.72	769.45
	% error		0.8	0.47
0.6067		746.10	740.90	749.76
	% error		0.7	0.49
0.8532		702.99	700.41	706.53
	% error		0.4	0.50
Av. Abs. %error			0.7	0.42

Table A.21: Comparisons between measured and predicted densities of Basrah crude oil with n-Nonane at 25 ^{0}C where ρ_{Cal2} is calculated by equation 4-15*at constant parameter.

n-Nonane X_2		Density kg/m^3 (exp.)	Density kg/m^3 (HBT)	Density kg/m^3 (Cal.2)
0.1002		852.58	850.02	855.00
	% error		0.3	0.28
0.2171		832.29	828.11	835.24
	% error		0.5	0.35
0.4504		793.50	790.17	796.69
	% error		0.4	0.40
0.5621		776.08	773.80	779.29
	% error		0.3	0.41
0.7487		748.47	748.32	751.53
	% error		0.0	0.41
0.8732		730.57	732.39	733.62
	% error		-0.2	0.41
Av. Abs. %error			0.3	0.38

Table A.22: Comparisons between measured and predicted densities of Kirkuk crude oil with Toluene at 25 ^{0}C where ρ_{Cal2} is calculated by equation 4-15*at constant parameter.

Toluene X_2		Density kg/m^3 (exp.)	Density kg/m^3 (HBT)	Density kg/m^3 (Cal.2)
0.1015		875.51	872.21	876.92
	% error		0.4	0.16
0.2458		872.68	869.91	874.96
	% error		0.3	0.26
0.4386		869.31	868.52	871.94
	% error		0.1	0.30
0.4918		868.50	868.52	871.12
	% error		0.0	0.30
0.6327		866.50	867.13	869.22
	% error		-0.1	0.31
0.8013		864.43	865.80	867.03
	% error		-0.2	0.30
Av. Abs. %error			0.2	0.27

Table A.23: Comparisons between measured and predicted densities of Kirkuk crude oil with n-Heptane at 25 ^{0}C where ρ_{Cal2} is calculated by equation 4-15*at constant parameter.

n-Heptane X_2		Density kg/m^3 (exp.)	Density kg/m^3 (HBT)	Density kg/m^3 (Cal.2)
0.1012		854.00	848.27	855.19
	% error		0.7	0.14
0.2458		821.53	813.83	823.92
	% error		0.9	0.29
0.4088		787.34	779.82	789.98
	% error		1.0	0.33
0.5232		764.53	757.87	767.37
	% error		1.0	0.37
0.6068		748.20	742.62	751.19
	% error		0.7	0.40
0.7533		721.29	717.32	724.43
	% error		0.6	0.44
Av. Abs. %error			0.8	0.33

Table A.24: Comparisons between measured and predicted densities of Byee-Hassin crude oil with Cyclohexane at 25 ^{0}C where ρ_{Cal2} is calculated by equation 4-15*at constant parameter.

Cyclohexane X_2		Density kg/m^3 (exp.)	Density kg/m^3 (HBT)	Density kg/m^3 (Cal.2)
0.0992		882.68	876.49	883.66
	% error		0.7	0.11
0.2930		855.98	850.24	858.00
	% error		0.7	0.24
0.4526		835.39	831.48	837.71
	% error		0.5	0.28
0.5088		828.45	825.11	830.84
	% error		0.4	0.29
0.7532		799.97	798.51	802.66
	% error		0.2	0.34
0.9217		781.70	781.24	784.56
	% error		0.1	0.37
Av. Abs. %error			0.1	0.27

Table A.25: Comparisons between measured and predicted densities of Byee-Hassin crude oil with Toluene at 25 ^{0}C where ρ_{Cal2} is calculated by equation 4-15*at constant parameter.

Toluene X_2		Density kg/m^3 (exp.)	Density kg/m^3 (HBT)	Density kg/m^3 (Cal.2)
0.1022		893.00	889.16	911.46
	% error		0.4	2.07
0.3135		884.74	882.57	899.89
	% error		0.2	1.71
0.4436		879.81	879.27	892.62
	% error		0.1	1.46
0.5027		877.66	877.74	889.43
	% error		0.0	1.34
0.7556		869.73	870.90	876.26
	% error		0.2	0.75
0.9367		863.82	865.93	867.50
	% error		0.2	0.43
Av. Abs. %error			0.2	1.29

Table A.26: Comparisons between measured and predicted densities of Byee-Hassin crude oil with n-Hexadecane at 25 ^{0}C where ρ_{Cal2} is calculated by equation 4-15*at constant parameter.

n-Hexadecane X_2		Density kg/m^3 (exp.)	Density kg/m^3 (HBT)	Density kg/m^3 (Cal.2)
0.1345		877.27	876.97	894.69
	% error		0.0	1.99
0.3163		852.00	852.20	865.78
	% error		0.0	1.62
0.4206		838.18	838.68	849.82
	% error		-0.1	1.39
0.4982		828.24	828.93	838.31
	% error		-0.1	1.22
0.7232		800.93	801.95	806.61
	% error		-0.1	0.71
0.9120		779.46	780.68	781.79
	% error		-0.2	0.30
Av. Abs. %error			0.1	1.20

Table A.27: Comparisons between measured and predicted densities of Baghdad crude oil with n-Hexadecane at 25 ^{0}C where ρ_{Cal2} is calculated by equation 4-15*at constant parameter.

n-Hexadecane X_2		Density kg/m^3 (exp.)	Density kg/m^3 (HBT)	Density kg/m^3 (Cal.2)
0.0887		891.24	890.94	892.09
	% error		0.0	0.10
0.3007		859.56	859.64	861.24
	% error		0.0	0.20
0.4630		836.77	837.27	838.43
	% error		-0.1	0.20
0.5397		826.44	827.12	828.03
	% error		-0.1	0.19
0.6557		811.37	812.25	812.79
	% error		-0.1	0.17
0.9326		777.65	778.87	778.69
	% error		-0.2	0.13
Av. Abs. %error			0.1	0.16

Table A.28: Comparisons between measured and predicted densities of Baghdad crude oil with n-Nonane at 25 ^{0}C where ρ_{Cal2} is calculated by equation 4-15*at constant parameter.

n-Nonane X_2		Density kg/m^3 (exp.)	Density kg/m^3 (HBT)	Density kg/m^3 (Cal.2)
0.2088		858.32	853.45	860.33
	% error		0.6	0.23
0.3114		837.13	832.10	839.44
	% error		0.6	0.28
0.4377		811.92	807.86	814.45
	% error		0.5	0.31
0.4922		801.44	797.95	804.05
	% error		0.4	0.33
0.5665		787.29	784.90	790.00
	% error		0.3	0.34
0.7422		755.39	755.65	758.28
	% error		0.0	0.38
Av. Abs. %error			0.4	0.31

Table A.29: Comparisons between measured and predicted densities of Baghdad crude oil with n-Heptane at 25 ^{0}C where ρ_{Cal2} is calculated by equation 4-15*at constant parameter.

n-Heptane X_2		Density kg/m^3 (exp.)	Density kg/m^3 (HBT)	Density kg/m^3 (Cal.2)
0.0308		896.48	893.86	896.17
	% error		0.3	0.03
0.2791		831.50	823.93	833.69
	% error		0.9	0.26
0.4734		785.61	779.10	788.44
	% error		0.8	0.36
0.5276		773.36	767.47	776.25
	% error		0.8	0.37
0.6025		756.70	751.92	759.82
	% error		0.6	0.41
0.7363		728.63	725.56	732.02
	% error		0.4	0.47
Av. Abs. %error			0.6	0.32

Table A.30: Comparisons between measured and predicted densities of Safyia crude oil with Cyclohexane at 25 ^{0}C where ρ_{Cal2} is calculated by equation 4-15*at constant parameter.

Cyclohexane X_2		Density kg/m^3 (exp.)	Density kg/m^3 (HBT)	Density kg/m^3 (Cal.2)
0.0900		896.52	890.94	897.38
	% error		0.6	0.10
0.3078		862.91	858.14	864.67
	% error		0.6	0.20
0.4343		844.58	841.39	846.78
	% error		0.4	0.26
0.5106		834.08	831.58	836.34
	% error		0.3	0.27
0.7943		797.69	796.86	800.33
	% error		0.1	0.33
0.9201		782.98	782.40	785.61
	% error		0.0	0.34
Av. Abs. %error			0.3	0.25

Table A.31: Comparisons between measured and predicted densities of Safyia crude oil with Toluene at 25 ^{0}C where ρ_{Cal2} is calculated by equation 4-15*at constant parameter.

Toluene X_2		Density kg/m^3 (exp.)	Density kg/m^3 (HBT)	Density kg/m^3 (Cal.2)
0.1034		910.72	902.21	906.88
	% error		0.9	0.42
0.3195		897.82	892.64	896.25
	% error		0.6	0.17
0.4908		888.02	885.75	887.78
	% error		0.3	0.03
0.5469		884.94	883.42	885.05
	% error		0.2	0.01
0.7533		874.32	874.66	875.52
	% error		0.0	0.14
0.8907		867.45	868.81	869.40
	% error		-0.2	0.22
Av. Abs. %error			0.4	0.17

Table A.32: Comparisons between measured densities and the corresponding calculated value of binary systems; Light naphtha and heavy naphtha at 25^0C where ρ_{Cal2} is calculated by equation 4-15*at constant parameter.

Light naphtha X_2		Density kg/m^3 (exp.)	Density kg/m^3 (HBT)	Density kg/m^3 (Cal.2)
0.0614		728.09	692.83	731.41
	% error		4.8	0.46
0.2079		714.96	688.78	719.25
	% error		3.7	0.60
0.4814		691.53	680.80	696.09
	% error		1.6	0.66
0.7084		673.02	673.90	677.52
	% error		-0.1	0.67
0.9022		657.91	667.90	662.26
	% error		-1.5	0.66
v. Abs. %error			2.3	0.61

Table A.33: Comparisons between measured densities and the corresponding calculated value of binary systems; Light naphtha with Kerosene at 25^0C where ρ_{Cal2} is calculated by Equation 4-15*at constant parameter.

Light naphtha X_2		Density kg/m^3 (exp.)	Density kg/m^3 (HBT)	Density kg/m^3 (Cal.2)
0.0378		771.06	726.53	774.03
	% error		5.8	0.39
0.1404		756.37	719.51	760.54
	% error		4.9	0.55
0.5245		705.49	694.32	710.10
	% error		1.6	0.65
0.5878		697.69	690.28	702.28
	% error		1.1	0.66
0.8026		672.37	676.83	676.80
	% error		-0.7	0.66
Av. Abs. %error			2.8	0.58

Table A.34: Comparisons between measured densities and the corresponding calculated value of binary systems; heavy naphtha and Kerosene at 25^0C where ρ_{Cal2} is calculated by equation 4-15*at constant parameter.

Heavy naphtha X_2		Density kg/m^3 (exp.)	Density kg/m^3 (HBT)	Density kg/m^3 (Cal.2)
0.1045		771.98	725.15	775.72
	% error		6.1	0.48
0.2562		756.37	719.51	769.38
	% error		6.0	0.52
0.4803		755.69	711.56	759.32
	% error		5.8	0.48
0.6914		746.65	704.42	749.74
	% error		5.7	0.41
0.9320		736.52	696.61	738.87
	% error		5.4	0.32
Av. Abs. %error			5.8	0.44

Table A.35: Comparisons between measured densities and the corresponding calculated value of binary systems; Kerosene with gas oil at 25^0C where ρ_{Cal2} is calculated by equation 4-15*at constant parameter.

Kerosene X_2		Density kg/m^3 (exp.)	Density kg/m^3 (HBT)	Density kg/m^3 (Cal.2)
0.1463		810.28	784.74	812.01
	% error		3.2	0.21
0.2955		804.26	773.01	806.45
	% error		3.9	0.27
0.4948		796.30	758.98	798.61
	% error		4.7	0.29
0.7067		787.96	745.64	790.19
	% error		5.4	0.28
0.8044		784.16	739.93	786.29
	% error		5.6	0.27
Av. Abs. %error			4.6	0.27

Table A.36: Comparisons between measured and predicted densities of binary systems; of Jamboor with Basrah cruds at 25, 30, 40, and 50^{o}C, where subscript 1, 2 indicates equation 4-18 and equation 4-16 respectively.

Jamboor X_2	Excess Volume Cm^3/Kg	Temperature ^{o}C				Av. Abs. % error
		25^{o}C	30^{o}C	40^{o}C	50^{o}C	
0.1057	$V^{E}_{\exp}$	-0.21	-0.22	-0.24	-0.26	
	V^{E}_{Cal1}	-0.208	-0.214	-0.233	-0.260	1.6
	V^{E}_{Cal2}	-0.209	-0.217	-0.236	-0.257	1.2
0.3071	$V^{E}_{\exp}$	-0.43	-0.44	-0.48	-0.52	
	V^{E}_{Cal1}	-0.435	-0.450	-0.493	-0.527	1.8
	V^{E}_{Cal2}	-0.435	-0.458	-0.501	-0.536	3.2
0.5001	$V^{E}_{\exp}$	-0.50	-0.52	-0.58	-0.61	
	V^{E}_{Cal1}	-0.492	-0.508	-0.563	-0.594	2.3
	V^{E}_{Cal2}	-0.491	-0.500	-0.556	-0.587	3.3
0.6943	$V^{E}_{\exp}$	-0.41	-0.42	-0.47	-0.50	
	V^{E}_{Cal1}	-0.418	-0.428	-0.483	-0.518	2.5
	V^{E}_{Cal2}	-0.415	-0.419	-0.470	-0.508	0.78
0.9124	$V^{E}_{\exp}$	-0.17	-0.17	-0.20	-0.23	
	V^{E}_{Cal1}	-0.165	-0.166	-0.192	-0.216	3.9
	V^{E}_{Cal2}	-0.169	-0.176	-0.206	-0.231	1.8
Av. Abs.% error (Cal 1)		1.7	2.3	3.0	2.7	
Av. Abs.% error (Cal 2)		0.99	2.6	2.6	2.0	

Table A.37: Comparisons between measured and predicted densities of binary systems; of Jamboor with Baghdad cruds at 25, 30, 40, and 50^{o}C, where subscript 1, 2 indicates equation 4-18 and equation 4-16 respectively.

Jamboor X_2	Excess Volume Cm^3/Kg	Temperature ^{o}C				Av. Abs. % error
		25^{o}C	30^{o}C	40^{o}C	50^{o}C	
0.1521	$V^E{}_{\exp}$	-0.56	-0.59	-0.76	-0.98	
	$V^E{}_{Cal1}$	-0.555	-0.584	-0.797	-0.978	1.8
	$V^E{}_{Cal2}$	-0.557	-0.578	-0.754	-0.950	1.6
0.2910	$V^E{}_{\exp}$	-0.86	-0.94	-1.32	-1.52	
	$V^E{}_{Cal1}$	-0.861	-0.953	-1.276	-1.525	1.3
	$V^E{}_{Cal2}$	-0.866	-0.977	-1.335	-1.594	2.7
0.4909	$V^E{}_{\exp}$	-1.06	-1.24	-1.57	-1.89	
	$V^E{}_{Cal1}$	-1.072	-1.223	-1.583	-1.885	0.9
	$V^E{}_{Cal2}$	-1.073	-1.211	-1.569	-1.866	1.2
0.6888	$V^E{}_{\exp}$	-1.04	-1.13	-1.14	-1.75	
	$V^E{}_{Cal1}$	-1.021	-1.146	-1.425	-1.755	1.2
	$V^E{}_{Cal2}$	-1.007	-1.119	-1.388	-1.673	2.5
0.8723	$V^E{}_{\exp}$	-0.60	-0.67	-0.81	-1.03	
	$V^E{}_{Cal1}$	-0.614	-0.660	-0.790	-1.027	1.6
	$V^E{}_{Cal2}$	-0.618	-0.684	-0.824	-1.085	3.1
Av. Abs.% error (Cal 1)		1.3	1.3	2.5	0.27	
Av. Abs.% error (Cal 2)		1.7	2.3	1.1	3.8	

Table A.38: Comparisons between measured and predicted densities of binary systems; of Basrah with Kirkuk cruds at 25, 30, 40, and 50^oC , where subscript 1, 2 indicates equation 4-18 and equation 4-16 respectively.

Basrah X_2	Excess Volume Cm^3/Kg	Temperature ^oC				Av. Abs. % error
		25^oC	30^oC	40^oC	50^oC	
0.0900	$V^E_{\exp}$	-0.13	-0.14	-0.16	-0.17	
	V^E_{Cal1}	-0.147	-0.153	-0.174	-0.188	10
	V^E_{Cal2}	-0.132	-0.139	-0.161	-0.178	1.7
0.3010	$V^E_{\exp}$	-0.31	-0.32	-0.36	-0.39	
	V^E_{Cal1}	-0.297	-0.312	-0.351	-0.377	3.1
	V^E_{Cal2}	-0.310	-0.328	-0.367	-0.370	2.4
0.5025	$V^E_{\exp}$	-0.37	-0.39	-0.43	-0.46	
	V^E_{Cal1}	-0.372	-0.389	-0.429	-0.461	0.3
	V^E_{Cal2}	-0.359	-0.376	-0.404	-0.452	3.6
0.6916	$V^E_{\exp}$	-0.31	-0.32	-0.35	-0.38	
	V^E_{Cal1}	-0.120	-0.123	-0.134	-0.144	62
	V^E_{Cal2}	-0.237	-0.286	-0.234	-0.177	30
0.9182	$V^E_{\exp}$	-0.12	-0.12	-0.13	-0.14	
	V^E_{Cal1}	-0.224	-0.230	-0.250	-0.270	91
	V^E_{Cal2}	-0.204	-0.161	-0.264	-0.365	92
Av. Abs.% error (Cal 1)		33	33	33	34	
Av. Abs.% error (Cal 2)		20	10	29	45	

Table A.39: Comparisons between measured and predicted densities of binary systems; of Kirkuk with Byee-Hassin cruds at 25, 30, 40, and 50 ^{o}C , where subscript 1, 2 indicates equation 4-18 and equation 4-16 respectively.

Byee-Hassin X_2	Excess Volume Cm^3/Kg	Temperature ^{o}C				Av. Abs. % error
		25 ^{o}C	30 ^{o}C	40 ^{o}C	50 ^{o}C	
0.1042	$V^{E}{}_{\exp}$	-0.16	-0.17	-0.19	-0.23	
	$V^{E}{}_{Cal1}$	-0.163	-0.176	-0.192	-0.232	1.7
	$V^{E}{}_{Cal2}$	-0.158	-0.167	-0.182	-0.225	2.3
0.3078	$V^{E}{}_{\exp}$	-0.38	-0.41	-0.48	-0.53	
	$V^{E}{}_{Cal1}$	-0.381	-0.408	-0.477	-0.529	0.39
	$V^{E}{}_{Cal2}$	-0.394	-0.423	-0.515	-0.555	4.7
0.4998	$V^{E}{}_{\exp}$	-0.45	-0.48	-0.57	-0.62	
	$V^{E}{}_{Cal1}$	-0.441	-0.473	-0.573	-0.618	1.1
	$V^{E}{}_{Cal2}$	-0.428	-0.460	-0.542	-0.598	4.4
0.6977	$V^{E}{}_{\exp}$	-0.34	-0.37	-0.47	-0.51	
	$V^{E}{}_{Cal1}$	-0.353	-0.384	-0.468	-0.514	2.2
	$V^{E}{}_{Cal2}$	-0.352	-0.381	-0.450	-0.499	3.2
0.8888	$V^{E}{}_{\exp}$	-0.16	-0.18	-0.20	-0.24	
	$V^{E}{}_{Cal1}$	-0.150	-0.168	-0.201	-0.236	3.7
	$V^{E}{}_{Cal2}$	-0.159	-0.179	-0.220	-0.253	4.3
Av. Abs.% error (Cal 1)		2.8	3.2	0.55	0.72	
Av. Abs.% error (Cal 2)		2.8	2.5	6.1	3.6	

Table A.40: Comparisons between measured and predicted densities of binary systems; of Kirkuk with Baghdad cruds at 25, 30, 40, and 50^oC , where subscript 1, 2 indicates equation 4-18 and equation 4-16 respectively.

Kirkuk X_2	Excess Volume Cm^3/Kg	Temperature ^oC				Av. Abs. % error
		25^oC	30^oC	40^oC	50^oC	
0.1107	$V^E_{\exp}$	**-0.36**	**-0.41**	**-0.55**	**-0.63**	
	V^E_{Cal1}	**-0.360**	**-0.401**	**-0.551**	**-0.633**	**0.72**
	V^E_{Cal2}	**-0.361**	**-0.404**	**-0.539**	**-0.615**	**1.6**
0.3034	$V^E_{\exp}$	**-0.82**	**-0.95**	**-1.31**	**-1.46**	
	V^E_{Cal1}	**-0.808**	**-0.956**	**-1.298**	**-1.450**	**0.94**
	V^E_{Cal2}	**-0.810**	**-0.982**	**-1.356**	**-1.525**	**3.1**
0.5009	$V^E_{\exp}$	**-0.94**	**-1.16**	**-1.54**	**-1.76**	
	V^E_{Cal1}	**-0.972**	**-1.166**	**-1.569**	**-1.780**	**1.7**
	V^E_{Cal2}	**-0.960**	**-1.122**	**-1.508**	**-1.707**	**2.6**
0.7049	$V^E_{\exp}$	**-0.84**	**-0.94**	**-1.27**	**-1.51**	
	V^E_{Cal1}	**-0.792**	**-0.920**	**-1.227**	**-1.483**	**3.3**
	V^E_{Cal2}	**-0.820**	**-0.943**	**-1.226**	**-1.462**	**2.3**
0.8401	$V^E_{\exp}$	**-0.47**	**-0.54**	**-0.71**	**-0.94**	
	V^E_{Cal1}	**-0.504**	**-0.557**	**-0.740**	**-0.958**	**4.2**
	V^E_{Cal2}	**-0.478**	**-0.550**	**-0.751**	**-0.991**	**3.7**
Av. Abs.% error (Cal 1)		**3.6**	**1.7**	**2.1**	**1.2**	
Av. Abs.% error (Cal 2)		**1.6**	**2.0**	**3.4**	**3.7**	

Table A.41: comparisons between measured and predicted excess volume of Jamboor crude oil with Heavy naphtha at 25^0C, where subscript 1, 2 indicates equation 4-18 and equation 4-16 respectively.

Heavy naphtha X_2	Excess volume (exp.R)	Excess volume (Cal.eq.2)	Abs. %error	Excess volume (Cal.eq.1)	Abs. %error
0.0987	-0.46	-0.46	0.4	-0.41	9.8
0.2732	-0.97	-0.97	0.39	-0.99	2.1
0.4223	-1.21	-1.25	2.9	-1.25	3.3
0.5215	-1.30	-1.26	3.0	-1.28	1.4
0.6589	-1.18	-1.18	0.06	-1.14	3.7
0.8625	-0.52	-0.53	1.5	-0.56	7.8
Over all abs. % error			1.4		4.7

Table A.42: comparisons between measured and predicted excess volume of Basrah crude oil with Heavy naphtha at 25^0C, where subscript 1, 2 indicates equation 4-18 and equation 4-16 respectively.

Heavy naphtha X_2	Excess volume (exp.R)	Excess volume (Cal.eq.2)	Abs. %error	Excess volume (Cal.eq.1)	Abs. %error
0.0943	-0.75	-0.73	2.8	-0.54	27
0.2506	-1.03	-1.11	7.4	-1.21	18
0.4760	-1.68	-1.60	4.7	-1.66	1.2
0.5445	-1.73	-1.76	1.4	-1.67	3.4
0.6402	-1.59	-1.55	2.3	-1.58	0.43
0.9102	-0.54	-0.58	6.6	-0.60	11
Over all abs. % error			4.2		10

Table A.43: comparisons between measured and predicted excess volume of Kirkuk crude oil with Heavy naphtha at $25^0 C$, where subscript 1, 2 indicates equation 4-18 and equation 4-16 respectively.

Heavy naphtha X_2	Excess volume (exp.R)	Excess volume (Cal.eq.2)	Abs. %error	Excess volume (Cal.eq.1)	Abs. %error
0.0902	-0.65	-0.65	0.69	-0.62	5.2
0.2705	-1.44	-1.46	1.2	-1.43	0.79
0.4234	-1.69	-1.67	1.3	-1.74	2.9
0.5438	-1.73	-1.79	3.6	-1.76	1.7
0.6802	-1.65	-1.56	5.4	-1.55	6.0
0.9142	-0.49	-0.53	7.2	-0.58	18
Over all abs. % error			3.3		5.7

Table A.44: comparisons between measured and predicted excess volume of Kirkuk crude oil with Light naphtha at $25^0 C$, where subscript 1, 2 indicates equation 4-18 and equation 4-16 respectively.

Light naphtha X_2	Excess volume (exp.R)	Excess volume (Cal.eq.2)	Abs. %error	Excess volume (Cal.eq.1)	Abs. %error
0.104	-2.51	-2.50	0.59	-0.31	87
0.3325	-7.29	-7.47	2.5	-7.63	4.6
0.4432	-8.86	-9.01	1.7	-8.89	0.31
0.5197	-9.43	-9.46	0.3	-9.31	1.3
0.6538	-9.22	-8.47	8.1	-8.99	2.5
0.9367	-2.32	-2.73	18	-2.72	17
Over all abs. % error			5.0		19

Table A.45: comparisons between measured and predicted excess volume of Byee-Hassin crude oil with Gas oil at $25^{0}C$, where subscript 1, 2 indicates equation 4-18 and equation 4-16 respectively.

Gas oil X_2	Excess volume (exp.R)	Excess volume (Cal.eq.2)	Abs. %error	Excess volume (Cal.eq.1)	Abs. %error
0.1082	-0.10	-0.10	2.3	-0.10	2.7
0.3122	-0.21	-0.20	4.5	-0.21	0.46
0.4968	-0.25	-0.25	0.90	-0.24	5.7
0.5567	-0.22	-0.23	6.2	-0.23	5.1
0.7534	-0.17	-0.17	0.20	-0.18	3.0
0.9345	-0.07	-0.07	5.2	-0.06	14
Over all abs. % error			3.2		5.2

Table A.46: comparisons between measured and predicted excess volume of Byee-Hassin crude oil with Kerosene at $25^{0}C$, where subscript 1, 2 indicates equation 4-18 and equation 4-16 respectively.

Kerosene X_2	Excess volume (exp.R)	Excess volume (Cal.eq.2)	Abs. %error	Excess volume (Cal.eq.1)	Abs. %error
0.0902	-0.24	-0.24	1.9	-0.24	0.78
0.2654	-0.59	-0.61	3.4	-0.60	1.9
0.4642	-0.79	-0.78	1.5	-0.76	3.2
0.5279	-0.76	-0.75	1.4	-0.75	0.88
0.6038	-0.67	-0.67	0.60	-0.70	4.6
0.8336	-0.35	-0.36	3.1	-0.34	3.1
Over all abs. % error			2.0		2.4

Table A.47: comparisons between measured and predicted excess volume of Byee-Hassin crude oil with Light naphtha at $25^{0}C$, where subscript 1, 2 indicates equation 4-18 and equation 4-16 respectively.

Light naphtha X_2	Excess volume (exp.R)	Excess volume (Cal.eq.2)	Abs. %error	Excess volume (Cal.eq.1)	Abs. %error
0.1112	-2.90	-2.88	0.84	-2.70	6.9
0.3786	-7.70	-7.82	1.6	-7.93	3.0
0.4534	-8.41	-8.71	3.6	-8.62	2.4
0.5122	-9.02	-8.76	2.9	-8.83	2.1
0.6234	-8.78	-8.33	5.2	-8.43	4.0
0.7778	-5.88	-6.20	5.4	-6.13	4.3
Over all abs. % error			3.2		3.8

Table A.48: comparisons between measured and predicted excess volume of Byee-Hassin crude oil with Heavy naphtha at $25^{0}C$, where subscript 1, 2 indicates equation 4-18 and equation 4-16 respectively.

Heavy naphtha X_2	Excess volume (exp.R)	Excess volume (Cal.eq.2)	Abs. %error	Excess volume (Cal.eq.1)	Abs. %error
0.1281	-0.75	-0.75	0.33	-0.73	3.2
0.2620	-1.25	-1.27	1.4	-1.34	7.5
0.3786	-1.88	-1.81	3.6	-1.78	5.4
0.4556	-2.04	-2.05	0.68	-2.00	1.8
0.5583	-2.11	-2.017	2.8	-2.20	4.1
0.8007	-1.86	-1.84	1.3	-1.83	1.4
Over all abs. % error			1.7		3.9

Table A.49: comparisons between measured and predicted excess volume of Baghdad crude oil with Heavy naphtha at $25^{0}C$, where subscript 1, 2 indicates equation 4-18 and equation 4-16 respectively.

Heavy naphtha X_2	Excess volume (exp.R)	Excess volume (Cal.eq.2)	Abs. %error	Excess volume (Cal.eq.1)	Abs. %error
0.1281	-0.88	-0.87	0.72	-0.87	1.5
0.2620	-1.65	-1.51	8.5	-1.62	1.8
0.3786	-1.96	-2.49	27	-2.05	4.7
0.4775	-2.26	-1.98	12	-2.21	2.1
0.5583	-2.21	-1.99	10	-2.19	0.94
0.8007	-1.32	-1.45	9.6	-1.34	1.2
Over all abs. % error			11		2.1

Table A.50: comparisons between measured and predicted excess volume of Baghdad crude oil with Light naphtha at $25^{0}C$, where subscript 1, 2 indicates equation 4-18 and equation 4-16 respectively.

Light naphtha X_2	Excess volume (exp.R)	Excess volume (Cal.eq.2)	Abs. %error	Excess volume (Cal.eq.1)	Abs. %error
0.1029	-4.42	-4.32	2.2	-3.81	14
0.3033	-7.16	-7.66	7.0	-7.78	8.6
0.4855	-8.31	-8.21	1.3	-8.39	0.92
0.5234	-8.47	-8.27	2.3	-8.23	2.8
0.6056	-7.89	-7.42	5.9	-7.61	3.5
0.8807	-2.78	-3.15	13	-3.08	11
Over all abs. % error			5.3		6.7

Table A.51: comparisons between measured and predicted excess volume of Safyia crude oil with Gas oil at $25^0 C$, where subscript 1, 2 indicates equation 4-18 and equation 4-16 respectively.

Gas oil X_2	Excess volume (exp.R)	Excess volume (Cal.eq.2)	Abs. %error	Excess volume (Cal.eq.1)	Abs. %error
0.0980	-0.12	-0.12	3.0	-0.13	5.2
0.2956	-0.26	-0.23	9.9	-0.25	3.0
0.3911	-0.28	-0.30	5.9	-0.28	0.00
0.4855	-0.29	-0.31	6.6	-0.30	2.1
0.5201	-0.30	-0.29	2.0	-0.30	0.11
0.7345	-0.28	-0.27	2.7	-0.28	0.70
Over all abs. % error			5.0		1.9

Table A.52: comparisons between measured and predicted excess volume of Safyia crude oil with Kerosene at $25^0 C$, where subscript 1, 2 indicates equation 4-18 and equation 4-16 respectively.

Kerosene X_2	Excess volume (exp.R)	Excess volume (Cal.eq.2)	Abs. %error	Excess volume (Cal.eq.1)	Abs. %error
0.1577	-0.58	-0.57	1.4	-0.54	6.8
0.2275	-0.64	-0.65	1.8	-0.67	5.0
0.4194	-0.79	-0.81	2.1	-0.82	3.4
0.4821	-0.83	-0.84	1.3	-0.82	1.7
0.5819	-0.80	-0.75	6.8	-0.78	3.0
0.7846	-0.54	-0.56	4.2	-0.55	2.6
Over all abs. % error			2.9		3.8

Table A.53: comparisons between measured and predicted excess volume of Safyia crude oil with Heavy naphtha at 25 ^{0}C, where subscript 1, 2 indicates equation 4-18 and equation 4-16 respectively.

Heavy naphtha X_2	Excess volume (exp.R)	Excess volume (Cal.eq.2)	Abs. %error	Excess volume (Cal.eq.1)	Abs. %error
0.2275	-2.75	-2.74	0.26	-2.69	2.4
0.4194	-3.28	-3.33	1.4	-3.42	4.3
0.5119	-3.35	-3.32	0.76	-3.34	0.37
0.5819	-3.20	-3.16	1.3	-3.11	2.8
0.6667	-2.69	-2.71	0.77	-2.67	0.58
0.9144	-0.68	-0.68	0.73	-0.74	9.5
Over all abs. % error			0.87		3.3

Table A.54: comparisons between measured and predicted excess volume of Jamboor crude oil with n-Hexadecane at 25^{0}C, where subscript 1, 2 indicates equation 4-18 and equation 4-16 respectively.

n-Hexadecane X_2	Excess volume (exp.R)	Excess volume (Cal.eq.2)	Abs. %error	Excess volume (Cal.eq.1)	Abs. %error
0.0993	0.39	0.39	0.68	0.42	6.4
0.3288	0.93	0.96	2.8	0.95	1.8
0.4234	1.11	1.09	2.1	1.07	4.1
0.5011	1.16	1.14	1.9	1.13	2.7
0.6717	1.04	1.07	2.8	1.14	9.1
0.8534	0.85	0.84	0.97	0.78	7.7
Over all abs. % error			1.9		5.3

Table A.55: comparisons between measured and predicted excess volume of Basrah crude oil with n-heptane at 25^0C, where subscript 1, 2 indicates equation 4-18 and equation 4-16 respectively.

n-heptane X_2	Excess volume (exp.R)	Excess volume (Cal.eq.2)	Abs. %error	Excess volume (Cal.eq.1)	Abs. %error
0.0674	-1.52	-1.51	0.87	-1.34	12
0.2538	-3.73	-3.81	2.1	-3.85	3.1
0.4378	-4.74	-4.68	1.3	-4.79	1.0
0.5011	-4.88	-4.81	1.4	-4.80	1.6
0.6067	-4.54	-4.58	0.94	-4.50	0.94
0.8532	-2.23	-2.25	0.97	-2.28	2.4
Over all abs. % error			1.3		3.5

Table A.56: comparisons between measured and predicted excess volume of Basrah crude oil with n-Nonane at 25^0C, where subscript 1, 2 indicates equation 4-18 and equation 4-16 respectively.

n-Nonane X_2	Excess volume (exp.R)	Excess volume (Cal.eq.2)	Abs. %error	Excess volume (Cal.eq.1)	Abs. %error
0.1002	-0.73	-0.73	0.26	-0.89	22
0.2171	-1.82	-1.81	0.40	-1.64	10
0.4504	-2.30	-2.30	0.02	-2.39	4.0
0.5621	-2.37	-2.41	1.7	-2.44	2.8
0.7487	-2.21	-2.13	3.5	-1.99	9.7
0.8732	-1.08	-1.12	4.0	-1.25	16
Over all abs. % error			1.7		11

Table A.57: comparisons between measured and predicted excess volume of Kirkuk crude oil with Toluene at $25^0 C$, where subscript 1, 2 indicates equation 4-18 and equation 4-16 respectively.

Toluene X_2	Excess volume (exp.R)	Excess volume (Cal.eq.2)	Abs. %error	Excess volume (Cal.eq.1)	Abs. %error
0.1015	0.65	0.65	0.12	0.64	1.6
0.2458	1.38	1.38	0.18	1.39	0.66
0.4386	1.86	1.85	0.79	1.86	0.23
0.4918	1.85	1.90	2.9	1.86	0.35
0.6327	1.61	1.56	3.4	1.60	0.61
0.8013	0.91	0.93	2.2	0.92	0.68
Over all abs. % error			1.6		0.69

Table A.58: comparisons between measured and predicted excess volume of Kirkuk crude oil with n-Heptane at $25^0 C$, where subscript 1, 2 indicates equation 4-18 and equation 4-16 respectively.

n-Heptane X_2	Excess volume (exp.R)	Excess volume (Cal.eq.2)	Abs. %error	Excess volume (Cal.eq.1)	Abs. %error
0.0902	-2.18	-2.18	0.21	-2.28	4.7
0.2705	-4.03	-4.05	0.44	-4.27	6.0
0.4234	-5.44	-5.42	0.42	-4.97	8.6
0.5438	-5.60	-5.66	1.1	-5.43	3.0
0.6802	-5.06	-4.97	1.8	-5.73	13
0.9142	-3.78	-3.82	0.94	-3.19	16
Over all abs. % error			0.81		8.5

Table A.59: comparisons between measured and predicted excess volume of Byee-Hassin crude oil with Cyclohexane at $25^{0}C$, where subscript 1, 2 indicates equation 4-18 and equation 4-16 respectively.

Cyclohexane X_2	Excess volume (exp.R)	Excess volume (Cal.eq.2)	Abs. %error	Excess volume (Cal.eq.1)	Abs. %error
0.0992	0.56	0.58	2.8	0.60	7.3
0.2930	1.49	1.42	4.8	1.49	0.22
0.4526	1.95	1.96	0.69	1.91	2.2
0.5088	1.99	2.04	2.7	1.98	0.58
0.7532	1.57	1.60	2.0	1.68	7.2
0.9217	0.87	083	5.0	0.72	17
Over all abs. % error			3.0		5.7

Table A.60: comparisons between measured and predicted excess volume of Byee-Hassin crude oil with Toluene at $25^{0}C$, where subscript 1, 2 indicates equation 4-18 and equation 4-16 respectively.

Toluene X_2	Excess volume (exp.R)	Excess volume (Cal.eq.2)	Abs. %error	Excess volume (Cal.eq.1)	Abs. %error
0.1022	0.45	0.45	3.6	0.42	6.0
0.3135	1.32	1.34	1.7	1.38	4.6
0.4436	1.79	1.72	3.7	1.76	1.5
0.5027	1.89	1.72	9.0	1.84	2.4
0.7556	1.36	1.80	33	1.42	4.6
0.9367	0.50	0.26	49	0.43	14
Over all abs. % error			17		5.5

Table A.61: comparisons between measured and predicted excess volume of Byee-Hassin crude oil with n-Hexadecane at $25^{0}C$, where subscript 1, 2 indicates equation 4-18 and equation 4-16 respectively.

n-Hexadecane X_2	Excess volume (exp.R)	Excess volume (Cal.eq.2)	Abs. %error	Excess volume (Cal.eq.1)	Abs. %error
0.1345	0.39	0.37	4.5	0.39	1.1
0.3163	0.73	0.80	10	0.75	3.0
0.4206	0.87	0.86	1.0	0.86	1.5
0.4982	0.90	0.84	6.2	0.88	2.2
0.7232	0.65	0.63	3.6	0.68	4.6
0.9120	0.28	0.31	11	0.25	9.8
Over all abs. % error			6.1		3.7

Table A.62: comparisons between measured and predicted excess volume of Baghdad crude oil with n-Hexadecane at $25^{0}C$, where subscript 1, 2 indicates equation 4-18 and equation 4-16 respectively.

n-Hexadecane X_2	Excess volume (exp.R)	Excess volume (Cal.eq.2)	Abs. %error	Excess volume (Cal.eq.1)	Abs. %error
0.0887	0.13	0.13	0.61	0.10	22
0.3007	0.32	0.32	0.15	0.35	9.6
0.4630	0.48	0.47	1.8	0.48	0.2
0.5397	0.53	0.52	2.0	0.50	4.8
0.6557	0.48	0.51	6.2	0.49	1.8
0.9326	0.14	0.13	7.7	0.15	6.5
Over all abs. % error			3.1		7.6

Table A.63: comparisons between measured and predicted excess volume of Baghdad crude oil with n-Nonane at 25^0C, where subscript 1, 2 indicates equation 4-18 and equation 4-16 respectively.

n-Nonane X_2	Excess volume (exp.R)	Excess volume (Cal.eq.2)	Abs. %error	Excess volume (Cal.eq.1)	Abs. %error
0.2088	-1.71	-1.70	0.38	-1.78	4.1
0.3114	-2.73	-2.75	0.62	-2.64	3.3
0.4377	-3.19	-3.19	0.01	-3.21	0.54
0.49212	-3.29	-3.27	0.49	-3.24	1.6
0.5665	-2.96	-2.96	0.06	-3.06	3.3
0.7422	-1.86	-1.87	0.33	-1.82	2.0
Over all abs. % error			0.32		2.5

Table A.64: comparisons between measured and predicted excess volume of Baghdad crude oil with n-Heptane at 25^0C, where subscript 1, 2 indicates equation 4-18 and equation 4-16 respectively.

n-Heptane X_2	Excess volume (exp.R)	Excess volume (Cal.eq.2)	Abs. %error	Excess volume (Cal.eq.1)	Abs. %error
0.0308	-0.53	-0.52	1.0	-0.49	7.5
0.2791	-4.64	-4.70	1.3	-4.69	1.0
0.4734	-5.81	-5.81	0.04	-5.74	1.3
0.5276	-5.57	-5.45	2.2	-5.49	1.4
0.6025	-4.64	-4.63	0.25	-4.81	3.6
0.7363	-2.91	-2.99	2.7	-2.86	1.9
Over all abs. % error			1.2		2.8

Table A.65: comparisons between measured and predicted excess volume of Safyia crude oil with Cyclohexane at $25^{0}C$, where subscript 1, 2 indicates equation 4-18 and equation 4-16 respectively.

Cyclohexane X_2	Excess volume (exp.R)	Excess volume (Cal.eq.2)	Abs. %error	Excess volume (Cal.eq.1)	Abs. %error
0.0900	0.67	0.65	3.0	0.58	13
0.3078	1.62	1.75	7.9	1.71	5.5
0.4343	2.09	1.99	5.0	2.05	1.9
0.5106	2.11	2.11	0.19	2.12	0.28
0.7943	1.46	1.36	6.6	1.38	5.6
0.9201	0.47	0.57	21	0.60	28
Over all abs. % error			7.2		9.0

Table A.66: comparisons between measured and predicted excess volume of Safyia crude oil with Toluene at $25^{0}C$, where subscript 1, 2 indicates equation 4-18 and equation 4-16 respectively.

Toluene X_2	Excess volume (exp.R)	Excess volume (Cal.eq.2)	Abs. %error	Excess volume (Cal.eq.1)	Abs. %error
0.1034	0.41	0.40	3.3	0.36	12
0.3195	1.15	1.23	7.0	1.22	5.8
0.4908	1.52	1.46	3.8	1.51	091
0.5469	1.54	1.48	3.8	1.48	3.6
0.7533	0.90	0.95	5.9	0.95	5.5
0.8907	0.40	0.40	1.1	0.38	5.7
Over all abs. % error			4.2		5.6

Table A.67: comparisons between measured and predicted excess volume of Light naphtha with Heavy naphtha at $25^{0}C$, where subscript 1, 2 indicates equation 4-18 and equation 4-16 respectively.

Light naphtha X_2	Excess volume (exp.R)	Excess volume (Cal.eq.2)	Abs. %error	Excess volume (Cal.eq.1)	Abs. %error
0.0614	-0.26	-0.262	0.65	-0.238	8.6
0.2079	-0.59	-0.586	0.65	-0.614	4.1
0.4814	-0.87	-0.866	0.51	-0.842	3.2
0.7084	-0.68	-0.697	2.5	-0.712	4.8
0.9022	-0.36	-0.35	2.9	-0.334	7.3
Over all abs. % error			1.4		5.6

Table A.68: comparisons between measured and predicted excess volume of Light naphtha with Kerosene at $25^{0}C$, where subscript 1, 2 indicates equation 4-18 and equation 4-16 respectively.

Light naphtha X_2	Excess volume (exp.R)	Excess volume (Cal.eq.2)	Abs. %error	Excess volume (Cal.eq.1)	Abs. %error
0.0378	-0.22	-0.22	0.53	-0.21	3.5
0.1404	-0.65	-0.65	0.62	-0.65	0.72
0.5245	-1.20	-1.19	0.85	-1.19	0.90
0.5878	-1.15	-1.15	0.37	-1.16	0.99
0.8026	-0.82	-0.82	0.33	-0.82	0.27
Over all abs. % error			0.54		1.3

Table A.69: comparisons between measured and predicted excess volume of Heavy naphtha with Kerosene at 25^{0}C, where subscript 1, 2 indicates equation 4-18 and equation 4-16 respectively.

Heavy naphtha X_2	Excess volume (exp.R)	Excess volume (Cal.eq.2)	Abs. %error	Excess volume (Cal.eq.1)	Abs. %error
0.1045	-0.20	-0.20	0.84	-0.21	5.7
0.2565	-0.44	-0.45	2.1	-0.43	1.6
0.4803	-0.57	-0.55	3.2	-0.56	0.99
0.6914	-0.46	-0.47	2.9	-0.47	2.7
0.9320	-0.15	-0.15	2.2	-0.13	10
Over all abs. % error			2.3		4.3

Table A.70: comparisons between measured and predicted excess volume of Kerosene with Gas oil at 25^{0}C, where subscript 1, 2 indicates equation 4-18 and equation 4-16 respectively.

Kerosene X_2	Excess volume (exp.R)	Excess volume (Cal.eq.2)	Abs. %error	Excess volume (Cal.eq.1)	Abs. %error
0.1463	-0.11	-0.11	1.4	-0.12	6.5
0.2955	-0.21	-0.21	0.64	-0.20	3.7
0.4948	-0.26	-0.26	1.0	-0.26	0.28
0.7067	-0.23	-0.24	5.6	-0.24	4.0
0.8044	-0.20	-0.19	4.9	-0.19	4.3
Over all abs. % error			2.7		3.7

Table A.71: Smoothing Coefficients equation 4-18 for the binary crude mixtures at 25, 30, 40, 50

		Temperature ^oC			
Crude		**25**	**30**	**40**	**50**
Jamboor and Basrah	A_o	**-1.96741**	**-2.04526**	**-2.25296**	**-2.37604**
	A_1	**-0.09875**	**-0.09047**	**-0.05165**	**-0.04807**
	A_2	**-0.25444**	**-0.22204**	**-0.28312**	**-0.53806**
Jamboor and Baghdad	A_o	**-4.30411**	**-4.91039**	**-6.34362**	**-7.55972**
	A_1	**0.78796**	**0.94112**	**0.60673**	**1.06395**
	A_2	**-1.12686**	**-0.57088**	**-0.53987**	**-1.57196**
Basrah and Kirkuk	A_o	**-1.45914**	**-1.52482**	**-1.68422**	**-1.81421**
	A_1	**-0.01361**	**-0.04276**	**-0.10740**	**-0.10605**
	A_2	**-0.14940**	**-0.11440**	**-0.15603**	**0.17347**
Basrah and Baghdad	A_o	**-4.01469**	**-4.49853**	**-5.0.3810**	**-5.89466**
	A_1	**0.17092**	**-0.02833**	**-0.11760**	**-0.08235**
	A_2	**0.15393**	**0.43475**	**0.27265**	**0.08786**
Kirkuk and Byee-hassin	A_o	**-1.76533**	**-1.89199**	**-2.29163**	**-2.47068**
	A_1	**-0.14656**	**-0.11845**	**-0.02104**	**-0.05881**
	A_2	**0.22310**	**0.16454**	**0.40479**	**0.05659**
Kirkuk and Baghdad	A_o	**-3.88071**	**-4.65439**	**-6.26331**	**-7.10588**
	A_1	**0.00752**	**-0.07989**	**-0.23531**	**0.388760**
	A_2	**0.34788**	**1.04511**	**1.38114**	**0.60102**

Table A.72: Smoothing Coefficients equation 4-18 for the binary crude-fraction systems at 25°C

Crude		Light naphtha	Heavy naphtha	Kerosene	Gas oil
Jamboor	A_o	**-28.4041**	**-5.1372**		
	A_1	**-0.9268**	**-0.0181**		
	A_2	**6.1416**	**0.7588**		
Basrah	A_o		**-6.7302**		
	A_1		**0.9842**		
	A_2		**0.8722**		
Kirkuk	A_o	**-37.3872**	**-7.0979**		
	A_1	**10.4176**	**-0.0892**		
	A_2	**5.5757**	**-0.5042**		
Byee-Hassin	A_o	**-35.2448**	**-8.4171**	**-3.0482**	**-0.9425**
	A_1	**4.4919**	**3.9840**	**-0.4175**	**-0.0613**
	A_2	**7.3477**	**1.8937**	**0.7274**	**-0.1196**
Baghdad	A_o	**-33.3513**	**-8.8774**		
	A_1	**-7.6010**	**0.2082**		
	A_2	**-3.0168**	**1.7441**		
Safiya	A_o		**-13.4521**	**-3.2542**	**-1.1913**
	A_1		**-3.9083**	**-0.4984**	**0.2073**
	A_2		**1.0233**	**-0.9970**	**-0.6242**

Table A.73: Smoothing Coefficients equation 4-18 for the binary crude-spike systems at 25°C

Crude		Cyclohexane	Toluene	n-Heptane	n-Nonane	n-Hexadecane
Jamboor	A_o		**9.0114**			**4.5124**
	A_1		**-2.0721**			**-1.2471**
	A_2		**-5.588**			**1.7550**
Basrah	A_o			**-19.2153**	**-9.7473**	
	A_1			**-1.8713**	**1.0132**	
	A_2			**-0.6857**	**-1.4133**	
Kirkuk	A_o		**3.4063**	**-22.0870**		
	A_1		**1.3474**	**-2.1810**		
	A_2		**-2.3139**	**2.3275**		
Byee-Hassin	A_o	**7.8811**	**7.3827**			**3.5197**
	A_1	**-1.9771**	**-1.6898**			**0.0621**
	A_2	**0.6679**	**-2.1248**			**-0.4737**
Baghdad	A_o			**-12.9471**	**-22.5824**	**1.9783**
	A_1			**-2.1903**	**-8.8820**	**-0.6781**
	A_2			**9.9074**	**16.4616**	**-0.2570**
Safiya	A_o	**8.4541**	**6.0267**			
	A_1	**-0.6616**	**0.0591**			
	A_2	**-1.1842**	**-3.4494**			

Table A.74: Smoothing Coefficients equation 4-18 for the binary combination system of petroleum fraction mixtures

Petroleum fraction pairs	T/°C	A_o	A_1	A_2
LN & HN	**25**	**-3.36571**	**-0.14273**	**-0.81936**
LN & KER	**25**	**-4.81201**	**-0.04989**	**-1.00218**
HN & KER	**25**	**-2.25796**	**-0.07780**	**0.09633**
KER & GO	**25**	**-1.04533**	**0.22166**	**-0.09863**

شكر و تقدير

أود أن أعبر عن إمتناني العميق و شكري الجزيل لمشرفي الدكتور جابر شنشول لما بذله من جهد كبير و إرشادات سديدة و قيمة طوال فترة إعداد الرسالة.

أود أيضاً أن أشكر السيد رئيس القسم و موظفي قسم الهندسة الكيمياوية لتعاونهم أثناء فترة البحث.

و الشكر الجزيل إلى عائلتي لما أبدوه من دعم و تشجيع طوال فترة البحث.

ذرى نصرت عبد الهادي

الخلاصة

تم مزج ثلاثة أنواع من النفوط الخام العراقية، والمأخوذة من آبار مختلفة، عند درجات حرارة مختلفة هي 15، 25، 30°م، وخضعت إلى حسابات الكثافة. تم تسجيل النتائج بصيغة معادلات للحجم النوعي الزائد لهذه الخلائط. إن أنواع النفط الخام المستخدم كانت ذات تنوع جيد حيث تراوحت من النفط الخفيف,كثافة 44.3 لنفط (خانة) ونفط البصرة, كثافة 31.4 علاوة على النفط الخام الثقيل شرق بغداد ذي الكثافة 24.2.

يحصل بصورة عامة عند مزج النفط الخفيف الى الثقيل انكماش ملحوظ في حجم الخلائط. إن درجة الحرارة ما بين 15-30°م لها تأثير قليل على الزيادة الحجمية لكل مزيج تمت دراستهُ.

إن مزيج النفوط مع الهيدروكاربونات الاروماتية ينتج زيادة موجبة في الحجم . إن هذا التأثير يكون أكبر عند أقل درجة غليان كما في التلوين . بينما وجود مجموعة المثيل في الحلقة(الزايلينات) يؤدي إلى نقصان الحجم الزائد الموجب. تأثر الكثافة القياسية للنفط الخام على التمدد الحجمي للخلائط النفطية الاروماتية , اذ يعطي نفط خام خانة ذو الكثافة الواطئة نحو أعلى قيمة للحجم الزائد 2,68 عند مزجه مع التلوين, بينما نفط شرق بغداد ذوالكثافة العالية ينتج 0.7كأقل زيادة في الحجم.

إن خلط النفط مع المشتقات النفطية ذات الطبيعة البرافينية يؤدي الى زيادة حجمية سالبة. إن الانكماش الحاصل يكون أكبر عند خلط الكيروسين مع النفط الخام مما هو عليه في حالة الخليط مع زيت الغاز ذي المدى الغليان الاعلى. كما إن لكثافة النفط الخام تأثير على نقصان الحجم عند مزج النفوط مع المشتقات النفطية, اذ يعطي الخليط الثنائي مع

نفط شرق بغداد ذي الكثافة العالية أقل انكماش في الحجم, بينما تعطي الخلائط النفط الخفيف خانة انكماش أعلى نسبياً.

تَمَ تعميم معادلة الحالة لـ (costald) عن طريق استعمال تقنية (HBT) لحساب الكثافة للخلائط الثنائية للنفوط المدروسة. بلغت نسبة الخطا الكلي عند حساب الكثافات نحو (0.874) للحالات المدروسة والمستحصلة من (54) تجربة علمية.

تَمَ تطوير علاقة عامة بين الكثافة ,درجة الحرارة , و التركيز . لِجميع الخلائط المدروسة لتمثيل البيانات لدرجات حرارة تتراوح بين 15- 50°م, وكما يلي:

$$\rho_{mix} = \rho_{15}\left[A_o + \frac{A_1(\rho_{15}X)}{(t-288)} + \frac{A_2(\rho_{15}X)^{A_3}}{(t-288)^{A_4}} \right]$$

إن التحليلات المفصلة بينت بأن العلاقة المفترضة تعطي نتائج متطابقة الى حد كبير اذ بلغت نسبة الخطأ المطلق الكلي نحو0.305% لـ 384 حالة.

تَمَ حساب الحجم الزائد بإستخدام معادلة التنبؤ بالكثافة المقترحة, تم تطبيق المعادلة لـ(384) مزيج ثنائي وقد أعطت نتائج مرضية وبمعدل خطأ مطلق كلي نحو 3.8 %

تقدير الزيادة الحجمية للخلائط النفطية

رسالة
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درجة ماجستير علوم في الهندسة الكيمياوية

من قبل
ذرى نصرت عبد الهادي
(بكالوريوس في الهندسة الكيمياوية ٢٠٠١)

رمضان ١٤٢٥هـ
تشرين الثاني ٢٠٠٤ م