EXCESS PROPERTIES IN DIMETHYL SULFOXIDE + 1-BUTANOL AND 1,4-DIOXANE+1-BUTANOL BINARY MIXTURES AT 298.15 K

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În lucrare sunt raportate densităţi şi viscozităţi pentru sistemele binare dimetilsulfoxid+1-butanol şi 1,4-dioxan+1-butanol în funcţie de compoziţie la temperatura de 298.15 K. Din datele experimentale s-au calculat volumul molar de exces, V^E, deviaţia în viscozitate, $\Delta\nu$, şi energia Gibbs de exces de activare a curgerii viscoase, G^{*E}. Apoi valorile calculate s-au fitat cu ajutorul ecuaţiei Redlich-Kister.

Ambele sisteme prezintă valori pozitive pentru V^E şi negative pentru $\Delta\nu$ şi G^{*E} pe întreg domeniul de compoziţii. Funcţiile de exces calculate au fost analizate în termeni de interacţii moleculare între componenţii amestecului. Datele de viscozitate au fost corelate cu ecuaţiile Grunberg-Nissan, Soliman şi McAllister.

In this paper densities and viscosities of the binary systems dimethyl sulfoxide+1-butanol and 1,4-dioxane+1-butanol have been reported as function of composition at 298.15 K. The excess molar volumes, V^E, viscosity deviation, $\Delta\nu$, and excess Gibbs energy of activation of viscous flow, G^{*E}, were calculated from experimental data. Then the computed quantities were fitted to the Redlich-Kister equation.

Both systems exhibit positive deviations of V^E and negative values for $\Delta\nu$ and G^{*E} over the whole composition range. The resulting excess functions were analyzed in terms of molecular interactions between the components of the mixture. The viscosity data have also been correlated with Grunberg-Nissan, Soliman and McAllister equations.

Keywords: density, viscosity, 1-butanol, dimethyl sulfoxide, 1,4-dioxane

1. Introduction

Studies of excess function of binary liquid mixtures have considerable importance in understanding the nature of molecular interaction between unlike molecules. The study of molecular interaction in mixed solvent systems is of great

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significance owing to the practical applications of these systems in various technologies, as they provide a wide choice of solutions with appropriate properties.

Research activities of our laboratory comprise, among others, the systematic measurements of volumetric and transport properties of different organic compounds [1, 2]. This work represents a study concerning the behavior of binary systems with alkanols, and reports new data for the binary systems dimethyl sulfoxide+1-butanol and 1,4-dioxane+1-butanol at 298.15 K and atmospheric pressure. Knowledge of the solution properties of these mixtures will be an important step in providing a better understanding of many chemical and biological processes in these media.

Dimethyl sulfoxide (DMSO) was particularly chosen because of its wide range of applicability as a solvent. DMSO is a highly associated solvent, which forms polymer chains by interaction between its sulphur and oxygen atoms. DMSO exhibits also dipole-dipole interactions in the pure state because of its fairly high dipole moment (μ=4.30 D). The alkanols are self-associated solvents through hydrogen bonds, and 1,4-dioxane is an unassociated and non-aprotic solvent.

The excess molar volumes, V^E, viscosity deviation, $\Delta\nu$, and excess Gibbs energy of activation of viscous flow, G^{*E}, were calculated from experimental data. The computed quantities were fitted to the Redlich-Kister type polynomial equation to derive the binary coefficients and estimate the standard deviations between experimental and calculated results. The viscosity data have been correlated with Grunberg-Nissan, Soliman and McAllister semiempirical equations.

In literature volumetric and transport properties for the binary systems DMSO+1-butanol [3-7] and 1,4-dioxane+1-butanol [8-11] were reported.

2. Experimental

Chemicals used in the experimental determination of the studied properties were supplied by Merck (dimethyl sulfoxide having a purity of 99.8%, 1,4-dioxane, and 1-butanol with a purity of 99.5%). They were used without further purification. Experimental density and viscosity of the pure components are in agreement with the literature values, as Table 1 shows.

Table 1

Densities and viscosities of pure components at 298.15

Compound	ρ, (g·cm^{-3})		η, (mPa·s)	
	experimental	literature	experimental	literature
dimethyl sulfoxide	1.09770	1.0962 [12]	1.9801	
1,4-dioxane	1.02760	1.02772 [8]	1.1925	1.196 [11]
1-butanol	0.80550	0.80554 [8] 0.80564 [10]	2.5516	2.564 [11]

All mixtures were prepared by weighing the appropriate volumes of liquids in airtight stoppered glass bottle. The experimental uncertainty in mole fractions was estimated to be less than ±0.0002. Densities of pure liquids and of mixtures were measured using an Anton Paar DMA 4500 densitometer with a precision of ±0.00005 g·cm^{-3}. The uncertainty in excess molar volume values was ±10^{-2} cm^3 mol^{-1}.

The kinematic viscosity $\nu\,(= \eta/\rho)$ of pure solvents and their mixture were measured with an Ubbelohde viscometer; the uncertainty in the kinematic viscosity was ±0.001 mPa·s. All measurements were performed in a thermostat maintained at desired temperature with accuracy of ± 0.05 K. The corresponding uncertainty in the kinematic viscosity is ± 0.001·10^{-6} m^2·s^{-1}.

3. Results and Discussions

The obtained experimental data of density and viscosity for the binary systems dimethyl sulfoxide+1-butanol and 1,4-dioxane+1-butanol at 298.15 K are shown in Table 2.

On the basis of experimental data, the corresponding excess properties were calculated as follows:

Excess molar volumes (V^E):

$$V^E = \sum X_i M_i \left(\rho^{-1} - \rho_i^{-1}\right) \tag{1}$$

where X_i is the mole fraction of component i of the mixture; ρ is the density of the mixture; M_i, ρ_i are the molar mass and density of the pure compounds, respectively.

The viscosity deviation ($\Delta\eta$):

$$\Delta\eta = \eta - \sum X_i \eta_i \tag{2}$$

where η and η_i are the dynamic viscosity of the mixture, and of the pure component i, respectively.

Excess Gibbs energy of activation of viscous flow (G^{*E}):

$$G^{*E} = RT\left[ln(V\eta) - \sum x_i \, ln(V_i\eta_i)\right] \tag{3}$$

where V and V_i are the molar volume of the mixture and of the pure components, respectively. R is the gas constant and T, the absolute temperature.

The excess properties data, Y^E, were correlated with Redlich – Kister equation:

$$Y^E = X_i X_j \sum_{k=0}^{p} A_k \left(X_i - X_j\right)^k \tag{4}$$

where A_k are the fitting parameters and p is the degree of polynomial expansion.

The standard deviation was defined:

$$\sigma = \left[\frac{\sum (Y_i^{exp} - Y_i^{calc})^2}{N_{exp} - N_{par}}\right]^{0.5} \tag{5}$$

where N_{exp} is the number of experimental data and N_{par} is the number of parameters.

The fitting parameters A_k (Eq. (4)) together with the standard deviations σ (Eq. (5)) are gathered in Table 3. It should be noted that for studied systems three parameters were necessary for correlation to obtain optimum standard deviation.

Table 2

Densities and viscosities of the binary systems DMSO (1) + 1-butanol (2) and 1,4-dioxane (1) + 1-butanol (2) at 298.15K

X_1	ρ, (g·cm^{-3})	η, (mPa·s)	X_1	ρ, (g·cm^{-3})	η, (mPa·s)
DMSO (1) + 1-butanol (2)			1,4-dioxane (1) + 1-butanol (2)		
0.1052	0.82851	2.2197	0.0887	0.82319	2.1650
0.2443	0.86133	1.9331	0.2112	0.84819	1.7329
0.3566	0.89025	1.8071	0.3146	0.86980	1.4789
0.4630	0.91965	1.7568	0.4166	0.89164	1.3114
0.5640	0.94935	1.7573	0.5171	0.91367	1.2123
0.6599	0.97918	1.7891	0.6163	0.93594	1.1646
0.7511	1.00901	1.8373	0.7142	0.95840	1.1526
0.8380	1.03877	1.8906	0.8108	0.98107	1.1621
0.9209	1.06836	1.9403	0.9060	1.00403	1.1795

(1 g·cm^{-3}= 10^{-3} kg·m^{-3})

Table 3

Parameters A_k and standard deviations of excess functions for DMSO + 1-butanol and 1,4-dioxane + 1-butanol systems

	A_0	A_1	A_2	σ
	DMSO + 1-butanol			
V^E, ($cm^3 \cdot mol^{-1}$)	0.9241	-0.9619	-0.0503	0.0046
$\Delta\eta$, (mPa·s)	-2.2368	1.7843	-0.1693	0.0009
G^{*E}, ($J \cdot mol^{-1}$)	-2.7410	0.2535	0.3722	0.0046
	1,4-dioxane + 1-butanol			
V^E, ($cm^3 \cdot mol^{-1}$)	1.0651	0.0791	0.1730	0.0041
$\Delta\eta$, (mPa·s)	-5.1119	-2.9213	1.5793	0.0336
G^{*E}, ($J \cdot mol^{-1}$)	-5.1579	-5.4890	-1.8012	0.0532

($1\ cm^3 \cdot mol^{-1} = 10^{-6}\ m^3 \cdot mol^{-1}$)

The viscosity data have been correlated using semiempirical or theoretical-based models of Grunberg-Nissan (eq. (6)), Soliman (eq. (7)), and McAllister (eq. (8)), with one or two adjustable parameters.

$$ln\,\eta = X_1\, ln\,\eta_1 + X_2\, ln\,\eta_2 + X_1 X_2 G_{12} \tag{6}$$

According to Grunberg and Nissan [13], the adjustable binary parameter, G_{12}, is regarded as measure of the strength of interactions between the mixing species.

McAllister's two-parameter equation [14], 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.

$$\begin{aligned} \ln\nu = {} & X_1^3 \ln\nu_1 + X_2^3 \ln\nu_2 + 3X_1^2 X_2 \ln\nu_{12} + 3X_2^2 X_1 \ln\nu_{21} + X_1^3 \ln M_1 + \\ & + X_2^3 \ln M_2 - \ln\left(X_1 M_1 + X_2 M_2\right) + 3X_1^2 X_2 \ln M_{12} + 3X_1 X_2^2 \ln M_{21} \\ & M_{12} = \left(2M_1 + M_2\right)/3 \qquad M_{21} = \left(M_1 + 2M_2\right)/3 \end{aligned} \tag{7}$$

where ν and ν_i are the kinematic viscosity of the mixture and pure components, respectively.

The data were also correlated with a modified form of the McAllister equation proposed by Soliman [15], using the form with two-parameters.

$$ln\,\nu = X_1^3\, ln\,\nu_1 + X_2^3\, ln\,\nu_2 + 3X_1^2 X_2\, ln\, A_{12} + \frac{\nu_{12} X_1 X_2}{\left(\frac{M_1}{M_2}\right)^2 X_1 + X_2} \tag{8}$$

For all these models the standard deviation (σ) was calculated using type (5) equation. The correlation parameters and standard deviation are presented in Table 4.

The binary systems DMSO + 1-butanol and 1,4-dioxane +1-butanol show positive deviations of V^E, and negative values for $\Delta\nu$ and G^{*E} over the whole composition range, as figures 1-3 show. The values of V^E and $\Delta\nu$ functions correspond well with literature [3, 11].

Experimental findings and literature survey reveals that for DMSO + 1-butanol system the effect due to the breaking up of self-associated structures of the pure compounds is dominant over effect of hydrogen bonding and dipole–dipole interaction between unlike molecules.

Positive values of excess molar volume for the 1,4-dioxane + 1-butanol system also indicate that the positive contributions from the breaking up of alcohol agglomerates and ether–ether interactions dominate over the negative contribution resulting from heteromolecular interaction.

Table 4

Adjustable parameters and standard deviation of the Grunberg-Nissan, Soliman and McAllister equations

	Equation	Parameters / σ	
DMSO + 1-butanol	Grunberg-Nissan	G_{12}	-0.9633
		σ	0.0555
	Soliman	A_{12}	1.1433
		ν_{21}	1.5687
		σ	0.0115
	McAllister	ν_{12}	1.8286
		ν_{21}	1.6851
		σ	0.0118
1,4-dioxane + 1-butanol	Grunberg-Nissan	G_{12}	-1.3482
		σ	0.0250
	Soliman	A_{12}	0.8468
		ν_{21}	1.0375
		σ	0.0246
	McAllister	ν_{12}	1.0856
		ν_{21}	1.3946
		σ	0.0233

According to Fort and Moore [16], negative values of excess viscosity are observed for the systems of different molecular size in which the dispersion forces are dominant. Negative excess in G^{*E} also indicates that dispersion forces are prevailing in mixtures, as suggested by other authors [17, 18]. Thus, the observed variation with composition of $\Delta\nu$ and G^{*E} suggest that dispersion forces are operative between unlike molecules of the investigated binary mixtures.

The viscosity data have been correlated with semi-empirical equations of Grunberg-Nissan, Soliman and McAllistar. For both studied systems, the values of the Grunberg-Nissan interaction parameters are negative, which suggest weak interactions between unlike molecules, which is in accordance with the excess properties analysis. The equations used for viscosity correlation present small deviations, less than 0.1, with very good results for theoretical based McAllister and Soliman equations for DMSO + 1-butanol system.

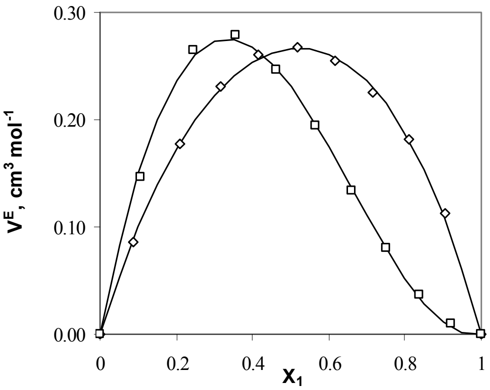

Fig. 1 Excess molar volumes, V^E, at 298.15K for the binary systems: (◊), 1,4-dioxane (1) +1-butanol (2) and (□), DMSO (1)+ 1-butanol (2)

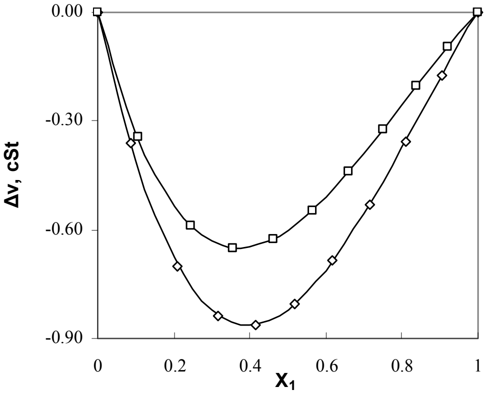

Fig. 2 Deviations of viscosities, Δν, at 298.15K for the binary systems: (◊), 1,4-dioxane (1) +1-butanol (2) and (□), DMSO (1)+ 1-butanol (2)

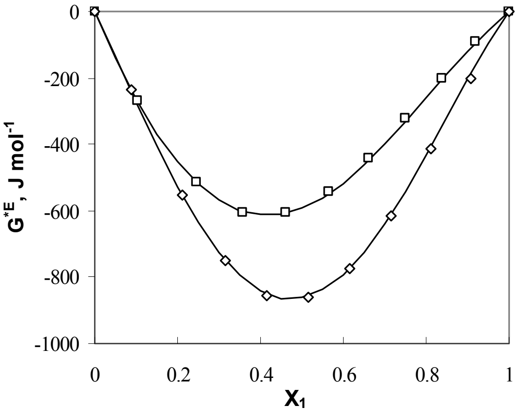

Fig. 3 Excess Gibbs energy of activation of viscous flow, G^{*E}, at 298.15K for the binary systems: (◊), 1,4-dioxane (1) +1-butanol (2) and (□), DMSO (1)+ 1-butanol (2)

4. Conclusions

New experimental data of densities and kinematic viscosities for the binary systems DMSO + 1-butanol and 1,4-dioxane + 1-butanol at 298.15 K have been reported. The obtained excess molar volumes are all positive and deviations in viscosity and excess Gibbs energy of activation of viscous flow, G^{*E}, are negative over the whole composition range. This suggests that breaking up of self-associated structures of the pure compounds is dominant over the hydrogen bonding and dipole–dipole interaction between unlike molecules.

For the studied systems the negative values of the Grunberg-Nissan parameters are in accordance with the excess properties analysis.

The Grunberg-Nissan, Soliman and McAllister equations are suitable to estimate the mixing viscosities in terms of the pure component data.

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