PREDICTING THE CHANGE IN VOLUME OF MIXED OIL STOCKS

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ABSTRACT

A typical local heavy crude oil is blended with light one in different ratios. Furthermore reduced crude (atmospheric residue) is blended with 5-25 vol. % Kerosene or Gas oil, in order to improve it's properties as industrial Fuel oil.

Density measurements for the different oil stocks over a temperature range between (15-60^{0}C) we used to develop a density predicting correlation. The validity of the density linear correlation is demonstrated by a good match between the calculated and experimental oil-stock densities.

The blended oil-stocks show negative excess volumes. This shrinkage increases with decreasing the value of light component and with increasing the temperature up to 35^{0}C.

A correlation was modified to estimate the relative excess volume of oil blends at different temperatures. This model suggests that the ideal volume of oil mixture is not a linear function of volume fraction and density. The validity of the correlation is shown to be accurate to predict the volumetric behavior of the studied oil mixtures, with AAD <0.015.

INTRODUCTION

Heavy crude oils and residual oil fractions we often blended with light oilstocks to meet certain specifications, such as lowering the viscosity and pour point. Different grades of crude oils from various fields are usually mixed and handled in the same pipelines to the consumer or to the refinery.

The blending of oil-stocks results in volume changes caused by the non-ideal ehavior f il systems as compared with the calculated ideal volume (1-3). Since the oil industry uses volume measurement in its balances, the apparent discrepancies, which in some cases financial complications, which in some cases have led to litigation (4).

A major study of spiked crude oils was done in the 1950s by Rossini on behalf of the US petroleum industry (2). These results form the basis of API procedure 2509C for determining the shrinkage of crude oils containing 50 vol. % spike (2). Robinson gave details of a theoretical approach based on the Costald equation of state (5).

Generally observed that the addition of paraffin hydrocarbons to a crude oil produces negative excess volume. This shrinkage effect is greatest for the lowest boiling spike. Furthermore, mixtures of crude oils with Toluene or Cyclohexane show positive excess volume, and thus exhibit expansion (3).

The current project was instigated to evaluate the volumetric behavior of blends of typical Iraqi heavy oil-stocks with light types. Furthermore, it was aimed to develop correlation to predict the densities and excess volumes of oil-stock blends at different temperatures.

EXPERIMENTAL WORK

Binary mixtures of a heavy crude oil (API^0 =20.7) with a light one (AP1^0 = 34.7) were prepared over a range of 10 - 90 % vol.% increment. Reduced crude (API^0= 16.4) was also blended with 5 - 25 vol.% Kerosene (AP1^0= 48.7) or Gas Oil (AP10 = 35.9) at 5 vol.% increment. The oil-stocks were supplied by Al-D aura Refinery, Baghdad. Densities of the studied oil-stocks at different temperatures are illustrated in table 1.

Density determinations of crude oils and petroleum products and their blends were made by means of 25 cm^3 Pycnometer according to the standard method IP-190 (6). The measurements were carried out at atmospheric pressure over a range of temperatures (15-60^{0}C), at 5^{0}C increment. The temperature was kept constant within i 0.1 ^{0}C of the selected temperature by means of a water bath (Julabo HC). Repeatability of sample densities was $\pm 10^{-4}$ gm/cm^3.

RESULTS AND DISCUSSION

The density measurements of the various oil-stock blends at different temperatures show, as it is expected, a gradual decrease with temperature increase and With vol.% increase of the light component. Fig. 1 shows the variation of density with temperature and composition for Reduced Crude/Gas oil blends. Similar observations are obtained for the other systems studied.

Thus, is seen to be that the effect of temperature on the density of oil- stock Systems followed linearity.

The following linear equation (7), was modified to predicate the density of oil-stock mixtures as function of temperature and vol.% of blending component.

$$\rho = a + b\,T \qquad (1)$$

The two parameters in eqn. 1 were obtained by least square method. It was found that the parameter (b) has values between -0.722 and -0.826 for binary mixtures of light and heavy crude oils. Therefore an optimum value equal 0.783 was taken, result the one-parameter eqn. 2 for binary crude oil Systems.

$$\rho = a - 0.783T \qquad (2)$$

Further observation was that, the parameter a is related to the concentration of light crude oil by the following linear equation:

$$a = 877.975 + 54.571\,x \qquad (3)$$

It is therefore appropriate to find the final expression between density, temperature and composition by substituting eqns. 2 and 3 to get the following equation for crude oil blends:

$$\rho = 877.975 - 0.783T + 54.571x \qquad (4)$$

Eqn. 4 predict the values of mixture densities over a whole composition range and at various temperatures with excellent agreement. The average standard deviation is 0.993 and average absolute error is 2.12 %.

The same procedure was done for the binary mixtures of Reduced Crude with Kerosene and light Gas Oil. Therefore, the resulting expression for the density as function of temperature and composition for reduced crude blends is as expressed in eqn. 5, which has an average standard deviation of 0.578 and average absolute error of 0.657 %.

$$\rho = 975.611 - 0.7234T - 163.131\,x \qquad (5)$$

Thus, combination of eqn.4 together with eqn.5 provides an overall density predication for all oil-studied mixtures, as follows:

$$\rho = 900 - 0.783\,T + 54.571\,x \qquad (6)$$

The predicated results using eqn.6 were in agreement with experimental data. The average standard deviation is 3.2 for crude oil blends and 2.9 for reduced crude blends. The average absolute error is 2.9 % and 4.7 % for crude oil and reduced crude blends respectively.

The density data obtained in this project were used to calculate the volume of each blend, in order to predict the excess volume.

The nonlinear ideal volume method was first used by Ashcroft etal. (3) to calculate the value of ideal volume of mixtures of crude oils and light hydrocarbons (Spike). The ideal volume V^{id} is given in terms of volume fraction of spike Φ_2 and the densities of crude oil ρ_1^0 and spike ρ_2^0 by equation. 7:

$$V^{id} = 1/\,[(1-\Phi_2)\,\rho_1^0 + \Phi_2\,\rho_2^0]\ \ cm^3.kg^{-1} \qquad (7)$$

The percentage relative excess volume ΔV^R is calculated by eqn. 8.

$$\Delta V^R = [\,(V_{mix} - V_{ideal}\,)\,/\,V_{ideal}]\ x\ 100 \qquad (8)$$

The density data for the various oil-stock mixtures in this project were expressed in form of the percentage relative excess volume, by means of eqns. 7 and 8. Figs. 2 and 3 represent plot of the relative excess volume of crude blends against volume percent of light crude oil for different temperatures. The obtained smooth curves pass through zero at 0% and 100% light crude. The maximum occurs at or close to 50%, indicating that ΔV^R at this point should be a good indicator of the interaction in these mixtures.

Mixtures of light with heavy crude oil show always-negative excess volume values. This "Shrinkage" effect increase with increasing the concentration of light crude oil up to about 50%. Further increase of light component leads in gradual decrease of "shrinkage" as shown in figs. 2 and 3.

Mixtures of Reduced Crude with Kerosene or Gas oil show also negative values of excess volume, as illustrate in figs.4-7. This *shrinkage* effect is greatest for the lowest-boiling component, Kerosene.

The effect of increasing temperature on relative excess volume of the oil blends is demonstrated in figs. 2-7. Generally, the increase of temperature up to 3 5^{0}C leads to gradual increase of relative excess volume of all studied systems.

Further increase of temperature lead in decrease of relative excess volume values for the same blends.

A correlation was modified to estimate the relative excess volume of oil blends at different temperatures. The following quartic equation proposed originally by Ashcroft (3) for mixtures of crude oils and light hydrocarbons (Spiked), was particularly relevant to this study.

$$\Delta V^R = \Phi_2(1-\Phi_2)(A_0+A_1(1-2\Phi_2)+A_2(1-2\Phi_2)^2) \quad (9)$$

Smoothing coefficients of eqn. 9 was tabulated for each crude oil-Spike system at 15 and 25 ^{0}C (3).

The predominate stage was how to formulate the constants of eqn. 9, A_0, A_1 and A_2 to predict the relative excess volumes of the studied oil mixtures at different temperatures. The values of these three constants were calculated at each temperature from the values of relative excess volume, given in figs. 2-7 by using the least square method. The results with the standard deviation are presented in tables 2-4 for Crude/Crude, Reduced crude/Kerosene and Reduced crude/Gas oil systems respectively. It can be calculated from table 2 for crude oil mixtures, that the parameters A_0 and A_1 are related to the temperature by the logarithmic eqns. 10 and 11, while A_2 is related to the temperature by the linear equation 12.

$$A_0 = -0.0032 + 0.0012 \log T \quad (10)$$

$$A_1 = (-84.2077+24.123 \log T) \times 10^{-6} \quad (11)$$

$$A_2 = (-15.2975+0.6492\ T) \times 10^{-8} \quad (12)$$

An examination of eqns. 9-12 resulted in excellent agreement with experimental data for predication the relative excess volume for crude oil mixtures. The average standard deviation is 0.0124 at the temperature range studied.

It was found, also that the constants, A_0, A_1 and A_2 are related to the temperature, in case of Reduced crude blends with Kerosene or Gas oil, as follows:

$$A_0 = -0.003 + 0.001 \log T \quad (13)$$

$$A_1 = (-80.183+30.095 \log T) \times 10^{-6} \quad (14)$$

$$A_2 = (-15.2975+0.6492T) \times 10^{-8} \quad (15)$$

The data of relative excess volume were calculated by means of eqns.9 and 13-15 with an average standard deviation of 0.0022.

Further attempt was done to formulate a generalized expression to calculate the relative excess volume for all considered oil systems at different temperatures. Thus, the constants A_0, A_1 and A_2 can readily be calculated by means of eqns. 16 -18.

$$A_0 = -0.003+0.001 \log T \quad (16)$$

$$A_1\ (-83.025+25.185 \log T) \times 10^{-6} \quad (17)$$

$$A_2 = (-16.829+0.649\ T) \times 10^{-8} \quad (18)$$

The correlation shown to be accurate with an average standard deviation of 0.019 for crude oil systems and 0.015 for reduced crude blends with Kerosene or Gas oil.

CONCLUSION

A total of 230 density measurements were obtained at different temperatures (15-60^0 C), of which 120 for heavy/light Crude blends and the remainder for Reduced Crude/Kerosene or Gas oil systems. A linear correlation was shown to be accurate for density predication as function of temperature and composition for all studied systems. Furthermore, the relative excess volume of the studied Systems can be predicted for different temperatures by a quartic equation with excellent accuracy.

NOMENCLATURE

a , b	Parameters in density model
A_i	Constants in eqn. 9
AAD	Average absolute deviation
T	Temperature, ^{0}C
ΔV^R	Percentage relative excess volume
ρ	Density, $Kg.m^{-3}$
x, Φ_2	Volume fraction of light component in the mixture
σ	Standard deviation between experimental and fitted values of ΔV^R

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Table (1) Densities of oil-stocks at different temperatures

Temperature (°C)	Densities				
	Light crude	Heavy crude	Reduced crude	Gas oil	Kerosene
15	851.615	926.943	957.135	845.490	785.086
20	846.686	923.964	955.875	843.966	783.590
25	840.563	918.745	954.554	841.153	780.094
30	835.093	914.580	951.714	838.681	777.416
35	829.052	909.927	948.525	935.577	774.284
40	826.477	904.427	944.033	932.607	764.706
45	823.505	900.513	940.042	827.292	764.706
50	818.441	897.318	935.362	823.129	759.586
55	814.525	895.041	926.746	815.867	754.488
60	809.879	893.100	925.097	810.558	752.534

Table (2) Smoothing coefficients and accuracy (eqn.9) for crude systems

Temperature (°C)	$A_o \times 10^3$	$A_1 \times 10^5$	$A_2 \times 10^7$	σ
15	0.6868	-2.7660	-0.8745	0.4109
20	0.4596	-0.9090	-0.4497	0.2195
25	0.2450	-3.4900	-0.6414	0.8070
30	0.9767	-0.8636	-0.3471	1.3852
35	1.4750	-0.8061	-0.1767	0.3263
40	1.5280	1.5800	1.7818	0.3867
45	2.3500	3.1300	2.2697	0.6487
50	1.4799	0.5641	1.7625	1.1679
55	1.1600	1.7800	1.6803	1.4645
60	0.7580	1.3500	2.3130	1.3124

Table (3) Smoothing coefficients and accuracy (eqn.9) for reduced crude – kerosene systems

Temperature (°C)	$A_o \times 10^3$	$A_1 \times 10^4$	$A_2 \times 10^6$	σ
15	2.299	1.256	1.657	0.0411
20	2.369	0.144	-0.657	0.0122
25	3.192	0.839	0.505	0.7368
30	2.090	0.010	-0.666	0.5064
35	8.165	3.450	3.725	0.1219
40	4.358	1.918	2.157	0.8476
45	0.041	1.285	-2.615	0.3046
50	4.090	1.606	1.613	0.0081
55	3.449	1.875	-0.6335	1.0399
60	1.889	1.001	1.351	0.3327

Table (4) Smoothing coefficients and accuracy (eqn.9) for reduced crude – gas oil systems

Temperature (°C)	$A_o \times 10^3$	$A_1 \times 10^4$	$A_2 \times 10^6$	σ
15	1.207	0.554	-0.654	0.1020
20	0.034	0.810	-1.663	0.1658
25	1.130	0.060	-0.527	0.3849
30	0.174	0.938	-1.765	0.3757
35	4.462	1.985	-2.230	0.1267
40	4.839	2.142	-2.389	0.3387
45	1.424	0.189	-0.946	0.4435
50	3.116	0.586	-0.017	0.9710
55	0.655	1.345	-3.003	0.8507
60	2.339	0.768	-0.618	0.4949

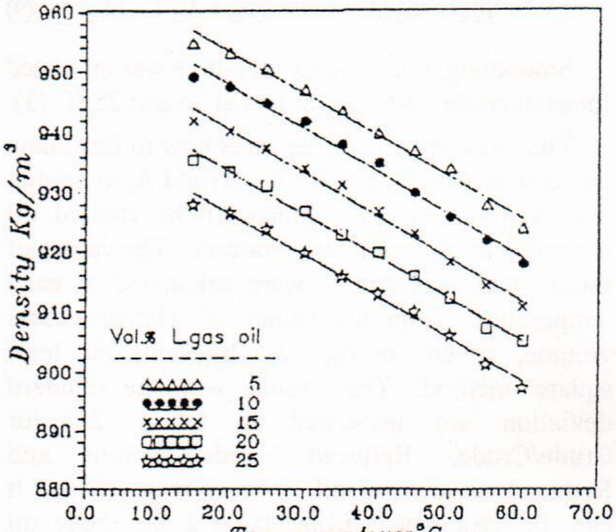

Fig. (1) Variation of density with temperature for reduced crude and gas oil mixtures

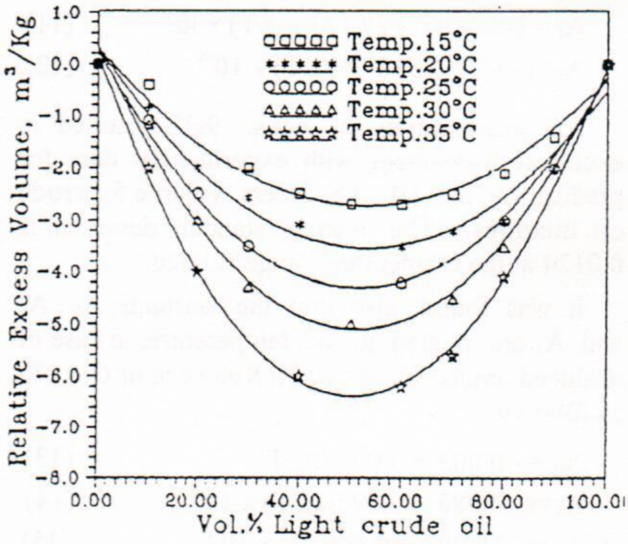

Fig. (2) Relative excess volume of light and heavy crude mixtures at 15-35°C

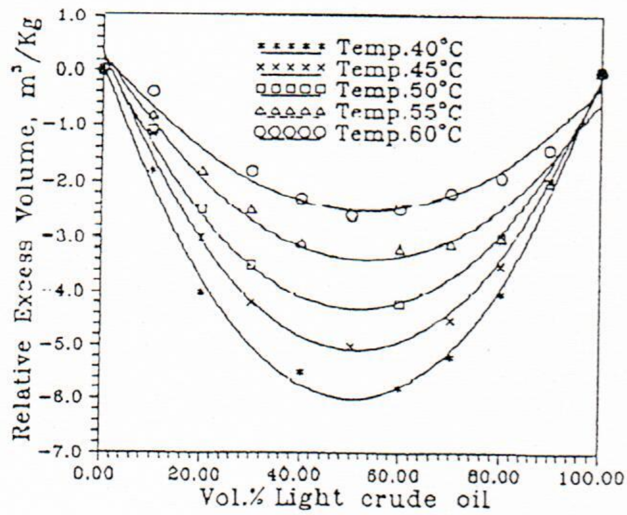

Fig. (3) Relative excess volume of light and heavy crude mixtures at 40-60°C

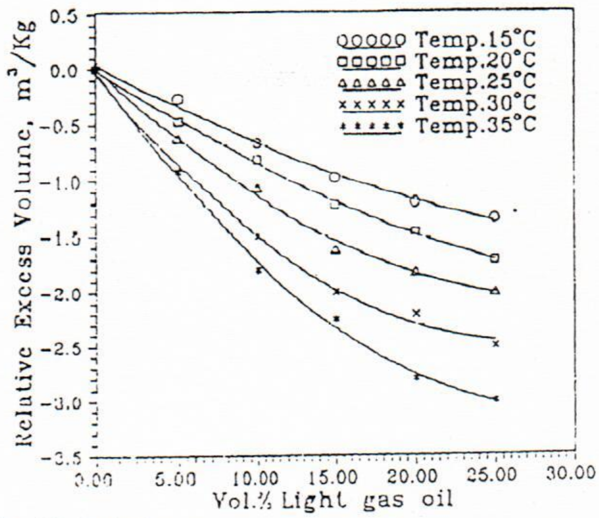

Fig. (6) Relative excess volume of reduced crude-gas oil at 15-35°C

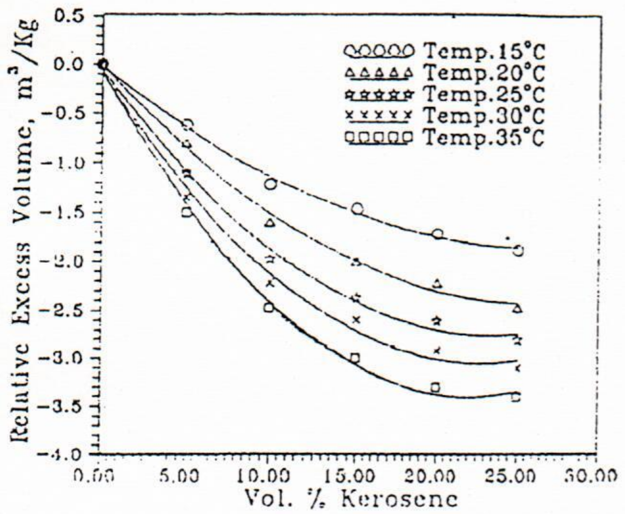

Fig. (4) Relative excess volume of reduced crude – kerosene blends at 15-35°C

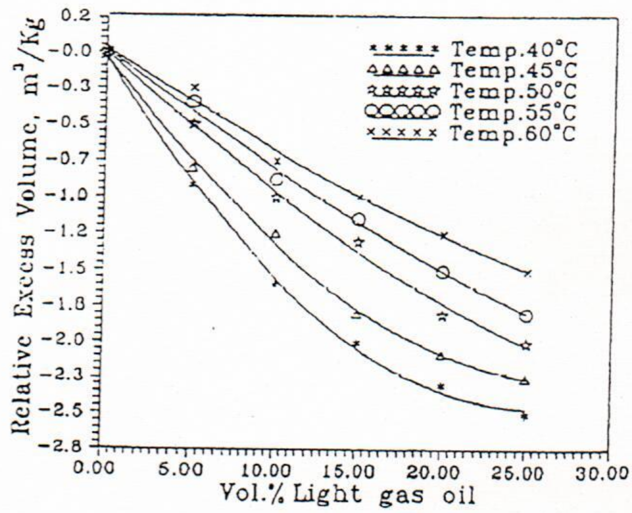

Fig. (7) Relative excess volume of reduced crude – gas oil at 40-60°C

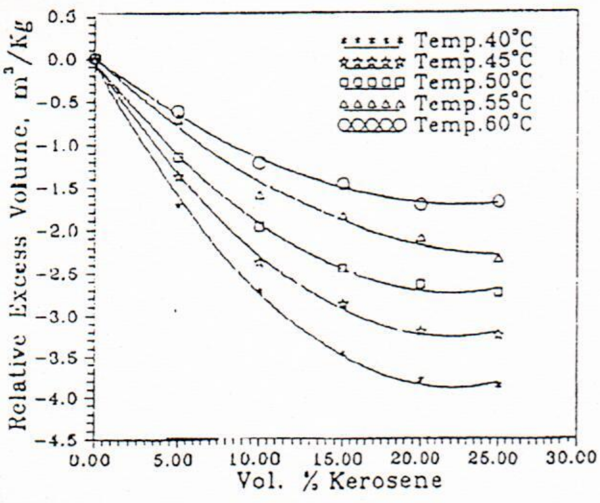

Fig. (5) Relative excess volume of reduced crude – kerosene blends at 40-60°C