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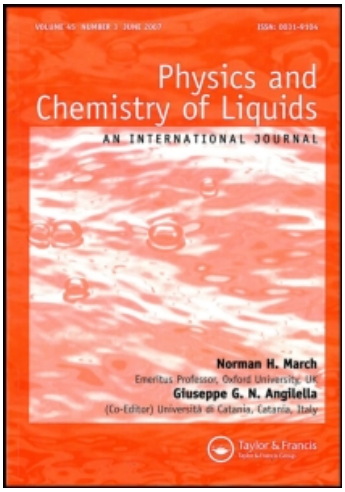

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Study on the internal structure of some ethylene glycols with sulfolane binary mixtures by means of measuring their viscosities at T = 303.15 K

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Study on the internal structure of some ethylene glycols with sulfolane binary mixtures by means of measuring their viscosities at $T = 303.15\,K$

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Viscosities of the binary mixtures of sulfolane with ethylene glycol, diethylene glycol, triethylene glycol and tetraethylene glycol were measured, at 303.15 K, at atmospheric pressure over the whole composition range. The experimental results are used to calculate viscosity deviations. The calculated binary data have been fitted to the Redlich–Kister equation to determinate the appropriate coefficients. This work also provides a test of the Hind *et al*., Grunberg and Nissan, Frenkel and McAllister equations for correlating the viscosities of binary mixtures with mole fractions. The results are discussed in terms of intermolecular interactions and structure of studied binary mixtures.

Keywords: sulfolane; ethylene glycol; diethylene glycol; triethylene glycol; tetraethylene glycol; viscosity

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1. Introduction

This article is a continuation of our studies on the thermodynamic and structural properties of some mixtures of sulfolane with ethylene glycols and alkoxyethanols [1,2]. In the present work, we have measured the viscosity (η) over the entire composition range, at 303.15 K, for binary mixtures of sulfolane (SU) with ethylene glycol (EG), diethylene glycol (DEG), triethylene glycol (DEG) and tetraethylene glycol (TETRAEG). The experimental results for η were used to calculate the viscosity deviations ($\Delta\eta$) and excess energies of activation for viscous flow (ΔG^{*E}) for all studied binary mixtures. These quantities have been fitted to the Redlich–Kister equation [3] to obtain the binary coefficients and standard deviations.

The studied solvents have found a wide variety of applications in the petroleum, cosmetics, textile, pharmaceutical and other industries [4–6].

2. Experimental section

2.1. *Materials*

The following materials with mole fraction purity as stated were used: sulfolane (Aldrich, purum, GC $\geq$ 0.98 mole fraction), ethylene glycol (Fluka, Switzerland, puriss. anhydrous, GC $>$ 0.99 mole fraction), diethylene glycol (Fluka, Switzerland, puriss. p.a.,

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Table 1. Viscosities and refractive indexes of pure components at $T = 303.15\,\mathrm{K}$.

	η (mPa s^{-1})	
Solvent	This work	Lit.
Sulfolane	10.121	10.290 [9] 13.550 [10]
Ethylene glycol	13.533	13.543 [11]
Diethylene glycol	21.875	21.754 [11]
Triethylene glycol	29.244	29.256 [11]
Tetraethylene glycol	35.686	34.989 [11]

GC ≥ 0.995 mole fraction), triethylene glycol (Fluka, Switzerland, puriss. anhydrous, GC > 0.99 mole fraction) and tetraethylene glycol (Fluka, Switzerland, purum, GC ≥ 0.99 mole fraction). All glycols were further purified by the methods described by us previously [1,2]. Sulfolane was purified by the method described by Domańska *et al.* [7]. The mixtures were prepared using a Sartorius balance. Conversion to molar quantities was based on the relative atomic mass table of 1985, issued by IUPAC in 1986. The maximum estimated error in the mole fractions is $\pm 1 \times 10^{-4}$. Liquids were stored in a dry-box over phosphorus pentoxide and degassed by ultrasound just before the experiment. Experimental viscosities for the pure solvents, at $T = 303.15\,\mathrm{K}$, are compared with values available in the literature and are listed in Table 1. The differences between the measured and literature values can be ascribed to the different measurement methods used, and to the different purification procedures employed by other authors [8].

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2.2. *Measurements*

The flow times of the mixtures and the pure liquids were measured in a ViscoClock (made by Schott), equipped with an Ubbelohde capillary viscometer. Double distilled, deionised and degassed water with a specific conductance of $1 \times 10^{-9}\,\mathrm{s\,m^{-1}}$ was used for the calibration. The time measurement tolerance was $\pm 0.005\%$, and the display accuracy was ± 0.01 s. The uncertainty in the viscosity measurements was $\pm 0.001\,\mathrm{mPa\,s^{-1}}$.

In all measurements of the viscosity and refractive index, a Haake model DC-30 thermostat was used at a constant digital temperature control of $\pm 0.01\,\mathrm{K}$.

3. Results and discussion

The experimental viscosities (η) obtained from the measurements of the pure solvents and for the studied binary mixtures, at $T = 303.15\,\mathrm{K}$, are summarised in Table 2. Many investigations of the viscosity and refractive behaviours of liquids have been reported in the literature, and the best representations of the results as a function of the binary composition are given by the following equation [12,13]:

$$\ln \eta(x_1) = \sum_{j=0}^{6} \beta_j \cdot x_1^j, \tag{1}$$

Table 2. Viscosities (η) and excess viscosities ($\Delta\eta$) for {SU(1) + EG(2), SU(1) + DEG(2), SU(1) + TEG(2) and SU(1) + TETRAEG(2)} binary mixtures at $T = 303.15$ K.

x_1	η (mPa s^{-1})	$\Delta\eta$ (mPa s^{-1})	x_1	η (mPa s^{-1})	$\Delta\eta$ (mPa s^{-1})
	SU(1) + EG(2)			SU(1) + DEG(2)	
0.0000	13.533	0.000	0.0000	21.875	0.000
0.0503	11.924	−1.437	0.0517	20.103	−1.164
0.0993	10.749	−2.445	0.0984	18.619	−2.099
0.2006	8.926	−3.923	0.2060	15.845	−3.609
0.2984	7.669	−4.846	0.2958	13.987	−4.411
0.3930	6.857	−5.335	0.3988	12.283	−4.905
0.4553	6.555	−5.425	0.4469	11.688	−4.934
0.5015	6.443	−5.379	0.4997	11.115	−4.887
0.5484	6.443	−5.219	0.5346	10.805	−4.786
0.6038	6.548	−4.925	0.6030	10.311	−4.476
0.7048	7.013	−4.115	0.7047	9.829	−3.763
0.8065	7.683	−3.098	0.7896	9.536	−3.058
0.9034	8.532	−1.919	0.8987	9.510	−1.802
0.9426	9.018	−1.299	0.9348	9.614	−1.273
1.0000	10.121	0.000	1.0000	10.121	0.000
	SU(1) + TEG(2)			SU(1) + TETRAEG(2)	
0.0000	29.244	0.000	0.0000	35.686	0.000
0.0435	27.750	−0.662	0.0511	33.893	−0.487
0.0985	25.877	−1.483	0.0993	32.168	−0.979
0.2083	22.542	−2.719	0.1997	28.585	−1.996
0.2999	20.021	−3.488	0.3005	25.148	−2.856
0.3966	17.634	−4.026	0.3969	22.217	−3.322
0.4473	16.493	−4.197	0.4521	20.700	−3.428
0.4985	15.445	−4.266	0.4986	19.510	−3.429
0.5498	14.465	−4.265	0.5500	18.274	−3.351
0.5855	13.851	−4.196	0.5937	17.282	−3.226
0.6913	12.237	−3.787	0.6989	15.037	−2.782
0.8065	10.899	−2.922	0.8010	13.019	−2.189
0.8984	10.175	−1.889	0.8990	11.288	−1.415
0.9458	10.084	−1.073	0.9457	10.653	−0.856
1.0000	10.121	0.000	1.0000	10.121	0.000

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which could be fitted to the experimental data, at $T = 303.15$ K, using a least-squares method. The β_j coefficients of this fitting procedure are listed in Table 3, along with the standard deviation $\sigma(\eta)$ for each binary mixtures.

The goodness-of-fit of this procedure is ascertained by a mean deviation $\overline{\Delta\eta} = \pm 0.5 \times 10^{-3}$ mPa s^{-1} for (SU + EG), $\overline{\Delta\eta} = \pm 0.8 \times 10^{-3}$ mPa s^{-1} for (SU + DEG), $\overline{\Delta\eta} = \pm 0.8 \times 10^{-3}$ mPa s^{-1} for (SU + TEG) and $\overline{\Delta\eta} = \pm 0.4 \times 10^{-3}$ mPa s^{-1} for (SU + TETRAEG) binary liquid mixtures.

From the measured viscosities, the viscosity deviations ($\Delta\eta$) of the mixtures at $T = 303.15$ K have been calculated from the relationship:

$$\Delta\eta = \eta - (x_1 \cdot \eta_1 + x_2 \cdot \eta_2), \tag{2}$$

where η_1, η_2 and η are the viscosities of the sulfolane, ethylene glycols and the mixtures, respectively. The values of $\Delta\eta$ at $T = 303.15$ K, are summarised in Table 2.

Table 3. Coefficients β_j and standard deviations $\sigma(\eta)$ of Equation (1) for {SU(1) + EG(2), SU(1) + DEG(2), SU(1) + TEG(2) and SU(1) + TETRAEG(2)} binary mixtures at $T = 303.15$ K.

T (K)	β_0	β_1	β_2	β_3	β_4	β_5	β_6	$\sigma(\eta)\cdot 10^3$
SU(1) + EG(2)								
303.15	2.6055	−2.8656	7.8800	−30.6076	67.3891	−64.4212	22.3343	1.9
SU(1) + DEG(2)								
303.15	3.0858	−1.7524	1.8272	−7.6428	19.2694	−19.9713	7.4987	1.3
SU(1) + TEG(2)								
303.15	3.3762	−1.2601	0.4829	−3.4473	8.0710	−8.2148	3.3074	1.6
SU(1) + TETRAEG(2)								
303.15	3.5749	−1.0047	−0.1387	−4.0044	13.0243	−15.3335	6.1966	0.6

Table 4. Coefficients a_j and standard deviations $\sigma(\Delta\eta)$ of Equation (5) for {SU(1) + EG(2), SU(1) + DEG(2), SU(1) + TEG(2) and SU(1) + TETRAEG(2)} binary mixtures at $T = 303.15$ K.

T (K)	a_0	a_1	a_2	a_3	a_4	$\sigma(\eta^E)$
SU + EG						
303.15	−21.5306	4.3869	2.3688	−1.4857	−11.3750	0.0082
SU + DEG						
303.15	−19.5287	4.3358	−0.3132	−3.3766	−4.6574	0.0170
SU + TEG						
303.15	−17.0701	−1.1393	−0.6529	−2.0412	−2.2510	0.0209
SU + TETRAEG						
303.15	−13.7186	1.5060	2.6043	−6.8151	−2.8519	0.0092

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The viscosity deviations were fitted by a Redlich–Kister-type equation [3]:

$$\Delta\eta\ (\mathrm{mPa\,s^{-1}}) = x_1 \cdot (1 - x_1) \sum_{j=0}^{4} a_j \cdot (2x_1 - 1)^j. \tag{3}$$

The parameters a_j of Equation (3) were evaluated by the least-squares method. The values of these parameters with standard deviation σ, are summarised in Table 4.

Standard deviation values were obtained from:

$$\sigma = \left[\frac{\sum (V_{\mathrm{exp\,tl}} - V_{\mathrm{calcd}})^2}{N - p}\right]^{1/2}, \tag{4}$$

where N is the number of experimental points, p is the number of parameters, V_{exptl} and V_{calcd} are the experimental and calculated properties.

The variations of $\Delta\eta$ values as a function of the mole fraction of sulfolane (x_1) for all studied mixtures are presented in Figure 1.

The viscosity deviations, presented in Figure 1, are negative over the entire composition range for all the studied systems. In all mixtures, the minimum occurs around $x_{\mathrm{sulfolane}} \approx 0.50$.

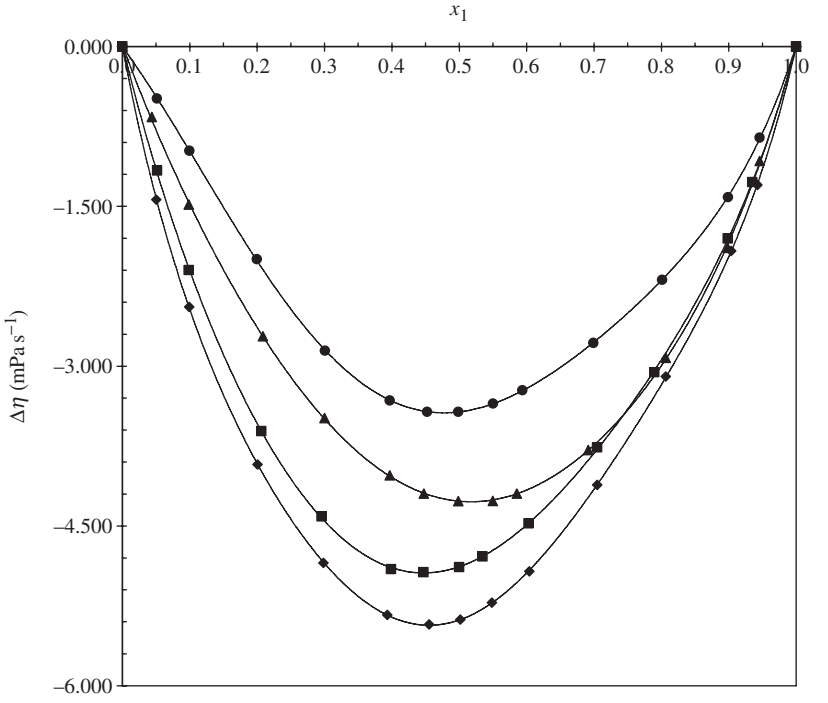

Figure 1. Plot of the excess viscosities ($\Delta\eta$) against mole fraction SU(x_1) for {(◆) SU(1) + EG(2), (■) SU(1) + DEG(2), (▲) SU(1) + TEG(2) and (●) SU(1) + TETRAEG(2)} binary liquid mixtures at $T = 303.15$ K.

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The study of this thermodynamic and structural parameter for binary liquid systems represents a unique tool for investigating the formation of intermolecular complexes, and provides a valuable aid for determining their stoichiometry and their relative thermostability [14–16]. The position of the relative maxima or minima in the plots of $\Delta\eta$ *versus* x_1 could be taken as the true composition of these intermolecular complexes. In particular, positive deviations should be detected in binary mixtures where strong specific interactions between unlike molecules, such as hydrogen bonding, take place [14–17]. In fact, in the studied mixtures we observed negative deviations in viscosity, which regularly increases as the size and/or viscosity of the ethylene glycols are decreased:

$$\Delta\eta_{\min}(\mathrm{SU} + \mathrm{EG}) > \Delta\eta_{\min}(\mathrm{SU} + \mathrm{DEG}) > \Delta\eta_{\min}(\mathrm{SU} + \mathrm{TEG}) > \Delta\eta_{\min}(\mathrm{SU} + \mathrm{TETRAEG}). \quad (5)$$

This reveals that the strength of a specific interaction is not the only factor influencing the viscosity deviation of the studied liquid mixtures. In the analysed mixtures, the molecular size and shape of the components and dispersion forces also play an equally important role.

The globular molecules of sulfolane have no significant intermolecular hydrogen bonding capability in a pure liquid [18–21]. On the other hand, the molecules of

ethylene glycols are self associated liquids through inter- and intramolecular hydrogen bonding [22–27]. Therefore, on the basis of the actual experimental evidence, we can suggest that the addition of pure sulfolane to ethylene glycols would disrupt their self-associated structure (hence, SU acts likewise as an inert solvent). These free SU, EG, DEG, TEG and TETRAEG molecules may interact by dipole–dipole forces and/or intermolecular hydrogen bonds forming the mixed intermolecular complexes [1,2,28].

This effect is also supported by the negative values of V^E and suggests that the strength of intermolecular interaction is not the only factor influencing the viscosity of the studied liquid mixtures, but the molecular size and internal structure of the components are also equally important [1].

Several semi-empirical equations have been used to estimate the viscosity of liquid mixtures in terms of pure component data.

The experimental viscosity data of analysed binary liquid mixtures were further fitted to:

- the Hind *et al*. equation [29]:

$$\eta = x_1^2 \cdot \eta_1 + x_2^2 + 2 \cdot x_1 \cdot x_2 \cdot H_{12} \tag{6}$$

- the Grunberg–Nissan equation [30]:

$$\eta = \exp(x_1 \cdot \ln \eta_1 + x_2 \cdot \ln \eta_2 + x_1 \cdot x_2 \cdot G_{12}), \tag{7}$$

  where G_{12} is a parameter proportional to the interaction energy;
- the Frenkel equation [31]:

$$\ln \eta = \sum_{i=1}^{n} x_i^2 \cdot \eta_i + 2 \cdot \left[\sum_{i=1}^{n} \sum_{j>1}^{n} x_i \cdot x_j \ln F_{ij} \right], \tag{8}$$

  where F_{21} are the parameters representing binary **12** interactions;
- the two parameters McAllister equation [32]:

$$\ln \upsilon = x_1^3 \cdot \ln \eta_1 + 3 \cdot x_1^2 \cdot x_2 \cdot \ln Z_{12} + 3 \cdot x_1 \cdot x_2^2 \cdot \ln Z_{21} + x_2^3 \cdot \ln \upsilon_2 - \ln(x_1 + x_2 \cdot M_2/M_1) + 3 \cdot x_1^2 \cdot x_2 \cdot \ln(2/3 + M_2/3M_1) + 3 \cdot x_1 \cdot x_2^2 \cdot \ln(1/3 + 2M_2/3M_1) + x_2^3 \cdot \ln(M_2/M_1), \tag{9}$$

where Z_{12} and Z_{21} are interaction parameters, M_1 and M_2 are the molecular mass, and υ_1 and υ_2 are the kinematic viscosity of pure component **1** and **2**.

To perform a numerical comparison of the correlating ability of Equations (6)–(9), we calculated the standard deviations (σ). The values of the parameters of Equations (6)–(9) were determined for the systems using a least-squares method, with equal weights assigned to each experimental datum. The correlation parameters and standard deviations (σ) for these equations are listed in Table 5. It is observed that the relation fit the McAllister experimental results better than the Hind, Grunberg–Nissan and Frenkel equations, as the σ values for the latter equations are larger than the values for the McAllister equation in the studied binary mixtures.

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Table 5. Adjustable parameters and standard deviations of several semiempirical equations for {SU(1) + EG(2), SU(1) + DEG(2), SU(1) + TEG(2) and SU(1) + TETRAEG(2)} binary mixtures at $T = 303.15$ K.

Equation	Values of the parameters	σ
SU + EG		
Grunberg–Nissan	$G_{12} = -2.3039$	0.118
Hind *et al.*	$H_{12} = 0.3621$	0.398
Frenkel	$F_{12} = 0.1181$	0.118
McAllister	$A = 4.2970$	0.101
	$B = 4.9662$	
SU + DEG		
Grunberg–Nissan	$G_{12} = -1.1937$	0.290
Hind *et al.*	$H_{12} = 5.7778$	0.284
Frenkel	$F_{12} = 8.2352$	0.279
McAllister	$A = 6.5389$	0.090
	$B = 11.1466$	
SU + TEG		
Grunberg–Nissan	$G_{12} = -0.5291$	0.647
Hind *et al.*	$H_{12} = 10.8666$	0.173
Frenkel	$F_{12} = 13.3699$	0.600
McAllister	$A = 8.6925$	0.153
	$B = 18.1171$	
SU + TETRAEG		
Grunberg–Nissan	$G_{12} = 0.0675$	0.307
Hind *et al.*	$H_{12} = 16.1873$	0.134
Frenkel	$F_{12} = 19.7169$	0.291
McAllister	$A = 12.7305$	0.108
	$B = 23.2538$	

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