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VOLUMETRIC BEHAVIOR OF MIXTURES OF DIFFERENT OIL-STOCKS

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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 (25 and 35˚C).

Binary mixtures of gas oil with the paraffinic spikes, light naphtha, heavy naphtha, kerosene and n-hexadecane produce negative excess volume values. This maximum shrinkage occurs for the lowest boiling spike. Where n-hexadecane results 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 affected 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 with some base oil stocks of different boiling range show positive excess volume. This expansion is greatest for lowest boiling stock.

Key Words: Excess volume; Blending; non-ideal mixtures; mixed petroleum fractions.

1. 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]. Furthermore, 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 [2].

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

Iloukhani, H. *et. al.* [4] 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, due to the molecular interactions, such as excess volume are an important thermodynamic property in process design calculation, and accurate prediction of this property is required.

Ashcroft *et al.* [5] carried out a series of experimental work to study the volumetric behavior of different types of world crude oils with different types of hydrocarbons as petroleum fractions or individual hydrocarbons. The results were reported in terms of equation for percentage relative excess specific volume of the mixtures, from which excess volume can be calculated.

A contribution was done in the present work to investigate the effect of chemical composition of blending species on excess volume of their mixtures with gas oil. Also 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 MEK as ketone and *iso*-octanol as an alcohol. Research was also made to describe the volumetric behavior of some lubricating oil base stocks with Methyl Ethyl Ketone, MEK.

2. Experimental work

2.1 Oil stocks

The petroleum fractions, light-naphtha, heavy naphtha, kerosene, gasoil and reduced crude were supplied as "stock tanks" products from Al-Daura Refinery in Baghdad. The specific gravities and other available specification of these cuts are given in Table 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 2. Other blend components were methyl ethyl ketone (Daura Refinery) *2*- ethylhexanol, toluene, a xylenes-mixture (sp. gravity, 25.6˚= 0.8701, BP =136-148˚C) and *n*-hexadecane (local market).

Table 1 Specification of petroleum fractions

Specification	Distillate Product				
	Kerosene	Heavy naphta	Light naphta	Reduced crude	Gas oil
Sp. gravity @ 25.6°C	0.7762	0.74125	0.65927	0.8901	0.8767
API gravity	50.8	59.4	83.1	27.5	29.9
Boiling range, °C	153-234	88-173	40-110	atm. Res	205-333
Flash point °C	39	—	—	102.5	64
Sulfur content %	0.2	0.1	Nil	1.5	0.9
Avg. Mwt. (gm/gmol)	168.56	126.72	83.59	400	241.33

Table 2 Properties of base oil - stocks

Specification	40 stock	60 stock	150 stock
Viscosity. @ 20°C	3.2	8.5	30.0
Sp. gravity @ 35°C	0.8505	0.8845	0.9526
VI	96	95	94
Pour point °C	-3	-3	0
Color	0.5	1.5	3.0
Flash point. °C	190	220	290

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.

3. Results and discussion

The density data obtained in the present project covers 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 volume fraction of spike ϕ_2 can readily be calculated by eq. 1.

$$\phi_2 = \frac{x_2\,\rho_1^\circ}{\left(\rho_2^\circ + x_2\;\rho_1^\circ - x_2\;\rho_2^\circ\right)} \qquad (1)$$

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.

$$V^E = V_{mix} - V^{id} \quad (2)$$

V^{id} was calculated using eq. 3. (5) (6)

$$V^{id} = \frac{\rho_2^\circ + x_2(\rho_1^\circ - \rho_2^\circ)}{\rho_1^\circ \rho_2^\circ} \quad (cm^3/kg) \quad (3)$$

The data for binary mixtures in form of excess specific volume V^E were plotted against mass fraction of spike, which give usually smooth curves, as shown in Figures. 1, 2 and 4. These curves pass through zero at 0 and 100 wt % spikes. While the maximum excess volume occur at/or close to 0.5 mass fraction.

3.1.Composition dependence of excess volume

Light naphtha, Heavy naphtha, Kerosene and reduced crude were chosen to study the effect of some oil-stocks on the excess volumes of their mixtures with gas oil. The results are plotted in Figure 1. Excess volumes V^E are negative for each of binary mixtures, Light naphtha, Heavy naphtha, Kerosene at 298.15 and 308.15 K and over the complete mass fraction range. Maximum shrinkage occur at/ or close to 0.5 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 3.

Table 3 Max. Excess volumes, in cm^3/kg at about 0.5 mass fractions at 298.15 and 308.15 K for petroleum fractions.

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

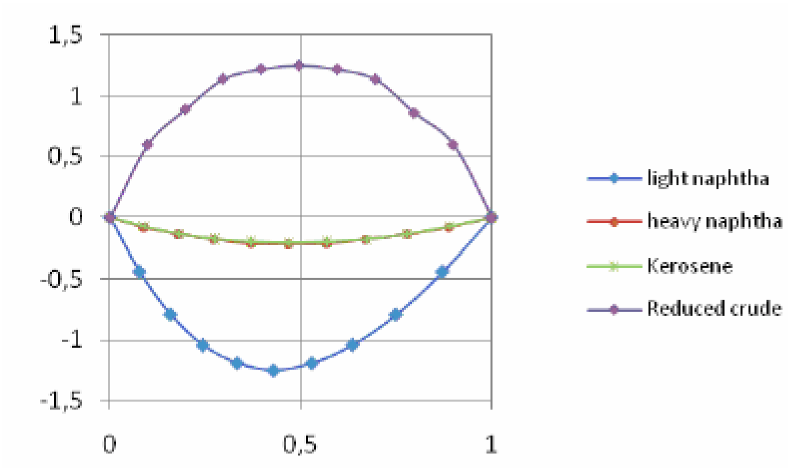

Fig. 1 Excess volume of gas oil mixed with some petroleum fractions at 298.15K.

Light naphtha, heavy naphtha and kerosene are considered usually as paraffinic spikes, particularly light naphtha. It is well known that linear paraffinic hydrocarbons resulted in volume shrinkage when mixed with crude oils or petroleum fractions [5,7]. The low boiling spike, light naphtha gives the largest negative excess volume, about -1.25 cm^3/kg at 25°C, within the present experimental results. While heavy naphtha and kerosene show a little deviation from ideal behavior, given about -0.21 cm^3/kg at 25°C excess volume.

Mixtures of reduced crude with gas oil exhibit positive excess volume as shown in figure 1. Reduced crude consists mainly of aromatics hydrocarbons. The aromatics as structure-breaking material leading to expansion where 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 3.

Temperatures increase in the range of 25-35°C affected the excess volume of all studied petroleum fractions mixtures. Thus decrease of shrinkage or expansion was observed by increasing the temperature as shown in Table 3.

3.2 Composition dependence of excess volume

The excess volume behavior of oil mixtures is influenced largely by the chemical composition of blending component. A contribution was done in the present work to investigate the effect of 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, methyl ethyl ketone as ketone and *iso*-octanol as an alcohol. The results are summarized in Figure 2.

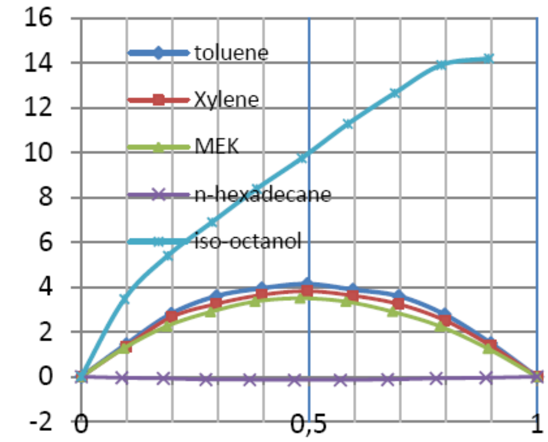

Figure 2 Excess volume of spiked gas oil.

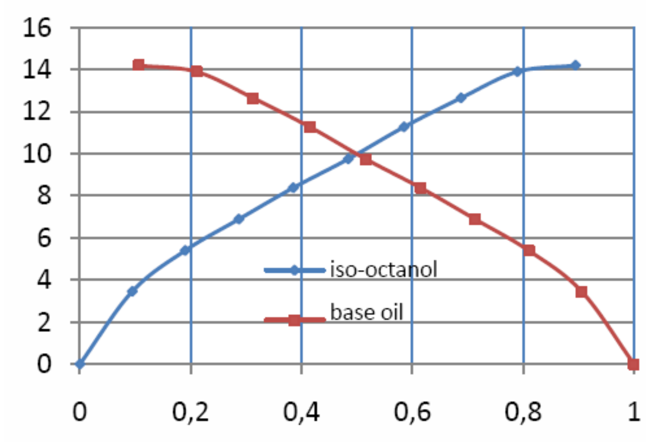

Fig 3 Excess volume of gas oil spiked /*iso*-octanol systems.

The binary mixtures of gas oil with aromatic components, 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 Figures 2 and 3. This effect could be related to the fact, that such compounds are "structure breaking" materials leading to positive excess volume [8].

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 [7]. 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 Figure 3 and Table 4, indicating that interactions between unlike molecules are weak and give rise to positive deviation.

Table 4 Max excess volumes, in cm^3/kg at about 0.5 mass fraction of spike at 298.15 and 308.15K for gas oil blends with different chemicals.

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

It is generally observed that paraffinic spikes usually produce negative excess volume values. This "shrinkage" effect is greatest for the lowest boiling point spikes. 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). It is also noticed that if the temperature increased the value of excess volume will be decreased.

It is interested to notice that *iso*-octanol spike produces positive excess volume values over the whole mass fractions, as shown in Figure 3. It was published else where [9] that mixture of alcohols with *n*-alkanes gives positive excess volumes over the entire mass fraction. Higher alcohols give even larger in magnitude than excess volumes observed for mixtures of low alcohols, such as methanol or ethanol with *n*-heptane [8]. Furthermore, Figure 3 indicates, that an equal positive value of excess volume about 9.8 cm^3/kg was achieved with a mass fraction of about 0.5 for both *iso*-octanol spiked gas oil or gas oil mixed with *iso*-octanol. While the maximum excess volume about +14 cm^3/kg was resulted by a mass fraction greatest than 0.9 and lowest than 1.0 for both systems.

3.3 Base Oils / MEK systems

The lubricating oil base stocks are produced usually from vacuum distillation of reduced crude oils and certain processes to meet the desired specifications. Dewaxing by means of methyl ethyl ketone is one of the lube oil processing aimed to reduce the cloud and pour points.

Therefore MEK considered in the present work to investigate its volumetric behavior by mixing with some base oils. Thus were stocks 40, 60 and 150 which are ordered according there increasing boiling range and viscosities, as shown in Table 2.

It is generally observed that the mixing of MEK to the three types of base oil stock produced positive excess volume values. In other word an "expansion" occurs relative to the calculated ideal volume, as shown in Figure 4. This behavior is indicating that interactions between unlike molecules are weak and give rise to positive deviations.

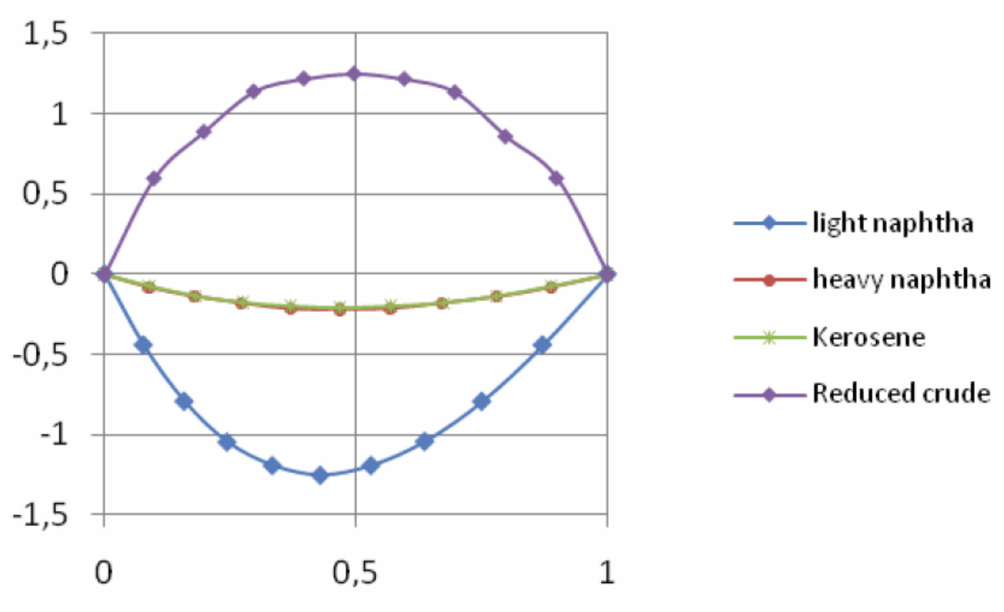

Fig. 4 Excess volumes of MEK/base oil stocks.

As shown in Figure 4, the boiling range as well as the viscosity of base oils have predominate effect on the expansion of MEK/ base oil systems. Thus, stock 40 of lowest viscosity gives the maximum positive excess volume about 6.5 cm^3/kg. The mixed stock 60 resulted in value about 3.5 cm^3/kg, while the heavy stock, 150 resulted in the lowest value of about 0.5 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 units.

4. Conclusions

Volumetric shrinkage is resulted from blending paraffinic petroleum fractions or hydrocarbons with gas oil. Blend of gas oil with aromatic nature hydrocarbons, MEK and *iso*-octanol are considered as "structure breaking" material, leading to high expansion effect. Furthermore mixing of *iso*-octanol with gas oil resulted in positive excess volume values over the whole mass fractions.

The blending of MEK with lube oil base stoke as unlike molecules resulted in expansion, which is greatest for the lowest boiling stock.

Nomenclature

V^E =Excess volume	cm^3/kg
x_2 = Mass fraction of spike	-
ϕ_2= Volume fraction of spike	-
$\rho_1°$ = Density of base oil stock	kg/m^3
$\rho_2°$ = Density of spike	kg/m^3

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