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E'XCESS VOLUMES OF HEAVY OIL – STOCKS MIXTURES + (KEROSENE OR XYLENE) AT 303 K

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ABSTRACT

Binary mixtures of three, heavy oil-stocks had been subjected to density measurements. The data had been acquired on the volumetric behavior of these systems. The heavy oil-stocks used were of good varity, namely 40 stock, 60 stock, and 150 stock. 40 stock is the lightest one with °API gravity 33.7 while 60 stock is middle type and 150 stock is heavy one, with °API gravity 27.7 and 23.8 respectively. Stocks with Kerosene or Xylene form non-ideal mixtures, for which excess volume can be positive or negative. Mixtures of heavy oil-stocks with paraffinic spike (kerosene) show negative excess volume. While, aromatic rings results a lower positive excess volume, as shown in xylene when blending with 40 stock and 60 stock but a negative excess volume when blending with 150 stock. The gravity of oil-stocks has an effect on excess volume when the oil-stocks spiked with Kerosene or Xylene. Those, 40 stock as typical light type resulted in minimum negative excess volume of -2.18, when it was spiked with the kerosene, while the spiked heavy oil-stock with kerosene gave a maximum excess volume of -11.2. The Redlich-Kister equation was used to fit the excess volume values, and the coefficients and estimate of the standard error values were presented.

Keywords: Excess Volume, Mixing Behavior, T.D. of mixing

INTRODUCTION

The mixing of different compounds gives rise to solutions that generally do not behave ideally. The deviation from ideality is expressed by many thermodynamic properties, particularly activity coefficients and excess or residual properties [1]. Excess thermodynamic properties are useful in the study of molecular interactions and arrangements [2]. In particular, they reflect the interactions that take place between solute

– solute, solute – solvent, and solvent – solvent species [3]. In general, positive excess volumes may be due to compensation between strong like interactions (such as those present in alcohols) and equally unlike H-bond interactions (such as those present between alcohol and ether) [3,4]. Negative excess volume will occur when the unlike interactions prevail over self-association [1,3]. Binary mixtures are an important class of solvents and solutions, and the behavior of their physical properties is still unclear [5].

In the blending of petroleum components having different physical properties, excess volumes occur because the components do not form ideal solutions. In an ideal solution, the total solution volume is equal to the sum of the volumes of the components. In order for a solution to approach ideality, the molecules of the materials blended together must be similar in size, shape, and properties. If the nature of the components differs appreciably, then deviation from ideal behavior may be expected. This deviation may be either positive or negative; that is, the total volume may increase or decrease when the components are blended [8]. The blending of oil stocks results in volume changes, caused by the non-ideal behavior of oil systems as compared with the calculated ideal volume. Since the oil industry uses volume measurement in its balances, the apparent discrepancies in material may cause financial complications, which in some cases have led to litigation [6].

The excess volume behavior of heavy oil-stocks mixtures is important. Since only small amount of database was published, especially on mixtures of heavy oil-stocks with pure hydrocarbons. While little studies were published on mixtures of different types of heavy oil-stocks.

A full understanding of thermodynamic and transport properties of binary liquid systems is essential in many chemical engineering processes such as design calculation, heat transfer, mass transfer, fluid flow, and so forth [7]. We have started a research program on the excess properties of mixtures containing (heavy oil-stocks + spikes). In this work we have reported experimental data such as density over the whole range of composition for binary liquid mixtures.

The present work was investigated to evaluate the volumetric behavior of blends of the heavy oil-stocks. Further aim of the work was to investigate the effect of hydrocarbons spikes such as kerosene and xylene on the excess volume of these mixtures.

Experimental work

Three heavy oil-stocks were obtained from al-Durra Refinery, namely 40 stock, 60 stock, and 150 stock. 40 stock is the lightest one with °API gravity 33.69 while 60 stock is middle type and 150 stock is heavy one, with °API gravity 27.74 and 23.79 respectively. The main properties of oil stocks (40 stock, 60 stock, and 150 stock) were measured in al-Durra Refinery laboratories according to API and ASTM specification, as listed in table 1.

Table 1: properties of oil stocks

Specification	40 stock	60 stock	150 stock
Kin. Viscosity at 40 °C, cSt	18.11	56.12	501.98
Kin. Viscosity at 100 °C, cSt	3.14	7.69	33.38
Viscosity index (VI)	95	95	93

Specific gravity at 15.6 °C	0.85	0.88	0.90
°API gravity	33.69	27.74	23.79
COC Flash,°C	n.d.	200-300	290-300
P.M. Flash,°C	160	n.d.	n.d.
Pour point,°C	-24	-6	-3
Sulfur content, wt.%	0.62	1.40	2.00

Kerosene was used as petroleum fraction to study the excess volume phenomena of heavy oil-stocks. This fraction was supplied by al-Durra Refinery, while the xylene was supplied from MERCK Company, Germany.

The method of mixing process was achieved by electrical mixer at room temperature (20-25 °C). Density measurements was made immediately, after preparing the mixtures to avoid deposit formation or vaporizing the light ends. All density measurements are carried out at atmospheric pressure.

The following mixtures were prepared in this study:

- Three heavy oil-stocks binary mixtures, over a range of weight percent (0-100) at temperature 30 °C.
- Binary mixtures of heavy oil-stocks with spikes (kerosene + xylene), over a range of weight percent (0-100) at temperature 30 °C.

Density determination of heavy oil-stocks, spikes and their blends were carried out using Pyknometer having a size of 50 cm^3 according to the standard methods (IP 190) [8].

The Pyknometer was placed in a water bath type (Julabo F25) as shown in Fig. 1. Which was capable of maintaining the temperature within ± 0.1 °C of the selected temperature. Thoroughly cleaning the Pyknometer and stopper with a surfactant cleaning fluid (gasoline), then with acetone and dried. Ensuring that all traces of moisture are removed by drying with a current hot air passing slowly through the Pyknometer and stopper capillary. Wiping the outside of Pyknometer and stopper with a clean, lint-free cloth. Normally Pyknometer cleaned by using (gasoline and acetone), and dried. All the density measurements were carried out at atmospheric pressure.

RESULTS AND DISCUSSION

The excess thermodynamic properties such as excess volumes of mixtures of heavy oil-stocks are considerable interest in the field of transportation. Usually light oil-stock blended with medium and also with heavy oil-stock to satisfy such specification for lubricating oil and another uses. Although these treatment have led to considerable insight into thermodynamic behavior of these mixtures. But these blending led mostly to loss in volume [6].

Fig. 1 Water bath

The heavy oil-stocks used were of good varity, namely 40 stock, 60 stock, and 150 stock. 40 stock is the lightest one with °API gravity 33.7 while 60 stock is middle type and 150 stock is heavy one, with °API gravity 27.7 and 23.8 respectively.

Three binary mixtures of heavy oil-stocks have been made. The volumetric behavior of the binary mixtures of heavy oil-stocks with different densities was evaluated. The ideal volume was calculated by the linear expression in terms of mass fraction of blending component as follows [9].

$$V^{id} = \frac{\rho_2^O + x_2(\rho_1^O - \rho_2^O)}{\rho_1^O \rho_2^O} \left(\frac{cm^3}{kg}\right) \ldots (1)$$

Excess volume is defined by the equation:-

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

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

Excess volumes for binary heavy oil-stocks mixtures are summarized in tables 2, 3 and 4.

If the data in the form of excess volumes are plotted against mass fraction of reference components, smooth curves are obtained as shown in figure 2. The curves pass through zero at 0 wt% and 100 wt% reference component, while the maximum excess volume occur at, or close to, mass fraction of 0.5, indicating that V^E at this point should be good indicator of the molecular interactions in the mixtures.

Table 2: Excess volume of binary systems; of Stock 40 with Stock 60.

Stock 40 X2	Density in g/cm³	V^E
0.2	0.8808	1.5577
0.4	0.8738	2.2448
0.5	0.87	3.0394
0.6	0.8684	1.9532
0.8	0.863	0.9494

Table 3: Excess volume of binary systems; of Stock 40 with Stock 150.

Stock 40 X2	Density in g/cm³	V^E
0.2	0.9006	-2.0735
0.4	0.8898	-3.5867
0.5	0.8856	-4.7520
0.6	0.881	-4.3514
0.8	0.8692	-2.9324

Table 4: Excess volume of binary systems; of Stock 60 with Stock 150.

Stock 60 X2	Density in g/cm³	V^E
0.2	0.9064	0.2294
0.4	0.9016	0.5207
0.5	0.899	0.9372
0.6	0.8974	0.3293
0.8	0.8934	0.1639

Excess volume are positive for (stock 40 + stock 60), and (stock 60 + stock 150) mixtures over the mass fraction range, as shown in Fig. 2.

As one can see from Fig. 2 the derived values of V^E for the stock 40 + stock 150 mixtures are very high (maximal value is about (-4.752

cm^3/kg) and negative over the whole composition range. V^E curves are almost symmetric with the maximum at 0.5 mass fractions. This negative excess volume (shrinkage) come from the changes in self-association (inter or intramolecular) and physical interaction (van der Waals interaction and dipole–dipole interaction) between like molecules decrease the volume [10]. On the other hand, free volume effects, interstitial accommodation or interactions between unlike molecules contribute to volume contraction.

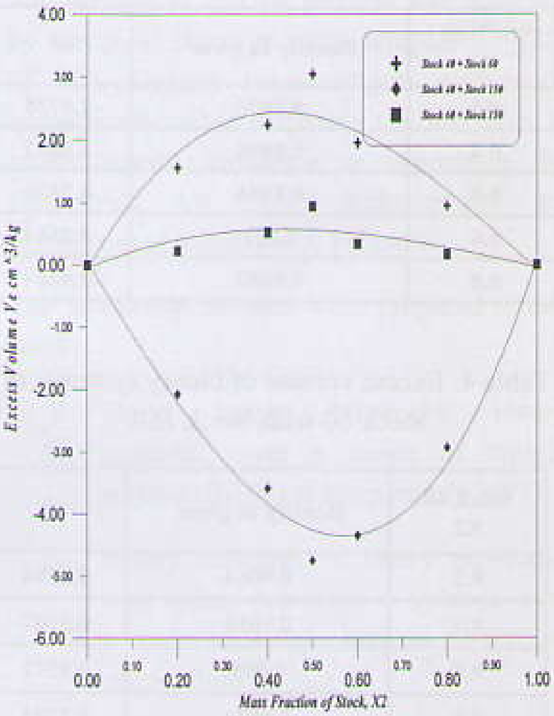

Fig. 2 Excess volume V^E for Binary mixtures of Stocks oil

The small values of the V^E is the result of the ideality of the stock 60 + stock 150 mixture, i.e. the difference between the mixture volume V_{mix} and the ideal mixture molar volume $V_{idel} = xV_1 + (1-x)V_2$ is very small (maximum value of about 0.94 cm^3 /kg. but it also gives excess volume (stock 60 +stock 150) mixture due to the different in the chemical composition and structure bonds between the molecules, in addition to the difference in specific gravity between these stocks

The three heavy oil-stocks were, also, blended with kerosene and xylene. The spiked heavy oil-stocks have been subjected to density measurements to evaluate the volumetric behavior of these systems. The density data obtained for each heavy oil-stocks/spike pairs are reported in the form of excess volume V^E at a given mass fraction of spike X_2 as shown in table 5, 6 and 7.

Table 5: Excess volumes V^E, for spiked stock 40

Stock 40 with:		
X_2	Kerosene	Xylene
0.2	-2.1838	0.9949
0.4	-4.5252	1.4089
0.5	-5.2453	2.0545
0.6	-5.0798	1.5732
0.8	-3.5347	1.0243

Table 6: Excess volumes V^E, for Spiked stock 60

Stock 60 with:		
X_2	Kerosene	Xylene
0.2	-2.9507	1.0557
0.4	-5.1751	1.6889
0.5	-6.9118	1.9706
0.6	-5.9727	1.5353
0.8	-5.3794	1.1375

Table 7: Excess volumes V^E, for Spiked stock 150

Stock 150 with:		
X_2	Kerosene	Xylene
0.2	-7.2927	-0.5592
0.4	-9.1326	-1.6145
0.5	-11.2026	-2.2891
0.6	-9.9023	-1.6666
0.8	-8.2446	-1.2037

If the data in the form of specific excess volume are plotted against mass fraction spike, smooth curves are obtained as shown in Figs. 3 and 4. The curves pass through zero at 0 wt% spike and 100 wt% spikes, while the maximum excess volume occur at, or close to, mass fraction of 0.5, indicating that V^E at this point should be good indicator of the interactions in these systems.

It is generally observed that the addition of middle petroleum fractions, such as kerosene to the three heavy oil-stocks of different densities produces negative excess volumes; in other words "shrinkage" occurs relative to calculated ideal volume, as shown in tables 5, 6 and 7.

This shrinkage effect is directly proportional with specific gravity of the oil-stocks, so that when the density of oil-stock increase the negative excess volume will increase.

As one can see from Fig. 3 the derived values of V^E for the (kerosene + heavy oil-stocks) mixtures are very high (maximal value is about (-11.202 cm^3/kg) and negative over the whole composition range. It seems that the position of paraffinic straight chains has great effect on the volumetric behavior of these mixtures. The n-paraffins behavior is consistent with a close-packed structure, the mixture having a more tightly packed structure than component liquids. These observations can be directly related to the existence of long-orientational order in hydrocarbons [12].

The negative V^E arises due to dominance of the following factors [11]:

(a) Chemical interaction between constituent molecules such as hetero-molecular association through the formation of H-bond, often termed as strong specific interaction.

(b) Association through weaker physical forces such a dipolar force or any other forces of this kind.

(c) Accommodation of molecules of one component into the interstitial positions of the structural network of molecules of the other component.

(d) Geometry of the molecular structure that favors fitting of the component molecules with each other.

The binary mixtures of stock 40 and stock 60 with xylene show positive values of excess volume, and thus exhibit expansion, as shown in Fig. 4. This effect is appreciable relate to the fact, that such compounds are "structure breaking" materials leading to positive excess volume [13].

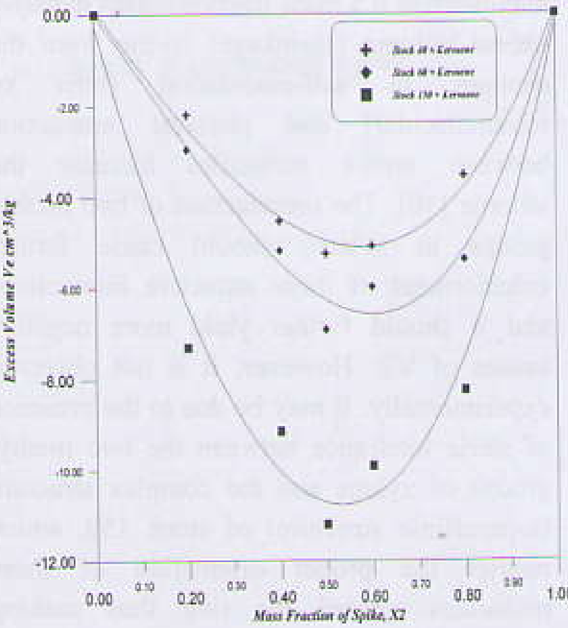

Fig. 3 Excess volume VE for Binary Mixtures of Stock oil/Kerosene

The factors that are mainly responsible for the volume expansion i.e., positive values of V^E, are [11]:

(a) Disruption of one or both components in a solution system. A suitable example of this, the rupture of H-bonding of one compound by the other, or breaking up of associates held together by weaker physical forces such as dipole or dipole-induced dipole interactions or by any other van der Waals forces.

(b) The geometry of molecular structure which does not favor fitting of the molecules with each other.

(c) Steric hindrance which opposes the proximity of the constituent molecules.

The binary mixture of stock 150 with xylene show negative values of excess volume over the whole composition range as shown in fig. 4. VE curves are almost symmetric with the maximum at 0.5 mass fractions. This negative excess volume (shrinkage) co-me from the changes in self-association (inter or intramolecular) and physical interaction between unlike molecules increase the volume [10]. The introduction of two methyl groups in xylene, should cause further enhancement of these attractive interactions and it should further yield more negative values of VE. However, it is not observed experimentally. It may be due to the presence of steric hindrance between the two methyl groups of xylene and the complex structure (n-paraffinic structure) of stock 150, which restrict the proper orientation of these molecules toward the ring thus making interactions weaker. Among the xylene is symmetrical molecule, thus it offers least steric hindrance. The VE values for this system are most negative [14].

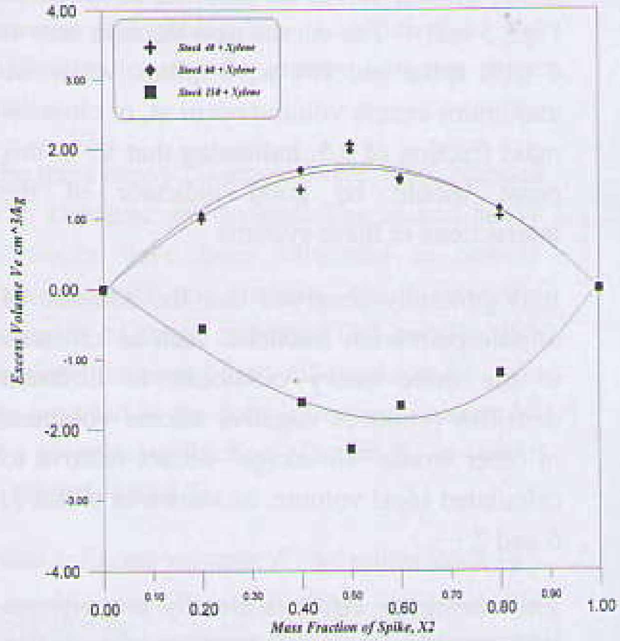

Fig. 4 Excess volume V^E for Binary Mixtures of Stock oil/Xylene

The well-known Redlich-Kister polynomial equation[15], which has the following form

$$V^E = x_1 x_2 \sum_{i=0}^{n} A_i (x_1 - x_2)^i \ldots \quad (3)$$

is used to correlate the experimental data. The coefficient Ai is determined by a multiple regression analysis based on the least-squares method and is summarized along with the standard deviations between the experimental and fitted values of the corresponding function in table 8.

A computer program was used to find the values of the constants A_1, A_2, A_3, A_4 and A_5 that give the best fitting of the experimental data. The coefficients for each system i.e., for each mixture are tabulated in table 8.

The values of the constants A_1, A_2, A_3, A_4 and A_5 where give the best fitting of the experimental data for each pipe diameter, were computed by Statistica program

The values of standard error (SD) [14] between the calculated and experimental datum points are obtained using the equation as follows:

$$SD = \left[\Sigma \left(V^E_{cal} - V^E_{exp}\right)^2 \Big/ (n-1) \right]^{1/2} \quad \ldots (4)$$

Where:

V^E_{Cal} is the calculated value and

V^E_{exp} is the experimental value.

CONCLUSIONS

It's generally observed that the blending of light and medium oil-stocks with heavy oil-stock results in volume "losses" caused by the non-ideal behavior of this system as compared with the calculated ideal volume. Also it's observed that the mixing of paraffinic hydrocarbon (kerosene) with heavy oil-stocks produces negative excess volume.

While the blends of aromatics hydrocarbons (xylene) with heavy oil-stocks produce positive excess volume except stock 150, so that this blends produce negative excess volume due to composition of stock -150 with high aromatics structure. These binary data were correlated well with the Redlich–Kister equation.

NOMENCLATURE

Ai: coefficients of Redlich-Kister polynomial equation

n: total number of experimental values

V^E: excess volume, cm3/kg

x_2 : mass fraction of component 2

ρ_{mix} : density of the mixture for binary system, g/cm^3

ρ_i° : density of component i, g/cm^3

Table 8: Coefficients of the Redlich-Kister equation Ai and standard deviation for V^E

Mixture	A1	A2	A3	A4	A5	SD
Stock 40 + Stock 60	12.1576	13.9594	-151.7479	-12.6318	359.2599	8.19539E -05
Stock 40 + Stock 150	-13.0080	31.1886	17.7445	-59.7412	-45.5127	1.99374E -05
Stock 60 + Stock 60	3.7488	4.1354	-65.7929	-1.4567	148.1778	3.11384E -05
Stock 40 + Kerosene	-20.9812	-7.1407	-30.6345	62.5277	70.5194	3.34821E -05
Stock 40 + Xylene	2.6180	5.8411	18.5475	-32.5651	-39.9121	4.7407E-05
Stock 60 + Kerosene	-23.6472	40.9688	191.7505	-35.2620	-623.3760	4.01008E -05
Stock 60 + Xylene	5.8824	-7.3264	21.2936	14.8275	-10.6623	4.09339E -05
Stock 150 + Kerosene	-32.8104	-16.9904	50.5631	104.3701	-334.2699	3.62272E -05
Stock 150 + Xylene	-1.1564	-11.2023	-101.2507	33.2080	283.8356	1.50759E -05

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تاثير المضافات الهيدروكاربونية (النفط الابيض+الزايلين) على الحجم الزائد للاساسات زيت التزليق

تم استخدام ثلاث انواع من اساسات زيت التزليق وهي الاستوك 40 وهو الاخف من حيث الحجم الجزيني والمتوسط وهو الاستوك 60 والاثقل وزنا جزنيا الاستوك 150 لمعرفة السلوك الحجمي لمخاليط تلك الزويت وكذلك سلوك تلك الزيوت حجميا عند اضافة المضافات الهيدروكاربونية مثل النفط الابيض والزايلين. حيث ان اضافة هذه المواد تؤدي الى زيادة في الحجم قد تكون موجبة او سالبة بمعنى اخر ان هذه الاضافات قد تودي الى انكماش او تمدد حجمي في تلك الخلائط. حيث تبين ان اضافة المادة الهيدروكاربونية ذات الطابع البرافييني (النفط الابيض) يؤدي الى حدوث انكماش ملحوظ في حجم الخلائط بينما اضافة المادة الهيدروكاربونية ذات الطابع الورومانتي (الزايلين) يؤدي الى تمدد تلك الخلائط ماعدا خلائط الاستوك 150 حيث ان اضافة الزايلين الى تلك الخلائط يؤدي الى انكماشها والسبب في سلوك الزايلين بصورة عامة يرجع الى التركيب الاروماتي المعقد للستوك 150. تم الحصول على اعلى نسبة من الحجم الزائد وهي 11,2 عند اضافة النفط الابيض الى الاستوك 150. تم حساب قيم الحجم الزائد باستخدام معادلة ردلخ – كايستر واعطت النتائج النظرية توافق كبير جدا مع النتائج العملية.