

Viscosity in Dimethyl Sulfoxide + 1,4-Dimethylbenzene System

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*This paper reports the viscosities measurements for the binary system dimethyl sulfoxide + 1,4-dimethylbenzene over the entire range of mole fraction at 298.15, 303.15, 313.15 and 323.15 K and atmospheric pressure. The experimental viscosities were correlated with the equations of Grunberg-Nissan, Katti-Chaudhri, Hind, Soliman and McAllister; the adjustable binary parameters have been obtained. The excess Gibbs energy of activation of viscous flow (G^{*E}) has been calculated from the experimental measurements and the results were fitted to Redlich-Kister polynomial equation. The obtained negative excess Gibbs free energy of activation and negative Grunberg-Nissan interaction parameter are discussed in structural and interactional terms.*

Keywords: dimethyl sulfoxide, 1,4-dimethylbenzene, viscosity, interaction parameter

Knowledge of the viscosity is very important in many chemical applications, such as design involving chemical separations, mass transport, heat transport, fluid flow, molecular structure, etc. Generally, the studies of excess properties such as molar volume, deviation in viscosity, excess Gibbs free energy of activation of viscous flow (G^{*E}) and Grunberg-Nissan interaction parameter are useful in understanding the nature of intermolecular interactions between two liquids, particularly when polar and nonpolar components are involved.

As a part of our ongoing research focusing on experimental and theoretical studies of volumetric and transport properties of aqueous and non-aqueous binary and ternary liquid mixtures [1,2], in this work we investigate viscosity for the binary system dimethyl sulfoxide (DMSO) + 1,4-dimethylbenzene in the temperature range from 298.15 to 323.15 K at four isotherms. For this system we previously reported VLE data, density, viscosity, refractive index and derived excess properties [3], and we present here new results of the viscosity correlation with some models from literature, along with the computed excess Gibbs free energy of activation of viscous flow (G^{*E}) and Grunberg-Nissan interaction parameter, the results being interpreted in structural and interactional terms. In literature there are no viscosity data for this system.

The viscosity data were correlated with equations of Grunberg-Nissan [4], Katti-Chaudhri [5], Hind [6], Soliman [7] and McAllister [8]. The excess Gibbs energy of activation (G^{*E}) results were fitted to the Redlich-Kister polynomial

equation to derive the binary coefficients and estimate the standard deviations between the experimental and calculated results.

Experimental Part

Materials

The used substances were purified by distillation. Dimethyl sulfoxide was distilled under vacuum at 0.8-0.9 kPa and 338.65 K. The analytical-reagent-grade 1,4-dimethylbenzene from Fluka (p.a.) was used without further purification. The pure substances were kept in airtight stoppered glass bottle to avoid air contact. The purity was checked by refractive index, density and gas chromatography. It was better than 99.5 mass per cent. We have checked the physical properties by repeated measurements over an interval of 2-3 days, during which time no changes were observed. The experimental values of density, refractive index and viscosity of the pure components are presented in table 1 and compared with literature values.

Apparatus and procedure

Kinematic viscosity measurements of pure solvents and their binary mixtures were carried out using an Ubbelohde viscosimeter. The viscosimeter was calibrated with double distilled water and pure solvents. The time of fall always exceeded 60 s; the accuracy of the flow time was ± 0.1 s. Consequently the errors of the measured values of the viscosity may be estimated as less than 1%. At least four time flow measurements were performed for each

Table 1
COMPARISON OF MEASURED DENSITIES, ρ , VISCOSITIES, η , WITH LITERATURE VALUES

T, K	$10^{-3} \rho, \text{kg}\cdot\text{m}^{-3}$		n_D		$\eta, \text{mPa}\cdot\text{s}$	
	lit.	exp.	lit.	exp.	lit.	exp.
dimethyl sulfoxide						
298.15	1.0957 [9]	1.09574	1.4770 [12]	1.4768		2.0388
303.15	1.09050 [10]	1.09074	1.4752 [13]	1.4733	1.830 [13]	1.8405
313.15	1.08046 [11]	1.08075	1.4700 [13]	1.4694	1.534 [13]	1.5373
1,4-dimethylbenzene						
298.15	0.8568 [9]	0.85712	1.4930 [14]	1.4930	0.603 [15]	0.6282

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Table 2
EXPERIMENTAL DYNAMIC VISCOSITIES AND EXCESS GIBBS ENERGY OF ACTIVATION (G^{*E})
FOR DMSO (1) + 1,4-DIMETHYLBENZENE (2) SYSTEM AT DIFFERENT TEMPERATURES

X_1	η , mPa·s	G^{*E} , kJ·mol ⁻¹	X_1	η , mPa·s	G^{*E} , kJ·mol ⁻¹
298.15 K					
0.0000	0.628	0.0000	0.5969	1.161	-0.1330
0.1056	0.688	-0.0553	0.7009	1.327	-0.1130
0.1975	0.749	-0.0886	0.8022	1.524	-0.0831
0.2988	0.828	-0.1177	0.8978	1.747	-0.0480
0.4033	0.925	-0.1357	1.0000	2.039	0.0000
0.5126	1.048	-0.1399			
303.15 K					
0.0000	0.590	0.0000	0.5969	1.070	-0.1215
0.1056	0.647	-0.0399	0.7009	1.216	-0.1055
0.1975	0.704	-0.0694	0.8022	1.389	-0.0789
0.2988	0.776	-0.0974	0.8978	1.585	-0.0458
0.4033	0.862	-0.1172	1.0000	1.841	0.0000
0.5126	0.971	-0.1250			
313.15 K					
0.0000	0.532	0.0000	0.5969	0.923	-0.1217
0.1056	0.578	-0.0452	0.7009	1.041	-0.1051
0.1975	0.624	-0.0754	0.8022	1.179	-0.0784
0.2988	0.683	-0.1025	0.8978	1.335	-0.0456
0.4033	0.754	-0.1205	1.0000	1.537	0.0000
0.5126	0.842	-0.1265			
323.15 K					
0.0000	0.483	0.0000	0.5969	0.810	-0.1188
0.1056	0.521	-0.0481	0.7009	0.908	-0.1015
0.1975	0.560	-0.0792	0.8022	1.022	-0.0753
0.2988	0.609	-0.1049	0.8978	1.149	-0.0433
0.4033	0.669	-0.1209	1.0000	1.313	0.0000
0.5126	0.743	-0.1246			

composition and temperature and the results were averaged. A thermostatically controlled bath was used to keep the temperature within ± 0.05 K.

The mixtures were prepared gravimetrically by using a HR-120 (A&D Japan) electronic balance with a precision of 0.0001 g and the accuracy of mole fraction is estimated to be less than 0.0002. All mixtures were completely miscible over the whole composition range.

Results and Discussions

The measured viscosities and excess Gibbs free energy of activation (G^{*E}) for dimethyl sulfoxide + 1,4-dimethylbenzene system in the temperature range from 298.15 to 323.15 K are given in table 2.

The excess Gibbs energy of activation of viscous flow (G^{*E}) was computed through the following equation:

$$G^{*E} = RT \left[\ln(V\eta) - \sum_{i=1}^N X_i \ln(V_i \eta_i) \right] \quad (1)$$

where η and η_i are the dynamic viscosity of the mixture, and of the pure component i , respectively; V and V_i are the molar volume of the mixture, and of the pure component i , respectively. X_i are the mole fractions, R is the gas constant and T is the absolute temperature. N represents the number of components in the mixture.

The composition dependence of the excess Gibbs energy of activation was represented by a Redlich-Kister type equation:

$$G^{*E} = X_i X_j \sum_{k=0}^p A_k (X_i - X_j)^k \quad (2)$$

where p is the degree of polynomial expansion. The adjustable parameters, A_k , were obtained by fitting the experimental data to the developed equation using Excel Solver. It was found that the best fits were obtained for the solution of equation (2) with 3 adjustable parameters. The

correlated results are shown in table 3 in which the tabulated standard deviation (σ) was defined as:

$$\sigma = \left[\frac{\sum (G_{\text{exp}}^{*E} - G_{\text{calc}}^{*E})^2}{n - p} \right]^{0.5} \quad (3)$$

where n is the number of experimental data, p is the number of parameters.

Table 3
ESTIMATED REDLICH-KISTER PARAMETERS OF EXCESS GIBBS
ENERGY OF ACTIVATION (G^{*E}) FOR DMSO (1) + 1,4-
DIMETHYLBENZENE (2) SYSTEM AT DIFFERENT TEMPERATURES

T, K	A_0	A_1	A_2	σ
298.15	-0.5859	-0.0246	0.0279	0.0010
303.15	-0.5701	-0.1932	0.0724	0.0006
313.15	-0.5450	-0.0962	0.0411	0.0006
323.15	-0.5204	-0.0234	0.0224	0.0005

Several relations have been proposed to evaluate the viscosity of liquid binary mixtures by using some empirical and theoretical based models with one or more adjustable parameters. The equations of Grunberg-Nissan, Katti-Chaudhri and Hind have one adjustable parameter, A_{ij} . According to Grunberg and Nissan, the adjustable binary parameter mentioned in Eq. (4) is regarded as measure of the strength of interactions between the mixing species.

Grunberg -Nissan:

$$\ln \eta = \sum_i X_i \ln \eta_i + \sum_i \sum_{j \neq i} X_i X_j A_{ij} \quad (4)$$

Katti -Chaudhri:

Table 4
THE RESULTS OF VISCOSITY CORRELATION FOR
DMSO (1) + 1,4-DIMETHYLBENZENE (2) SYSTEM AT DIFFERENT TEMPERATURES

Equation	A _{ij}	A _{ji}	v _{ij}	σ	A _{ij}	A _{ji}	v _{ij}	σ
	298.15 K				303.15 K			
Grunberg-Nissan	-0.3675			0.0009	-0.3426			0.0027
Katti-Chaudhri	-0.2213			0.0013	-0.1959			0.0012
Hind	0.7229			0.0285	0.6924			0.0257
Soliman	1.5002		-0.3148	0.0018	1.5230		-0.4863	0.0029
Soliman	1.1932	0.8889	0.0811	0.0004	1.0232	0.8147	0.2018	0.0003
McAllister	1.2587	0.9141		0.0005	1.1575	0.8683		0.0009
313.15 K				323.15 K				
Grunberg-Nissan	-0.3384			0.0017	-0.3295			0.0008
Katti-Chaudhri	-0.1918			0.0004	-0.1829			0.0005
Hind	0.6227			0.0191	0.5649			0.0145
Soliman	1.6756		-0.8956	0.0036	1.8279		-1.2566	0.0041
Soliman	0.9370	0.7405	0.1109	0.0002	0.8573	0.6755	0.0555	0.0001
McAllister	1.0056	0.7683		0.0005	0.8911	0.6895		0.0002

$$\ln(\eta V) = \sum_i^n X_i \ln(\eta_i V_i) + \sum_i^n \sum_{j>i}^n X_i X_j A_{ij} \quad (5)$$

Hind:

$$\eta = \sum_i^n X_i^2 \eta_i + \sum_i^n \sum_{j>i}^n X_i X_j A_{ij} \quad (6)$$

McAllister's two-parameters equation, based on Eyring's theory of absolute reaction rates, takes into account interactions both of like and unlike molecules by a two-dimensional three-body interaction. This model is recommended for the systems where the volumetric size ratio of components is about 1.5.

$$\ln v = \sum_{i=1}^n X_i^3 \ln(v_i M_i) - \ln \sum_{i=1}^n X_i M_i + 3 \sum_{i=1}^n \sum_{\substack{j=1 \\ j \neq i}}^n X_i^2 X_j \ln(A_{ij} M_{ij})$$

$$M_{ij} = \frac{2M_i + M_j}{3} \quad (7)$$

where v , v_i are the kinematic viscosity of the mixture, and of pure component i , respectively, M_i is the molecular mass of the components.

The data were also correlated with a modified form of the McAllister equation proposed by Soliman. The general form of the equation is as follows, and it could be used with two or three parameters:

$$\ln v = \sum_{i=1}^n X_i^3 \ln v_i + 3 \sum_{i=1}^n \sum_{\substack{j=1 \\ j \neq i}}^n X_i^2 X_j \ln A_{ij} + \sum_{i=1}^n \sum_{\substack{j=1 \\ j \neq i}}^n \frac{v_{ij} X_i X_j}{\left(\frac{M_i}{M_j}\right)^2 X_i + X_j} \quad (8)$$

For all these models the standard deviation (σ) was calculated using type (3) equation. The correlation parameters and standard deviation are presented in table 4. Our analysis shows that the Hind equation gives relatively large standard deviation and it decreases as the temperature increases, while the other four equations leads to smaller standard deviation values indicating the suitability of all the four relations for representing the mixing viscosities of dimethyl sulfoxide + 1,4-dimethylbenzene binary mixtures. The best correlation method for our binary system data is found using Mc Allister two parameters and Soliman three parameters models, and the worst using the Hind model. The standard deviation was improved in the case of Soliman equation by using three parameters instead

two; moreover it decreases as the temperature increases. It is worthy to note that the theoretical based McAllister equation gives very good results, even if the components have different molar volumes (71.30 for DMSO and 123.87 cm³ mol⁻¹ for 1,4-dimethylbenzene at 298.15 K).

Figure 1 depicts the correlation results with the mentioned models; it is mentioned that curves which are based on exponential type equations overlap.

Figure 2 shows that the excess Gibbs energy of activation (G^{*E}) values are negative throughout the mixture composition and become slightly more positive as the temperature of the mixtures increases from 298.15 K to 323.15 K. The values of Grunberg-Nissan parameters, as shown in table 4, are negative for all investigated temperatures.

In order to elucidate the forces that are acting between unlike molecules, the help of excess Gibbs free energy of activation of viscous flow (G^{*E}) and Grunberg-Nissan interaction parameter have become indispensable and essential. Generally, the positive G^{*E} values indicate specific interactions while negative values indicate the dominance of dispersion forces; moreover if Grunberg-Nissan interaction parameter values are positive, the interactions between unlike molecules are strong whereas negative values means weak interactions [16].

Therefore, the negative excess Gibbs free energy of activation (G^{*E}) and negative Grunberg-Nissan interaction parameter indicate weak interactions in the present system. This is in accordance with the obtained results in

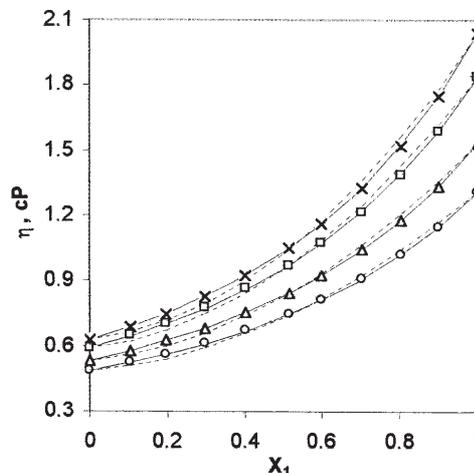


Fig. 1 Dynamic viscosity of the DMSO (1) + 1,4-dimethylbenzene (2) system at 298.15 K (x); 303.15 K (□); 313.15 K (Δ) and 323.15 K (o); correlation with Grunberg-Nissan (—) and Hind (---) models

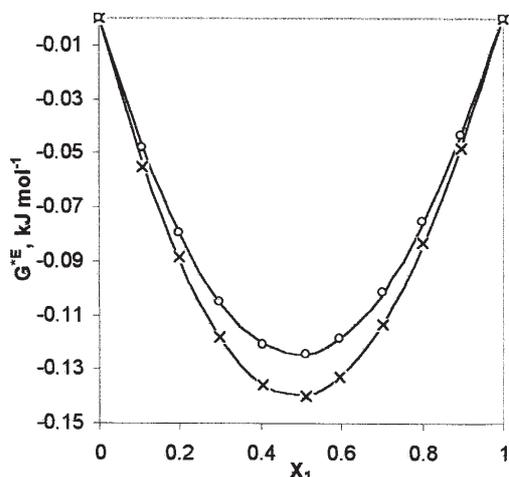


Fig. 2 Excess molar Gibbs of activation of viscous flow (G^E) of the DMSO (1) + 1,4-dimethylbenzene (2) system at 298.15 K (x) and 323.15 K (o); (—) Redlich-Kister's correlation

our earlier study, where the moderate negative excess molar volumes, negative deviations in viscosity and positive deviations of Raoult's law for this system have been explained by the predominance of structural effects over interactional ones [3].

Structural information confirms these statements. DMSO is an aprotic, highly polar self-associated solvent, having a dipole moment $\mu = 3.96$ D [17]; 1,4-dimethylbenzene is a nonpolar, stable substance with a large quadrupole moment [18], which causes molecular order in the pure state. On mixing, the molecular order in aromatic hydrocarbon decreases because of DMSO molecules, whereas the molecular associations in pure DMSO are disrupted by 1,4-dimethylbenzene. Their binary mixtures are characterized by weak electron donor-acceptor type interactions in which aromatic hydrocarbon behave as electron donor [19].

Conclusions

Experimental dynamic viscosities data for the binary system DMSO + 1,4-dimethylbenzene in the temperature range from 298.15 to 323.15 K at four isotherms have been reported. The viscosity data were correlated with equations

of Grunberg-Nissan, Katti-Chaudhri, Hind, Soliman and McAllister, the best correlation being found using Mc Allister two parameters and Soliman three parameters models.

Excess Gibbs free energy of activation of viscous flow (G^E) and Grunberg-Nissan interaction parameter were calculated. The obtained negative excess Gibbs free energy of activation and negative Grunberg-Nissan interaction parameter, in accordance with the previous reported results, shows the predominance of structural effect over interactional on mixing.

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