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RESEARCH ARTICLE

VISCOSITY AND THERMODYNAMIC STUDY OF CRUDE OILS IN BENZENE

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ABSTRACT

Viscosities for different concentrations of crude oil solutions from 10 to 50 %(v/v) have been studied using benzene as a solvent at temperature ranging from 303 to 318 K. Four different relations: Huggins, Kraemer, Martin and Schulz-Blaschke were used to study the oil solution interaction in benzene by viscosity measurement. Viscometric constant values in terms of solute-solvent interaction. These relations were successfully applied for the study of macromolecular interaction. The validity of these relations concerning the interaction of crude oils with benzene was studied. Thermodynamic parameters for viscous flow were also evaluated such as free energy change of activation (ΔG^*), enthalpy change of activation (ΔH^*) and entropy change of activation (ΔS^*) as a function of concentration of crude oil solutions and temperature.

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INTRODUCTION

Crude oil is the raw form of petroleum which is unrefined and chemically is a complex mixture of hydrocarbons, with small amounts of sulphur, oxygen, and nitrogen, as well as various metallic constituents. It is a source to produce energy using as a fuel, power generation, heat production for our homes, etc. are several important domestic and industrial applications of crude oil (Oyekunle, *et al*., 2004; Ghannama, *et al*., 2006; Elsharkwy, *et al*., 2001; Lesaint, *et al*., 2010). Viscosity and density data of liquids and liquid mixtures find broad application in solution theory and molecular dynamics which is essential for thermo chemical, electrochemical, biochemical and kinetic studies. Study for viscosity of crude oils provides valuable information about solvent-solvent interaction required in petroleum engineering (Hashim, *et al*., 2003; Poindexter, *et al*., 2002). The behavior of petroleum fluids at oil field conditions can understand by knowing the viscosities of pure hydrocarbons and their mixtures (Hernandez-Galvan, *et al*., 2007). It is an important technique for the study of thermodynamic and various physical properties such as pressure, temperature, solution gas–oil ratio, bubble point pressure, gas gravity and oil gravity etc (Torabia, *et al*., 2011; Evdokimova, 2010; Kouzel, 1965). In petroleum industry, water-in-oil (w/o) emulsions can lead to massive economic losses if not treated properly. Research data (Hannisdala, *et al*., 2007; Fournantyab, *et al*., 2008; Hasan, *et al*., 2010) for water-in-oil emulsions is available but in pure solvent require more study.

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Crude oils obtained from different geographical locations vary in physical properties. The purpose of this study is to use the viscosity data of crude oil samples taken from local and international areas in benzene as a solvent to evaluate crude oil solvent interaction using different relations. The validity of macromolecular relations is applied on the crude oils. Physicochemical properties and thermodynamic parameters for viscous flow of crude oils as a function of concentration of crude oil solutions were also calculated.

MATERIALS AND METHODS

All the glassware used were of Pyrex 'A' grade quality. Crude oils used in the experimental work was obtained from different local and international areas like Upper zukkum, Mazari, Lashari, Pasaki, Sono and Iranian light, Arabian light, termed as sample A, B, C, D, E, F and G respectively. Benzene (C_6H_6, HPLC grade, 99 % pure of Merck) was used without further purification. Densities and viscosities of pure benzene obtained from literature (Parthasarathi, *et al*., 2011; Al-Kandary, *et al*., 2006). An Ostwald viscometer type Techniconominal constant 0.05 $Cs.s^{-1}$ capillary ASTM D 445, was used to measure the viscosity at different temperatures ranging from 303 to 318 K with the interval of 5 K. For keeping the temperature constant throughout the experiment work, a thermostatic water bath (type Haake-13, Karlsruhe, Germany) was used. Different percent compositions of crude oil samples were prepared in pure benzene as a solvent by taking a known volume of samples concentrations (10, 20, 30, 40 and 50 %v/v). Particular volumes of crude oils sample solutions was taken in viscometer, which is vertically placed in a glass tube attached with thermostatic water bath having a constant circulation of water to maintain constant temperature during the experimental work. Time of flow for solutions between two marks was taken by stopwatch having a least count of + 0.5 seconds. Pipette filler used to fill the crude oil sample to the upper mark in the viscometer. The densities of crude oil solutions (10, 20, 30, 40 and 50 %v/v) A to G were also measured with relative density bottle having the capacity of 10 cm^3. Reproducibility of the results was checked by taking each measurement three times. The values of uncertainty for viscosity and density measurement are ±0.002 mPa.s and ±0.001 $g.cm^{-3}$ respectively. All the precautions were made during experimental work due to hazards of benzene. Reproducibility of the results was checked by taking each measurement three times.

RESULTS AND DISCUSSION

Viscosities of different percent compositions (10, 20, 30, 40 and 50 %v/v) of crude oils sample (A, B, C, D, E, F and G) solution in benzene as a solvent at different temperatures ranging from 303 to 318 K with the interval of 5 K is tabulated in Table 1.

Table 1. Viscosities of crude oil mixtures in benzene at different temperatures

Percent composition of crude oil % (*v/v*)	Viscosities (*m.Pa.s*) at temperatures (*K*)			
	303	308	313	318
Sample A				
10	11.890	11.836	11.693	11.560
20	12.253	12.125	11.982	11.940
30	12.396	12.358	12.318	12. 247
40	12. 610	12. 528	12. 445	12. 260
50	12.700	12.956	12.850	12.688
Sample B				
10	11.875	11.663	11.500	11.380
20	11.900	11.699	11.536	11.452
30	12.330	11.990	11.856	11.461
40	12.657	12.126	11.856	11.565
50	12.850	12.150	12.056	11.823
Sample C				
10	11.607	11.380	11.309	11.278
20	11.840	11.465	11.423	11.338
30	12.039	11.768	11.615	11.491
40	12.100	11.900	11.754	11.557
50	12.260	12.032	11.849	11.806
Sample D				
10	11.906	11.700	11.544	11.430
20	12.125	11.848	11.598	11.494
30	12.205	12.107	11.875	11.790
40	12.496	12.153	11.960	11.812
50	12.789	12.262	12.203	12.098
Sample E				
10	11.976	11.795	11.629	11.522
20	12.367	12.126	11.823	11.547
30	12.692	12.193	11.996	11.709
40	12.839	12.226	12.081	11.885
50	12.982	12.247	12.108	11.984
Sample F				
10	12.121	11.994	11.851	11.754
20	12.334	12.124	11.994	11.868
30	12.643	12.449	12.251	12.142
40	13.040	12.844	12.558	12.424
50	13.873	13.393	13.286	12.980
Sample G				
10	12.182	12.024	11.983	11.912
20	12.285	12.152	12.048	12.045
30	12.687	12.613	12.540	12.429
40	13.004	12.876	12.817	12.701
50	13.784	13.774	13.670	13.477

The intrinsic viscosities [η] were calculated by using viscometric data, through graphical extrapolation method. The most commonly employed equations are Huggins, Kraemer, Martin and Schulz-Blaschke; equations 1 to 4, respectively. In order to apply these relations, practical determinations using different concentrations are carried out by counting the efflux time of these solutions through a capillary.

$$\eta_{sp}/C = [\eta]_h + k_h [\eta]_h^2 C \quad \text{..........(1)}$$
$$\ln \eta_r /C = [\eta]_k - k_k [\eta]_k^2 C \quad \text{.........(2)}$$
$$\ln \eta_{sp}/C = \ln[\eta]_m + k_m [\eta]_m C \quad \text{.........(3)}$$
$$\eta_{sp}/C = [\eta]_{sb} + k_{sb} [\eta]_{sb} \eta_{sp} \quad \text{.........(4)}$$

where: C is the concentration of crude oil solution, $\eta_r = \eta / \eta_o$ is the viscosity of a solution with respect to the viscosity of a solvent; η_{sp} is the specific viscosity ($\eta_{sp} = \eta_r$ -1); $[\eta]_h$ is the intrinsic viscosity or limiting viscosity number with respect to Huggins equation; $[\eta]_k$ (Huggin, 1942) is the intrinsic viscosity with respect to Kraemer equation; $[\eta]_m$ is the intrinsic viscosity with respect to Martin equation; $[\eta]_{sb}$ is the intrinsic viscosity with respect to Schulz-Blaschke equation; k_h, k_k, k_m and k_{sb} are the Huggins, Kraemer, Martin and Schulz-Blaschke coefficients, respectively.

Table 2. Densities of crude oil mixtures in benzene at different temperatures

Percent composition of crude oil (*v/v*)	Densities ($g.cm^{-3}$) at temperatures (*K*)			
	303	308	313	318
Sample A				
10	0.8748	0.8748	0.8684	0.8650
20	0.8774	0.8730	0.8673	0.8690
30	0.8773	0.8700	0.8700	0.8680
40	0.8700	0.8680	0.8660	0.8650
50	0.8670	0.8620	0.8600	0.8590
Sample B				
10	0.8649	0.8610	0.8580	0.8550
20	0.8599	0.8540	0.8510	0.8490
30	0.8559	0.8500	0.8480	0.8450
40	0.8517	0.8460	0.8460	0.8380
50	0.8460	0.8430	0.8420	0.8370
Sample C				
10	0.8669	0.8629	0.8600	0.8580
20	0.8610	0.8550	0.8540	0.8520
30	0.8580	0.8520	0.8490	0.8450
40	0.8530	0.8496	0.8460	0.8440
50	0.8480	0.8440	0.8420	0.8400
Sample D				
10	0.8511	0.8483	0.8440	0.8415
20	0.8446	0.8409	0.8350	0.8330
30	0.8410	0.8358	0.8350	0.8330
40	0.8380	0.8328	0.8310	0.8290
50	0.8790	0.8320	0.8293	0.8260
Sample E				
10	0.8520	0.8470	0.8410	0.8380
20	0.8435	0.8380	0.8370	0.8330
30	0.8410	0.8350	0.8340	0.8320
40	0.8368	0.8320	0.8290	0.8270
50	0.8311	0.8280	0.8250	0.8220
Sample F				
10	0.8530	0.8502	0.8499	0.8470
20	0.8550	0.8497	0.8480	0.8460
30	0.8520	0.8496	0.8470	0.8460
40	0.8510	0.8510	0.8460	0.8442
50	0.8500	0.8510	0.8460	0.8440
Sample G				
10	0.8710	0.8660	0.8660	0.8560
20	0.8640	0.8630	0. 8623	0.8550
30	0.8630	0.8620	0. 8620	0.8550
40	0.8630	0.8610	0. 8604	0.8500
50	0.8620	0.8600	0. 8561	0.8480

Results for viscosity and density data are tabulated in Tables 1 and 2 respectively. The results show an increase in viscosity with the increase in concentration of crude oil at fixed temperature and decreased with increasing temperature.

Table 3. Intrinsic viscosity and viscometric constants of crude oil mixtures in benzene at 308 K

Crude oil samples	Intrinsic viscosities (dL.g^{-1})				
	$[\eta]_h$	$[\eta]_k$	$[\eta]_m$	$[\eta]_{sb}$	
A	1.100	0.250	1.317	8.666	
B	1.075	0.248	1.303	16.31	
C	1.048	0.245	1.265	11.57	
D	1.082	0.248	1.313	15.37	
E	1.089	0.249	1.323	17.96	
F	1.105	0.250	1.308	6.045	
G	1.004	0.250	1.291	4.621	
Crude oil samples	Viscometric constants				
	k_{h} x 10	k_{k} x 10	k_{m} x 10	k_{sb} x 10	$k_h + k_k$ x 10
A	-0.162	-0.717	-0.279	-0.827	-0.879
B	-0.168	-0.730	-0.291	-0.894	-0.898
C	-0.172	-0.744	-0.297	-0.895	-0.916
D	-0.167	-0.726	-0.288	-0.881	-0.893
E	-0.165	-0.723	-0.287	-0.885	-0.888
F	-0.147	-0.715	-0.275	-0.791	-0.862
G	-0.192	-0.717	-0.274	-0.761	-0.909

Table 4. Thermodynamic parameters for 20 % crude oil mixtures in benzene at different temperatures

Temperature (*K*)	Enthalpy change of Activation (ΔH^*) (kJ mol^{-1})	Free Energy change of Activation ($-\Delta G^*$) (kJ mol^{-1})	Entropy change of Activation (ΔS^*) (kJ mol^{-1})
Sample A			
303		11.092	31.935
308	1.415	11.299	32.097
313		11.515	32.270
318		11.709	32.371
Sample B			
303		11.170	30.469
308	1.938	11.393	30.697
313		11.614	30.915
318		11.819	31.073
Sample C			
303		11.178	29.829
308	2.139	11.444	30.213
313		11.640	30.353
318		11.846	30.523
Sample D			
303		11.118	26.998
308	2.937	11.360	27.347
313		11.612	27.716
318		11.809	27.899
Sample E			
303		11.121	28.653
308	2.438	11.366	28.984
313		11.579	29.203
318		11.797	29.429
Sample F			
303		11.015	29.785
308	1.990	11.302	30.232
313		11.513	30.425
318		11.725	30.613
Sample G			
303		11.085	33.922
308	0.806	11.318	34.129
313		11.479	34.101
318		11.685	34.210

Results show that with the increase in temperature kinetic energy of molecules increases which decreased the viscosity of oil solution because heat has a strong influence on viscosity of high molecular weight components in the crude oil.

From density data it is shown that with the increase in concentration and temperature of crude oil solutions density decreased as shown in Table 2. This decreased may be due to disturbance in composition of crude oil solutions in Benzene. As crude oils comprises of two heaviest, most polar fractions that is asphaltenes and resins. Asphaltenes which is structurally quite complex, have some common features: a polynuclear aromatic core, certain degree of saturated substituents, and little content of nitrogen, oxygen, and/or sulfur. This portion of crude oil is insoluble in alkane solvents but soluble in aromatic solvents (benzene or toluene).

Resins, is a low molecular weight versions of asphaltenes with a higher degree of overall saturation. Due to the solubility of asphaltenes in benzene causing decreased in density while viscosity increased (Parthasarathi, *et al*., 2011). The results tabulated in Table 1 also show that for sample G highest value of viscosity were obtained while for sample C least values were observed in benzene. The specific viscosity determines the contribution of the solute to the viscosity of the solution. Thus, from measurements of specific viscosity, it is possible to attain the intrinsic viscosity through graphic extrapolations by using different relations as Huggins, Kraemer, Martin and Schulz-Blaschke; equations. The intrinsic viscosity [η] provides information about the hydrodynamic volume of a macromolecule in a solvent. Intrinsic viscosity and viscometric constant using different relations for crude oils in benzene are tabulated in Table 3. The respective intrinsic viscosity was calculated by graphic extrapolations as shown in Fig. 1. It was observed that best straight line obtained by Martin equation. Huggins and Kraemer coefficients are used to evaluate the solvent quality and used for very dilute solutions while Martin Schulz-Blaschke equations were used for a long range of concentration. Basically these relations (1-4) used for high molecular weight solute related to macromolecule-solvent interactions.

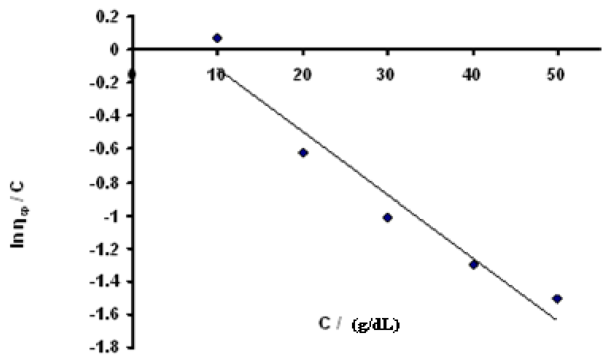

Fig. 1. Plot of ln η_{sp}/C versus C (concentration of crude oil) sample E solution at 308 K

Results tabulated in Table 3, show that for all samples of crude oil the values of intrinsic viscosity were positive, hence benzene would be considered as a good solvent for crude oil samples. In a good solvent where the energy of interaction between a solute segment and a solvent molecule adjacent to it exceeds the mean of the energies of interaction between the solute-solute and solvent-solvent pairs, the macromolecule will tend to expand further so as to reduce the number of contacts between pairs of macromolecule elements.

Therefore, the solute molecule will be in a much extended form in a good solvent. The value of the intrinsic viscosity will be high in a good solvent, as the molecule is much extended. The highest value of intrinsic viscosity obtained for Schulz-Blaschke equation. In a poor solvent, on the other hand, where the energy of interaction is unfavorable, a small configuration in which solute-solute contacts occur more frequently will be favored, and the solute will tend to occupy a tightly rigid form, resulting in a lowering of the intrinsic viscosity. The plots of equations 1 to 4 are linear and values of k_h, k_k, k_m and k_{sb} are negative. The negative values of viscometric constants show that the higher the affinity between macromolecule and solvent, the lower the value of viscometric constants. From Table 3 it was shown that for all samples of crude oil the values of viscometric constants were negative, hence benzene should be considered as a good solvent. This behavior was also supported by Kraemer constant (k_k) because negative values of Kraemer coefficients indicate good macromolecule solvation.

The intrinsic viscosity is a measure of the shape and size of the isolated macromolecule and a measure of the solvent power and Huggins constant (k_h) is a measure of the hydrodynamic interaction. A change of temperature affects the coefficient values; (k_h, k_k, km and k_{sb}), due to modifications in the macromolecule-macromolecule and macromolecule-solvents interactions. Thus the interpretation of different temperature data provides a useful way to obtain information about the interactions particularly (Saeed *et al*., 2014). From Table 3 it was shown that the vales of k_h, k_m and k_k, k_{sb} are close for all the samples of crude oils.

Thermodynamic data of crude oil viscosity as a function of temperature and composition are required for reservoir studies and hot pipelines (Hemmingsena**,** *et al*., 2005). The values of thermodynamic parameters for viscous flow were also calculated for all the samples of crude oil solutions as shown in Table 4.

$$\log \eta = (\log 103 - \Delta S^*/R) + \Delta H^*/RT \quad (5)$$

where, η is the viscosity of solution, R is the gas constant, ΔS* is the entropy change of activation, ΔH* is the enthalpy change of activation and T is the absolute temperature.

The results for enthalpy change of activation (ΔH*) tabulated in Table 4, it was observed that highest value of ΔH* obtained for sample D while least value obtained for sample G. From equation 5 by plotting a graph between log η versus 1/T as shown in Fig. 2, and slope gives the values of enthalpy change of activation (ΔH*) which increased with the increase in concentration due to production of strong forces between solute and solvent molecules.

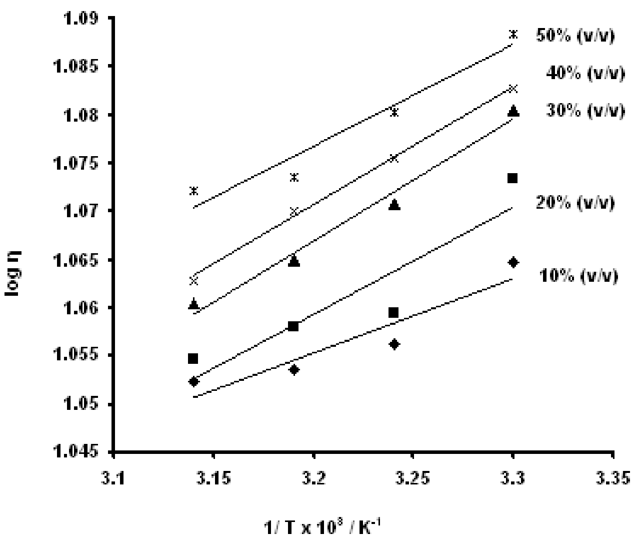

Fig. 2. Plot of log η versus 1/T of sample C solution in different percent composition of benzene

The values of free energy change of activation (ΔG*) controls the rate of flow in fluid processes. The free energy change of activation (ΔG*) of viscous flow is given by the equation.

$$\Delta G^* = 2.303 \ RT \log (\eta/103) \quad (6)$$

The values of free energy change of activation (ΔG*) decreased with the increase in temperature of crude oil solutions as shown in Table 4.
The relation between activation entropy and enthalpy is given by the equation as shown in Table 5:

$$\Delta S^* = \Delta H^* - \Delta G^* /T \quad (7)$$

The values of entropy change of activation (ΔS*) increased with increase in temperature of crude oil solutions for all samples indicates the disordered system and orientation of molecules disturbed with the change in temperature.

Conclusion

The validity of different relations for crude oils and benzene system was studied and concluded that they can be applied for evaluation of interaction of crude oils and benzene as applied for macromolecule and solvent systems. The positive values of intrinsic viscosity show that benzene act as a good solvent for all crude oil samples. Thermodynamic parameters were also evaluated by the viscosity data as a function of temperature and crude oil concentration. The increased in entropy change of activation also confirmed the disorderness in solvent system.

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