



## DENSITY AND REFRACTIVE INDICES OF DIMETHYL SULFOXIDE + 1-HEXANOL SYSTEM AT TEMPERATURES FROM (298.15 TO 323.15) K

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Densities and refractive indices of the binary system dimethyl sulfoxide + 1-hexanol have been measured at  $T = (298.15, 303.15, 313.15 \text{ and } 323.15 \text{ K})$  and atmospheric pressure, over the whole composition range. From these experimental data, excess molar volumes, ( $V^E$ ), molar refractions ( $R$ ) and deviations in molar refraction ( $\Delta R$ ) have been calculated and the excess properties have been fitted to the Redlich-Kister polynomial equation. The system exhibits positive values for  $V^E$  and negative values for  $\Delta R$  over the whole composition range at all investigated temperatures. The experimental results have been used to test the applicability of the Prigogine-Flory-Patterson theory. The resulting excess functions were analyzed in terms of molecular interactions between the components of the mixture.

### INTRODUCTION

The study of molecular interaction in mixed solvent systems is of great significance owing to the practical applications of these systems in various technologies, as they provide a wide choice of solutions with appropriate properties. Excess functions are of considerable importance for understanding the nature of molecular interaction. The negative or positive deviation from the ideal value depend on the type and the extent of the interactions between the unlike molecules, as well as, on the composition and the temperature.

This paper is a continuation of our earlier work on properties and excess properties of nonelectrolyte liquid mixtures.<sup>1-3</sup>

Dimethyl sulfoxide (DMSO) and  $n$ -alcohols are important solvents in chemistry owing to their miscibility with almost all common polar and nonpolar solvents, resulting from their wide application in industrial and medical fields. DMSO is a typical aprotic self-associated solvent due to S=O group, with large dipole moment ( $\mu = 3.96 \text{ D}$  at 298.15 K) and 1-hexanol is a self-associated

solvent through hydrogen bonding, with relatively low values of dipole moment. A deeper knowledge of the solution properties of DMSO + 1-hexanol mixtures will be important in providing a better understanding of many chemical and biological processes in these media.

Volumetric properties of binary mixtures of DMSO with 1-hexanol have also been studied by Ali *et al.*<sup>4</sup> only at 303.15 K; no literature data at other temperatures are available for this system.

### EXPERIMENTAL

**Materials.** Dimethyl sulfoxide and 1-hexanol (Merck, purities > 99.5% in mole fraction) were used without further purification. Experimental densities,  $\rho$ , and refractive indices,  $n_D$ , of the pure components are in agreement with the literature values, as can be seen in Table 1.

**Apparatus and procedure.** All mixtures were prepared by mixing the appropriate volumes of liquids in airtight glass bottle and weighed using a HR-120 (A&D Japan) electronic balance with a precision of 0.1 mg. The experimental uncertainty in mole fraction was estimated to be less than  $\pm 0.0002$ . Densities of pure liquids and of mixtures were measured using an Anton Paar DMA 4500 densitometer with a

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precision of  $\pm 5 \cdot 10^{-5} \text{ g} \cdot \text{cm}^{-3}$ . The uncertainty in  $V^E$  calculation is less than  $\pm 10^{-2} \text{ cm}^3 \text{ mol}^{-1}$ .

Refractive indices values for the D-line were measured with a thermostated Abbe refractometer with a precision of  $\pm 0.0001$ . All

measurements were performed in a thermostat with the temperature kept constant with a precision of  $5 \cdot 10^{-2} \text{ K}$ .

Table 1

Densities, dynamic viscosities and refractive indices of pure components at 298.15 K

Compound	$\rho, \text{ g cm}^{-3}$		$n_D$	
	Exp.	Lit.	Exp.	Lit.
Dimethyl sulfoxide	1.09536	1.09533 <sup>5</sup> , 1.095278 <sup>6</sup>	1.4778	1.4770 <sup>7</sup>
1-hexanol	0.81513	0.81494 <sup>8</sup> , 0.81523 <sup>9</sup>	1.4163	1.4154 <sup>9</sup> , 1.4161 <sup>10</sup>

## RESULTS AND DISCUSSION

The experimental data of density and refractive index obtained at  $T = (298.15, 303.15, 313.15 \text{ and } 323.15 \text{ K})$  for the binary system DMSO (1) + 1-hexanol (2) are shown in Table 2.

The molar refraction,  $R$ , can be defined from refractive index and molar volume,  $V$ , of the mixture as:

$$R = \frac{n_D^2 - 1}{n_D^2 + 2} V \quad (1)$$

The values of excess molar volume,  $V^E$ , and deviation in molar refraction,  $\Delta R$ , were calculated

from the experimental data according to the following equations:

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

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

where  $X_i$  and  $\varphi_i$  represent the mole fraction and volume fraction of pure component  $i$ , respectively; and  $V_i$ ,  $R_i$ , are the molar volume and molar refraction of the pure component  $i$ , respectively.

Table 2

Densities and refractive index for the DMSO (1)+1-hexanol (2) system at different temperatures

$X_1$	$\rho, \text{ g} \cdot \text{cm}^{-3}$	$n_D$	$X_1$	$\rho, \text{ g} \cdot \text{cm}^{-3}$	$n_D$
<b>298.15 K</b>			<b>303.15 K</b>		
0.0000	0.81513	1.4163	0.0000	0.81155	1.4149
0.1115	0.83303	1.4200	0.1115	0.82934	1.4182
0.2124	0.85092	1.4239	0.2124	0.84712	1.4222
0.3032	0.86863	1.4278	0.3032	0.86474	1.4258
0.3919	0.88768	1.4318	0.3919	0.88368	1.4299
0.5036	0.91455	1.4374	0.5036	0.91040	1.4358
0.6043	0.94202	1.4432	0.6043	0.93774	1.4415
0.6983	0.97103	1.4497	0.6983	0.96661	1.4481
0.8008	1.00712	1.4580	0.8008	1.00252	1.4562
0.8983	1.04691	1.4669	0.8983	1.04212	1.4651
1.0000	1.09536	1.4778	1.0000	1.09033	1.4758
<b>313.15</b>			<b>323.15</b>		
0.0000	0.80429	1.4110	0.0000	0.79688	1.4067
0.1115	0.82189	1.4141	0.1115	0.81435	1.4100
0.2124	0.83949	1.4188	0.2124	0.83177	1.4135
0.3032	0.85691	1.4219	0.3032	0.84902	1.4181
0.3919	0.87566	1.4258	0.3919	0.86758	1.4219
0.5036	0.90210	1.4314	0.5036	0.89376	1.4275
0.6043	0.92917	1.4376	0.6043	0.92056	1.4332
0.6983	0.95775	1.4439	0.6983	0.94888	1.4392
0.8008	0.99332	1.4519	0.8008	0.98410	1.4471
0.8983	1.03254	1.4610	0.8983	1.02295	1.4559
1.0000	1.08028	1.4717	1.0000	1.07023	1.4665

The experimental values of  $V^E$ , and  $\Delta R$  were fitted to the Redlich-Kister type polynomials:

$$Y = X_i X_j \sum_{k=0}^p A_k (X_i - X_j)^k \quad (4)$$

where  $Y$  is  $V^E$  or  $\Delta R$  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 3, along with the standard deviation,  $\sigma$ , defined as follows:

$$\sigma = \left[ \frac{\sum_{i=1}^n (Y_i^{\text{exp}} - Y_i^{\text{calc}})^2}{n - m} \right]^{0.5} \quad (5)$$

where  $n$  is the number of experimental data and  $m$  is the number of parameters. It should be noted that for DMSO + 1-hexanol system three parameters were necessary for correlation to obtain optimum standard deviation.

The variation of the excess or deviation properties along with the smoothed curves using Eq. (4) are presented in Figs. 1-2. As can be seen from the figures, the DMSO + 1-hexanol system show positive values for  $V^E$  and negative values for deviations in molar refraction over the whole composition range at temperatures between 298.15 and 323.15 K.

Table 3

Parameters  $A_k$  and standard deviations of excess functions for DMSO + 1-hexanol system at different temperatures

	$T, \text{K}$	$A_0$	$A_1$	$A_2$	$\sigma$
$V^E, (\text{cm}^3 \cdot \text{mol}^{-1})$	298.15	1.3507	0.2690	0.0037	0.0018
$\Delta R, (\text{cm}^3 \cdot \text{mol}^{-1})$		-6.1589	1.6684	-0.3026	0.0066
$V^E, (\text{cm}^3 \cdot \text{mol}^{-1})$	303.15	1.3824	0.2610	-0.0025	0.0018
$\Delta R, (\text{cm}^3 \cdot \text{mol}^{-1})$		-6.1536	1.7815	-0.5204	0.0089
$V^E, (\text{cm}^3 \cdot \text{mol}^{-1})$	313.15	1.4233	0.2644	-0.0180	0.0018
$\Delta R, (\text{cm}^3 \cdot \text{mol}^{-1})$		-6.1854	1.7463	-0.3821	0.0172
$V^E, (\text{cm}^3 \cdot \text{mol}^{-1})$	323.15	1.4375	0.2897	-0.0582	0.0023
$\Delta R, (\text{cm}^3 \cdot \text{mol}^{-1})$		-6.0924	1.6404	-0.6271	0.0187

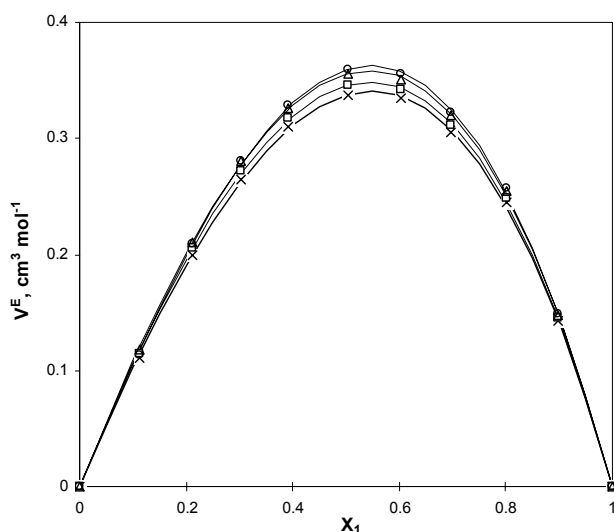


Fig. 1 – Excess molar volumes for DMSO (1) + 1-hexanol (2) system at 298.15 K (×); 303.15 K (□); 313.15 K (Δ); 323.15 K (o); correlation with Redlich-Kister equation (—).

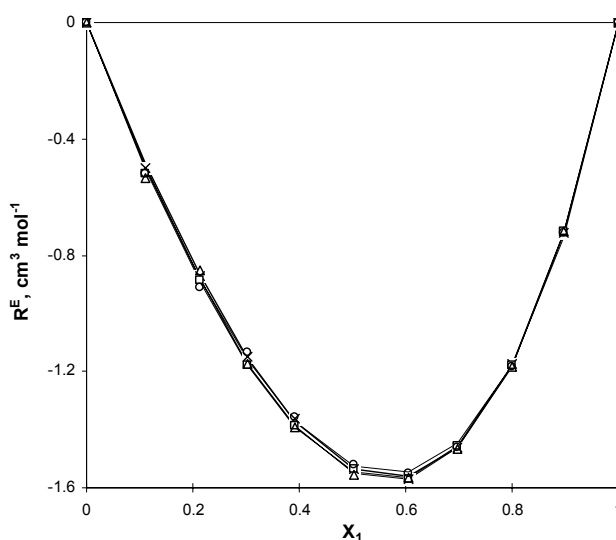


Fig. 2 – Deviations in molar refraction for DMSO (1) + 1-hexanol (2) system at 298.15 K (×); 303.15 K (□); 313.15 K (Δ); 323.15 K (o); correlation with Redlich-Kister equation (—).

The excess molar volumes values are moderate positive and become slightly more positive as the temperature of the mixtures increases from 298.15 K to 323.15 K. For DMSO + 1-hexanol system this behavior indicate that the effect of disruption of alkanol multimers and weakening of interactions between DMSO molecules is dominant over the combined effects of H-bonding and dipole-dipole interactions between unlike molecules. This is in accordance/correlated with the negative values of viscosity deviations obtained for this system,<sup>11</sup> which indicate weak intermolecular interactions between components.

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

All the obtained excess or deviation properties are in accordance with those reported in literature<sup>4</sup> at 303.15 K.

$$\frac{V_{PPF}^E}{X_1V_1^* + X_2V_2^*} = V_{int}^E + V_{fv}^E + V_{ip}^E = \frac{(\tilde{v}^{1/3} - 1)\tilde{v}^{2/3}\Psi_1\theta_2\chi_{12}}{[(4/3)\tilde{v}^{-1/3} - 1]P_1^*} - \frac{(\tilde{v}_1 - \tilde{v}_2)^2((14/9)\tilde{v}^{-1/3} - 1)\Psi_1\Psi_2}{[(4/3)\tilde{v}^{-1/3} - 1]\tilde{v}} + \frac{(\tilde{v}_1 - \tilde{v}_2)(P_1^* - P_2^*)\Psi_1\Psi_2}{P_2^*\Psi_1 + P_1^*\Psi_2} \quad (6)$$

where  $\tilde{v}_i$  and  $\tilde{v}$  are the reduced volume of pure components and mixtures, respectively,  $V_i^*$  is the characteristic volume, and  $P_i^*$  is the characteristic pressure of pure components; they are obtained from thermal expansion coefficient,  $\alpha$ , and isothermal compressibility,  $k_T$ . In Eq. (6),  $\Psi_i$  is the molecular contact energy fraction and  $\theta_2$ , the molecular surface fraction. The various characteristic and reduced parameters of pure liquids needed for

The  $V^E$  behavior of DMSO + 1-hexanol system can be predicted and correlated using the Prigogine-Flory-Patterson (PFP) theory, which has been widely used to analyze the excess thermodynamic properties for different kinds of mixtures. The PFP theory considers the  $V^E$  of binary mixtures to be the sum of three contributions: (i) the interactional contribution, which is proportional to the only interaction parameter,  $\chi_{12}$ ; (ii) the free volume contribution, which arises from the dependence of the reduced volume upon the reduced temperature as a result of the difference between the degree of expansion of the two components; and (iii) the internal pressure contribution, which depends both on the differences of internal pressures and on the differences of reduced volumes of the components and can be related to the structure-breaking effect on mixing.

In the present study, the following equation form has been used to estimate  $V^E$  values according with PFP theory:

the  $V^E$  estimation were calculated by using the expressions given in literature<sup>12-15</sup> and are listed in Table 4.

The experimental and calculated  $V^E$  using PFP model and three PFP contributions for near equimolar composition at 298.15, 303.15, 313.15 and 323.15 K are summarized in Table 5 and suggestively reflected in Fig. 3 at 298.15 K.

Table 4

Physico-chemical data of pure components used in Flory and PFP theories at 298.15K

	$\alpha$ K <sup>-1</sup>	$k_T$ cm <sup>3</sup> J <sup>-1</sup>	$\tilde{v}_i$	$V_i$ cm <sup>3</sup> mol <sup>-1</sup>	$V_i^*$ cm <sup>3</sup> mol <sup>-1</sup>	$P_i^*$ J cm <sup>-3</sup>	$\tilde{T}_i$
DMSO	0.000887 <sup>a</sup>	0.00052193 <sup>a</sup>	1.2241	71.31	58.25	759.20	0.05324
1-hexanol	0.000916	0.0008519 <sup>b</sup>	1.2302	125.35	101.90	485.19	0.05425

<sup>a</sup> from ref. 16. <sup>b</sup> estimated from ref. 17.

Table 5

Experimental and calculated  $V^E$  and three PFP contributions for near equimolar composition at different temperatures

T, K	$V_{\text{exp}}^E$ $\text{cm}^3 \text{mol}^{-1}$	$V_{\text{PFP}}^E$ $\text{cm}^3 \text{mol}^{-1}$	$V_{\text{int}}^E$ $\text{cm}^3 \text{mol}^{-1}$	$V_{\text{fv}}^E$ $\text{cm}^3 \text{mol}^{-1}$	$V_{\text{ip}}^E$ $\text{cm}^3 \text{mol}^{-1}$	$\chi_{12}$ $\text{J cm}^{-3}$	$\sigma$ $\text{cm}^3 \text{mol}^{-1}$
298.15	0.337	0.340	0.394	-0.001	-0.053	38.7	0.023
303.15	0.346	0.347	0.403	-0.001	-0.055	39.7	0.022
313.15	0.356	0.357	0.419	-0.001	-0.061	40.8	0.025
323.15	0.360	0.359	0.424	-0.001	-0.065	41.3	0.028

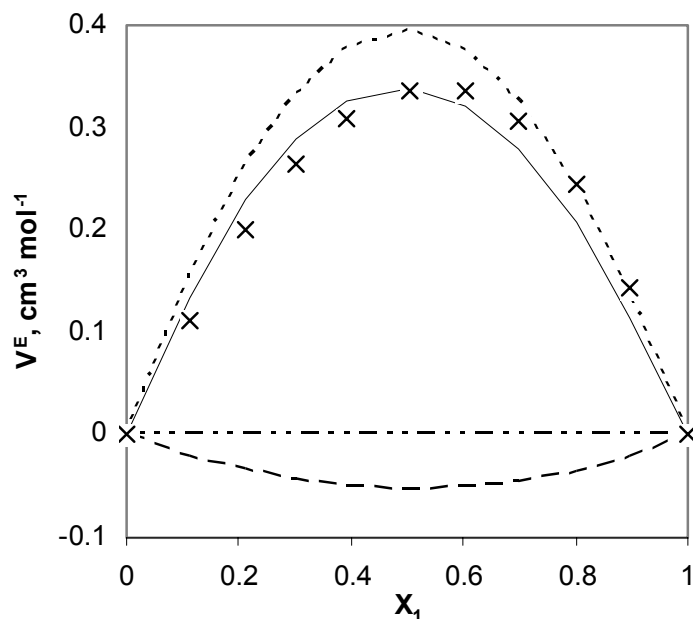


Fig. 3 – Excess molar volumes for DMSO (1) + 1-hexanol (2) system at 298.15 K calculated with the PFP theory: interactional contribution (---); free volume contribution (-.-.-); internal pressure contribution (- -); total excess molar volume predicted by PFP theory (—).

The interactional parameter  $\chi_{12}$  was evaluated, fitting the experimental  $V^E$  values to Eq. (6) and using the least-squares method over the whole composition range; the obtained values are indicated also in Table 5, together with standard deviation,  $\sigma$ , calculated using type (5) equation.

A perusal of the Table 5 reveals that the interactional contribution has positive values; also the interactional parameter  $\chi_{12}$  is positive, increasing when temperature increases. In the original PFP theory the  $V_{\text{int}}^E$  is generally positive in the absence of a H-bond and other specific interactions. This is indeed the case for DMSO + 1-hexanol mixture, as was stated above to the  $V^E$  analysis. Since the  $V_{\text{int}}^E$  term is dominant in  $V^E$ , these values are positive. Internal pressure contributes negatively to the  $V_{\text{PFP}}^E$  values,

decreasing when temperature increases. It is also clear from Table 5 that the contribution due to free volume,  $V_{\text{fv}}^E$  does not seem to play a dominant role in deciding the sign and magnitude of the excess molar volume.

## CONCLUSIONS

New experimental data of densities and refractive indices for the binary systems DMSO + 1-hexanol at 298.15, 303.15, 313.15 and 323.15 K have been reported. The obtained excess molar volumes are all positive. 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.

The PFP theory has a good performance in predicting excess molar volumes of mixtures of DMSO + 1-hexanol, despite using only one fitting parameter. The interactional contribution has positive values and represent the most significant term in the  $V^E$  values; internal pressure contributes negatively to the  $V_{PFP}^E$  values. The analysis of relative contributions suggests the absence of H-bond and other specific interactions in the mixtures.

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