# EFFECT OF THE CHEMICAL COMPOSITION ON EXCESS VOLUME OF MIXTURES WITH PETROLEUM FRACTION

**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**

**Shymaa Kareem Abd-Alsada**
**(B.Sc. in Chemical Engineering 2001)**

**Rabee el-awal** **1426**

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# *CERTIFICATION*

We certify that the preparation of this thesis titled "**Effect of the Chemical Composition on Excess Volume of Mixtures with Petroleum Fractions**" was made by **Shymaa Kareem Abdul-sada** under our supervision at Al-Nahrain University, College of Engineering, in partial fulfillment of the requirement for the degree of Master of Science in Chemical engineering.

| | |
|---|---|
| Signature: J. Shanshool | Signature: |
| Name: **Prof. Dr. Jabir Shanshool** | Name: **Dr. Naseer Habobi** |
| (Supervisor) | (Supervisor) |
| Date: 22/ 6 /2005 | Date: 22 / 6 / 2005 |

Signature:

Name: **Prof. Dr. Qasim.J.Slaiman**

(Head of Department)

Date: 4 / 7 / 2005

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Signature: J. Shanshool
Name: **Prof. Dr. Jabir Shanshool**
(Supervisor)
Date: 22/ 6 / 2005

Signature:
Name: **Dr. Naseer Habobi**
(Supervisor)
Date: 22 / 6 / 2005

Signature: M. A-R. Mohammed
Name: **Dr. Muhanned A.R.Mohammed**
(Member)
Date: 28/6 / 2005

Signature: N. K. Ibrah
Name: **Dr. Neran K.Ibrahem**
(Member)
Date: 3 / 7 / 2005

Signature: A-H. Mohamed
Name: **Prof. Dr. Abdul-Halim A-K Mohammed**
(Chairman)
Date: 29/ 6 / 2005

Approval of the College of Engineering

Signature: MM Naima
Name: **Prof. Dr. Fawzi M.Al-Naima**
(Dean)
Date: 5/9 /2005

# ABSTRACT

Blending of oil stocks with hydrocarbons form non-ideal mixtures, for which excess volumes can be positive or negative depending to the nature of species. Gas oil mixed with nine petroleum fractions or individual hydrocarbons consisting of aromatics, and paraffinic nature in addition to an alcohol and a ketone. The systems have been subjected to density measurements at two temperatures. The results are reported in terms of excess volume, $V^E$.

Binary mixtures of gas oil with the paraffinic spikes, light naphtha heavy naphtha, kerosene and n-hexadecane produce negative excess volume values. This shrinkage effect is greatest for the lowest boiling spike. N-hexadecane results for in very small negative excess volume and seem to form nearly ideal volumes with gas oil.

The spiking of gas oil with, toluene, xylene, MEK or reduced crude show positive excess volume, indicating that such spikes are effected as "structure breaking" materials leading to expansion.

The spiked gas oil with iso-octanol shows an expansion. The excess volume values increases as the mass fraction of iso-octanol increased.

Methyl ethyl ketone is used usually as solvent for dewaxing of lube oil base stocks. Its binary mixtures with some base oil stocks of different boiling range show positive excess volume. This expansion is greatest for lowest boiling stock.

Excess specific volume of ternary mixtures was studied for spiked gas oil using different nature of spices. For all spiked gas oil ternary system used in this study, the excess volumes seems to be as a result for the corresponding excess volumes of the binary mixtures.

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# 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, °API

C = concentration of spike.

CI = correlation index.

G = gravity difference (crude spike -), °API

K,$K_0$,Kp = experimental constants

$K_w$ = Watson characterisation factor.

MABP = molal average boiling point, K

$M_w$ = molecular weight, gm / g mole.

P = pressure, N / $m^2$

Pc = critical pressure, N / $m^2$

$P_r$ = reduced pressure, P/Pc

$P_s$ = saturation pressure, N / $m^2$

SG = specific gravity 15°C

T,t = temperature, °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 mol

V* = characterisation volume $cm^3$/ g mol

VCF = volume correlation factor

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

$V^E$ = excess volume $cm^3$/ mol

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

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

x = mass fraction of reference component

Z = compressibility factor

Greek Letters

$\alpha$ = Correlation coefficient of thermal expansion $m^3$/ kg

$\rho$ = Density, kg/$m^3$

$\rho_{15}$ = Density at 15 ˚C, kg/$m^3$

$\Phi$ = Volume fraction

A, $\beta$, $\gamma$ = Constants

$\omega$ = A centric fraction

$\omega_{SRK}$ = A centric factor from Soave equation of state

$\Delta v$ = Specific volume change for petroleum fractions

$\Delta V$ = Change in molar volumes for hydrocarbon mixtures.

$\Delta V^R$ = Relative excess volume of oil blend, $m^3$ / kg

$\sigma$ = Standard deviation between experimental and fitted value.

Superscript

Cal.= calculated value.

Exp.= experimental value.

mix., m= mixture.

I,j=components.

Superscripts

E = Excess

id = Ideal

(o) = Simple fluid

MEK = methyl ethyl ketone

# CHAPTER ONE
# INTRODUCTION

The objective of product blending is to allocate the available blending components in such away as to meet product demands and specifications at the least cost and to produce incremental products which maximize overall profit (1).

As apart of conservation effort of the pipe line industry, the cases of oil losses in transit are being investigated continuously. Such investigations 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 components and the heavier crude oil. That is, 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 volume basis, while of course, no loss of weight as a result of the mixing operation (2).

The appearance and characteristics of crude oils vary widely from oil field and even from well in the same oil field. Knowledge of the physical and chemical properties of oils is necessary for the marketing requirements and for understanding of the need for the various refinery process (3).

Density is a property, which has the greatest influence on the value of crude oil and its products and together with viscosity have active roles in selling, transportation and other industrial applications (4). The variation of density with temperature is a property of great technical importance, since most petroleum products are sold at the prevailing temperatures rather than at the standard 15.6ºC (5).

In fact 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 pipe lines to the consumer or to the refiner (6).

In the blending of petroleum components having different physical properties, excess volumes occur because the components do not form ideal solutions. In ideal solutions, the total 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.

Glasstone(7) states that if a solution of two or more components exhibits positive deviation from Raoult's law, the observed vapour 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 megatire deviation from Raoult's law, usually, there is a decrease in both vapour pressure and volume on mixing. This is attributed to the mean attractire forces between the molecules in the mixture being greater than for the constituents separately.

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 the thermodynamic. Property (excess volume) is an important thermodynamic property in process design calculation, and accurate prediction of this property is required.

The current project was investigated to study the effect of chemical composition of species on volumetric behavior of oil product mixtures. Further aim of the work was investigated to evaluate the volumetric behavior of blends of lubricating base oils with methyl-ethyl ketone. Since the base oils are usually treated with methyl-ethyl ketone for dewaxing purposes. Also to develop appropriate equations to predicate the excess volumes of the blends at different composition.

# CHAPTER TWO
# LITERATURE SURVEY

## 2.1 Characterization of Oil Stocks

### 2.1.1 General Properties

The chemical compositions of crude oils are surprisingly uniform even though their physical characteristics vary widely. The hydrocarbons present in crude petrol petroleum are classified into three general types; paraffin's, naphthenes, and aromatics, in addition, to olefins that are formed during processing by the de-hydrogenation of paraffin's and naphthenes (8). In this way, the differences between crude oils could be explained by the relative amounts of each series, paraffin's, naphenes and aromatics present in oil, and the extent to which individual members of a series appear in the crude. This view has been corroborated by modern studies.

There are several correlations between yield and the aromaticity and paraffinicity of crude oil and their fractions, but the two most widely used are the uop or "Watson characterization", factor kw and the u.s. Bureau of mines "correlation Index". CI, as given in equation (2-1) and (2-2) respectively (1).

$$\mathbf{Kw = (TB)^{1/3} / SG} \qquad \ldots\ldots\ldots\ldots\ldots \text{(2-1)}$$

$$\mathbf{CI = (87552/TB) + 473.7\ SG - 456.8} \qquad \ldots\ldots\ldots\ldots\ldots \text{(2-2)}$$

Where, TB = average boiling point, ºR.

SG = specific gravity at 60ºF

Crude oils show a narrow range of Kw and vary from less than 10.5 for highly aromatic crude to 15 for highly paraffinic base crude (1). For petroleum fractions, the values of Kw are usually between 12.5 to 13.0 for paraffinic, 11.0 to 12.0 for naphthenes and between 9.0 to 12.0 for aromatic types (9). Therefore the correlation index is useful in evaluating individual fractions from crude oils.

The CI scale is based upon straight – chain paraffin's having a CI value of 0 and benzene having a CI value of 100. The CI values are not quantitative, but the lower the CI value the greater the concentration of paraffin hydrocarbons in the fraction, and the higher the CI value the greater the concentrations of naphthenes and aromatics (1).

Pour point gives an indication of minimum temperature at which the oil will flow and is an important property of fuel oil and lubricating oils (7). The lower pours point the lower paraffin content and the greater content of aromatics (1).

Carbon residue gives a measure of the quantity of solid deposits obtained when medium and heavy fuel oils are subjected to evaporation and pyrolysis at high temperatures. The bulk of the oil will evaporate; but the heavier and more complex material will decompose and form carbon a ceous deposit (8). The carbon residue is roughly related to the asphalt content of the crude and the quantily of lubricating oil fraction that can be recovered. In most cases the lower the carbon residue the more valuable is the crude.

The distillation properties of petroleum fraction are carried out according standard methods such as ASTM or TBP in a procedure of evaluating the percentage distillate with the corresponding temperature. The results are usually plotted as distillation curves. The distillation curves give in formation about initial boiling point, End boiling point and the temperature of any particulate cut.

Distillation curves are of value in assessing the suitability of petroleum fractions for various applications, particularly in respect to volatility. Such information is also needed for the deign and control of distillation columns. It is also useful, usually in conjunction with some other physical properties such as density, in characterizing petroleum fractions to permit prediction of other properties (3).

### 2.1.2 Critical Properties

For undefined petroleum fractions, it is a common practice that only inspection data, namely, true boiling point ($T_b$), specific gravity (SG), and molecular weight (Mw) are experimentally measured. However, in order to predict thermophysical properties of these fluids using corresponding states correlations, values of the critical constants, acentric factor and other characterization parameters for fractions are necessary (3). Therefore, correlations for estimating these characterization parameters as functions of the fractions $T_b$, and SG have been listed below:

1- Critical Temperature and Critical Pressure

Due to Winn (10), the critical temperature and critical pressure are formulated as follows

$$P_c = 6.1488\times10^7\ MABP^{-2.3177}\ SG^{2.4853} \qquad \text{………..} \ (2\text{-}3)$$

$$T_c = 0.55556\ \exp\left[4.2009\ MABP^{0.08615}\ SG^{0.04614}\right] \qquad \text{……….} \ (2\text{-}4)$$

2- Critical Volume, can be expressed as follows (11)

$$In\ (V_c) = 80.4479 - 129.8038\ SG + 63.1750\ SG^2 - 13.1750\ SG^3 + 1.10108\ \ln(Mw) + 42.1958\ in(SG) \qquad \text{………...}(2\text{-}5)$$

3- Molecular Weight, is expressed as follows (12)

$$Mw = -12272.6 + 9486.4SG + (4.6523-3.3287SG)\ T_b + [1-0.77085SG-0.02058SG^2)1.3437-720.79/(T_b)10^7/T_b+(1-0.80882SG+0.02226\ SG^2)(1.8828 - 181.98/T_b)10^{12}/T_b^3 \qquad \text{………..}(2\text{-}6)$$

4- Acentric Factor

Due to Lee and Kesler(13) in which the Watson characterization factor $W=(1.80MABP)^{1/3}/SG$, $T_{Br}=MABP/T_c$ and $P_{Br}=1.01325/P_c$: for $T_{Br}< 0.8$

$$\omega = [192P_{Br}-5.92714+6.09648/T_{Br}+1.28862\ \ln T_{Br}-0.16947\ T_{Br}^6]/[15.2518-15.6875/T_{Br}-13.4721\ \ln T_{Br}+0.3577\ T_{Br}^6] \qquad \text{………...}(2\text{-}7)$$

for $T_{Br} > 0.8$

$$\omega = 7.904+0.1352W-0.00465W^2+8.359T_{Br}+(1.408-0.01063W)/T_{Br} \ldots(2\text{-}8)$$

where: $T_c$= critical temperature, K; SG= specific gravity at 15°C

$P_c$= critical pressure, bar; MABP=Molal average boiling point, K

$V_c$= critical volume, $cm^3$/g-mol

## 2.2 Blending

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 (1). 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.

The major refinery products produced by blending are gasoline, jet fuels, heating oils, diesel fuels and lubricating oils. The objective of product blending is to allocate the available blending components in such away as to meet product demands and specifications at the least cost and to produce incremental products which maximize overall profit (1).

Motor gasoline is produced from products of many sources made available by oil refineries. Normal butane is added to gasoline to give the desired vapour pressure. Some additives are mixed in suitable proportion to get the desired octane number (14).

Heavy fuel oils are usually blended with low-viscosity oil-stocks to reduce there viscosities and pour point, or to easy pipelining. The large numbers of lubricating oils sold today are produced by blending a small number of lubricating oil base stocks and additives to give the oils desirable characteristics or to enhance and improve existing properties.

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 over all cost or profit.

Prediction of the true volume of an oil blend is important to the refiners since small changes can have considerable economic significance when products are measured in thousands of barrels. Several investigators have presented charts and equations for estimating these volumetric contractions (15).

## 2.3 Estimation Oil Stocks Densities

### 2.3.1 Background

Density and specific gravity are extensively used in connection with petroleum products, while the term API gravity is widely preferred in oil industries. API gravity is usually reported as apart of a crude oil or product analysis, and hence no short-cut methods of estimation are needed (5).

Data on density at specified temperatures are required daily in a variety of chemical engineering computations involve: fluid flow, heat and mass transfer, pumping mixing, estimate of other properties, and interconvsions of volumetric and mass flow rates (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 (16).

## 2.3.2 Standard Techniques for Calculating Oil Stocks Density

The common stander techniques for estimating the densities of oil stocks are as follows:

### I- API Standard 2530 (17)

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

$$\boldsymbol{\alpha = K_o/\rho^2_{15}} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ (2\text{-}9)$$

Where $K_0$ = 613.9723, in the metric measurement system.

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

$$\mathbf{VCF = Exp\ [-a\ (T-15)-0.8\ a^2\ (T-15)^2]} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ (2\text{-}10)$$

Where T is the temperature (°C) to which correlation is to be made.

To determine the density from an input density at a temperature other than 15°C requires an iterative process assuming a value for the density at 15°C, calculating the VCF and comparing the density calculated from this with the input value.

The accuracy of the API standard 2530 is given by the following statement:

**Table 2-1** VCF precision at 95 percent confidence level

| **Temperature, °F** | 100 | 150 | 200 | 250 |
|---|---|---|---|---|
| **Precision, %** | ±0.05 | ±0.15 | ±0.25 | ±0.35 |

Standard tables are exist for both crudes and products, which include a rigorous procedure for rounding and truncating results at each calculation stage to ensure reproduction uniformity from any calculating machine.

## II- IP Petroleum Measurement Manual Part X, Section I, Table 3(18)

Compressibility of crude can be evaluated from the relationship:

$$C^* = \mathrm{Exp}\,(1.38315 + 0.00343804\,T - 3.02909\,\ln(P_{15}/1000) - 0.0161654T\,\ln(P_{15}/1000)) \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{(2-11)}$$

Where, $C^*$ is compressibility ($\times 10^5$/bar)
The range of applicability is given as 0 to 35 bar.

## III- IP Tables 53 and 54(19)

Densities of oils at any temperature can be calculated from a single input value of 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 to 600kg/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$^o$F to 0.03% below 0$^o$F. No conclusion on the accuracy of the tables for use with mixtures is possible.

**IV- API "Shrinkage" Procedure (20)**

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

$$\mathbf{S = 0.00214\, C^{-0.0704}\, G^{1.76}} \qquad \text{.................... (2-12)}$$

Where, S = shrinkage factor, as vol. % of spike

### 2.3.3 Hankinson-Brobst-Thomson (HBT) Technique

Hankinson et. al. (21) obtained a fine tuned version of the Costald correlation that predicts the density for 40 "LNG – Like" mixtures with an average absolute percent error of 0.078 percent. This correlation relates the saturated molar volume of a liquid, $V_s$, to a characteristic volume, $V^*$, the reduced temperature, and a modified a centric factor, $\omega_{SRK}$, for each stream component as shown in the following Eqs:

$$V_s / V^* = V_R^{(0)} (1 - \omega_{SRK} V_R^{(8)}) \quad \text{.................(2-13)}$$

$$V_R^{(0)} = 1 + a(1-T_r)^{1/3} + b(1-T_r)^{2/3} + c(1-T_r) + d(1-T_r)^{4/3} \quad 0.25 < T_r < 0.95 \text{ ..... (2-14)}$$

$$V_R^{(8)} = (e + fT_r + gT_r^2 + hT_r^3)/(T_r - 1.0001) \quad 0.25 < T_r < 0.95 \quad \text{...............(2-15)}$$

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 = - 0.048065 |

Thomson et al (22) have extended the HBT method to allow the calculation of compressed liquid volume by generalizing the constants in Tail equation (26) (28). Thus:

$$V = Vs\,(1 - C^* \log((B+P)/(B+P_S))) \quad \text{............ (2-16)}$$

Where, $V_S$= saturated volume from Eq.2-13

$$B = P_C(-1.0 + a(1-T_r)^{1/3} + b(1-T_r)^{2/3} + d(1-T_r) + e(1-T_r)^{4/3}) \quad \text{..........(2-17)}$$

$$e = \mathrm{Exp}\,(f + g\,\omega_{SRK} + h\,\omega^2_{SRK}) \quad \text{.......... (2-18)}$$

And

$$C = j + k\,\omega_{SRK} \quad \text{............... (2-19)}$$

The parameters a through k is given in table 2-1.

**Table 2-2** Parameter for Eqs. (2-22), (2-23) and (2-24)

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

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 vapour pressure relationship. The generalized relationship by Hankinson et al. (23) is as follows:

$$\mathbf{Log\ (P_r) = P_r^{(0)} + \omega\ P_r^{(1)}} \qquad \text{……… (2-20)}$$

Where,

$$\mathbf{F = 35.0 - 36.01\ T_r - 96.736\ log\ (T_r) + T_r^{6}} \qquad \text{……..… (2-21)}$$

$$\mathbf{G = log\ (T_r) + 0.03721754\ (F)} \qquad \text{……..… (2-22)}$$

$$\mathbf{P_r^{(1)} = 4.86601\ (G)} \qquad \text{…….… (2-23)}$$

$$\mathbf{P_r^{(0)} = 5.8031817\ log\ (T_r) + 0.07608141} \qquad \text{……... (2-24)}$$

The values of any mixtures property (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)

$T_{cm} = [\, \sum \sum x_i x_I V_{ij}^{*} T_{cij} \,] / V^{*}_{m}$ ………(2-25)

$V^{*}_{m} = \frac{1}{4} \{ \Sigma_i \, x_i \, v^{*}_{i} + 3(\Sigma \, x_i v_i^{*1/3}) \}$ …….. (2-26)

$V_{ij}^{*} T_{cij} = (V_I^{*} T_{ci} V_j^{*} T_{cj})^{1/2}$ …….. (2-27)

And $\omega_m = \Sigma_i \, x_i \, \omega_{SRK}$ …….. (2-28)

Mixture critical pressure is calculated from:

$P_{cm} = (Z_{cm} \, RT_{cm}) / V^{*}_{cm}$ …….. (2-29)

Where $V^{*}_{m}$ comes from Eq.2-31 and $Z_{cm}$ from:

$Z_{cm} = 0.291 - 0.08 \, \omega_{SRK}$ ……. (2-30)

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 point was 6.1 percent (24).

## 2.3.4 Prediction of mixtures densities

A number of graphical and mathematical methods have been published to suggest ways to estimate the density of petroleum oil and its fractions when no experimental data are available; most of then suffer from various short comings (16).

Teja(25) 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.

Rice and Teja (26)(27) measured the densities of binary mixtures of benzene with n-propyl benzene at 298.15 K and 308.15 K and benzene with n-butyl benzene at 298.15 K and a ternary mixture of hexane, hexadecane and n-propyl alcohol at 298.15 and 323.15 K using a 10 ml pyconmeter.

The variation of density with temperature, or effectively, the thermal coefficient 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°F. Consequently, much work has been expended on the investigation of this function (5).

Orwoll and Flory (28) measured the values of the thermal expansion coefficients $a = 1/v\ (\delta v/\ \delta T)\ P$ of n-hexane and n-heptane. The values of $((v/\ T)_P)$ 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:

$$\mathbf{V = f\,(A+Bt^1+Ct^3)\,dt^1 + V_o} \qquad \text{………… (2-31)}$$

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

Some of the equations by Orwoll and Flory are detailed in table 2.3. In this table, densities are given by thepolynomials in powers of temperature. The estimated ranges of error in densities were $\pm$ 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, °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 (29) 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 coefficient of expansion.

Downer and Inkely (29) demonstrated that the change of the density with temperature has a linear relationship with a slope represent the coefficient of expansion. For the purpose of transfer of bulk petroleum oils and stated at a fixed reference or base temperature, which are 60°F in countries dealing with U.S.A and 15°C or 20°C in a significant number of nation. Rolumes metered at temperatures other than base value are adjusted to the base value by factors developed and tabulated in the petroleum measurement (30).

AL-Najjar, etal (31) demonstrated that of density of crude oil with temperature in the range of (15-50°C) had a linear relationship:

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

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

Shiomi (32) measured the densities and thermal expansion coefficients for poly (vinly methyl ether), over a temperature range of (25-120)°C, then get a predicting equation for $\rho$ and $a$.

$$\rho\ (\mathrm{g/cm^3}) = 1.0725 - 7.259*10^{-4}t + 1.16*10^{-7}t^2 \qquad \text{........... (2-33)}$$

$$a\ (\mathrm{deg^{-1}}) = 6.77*10^{-4} + 2.42*10^{-7}t \qquad \text{............(2-34)}$$

Where t is the temperature in °C.

Tongfan and Danithly (33) measured the densities of acetic acid-water mixtures at temperature between 290 and 460 K and concentrations ranging from 25 wt % to 100 wt % acetic acid. The data were correlated with a polynomial function in temperature and concentration and were extrapolated using two association models and model based on the generalized corresponding state principle (GCSP).

Although the association models provide more information on the structure of solution the GCSP method as given in equation (2-35) required much less information and could apparently be extrapolated over a significant range of temperatures, with accuracy of ± 0.1%.

$$\rho/Kg.m^{-3} = A_o + A_1T/K + A_2T^2/K^2 + A_3T^3/K^3 \quad \text{……….. (2-35)}$$

With:

$$A_o = 534.613 + 1950.54\,x - 1054.32\,x^2 + 174.019\,x^3 \quad \text{…… (2-36)}$$

$$A_1 = 4.1964 - 10.525\,x + 3.1592\,x^2 \quad \text{…… (2-37)}$$

$$A_2 = -\,0.01135 + 0.01214x - 0.00366x^2 \quad \text{…… (2-38)}$$

$$A_3 = 8.4358*10^{-6} - 1.4764*10^{-5}x \quad \text{…… (2-39)}$$

Where, T=is the temperature in K, and X is the mole fraction of acetic acid.

Shanshool and Hashim had generalized the costarred equation to calculate the densities of oil stocks and their mixtures using critical temperature, critical pressure, characteristic volume, suave Redlich-Kowng acentric factor and molecular weight (24). This new method provides accurate and computationally reliable predication of oil stocks densities (24).

## 2.4 Volumetric Behavior of Mixtures

### 2.4.1 Phenomena of excess Volume

The change in volume on mixing liquids is not a recently observed phenomenon, but has been reported by a number of authors. There are many volumes change data in the literature on blends of pure hydrocarbons, and blends of individual chemical (34).

A mixture of typical hydrocarbons forms non-ideal systems for which excess volume may be positive or negative according to the nature of species (9). The phenomenon of volume shrinkage experienced in blending light petroleum components with crude oil is due to the fact that they do not form ideal solution.

An ideal solution may be defined as one in which no specific forces of attractions exist between the components of solution and no change occur in the properties of the components when mixed, merely a dilution of one into the other. Thus in an ideal solution, the total solution volume equal to the sum of volumes of the components and the other physical properties such as refractive index, fluidity and vapor pressure can be calculated by taking the molal average of the components properties (7).

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, than 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 of negative direction. That is it can result in either expansion or shrinkage of total volume upon mixing.

### 2.4.2 Individual components

The excess volume of Individual 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. A number of equations are available in the literature to calculate the value of excess volumes for different Individual component mixtures when no experimental data are available.

Hossein, K. (35) were 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 showed 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. (36) measured the excess volumes of 1,1,2,2-tetrachloroethane with methyl ethyl ketone, dithyl ketone, and methyl propyl ketone between 303.15 and 313.15 K. they showed that the excess volumes were negative over the entire composition range in all the mixtures at both the temperatures. The negative value of excess volume 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. Krishnaiah, and Puligundia (37) measured the excess volumes for six binary mixtures of 1,1,2,2- tetrachloroethane with 1-alkanols (1-propanol, l-butanol, l-pentanol, l-hexanol, l-heptanol, and l-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. (38) were measured the molar excess volumes as a function of mole fraction at 298.15, 308.15 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 for any mixture containing an $m_c$-membered cyclic dirther 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 (39) 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, $CH_2ClCH_2Cl$-pxylene, 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 behighly positive in comparison to those for the systems $CH_2ClCH_2Cl$-benzene, $CH_2ClCH_2Cl$-benze, $CH_2ClCH_2Cl$-p-xylene, and $CH_2CH_2Cl$-cyclohexane.

Reamer, Sage and Lacey (40) determined the volumetric behavior of four mixtures of n-butane and decane experimentally at seven temperatures from 100 to 460 $^oF$, 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 (41) determined the volumetric behavior of four mixtures of propene and l-butene experimentally at temperature range (40-280) $^{o}$F. For up to 10,000 psig. The results are presented in graphical and tabular from.

Winnick and Kong (42) measured the excess volumes for five binary polar liquid mixtures using pyconmeter 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 (43) 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.

### 2.4.3 Oil Stocks

The volumetric properties of binary mixtures of long-chainlinear paraffinic hydrocarbons have been extensively studied. Generally, they exhibit negative volumes, particularly when there is a large difference between the carbon-chain length of the component (44).

It is generally observed that the addition of light paraffinic hydrocarbons to a crude oil produces negative excess volumes; in other words a small "shrinkage occurs relative to the calculated ideal volume. The effect is less pronounced as the molecular size of the ajjed hydrocarbon increases, and it may become an expansion (44).

The volumetric behavior was studied for six Iraqi crude oils from different wells combined with nine light hydrocarbons or light petroleum fractions (1). It was observed, that the mixtures of crude oils with paraffinc spikes give negative excess volume and this value becomes larger as API gravity difference increased. Mixtures of crude oils with aromatic components give positive excess volume (44).

Mixtures of kerosene with aromatic oil stocks show positive excess volume. This expansion effect is greatest for the lowest boiling point spikes as in case of benzene. While spiking of non-aromatic oil products and kerosene results in negative excess volume. This shrinkage effect is greatest for lowest boiling spike (45).

Loffe (46) presented a similar equation to (2-40) for predicting the specific volume change ($\Delta v$) in systems of petroleum fractions. Loffe's is:

$$\mathbf{\Delta v = K_pP_1P_2} \qquad \text{…… (2-40)}$$

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, $K_p$ varies considerably with composition. Inspection of the curve plotted by Reeves (15) indicates that the volume change is a function of the composition and the molecular weights of the components. Accordingly, it was assumed that the following empirical relation could express the volumetric contraction:

$$\mathbf{\text{Log } C = \alpha \log P + \beta \log M_1 + \gamma \log (M_2 - M_1) + K} \qquad \text{…… (2-41)}$$

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 weight of the lighter component and heavier component respectively. $\alpha$, $\beta$ and $\gamma$ are experimental constants. Volume changes in seven different blends of petroleum fractions at (60-70) $^{o}$F with a total of 44 experimental points were used to determine the values of constants in Eq.2-41.

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:

$$\mathbf{Log\ C=0.6107\ log\ P+\ \beta\ log\ M_1+0.537\ log\ (M_2-M_1)+4.418} \quad \text{........ (2-42)}$$

Eq.2-42 is valid for concentration (P) of 50% or less of the heavier component, while for higher concentrations the relation becomes:

$$\mathbf{Log\ C=0.6107\ log\ (100-P)+\beta\ log\ M_1+0.537\ log\ (M_2-M_1)+4.41} \quad \text{...... (4-43)}$$

B 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.

## 2.5 Estimation of Excess volume

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

Kumaran (47) measured molar volume of benzenetn – hexane systems 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:

$$V^E = x\,(1-x)\,[1.612-0.09(1-2x)+0.127(1-2x)^2-0.08(1-2x)^3] \quad \ldots\ldots (2\text{-}44)$$

At 298.15K with a standard deviation of 0.0005, and

$$V^E = x\,(1-x)\,[1.44-0.003(1-2x)+0.073(1-2x)^2-0.057(1-2x)^3] \quad \ldots\ldots (2\text{-}45)$$

At 323.15K with a standard deviation of 0.0006

Cokele (48) measurd 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°C. The molar volume of a mixture calculated as the mole fraction weighted average of the pure component molar volume is within 0.14% of correct value. The resulting equation for mixture molar volume is:

$$V^E = (114.86 + 0.0876t \text{ ml/mole}) + (120.6 + 0.117t \text{ ml/mole})\,x \quad \ldots\ldots.. (2\text{-}46)$$

Where $V^E$ in ml/mole.

Rex Goates et al. (49) measured the densities of binary mixture 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 volume were fitted by a least squares method to an equation of the type:

$$V^E = x\,(1-x)\,\Sigma_{ai}\,(1-2x)^i \quad \ldots\ldots (2\text{-}47)$$

Subramanyam Reddy (43) measured the density of mixtures of benzene + 2-ethoxyethanol of 303.15 and 323.15 K over the entire composition range.

The excess volume were positive at small x 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 0.2 303.15, 313.15 and 323.15K respectively. The results for the excess volumes were fitted by Eq.2-47.

Biron (51) proposed the following relation for calculating the change in molar volumes ΔV for hydrocarbon mixtures.

$$\Delta V = KN_1 N_2 \qquad \text{...... (2-48)}$$

$N_1$ 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.

It is generally observed that the addition of light paraffinic hydrocarbons to a crude oil produces negative excess volumes; in other words a small “shrinkage occurs relative to the calculated ideal volume. The effect is less pronounced as the molecular size of the ajjed hydrocarbon increases, and it may become an expansion.

Ashcroft et al. (53) carried out a series of experimental work to study the volumetric behavior of different types of world crude oils with the 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 quantitative expressions on a volumetric basis, these results were expressed in the from of a dimensionless quantity – the percentage relative excess volume, given by:

$$\Delta V^R = 100 \times [(V_{mix} - V_{ideal})/V_{ideal}] \qquad \ldots\ldots (2\text{-}49)$$

The data were fitted for each crude / spike pair mostly by quadratic equations of the from of Eq.2-54 in terms of volume fraction of spike $\Phi_2$:

$$\Delta V^R = \Phi_2 (1- \Phi_2) (A_0 + A_1 (1-2 \Phi_2) + A_2 (1-2 \Phi_2)^2) \qquad \ldots\ldots (2\text{-}50)$$

The results of excess specific volume for different Iraqi crude oils with light hydrocarbons were fitted for each crude/spike pair by quadratic equation of the following form in terms of mass fraction of spike $x_2$ (1).

$$V^E = x_2(1-x_2) (Ao+A_1) (1-2x_2) +A_2 (1-2x_2^2) \qquad \ldots\ldots (2\text{-}51)$$

J.Shanshool and E.T.Hashim had developed a shrinkage formula for crude oils of diverse origin and individual hydrocarbons or petroleum fraction systems, as follows (50)

$$\mathbf{S = 8.6 \times 10^{-7} (100-C) G^{2.64} u^{-0.14}} \quad \text{……… (2-52)}$$

The purposed equation is more accurate than other known forms.

# CHAPTER THREE
# EXPERMINTAL WORK

## 3.1 Oil Stocks

The petroleum fractions, lightnaphtha, heavy naphtha, kerosene, gasoil and reduced crude were supplied as "stock tanks" products by Al-Daura Refinery in Baghdad. The specific gravities and other available specification of these cuts are given in table 3-1. Three base oils namely stocks 40, 60 and 150 were also obtained from AL-Daura Refinery, while there main properties are listed in table 3-2. Other blend components were Methyl ethyl ketone (Daura Refinery) 2-ethylhexanol (National co. for chemical and plastics industries) and Toluene, Xylenes and n-hexadecaue (local market), for which the available specifications are listed in table 3-3.

**Table 3-1** specification of petroleum fractions

| **Specification** | **Distillate Product** | | | | |
|---|---|---|---|---|---|
| | **Kerosene** | **Heavy napths** | **Light napths** | **Reduced crude** | **Gas oil** |
| **Sp.gravity at 25.6°C** | 0.7762 | 0.74125 | 0.65927 | 0.8901 | 0.8767 |
| **API gravity** | 50.79837 | 59.39376 | 83.13133 | 27.4709 | 29.9007 |
| **Boiling range, °C** | 153-234 | 88-173 | 40-110 | Atm.Res | 205-333 |
| **Flash point °C** | 39 | — | — | 102.5 | 64 |
| **Slupher content,%** | 0.2 | 0.1 | Nil | 147.8 | 0.9 |
| **$M_W$ (gm/g mol)** | 168.56 | 126.72 | 83.59 | 400 | 241.33 |

**Table 3-2** Properties of Base Oil – Stocks

| Specification | 40 stock | 60 stock | 150 stock |
|---|---|---|---|
| **VIS at 20ºC** | 3-3.2 | 8-9 | 28-32 |
| **Sp.gr.d 35ºC** | 0.8505 | 0.8845 | 0.9526 |
| **VI** | 96 | 95 | 94 |
| **Pour point ºC** | -3 | -3 to -6 | 0 |
| **Colour** | 0.5 | 1.5 | 3.0 |
| **Coc.ºC** | 190 | 220 | 290 |

**Table 3-3** specification of light hydro carbons components

| Specification | Toluene | Xylene | Methyl ethyl ketone | n-hexa decanc | 2-ethyl hexanol |
|---|---|---|---|---|---|
| **Sp.gr.at 15.6ºC** | 0.8710 | 0.8701 | 0.806 | — | 0.8323 |
| **API gravity** | 30.95 | 31.12 | — | — | 1 |
| **$M_W$ (gm/g mol)** | 92.14 | 111 | 72.1 | 226.45 | 130.23 |
| **Boiling point,ºC** | 110-111 | — | — | 286.5 | — |
| **Purity** | 99.5% | — | Not less than 18% | 99% | 99% |

## 3.2 Blending

The composition of each oil – products Mixture is prepared as volume percentage and then converted to the weight percent by sensitive digital balance type (sartorius hardy GMBH Gottingen – sensitivity 0.0001 gm).

Mixing process was undertaken by shaking the considered amounts of the samples in a closed 250ml flask at room temperature. Density measurements are made immediately after preparing the mixture to avoid vaporizing the light components.

The following mixtures were prepared in this study:

1. Binary mixtures of gas oil with petroleum fractions and other blend components over range of weight percent (0-100) wt % with random wt % increment had chosen at two temperatures 298.15 K and 308.15 K.

2. Binary mixtures of methyl ethyl ketone with three Base oil–stocks, 40 stocks, 60 stocks, 150 stocks, over range of 0-100 weight percent with random wt % increment at 308.15 K only.

3. Ternary mixtures.

## 2.3 Density measurements

Densities of oil – products and their mixtures are measured at 298.15 K and 308.15 K with an Anton paar digital densitometer (Model DMA 48) and controlled thermostatically with a precision of ±0.01 K; all density measurements are carried out at one atmospheric pressure. Fig, 3-1 shows photograph of DMA 48 densitometer, while its specifications are listed in table 3-4.

**Table 3-4** specification of DMA 48

| | |
|---|---|
| **Measuring range** | 0 to 39 /cm$^3$ |
| **Accuracy** | $\pm 1\times 15^{-5}$ g/cm$^3$ |
| **Precision** | $\pm 3\times 15^{-5}$ g/cm$^3$ |
| **Sample size** | Approx. 0.7 ml |
| **Sample temperature range** | -10 to 70ºC |
| **Temperature equilibrium** | 0.5 to 3.5 min |
| **Typical test cycling time** | 1 to 8 min |
| **Pressure** | Up to 10 bar (150 psig) |

# CHAPTER FOUR
# RESULTS AND DISCUSION

## 4-1 Introduction

The density data obtained in present project cover the entire composition range from 0 to 100 vol.% spike for all mixtures .The density data for each blend were reported in the form of excess specific volume $V^E$ at a given mass fraction of blending component.

The measurements were carried out by using weight fraction rather than volume fraction to get more accurate composition values of the blending stock $\Phi_2$can readily are calculated as follows (44)(52)

$$\Phi_2 = x_2\rho_1^0 / [\rho_2^0 + x_2\rho_1^0 - x_2\,\rho_2^0] \qquad \text{........ (4-1)}$$

Where

$x_2$ = Mass fraction of spike

$\Phi_2$= Volume fraction of spike

$\rho_1^0$= Density of base oil stock

$\rho_2^0$= Density of spike

In view of need to establish quantitative expressions, the results were expressed in the form of excess specific volume $V^E$ according to the following equation.

$$V^E = V_{mix} - V^{id} \qquad \text{..........(4-2)}$$

Where $V_{mix}$ is the actual (total) volume, which is equal to $(1/\rho_{mix})$ in ($cm^3/kg$) and $(\rho_{mix})$ measured density in $kg/m^3$, by combine the data listed in appendix (A), to calculate the excess volume (listed in appendix B). Linear expression for the ideal volume could be gets in terms of mass fraction (45) (35)

$$V^{id} = [\rho_2^0 + x_2 (\rho_1^0 - \rho_1^0)] / \rho_1^0 \rho_2^0 \qquad (cm^3/kg) \qquad \ldots\ldots\ldots (4\text{-}3)$$

The data for binary mixtures in form of excess specific volume $V^E$ plotted against mass fraction of spike, which give usually smooth curves. These curves obtained as shown in Figs. 4-1 to 4-13. These curves pass through zero at 0 and to 100 wt % spikes. While the maximum occur at or close to 0.5 mass fraction.

## 4.2 Excess volume of Petroleum fraction mixtures

Kerosene, Heavy naphtha, light naphtha and reduced crude were chosen to study the effect of such oil – stocks on the excess volumes of their mixtures with gas oil. The results are plotted in Figs 4-1 through 4-4 for two temperatures. See tables B-1 through B-4.

Excess volumes ($V^E$) are negative for each of binary mixtures, Kerosene, Heavy naphtha and light naphtha at 298.15 and 308.15 k and over the complete mass fraction range maximum shrinkage occur at close to 50% mass fraction, indicating that excess volume at this point should be a good indicator of the interactions in these mixtures. Values of excess volume at mass fraction 0.5 are given in table 4-1.

**Table 4-1** Max. Excess volumes, in cm$^3$/kg at about 0.5 mass fractions at 298.15 and 308.15 k.

| Gas oil + | $V^E_{298.15}$ | $V^E_{308.15}$ |
|---|---|---|
| **Reduced crude** | **1.25** | **0.83** |
| **Kerosene** | **-0.21** | **-0.25** |
| **Heavy naphtha** | **-0.22** | **-0.2617** |
| **Light naphtha** | **-1.25** | **-1.518** |

Light naphtha, heavy naphtha and kerosene are considered usually as paraffinic spikes, particularly light naphtha. It well known that linear paraffinic hydrocarbons resulted in volume shrinkage when mixed with crude oils or petroleum fractions (35) (46). The low boiling spike, light naphtha given the largest negative excess volume, about -1.25 cm$^3$/kg at 25˚C, with in the present experimental results. While kerosene show a littlie deviation from ideal behavior, given about -0.21 cm$^3$/kg at 25˚C excess volume.

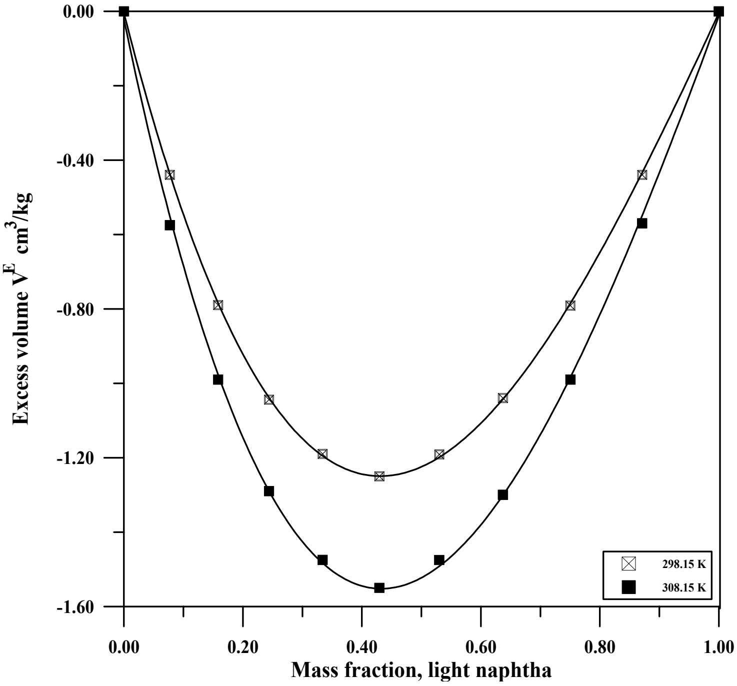

**Fig 4-1** Excess volume of gas oil and light naphtha

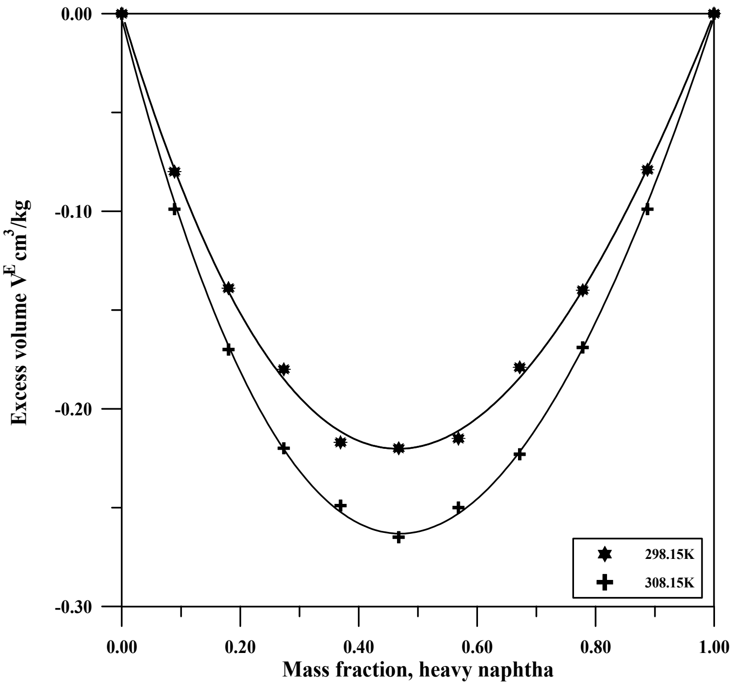

**Fig 4-2** Excess volume of gas oil and heavy naphtha

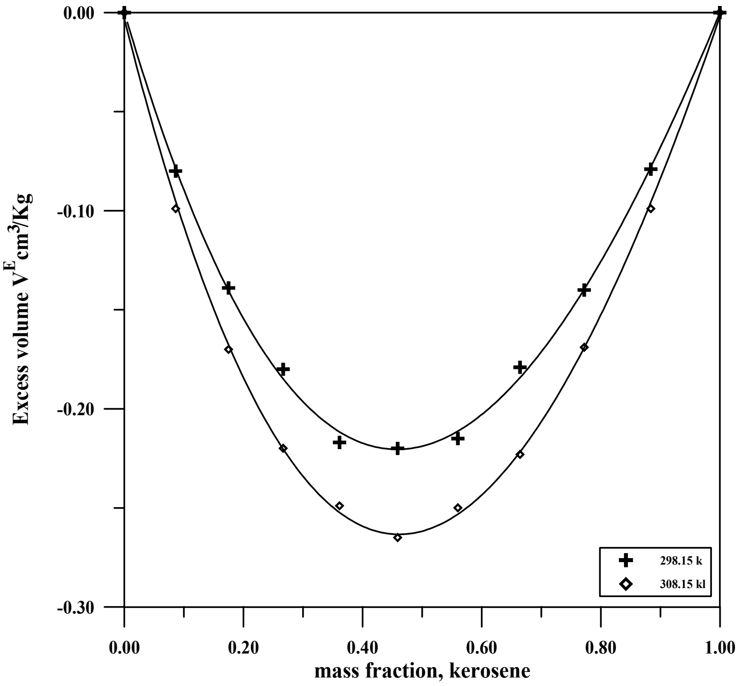

**Fig 4-3** Excess volume of gas oil and kerosene

Mixtures of reduced crude with gas oil exhibit positive excess volume as shown in Fig (4-4). Reduced crude consist mainly of aromatics hydrocarbons. The aromatics as structure- breaking material leading to expansion. The maximum expansion, about 1.2 $cm^3$/kg at 25°C is achieved in this system also at about 0.5 mass fractions, as given in table (4-1).

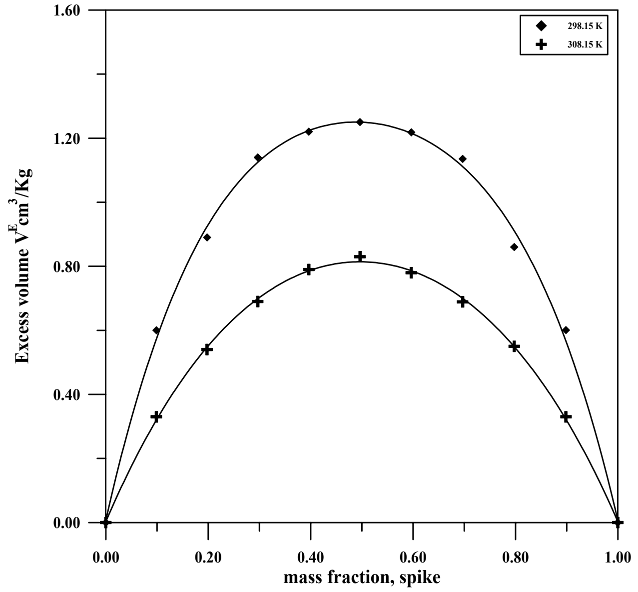

**Fig 4-4** Excess volume of gas oil and reduced crude

Temperatures increase in the range of 25-35°C affected the excess volume of all studied petroleum fractions mixtures. Thus decrease of shrinkage or increase of expansion is observed by increasing the temperature as shown in figs. 4-1through 4-4 and table 4-1. Figs 4-5 and 4-6 summarized the results of excess volume by spiking of gas oil with the considered petroleum fractions at 25and 35°C respectively. It is noticed that light naphtha given the maximum shrinkage while reduced crude resulted maximum expansion.

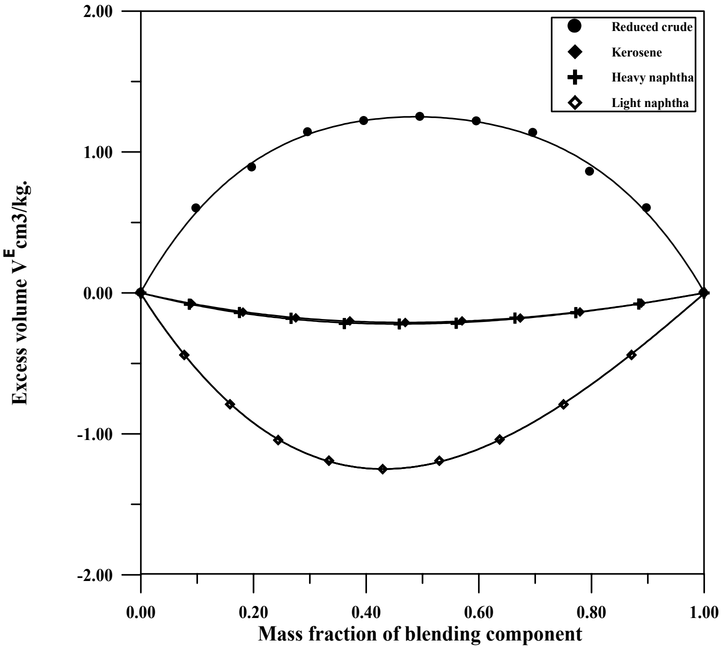

**Fig 4-5** Excess volume of gas oil mixed with some petroleum fractions at 298.15 K

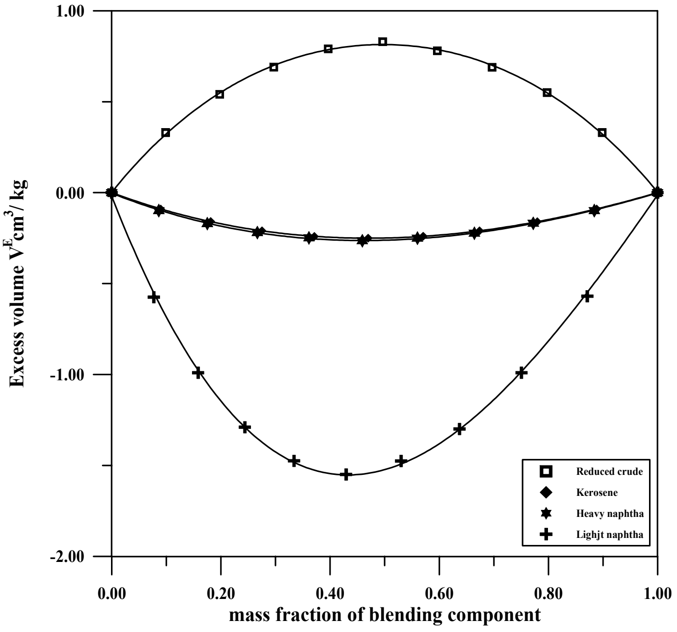

**Fig 4-6** Excess volume of gas oil mixed with some petroleum fractions at 308.15 k

## 4.3 Composition Dependence of Excess volume

The blending of oil stocks results usually in volume change, caused by non–ideal behavior of oil systems as compared with calculated volume. The excess volume behavior of oil mixtures is influenced largely by the chemicals composition of blending component. A contribution was done in the present work to investigate the effect chemical composition of blending species on excess volume of their mixtures with gas oil. Some individual chemicals provided a diverse chemical nature were chosen for this purpose. These are toluene and xylenes as aromatics, n-hexadecane as straight-chain paraffin, and methyl ethyl ketone as ketone and iso-octanol as an alcohol. The results are illustrated in Figs 4-7 through 4-12. The results are listed in tables B-5 through B-10.

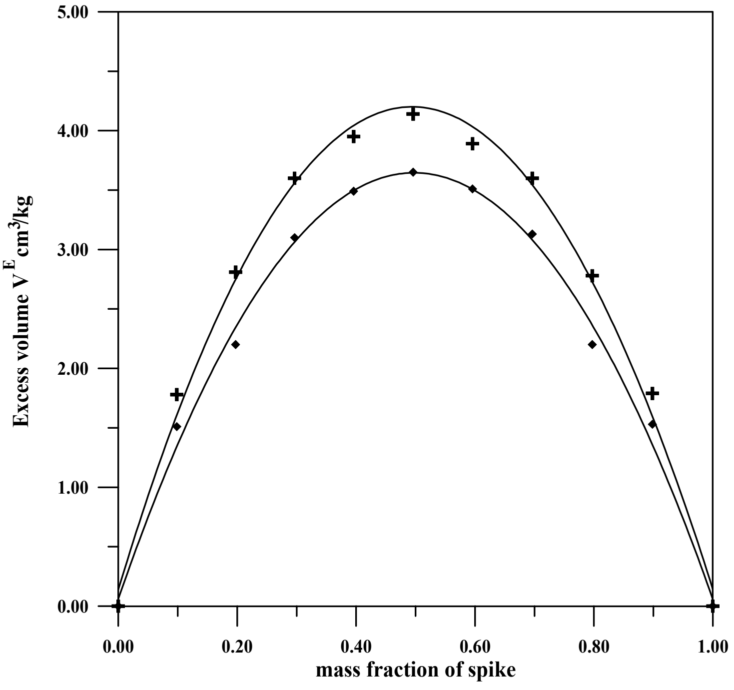

**Fig 4-7** Excess volume of gas oil spiked with toluene

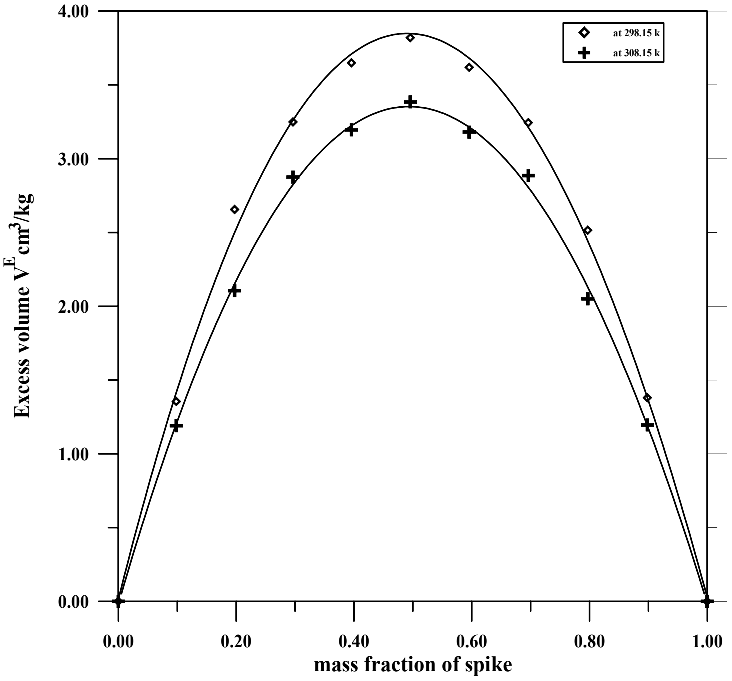

**Fig 4-8** Excess volume of gas oil spiked with xylenes mixture

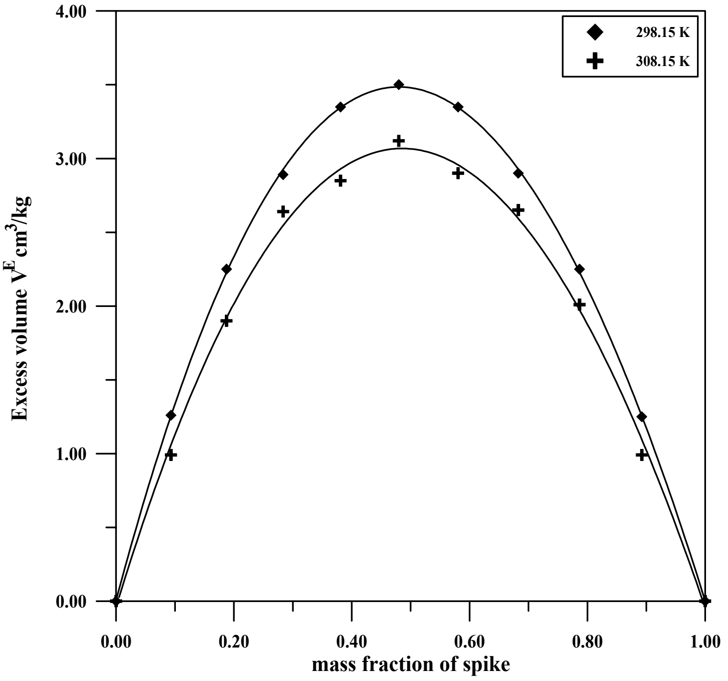

**Fig 4-9** Excess volume of gas oil spiked with MEK

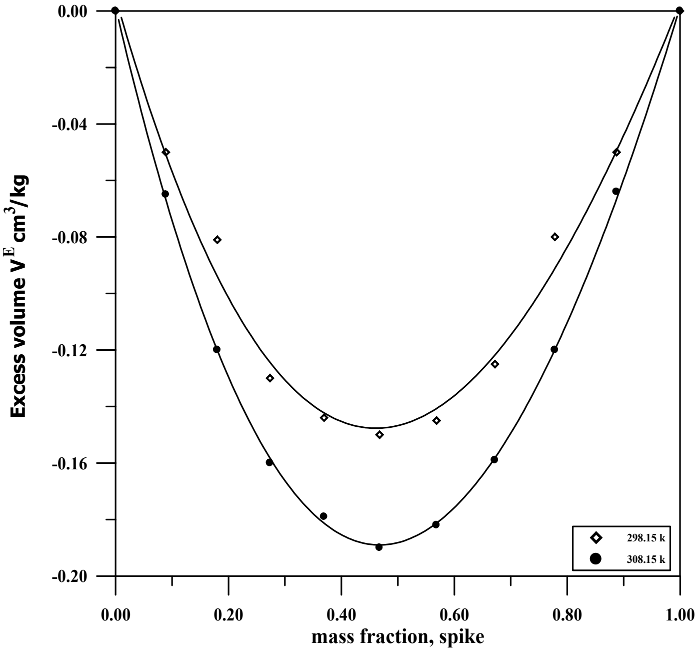

**Fig 4-10** Excess volume of gas oil spiked with n-hexadecane

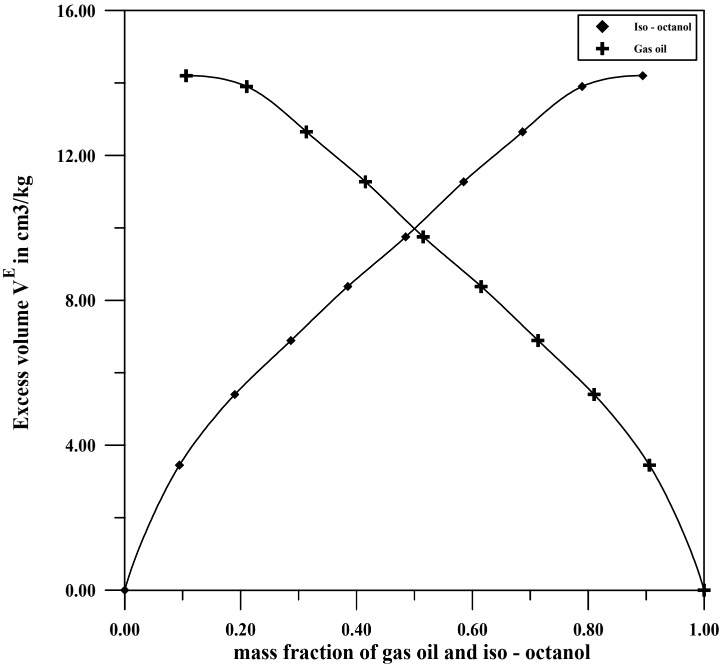

**Fig 4-11** Excess volume of gas oil / Iso-Octanol systems at 298.15 K

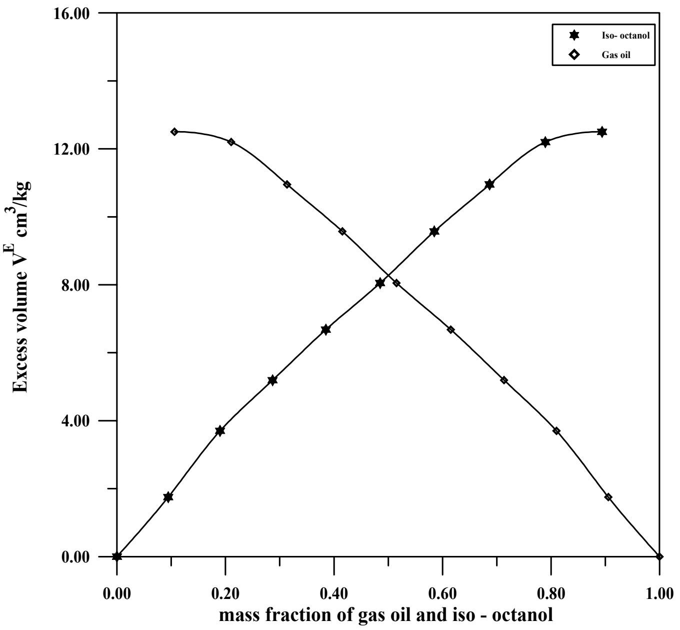

**Fig 4-12** Excess volume of gas oil / Iso-Octanol systems at 308.15 K

The binary mixtures of gas oil with aromatic component, methyl ethyl ketone or iso-octanol show positive values of excess volume, and thus exhibit expansion, iso- octanol being particularly more effective, as shown in Figs 4-13 and 4-14. This effect is appreiable relate to the fact, that such compounds are "structure breaking" materials leading to positive excess volume (54).

Toluene spike results in higher expansion than xylenes, probably due to the presence of an additional methyl group in the later, it was published that benzene as aromatics spike in kerosene produces the highest expansion than toluene and xylenes (46). Mixtures of methyl ethyl ketone with gas oil produce also positive excess volume, but slightly lower than in case of xylenes spike, as shown in Fig.4-14 and table 4-2. Indicating that interactions between unlike molecules are weak and give rise to positive deviation, as in case of aromatic spikes.

**Table 4-2** Max excess volumes, in cm$^3$/kg at about 0.5 mass fraction of spike at 298.15 and 308.15k

| Gas oil + | $V^E$ (298.15) | $V^E$ (308.15) |
|---|---|---|
| **Toluene** | 4.14 | 3.65 |
| **Xylene Mixtures** | 3.805 | 3.385 |
| **Methyl ethyl ketone** | 3.501 | 3.12 |
| **n-hexadecane** | -0.15 | -0.19 |
| **Iso-octanol** | 9.75 | 8.05 |

The spiked gas oil with n-hexadecane resulted in negative values of excess volume, as shown in Fig.4-10. It is generally observed that paraffinic spikes usually produce negative excess volume values. This "shrinkage" effect is greatest for the lowest boiling point spikes (53). It was previous observed that light naphtha, as boiling paraffinic spike with gas oil, gives the highest shrinkage within the present experimental results, as illustrated in Fig 4-1. The maximum value of excess volume with light naphtha (boiling rang = 40 to 110˚C) is about -1.25 cm$^3$/kg at 25˚C, while it is about -0.15 cm$^3$/kg at 25˚C for n-hexadecane (boiling point = 286.5˚C). These indicates that n-hexadecane caused with gas oil, lead to small negative values of excess volume. It is also noticed that if the temperature increased the value of excess volume will be decreased.

The results of excess volume values for spiking of gas oil with iso-octanol are illustrated in Figs 4-11 and 4-12 for temperatures 25˚C and 35˚C respectively. It is interested to notice that Iso–octanol spike produce positive excess volume values over the whole mass fractions .it was published elsewhere (53) that mixtures of alcohols with n-alkanes give positive excess volumes over the entire mass fraction. Higher alcohols give even lager in magnitude than excess volumes observed for mixtures of low alcohols, such as methanol or ethanol with n-heptane (54).

It must be observed that the blend of gas oil in to iso-octanol resulted in negative excess volume values over the whole mass fractions as shown Figs 4-11 and 4-12. It is also noticed that an equal positive value of excess volume about 9.8 $cm^3/kg$ was achieved a mass fraction of about o.5 $cm^3/kg$ for both iso-octanol spiked gas oil or gas oil mixed with iso–octanol. While the maximum excess volume about +14 $cm^3/kg$ is resulted by a mass fraction greater than 0.9 and lower than 1.0 for both systems

.

Temperature increase in the range 25-35˚C, have a low effect on excess volume values for both systems, leading to in decrease of expansion, as shown in Figs 4-11 and 4-12. Figs 4-13 and 4-14 summarized the results of excess volume by spiking of gas oil with the considered of blending component.

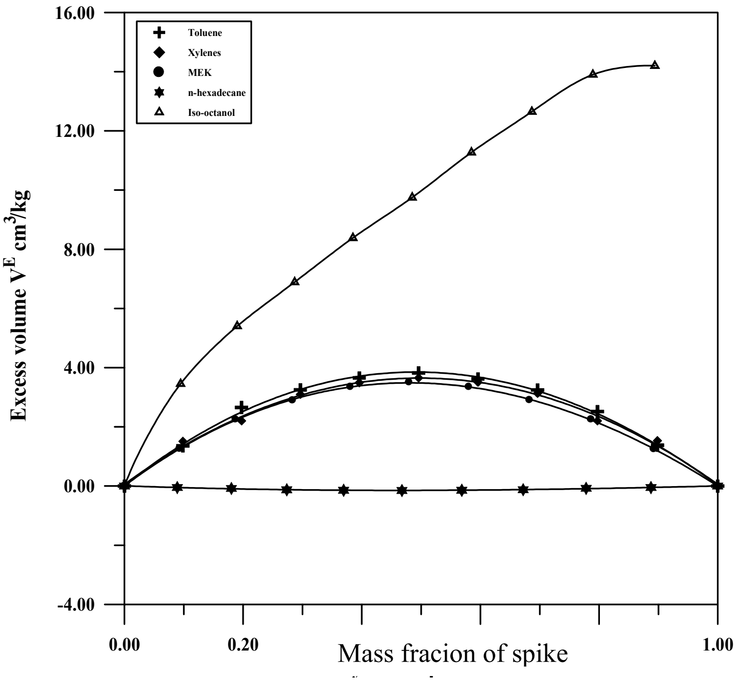

**Fig 4-13** Excess volume of spiked gas oil at 298.15 K

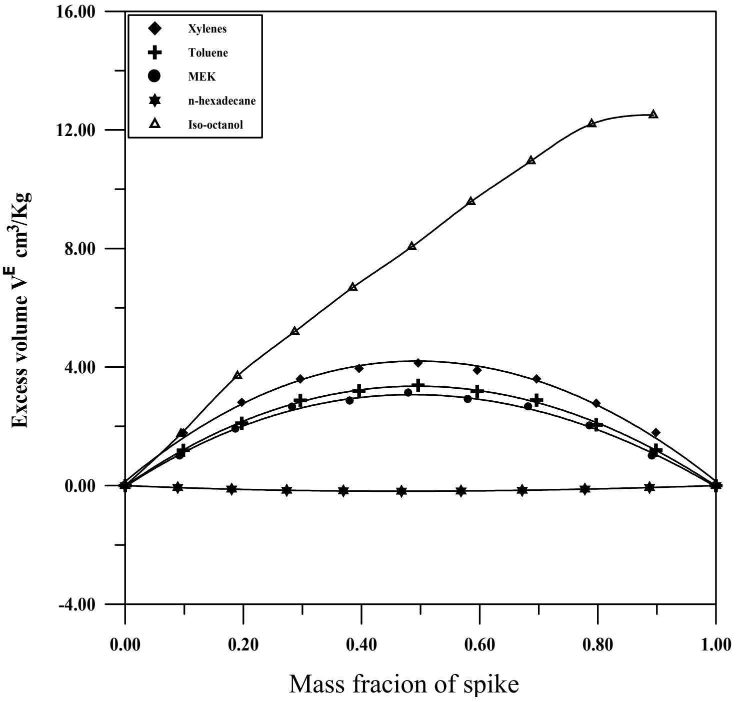

**Fig 4-14** Excess volume of spiked gas oil at 308.15 K

## 4.4 Volumetric Behavior of Base oils / MEK systems

The lubricating oil base stocks are produced usually from vacume distillation of reduced crude and special processing to meet the desired specification (55). The distillation step aimed to separate individual fractions called "Base oils" according to viscosity and boiling range specifications. Therefore stocks 40,60and 150 are considered as some oil base oils, which are ordered according as there increasing boiling range.

Dewaxing by means of methyl ethyl ketone is one of important lube oils processing, aimed to reduce the cloud and pour points. There for MEK was choosen to investigate its volumetric behavior by mixing with the base oil, The excess volume values are illustrated in Fig 4-15 for all base oils considered. It is generally observed that the addition of MEK to the three types of base oil stocks of different boiling ranges produces positive excess volume values. In other words an "expansion" occurs relative to the calculated ideal volume, as shown in Fig 4-15. This behavior is indicating that interactions between unlike molecules are weak and give rise to positive deviations. This expansion effect is greatest for the lowest boiling range, stock 40.

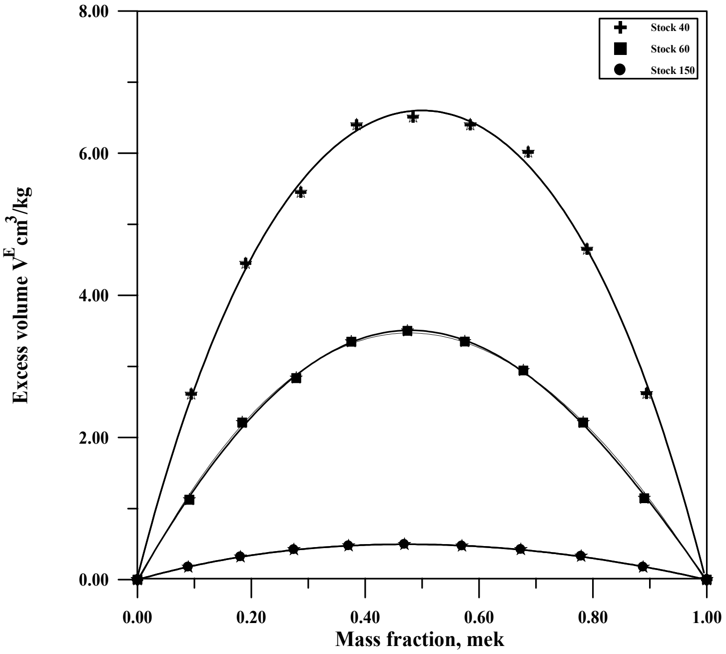

**Fig 4-15** Excess volume of MEK / base oil stocks

As shown in Fig 4-15, the boiling range of base oils has predominate effect on the expansion of MEK spiked base oils, Those stock 40 gives the maximum positive excess volume value of about 6.0 $cm^3/kg$. The spiked stock 60 resulted in a value of about 3.5 $cm^3/kg$, while the heavy base oil, stock 150 resulted in the lowest value of about 0.7 $cm^3/kg$.

The expansion effect of base oils with MEK must be taken in account by design and operation of Dewaxing of lube oil processing unites.

## 4.5 Ternary Mixtures

Four ternary mixture of spiked gas oil were done to satisfy and study the excess volume behavior of such systems. The considered mixtures were composed of gas oil spiked with one gives a negative excess volume and another results in a positive excess volume with gas oil, as follows:

1. Gas oil / Light naphtha / MEK
2. Gas oil / Heavy naphtha / MEK
3. Gas oil / Light naphtha / Toluene
4. Gas oil / Heavy naphtha / Toluene

The mass fraction of gas oil was taken about 0.4 for all systems. The results are illustrated in tables 4-3 through 4-6.

Fig 4-16 shows the excess volume for Gas oil/Light naphtha/Methyl ethyl ketone system. Light naphtha resulted in negative excess volume in gas oil ternary mixtures, while MEK give positive $V^E$ values. As its expected the expansion increase as the mass fraction of MEK increased. While increased mass fraction of light naphtha resulted in negative excess volume. Equal mass fraction for both light naphtha and MEK resulted in close to zero value of excess volume, and seems to form ideal volumes. This effect can be attributed to the fact that light naphtha and MEK spikes have dual effects. MEK as structure breaking material leading to expansion and at the same time the paraffinic spike light naphtha exhibit negative excess volume. Both effects seem to be having of equal in such system, as shown in Fig 4-16 and table 4-3.

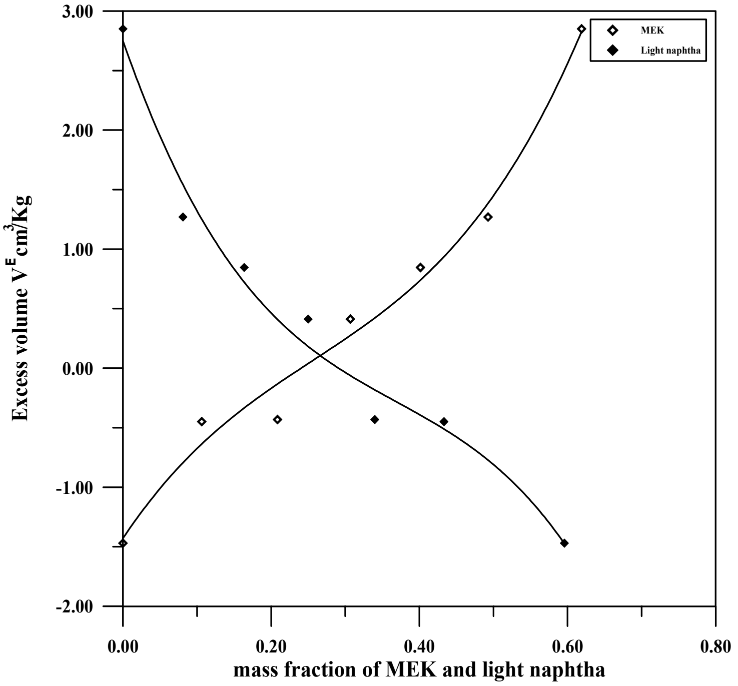

**Fig 4-16** Excess volume of ternary mixtures of gas oil/ light naphtha/ MEK

Heavy naphtha and MEK ternary mixtures show similar excess volume behavior, as discussed previously. Except that the shrinkage effect is lower as in case with light naphtha system. Heavy naphtha exhibits low negative excess volumes. The achieved excess volumes were to be positive the entire range of mass fraction for such over ternary system, as illustrated in table 4-4 and Fig 4-17. Similar effect was noticed for heavy naphtha and toluene spikes in gas oil. The excess volumes were to be positive also over the entire range of mass fractions, as shown in table 4-5 and Fig 4-18.

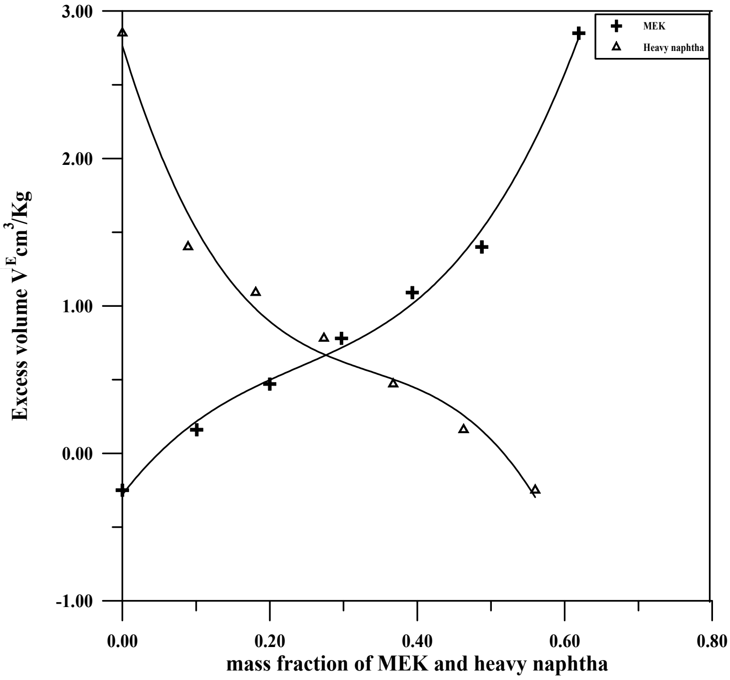

**Fig 4-17** Excess volume of ternary mixtures of gas oil/heavy naphtha/MEK

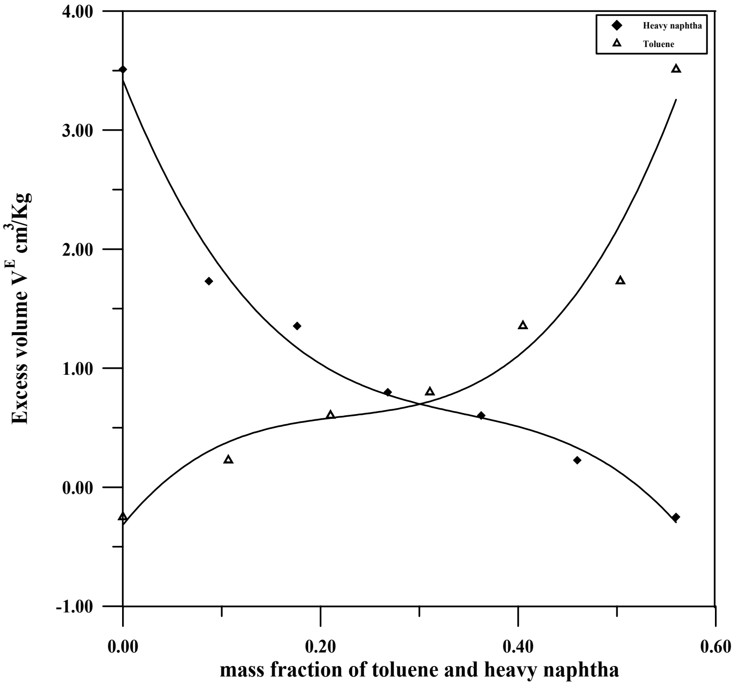

**Fig 4-18** Excess volume of ternary mixtures of gas oil/heavy naphtha/toluene

Toluene results in higher expansion as MEK in there ternary mixtures with gas oil. The results of ternary mixtures of Toluene, Light naphtha spikes are illustrated in table 4-6 and Fig 4-19. Here a gain, toluene as strong structure breaking material resulted in expansion, while light naphtha as high paraffinic spike gives shrinkage. The effect of former is greater.

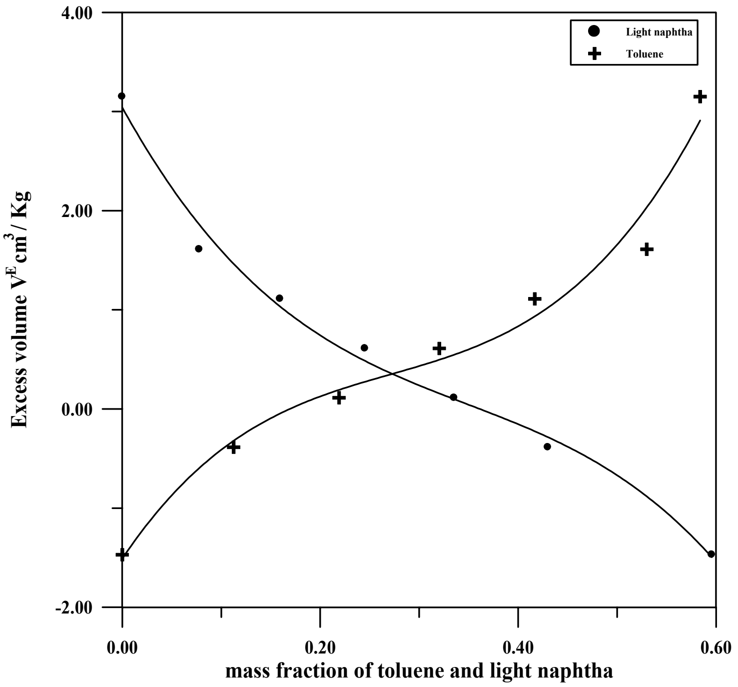

**Fig 4-19** Excess volume of ternary mixtures of gas oil/light naphtha/toluene

**Table 4-3** Excess volume in $cm^3$/kg for ternary mixtures, gas oil, light naphtha and methyl ethyl ketone at 298.15k.

| Mix. | $X_1$ Gas Oil | $X_2$ Light Naphtha | $X_3$ MEK | $V^E$ $Cm^3$/kg |
|---|---|---|---|---|
| 1 | 0.3809 | - | 0.6191 | 2.85 |
| 2 | 0.4271 | 0.0802 | 0.4927 | 1.27 |
| 3 | 0.4350 | 0.1636 | 0.4014 | 0.8450 |
| 4 | 0.4433 | 0.2500 | 0.3067 | 0.4125 |
| 5 | 0.4517 | 0.3398 | 0.2085 | -0.432 |
| 6 | 0.4607 | 0.4331 | 0.1062 | -0.45 |
| 7 | 0.4042 | 0.5958 | - | -1.47 |

**Table 4-4** Ternary excess volume in $cm^3$/kg of gas oil, heavy naphtha and methyl ethyl ketone at 298.15k.

| Mix. | $X_1$ Gas Oil | $X_2$ Light Naphtha | $X_3$ MEK | $V^E$ $Cm^3$/kg |
|---|---|---|---|---|
| 1 | 0.3809 | - | 0.6191 | 2.85 |
| 2 | 0.4227 | 0.0897 | 0.4876 | 1.4 |
| 3 | 0.4261 | 0.187 | 0.3932 | 1.09 |
| 4 | 0.4296 | 0.2732 | 0.2972 | 0.78 |
| 5 | 0.4329 | 0.3673 | 0.1998 | 0.47 |
| 6 | 0.4365 | 0.4628 | 0.1007 | 0.16 |
| 7 | 0.4401 | 0.5599 | - | -0.25 |

**Table 4-5** Ternary excess volume in $cm^3$/kg of gas oil, heavy naphtha and toluene at 298.15k.

| Mix. | $X_1$ Gas Oil | $X_2$ Heavy Naphtha | $X_3$ Toluene | $V^E$ $Cm^3$/kg |
|---|---|---|---|---|
| 1 | 0.4041 | - | 0.5959 | 3.51 |
| 2 | 0.4097 | 0.0869 | 0.5034 | 1.73 |
| 3 | 0.4190 | 0.1762 | 0.4048 | 1.354 |
| 4 | 04213 | 0.2681 | 0.3106 | 0.798 |
| 5 | 0.4273 | 0.3626 | 0.2101 | 0.602 |
| 6 | 0.4336 | 0.4598 | 0.1066 | 0.226 |
| 7 | 0.4401 | 0.5599 | - | -0.25 |

**Table 4-6** Ternary excess volume in $cm^3$/kg of gas oil, light naphtha and toluene at 298.15k.

| Mix. | $X_1$ Gas Oil | $X_2$ Heavy Naphtha | $X_3$ Toluene | $V^E$ $Cm^3$/kg |
|---|---|---|---|---|
| 1 | 0.4699 | - | 0.5301 | 3.15 |
| 2 | 0.3382 | 0.0778 | 0.5840 | 1.61 |
| 3 | 0.4239 | 0.1594 | 0.4167 | 1.11 |
| 4 | 0.4345 | 0.2451 | 0.3204 | 0.610 |
| 5 | 0.4457 | 0.3352 | 0.2191 | 0.112 |
| 6 | 0.4575 | 0.4301 | 0.1124 | -0.386 |
| 7 | 0.4042 | 0.5958 | - | -0.147 |

## 4.6 Fitting Data

The following excess volume correlation, proposed originally for binary mixtures of individual hydrocarbons[(56)], is particularly relevant to this study:

$$\mathbf{V^E_m\ (cm^3.mol^{-1}) = x\ (1\text{-}x)\ (a_1x^o + a_2x + a_3\,x^2)} \qquad \text{………. (4-4)}$$

Where $V^E_m$ molar excess volume $cm^3/mol^{-1}$, x mole fraction of spike.

Modification has been made on equation (4-4) to get accurate data for excess volume of oil stock mixtures. The modification has been done on equation (4-5) by replacing x (1-x) by x only and changing the constants as follows:

$$\mathbf{V^E\ (cm^3/kg) = A_0+A_1x + A_2x^2 + A_3x^3} \qquad \text{……….. (4-5)}$$

Where $V^E$ excess volume in $cm^3/kg$, the coefficients $a_o$, $a_1$, $a_2$ and $a_3$ were calculated by least square methods using statistic program. Thus values are listed in table 4-7 for temperatures.

**Table 4-7** Smoothing coefficients eq.4-3 for binary blend systems gas oil with oil stocks at 298.15 and 308.15K

| GAS OIL + | T/K | $A_o$ | $A_1$ | $A_2$ | $A_3$ |
|---|---|---|---|---|---|
| **Toluene** | 298.15 | 1.270609E-2 | 17.082 | -17.868 | 0.80281 |
| | 308.15 | 1.266653E-2 | 14.667 | -14.983 | 0.312551 |
| **Xylenes Mixtures** | 298.15 | 1.394456E-2 | 15.916 | -17.092 | 1.19019 |
| | 308.15 | -1.7755E-2 | 13.830 | -14.531 | 0.704632 |
| **MEK** | 298.15 | 6.109728E-3 | 15.602 | -17.213 | 2.20635 |
| | 308.15 | -0.03897 | 13.125 | -14.953 | 1.40454 |
| **Reduced crude** | 298.15 | 0.06393 | 5.1109 | -5.3904 | 0.28 |
| | 308.15 | 0.01587 | 3.2852 | -3.365 | 0.082 |
| **n-hexadecane** | 298.15 | 4.572E-3 | -0.7027 | 0.8991 | -0.19833 |
| | 308.15 | 1.136488E-3 | -0.8566 | 1.05822 | -0.19948 |
| **Kerosene** | 298.15 | -0.169600E-4 | -0.938 | 1.14255 | -0.2044 |
| | 308.15 | -1.5069E-4 | -1.1182 | 1.36216 | -0.24295 |
| **Heavy naphtha** | 298.15 | 1.83299E-4 | -1.0268 | 1.32824 | -0.30172 |
| | 308.15 | 2.88017E-3 | -1.1644 | 1.41968 | -0.25365 |
| **Light naphtha** | 298.15 | -5.07813E-3 | -6.3011 | 9.146 | -2.8447 |
| | 308.15 | -0.008237E-4 | -7.9333 | 11.834 | -3.9891 |

The values of coefficients in table 4-7 were plotted against the Mw of corresponding spike, resulted in the following equations to estimate the values of the coefficients in equation 4-5:

$$\mathbf{A_0 = a_0 + a_1M_W + a_2M^2_W + a_3M^3_W} \quad \text{.........4-6}$$

$$\mathbf{A_1 = b_0 + b_1M_W + b_2M^2_W + b_3M^3_W} \quad \text{.........4-7}$$

$$\mathbf{A_2 = c_0 + c_1M_W + c_2M^2_W + c_3M^3_W} \quad \text{.........4-8}$$

$$\mathbf{A_3 = d_0 + d_1M_W + d_2M^2_W + d_3M^3_W} \quad \text{.........4-9}$$

Values for the coefficients $a_0$, $a_1$, $a_2$, $a_3$, $b_0$, $b_1$, $b_2$, $b_3$, $c_0$, $c_1$, $c_2$, $c_3$, $d_0$, $d_1$, $d_2$, and $d_3$ are given in table (4-8), (4-9), (4-10) and (4-11).

**Table 4-8** Best values of coefficients for equations 4-4 of gas oil combined with eight oil products at 298.15 and 308.15K

| | $A_0$ | | | |
|---|---|---|---|---|
| | $a_0$ | $a_1$ | $a_2$ | $a_3$ |
| **Negative $V^E$ at 298.15 k** | -0.06204 | 0.001231 | -8.008E-006 | 1.7086E-008 |
| **Negative $V^E$ at 308.15 k** | -0.13135 | 0.002633 | -1.67106E-005 | 3.38491E-008 |
| **Positive $V^E$ at 298.15 k** | -0.07806 | 0.001966 | -1.26309E-005 | 2.1506E-008 |
| **Positive $V^E$ at 308.15 k** | -1.15661 | 0.0278 | -0.000194 | 3.31102E-007 |

**Table 4-9** Best values of coefficients for equations 4-4 of gas oil combined with eight oil products at 298.15 and 308.15K

| | $A_1$ | | | |
|---|---|---|---|---|
| | $b_0$ | $b_1$ | $b_2$ | $b_3$ |
| **Negative $V^E$ at 298.15 k** | -49.4194 | 0.881718 | -0.05215 | 1.00346E-005 |
| **Negative $V^E$ at 308.15 k** | -3.24597 | 0.383429 | -0.001076 | 0 |
| **Positive $V^E$ at 298.15 k** | -28/.9995 | 1.09072 | -0.0075761 | 1.26561E-005 |
| **Positive $V^E$ at 308.15 k** | -19.1232 | 0.798018 | -0.0055265 | 9.17882E-006 |

**Table 4-10** Best values of coefficients for equations 4-4 of gas oil combined with eight oil products at 298.15 and 308.15K

| | $A_2$ | | | |
|---|---|---|---|---|
| | $c_0$ | $c_1$ | $c_2$ | $c_3$ |
| **Negative $V^E$ at 298.15 k** | 72.3211 | -1.2888 | 0.00759 | -1.455E-005 |
| **Negative $V^E$ at 308.15 k** | 49.653 | -0.591 | 0.00166 | 0 |
| **Positive $V^E$ at 298.15 k** | 1.19132 | -0.465888 | .00331644 | -5.4214E-006 |
| **Positive $V^E$ at 308.15 k** | -2.95802 | -0.290689 | 0.00204194 | -3.29454E-006 |

**Table 4-11** Best values of coefficients for equations 4-4 of gas oil combined with eight oil products at 298.15 and 308.15K

| | $A_3$ | | | |
|---|---|---|---|---|
| | $d_0$ | $d_1$ | $d_2$ | $d_3$ |
| **Negative $V^E$ at 298.15 k** | -22.8822 | 0.406704 | -.00237 | 4.508E-008 |
| **Negative $V^E$ at 308.15 k** | -17.6106 | 0.2133 | -0.00060 | 0 |
| **Positive $V^E$ at 298.15 k** | 27.4584 | -0.6165 | 0.00420 | -7.0815E-006 |
| **Positive $V^E$ at 308.15 k** | 22.1064 | -0.58377 | .0034941 | -5.9023E-006 |

# CHAPTER FIVE
# CONCLUSION AND RECOMMENDATIONS

## 5-1 CONCLUSIONS

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

1. Mixtures of gas oil with light petroleum fractions, light naphtha, heavy naphtha and kerosene show negative values of excess volume. This shrinkage effect is greatest for the lowest boiling spikes as in case of light naphtha. While the blending of reduced crude as a "structure breaking" material with gas oil resulted in positive excess volume.

2. The spiking of gas oil with some individual compounds of different chemical nature could be give an ideal abut the effect of chemical composition on the volumetric behavior of oil stock systems.

3. The binary mixtures of gas oil with aromatic compounds and methyl ethyl ketone show positive excess volume. While the spiked gas oil with material, resulted low shrinkage.

4. Mixing iso-octanol with gas oil resulted in positive excess volume values over the whole mass fraction. Therefore iso-octanol is considered as strong "structure breaking" material, leading to high expansion effect.

5. The blending of methyl ethyl ketone with lubricating oil base stocks produces positive excess volume. This expansion effect is greatest for the lowest boiling range base stock.

6. The spiked gas oil ternary mixtures show excess volumes so close to the sum of its binary systems with the considered spikes.

## 5.2 RCOMMENDATIONS

1. Study the pressure effect on volumetric behavior of oil stocks mixtures.

2. More work to be done on excess volumes of different gravities crude oil binary and ternary mixtures.

3. Contribution can be done to clarify the volumetric behavior of spiked oil stock by alcohols.

4. Developing a correlations to predict excess volume of oil stock mixtures based on the some of there properties.

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# Appendix A

# Densities

**Table A-1** The densities for values of binary system of gas oil and individual component.

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| component | Density kg /$m^3$ at temperature., K | |
|---|---|---|
| | 298.15 | 308.15 |
| Toluene | 861.80 | 850.10 |
| MEK | 809.10 | 798.10 |
| Xylenes | 861.61 | 850.01 |
| Reduced crude | 890.10 | 877.70 |
| Iso-octanol | 823.01 | 811.6 |
| n-hexadecane | 769.90 | 759.23 |
| Kerosene | 776.20 | 765.40 |
| Heavy naphtha | 741.28 | 733.67 |
| Light naphtha | 659.27 | 650.46 |

**Table A-2** The measured densities values for binary system of gas oil and light naphtha.

| Mass fraction of spike, x | Density(kg /m$^3$) at Temperature, k | |
|---|---|---|
| | 298.15 | 298.15 |
| 0.0771 | 855.28 | 843.78 |
| 0.1582 | 833.78 | 822.62 |
| 0.2437 | 812.17 | 801.34 |
| 0.3339 | 790.48 | 779.98 |
| 0.4292 | 768.73 | 758.54 |
| 0.5301 | 746.9 | 737.00 |
| 0.637 | 725.04 | 715.43 |
| 0.7505 | 703.15 | 693.81 |

**Table A-3** The measured densities values for binary system of gas oil and heavy naphtha.

| Mass fraction of spike, x | Density(kg /m$^3$) at Temperature, k | |
|---|---|---|
| | 298.15 | 308.15 |
| 0.0889 | 0.851 | 862.8 |
| 0.18 | 0.838 | 848.9 |
| 0.2734 | 0.825 | 835.1 |
| 0.3692 | 0.811 | 821.5 |
| 0.4675 | 0.798 | 807.9 |
| 0.5684 | 0.785 | 794.4 |
| 0.6719 | 0.772 | 781. |
| 0.7783 | 0.759 | 767.6 |
| 0.8870 | 0.746 | 754.4 |

**Table A-4** The measured densities values for binary system of gas oil and kerosene.

| Mass fraction of spike, x | Density(kg /m$^3$) at Temperature, k | |
|---|---|---|
| | 298.15 | 308.15 |
| 0.0895 | 866.71 | 854.93 |
| 0.1812 | 856.70 | 845.04 |
| 0.275 | 846.68 | 835.13 |
| 0.3711 | 836.65 | 825.21 |
| 0.4695 | 826.60 | 815.28 |
| 0.5704 | 816.54 | 805.32 |
| 0.6738 | 806.47 | 795.36 |
| 0.7798 | 796.39 | 785.39 |
| 0.8884 | 786.30 | 775.42 |

**Table A-5** The measured densities values for binary system of gas oil and reduced crude.

| Mass fraction of spike, x | Density(kg /m$^3$) at Temperature, k | |
|---|---|---|
| | 298.15 | 308.15 |
| 0.0986 | 888.29 | 876.16 |
| 0.1976 | 886.72 | 874.71 |
| 0.2968 | 885.19 | 873.30 |
| 0.3964 | 883.79 | 871.94 |
| 0.4962 | 882.43 | 870.62 |
| 0.5964 | 881.11 | 869.37 |
| 0.6968 | 879.84 | 868.15 |
| 0.7976 | 878.72 | 866.97 |
| 0.8986 | 877.58 | 865.84 |

**Table A-6** The measured densities values for binary system of gas oil and toluene.

| Mass fraction of spike, x | Density(kg /m$^3$) at Temperature, k | |
|---|---|---|
| | 298.15 | 308.15 |
| 0.0984 | 874.09 | 862.30 |
| 0.1972 | 871.58 | 860.23 |
| 0.2964 | 869.50 | 858.10 |
| 0.3958 | 867.76 | 856.35 |
| 0.4957 | 866.13 | 854.78 |
| 0.5958 | 864.84 | 853.42 |
| 0.6963 | 863.58 | 852.23 |
| 0.7972 | 862.71 | 851.44 |
| 0.8984 | 862.17 | 850.56 |

**Table A-7** The measured densities values for binary system of gas oil and xylenes.

| Mass fraction of spike, x | Density(kg /m$^3$) at Temperature, k | |
|---|---|---|
| | 298.15 | 308.15 |
| 0.0984 | 874.15 | 863.40 |
| 0.1972 | 871.66 | 862.02 |
| 0.2964 | 869.71 | 860.65 |
| 0.3958 | 867.90 | 859.31 |
| 0.4957 | 866.27 | 857.98 |
| 0.5958 | 864.93 | 856.67 |
| 0.6963 | 863.71 | 855.37 |
| 0.7972 | 862.75 | 854.11 |
| 0.8984 | 861.76 | 853.01 |

**Table A-8** The measured densities values for binary system of gas oil and MEK.

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| Mass fraction of spike, x | Density(kg /m$^3$) at Temperature, k | |
|---|---|---|
| | 298.15 | 308.15 |
| 0.0930 | 868.99 | 857.40 |
| 0.1874 | 861.51 | 850.09 |
| 0.2834 | 854.31 | 842.91 |
| 0.3809 | 847.25 | 836.12 |
| 0.4799 | 840.42 | 829.30 |
| 0.5805 | 833.81 | 822.82 |
| 0.6828 | 827.40 | 816.35 |
| 0.7868 | 821.10 | 810.12 |
| 0.8925 | 815.03 | 804.13 |

**Table A-9** The measured densities values for binary system of gas oil and n-hexadecane.

| Mass fraction of spike, x | Density(kg /m$^3$) at Temperature, k | |
|---|---|---|
| | 298.15 | 308.15 |
| 0.0889 | 866.06 | 854.29 |
| 0.1800 | 855.40 | 843.77 |
| 0.2734 | 844.76 | 833.24 |
| 0.3692 | 834.09 | 822.69 |
| 0.4675 | 823.41 | 812.14 |
| 0.5684 | 812.72 | 801.57 |
| 0.6719 | 802.03 | 791.01 |
| 0.7783 | 791.32 | 780.42 |
| 0.8876 | 780.62 | 769.83 |

**Table A-10** The measured densities values for binary system of gas oil and iso-octanol.

| Mass fraction of spike, x | Density(kg /m$^3$) at Temperature, k | |
|---|---|---|
| | 298.15 | 308.15 |
| 0.0944 | 869.00 | 858.19 |
| 0.1900 | 862.00 | 851.47 |
| 0.2868 | 855.00 | 845.79 |
| 0.3849 | 849.00 | 837.79 |
| 0.4841 | 843.00 | 832.58 |
| 0.5847 | 836.00 | 826.29 |
| 0.6876 | 830.00 | 820.12 |
| 0.7896 | 824.00 | 814.07 |
| 0.8941 | 819.00 | 808.66 |

**Table A-11** The measured densities values for binary system of gas oil and base oil stock (40, 60 and 150).

| Mass fraction of spike, x base oil stock(40) | Density(kg /m$^3$) at 298.15 k | Mass fraction of spike, x base oil stock(60) | Density(kg /m$^3$) at 298.15 k | Mass fraction of spike, x base oil stock(150) | Density(kg /m$^3$) at 298.15 k |
|---|---|---|---|---|---|
| 0.0944 | 843.40 | 0.0911 | 875.00 | 0.0894 | 892.01 |
| 0.1900 | 836.80 | 0.1840 | 865.50 | 0.1810 | 881.45 |
| 0.2868 | 831.00 | 0.2788 | 856.55 | 0.2748 | 870.93 |
| 0.3848 | 825.11 | 0.3756 | 847.50 | 0.3708 | 860.45 |
| 0.4841 | 819.90 | 0.4743 | 838.83 | 0.4692 | 850.00 |
| 0.5846 | 814.79 | 0.5750 | 830.35 | 0.5701 | 839.56 |
| 0.6864 | 809.86 | 0.6779 | 822.03 | 0.6735 | 829.16 |
| 0.7896 | 805.55 | 0.7830 | 813.91 | 0.7795 | 818.78 |
| 0.8941 | 801.65 | 0.8903 | 806.00 | 0.8883 | 808.44 |

# Appendix B

# Excess Volume

**TableB-1:Comparisons between measured excess volumes and the corresponding calculated values of binary system of gas oil and light naphtha.**

| Mass fraction of Spike, x | Excess Volumes, in cm³ /kg | Temperature, °C | | Av.abs %error |
|---|---|---|---|---|
| | | 25 | 35 | |
| 0.0771 | $V^E$ exp. | -0.44 | -0.57 | |
| | $V^E$ cal. | -0.49 | -0.55 | |
| | % error | 0.49 | 4.10 | 2.29 |
| 0.1582 | $V^E$ exp. | -0.79 | -0.99 | |
| | $V^E$ cal. | -0.78 | -0.98 | |
| | % error | 0.72 | 0.70 | 0.71 |
| 0.2437 | $V^E$ exp. | -1.044 | -1.29 | |
| | $V^E$ cal. | -1.04 | -1.29 | |
| | % error | 0.51 | 0.51 | 0.51 |
| 0.3339 | $V^E$ exp. | -1.19 | -1.47 | |
| | $V^E$ cal. | -1.19 | -1.48 | |
| | % error | -0.44 | -0.78 | 0.61 |
| 0.4292 | $V^E$ exp. | -1.25 | -1.55 | |
| | $V^E$ cal. | -1.25 | -1.54 | |
| | % error | 0.03 | 0.07 | .05 |
| 0.5301 | $V^E$ exp. | -1.19 | -1.48 | |
| | $V^E$ cal. | -1.19 | -1.48 | |
| | % error | -0.67 | -0.51 | 0.59 |
| 0.637 | $V^E$ exp. | -1.04 | -1.3 | |
| | $V^E$ cal. | -1.04 | -1.29 | |
| | % error | -0.28 | 0.68 | 0.48 |
| 0.7505 | $V^E$ exp. | -0.791 | -0.99 | |
| | $V^E$ cal. | -0.78 | -0.98 | |
| | % error | 0.75 | 0.69 | 0.72 |
| 0.8712 | $V^E$ exp. | -0.44 | -0.57 | |
| | $V^E$ cal. | -0.43 | -0.57 | |
| | % error | 1.39 | -1.00 | 1.19 |

**Table B-2: Comparisons between measured excess volumes and the corresponding calculated values of binary system of gas oil and heavy naphtha.**

| Mass fraction of Spike, x | Excess Volumes, in cm³ /kg | Temperature, °C | | Av.abs %error |
|---|---|---|---|---|
| | | 25 | 35 | |
| 0.0889 | $V^E$ exp. | -0.08 | -0.099 | |
| | $V^E$ cal. | -0.081 | 0.09 | |
| | % error | 9.45 | 1.03 | 5.23 |
| 0.18 | $V^E$ exp. | -0.139 | -0.17 | |
| | $V^E$ cal. | -0.14 | -0.16 | |
| | % error | 4.53 | 3.15 | 3.84 |
| 0.2734 | $V^E$ exp. | -0.18 | -0.22 | |
| | $V^E$ cal. | -0.187 | -0.21 | |
| | % error | 2.41 | 4.13 | 3.27 |
| 0.3692 | $V^E$ exp. | -0.217 | -0.24 | |
| | $V^E$ cal. | -0.213 | -0.246 | |
| | % error | 1.01 | 1.81 | 1.40 |
| 0.4675 | $V^E$ exp. | -0.22 | -0.265 | |
| | $V^E$ cal. | -0.22 | -0.257 | |
| | % error | 2.86 | 0.19 | 1.53 |
| 0.5684 | $V^E$ exp. | -0.215 | -0.25 | |
| | $V^E$ cal. | -0.21 | -0.247 | |
| | % error | 1.104 | 2.41 | 1.75 |
| 0.6719 | $V^E$ exp. | -0.179 | -0.223 | |
| | $V^E$ cal. | -0.182 | -0.216 | |
| | % error | 3.16 | 1.52 | 2.34 |
| 0.7783 | $V^E$ exp. | -0.14 | -0169 | |
| | $V^E$ cal. | -0.137 | -0.163 | |
| | % error | 3.25 | 2.29 | 2.77 |
| 0.8876 | $V^E$ exp. | -0.079 | -0.099 | |
| | $V^E$ cal. | -0.076 | -0.09 | |
| | % error | 8.95 | 3.83 | 6039 |

**Table B-3: Comparisons between measured excess volumes and the corresponding calculated values of binary system of gas oil and kerosene.**

| Mass fraction of Spike, x | Excess Volumes, in cm³ /kg | Temperature, °C | | Av.abs %error |
|---|---|---|---|---|
| | | 25 | 35 | |
| 0.0895 | $V^E$ exp. | -0.074 | -0.09 | |
| | $V^E$ cal. | -0.075 | -0.091 | |
| | % error | 1.48 | 0.94 | 1.21 |
| 0.1812 | $V^E$ exp. | -0.136 | -0.159 | |
| | $V^E$ cal. | -0.134 | -0.161 | |
| | % error | 1.61 | 1.15 | 1.38 |
| 0.275 | $V^E$ exp. | -0.177 | -0.21 | |
| | $V^E$ cal. | -0.176 | -0.211 | |
| | % error | 0.60 | 0.49 | 0.55 |
| 0.3711 | $V^E$ exp. | -0.199 | -0.241 | |
| | $V^E$ cal. | -0.201 | -0.241 | |
| | % error | 1.15 | 0.11 | 0.63 |
| 0.4695 | $V^E$ exp. | -0.21 | -0.25 | |
| | $V^E$ cal. | -0.21 | -0.251 | |
| | % error | 0.09 | 0.54 | 0.32 |
| 0.5704 | $V^E$ exp. | -0.199 | -0.24 | |
| | $V^E$ cal. | -0.201 | -0.241 | |
| | % error | 1.16 | 0.50 | 0.83 |
| 0.6738 | $V^E$ exp. | -0.178 | -0.21 | |
| | $V^E$ cal. | -0.176 | -0.211 | |
| | % error | 1.17 | 0.38 | 0.78 |
| 0.7798 | $V^E$ exp. | -0.135 | -0.16 | |
| | $V^E$ cal. | -0.134 | -0.16 | |
| | % error | 0.98 | 0.20 | 0.59 |
| 0.8884 | $V^E$ exp. | -0.073 | -0.09 | |
| | $V^E$ cal. | -0.075 | -0.09 | |
| | % error | 2.64 | 0.138 | 1.39 |

**Table B-4: Comparisons between measured excess volumes and the corresponding calculated values of binary system of gas oil and reduced crude.**

| Mass fraction of Spike, x | Excess Volumes, in cm³ /kg | Temperature, °C | | Av.abs %error |
|---|---|---|---|---|
| | | 25 | 35 | |
| 0.0986 | $V^E$ exp. | 0.6 | 0.33 | |
| | $V^E$ cal. | 0.52 | 0.31 | |
| | % error | 14.04 | 6.92 | 10.48 |
| 0.1976 | $V^E$ exp. | 0.89 | 0.54 | |
| | $V^E$ cal. | 0.87 | 0.53 | |
| | % error | 2.75 | 1.06 | 1.90 |
| 0.2968 | $V^E$ exp. | 1.14 | 0.69 | |
| | $V^E$ cal. | 1.11 | 0.69 | |
| | % error | 2.34 | -0.95 | 1.64 |
| 0.3964 | $V^E$ exp. | 1.22 | 0.79 | |
| | $V^E$ cal. | 1.26 | 0.79 | |
| | % error | -3.30 | -0.56 | 1.93 |
| 0.4962 | $V^E$ exp. | 1.25 | 0.83 | |
| | $V^E$ cal. | 1.307 | 0.827 | |
| | % error | -4.56 | 0.32 | 2.43 |
| 0.5964 | $V^E$ exp. | 1.218 | 0.78 | |
| | $V^E$ cal. | 1.25 | 0.79 | |
| | % error | -2.96 | -1.98 | 2.47 |
| 0.6968 | $V^E$ exp. | 1.135 | 0.689 | |
| | $V^E$ cal. | 1.10 | 0.69 | |
| | % error | 2.84 | -1.39 | 2.11 |
| 0.7976 | $V^E$ exp. | 0.86 | 0.55 | |
| | $V^E$ cal. | 0.85 | 0.53 | |
| | % error | 0.78 | 2.43 | 1.61 |
| 0.8986 | $V^E$ exp. | 0.601 | 0.33 | |
| | $V^E$ cal. | 0.50 | 0.31 | |
| | % error | 15.62 | 6.14 | 10.88 |

**Table B-5: Comparisons between measured excess volumes and the corresponding calculated values of binary system of gas oil and toluene.**

| Mass fraction of Spike, x | Excess Volumes, in cm³ /kg | Temperature, °C | | Av.abs %error |
|---|---|---|---|---|
| | | 25 | 35 | |
| 0.0984 | $V^E$ exp. | 1.45 | 1.39 | |
| | $V^E$ cal. | 1.52 | 1.31 | |
| | % error | -4.27 | 5.67 | 4.97 |
| 0.1972 | $V^E$ exp. | 2.81 | 2.2 | |
| | $V^E$ cal. | 2.69 | 2.32 | |
| | % error | 4.17 | -5.67 | 4.93 |
| 0.2964 | $V^E$ exp. | 3.6 | 3.1 | |
| | $V^E$ cal. | 3.52 | 3.05 | |
| | % error | 2.02 | 1.55 | 1.79 |
| 0.3958 | $V^E$ exp. | 3.95 | 3.49 | |
| | $V^E$ cal. | 4.024 | 3.49 | |
| | % error | -1.88 | -0.004 | 0.94 |
| 0.4957 | $V^E$ exp. | 4.14 | 3.65 | |
| | $V^E$ cal. | 4.18 | 3.63 | |
| | % error | -1.15 | 0.28 | 0.72 |
| 0.5958 | $V^E$ exp. | 3.89 | 3.51 | |
| | $V^E$ cal. | 4.02 | 3.49 | |
| | % error | -3.27 | 0.32 | 1.79 |
| 0.6963 | $V^E$ exp. | 3.6 | 3.13 | |
| | $V^E$ cal. | 3.52 | 3.07 | |
| | % error | 2.36 | 2.02 | 2.19 |
| 0.7972 | $V^E$ exp. | 2.78 | 2.2 | |
| | $V^E$ cal. | 2.28 | 2.34 | |
| | % error | 3.54 | -6.4 | 4.98 |
| 0.8984 | $V^E$ exp. | 1.5 | 1.4 | |
| | $V^E$ cal. | 1.52 | 1.32 | |
| | % error | -1.31 | 5.49 | 3.39 |

**Table B-6: Comparisons between measured excess volumes and the corresponding calculated values of binary system of gas oil and xylenes mixtures.**

| Mass fraction of Spike, x | Excess Volumes, in cm³ /kg | Temperature, °C | | Av.abs %error |
|---|---|---|---|---|
| | | 25 | 35 | |
| 0.0984 | $V^E$ exp. | 1.35 | 1.19 | |
| | $V^E$ cal. | 1.42 | 1.20 | |
| | % error | 1.19 | 0.42 | 0.80 |
| o.1972 | $V^E$ exp. | 2.65 | 2.11 | |
| | $V^E$ cal. | 2.491 | 2.14 | |
| | % error | 2.13 | -3.89 | 3.01 |
| 0.2964 | $V^E$ exp. | 3.25 | 2.88 | |
| | $V^E$ cal. | 3.26 | 2.82 | |
| | % error | 2.81 | 2.77 | 2.78 |
| 0.3958 | $V^E$ exp. | 3.65 | 3.195 | |
| | $V^E$ cal. | 3.71 | 3.22 | |
| | % error | 3.21 | -1.04 | 2.13 |
| 0.4957 | $V^E$ exp. | 3.82 | 3.39 | |
| | $V^E$ cal. | 3.85 | 3.35 | |
| | % error | 3.35 | 0.94 | 2.15 |
| 0.5958 | $V^E$ exp. | 3.62 | 3.18 | |
| | $V^E$ cal. | 3.68 | 3.21 | |
| | % error | 3.22 | -0.89 | 2.06 |
| 0.6963 | $V^E$ exp. | 3.24 | 2.89 | |
| | $V^E$ cal. | 3.21 | 2.81 | |
| | % error | 2.82 | 1.79 | 2.31 |
| 0.7972 | $V^E$ exp. | 2.52 | 2.05 | |
| | $V^E$ cal. | 2.44 | 2.13 | |
| | % error | 2.11 | 2.15 | 2.13 |
| 0.8984 | $V^E$ exp. | 1.38 | 1.195 | |
| | $V^E$ cal. | 1.38 | 1.19 | |
| | % error | 1.20 | -1.10 | 1.15 |

**Table B-7: Comparisons between measured excess volumes and the corresponding calculated values of binary system of gas oil and methyl ethyl ketone.**

| Mass fraction of Spike, x | Excess Volumes, in cm³ /kg | Temperature, °C | | Av.abs %error |
|---|---|---|---|---|
| | | 25 | 35 | |
| 0.093 | $V^E$ exp. | 1.26 | 0.99 | |
| | $V^E$ cal. | 1.31 | 1.057 | |
| | % error | -3.97 | -6.77 | 5.37 |
| 0.1874 | $V^E$ exp. | 2.25 | 1.9 | |
| | $V^E$ cal. | 2.34 | 1.919 | |
| | % error | -4 | -1.02 | 2.511 |
| 0.2834 | $V^E$ exp. | 2.89 | 2.64 | |
| | $V^E$ cal. | 3.09 | 2.55 | |
| | % error | -7.11 | 3.59 | 5.35 |
| 0.3809 | $V^E$ exp. | 3.35 | 2.85 | |
| | $V^E$ cal. | 3.57 | 2.93 | |
| | % error | -6.68 | -2.77 | 4.72 |
| 0.4799 | $V^E$ exp. | 3.50 | 3.12 | |
| | $V^E$ cal. | 3.77 | 3.067 | |
| | % error | -7.78 | 1.69 | 4.74 |
| 0.5805 | $V^E$ exp. | 3.35 | 2.9 | |
| | $V^E$ cal. | 3.69 | 2.96 | |
| | % error | -10.3 | -1.94 | 6.11 |
| 0.6828 | $V^E$ exp. | 2.9 | 2.65 | |
| | $V^E$ cal. | 3.34 | 2.59 | |
| | % error | -15.1 | 2.158 | 8.61 |
| 0.7868 | $V^E$ exp. | 2.25 | 2.01 | |
| | $V^E$ cal. | 2.7 | 1.97 | |
| | % error | -20 | 1.84 | 10.93 |
| 0.8925 | $V^E$ exp. | 1.25 | 0.99 | |
| | $V^E$ cal. | 1.7 | 1.09 | |
| | % error | -43.1 | -10.6 | 26.81 |

**Table B-8: Comparisons between measured excess volumes and the corresponding calculated values of binary system of gas oil and n-hexadecane**

| Mass fraction of Spike, x | Excess Volumes, in cm$^3$ /kg | Temperature, °C | | Av.abs %error |
|---|---|---|---|---|
| | | 25 | 35 | |
| 0.0889 | $V^E$ exp. | -0.05 | -0.065 | |
| | $V^E$ cal. | -0.051 | -0.067 | |
| | % error | -1.87 | -2.76 | 2.31 |
| 0.18 | $V^E$ exp. | -0.081 | -0.12 | |
| | $V^E$ cal. | -0.12 | -15.99 | |
| | % error | -15.99 | 0.056 | 8.02 |
| 0.2734 | $V^E$ exp. | -0.13 | -0.16 | |
| | $V^E$ cal. | -0.15 | 4.29 | |
| | % error | 4.29 | 1.22 | 2.76 |
| 0.3692 | $V^E$ exp. | -0.14 | -0.17 | |
| | $V^E$ cal. | -0.18 | 1.16 | |
| | % error | 1.16 | -1.07 | 1.12 |
| 0.4675 | $V^E$ exp. | -0.15 | -0.19 | |
| | $V^E$ cal. | -0.18 | 1.51 | |
| | % error | 1.51 | 0.82 | 1.17 |
| 0.5684 | $V^E$ exp. | -0.15 | -0.18 | |
| | $V^E$ cal. | -0.18 | 2.88 | |
| | % error | 2.88 | 0.81 | 1.84 |
| 0.6719 | $V^E$ exp. | -0.13 | -0.159 | |
| | $V^E$ cal. | -0.12 | -0.157 | |
| | % error | 2.49 | 1.13 | 1.81 |
| 0.7783 | $V^E$ exp. | -0.08 | -0.12 | |
| | $V^E$ cal. | -0.12 | -14.08 | |
| | % error | -14.08 | 1.168 | 7.63 |
| 0.8876 | $V^E$ exp. | -0.05 | -0.064 | |
| | $V^E$ cal. | -0.05 | -0.065 | |
| | % error | 0.89 | -1.54 | 1.22 |

**Table B-9: Comparisons between measured excess volumes and the corresponding calculated values of binary system of gas oil and iso-octanol**

| Mass fraction 0f spike, x | Excess volume $V^E$ experimental cm³/kg | |
|---|---|---|
| | 298.15 k | 308.15 k |
| 0.0944 | 3.45 | 1.75 |
| 0.1900 | 5.4 | 3.7 |
| 0.2868 | 6.89 | 5.19 |
| 0.3849 | 8.38 | 6.68 |
| 0.4841 | 9.75 | 8.05 |
| 0.5847 | 11.27 | 9.57 |
| 0.6876 | 12.65 | 10.95 |
| 0.7896 | 13.9 | 12.2 |
| 0.8941 | 14.2 | 12.5 |

**Table B-10: Comparisons between measured excess volumes and the corresponding calculated values of binary system of gas oil and base oil stocks 40,60 and 150**

| Base oil stock 40,x | Excess Volumes, In cm³/kg | Base oil Stock 60, x | Excess volumes, in cm³/kg | Base oil stock 150, x | Excess volumes, in cm³/kg |
|---|---|---|---|---|---|
| 0.0944 | 2.61 | 0.0911 | 1.12 | 0.0894 | 0.17 |
| 0.1900 | 4.45 | 0.1840 | 2.21 | 0.1810 | 0.32 |
| 0.2868 | 5.45 | 0.2788 | 2.83 | 0.2748 | 0.42 |
| 0.3848 | 6.39 | 0.3756 | 3.34 | 0.3708 | 0.47 |
| 0.4841 | 6.51 | 0.4743 | 3.50 | 0.4692 | 0.49 |
| 0.5846 | 6.4 | 0.5750 | 3.34 | 0.5701 | 0.47 |
| 0.6864 | 6.01 | 0.6779 | 2.94 | 0.6735 | 0.42 |
| 0.7896 | 4.65 | 0.7830 | 2.21 | 0.7795 | 0.33 |
| 0.8941 | 2.62 | 0.8903 | 1.144 | 0.8883 | 0.17 |

# الخلاصة

خلائط الخامات النفطية مع الهيدروكاربونات تكون محلول غير مثالي والتي لوحظ فيها ان التغير الحجمي ذو اتجاه موجب أو سالب معتمداً على طبيعة هذه الخلائط، زيت الغاز مزج مع تسعة مشتقات نفطية او مركبات هيدروكاربونية أو منتجات نفطية ومركبات بارافينية بالإضافة الى الكحول والكيتون. استخدم فيها قياسات الكثافة تحت درجات حرارة مختلفة. تم تسجيل النتائج بصيغة الحجم النوعي للمزيج.

الخلائط الثنائية لزيت الغاز مع الغاز مع البارافينك ( light naphtha, heavy naphtha Kerosene) يؤدي الى زيادة حجمية سالبة. ان تأثير الانكماش يكون اكبر ما يمكن عند أقل درجة غليان. ان نتائج ال(n-hexadecane) تكون زيادة حجمية سالبة قليلة نوعاً ما ويتجه النظام نحو الحجوم المثالية مع زيت الغاز.

إن خلائط زيت الغاز مع( التولوين، زايلين ، مثيل أثيل كيتون والنفط الخام الثقيل) يظهر زيادة حجمية موجبة. ان هذه الزيادة تشير الى ان "structure breaking" للمواد يتأثر مما يؤدي الى الأنكماش.

خلائط زيت الغاز مع (Iso- octanol ) تؤدي الى زيادة حجمية موجبة، هذه الزيادة تزداد بزيادة النسبة الوزنية لل (Iso- octanol ).

مثيل أثيل كيتون يستخدم عادة كمذيب للمواد الشمعية وزيوت الأساس. الخلائط الثنائية للمثيل أثيل كيتون مع بعض زيوت الأساس التي لها درجات غليان مختلفة تؤدي الى زيادة حجمية موجبة. ان هذا الأنكماش يكون اكبر مايمكن عند اقل درجة غليان.

درست الزيادة الحجمية للخلاط الثلاثية لزيت الغاز بأستخدام مركبات ذات طبيعة مختلفة. درست الخلائط الثلاثية لزيت الغاز، بالأستناد على الزيادة الحجمية الثنائية.

# شكر و تقدير

اودُ أن أعبر عن خالص شكري وتقديري وَ امتناني العميق للمشرفين الاستاذ الدكتور جابر شنشول جمالي و الدكتورنصير الحبوبي لما بذلوه من جهد كبير و ارشادات سديدة و قيمة طوال فترة اعداد الرسالة.

أودُ أيضاً أن أشكر السيد رئيس القسم و موظفي قسم الهندسة الكيماوية لإبدائهم المساعدة اللازمة أثناء فترة البحث.

ولا أنسى أن أتقدم بالشكر و الامتنان إلى من لازمني طوال فترة البحث وخلال أصعب الظروف إلى أعز من في الوجود أمي و جميع أفراد عائلتي فلهم جزيل الشكر و التقدير.

**م. شيماء كريم عبد السادة**

# تاثير المكونات الكيمياوية على الزيادة الحجمية للخلائط مع المشتقات النفطية

رسالة

مقدمة الى كلية الهندسة في جامعة النهرين و هي جزء من متطلبات نيل
درجة ماجستير علوم في الهندسة الكيمياوية

من قبل

**شيماء كريم عبد السادة**

(بكالوريوس في الهندسة الكيمياوية ٢٠٠١ )

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