



Density, viscosity and refractive index of the dimethyl sulfoxide + *o*-xylene system

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Abstract: This work reports the experimental results of the densities, viscosities and refractive indices between 298.15 and 323.15 K of the dimethyl sulfoxide + *o*-xylene system over the entire composition range of the mixtures. The excess molar volumes (V^E), viscosity deviations ($\Delta\nu$), excess Gibbs energy of activation of viscous flow (G^{*E}) and deviations in the refraction (ΔR) were calculated from the experimental data; all the computed quantities were fitted to the Redlich–Kister equation. The system exhibits moderate negative values for the investigated excess properties. The resulting excess functions were interpreted in structural and interactional terms. From the experimental data, the thermodynamic functions of the activation of viscous flow were estimated. The viscosity data were correlated with several semi-empirical equations. The two-parameter McAllister equation can give very good results.

Keywords: dimethyl sulfoxide; *o*-xylene; density; viscosity; excess properties.

INTRODUCTION

Thermodynamic and physical properties data have a well recognized importance in design calculations involving chemical separations, fluid flow and heat transfer. Studies on the volumetric and transport properties of binary liquid mixtures provide information on the nature of the interactions between the constituents.

The present work is a continuation of our systematic experimental studies on the physico-chemical properties of binary mixtures of dimethyl sulfoxide with xylenes. The effects of molecular size and geometrical fitting of the molecules on the volumetric and viscometric properties of binary mixture containing dimethyl sulfoxide and *p*-xylene were reported earlier.¹

This work reports experimental data of density, viscosity and refractive index for the dimethyl sulfoxide + *o*-xylene system at temperatures 298.15, 303.15,

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313.15 and 323.15 K. The excess molar volumes, viscosity deviations, excess Gibbs energy of activation of viscous flow (G^{*E}) and deviations in refraction were calculated from the experimental data and fitted to the Redlich–Kister type polynomial equation.

The variation of the excess or deviation properties with the composition were discussed from the interactional and structural point of view. The thermodynamic functions of activation of viscous flow were estimated from the dynamic viscosity values. The viscosity data were correlated with the Grunberg–Nissan, Hind and McAllister semi-empirical equations.

Dimethyl sulfoxide (DMSO), a typical aprotic highly polar self-associated solvent (dipole moment $\mu = 1.32 \times 10^{-29}$ C m),² is an important solvent in chemistry, biotechnology, and medicine. The aromatic hydrocarbon molecules possess large quadrupole moments, causing an orientational order in these liquids.³ The objective underlying the present work was to obtain information regarding molecular interactions in mixtures of a polar liquid with non-polar liquids, which is essential for an understanding of many chemical and industrial processes in these media. Moreover, the binary mixtures containing aromatic hydrocarbons are of interest as these systems find applications in studies of polymer miscibility, polymer phase diagrams, and preferential interactions in mixed solvents.⁴

The volumetric properties of binary mixtures of DMSO with *o*-xylene were studied by Ali *et al.*⁵ and Wang *et al.*⁶ However, no literature data on viscosities and refractive indices are available for this system.

EXPERIMENTAL

Materials

DMSO (Merck, mole fraction purity > 0.998) and *o*-xylene (Merck, mole fraction purity > 0.995) were used without further purification. The experimental density, refractive index and viscosity of the pure components are in agreement with the literature values, as can be seen in Table I.

TABLE I. Experimental and literature values for density, refractive index and viscosity of the pure components

T / K	$\rho \times 10^{-3} / \text{kg m}^{-3}$		n_D		$\eta / \text{mPa s}$	
	Lit.	Exp.	Lit.	Exp.	Lit.	Exp.
Dimethyl sulfoxide						
298.15	1.0954 ⁷ , 1.095240 ⁸	1.09530	1.4770 ⁴	1.4778	1.991 ⁷	1.993
303.15	1.09045 ⁹ , 1.09049 ¹⁰	1.09027	1.4752 ¹⁰	1.4748	1.830 ¹⁰	1.811
313.15	1.08046 ¹¹	1.08024	1.4700 ¹⁰	1.4702	1.534 ¹⁰	1.505
<i>o</i> -Xylene						
298.15	0.87557 ⁶ , 0.87558 ¹²	0.87560	1.50295 ¹³	1.5020	0.758 ¹⁴	0.759
303.15	0.8714 ⁵ , 0.87136 ¹⁵	0.87131		1.4998		0.715
313.15	0.8627 ⁵	0.86273		1.4948		0.634

Procedure

The binary mixtures were prepared by mixing the appropriate volumes of the liquids in airtight stoppered glass bottles, which were weighed using a HR-120 (A & D Japan) electronic balance with a precision of ± 0.0001 g. The experimental uncertainty in the mole fractions was estimated to be less than ± 0.0002 .

The density measurements of the pure solvents and the mixtures were performed by means of an Anton Paar DMA 4500 densimeter with a precision of ± 0.00005 g cm⁻³, between 298.15 and 323.15 K. The DMA cell was calibrated with dry air and ultra pure water at atmospheric pressure. The sample size was 0.70 cm³ and the sample thermostat was controlled to ± 0.01 K. Triplicate measurements of the density were performed for all the mixtures and pure components. The accuracy in the determination of the density is believed to be less than ± 0.2 kg·m⁻³ and $\pm 10^{-8}$ m³·mol⁻¹ for the calculation of V^E .

The kinematic viscosities of the pure components and their mixtures were determined at the same temperatures as for the density determinations, using an Ubbelohde capillary viscometer having a capacity of about 15 ml, a length of about 90 mm and 0.5 mm internal diameter. The viscometer was calibrated using double distilled water. At least four time flow measurements were performed for each composition and temperature, and the results were averaged. The viscometer was kept vertically in a transparent-walled bath with a thermal stability of ± 0.05 K for about 30 min to attain thermal equilibrium. The uncertainty of the flow time measurement was ± 0.1 s. The corresponding uncertainty in the kinematic viscosity is $\pm 0.001 \times 10^{-6}$ m² s⁻¹.

Refractive indices values for the D-line were measured with a thermostated Abbe refractometer with a precision of ± 0.0001 . All measurements were performed in a thermostat maintained at ± 0.05 K.

RESULTS AND DISCUSSION

Experimental data and excess or deviation values

The densities, ρ , kinematic viscosities, ν , and refractive indices, n_D , were measured in the temperature range from 298.15 to 323.15 K and the measured values are presented in Table II.

The values of the excess molar volume, V^E , viscosity deviation, $\Delta\nu$, deviation in molar refraction, ΔR , and the excess Gibbs energy of activation of viscous flow, G^{*E} , were calculated from the experimental data according to the following equations:

$$V^E = V - \sum_{i=1}^2 V_i x_i \quad (1)$$

$$\Delta\nu = \nu - \sum_{i=1}^2 \nu_i x_i \quad (2)$$

$$\Delta R_m = R_m - \sum_{i=1}^2 R_i \varphi_i \quad (3)$$

$$G^{*E} = RT \left[\ln(V\eta) - \sum_{i=1}^2 x_i \ln(V_i \eta_i) \right] \quad (4)$$

where x_i and φ_i represent the mole fraction and volume fraction of the pure component i , respectively; V , ν , η and R_m are the molar volume, kinematic and dynamic viscosity, and molar refraction of the mixtures, respectively, and V_i , ν_i , η_i , and R_i the corresponding properties of the pure components. The molar refraction was calculated from the Lorentz–Lorentz equation.¹⁶ R is the gas constant and T the absolute temperature. The experimental excess properties are also reported in Table II.

TABLE II. Densities, kinematic viscosities, refractive index, excess molar volumes, viscosity deviations, excess Gibbs energy of activation for viscous flow and deviations in molar refraction for the dimethyl sulfoxide (1) + *o*-xylene (2) system from 298.15 to 323.15 K

x_1	$\rho \times 10^{-3}$ kg m ⁻³	$\nu \times 10^6$ m ² s ⁻¹	n_D	$V^E \times 10^6$ m ³ mol ⁻¹	$\Delta \nu \times 10^6$ m ² s ⁻¹	G^{*E} kJ mol ⁻¹	$\Delta R_m \times 10^6$ m ³ mol ⁻¹
298.15 K							
0.0000	0.87560	0.8666	1.5020	0.000	0.000	0.000	0.000
0.1320	0.89390	0.9477	1.5005	-0.033	-0.045	-0.009	-0.759
0.2540	0.91281	1.0364	1.4988	-0.065	-0.072	-0.003	-1.330
0.3602	0.93100	1.1225	1.4973	-0.082	-0.087	0.005	-1.689
0.4729	0.95236	1.2229	1.4945	-0.088	-0.094	0.013	-1.964
0.5640	0.97145	1.3110	1.4923	-0.087	-0.093	0.018	-2.038
0.6602	0.99366	1.4106	1.4871	-0.078	-0.085	0.021	-1.947
0.7602	1.01934	1.5214	1.4831	-0.059	-0.070	0.020	-1.676
0.8597	1.04805	1.6390	1.4783	-0.035	-0.047	0.014	-1.200
1.0000	1.09530	1.8195	1.4778	0.000	0.000	0.000	0.000
303.15 K							
0.0000	0.87131	0.8200	1.4998	0.000	0.000	0.000	0.000
0.1320	0.88962	0.8942	1.4979	-0.043	-0.037	-0.004	-0.782
0.2540	0.90844	0.9723	1.4963	-0.072	-0.061	-0.001	-1.342
0.3602	0.92655	1.0474	1.4944	-0.087	-0.076	0.003	-1.717
0.4729	0.94783	1.1347	1.4919	-0.092	-0.083	0.007	-1.972
0.5640	0.96686	1.2113	1.4897	-0.092	-0.083	0.009	-2.041
0.6602	0.98897	1.2982	1.4835	-0.080	-0.077	0.011	-1.983
0.7602	1.01457	1.3955	1.4804	-0.061	-0.064	0.010	-1.706
0.8597	1.04318	1.4997	1.4761	-0.036	-0.043	0.008	-1.184
1.0000	1.09027	1.6608	1.4748	0.000	0.000	0.000	0.000
313.15 K							
0.0000	0.86273	0.7344	1.4948	0.000	0.000	0.000	0.000
0.1320	0.88097	0.7911	1.4932	-0.052	-0.030	-0.013	-0.773
0.2540	0.89966	0.8524	1.4912	-0.081	-0.049	-0.013	-1.361
0.3602	0.91763	0.9119	1.4891	-0.094	-0.060	-0.010	-1.750
0.4729	0.93876	0.9814	1.4870	-0.099	-0.065	-0.003	-1.989
0.5640	0.95764	1.0424	1.4852	-0.095	-0.064	0.002	-2.042
0.6602	0.97960	1.1113	1.4793	-0.083	-0.058	0.006	-1.979
0.7602	1.00502	1.1880	1.4762	-0.063	-0.047	0.009	-1.704
0.8597	1.03345	1.2692	1.4721	-0.037	-0.032	0.007	-1.185
1.0000	1.08024	1.3931	1.4702	0.000	0.000	0.000	0.000

TABLE II. Continued

x_1	$\rho \times 10^{-3}$ kg m ⁻³	$\nu \times 10^6$ m ² s ⁻¹	n_D	$V^E \times 10^6$ m ³ mol ⁻¹	$\Delta \nu \times 10^6$ m ² s ⁻¹	G^{*E} kJ mol ⁻¹	$\Delta R_m \times 10^6$ m ³ mol ⁻¹
323.15 K							
0.0000	0.85410	0.6591	1.4892	0.000	0.000	0.000	0.000
0.1320	0.87226	0.7062	1.4878	-0.060	-0.023	-0.011	-0.769
0.2540	0.89081	0.7572	1.4864	-0.087	-0.037	-0.009	-1.330
0.3602	0.90866	0.8073	1.4841	-0.101	-0.044	0.000	-1.737
0.4729	0.92964	0.8656	1.4820	-0.105	-0.045	0.011	-1.983
0.5640	0.94840	0.9163	1.4800	-0.101	-0.043	0.019	-2.051
0.6602	0.97020	0.9729	1.4744	-0.087	-0.038	0.025	-1.985
0.7602	0.99546	1.0345	1.4710	-0.067	-0.030	0.026	-1.711
0.8597	1.02371	1.0983	1.4672	-0.040	-0.019	0.020	-1.212
1.0000	1.07019	1.1917	1.4659	0.000	0.000	0.000	0.000

The experimental values of V^E , $\Delta \nu$, ΔR_m and G^{*E} were fitted to the Redlich–Kister¹⁷ type polynomials:

$$Y = x_i x_j \sum_{k=0}^p A_k (x_i - x_j)^k \quad (5)$$

where Y is V^E , $\Delta \nu$, ΔR_m or G^{*E} and p is the degree of polynomial expansion. The adjustable parameters A_k obtained by fitting the equations to the experimental values with a least-squares algorithm are given in Table III, along with the standard deviation, σ , defined as follows:

$$\sigma = \left[\frac{\sum_{i=1}^n (Y_i^{\text{exp}} - Y_i^{\text{calc}})^2}{n - m} \right]^{0.5} \quad (6)$$

where n is the number of experimental data and m is the number of parameters.

The variation of the excess or deviation properties along with the smoothed curves using Eq. (5) are presented in Figs. 1a–1d. As can be seen from the Figures, the main features of the system are that the excess molar volumes, deviations in viscosity, and deviations in molar refraction are all negative, while the excess Gibbs energy of activation of viscous flow has an S-shape allure, with positive and negative values.

The values of the excess molar volumes are moderately negative and become slightly more negative as the temperature of the mixtures increases from 298.15 to 323.15 K, with minima between -0.09 and -0.1×10^{-6} m³ mol⁻¹.

This trend would seem to indicate: (a) a packing effect due to the geometrical fitting of the molecules of different molecular sizes into each others structure (71.30×10^{-6} for DMSO and 121.24×10^{-6} m³ mol⁻¹ for *o*-xylene at 298.15 K)

and (b) electron donor–acceptor type interactions in which the aromatic hydrocarbon behaves as electron donor.¹⁸ A factor that would cause an increase of the V^E values (a positive effect) is the breakdown of DMSO self-association and the destruction of molecular order in the aromatic hydrocarbon on mixing, as is reflected by the positive heats of mixing reported in literature for this system.¹⁹ All these above factors play a role in deciding the magnitude of the excess molar volumes; hence the obtained V^E values are moderately negative. As the temperature is lowered, the packing effect of the compounds is lowered; therefore V^E became less negative, as was observed by Pal and Kumar²⁰ for mixtures exhibiting a similar behavior.

TABLE III. The adjustable parameters and standard deviations of the excess functions of the dimethyl sulfoxide (1) + *o*-xylene (2) system

Function	A_0	A_1	A_2	A_3	σ
298.15 K					
$V^E \times 10^6 / \text{m}^3 \text{mol}^{-1}$	-0.3600	0.0140	0.1201	-0.0141	0.0012
$\Delta \nu \times 10^6 / \text{m}^2 \text{s}^{-1}$	-0.3590	0.0378	-0.0187	–	0.0002
$\Delta R \times 10^6 / \text{m}^3 \text{mol}^{-1}$	-7.9785	1.9901	-0.5406	–	0.0097
$G^{*E} / \text{kJ mol}^{-1}$	0.1802	0.3288	-0.1472	0.0272	0.0004
303.15 K					
$V^E \times 10^6 / \text{m}^3 \text{mol}^{-1}$	-0.3736	0.0232	0.0656	0.0678	0.0006
$\Delta \nu \times 10^6 / \text{m}^2 \text{s}^{-1}$	-0.3235	-0.0049	-0.0103	–	0.0001
$\Delta R \times 10^6 / \text{m}^3 \text{mol}^{-1}$	-8.0778	1.8382	-0.2766	0.8832	0.0040
$G^{*E} / \text{kJ mol}^{-1}$	0.0740	0.1394	-0.0518	0.0085	0.0001
313.15 K					
$V^E \times 10^6 / \text{m}^3 \text{mol}^{-1}$	-0.3942	0.0538	0.0267	0.0941	0.0003
$\Delta \nu \times 10^6 / \text{m}^2 \text{s}^{-1}$	-0.2517	0.0151	-0.0067	–	0.0001
$\Delta R \times 10^6 / \text{m}^3 \text{mol}^{-1}$	-8.0712	2.1884	-0.5766	–	0.0082
$G^{*E} / \text{kJ mol}^{-1}$	0.0527	0.2216	-0.0687	0.0103	0.0002
323.15 K					
$V^E \times 10^6 / \text{m}^3 \text{mol}^{-1}$	-0.4161	0.0632	-0.0070	0.1273	0.0006
$\Delta \nu \times 10^6 / \text{m}^2 \text{s}^{-1}$	-0.1829	0.0280	0.0028	–	0.0001
$\Delta R \times 10^6 / \text{m}^3 \text{mol}^{-1}$	-8.0967	2.0085	-0.5193	–	0.0073
$G^{*E} / \text{kJ mol}^{-1}$	0.0680	0.2250	-0.0039	-0.0098	0.0001

The deviations in the viscosity are moderately negative over the whole composition range at the investigated temperatures. The viscosity deviations are a function of the intermolecular interaction as well as of the size and shape of the molecules. Fort and Moore²¹ state that a positive viscosity deviation is a characteristic of systems where intermolecular interactions predominate, whereas mixtures without strong interactions present a negative viscosity deviation. The obtained negative $\Delta \nu$ values for DMSO + *o*-xylene mixtures indicate weak interactions in this system. Moreover, V^E and $\Delta \nu$ do not obey the general rule, according which they should have the opposite sign (specific for systems where inter-

molecular interactions predominate), therefore, for this system, the geometrical fitting of the molecules prevails.

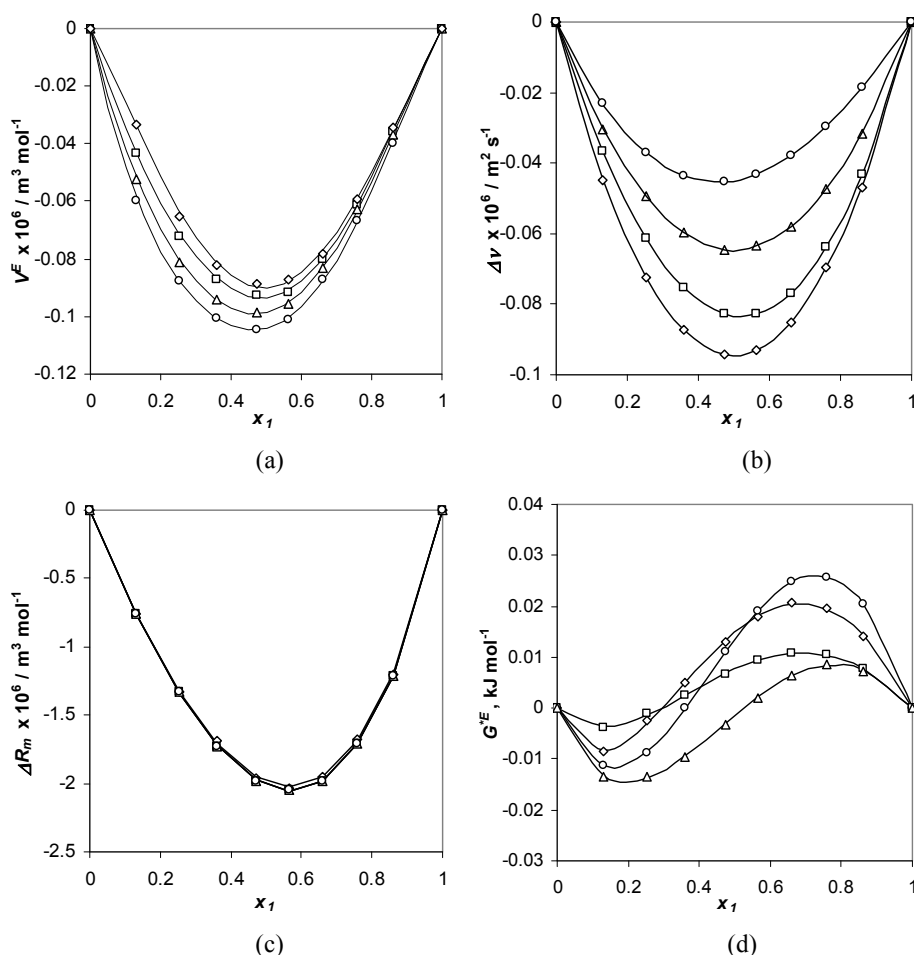


Fig. 1. Excess molar volumes (a), viscosity deviations (b), deviations in molar refraction (c) and excess Gibbs energy of activation of viscous flow (d) for the dimethyl sulfoxide (1) + *o*-xylene (2) system at 298.15 (◇); 303.15 K (□); 313.15 K (Δ); 323.15 K (○); correlation with the Redlich–Kister equation (—).

An increase of temperature diminishes the interactions in the pure components and also the interactions between unlike molecules, because of the increase in the thermal energy. This leads to less negative values of Δv with increasing temperature, as was observed in the present study.

The V^E values at 303.15 K compare well with the reported results of Wang *et al.*⁶ using the same experimental method, as is reflected in Fig. 2. There are no literature data with which to compare the values of Δv .

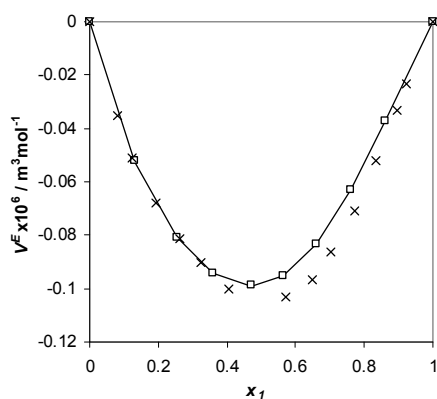


Fig. 2. Comparison of the excess molar volumes for the dimethyl sulfoxide (1) + *o*-xylene (2) system at 313.15 K: present data – □; Ref. 6 – ×; correlation with the Redlich–Kister equation: —.

The deviations in molar refraction are negative for the whole composition range for all mixtures. The values are independent of temperature, according to the theory, the molar refraction depending only on the wavelength of light used for the measurement.

From the viscosity and density data, the excess free energy of activation for viscous flow was calculated. The G^{*E} dependence with the mole fraction of DMSO and temperature is shown in Fig. 1d. For all the studied temperatures, the G^{*E} values vary from slightly negative in the *o*-xylene rich region to slightly positive with increasing DMSO mole fraction. Only a slight influence of temperature on the excess free energy of activation was observed. As suggested by other authors,^{22–23} a large negative excess in G^{*E} indicates the presence of weak interactions, whereas a large positive excess in G^{*E} suggests a specific association between the molecules in the solvent mixture. Due to the small obtained G^{*E} values (about $\pm 0.02 \text{ kJ mol}^{-1}$) for this system, it is difficult to explain the variation of G^{*E} with composition. For this purpose, non-thermodynamic information concerning the structure of the mixtures would be necessary.

A similar behavior, namely negative excess molar volumes, negative deviations in viscosity, negative deviations in molar refractivity and the same variation with temperature of the excess functions, was found in the case of the DMSO + *p*-xylene system, which was presented in a previous paper.¹

Thermodynamic functions of activation

The thermodynamic functions of activation for viscous flow were evaluated from the dynamic viscosity values of the binary mixtures considering the Eyring transition state theory. The absolute rate approach of Eyring provides the following expression for the viscosity of a liquid mixture:^{24–26}

$$\eta = \frac{h N_A}{V} \exp\left(\frac{\Delta G^*}{RT}\right) \quad (7)$$

where h is the Planck constant, N_A is Avogadro constant and ΔG^* is the molar Gibbs energy change of activation for the viscous flow process. Combining with:

$$\Delta G^* = \Delta H^* - T\Delta S^* \quad (8)$$

yields the equation:

$$\ln\left(\frac{\eta V}{h N_A}\right) = \frac{\Delta H^*}{RT} - \frac{\Delta S^*}{R} \quad (9)$$

From the experimental density and viscosity data, plots of $\ln(\eta V/hN_A)$ against $1/T$ give a straight line for each mixture and the enthalpy and entropy changes of activation of viscous flow can be estimated from its slope and intercept, respectively. The ΔH^* values are constant in the studied temperature range. The obtained thermodynamic functions of activation at 298.15 K are pre-

TABLE IV. The thermodynamic functions of the activation of viscous flow, ΔH^* , ΔS^* and ΔG^* , for the dimethyl sulfoxide (1) + *o*-xylene (2) system at 298.15 K

x_1	$\Delta H^* / \text{kJ mol}^{-1}$	$-\Delta S^* / \text{J mol}^{-1} \text{K}^{-1}$	$\Delta G^* / \text{kJ mol}^{-1}$
0.0000	8.78	54.10	-7.35
0.1320	9.47	52.22	-6.10
0.2540	10.11	50.54	-4.96
0.3602	10.61	49.27	-4.08
0.4729	11.11	48.01	-3.20
0.5640	11.51	47.01	-2.51
0.6602	11.93	45.95	-1.77
0.7602	12.38	44.80	-0.98
0.8597	12.85	43.56	-0.14
1.0000	13.59	41.55	1.20

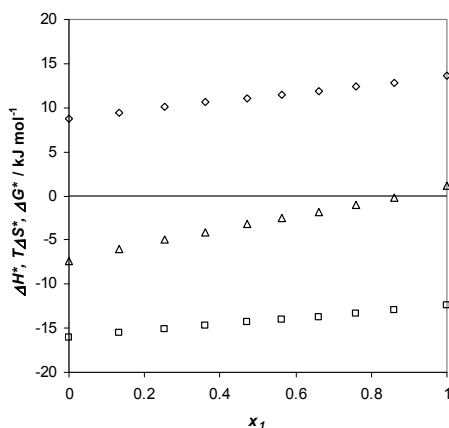


Fig. 3. Thermodynamic functions of activation vs. composition for the dimethyl sulfoxide (1) + *o*-xylene (2) system at 298.15 K; ΔH^* (\diamond); $T\Delta S^*$ (\square); ΔG^* (Δ).

sented in Table IV. The contributions of enthalpy and entropy changes to the Gibbs energy change of activation of viscous flow for dimethyl sulfoxide + *o*-xylene mixtures are shown in Fig. 3 at 298.15 K; they increase with increasing concentration of DMSO in the mixture. The same behavior was observed at all investigated temperatures. The values of ΔH^* are positive and of ΔS^* negative, indicating that the attainment of the transition state for viscous flow is accompanied by bond breaking. The entropy change of activation from the initial state to the transition at a given composition is significant during an activated viscous flow process; therefore this process is entropy-controlled for DMSO + *o*-xylene mixtures. It seems that for the viscous flow process, the structural factor dominates over the interactional one, as in the case of the mixing properties.

The viscosity data correlation

Several semi-empirical relations have been proposed to estimate the viscosity of liquid mixtures, in terms of pure component data. In the present work, the experimental viscosity data of the binary DMSO + *o*-xylene system at 298.15, 303.15, 313.15 and 323.15 K were fitted to the Grunberg–Nissan,²⁷ Hind²⁸ and McAllister²⁹ equations. According to Grunberg and Nissan, the adjustable binary parameter mentioned in Eq. (10) is regarded as a measure of the strength of the interactions between the mixing species. The single parameter correlation of Grunberg–Nissan and Hind equations are:

$$\ln \eta = \sum_i x_i \ln \eta_i + \sum_i \sum_{j>i} x_i x_j A_{ij} \quad (10)$$

$$\eta = \sum_i x_i^2 \eta_i + \sum_i \sum_{j>i} x_i x_j A_{ij} \quad (11)$$

where A_{ij} is the interaction parameter.

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

$$\ln \nu = \sum_{i=1}^n x_i^3 \ln (\nu_i M_i) - \ln \sum_{i=1}^n x_i M_i + 3 \sum_{i=1}^n \sum_{\substack{j=1 \\ j \neq i}}^n x_i^2 x_j \ln A_{ij} M_{ij} \quad (12)$$

$$M_{ij} = \frac{2M_i + M_j}{3} \quad (13)$$

where A_{ij} are the interaction parameters and M_i is the molar mass of the components. For all these models, the standard deviation, σ , was calculated using a type (6) equation.

The correlation parameters along with the average percentage deviation:

$$Dev = \frac{100}{n} \sum_{i=1}^n \frac{|\eta_i^{\text{exp}} - \eta_i^{\text{calc}}|}{\eta_i^{\text{exp}}} \quad (14)$$

and the standard deviation for the binary DMSO + *o*-xylene system at each temperature are listed in Table V.

TABLE V. Correlation deviations and adjustable parameters of the viscosity Equations for the dimethyl sulfoxide (1) + *o*-xylene (2) system

<i>T</i> / K	Grunberg–Nissan			Hind			McAllister			
	<i>A</i> _{<i>ij</i>}	σ mPa s	<i>Dev</i> %	<i>A</i> _{<i>ij</i>}	σ mPa s	<i>Dev</i> %	<i>A</i> _{<i>ij</i>}	<i>A</i> _{<i>ji</i>}	$\sigma \times 10^6$ m ² s ⁻¹	<i>Dev</i> %
298.15	-0.1120	0.0020	0.14	1.0114	0.0093	0.60	1.4373	1.0896	0.0009	0.06
303.15	-0.1251	0.0005	0.04	0.9391	0.0099	0.70	1.3139	1.0227	0.0003	0.02
313.15	-0.1378	0.0013	0.11	0.8146	0.0065	0.53	1.1280	0.8860	0.0004	0.03
323.15	-0.1126	0.0024	0.24	0.7260	0.0030	0.28	0.9957	0.7823	0.0003	0.03

The analysis showed that all the equations present small deviations, less than 1 %. The theoretically based McAllister equation gives very good results, with deviations from 0.02 to 0.06 %, even though the components have different molar volumes (molar volume ratio is 1.7). The values of the Grunberg–Nissan interaction parameter are negative for this system, which suggest weak interactions between unlike molecules, which is in accordance with the excess properties analysis.

CONCLUSIONS

Experimental data of the densities, kinematic viscosities and refractive indices for the binary system DMSO + *o*-xylene at 298.15, 303.15, 313.15 and 323.15 K are reported. The calculated excess molar volumes, viscosity deviations, excess Gibbs energy of activation of viscous flow and deviations in refraction were fitted to the Redlich–Kister equation. The excess molar volumes, deviations in viscosity and deviations in molar refraction are all negative, while the excess Gibbs energy of activation of viscous flow has an S-shape allure, with positive and negative values. The temperature has a significant effect on Δv and a relatively slight effect on V^E , ΔR_m and G^{*E} .

The moderate negative excess molar volumes and negative Δv values suggest that the geometrical fitting of the molecules is more important than the interactional factor for this system. The thermodynamic functions of activation for the viscous flow process indicate that this process is entropy-controlled. The Grunberg–Nissan, Hind and McAllister equations are suitable for estimating the mixing viscosities in terms of the pure component data.

NOMENCLATURE

A_k – Redlich–Kister parameters

- A_{ij} – Interaction parameters
 Dev – Average percentage deviation
 G^{*E} – Excess Gibbs energy of activation of viscous flow
 ΔG^* – Gibbs energy change of activation of viscous flow
 h – Planck constant
 ΔH^* – Enthalpy change of activation of viscous flow
 m – Number of model parameters
 M_i – Molar mass of the i -th pure component
 n – Number of experimental points
 N_A – Avogadro constant
 n_D – Refractive index
 ΔR_m – Deviation in molar refraction
 R_m – Molar refraction of mixture
 R_i – Molar refraction of the i -th pure component
 R – The gas constant
 ΔS^* – Entropy change of activation of viscous flow
 T – Absolute temperature
 V^E – Excess molar volume
 V – Molar volume of mixture
 V_i – Molar volume of the i -th pure component
 x_i – Liquid-phase mole fractions

Greek letters

- μ – Dipole moment
 η, ν – Dynamic and kinematic viscosity of the mixture, respectively
 η_i, ν_i – Dynamic and kinematic viscosity of the i -th pure component
 $\Delta \nu$ – Viscosity deviation
 ρ – Density
 σ – Standard deviation
 φ_i – Volume fraction.

ИЗВОД

ГУСТИНА, ВИСКОЗНОСТ И ИНДЕКС РЕФРАКЦИЈЕ СИСТЕМА
ДИМЕТИЛ СУЛФОКСИД + *o*-КСИЛЕН

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У раду су приказани експериментални подаци за густине, вискозности и индексе рефракције на температурама од 298,15 до 323,15 К система диметил сулфоксид + *o*-ксилен за комплетан опсег састава смеше. Вишак моларне завремице, одступање вискозности, вишак Gibbs-ове енергије вискозног течења и одступање индекса рефракције израчунати су на основу експерименталних података; израчунате вредности фитоване су Redlich–Kister једначином. Систем показује умерено негативно одступање вишкова испитиваних величина. Резултујуће функције вишкова тумачене су са становишта структурних промена и интеракције компоненти. На основу експерименталних података одређене су термодинамичке функције за активацију вискозног течења. Подаци за вискозност корелисани су са неколико полуемиријских једначина. Двопараметарска McAllister једначина може да да веома добра слагања.

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REFERENCES

1. O. Ciocirlan, O. Iulian, *J. Serb. Chem. Soc.* **73** (2008) 73
2. J. A. Dean, *Lange's Handbook of Chemistry*, McGraw-Hill, New York, 1956
3. D. Patterson, *J. Solution Chem.* **23** (1994) 105
4. M. I. Aralaguppi, T. M. Aminabhavi, S. B. Harogopad, R. H. Balundgi, *J. Chem. Eng. Data* **37** (1992) 298
5. A. Ali, A. K. Nain, D. Chand, R. Ahmad, *Bull. Chem. Soc. Jpn.* **79** (2006) 702
6. H. Wang, W. Liu, J. Huang, *J. Chem. Thermodyn.* **36** (2004) 743
7. J. A. Riddick, W. B. Bunger, T. K. Sakano, *Techniques of Chemistry. Vol. II, Organic Solvents*, 4th Ed., Wiley, 1986
8. R. D. Peralta, R. Infante, G. Cortez, J. Wisniak, *J. Solution Chem.* **34** (2004) 515
9. K. Rubini, R. Francesconi, A. Bigi, F. Comelli, *Thermochim. Acta* **452** (2007) 124
10. N. G. Tsierkezos, A. E. Kelarakis, M. A. Palaiologou, *J. Chem. Eng. Data* **45** (2000) 395
11. D. J. Pruet, L. K. Felker, *J. Chem. Eng. Data* **30** (1985) 452
12. L. Serrano, J. A. Silva, F. Farelo, *J. Chem. Eng. Data* **35** (1990) 288
13. T. E. Daubert, R. P. Danner, *Technical data book-petroleum refining*, 5th Ed., American Petroleum Institute, Washington, D.C., 1992-extant, in: DIPPR AIChE, 2005
14. M. Georgios, R. Christos, R. George, *J. Chem. Eng. Data* **44** (1999) 1187
15. C. Yang, P. Ma, Q. Yhou, *J. Chem. Eng. Data* **49** (2004) 881
16. H. A Lorentz, *Theory of electrons*, Teubner, Leipzig, Germany, 1909
17. O. Redlich, A. T. Kister, *Ind. Eng. Chem.* **40** (1948) 345
18. D. V. Fenby, G. B. Billing, D. B. Smythe, *J. Chem. Thermodyn.* **5** (1973) 49
19. E. I. Shcherbina, A. E. Tenenbaum, L. L. Gurarii, *Russ. J. Phys. Chem.* **49** (1975) 450
20. A. Pal, H. Kumar, *Fluid Phase Equilib.* **181** (2001) 17
21. R. Fort, W. R. Moore, *Trans. Faraday Soc.* **62** (1966) 1112
22. B. Sathyanarayana, B. Ranjithkumar, T. S. Jyostna, N. Sathyanarayana, *J. Chem. Thermodyn.* **39** (2007) 16
23. A. S. Al-Jimaz, J. A. Al-Kandary, A.-H. Al-Latif, *Fluid Phase Equilib.* **218** (2004) 247
24. H. Eyring, M. S. John, *Significant Liquid Structure*, Wiley, New York, 1969
25. R. J. Martins, M. J. E. de M. Cardoso, O. E. Barcia, *Ind. Eng. Chem. Res.* **39** (2000) 849
26. A. Ali, A. K. Nain, S. Hyder, *J. Indian Chem. Soc.* **75** (1998) 501
27. L. Grunberg, A. H. Nissan, *Nature* **164** (1949) 799
28. R. K. Hind, E. McLaughlin, A. R. Ubbelohde, *Trans. Faraday Soc.* **56** (1960) 328
29. R. A. McAllister, *AIChE J.* **6** (1960) 427.