THERMODYNAMIC AND TRANSPORT PROPERTIES OF BINARY LIQUID MIXTURES OF SULFOLANE WITH SOME METHYL ALKANOATES AT T = 308.15 K

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ABSTRACT

Measurement of densities ρ and viscosities η, have been carried out for binary mixtures of sulfolane (SUL) with methyl ethanoate (ME), methyl propionate (MP) and methyl butanoate (MB) and their pure liquids at T = 308.15 K over the entire composition range. From these experimental data, excess molar volumes V^{E}, and deviations in viscosity $\Delta\eta$, of methyl alkanoates with sulfolane have been calculated. These results have been fitted to the Redlich-Kister type polynomial using multiparametric non-linear regression analysis to estimate the binary coefficients and standard errors.

Key words: Binary mixtures, Viscosities, Sulfolane, Methyl alkanoates.

INTRODUCTION

Thermodynamic behavior of liquid mixtures containing sulfolane (SUL) and methyl alkanoates are of considerable interest because of their industrial importance. SUL and methyl alkanoates are good industrial solvents having various applications in the synthesis of perfumes, intermediates of pesticides, medicines, pharmaceutics and petroleum industry. Thus, correlation of the molecular structures with thermodynamic properties of such mixtures are necessary to obtain a systematic information on the behavior of components in the binary mixtures of [{(SUL + methyl ethanoate (ME)), + methyl propionate (MP) and + methyl butanoate (MB)]. It is easy to understand the importance of the availability of the solvent thermodynamic parameters, such as density (ρ), and viscosity (η), are important physical properties of solvent systems and are often used to explain the medium effects of solvent, electrolyte behavior, transport phenomena and reaction mechanisms in solutions[1].

These well-known properties are functionally dependent on the temperature and binary mixtures of the composition of the solvent systems[2]. To the best of our knowledge,

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for the mixtures of SUL with methyl alkanoates (ME, MP and MB) studied in this paper; no experimental data on density and viscosity are available in the accessible literature.

The aim of the present work was to analyze the changes in the thermodynamic properties, and to explain interactions present between unlike molecules. As a continuation of our research work[3-8], we now report the experimental data for density ρ, and viscosity η, for the binary mixtures of SUL with methyl alkanoates (ME, MP and MB) over the entire range of composition at the temperature of 308.15K. The measured values are used to calculate the various properties such as excess molar volumes V^{E} and deviations in viscosity $\Delta\eta$. The results are discussed in terms of molecular interactions present in the mixtures.

EXPERIMENTAL

Materials

All of the component liquids are of analytical grade. The SUL, ME, MP and MB were supplied by Aldrich Chemicals, U.S. The stated mass fraction purities of these are as follows: SUL (0.99), ME (0.995), MP (0.99) and MB (0.98). To minimize the contact of this deliquescent reagent with moist air, the product was kept in sealed bottles in a desiccator. The purity of the chemicals is checked by comparing densities and viscosities of the pure liquids with literature[9-17] (Table 1).

Table 1: Experimental density (ρ), and viscosity (η) and of pure liquids at T = 298.15 K

Component	$10^{3}.\rho/(Kg.m^{3})$	$10^{3}.\rho/(Kg.m^{3})$	$10^{3}.\eta/(mPa.s)$	$10^{3}.\eta/(mPa.s)$
	Exptl.	Lit.	Exptl.	Lit.
Sulfolane	1.2642	1.2640 [a]	8.7947 [y]	8.7947 [b]
Methyl ethanoate	0.9284	0.9282 [c]	0.3711	0.3710 [h]
Methyl propionate	0.91284	0.91280 [d]	0.4372 [y]	0.4370 [e]
Methyl butanoate	0.89250	0.89249 [g]	0.5450	0.5430 [f]

[x]Values at T = 303.15 K   reference [a=9, b=10, c=11, d=12, e=13, f=14, g=15, h=16, i=17]
[y]Values at T = 308.15 K

Apparatus and procedure

Binary mixtures were prepared by mass using of airtight bottles. The mass measurements were performed on a Dhona 100 DS; India, single-pan analytical balance with a resolution of 0.01×10^{-6} Kg. The properties of the mixture were measured on the same day after their preparation. The uncertainty in mole fraction was predictable to be less than $\pm 1\times10^{-4}$.

Densities of pure liquids and their mixtures were determined by using a $1 \times 10^{-5} m^3$ double arm pycnometer[17]. The uncertainty in density and excess molar volume values was found to be $\pm\, 0.04\ Kg.m^{-3}$ and $\pm\, 0.01\ m^3.mol^{-1}$, respectively.

A suspended level viscometer[18,19] was used to measure the flow times of pure liquids and liquid mixtures, and it was calibrated with doubly distilled water (water conductivity less than $1 \times 10^{-6}\ \Omega^{-1}.cm^{-1}$ with (0.9970 and 0.9940) $g.cm^{-3}$ as its density at (298.15 and 308.15) K, respectively, and also with benzene of density (0.87381 and 0.87341) $g.cm^{-3}$ at (298.15 and 308.15) K, respectively). Viscosity values (η) of pure liquids and mixtures were calculated using the flow times by relation

$$\eta = (at - b/t)\, \rho \qquad \qquad \text{…(1)}$$

Where *a* and *b* are the characteristic constants of the viscometer; 'ρ' is the density; and '*t*' represents the flow time of components. The flow times of pure liquids and liquid mixtures were determined by the average of five measurements. The uncertainty of viscosity was found to be $\pm\, 0.005$ mPa.s.

RESULTS AND DISCUSSION

Table 2 reports the experimental data of density (ρ), excess molar volume (V^E) and deviations in viscosity ($\Delta\eta$) for the binary mixtures of sulfolane +ME, +MP and + MB at T = 308.15 K along with the mole fraction of sulfolane.

Table 2: The values of density (ρ), viscosity (η), excess molar volume (V^E) and deviation in viscosity ($\Delta\eta$), Gibbs free energy of activation of viscous flow (G^{*E}) and Grunberg Nissan interaction parameter (d´) for the binary liquid mixtures at T = 308.15 K

x_1	$10^{-3}.\rho$ $(kg.m^{-3})$	$10^3.\eta$ $(Kg.m^{-1}.s^{-1})$	$10^6.V^E$ $(m^3.mol^{-1})$	$10^3.\Delta\eta$ $(kg.m^{-1}.s^{-1})$	G^*	d´
		Sulfolane (1) + Methyl ethanoate (2)				
0.0000	0.9153	0.3520	0.0000	0.0000	0.0000	---
0.0208	0.9260	0.3719	-0.2051	-0.1557	-8.6800	-0.5866
0.1501	0.9856	0.5175	-0.9561	-1.1017	-65.790	-0.7659
0.2738	1.0383	0.7189	-1.4513	-1.9447	-111.15	-0.8404
0.4002	1.0885	1.0350	-1.8049	-2.6958	-139.07	-0.8726
0.5058	1.1269	1.3911	-1.9318	-3.2312	-166.73	-1.0147

x_1	$10^{-3} \cdot \rho$ (kg.m^{-3})	$10^3 \cdot \eta$ (Kg.m^{-1}.s^{-1})	$10^6 \cdot V^E$ (m$^3 \cdot$mol^{-1})	$10^3 \cdot \Delta\eta$ (kg.m^{-1}.s^{-1})	G^*	d'
0.5970	1.1561	1.8750	-1.8170	-3.5173	-162.76	-1.0334
0.7321	1.1950	2.9195	-1.4493	-3.6134	-155.47	-1.2268
0.8538	1.2253	4.7520	-0.8885	-2.8084	-93.680	-1.1624
0.9789	1.2539	8.0829	-0.2372	-0.5337	-11.460	-0.7987
1.0000	1.2569	8.7947	0.0000	0.0000	0.0000	---
Sulfolane (1) + Methyl propionate (2)						
0.0000	0.9006	0.4372	0.0000	0.0000	0.0000	---
0.0237	0.9105	0.4608	-0.1764	-0.1745	-12.470	-0.8024
0.1736	0.9691	0.6578	-0.7854	-1.2303	-73.870	-0.7847
0.3100	1.0219	0.9285	-1.1967	-2.0995	-116.14	-0.8290
0.4406	1.0722	1.3125	-1.5020	-2.8070	-146.22	-0.9056
0.5458	1.1113	1.7515	-1.5877	-3.2472	-163.46	-1.0102
0.6479	1.1476	2.3673	-1.5141	-3.4847	-166.19	-1.1205
0.7629	1.1853	3.5014	-1.1653	-3.3117	-135.65	-1.1575
0.8723	1.2197	5.2138	-0.7248	-2.5136	-90.100	-1.2530
0.9813	1.2529	8.1315	-0.2149	-0.5069	-15.020	-1.2141
1.0000	1.2569	8.7947	0.0000	0.0000	0.0000	---
Sulfolane (1) + Methyl butanoate (2)						
0.0000	0.8814	0.5061	0.0000	0.0000	0.0000	---
0.0303	0.8923	0.5408	-0.1889	-0.2160	-13.060	-0.6875
0.1893	0.9487	0.7741	-0.7842	-1.3010	-73.380	-0.7529
0.3390	1.0036	1.1037	-1.1456	-2.2120	-119.30	-0.8401
0.4730	1.0541	1.5440	-1.3042	-2.8830	-148.70	-0.9433
0.5779	1.0947	2.0551	-1.3434	-3.2410	-157.50	-1.0196
0.6783	1.1339	2.6971	-1.2660	-3.4310	-166.50	-1.2076
0.7877	1.1770	3.8234	-1.0657	-3.2120	-143.60	-1.3568
0.8866	1.2161	5.4917	-0.7725	-2.3630	-93.770	-1.4637
0.9826	1.2516	7.9240	-0.1985	-0.7270	-34.490	-3.1925
1.0000	1.2569	8.7947	0.0000	0.0000	0.0000	---

The excess molar volumes (V^E) have been evaluated from density using

$$V^E = (x_1M_1 + x_2M_2)/\rho_m - (x_1M_1/\rho_1 + x_2M_2/\rho_2) \qquad \ldots(2)$$

Where ρ_m is the density of the mixture; x_1, M_1, ρ_1, and x_2, M_2, ρ_2 are the mole fraction, molar mass, and density of pure components 1 and 2, respectively.

The deviation in viscosity of a binary mixture is calculated from the equation

$$\Delta\eta = \eta - (x_1\,\eta_1 + x_2\,\eta_2) \qquad \ldots(3)$$

Where η, η_1, η_2 are viscosities of the liquid mixture and of the pure components 1 and 2, respectively; x_1, x_2 are the mole fractions of the components 1 and 2.

The excess Gibbs free energy of activation of viscous flow (G^{*E}) is obtained by the equation

$$G^{*E} = RT\,[\ln\eta\,V - (x_1 \ln\eta_1 V_1 + x_2 \ln\eta_2 V_2)] \qquad \ldots(4)$$

Where V is the molar volume of the mixture and V_1 and V_2 are the molar volume of the pure components 1 and 2, respectively. R and T have their usual meanings.

Various equations exist in the literatures were used to estimate the dynamic viscosity η, Gruenberg and Nissan suggested the expression:

$$\ln\eta = x_1 \ln\eta_1 + x_2 \ln\eta_2 + x_1x_2\,d' \qquad \ldots(5)$$

where d' is a parameter proportional to interchange energy, which reflects the non-ideality of the system. This parameter has been considered as valid measure for detecting the presence of interactions between the components.

The excess or deviation properties ΔY are fitted by the method of nonlinear least-squares to the fourth-order Redlich-Kister type polynomial equation.

$$\Delta Y = x_1x_2 \sum A_i (x_1 - x_2)^i \qquad \ldots(6)$$

Where A_0, A_1, A_2, A_3 and A_4 are adjustable binary coefficients. The coefficients A_i were estimated using multiparametric regression analysis based on a non-linear least-squares method. The number of A_i parameters was optimized using the F-test and is found to be points and m is the number of coefficients ($m = 5$) used in fitting the data.

In each case, the optimum number of coefficients A_i is determined from an examination of the variation of standard deviation (σ) as calculated by -

$$\sigma\,(Y^E) = [\Sigma(\Delta Y_{obs} - \Delta Y_{cal})^2 / (n - m)]^{1/2} \qquad \ldots(7)$$

Where n represents the number of experimental points and m is the number of coefficients ($m = 5$) used in fitting the data. The coefficients Ai and standard deviations

(σ) V^E and (σ) $\Delta\eta$ of the fit are summarized in Table 3.

Table 3: Binary coefficients (A_i) and corresponding standard deviation (σ) of equation (6) of Sulfolane + Methyl alkanoates

Excess property	A_0	A_1	A_2	A_3	A_4	σ
Sulfolane (1) + Methyl ethanoate (2)						
$10^6.V^E/(m^3.mol^{-1})$	-7.87	0.25	3.577	0.477	-5.83	0.017
$10^3.\eta/(Kg.m^{-1}.s^{-1})$	-11.22	-7.27	-3.87	-2.925	-2.38	0.026
Sulfolane (1) + Methyl propionate (2)						
$10^6.V^E/(m^3.mol^{-1})$	-6.67	-1.084	3.089	0.92	-5.55	0.024
$10^3.\eta/(Kg.m^{-1}.s^{-1})$	-10.85	-6.925	-3.64	-2.885	-2.44	0.012
Sulfolane (1) + Methyl butanoate (2)						
$10^6.V^E/(m^3.mol^{-1})$	-5.098	-0.97	-0.81	-0.438	-1.91	0.009
$10^3.\eta/(Kg.m^{-1}.s^{-1})$	-10.59	-6.605	-2.93	-4.89	-6.06	0.101

Excess molar volume

Excess molar volumes of (sulfolane + Methyl alkanoates) at $T = 308.15$ K are shown in Fig. 1. The values of V^E are negative for all mixtures (sulfolane +ME, +MP and +MB) over the whole mole fraction range and are less negative with increasing chain length of the alkanoate molecules. The negative values of V^E vary in the following order –

$$ME\ \ < M\,P < MB < 0$$

The variation of V^E with mole fraction of sulfolane with alkanoates is graphically shown in Fig. 1. The excess volume curves are almost in symmetric and parabolic indicating negative deviations over the entire range of mole fraction. The minimum value of each isotherm is falled around the mole fraction $x_1 = 0.5$.
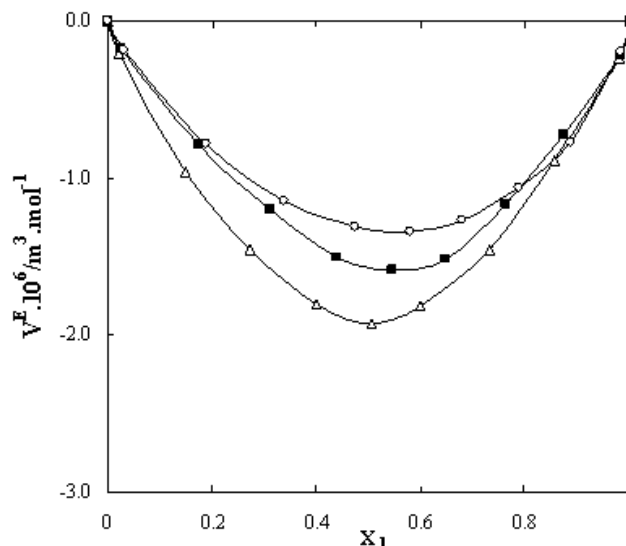
Fig. 1: Plots of excess molar volumes V^E against mole fraction x_1 of Sulfolane
(1) with Δ, Methyl ethanoate (2); ■ Methyl propionate (2);
○ Methyl butanoate (2) at T = 308.15 K

The observed negative values of V^E for the mixture of SUL+ ME are larger than the other mixtures. This is attributed to the interstitial accommodation of methyl ethanoate molecules within the structure of sulfolane due to smaller size.

Deviations in viscosity

Fig. 2 depicts the graphical representation of deviation in viscosity (Δη) for SUL with ME, MP and MB at 308.15 K. The observed values of Δη are negative for all the systems. A correlation between the sign of Δη and V^E has been observed for a number of binary solvent systems. Δη being positive where V^E is negative or vice versa.[20] Figures 1 and 2 clearly indicate that the isotherms of V^E and Δη do not obey the general statement. The viscosity of a mixture[21, 22] depends on the molecular interactions between the components mixture with strong interactions between different molecules show positive viscosity deviations, while for mixtures with absence of specific interactions indicates negative deviations in viscosity. Therefore the strength of the specific forces is not the only factor influencing the viscosity deviation of liquid mixtures, but molecular size and shapes of the components are also equally important. For the present system Δη are negative. The negative Δη values at equimolar concentrations of sulfolane and methyl alkanoates follow the order:

$$ME < M P < MB < 0$$

Rastogi et al.[23], suggested that the observed excess property is a combination of an interaction part and non-interaction part. The non-interaction part in the form of the size effect can be comparable to the interaction part and may be sufficient to reverse the trend set by the latter. Based on this theory the observed anomaly in the isotherms may be attributed to the size effect.
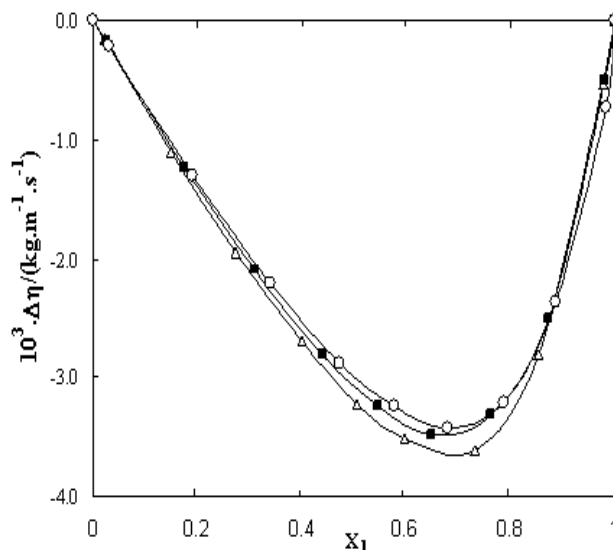

Fig. 2: Plots of deviation in viscosity Δη against mole fraction x₁ of Sulfolane (1) with Δ Methyl ethanoate (2); ■ Methyl propionate (2); ○ Methyl butanoate (2) at T= 308.15 K

The observed negative values of $\Delta\eta$ in the Table 2 indicate that there are no strong specific interactions present between the mixtures of methyl alkanoates and sulfolane, which are also reflected from the observed negative value of V^E for system. According to Reed and Taylor[24] positive G^{*E} values indicate specific interactions while negative values indicate the dominance of dispersion forces; similarly, if d′ values are positive interactions between like molecules are strong where weak with negative values.

The values of Table 2 incontrovertibly indicate that excess Gibbs free energy of activation of viscous flow (G^{*E}) and Grunberg Nissan interaction parameter (d′) are both negative for all the systems over the entire range of mole fraction. Hence, a cerebral conclusion can be made that physical forces are dominating over the chemical forces in all the system.

CONCLUSION

The excess molar volumes and deviation in viscosity of sulfolane with methyl ethanoate, methyl propionate and methyl butanoate have been reported at T = 308.15 K. Thus, it can be concluded that the evaluated experimental results are interpreted in terms of dispersion forces operating between unlike molecules and contribution of size and shape of the molecules.

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