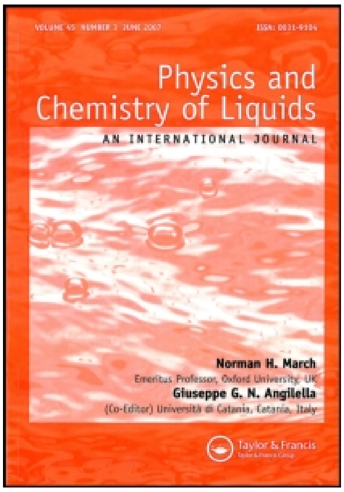

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Density, viscosity and thermodynamic activation for viscous flow of water sulfolane

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Density, viscosity and thermodynamic activation for viscous flow of water + sulfolane

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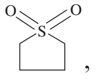
Densities and viscosities for the system, water (W) + sulfolane (SFL), have been determined for the entire range of composition at temperatures ranging from 303.15 to 323.15 K. Density, excess molar volume, viscosity, excess viscosity and thermodynamic activation parameters for viscous flow have been calculated and plotted against the mole fraction of SFL. The measured properties and some of the derived properties have been fitted to appropriate polynomial equations. These have been explained in terms of such factors, as, dipole–dipole interaction, partial accommodation of water molecules into the structural network of SFL and H-bonding between SFL and H_2O.

Keywords: Density; Excess molar volume; Viscosity; Thermodynamic activation parameters for viscous flow; Sulfolane

1. Introduction

We have undertaken a program of studying physical properties of aqueous solutions of highly polar organic solutes, i.e., the compounds with high dipole moments. As a part of this program we studied the volumetric and viscometric properties of aqueous solutions of dimethylsulfoxide [1,2] ($\mu = 4.06$ D) and ethylenecarbonate [3] ($\mu = 4.6$ D). The present study is a continuation of this program.

Sulfolane, , is a globular molecule [4] with a moderately high dielectric constant [5] ($\varepsilon = 43.4$ at 30°C) and a high dipole moment ($\mu = 4.80$ D) [6]. The freezing point of sulfolane (SFL) ranges between 25 and 27°C and its boiling point is 285°C. It is completely miscible with water at the studied temperatures. Yu *et al.* [7] reported the excess volumes at 298.15 K, Sacco *et al.* [8] on excess volumes and viscosity at 30, 40 and 50°C, Mcdonald *et al.* [9] on the influence of a small addition of SFL

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on the temperature of maximum density of water and Benoit and Choux [10] on the heat of mixing and vapor pressure of SFL + water system (W). Here we are reporting the density, excess molar volume, viscosity and thermodynamic properties of viscous flow of the system, SFL + W, for the entire range of concentration at temperatures from 303.15 to 323.15 K, with an interval of 5 K. Recently we have also reported the volumetric, viscometric and thermodynamic properties of viscous flow of aqueous solutions of protic and aprotic solvents, such as alcohols [11–13], diols [14–16], acetone [17], amines and diamines [18–22] and amides [23], the results of which are in some respects similar to those of the present system.

2. Experimental

Sulfolane was procured from Merck-Schuchardt, with quoted purity, 99.7%. The substance was used without any further purification. Redistilled water was used in the preparation of the solutions. An analytical balance of accuracy ±0.00001 g was used in density measurement. The solutions were prepared by weighing masses of the components by the same balance. The mole fraction was accurate up to the fourth decimal place. The density was measured by a 10 mL pycnometer previously calibrated with redistilled water. In viscosity measurement an Ostwald U-tube viscometer of British Standard Institution with sufficiently long efflux time was used, so that no kinetic energy correction was necessary. The flow time was recorded by an electronic timer accurate up to ±0.01 s. For every measurement, a thermostatic water bath controlled to ±0.05 K was used. The average uncertainties in the measured density and viscosity were not more than $0.02\,\mathrm{kg\,m^{-3}}$ and $4\times10^{-7}\,\mathrm{kg\,m^{-1}\,s^{-1}}$, respectively.

3. Results and discussion

The densities and viscosities of pure SFL at different temperatures are listed in table 1 together with literature values, wherever possible, for comparison, in which

Table 1. Densities, $\rho\times10^{-3}$ ($\mathrm{kg\,m^{-3}}$), and viscosities, $\eta\times10^{4}$ ($\mathrm{kg\,m^{-1}\,s^{-1}}$), of pure SFL at different temperatures.

		Temperature (K)					
Compound	Property	298.15	303.15	308.15	313.15	318.15	323.15
Sulfolane	ρ	1.26654 1.26654[a] 1.26540[b] 1.26564[c]	1.26202 1.26184[d] 1.26230[e] 1.26228[f] 1.2619[g] 1.262331[h]	1.25757	1.25317 1.253512[h] 1.2532[i]	1.2487	1.24421 1.24336[b] 1.244701[h]
	η	115.3085	100.5201 100.742[b] 103.56[d] 102.84[g] 102.9[h]	88.3331	77.8517 79.53[g] 79.47[h]	69.1145	61.6449 61.936[b] 63.06[h]

[a] Ref [29]; [b] Ref [24]; [c] Ref [30]; [d] Ref [27]; [e] Ref [5]; [f] Ref [26]; [g] Ref [28]; [h] Ref [8]; [i] Ref [25].

the agreement between the measured and literature values has been found to be satisfactory. Sulfolane is highly polar as indicated by its high dipole moment and dielectric constant, as mentioned earlier. The high values of boiling point (285°C), density ($1.26654\,\mathrm{g\,cm^{-3}}$ at 25°C) and viscosity ($115.308 \times 10^{-4}\,\mathrm{kg\,m^{-1}s^{-1}}$ at 25°C) of SFL indicate that the molecule is strongly associated through dipolar interaction.

Densities and excess molar volumes of the system, W + SFL, at temperatures, 303.15, 308.15, 313.15, 318.15 and 323.15 K, have been shown in table 2. The densities at temperatures, 303.15 and 323.15 K have been plotted against the mole fraction of SFL, x_2, in figure 1, which shows a rapid initial increase in density upon addition of SFL to W, following which the rate of increase decreases continuously with the increasing concentration of SFL. Exactly similar type of variation in density curves was observed by Sacco *et al.* [8]. Densities, ρ ($\mathrm{kg\,m^{-3}}$), viscosities, η ($\mathrm{kg\,m^{-1}\,s^{-1}}$), and free energies of activation for viscous flow, $\Delta G^{\neq}$ ($\mathrm{kJ\,mol^{-1}}$), have been fitted to the general polynomial equation of the form

$$Y = \sum_{i=0}^{n} A_i x_2^i \tag{1}$$

where Y stands for each of the above properties. The coefficients, A_i, and the squares of the regression coefficients, r^2, are shown in table 6.

The excess molar volumes, V_m^E, have been calculated by the following equation,

$$V_\mathrm{m}^\mathrm{E} = [(x_1M_1 + x_2M_2)/\rho - \{(x_1M_1)/\rho_1 + (x_2M_2)/\rho_2\}] \tag{2}$$

Table 2. Densities, $\rho \times 10^{-3}$ ($\mathrm{kg\,m^{-3}}$), excess molar volumes, $V_\mathrm{m}^\mathrm{E} \times 10^6$ ($\mathrm{m^3mol^{-1}}$), of the system, W (x_1) + SFL (x_2), at different temperatures.

T (K)	303.15		308.15		313.15		318.15		323.15	
x_2	ρ	V_m^E	ρ	V_m^E	ρ	V_m^E	ρ	V_m^E	ρ	V_m^E
Water (x_1) + sulfolane (x_2)										
0.00000	0.99560	0.0000	0.99410	0.0000	0.99220	0.0000	0.99030	0.0000	0.98810	0.0000
0.04934	1.05800	−0.1089	1.05524	−0.0944	1.05237	−0.0844	1.04928	−0.0699	1.04599	−0.0565
0.10013	1.10004	−0.1424	1.09676	−0.1239	1.09325	−0.1061	1.08976	−0.0891	1.08598	−0.0701
0.15038	1.13007	−0.1579	1.12632	−0.1334	1.12255	−0.1138	1.11886	−0.0970	1.11478	−0.0744
0.20131	1.15282	−0.1557	1.14873	−0.1262	1.14473	−0.1041	1.14064	−0.0802	1.13649	−0.0589
0.24960	1.17053	−0.1721	1.16643	−0.146	1.16227	−0.1223	1.15802	−0.0967	1.15369	−0.0727
0.29777	1.18422	−0.1617	1.17997	−0.1339	1.17562	−0.1063	1.17135	−0.0827	1.16712	−0.0647
0.35203	1.19611	−0.1189	1.19174	−0.0898	1.18739	−0.0644	1.18299	−0.0388	1.17846	−0.0119
0.40130	1.20573	−0.1046	1.20127	−0.0744	1.19681	−0.0468	1.19246	−0.0255	1.18783	0.0038
0.45239	1.21350	−0.0574	1.20911	−0.0326	1.20463	−0.0058	1.20015	0.0188	1.19564	0.0414
0.50246	1.22024	−0.0336	1.21601	−0.0049	1.21158	0.0178	1.20708	0.0413	1.20266	0.0578
0.54965	1.22638	−0.0129	1.22189	0.0118	1.21731	0.0402	1.21284	0.0603	1.20843	0.0744
0.60199	1.23221	0.0035	1.22757	0.0337	1.22301	0.0594	1.21859	0.0747	1.21393	0.1000
0.65076	1.23666	0.0386	1.23210	0.0626	1.22752	0.0880	1.22321	0.0950	1.21862	0.1150
0.70075	1.24122	0.0464	1.23663	0.0700	1.23218	0.0862	1.22783	0.0928	1.22305	0.1226
0.75228	1.24557	0.0462	1.24088	0.0738	1.23631	0.0954	1.23199	0.0976	1.22732	0.1193
0.80216	1.24926	0.0531	1.24474	0.0680	1.24026	0.0820	1.23574	0.0946	1.23120	0.1063
0.85257	1.25263	0.0610	1.24810	0.0743	1.24360	0.0879	1.23927	0.0854	1.23479	0.0910
0.89849	1.25558	0.0584	1.25109	0.0667	1.24664	0.0750	1.24219	0.0786	1.23772	0.0817
0.95107	1.25923	0.0225	1.25443	0.0434	1.24995	0.0517	1.24551	0.0520	1.24106	0.0513
1.00000	1.26202	0.0000	1.25757	0.0000	1.25317	0.0000	1.24870	0.0000	1.24421	0.0000

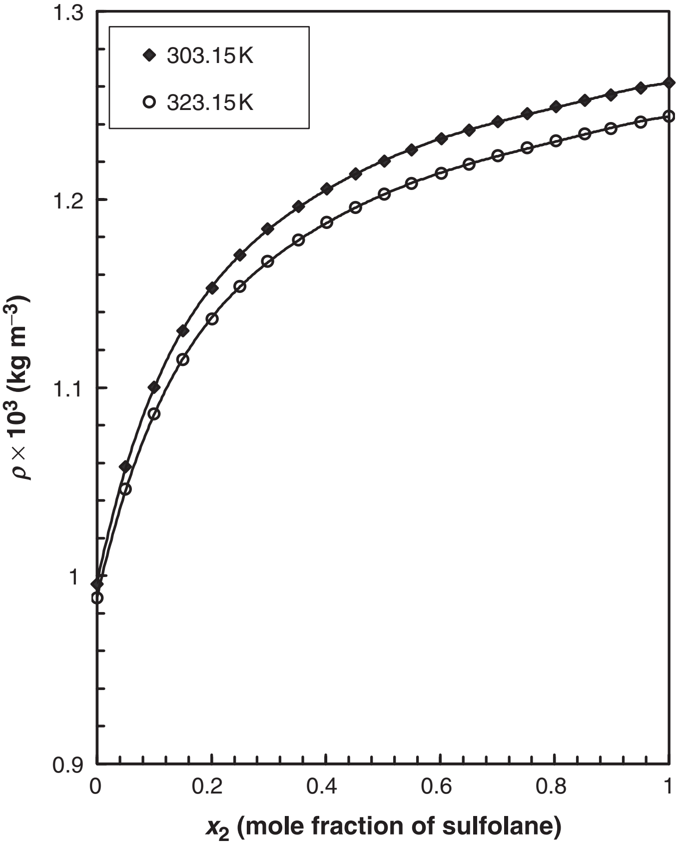

Figure 1. Variation of density, ρ, against mole fraction of SFL for the system, W $(x_1)+$SFL (x_2).

where, x_1, M_1 and ρ_1 are the mole fraction, molar mass and density respectively of pure water; x_2, M_2, and ρ_2 are the corresponding quantities for SFL, and ρ is the density of the solution. Excess molar volumes have been plotted against the mole fraction of SFL, x_2, in figure 2. The excess properties have been fitted to a Redlich–Kister polynomial equation of the form,

$$Y^{\mathrm{E}} = x_1 x_2 \sum_{i=0}^{n} A_i (1-2x_1)^i \tag{3}$$

where, Y^{E} represents each of $V_{\mathrm{m}}^{\mathrm{E}}$, η^{E} and $\Delta G^{\neq \mathrm{E}}$. The coefficients of the equation, A_i, and the standard deviations, σ, are listed in table 7.

An examination of $V_{\mathrm{m}}^{\mathrm{E}}$ *versus* x_2 curves reveals that:

(a) $V_{\mathrm{m}}^{\mathrm{E}}$ are negative in a water-rich region, but positive in a SFL-rich region, the magnitude being small in both cases. Such sigmoid type of curves for $V_{\mathrm{m}}^{\mathrm{E}}$ was observed for the systems W + SFL [8] and water + ethylenecarbonate [3].

(b) The system showed extrema. Minima and maxima have been observed respectively at ≈0.2 and ≈0.75 mole fraction of SFL.

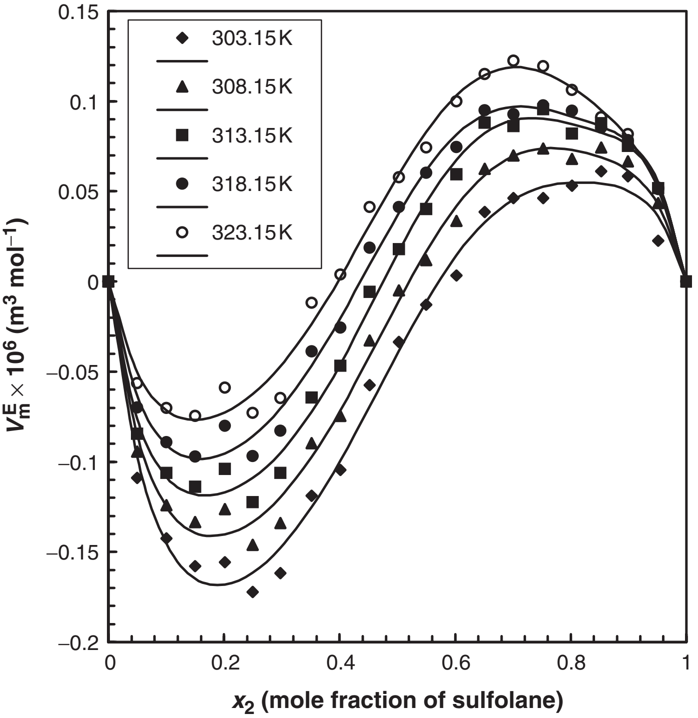

Figure 2. Variation of excess molar volume, V_m^E, against mole fraction of SFL for the system W (x_1) + SFL (x_2) at different temperatures.

Table 3. Experimental viscosities, η, and excess viscosities, $\eta^E \times 10^4$ (kg m^{-1} s^{-1}), of the system, W (x_1) + SFL (x_2), at different temperatures.

T (K)	303.15		308.15		313.15		318.15		323.15	
x_2	η	η^E	η	η^E	η	η^E	η	η^E	η	η^E
Water (x_1) + sulfolane (x_2)										
0.00000	8.007	0.000	7.2250	0.000	6.5600	0.000	5.988	0.000	5.4940	0.000
0.04934	11.255	2.184	10.130	1.955	9.177	1.765	8.357	1.600	7.662	1.471
0.10013	14.663	4.347	13.147	3.863	11.850	3.446	10.753	3.104	9.827	2.828
0.15038	18.132	6.418	16.246	5.718	14.580	5.064	13.178	4.528	12.010	4.107
0.20131	21.704	8.379	19.299	7.340	17.337	6.543	15.654	5.856	14.216	5.278
0.2496	25.033	9.977	22.302	8.805	19.973	7.809	17.993	6.966	16.293	6.247
0.29777	28.388	11.379	25.224	9.997	22.566	8.863	20.312	7.907	18.399	7.113
0.35203	31.764	12.252	28.238	10.796	25.268	9.597	22.742	8.576	20.526	7.658
0.4013	35.040	12.939	31.051	11.320	27.686	9.983	24.912	8.932	22.520	8.024
0.45239	38.282	13.131	33.969	11.545	30.383	10.295	27.262	9.154	24.619	8.217
0.50246	41.463	12.915	36.869	11.450	32.931	10.194	29.549	9.083	26.618	8.105
0.54965	44.799	12.631	39.760	11.153	35.455	9.903	31.930	8.960	28.802	8.051
0.60199	48.421	11.699	42.974	10.363	38.330	9.246	34.482	8.375	31.083	7.533
0.65076	52.053	10.508	46.253	9.406	41.152	8.338	37.032	7.616	33.369	6.873
0.70075	56.200	9.054	49.804	8.045	44.608	7.475	40.049	6.808	36.118	6.217
0.75228	60.893	7.182	53.969	6.460	48.134	5.952	43.199	5.492	38.950	5.082
0.80216	66.142	5.207	58.674	4.845	52.275	4.553	46.912	4.312	42.248	4.039
0.85257	72.277	3.052	64.061	2.992	57.197	3.137	50.687	2.497	46.072	2.911
0.89849	79.211	1.459	69.999	1.489	62.240	1.676	55.771	1.853	50.082	1.852
0.95107	88.982	0.166	78.273	0.125	69.277	0.301	61.861	0.543	55.363	0.596
1.00000	100.520	0.000	88.3331	0.000	77.8517	0.000	69.1145	0.000	61.6449	0.000

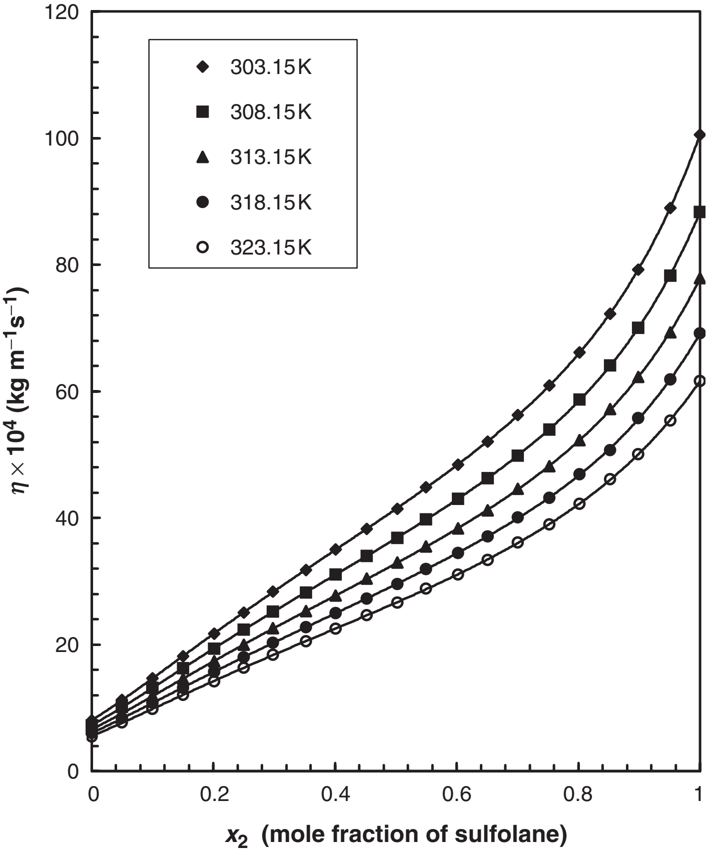

Figure 3. Variation of viscosity, η, against mole fraction of SFL for the system, W (x_1) + SFL (x_2) at different temperatures.

(c) With the rise of temperature, both the minima and maxima shift slightly towards the left along the composition axis.
(d) The effect of temperature on V_m^E for the system is positive i.e., $(\delta V_m^E/\delta T)$ is positive, for the whole range of composition.

The sign of V_m^E depends upon the relative strengths between the contractive factors and the expansive factors. The factors responsible for volume contraction are:

(a) Specific interaction between the component molecules.
(b) Interstitial accommodation of molecules of one component into the vacant spaces of molecules of the other component, which occurs preferentially when the size difference between the component molecules is large, or when large gaps are available in the structural network of molecules.
(c) Weak physical forces, such as dipole–dipole or dipole-induced dipole interactions or van der Waals forces.

The factors, which cause expansion in volume, are the following: (a) dispersion force; (b) steric hindrance of component molecules; (c) unfavorable geometric fitting; (d) electrostatic repulsion, etc.

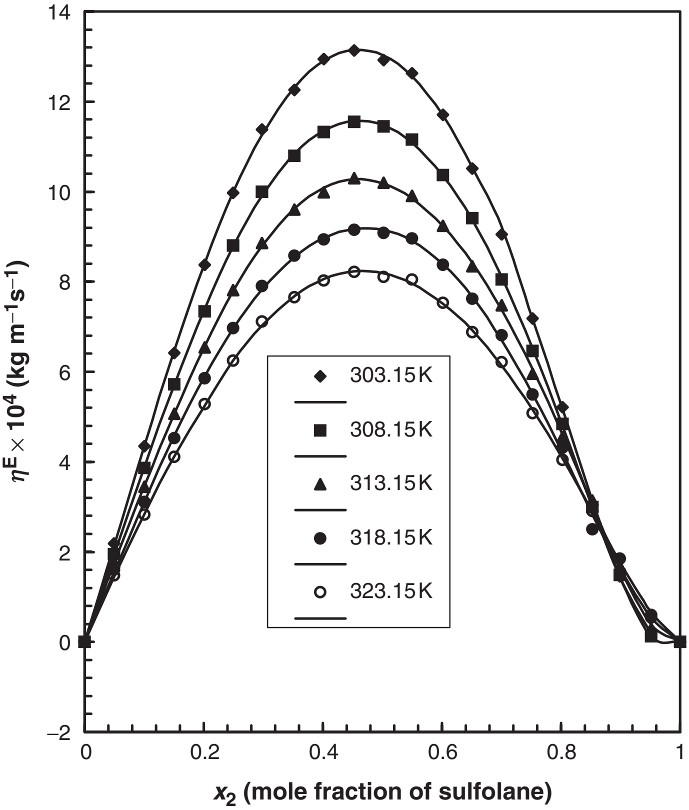

Figure 4. Variation of excess viscosity, η^E, against mole fraction of SFL for the system, W (x_1) + SFL (x_2) at different temperatures.

The negative part of V_m^E curves of the system asserts that the combined effect of the factors responsible for volume contraction outweigh the combined effect of the factors causing volume expansion. Sulfolane, with lone pairs of electrons on several sites, is highly prone to form H-bonding with water. Again, since the component molecules are highly polar, we expect the dipole–dipole type of interaction to take place between them. The ratio of the molar volumes of SFL to water, calculated on the basis of molar masses and densities at 303.15 K, is 5.26, which is indeed very high, indicating quite a large size difference between W and SFL molecules. This implies that the probability is high for the smaller water molecules, either in segregated or monomeric forms, to occupy the vacant spaces offered by the structural network of large SFL molecules. Sacco *et al.* [8,31], Mcdonald *et al.* [9] and Benoit and Choux [10] concluded from conductometric, volumetric, viscometric and calorimetric study of this system that SFL is a water structure breaker.

The positive part of V_m^E in the SFL-rich region of the system implies that the combined effect of the factors responsible for volume expansion outweigh the combined effect of the factors causing volume contraction.

Table 3 lists the viscosities, η, and excess viscosities, η^E, at different temperatures. Figure 3 shows the variation of viscosity against mole fraction of SFL. The viscosity increases rather monotonously up to ≈0.6 mole fraction of SFL, followed by

Table 4. Free energy of activation, $\Delta G^{\neq}$(kJ mol^{-1}), and excess free energy of activation, $\Delta G^{\neq E}$ (kJ mol^{-1}), for viscous flow of the system, water (x_1) + sulfolane (x_2) at different temperatures.

T (K)	303.15		308.15		313.15		318.15		323.15	
x_2	$\Delta G^{\neq}$	$\Delta G^{\neq E}$	$\Delta G^{\neq}$	$\Delta G^{\neq E}$	$\Delta G^{\neq}$	$\Delta G^{\neq E}$	$\Delta G^{\neq}$	$\Delta G^{\neq E}$	$\Delta G^{\neq}$	$\Delta G^{\neq E}$
Water (x_1) + sulfolane (x_2)										
0.00000	9.047	0.000	8.948	0.000	8.850	0.000	8.751	0.000	8.652	0.000
0.04934	10.373	0.805	10.293	0.818	10.213	0.832	10.134	0.846	10.054	0.860
0.10013	11.453	1.348	11.381	1.364	11.310	1.381	11.238	1.399	11.166	1.415
0.15038	12.344	1.708	12.279	1.726	12.214	1.745	12.149	1.764	12.084	1.781
0.20131	13.107	1.933	13.049	1.953	12.991	1.973	12.933	1.994	12.875	2.013
0.2496	13.736	2.052	13.684	2.072	13.632	2.093	13.579	2.115	13.527	2.135
0.29777	14.292	2.098	14.246	2.121	14.200	2.143	14.154	2.167	14.108	2.187
0.35203	14.825	2.059	14.787	2.082	14.748	2.107	14.710	2.133	14.672	2.155
0.4013	15.273	1.986	15.238	2.009	15.204	2.031	15.169	2.056	15.134	2.076
0.45239	15.697	1.870	15.669	1.894	15.642	1.919	15.614	1.946	15.587	1.968
0.50246	16.080	1.724	16.058	1.748	16.035	1.773	16.012	1.800	15.990	1.822
0.54965	16.428	1.574	16.413	1.600	16.397	1.627	16.382	1.656	16.366	1.680
0.60199	16.789	1.381	16.778	1.407	16.768	1.433	16.757	1.463	16.746	1.485
0.65076	17.116	1.193	17.110	1.218	17.103	1.243	17.096	1.272	17.090	1.293
0.70075	17.446	0.995	17.447	1.023	17.449	1.050	17.450	1.083	17.451	1.106
0.75228	17.784	0.788	17.787	0.813	17.790	0.837	17.793	0.866	17.796	0.886
0.80216	18.118	0.595	18.126	0.619	18.133	0.643	18.141	0.671	18.148	0.690
0.85257	18.463	0.407	18.472	0.427	18.481	0.447	18.490	0.472	18.499	0.487
0.89849	18.795	0.255	18.807	0.273	18.819	0.291	18.831	0.315	18.843	0.328
0.95107	19.201	0.105	19.209	0.114	19.217	0.122	19.225	0.137	19.233	0.140
1.00000	19.613	0.000	19.617	0.000	19.622	0.000	19.626	0.000	19.630	0.000

an accelerated rate of increase, as more and more SFL is added. This accelerated rate is thought to be due to increasing degree of association of SFL through dipolar interaction. The nature of variation of viscosity curves is in full accord with that observed by Sacco *et al.* [8].

Excess viscosities, η^E, have been calculated by using the following equation,

$$\eta^E = \eta - \exp(x_1 \ln \eta_1 + x_2 \ln \eta_2). \tag{4}$$

Figure 4 represents the variation of excess viscosities, η^E, as a function of mole fraction of SFL showing positive values throughout the whole range of composition, which can be viewed as due primarily to the formation of H-bonding between SFL and W. The maxima occur at ≈0.5 mole fraction of SFL.

Enthalpies of activation, $\Delta H^{\neq}$, and entropies of activation, $\Delta S^{\neq}$, for viscous flow have been determined by using the following equation,

$$\ln\left(\frac{\eta V_m}{hN}\right) = \frac{\Delta H^{\neq}}{RT} - \frac{\Delta S^{\neq}}{R}. \tag{5}$$

From the slopes and intercepts of the above equation, obtained by the least squares method, $\Delta H^{\neq}$ and $\Delta S^{\neq}$ have been calculated.

The $\Delta G^{\neq}$ values have been obtained by using the equation,

$$\Delta G^{\neq} = \Delta H^{\neq} - T\Delta S^{\neq}. \tag{6}$$

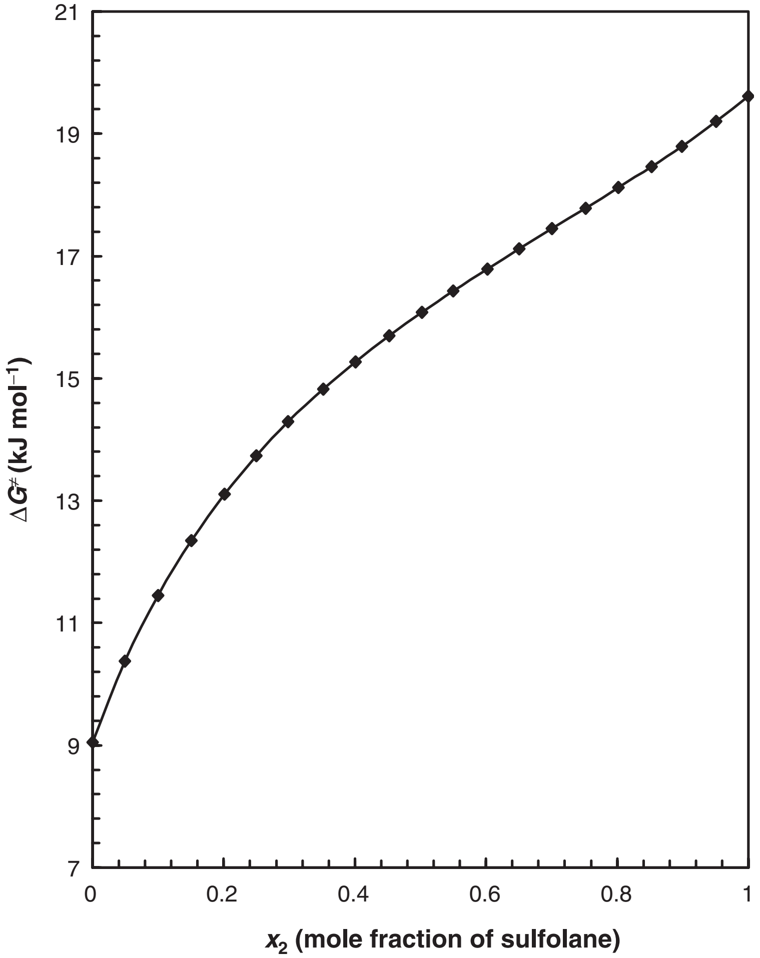

Figure 5. Variation of free energy of activation for viscous flow, $\Delta G^{\neq}$, against mole fraction of SFL for the system, water (x_1) + SFL (x_2) at 303.15 K.

Excess thermodynamic properties have been calculated by the following equation,

$$Y^{\mathrm{E}} = Y - (x_1 Y_1 + x_2 Y_2). \tag{7}$$

The significances of Y and Y^{E} have been described earlier. Y_1 and Y_2 are the respective properties of the pure components, 1 and 2.

Table 4 lists the free energies of activation for viscous flow, $\Delta G^{\neq}$, and their excess values, $\Delta G^{\neq \mathrm{E}}$, at temperatures 303.15 and 323.15 K. Figure 5 shows the variation of free energy at 303.15 K. The free energies increase systematically with the mole fraction of SFL. The effect of temperature on $\Delta G^{\neq}$ is extremely low (table 4), and in order to avoid undesirable crowding of the curves, the variation of this property is shown only at one temperature, 303.15 K. Figure 6 shows the variation of $\Delta G^{\neq \mathrm{E}}$ as a function of mole fraction of SFL, with clear maxima at ≈0.3 mole fraction of SFL.

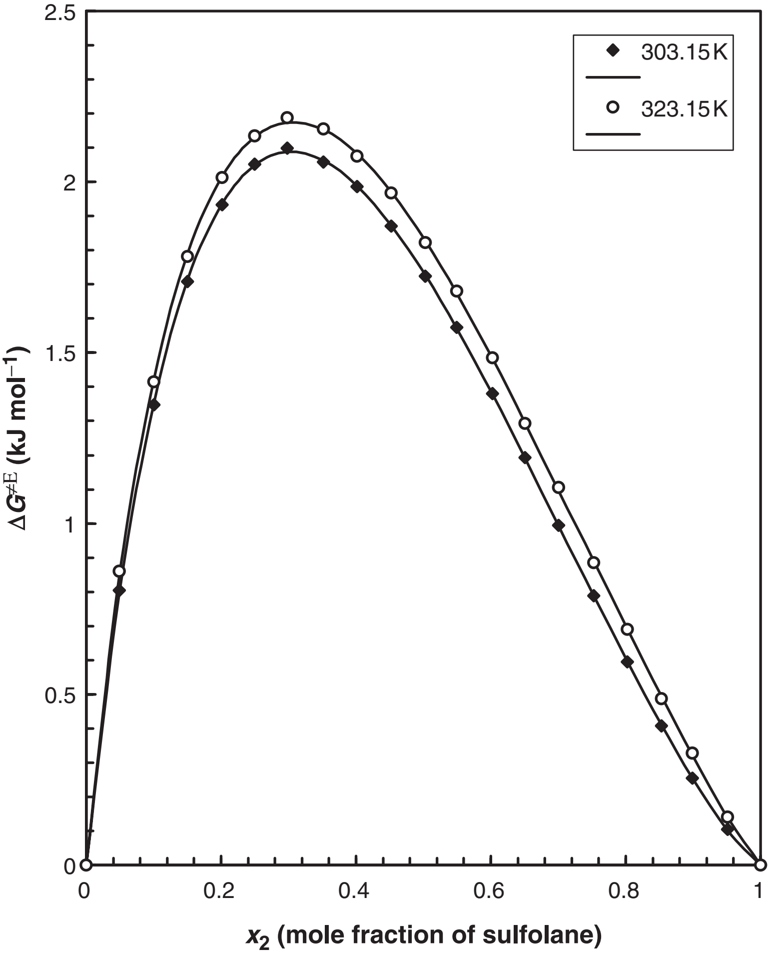

Figure 6. Variation of excess free energy of activation for viscous flow, $\Delta G^{\neq E}$, against mole fraction SFL for the system, water $(x_1) + \text{SFL}$ (x_2).

The maximum observed by Sacco *et al.* [8] corresponds almost quantitatively with ours both in magnitude and composition. The excess viscosity and excess free energy, both being positive, for the whole range of composition, indicate that the species formed in the solution system experience a somewhat greater resistive force in the flow process than usual.

The enthalpies and entropies of activation for viscous flow, $\Delta H^{\neq}$ and $\Delta S^{\neq}$, and their excess values, $\Delta H^{\neq E}$ and $\Delta S^{\neq E}$, have been listed in table 5. Figure 7 shows the variation of $\Delta H^{\neq}$ and $\Delta S^{\neq}$ of the system as a function of mole fraction of SFL. The $\Delta S^{\neq}$ has been found to decrease almost linearly with the addition of SFL to water up to $\approx$0.9 mole fraction of SFL and then increases until the pure state of SFL, giving rise to an ill-defined minimum, but $\Delta H^{\neq}$ shows a sigmoid nature of curve. It is to be noted from table 5 that, excess entropies, $\Delta S^{\neq E}$, are negative for the whole range of composition, indicating that the species formed in the activated state of the flow process are more ordered than what can be expected ideally.

Table 5. Enthalpies, $\Delta H^{\neq}$ (kJ mol^{-1}), excess enthalpies, $\Delta H^{\neq E}$ (kJ mol^{-1}), entropies, $\Delta S^{\neq}$ (J mol^{-1}K^{-1}) and excess entropies, $\Delta S^{\neq E}$ (J mol^{-1}K^{-1}), of activation for viscous flow for the system, W (x_1) + SFL (x_2).

x_2	$\Delta H^{\neq}$	$\Delta H^{\neq E}$	$\Delta S^{\neq}$	$\Delta S^{\neq E}$
Water (x) + sulfolane (x_2)				
0.00000	15.030	0.000	19.734	0.000
0.04934	15.211	−0.032	15.958	−2.760
0.10013	15.796	0.334	14.327	−3.344
0.15038	16.285	0.606	13.000	−3.637
0.20131	16.625	0.725	11.603	−3.984
0.2496	16.907	0.799	10.459	−4.134
0.29777	17.071	0.755	9.169	−4.432
0.35203	17.153	0.602	7.679	−4.804
0.4013	17.395	0.631	6.998	−4.471
0.45239	17.369	0.384	5.514	−4.902
0.50246	17.449	0.248	4.514	−4.871
0.54965	17.371	−0.034	3.111	−5.302
0.60199	17.429	−0.202	2.113	−5.221
0.65076	17.518	−0.324	1.325	−5.005
0.70075	17.366	−0.692	−0.265	−5.566
0.75228	17.593	−0.687	−0.629	−4.868
0.80216	17.663	−0.834	−1.502	−4.714
0.85257	17.910	−0.804	−1.824	−3.997
0.89849	18.062	−0.850	−2.418	−3.645
0.95107	18.714	−0.426	−1.607	−1.752
1.00000	19.355	0.000	−0.863	0.000

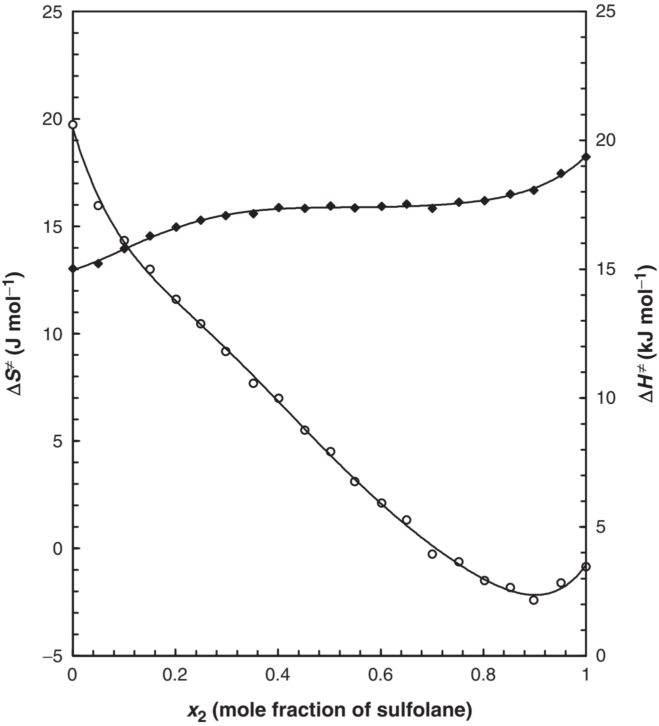

Figure 7. Variation of enthalpy, $\Delta H^{\neq}$ (◆), and entropy, $\Delta S^{\neq}$ (○), of activation for viscous flow against mole fraction of SFL for the system water (x_1) + SFL (x_2).

Table 6. Coefficients, A_i, of equation (1) expressing density, $\rho \times 10^{-3}$ (kg m^{-3}), coefficient of viscosity, $\eta \times 10^4$ (kg m^{-1} s^{-1}), free energy of activation, $\Delta G^{\neq}$ (kJ mol^{-1}) and the squares of the regression coefficients, r^2, for the system, W (x_1) + SFL (x_2) at different temperatures.

Property	Temperature (K)	A_0	A_1	A_2	A_3	A_4	A_5	A_6	r^2
ρ	303.15	0.9964	9.5479	−14.004	10.851	−4.9218	1.4326	−2.6402	0.9999
	308.15	0.9948	9.3154	−13.65	10.572	−4.8015	1.4047	−2.5781	0.9999
	313.15	0.9929	9.0319	−13.26	10.298	−4.6944	1.3809	−2.4961	0.9999
	318.15	0.9910	8.5588	−12.667	9.9252	−4.5663	1.3558	−2.3488	0.9999
	323.15	0.9887	8.3751	−12.35	9.6624	−4.4548	1.3318	−2.309	0.9999
η	303.15	8.0454	58.9940	108.44	458.06	858.82	−783.21	307.49	> 0.9999
	308.15	7.2621	53.008	89.696	391.13	746.84	−685.57	268.18	> 0.9999
	313.15	6.6022	47.312	78.671	341.97	640.67	−570.31	216.81	> 0.9999
	318.15	6.0091	44.574	46.925	215.8	415.19	−380.37	152.6	> 0.9999
	323.15	5.5213	40.642	38.887	183.23	342.68	−296.27	113.38	> 0.9999
$\Delta G^{\neq}$	303.15	9.0532	29.312	−62.786	107.07	−116.24	70.579	−17.377	> 0.9999
	308.15	8.9554	29.707	−64.54	112.43	−124.67	77.174	−19.443	> 0.9999
	313.15	8.8577	30.101	−66.295	117.79	−133.1	83.768	−21.509	> 0.9999
	318.15	8.7599	30.495	−68.049	123.16	−141.53	90.362	−23.575	> 0.9999
	323.15	8.6622	30.89	−69.803	128.52	−149.96	96.957	−25.641	> 0.9999

Table 7. Coefficients, A_i, of Redlich–Kister equation, equation (3), expressing excess molar volumes, $V_m^E \times 10^6$ (m^3 mol^{-1}), excess viscosity, $\eta^E \times 10^4$ (kg m^{-1} s^{-1}), excess free energy of activation, $\Delta G^{\neq E}$ (kJ mol^{-1}) and standard deviation, σ for the system, W (x_1) + SFL (x_2) at different temperatures.

Property	Temperature (K)	A_0	A_1	A_2	A_3	A_4	A_5	σ
V_m^E	303.15	−0.1604	1.2061	−0.4888	−0.5863	−0.1366	1.2809	0.01032
	308.15	0.0486	1.2095	−0.4158	−0.7797	−0.0979	1.4159	0.00940
	313.15	0.0608	1.2216	−0.4779	−1.0964	0.1499	1.8408	0.00837
	318.15	0.1469	1.0951	−0.5689	−0.8990	0.3527	1.5727	0.00799
	323.15	0.2321	1.0822	−0.3934	−0.8204	0.1502	1.1919	0.00888
η^E	303.15	52.1265	−11.7348	−19.9543	−9.9508	−18.1049	−5.8271	0.06396
	308.15	45.9188	−9.8897	−15.4827	−4.5398	−16.3439	−10.7069	0.05369
	313.15	40.7501	−8.5944	−11.2046	2.0152	−13.3943	−13.7343	0.07490
	318.15	36.6316	−5.3286	−10.7502	−9.2542	−8.6484	2.0219	0.12674
	323.15	32.7489	−5.3607	−6.9803	0.6807	−6.8731	−6.4731	0.06319
$\Delta G^{\neq E}$	303.15	6.9429	−6.2269	2.3233	−1.5112	1.1290	−1.1183	0.00505
	308.15	7.0438	−6.2078	2.3750	−1.4425	1.2609	−1.2857	0.00572
	313.15	7.1451	−6.1888	2.4263	−1.3734	1.3954	−1.4540	0.00656
	318.15	7.2589	−6.1537	2.4706	−1.3378	1.5977	−1.5201	0.00758
	323.15	7.3475	−6.1510	2.5292	−1.2347	1.6629	−1.7919	0.00850

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