Research Article

Excess Molar Volume and Excess Viscosity of Sulfolane-Chloromethane Binary Systems

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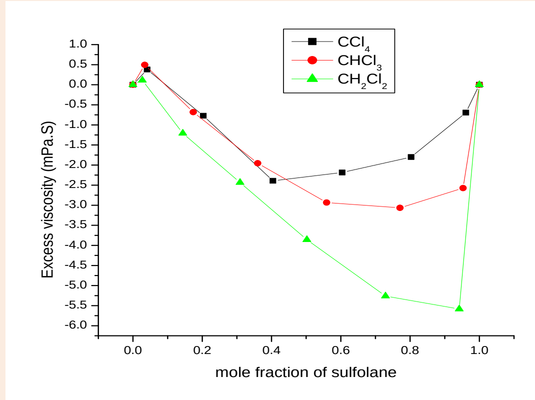
Abstract

Excess molar volume (V^E) at 303K and one atmospheric pressure have been measured over whole composition range for the binary mixtures of sulfolane with halomethanes (carbontetrachloride, chloroform and dichloromethane). Negative V^E values were observed for sulfolane- carbon tetrachloride binary mixture, where as positive V^E values were observed for sulfolane-chloroform and sulfolane – dichloromethane binary liquid mixtures. These data are fitted with Redlich-polynomial equation and from the coefficients; the partial molar properties have been calculated. The results are discussed in terms of molecular interactions.

Keywords: sulfolane, carbontetrachloride, chloroform and dichloromethane , density, viscosity



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Introduction

Sulfolane is a polar solvent, used to extract aromatic hydrocarbon from petroleum products[1]. The polarity of any solvent can be tuned by adding another less polar or non-polar solvent. Carbonterachloride(non-polar),Chloroform and Dichloromethane(polar) are widely used as solvent in many organic synthesis and chromatographic techniques. In many synthetic processes, mixed solvents render more beneficial results than any one of the individual component. Though these observations are generally dispensed with as synergestic effect, interactions between solvents molecules and hence the change in the liquid structural properties should play significant role. This can be understood by observing certain parameters like excess volume, internal pressure etc. Literature survey shows many authors have studied the excess molar volumes of binary mixtures of sulfolane with many other hydrocarbons, esters etc.(2-6). This paper concerns with the determination of excess molar volume for the binary mixtures consisting of an alicyclicdiketone solvent, sulfolane and any one of the chloromethanes, viz: dichloromethne (CH_2Cl_2), chloroform ($CHCl_3$) and carbontetrachloride (CCl_4).

Experimental

The chemicals used in the present work were of analytical grade with minimum assay of 99.9% (sd fine chemicals India and Merck, Germany). Densities for pure chemicals and binary mixtures were determined using pyconometer having a bulb volume of about 10mL capacity. The pycnometer was calibrated using double distilled water at the desired experimental temperature. The weight measurements were carried out using digital balance (shimadzu model with accuracy of +/- 0.01mg). An Oswald's viscometer of 10 mL capacity was used for the viscosity measurement of pure liquids and liquid mixtures and efflux time was determined using a digital chronometer to within +/-0.01s.

Results and Discussion

For binary mixtures of various mole fractions of sulfolane and chloromethane of a given volume, density and viscosity are determined. Using these data excess volumes and excess viscosities were calculated according to the following equations.

$$V^E = x_i m_i/\rho - x_1 m_1/\rho_1 - x_2 m_2/\rho_2$$

Where, X_i, x_1 and x_2 are mole fractions, ρ, ρ_1 and ρ_2 are densities of binary mixture, pure components 1 and 2 respectively. m_1 and m_2 are the molar masses components 1 and 2 respectively.

The viscosity deviations were calculated from the following relation,

$$\Delta\eta = \eta-(x_1\eta_1+x_2\eta_2)$$

Where, η is the viscosity of mixtures and η_1 and η_2 are the viscosity of the pure components 1 and 2 respectively. The density and viscosity values determined are given in table-1, along with literature value for comparison. The excess parameters calculated for binary mixtures of sulfolane with chloromethane are presented in **Table 2**. The observed excess molar volume $V^E{}_m$ are negative over the whole composition range of the mixtures of sulfolane with carbontetrachloride. On the other hand positive values are observed for sulfolane-chloroform and sulfolane-dichloromethane binary mixtures. When the excess volumes are plotted (**Figure 1**) against increasing sulfolane compostion a concave-up curve is generated for CCl_4 while concave-down curves results for other chloromethanes. It can also be seen that up to about 50% addition of sulfolane to CCl_4, the V^E values progressively decrease and further addition of sulfolane reverse the trend and becomes less negative. Thus the sulfolane- CCl_4 system is more tight and compact at almost equimolar composition. On the other hand, similar observation with $CHCl_3$ reveals that the sulfolane- $CHCl_3$ system is very much loosely packed and the liquid structure is more labile at equimolar compositions. These deductions are also corroborated with η^E plot,(**Figure 2**), The positive value of V^E and negative value of η^E for sulfolane-chloroform and sulfolane-dichloromethane system may indicate that dispersion and dipolar repulsion predominate.

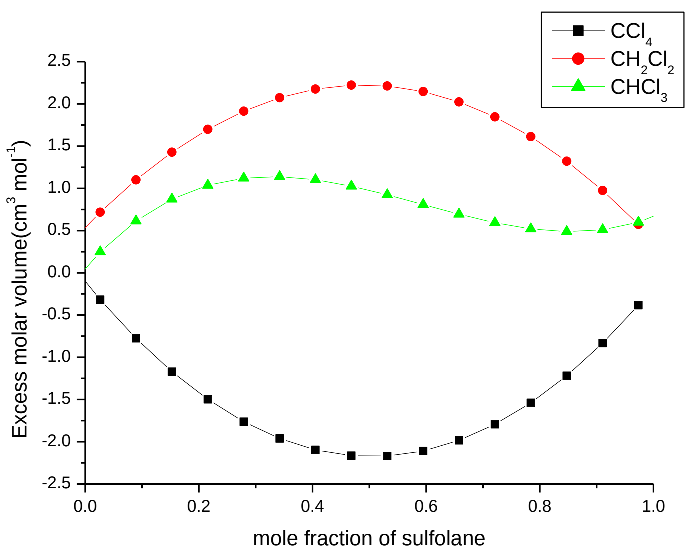

Figure 1 Plot of the excess molar volume of the binary mixtures Sulfolane-Chloromethane, 303 K

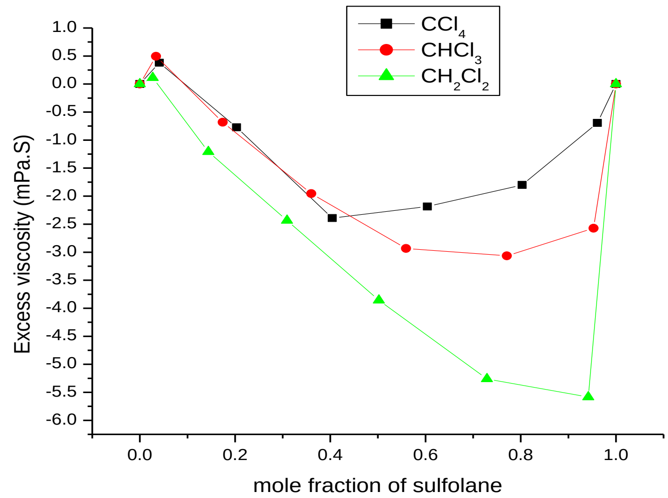

Figure 2 Plot of the excess viscosity of the binary mixtures Sulfolane- Chloromethane, at 303 K

The values of v^E and Δŋ for each mixture were fitted to the redlich-kister polynomial equation,

$$\mathbf{Y} = X_1 X_2 \sum_{i=0}^{n} Ai(2X_1 - 1)$$

Where, Y is v^E or η^E . The coefficients A_i are adjustable parameters and x_1 is the mole fraction of component 1. The fitted equations for V^E and η^E are given in **Table 3 and Table 4** respectively. The partial molar volume and the partial molar viscosity values $V\alpha_{m1}$, $V\alpha_{m2}$, $ŋ^{\alpha}_{m1}$ and $ŋ^{\alpha}_{m2}$ are calculated from the coefficients Ai using the relationship

Y^{α} m1 = Σ Ai and Y^{α} m2 = $(-1)^i$ Σ Ai

Where, the summation is from i=0, 1, 2, 3 ….and the values are also given in the respective tables.

Table 1 Density and Viscosity values of the pure solvents

Compound	**Density (g cm^{-3})**	**Viscosity (m.Pa.s)**
Sulfolane	1.2654(1.2654)	10.0742(10.0720)
Carbon tetrachloride	1.5867(1.5843)	0.9152(0.9050)
Chloroform	1.4723(1.4794)	0.5360(0.5320)
Dichloromethane	1.3250(1.3163)	0.3900(0.4060)

The density and viscosity values reported in reference 7,8 respectively are given in paranthesis

Table 2 Density (ρ), Viscosity (η), excess molar volume (V^E) and Excess viscosity (η^E) for binary mixtures of Sulfolane+ chloromethanes at 303 K

Mole fraction of sulfolane x_1	ρ g/ cm^3	V^E $cm^3\ mol^{-1}$	η m.Pa.s	η^E m.Pa.s
		Sulfolane + CCl_4		
0	1.5867	0	0.9152	0.0000
0.041	1.5765	-0.3006	1.6572	0.3796
0.203	1.5501	-1.82613	1.992	-0.7709
0.404	1.5	-2.74692	2.2174	-2.3913
0.604	1.4089	-1.05379	4.2579	-2.1845
0.803	1.3422	-0.90425	6.4653	-1.7989
0.961	1.2871	-0.65525	9.0205	-0.6926
1	1.2654	0	10.0742	0.0000
		Sulfolane + $CHCl_3$		
0	1.4723	0	0.5360	0.0000
0.034	1.4634	0.039849	1.3518	0.4956
0.174	1.4024	1.720786	1.5136	-0.6811
0.360	1.3805	0.599321	2.0133	-1.9547
0.559	1.3367	0.799711	2.9296	-2.9337
0.771	1.2995	0.54127	4.828	-3.0657
0.953	1.2557	1.357049	7.0526	-2.5727
1	1.2654	0	10.0742	0.0000
		Sulfolane + CH_2Cl_2		
0	1.3250	0	0.3900	0.0000
0.027	1.3056	0.846841	1.0147	0.1191
0.144	1.2885	1.309637	1.0679	-1.2031
0.309	1.2347	3.967949	1.1841	-2.4291
0.502	1.2701	1.203298	1.8841	-3.8553
0.729	1.256	1.472756	2.9656	-5.2588
0.942	1.2393	2.142014	5.3506	-5.5842
1	1.2654	0	10.0742	0.0000

Table 3

Mixture	Equations	$V\alpha_{m1}$	$V\alpha_{m2}$
Sulfolane +CCl_4	$V^E = -9.44291+7.97166\ X+3.93251\ X^2-10.81137\ X^3$	-8.35011	-2.67069
Sulfolane+ $CHCl_3$	$V^E = 5.23323-1.71595\ X+2.57915\ X^2+8.00214\ X^3$	14.09857	1.52619
Sulfolane+CH_2Cl_2	$V^E = 11.637-0.40539\ X+4.33214\ X^2+1.32971\ X^3$	16.89346	15.04482

Table 4

Mixture	Equations	η^{α}_{m1}	η^{α}_{m2}
Sulfolane + CCl_4	η^E = -10.55437-10.02757 X+9.09874 X^2+4.15054 X^3	-7.332	4.421
Sulfolane+ $CHCl_3$	η^E = -13.88179-26.21676 X+4.63294 X^2+11.71575 X^3	-23.749	5.252
Sulfolane+CH_2Cl_2	η^E = -10.55437-10.02757 X+9.09874 X^2+4.15054 X^3	-7.144	-152.311

Conclusion

Densities p and viscosities η for binary mixtures of sulfolane-chloramethanes have been measured at 303K. From the experimental values of the densities and visicosities, the excess molar volumes have been calculated and correlated by redlich-kister polynomial equation to derive the co-efficients. The excess molar volumes for sulfolane-CCl_4 are negative over the whole component range.The results indicate that at equimolar compositions of sulfolane-dichloromethane and sulfolane-chloroform mixtures, the system is loosely packed while that of sulfolane-carbontetrachloride system is closely packed.

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