

# DENSITIES AND DERIVED PROPERTIES OF WATER, 1,4-DIOXANE AND DIMETHYL SULFOXIDE BINARY AND TERNARY SYSTEMS AT TEMPERATURES FROM 293.15 K TO 313.15 K

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Excess molar volumes ( $V^E$ ) and excess partial molar volumes ( $\bar{V}_i^E$ ) of the binary systems: water+1,4-dioxane, 1,4-dioxane+dimethyl sulfoxide, water+dimethyl sulfoxide and of the corresponding ternary system water+1,4-dioxane+dimethyl sulfoxide have been evaluated from experimental density at five temperatures ranging from 293.15 K to 313.15 K. For all binary mixtures, the experimental data were correlated with Redlich-Kister's equation. For ternary system, the excess molar volume was estimated by correlative and predictive (symmetrical and asymmetrical) methods and the results were compared. The calculated functions have been used to explain the intermolecular interactions between the mixing components.

## INTRODUCTION

There is an increasing interest in thermodynamic behaviour of the liquid mixtures containing water and polar organic components. Generally, these mixtures are characterised by important property deviations from ideal behaviour, as for example: deviations of density, viscosity, ultrasound velocity, etc. A better understanding of molecular interactions and a better description by mixing rules of these mixtures are relevant in kinetic studies, biochemistry, organic synthesis, product design and can be further extended in industrial area, as for example, in design, simulation and process optimisation.

This paper is an extension of our studies on physico-chemical properties of the solvent mixtures. In earlier papers<sup>1-3</sup> we have reported the vapour-liquid equilibrium (VLE) measurements for the binary and ternary systems containing water, 1,4-dioxane and dimethyl sulfoxide (DMSO). For the same systems, in this work we have made an extended study of binary and ternary systems concerning the experimental data of densities as well as the calculation of the properties related to

density, excess molar volumes  $V^E$  and excess partial molar volumes  $\bar{V}_i^E$ . For this purpose we have put together previous published density data<sup>4-7</sup> and new data for binary systems. Important matters of our paper are to test the performance of several correlative and predictive (symmetrical and asymmetrical)  $V^E$  equations and to obtain property-structure correlation for the mentioned binary and ternary systems.

The presented experimental density data at five temperatures ranging from 293.15 to 313.15 K cover the whole composition range. The excess molar volumes for all binary systems were correlated with Redlich-Kister's equation. The parameters estimated for the binary systems were further used for the correlation and prediction of excess molar volumes in ternary system. Most of the experimental densities available in the literature were reported at few temperatures and only for binary systems;<sup>8-11</sup> the ternary water+1,4-dioxane+DMSO system has not been studied, except our previous published data.<sup>6</sup>

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## EXPERIMENTAL

**Materials.** The analytical reagent grade 1,4-dioxane from Merck was distilled at 374.35 K. DMSO was distilled under vacuum of 0.8-0.9 kPa at 338.65 K. The water was

bidistilled. The purity of all chemicals was checked by gas chromatography being more than 99.8 wt.% and by the measurements of the density and refractive indices. In Table 1 the values of these properties for the purified reagents are given and compared with the literature values.

Table 1

Densities and refractive indices of pure components at 298.15 K

Compound	$\rho, \text{g cm}^{-3}$		$n_D$	
	expt.	lit.	expt.	lit.
Water	0.9971	0.99705 <sup>12</sup>	1.3325	1.3325 <sup>13</sup>
Dimethyl sulfoxide	1.0957	1.0954 <sup>13</sup> , 1.09547 <sup>14</sup> 1.0956 <sup>15</sup>	1.4768	1.4768 <sup>14</sup> 1.4767 <sup>16</sup>
1,4-dioxane	1.0280	1.02797 <sup>13</sup> , 1.0280 <sup>16</sup>	1.4198	1.4194 <sup>16</sup>

**Apparatus and Procedure.** All mixtures were prepared by weighing the appropriate volumes of liquids in airtight stoppered glass bottle. The reproducibility in mole fraction was within  $\pm 0.0002$ . Densities of pure liquids and of mixtures were measured using a double-walled calibrated pycnometer having a bulb volume of 25 cm<sup>3</sup> and a capillary with an internal diameter of 1 mm. An average of triplicate measurements was considered and this was accurate to  $\pm 0.0002 \text{ g}\cdot\text{cm}^{-3}$ . The weighings were done on a HR-120 (A&D Japan) balance with a precision of  $0.1\cdot 10^{-3}$  g. Refractive indices values for the sodium D-line were measured with a thermostated Abbe refractometer with a precision of  $\pm 0.0001$ . All measurements were performed in a thermostat maintained at desired temperature with accuracy of  $\pm 0.05$  K. The uncertainty in excess molar volume values was  $\pm 10^{-2} \text{ cm}^3\cdot\text{mol}^{-1}$ .

## RESULTS AND DISCUSSION

### Binary Systems

The densities ( $\rho$ ) of all three binary systems measured at five temperatures ranging from 293.15 K to 313.15 K are shown in Table 2. The excess molar volumes ( $V^E$ ) and excess partial molar volumes of the components ( $\bar{V}_1^E, \bar{V}_2^E$ ) were calculated as follows:

$$V^E = \sum X_i M_i (\rho^{-1} - \rho_i^{\circ-1}) \quad (1)$$

$$\bar{V}_1^E = \bar{V}_1 - V_1^0 = V + X_2 \left( \frac{dV}{dX_1} \right) - V_1^0 \quad (2)$$

$$\bar{V}_2^E = \bar{V}_2 - V_2^0 = V - X_1 \left( \frac{dV}{dX_1} \right) - V_2^0 \quad (3)$$

where  $X_i$  is the mole fraction of component  $i$ ;  $\rho$ ,  $V$  are the density and molar volume of the mixture;  $M_i$ ,  $\rho_i^{\circ}$ ,  $V_i^0$ , the molar mass, density and molar volume of the pure component  $i$ , respectively,  $\bar{V}_i$ , the partial molar volumes.

The excess molar volumes calculated from density measurements were fitted by the Redlich-Kister's<sup>17</sup> expression for every binary mixture, according to the next equation:

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

where  $A_k$  are the fitting parameters and  $p$  is the degree of polynomial expansion. The standard deviations were computed using the following equation:

$$\sigma = \left[ \frac{\sum (V_{\text{exp}}^E - V_{\text{calc}}^E)^2}{N_{\text{exp}} - N_{\text{par}}} \right]^{0.5} \quad (5)$$

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

The fitting parameters  $A_k$  (Eq. (4)) together with the standard deviations  $\sigma$  (Eq. (5)), at the investigated temperatures, are gathered in Table 3. It should be noted that for 1,4-dioxane+DMSO system only two parameters were necessary for correlation to obtain optimum standard deviation.

The excess molar volumes versus mole fraction for the three binary systems at various temperatures are plotted in Fig. 1a-c.

Table 2

Densities for the binary systems at different temperatures

$X_1$	$\rho, \text{g cm}^{-3}$				
	293.15 K	298.15 K	303.15 K	308.15 K	313.15 K
Water(1)+1,4-Dioxane(2)*					
0.0000	1.0339	1.0280	1.0225	1.0172	1.0121
0.1007	1.0354	1.0294	1.0239	1.0186	1.0135
0.1995	1.0366	1.0308	1.0254	1.0200	1.0147
0.3422	1.0385	1.0328	1.0275	1.0222	1.0170
0.4256	1.0396	1.0340	1.0288	1.0236	1.0186
0.5379	1.0412	1.0357	1.0306	1.0256	1.0208
0.6640	1.0424	1.0372	1.0323	1.0275	1.0227
0.7530	1.0415	1.0368	1.0321	1.0274	1.0226
0.8197	1.0386	1.0343	1.0299	1.0255	1.0210
0.8710	1.0338	1.0298	1.0258	1.0218	1.0177
0.9130	1.0270	1.0234	1.0200	1.0166	1.0133
0.9470	1.0188	1.0158	1.0128	1.0100	1.0073
0.9760	1.0091	1.0068	1.0045	1.0022	1.0000
1.0000	0.9982	0.9971	0.9956	0.9940	0.9922
Water(1)+DMSO(2)					
0.0000	1.1012	1.0957	1.0901	1.0850	1.0804
0.0915	1.1015	1.0966	1.0924	1.0883	1.0843
0.1713	1.1021	1.0979	1.0942	1.0908	1.0873
0.2415	1.1026	1.0989	1.0956	1.0926	1.0895
0.3038	1.1028	1.0997	1.0966	1.0939	1.0910
0.3594	1.1029	1.1001	1.0972	1.0947	1.0921
0.4795	1.1019	1.0996	1.0972	1.0952	1.0930
0.5669	1.0994	1.0973	1.0953	1.0937	1.0919
0.6541	1.0941	1.0922	1.0906	1.0894	1.0881
0.7021	1.0894	1.0876	1.0861	1.0852	1.0843
0.7842	1.0769	1.0756	1.0741	1.0735	1.0730
0.8637	1.0575	1.0563	1.0550	1.0545	1.0542
0.9218	1.0370	1.0361	1.0346	1.0339	1.0333
0.9649	1.0174	1.0166	1.0150	1.0139	1.0128
1.0000	0.9982	0.9971	0.9956	0.9940	0.9922
1,4-Dioxane(1)+DMSO(2)					
0.0000	1.1012	1.0957	1.0901	1.0850	1.0804
0.0419	1.0983	1.0934	1.0880	1.0831	1.0787
0.1062	1.0939	1.0895	1.0845	1.0800	1.0759
0.2171	1.0864	1.0825	1.0781	1.0740	1.0703
0.3094	1.0801	1.0764	1.0723	1.0685	1.0649
0.4050	1.0737	1.0699	1.0660	1.0623	1.0588
0.4541	1.0704	1.0665	1.0627	1.0589	1.0554
0.5041	1.0670	1.0630	1.0592	1.0554	1.0519
0.6071	1.0601	1.0558	1.0518	1.0479	1.0442
0.7139	1.0529	1.0482	1.0440	1.0399	1.0359
0.8250	1.0455	1.0403	1.0357	1.0312	1.0268
0.9112	1.0398	1.0343	1.0292	1.0243	1.0196
0.9530	1.0370	1.0313	1.0260	1.0210	1.0161
1.0000	1.0339	1.0280	1.0225	1.0172	1.0121

\* data reported in ref. 6

Table 3

Redlich-Kister parameters,  $A_k$  and standard deviations,  $\sigma$ , in representation of  $V^E$  for the binary systems

$T, K$	$A_0$	$A_1$	$A_2$	$A_3$	$A_4$	$\sigma$
Water(1)+1,4-Dioxane(2)						
293.15	-2.5943	1.7545	-1.3001	0.3404	-0.2122	0.0016
298.15	-2.5058	1.6902	-1.5641	0.3544	0.4788	0.0012
303.15	-2.4581	1.6147	-1.4989	0.3404	0.5585	0.0011
308.15	-2.4037	1.6247	-1.1480	0.2199	0.1491	0.0007
313.15	-2.3525	1.6414	-0.6823	0.0384	-0.4206	0.0012
Water(1)+DMSO(2)						
293.15	-3.4295	1.5903	0.1123	-0.6966	0.7269	0.0002
298.15	-3.8264	1.3438	0.1426	-0.3202	0.7829	0.0013
303.15	-4.2413	1.2466	-0.1571	-0.7364	0.7666	0.0001
308.15	-4.6629	1.1830	-0.4751	-0.8016	0.8288	0.0001
313.15	-5.0063	1.1979	-0.8525	-0.7389	0.9877	0.0001
1,4-Dioxane(1)+DMSO(2)						
293.15	-0.8183					0.0011
298.15	-1.3608	-0.2454				0.0011
303.15	-1.8635	-0.2539				0.0012
308.15	-2.3273	-0.2518				0.0013
313.15	-2.7476	-0.2714				0.0013

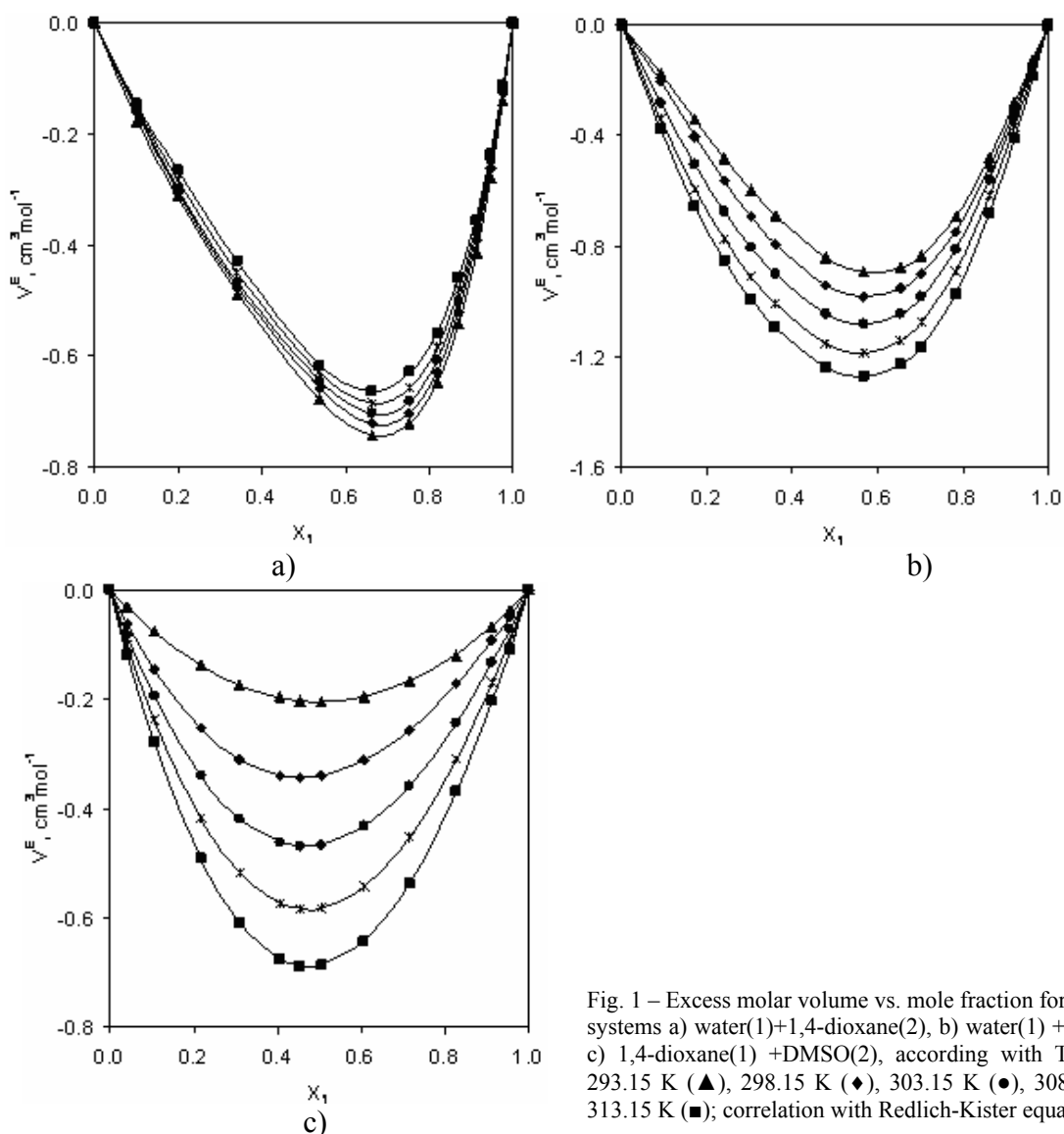


Fig. 1 – Excess molar volume vs. mole fraction for the binary systems a) water(1)+1,4-dioxane(2), b) water(1) +DMSO(2), c) 1,4-dioxane(1) +DMSO(2), according with Table 2, at 293.15 K ( $\blacktriangle$ ), 298.15 K ( $\blacklozenge$ ), 303.15 K ( $\bullet$ ), 308.15 K ( $*$ ), 313.15 K ( $\blacksquare$ ); correlation with Redlich-Kister equation (—).

All binary systems show negative deviations of  $V^E$  over the whole composition range at temperatures between 293.15 and 313.15 K. The most negative deviations are observed in the case of the binary water + DMSO system that presents the  $V^E$  minima between  $-0.85$  and  $-1.25$   $\text{cm}^3 \text{mol}^{-1}$  at the studied temperatures. The binary mixture 1,4-dioxane+DMSO shows the lowest  $V^E$  deviations with the minima between  $-0.2$  and  $-0.7$   $\text{cm}^3 \text{mol}^{-1}$ , and the binary system water+1,4-dioxane presents  $V^E$  minima between  $-0.65$  and  $-0.75$   $\text{cm}^3 \text{mol}^{-1}$ . The aqueous systems have asymmetrical curves according to  $X=0.5$  with the minimum values in the water-rich region. Our observed  $V^E$  minima values of  $-0.72$   $\text{cm}^3 \text{mol}^{-1}$  and  $-0.95$   $\text{cm}^3 \text{mol}^{-1}$  for water+1,4-dioxane and water + DMSO at 298.15 K are in satisfactory agreement with the  $V^E$  minima values of  $-0.80$   $\text{cm}^3 \text{mol}^{-1}$  and  $-0.97$   $\text{cm}^3 \text{mol}^{-1}$ , respectively, of Aminabhavi *et al.*<sup>8</sup>

Generally, the deviations observed on the excess molar volumes could be related with the molecular structure of the mixture. Usually, the positive deviations of  $V^E$  are determined by an advanced degree of unpacking of the molecules in the mixture and by the weak intermolecular interactions; the negative deviation of  $V^E$  suggests the presence of specific interactions between the components and/or geometrical accommodation of molecules on mixing.<sup>18</sup> In this present case, DMSO is a highly associated solvent, which forms polymer chains by interaction between its sulphur and oxygen atoms; self-associated forms of DMSO can dissociate because of the presence of proton-donor solvents. Like DMSO, water is self-associated by hydrogen bonds. Both water and DMSO are highly polar solvents, DMSO being at the top of the solvent polarity/polarizability scale. DMSO is a very weakly acidic and fairly basic, while water was reported as highly acidic and negligibly basic.<sup>19</sup> The both solvents can give strong intermolecular interactions by H-bonding between unlike molecules. The molecular clusters formed between water and DMSO are believed to possess a well-defined geometry and to be responsible for the strongly non-ideal mixing reflected in maxima or minima in the variation of some physico-chemical properties (density, viscosity, vapour pressure) with the mole fraction of water or DMSO. The spectroscopic (IR, NMR) analysis<sup>18</sup> and the

molecular dynamic simulation<sup>20</sup> reveal that the mixtures with  $X_w \leq 0.4$  are governed by the presence of DMSO: water complex in the ratio of 1:1. On the other hand, the behaviour of mixtures with  $0.4 \leq X_w \leq 0.6$  is governed by the presence of 1:1 and 1:2 DMSO: water complexes, and those with  $X_w \geq 0.6$  by the prevalence of the 1:2 DMSO: water complex and pure water, which endows the mixture with a high acidity and a low basicity. Moreover, DMSO has a large dipole moment ( $\mu = 3.96$  D), water molecules are polar ( $\mu = 1.89$  D). For this reason, the dipole-dipole interactions exist in the pure liquid and the same type of interactions could appear between DMSO and water. This could explain high negative  $V^E$  for this system with the minima at  $X_w \approx 0.6$ .

The water+1,4-dioxane system contains polar and very weakly polar components. Dioxane ( $\mu = 0.4$  D) and water ( $\mu = 1.89$  D) are miscible at all compositions and some of their physical properties, such as boiling point, vapour pressure and density are identical but their dielectric constants and dipole moments are very different. Dioxane is an aprotic solvent, whereas water is both an electron donor and acceptor. Dioxane is more basic and less acidic than water, because of the electron-releasing tendency of the methylene group in the molecule. A water molecule which is hydrogen bonded to the oxygen atom of a 1,4-dioxane molecule also becomes more basic and less acidic than pure water. X ray diffraction, mass spectroscopy and MNR measurements<sup>21</sup> show that: 1) in water rich domain ( $X_w > \approx 0.9$ ) hydrogen bonded clusters, characteristic to pure water (ice-like structure), are dominant; 2) in the  $X_w \approx 0.8-0.6$  domain, because of unlike interactions, both opened ice-like structure of water and inherent structure of 1,4-dioxane are broken down, and the hydrogen-bonded clusters of 1,4-dioxane and water molecules are the main species in the binary solutions; 3) when  $X_w$  is less than 0.6, the clusters characteristic of pure 1,4 dioxane are gradually formed. In this domain the structure of pure 1,4-dioxane is dominant; the water molecules forms hydrogen bonds with pure 1,4-dioxane clusters without altering its bulk structure. The obtained  $V^E$  vs. compositions curves, having negatives values and accentuated minima at  $X_w \approx 0.65-0.7$  are in agreement with the mentioned structural information.

Moderate negative values of  $V^E$  for the binary system DMSO+1,4-dioxane are due, probably, to the poor unlike dipole-dipole interactions between SO groups of the DMSO and the O group of 1,4-dioxane.<sup>11</sup> Also, the 1,4-dioxane molecules could break the polymer chains of DMSO.

A further comparison of the Fig. 1a-c shows an interesting difference in behaviour with respect to the variation in  $V^E$  with temperature at a fixed composition. The  $V^E$  of the binary system water+1,4-dioxane decreases with the increase of the temperature, becoming less negative, having an usual variation with temperature. In contrast with this system, the excess molar volume of the other two binary systems containing DMSO becomes more negative with the increase of the temperature. On the other hand, the influence of the temperature seems to be more important for the mixtures with DMSO. For example, in the 1,4-dioxane+DMSO system the minimum value of the  $V^E$  at 313.15K is around three times greater than the minimum value of the  $V^E$  at 293.15 K. It results that the systems

with DMSO have a different behaviour with temperature compared with water+1,4-dioxane system.

The  $V^E(T)$  behaviour for water-1,4-dioxane system can be explained by influence of temperature on kinetic energy of molecules which increase when temperature increase. This leads to decrease of the interactions between molecules, so  $V^E$  values become more positives as temperatures increase. The systems containing DMSO present a contrary variation, probably due to other factors than interactional, like structural effects and changes in the orientational positions of the molecules on mixing. The curves  $\bar{V}_1^E(X)$  and  $\bar{V}_2^E(X)$  for the three binary systems, at 313.15 K, are depicted in Fig. 2. All binary systems have negative excess partial molar volumes. The infinite dilution values for partial excess molar volumes, at all investigated temperatures, are listed in Table 4.

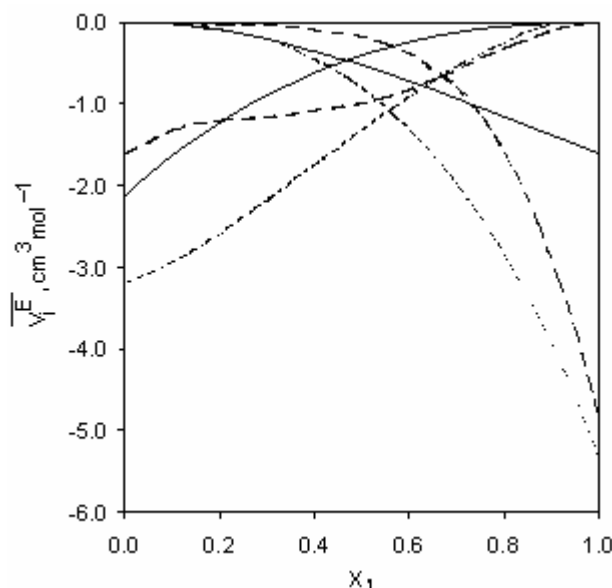


Fig. 2 – Partial excess molar volumes of the binary systems at T=313.15 K for: water (1) +1,4-dioxane(2) (---), water (1) + DMSO(2) (-.-.-), 1,4-dioxane (1) + DMSO(2) (—).

Table 4

Partial excess molar volumes at infinite dilution of the binary systems

T, K	$\bar{V}_1^{E,\infty}$ , $cm^3 mol^{-1}$	$\bar{V}_2^{E,\infty}$ , $cm^3 mol^{-1}$	$\bar{V}_1^{E,\infty}$ , $cm^3 mol^{-1}$	$\bar{V}_2^{E,\infty}$ , $cm^3 mol^{-1}$	$\bar{V}_1^{E,\infty}$ , $cm^3 mol^{-1}$	$\bar{V}_2^{E,\infty}$ , $cm^3 mol^{-1}$
	Water+1,4-Dioxane		Water+DMSO		1,4-Dioxane+DMSO	
293.15	-2.171	-6.002	-2.023	-4.945	-0.801	-0.837
298.15	-2.054	-5.657	-2.589	-5.167	-1.611	-1.123
303.15	-1.981	-5.432	-3.190	-5.403	-2.122	-1.618
308.15	-1.801	-5.196	-3.694	-5.746	-2.584	-2.084
313.15	-1.621	-4.907	-4.018	-6.120	-3.024	-2.485

### Ternary System

Table 5 shows the densities<sup>6</sup> and excess molar volumes calculated in ternary system at different temperatures and compositions.

Experimental data were reduced with correlative and predictive methods. The excess molar volume in ternary system is frequently described by the following expression:

$$V_{123}^E = V_{12}^E + V_{13}^E + V_{23}^E + X_1 X_2 X_3 \Delta_{123} \quad (6)$$

where  $V_{ij}^E$  are the binary contributions and  $\Delta_{123}$  stands for the so-called ternary contribution.

In this work the binary contributions were identified by regression of experimental data measured for each binary system and using Redlich-Kister equation. The ternary contribution was calculated by correlation of ternary experimental data with different equations: Cibulka<sup>22</sup>, Singh,<sup>23</sup> Jasinski,<sup>24</sup> and Nagata.<sup>25</sup> Table 6 shows the correlation results, estimated parameters and standard deviations at different temperatures. As example, Fig. 3 illustrates the isolines of the excess molar volume calculated with Cibulka equation at 298.15K.

Several methods for prediction of the excess molar volumes have been developed using additive binary contributions:

$$V_{123}^E = \sum \frac{X_i X_j}{X_i' X_j'} V_{ij}^E(X_i', X_j') \quad (7)$$

where  $X_i, X_j$  are the mole fractions of the components in the ternary mixture; the mole fractions in the binary mixture,  $X_i', X_j'$  are defined so that  $X_i' + X_j' = 1$ . The binary contribution  $V_{ij}^E$  is the excess property of  $i$ - $j$  binary system, evaluated at the point  $X_i', X_j'$ .

The predictive methods are divided in symmetrical and asymmetrical. In the first case, all three components of the mixture are treated identically, whereas in the second, one of the components plays the most important role. In the first category the equations of Kohler,<sup>26</sup> Jacob and Fitzner<sup>27</sup> and Colinet<sup>28</sup> and simple sum of binary contributions are included, whereas in the second category, the equations of Tsao,<sup>29</sup> Toop,<sup>30</sup> Scatchard<sup>31</sup> and Hillert.<sup>32</sup> For the predictive equations, the standard deviation was calculated with Eq. (8). The results are listed in Table 7.

$$\sigma = \left[ \frac{\sum (V_{\text{exp}}^E - V_{\text{calc}}^E)^2}{N_{\text{exp}}} \right]^{0.5} \quad (8)$$

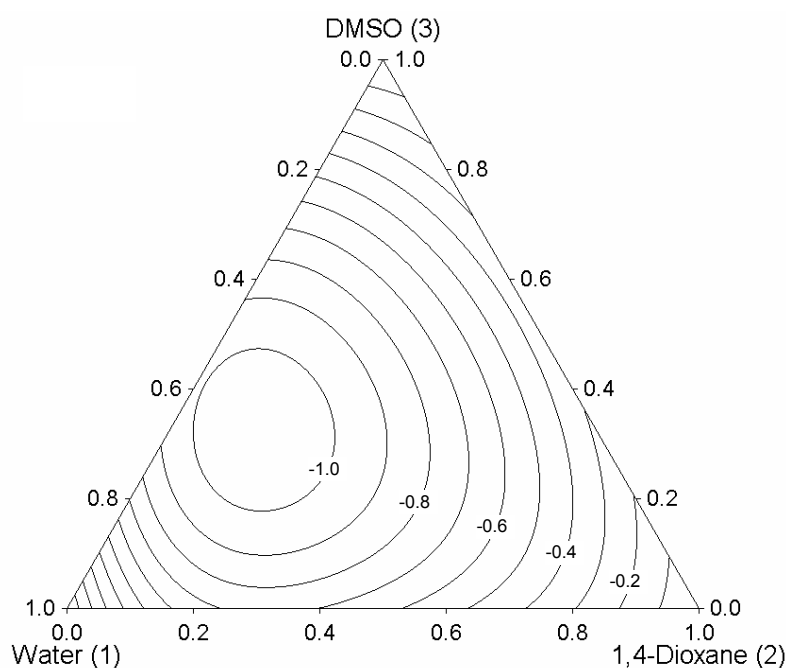


Fig. 3 – Curves of the constant excess molar volume,  $V^E$ , calculated with Cibulka equation for the water (1)+1,4-dioxane(2)+DMSO(3) system at 298.15 K.

Table 5

Densities and excess molar volumes for the ternary system

$X_1$	$X_2$	293.15 K		298.15 K		303.15 K		308.15 K		313.15 K	
		$\rho, \text{g cm}^{-3}$	$V^E, \text{cm}^3 \text{mol}^{-1}$	$\rho, \text{g cm}^{-3}$	$V^E, \text{cm}^3 \text{mol}^{-1}$	$\rho, \text{g cm}^{-3}$	$V^E, \text{cm}^3 \text{mol}^{-1}$	$\rho, \text{g cm}^{-3}$	$V^E, \text{cm}^3 \text{mol}^{-1}$	$\rho, \text{g cm}^{-3}$	$V^E, \text{cm}^3 \text{mol}^{-1}$
0.0999	0.8001	1.0427	-0.255	1.0376	-0.306	1.0335	-0.408	1.0290	-0.465	1.0248	-0.529
0.1000	0.5998	1.0577	-0.377	1.0535	-0.484	1.0509	-0.690	1.0469	-0.779	1.0432	-0.872
0.0998	0.4010	1.0731	-0.448	1.0691	-0.558	1.0680	-0.855	1.0632	-0.884	1.0590	-0.932
0.1000	0.1999	1.0881	-0.400	1.0838	-0.479	1.0809	-0.647	1.0778	-0.778	1.0750	-0.904
0.1997	0.6000	1.0530	-0.465	1.0490	-0.573	1.0461	-0.738	1.0421	-0.816	1.0380	-0.872
0.1998	0.4020	1.0704	-0.600	1.0662	-0.684	1.0632	-0.835	1.0608	-1.006	1.0577	-1.116
0.2000	0.2001	1.0877	-0.613	1.0835	-0.686	1.0807	-0.841	1.0781	-0.986	1.0752	-1.094
0.1998	0.1000	1.0964	-0.592	1.0927	-0.687	1.0897	-0.826	1.0881	-1.022	1.0845	-1.082
0.3002	0.5999	1.0480	-0.586	1.0442	-0.692	1.0404	-0.782	1.0374	-0.910	1.0332	-0.954
0.3000	0.4000	1.0667	-0.709	1.0627	-0.791	1.0591	-0.888	1.0562	-1.012	1.0536	-1.138
0.3000	0.2000	1.0856	-0.739	1.0835	-0.910	1.0801	-1.013	1.0759	-1.056	1.0734	-1.172
0.2999	0.1002	1.0949	-0.710	1.0918	-0.820	1.0889	-0.945	1.0854	-1.020	1.0835	-1.159
0.3997	0.5001	1.0499	-0.658	1.0465	-0.764	1.0426	-0.831	1.0405	-0.986	1.0365	-1.029
0.4000	0.4002	1.0609	-0.758	1.0573	-0.846	1.0540	-0.943	1.0506	-1.023	1.0478	-1.124
0.4002	0.1998	1.0852	-0.967	1.0812	-1.024	1.0778	-1.110	1.0754	-1.230	1.0723	-1.302
0.3998	0.1002	1.0950	-0.915	1.0911	-0.970	1.0881	-1.071	1.0847	-1.138	1.0825	-1.244
0.5000	0.4001	1.0535	-0.789	1.0503	-0.879	1.0464	-0.929	1.0432	-1.004	1.0401	-1.077
0.5001	0.3000	1.0666	-0.904	1.0629	-0.965	1.0597	-1.045	1.0565	-1.116	1.0538	-1.201
0.5002	0.1998	1.0796	-0.978	1.0751	-0.998	1.0729	-1.118	1.0700	-1.197	1.0677	-1.292
0.4998	0.1002	1.0915	-0.972	1.0884	-1.045	1.0856	-1.135	1.0831	-1.225	1.0805	-1.298
0.5997	0.3002	1.0568	-0.858	1.0528	-0.890	1.0502	-0.975	1.0465	-1.010	1.0437	-1.076
0.6001	0.1997	1.0723	-0.977	1.0685	-1.012	1.0654	-1.074	1.0633	-1.167	1.0616	-1.268
0.6000	0.1000	1.0860	-0.989	1.0826	-1.032	1.0805	-1.127	1.0780	-1.198	1.0747	-1.230
0.7000	0.2001	1.0588	-0.842	1.0564	-0.908	1.0538	-0.967	1.0508	-1.008	1.0488	-1.080
0.6998	0.1000	1.0760	-0.916	1.0734	-0.967	1.0710	-1.028	1.0685	-1.080	1.0663	-1.136
0.8001	0.1500	1.0492	-0.715	1.0466	-0.747	1.0447	-0.802	1.0421	-0.834	1.0399	-0.877
0.7990	0.0500	1.0672	-0.727	1.0645	-0.748	1.0623	-0.788	1.0603	-0.831	1.0586	-0.879
0.9000	0.0500	1.0385	-0.437	1.0366	-0.454	1.0355	-0.494	1.0342	-0.530	1.0331	-0.572
0.9000	0.0250	1.0422	-0.403	1.0407	-0.427	1.0399	-0.472	1.0385	-0.503	1.0378	-0.551



Table 6

Parameters,  $C_k$ , and standard deviations,  $\sigma$ , for representation of  $V^E$  with different correlative equations for the ternary system

Model	$C_0$	$C_1$	$C_2$	$C_3$	$C_4$	$C_5$	$C_6$	$C_7$	$C_8$	$\sigma$
293.15 K										
Cibulka	-6.1262	5.0960	9.3929							0.0249
Singh	-1.1735	13.5206	-17.0520							0.0265
Jasinski	-1.1293	-0.9323	-3.0029	-0.1278						0.0376
Nagata	-0.0057	-0.0193	-0.0127	0.0330	0.0073	0.0211	-0.0179	0.0003	-0.0248	0.0248
298.15 K										
Cibulka	-1.0314	-0.6559	-0.4094							0.0342
Singh	-0.6467	-2.4543	-99.7669							0.0289
Jasinski	-1.0317	-0.1054	-6.8152	-8.3062						0.0332
Nagata	-0.0041	-0.0025	-0.0223	-0.0324	0.0316	0.0097	0.0319	-0.0110	0.0236	0.0269
303.15 K										
Cibulka	-8.2805	43.2255	-5.6791	-53.9068						0.0456
Singh	-2.2224	-10.2614	-70.1687							0.0568
Jasinski	-1.6090	-4.3357	-12.5838	1.7904						0.0488
Nagata	-0.0086	-0.0208	-0.0275	0.0068	0.0493	-0.0008	0.0118	-0.0226	0.0512	0.0384
308.15 K										
Cibulka	-4.9428	34.9651	-12.3910	-46.9995						0.0686
Singh	-2.5184	-22.9237	-125.2672							0.0683
Jasinski	-2.2506	-3.2851	-11.9680							0.0769
Nagata	-0.0137	-0.0464	-0.0447	0.0383	0.0493	0.0727	0.0044	-0.0097	-0.0177	0.0504
313.15 K										
Cibulka	-3.4772	30.4765	-15.1839	-45.4627						0.0749
Singh	-3.2695	-28.8583	-135.5888							0.0689
Jasinski	-3.3304	-4.1452	-11.6330							0.0866
Nagata	-0.0110	-0.0214	-0.0375	-0.0296	0.0317	0.0487	0.0538	0.0083	0.0365	0.0462

Table 7

Standard deviations,  $\sigma$ , in representation of  $V^E$  for the ternary system by different predictive equations

T, K	Asymmetrical methods				Symmetrical methods			
	Tsao	Toop	Scatchard	Hillert	Simple	Kohler	Jacob	Colinet
293.15	0.0755	0.1032	0.1032	0.1030	0.0464	0.0447	0.0467	0.0375
298.15	0.0526	0.0983	0.0985	0.0985	0.0443	0.0448	0.0429	0.0403
303.15	0.0723	0.1261	0.1259	0.1259	0.0839	0.0833	0.0637	0.0776
308.15	0.0889	0.1463	0.1458	0.1458	0.1256	0.1078	0.0852	0.1027
313.15	0.0967	0.1656	0.1651	0.1651	0.1255	0.1228	0.1009	0.1187

The comparison between the correlative equations (Table 6) shows that the best results are obtained by using the Nagata's relation. This equation is more flexible from mathematical point of view comparing with the other equations. In addition, the Nagata's equation takes into account the influence of the temperature on the properties. These two features lead to the improvement of the correlation results. The Cibulka and Singh equations give similar standard deviations.

As is shown in Table 7, the results obtained by Tsao predictive equation are slightly better than the other asymmetrical equations used. For this ternary system, the symmetrical methods give better results than asymmetrical methods. The notation "Simple" in Table 7 represents the sum only of binary contributions from Eq. (6). The correlative methods, as can be expected, show better results than the predictive equations. However, the

predictive relations are useful when experimental ternary data are not available and only the parameters of binary systems are known.

The ternary mixture shows negative values of  $V^E$  for all compositions and temperatures, as already found for binary mixtures. At 298.15 K, the minimum value of the excess molar volume is  $V^E \approx -1.04 \text{ cm}^3 \text{ mol}^{-1}$  corresponding to a mixture with  $X_{\text{water}} \approx 0.5$ ,  $X_{\text{dioxane}} \approx 0.1$ . This behaviour is explained by complex interactions existing in the mixture: intra- and intermolecular H-bondings and dipole-dipole interactions between water, DMSO and 1,4-dioxane molecules.

The excess partial molar volume of each component of the water+1,4-dioxane+DMSO system has been computed from excess molar volume data by means of the following relation:

$$\bar{V}_i^E = V^E + \left( \frac{\partial V^E}{\partial X_i} \right)_{T,P,X_j, j \neq i} - \sum_{k=1}^N X_k \left( \frac{\partial V^E}{\partial X_k} \right)_{T,P,X_j, j \neq k} \quad (9)$$

In this relation, the Cibulka equation and parameters reported in Tables 3 and 6 have been

used. The computational results are graphically represented in Fig. 4a-c at 298.15 K.

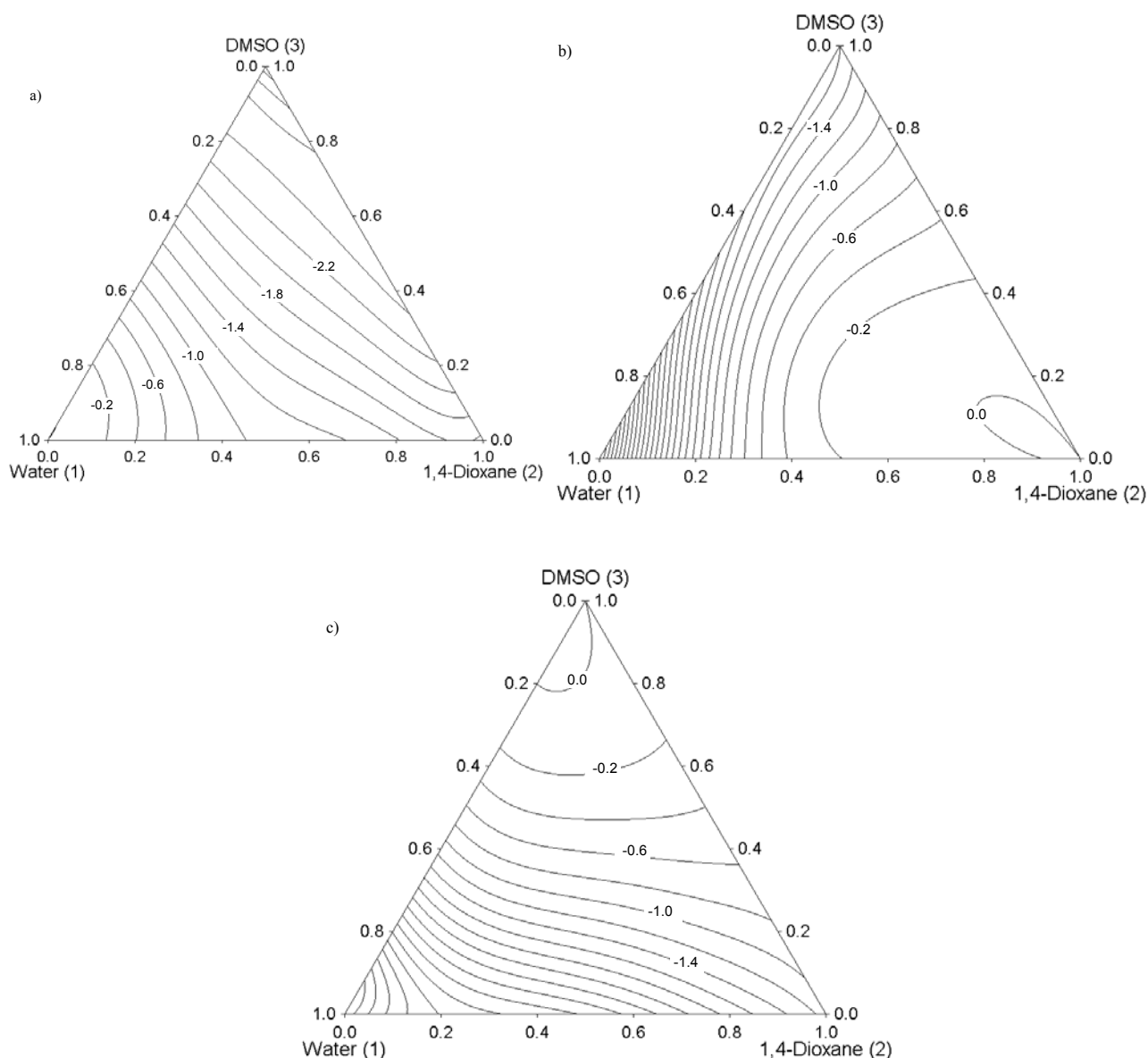


Fig. 4 – Partial excess molar volumes for water (1)+1,4-dioxane (2)+DMSO (3) system at 298.15 K for: a)  $\bar{V}_1^E$  b)  $\bar{V}_2^E$  c)  $\bar{V}_3^E$ .

## CONCLUSION

An extended study of binary and ternary systems with water, 1,4-dioxane and DMSO concerning the experimental data of densities as well as the calculation of the properties related to

density (excess molar volumes and excess partial molar volumes) have been presented.

The excess molar volumes and excess partial molar volumes for binary systems have been calculated and correlated with structural studies. All binary systems present negative  $V^E$  values in

the order: water+DMSO > water+1,4-dioxane > 1,4-dioxane+DMSO. The systems with DMSO have a peculiar behaviour concerning  $V^E$  temperature dependence, probably due structural effects.

The excess molar volumes of the ternary system water+1,4-dioxane+DMSO have been computed by means of correlative and predictive symmetrical and asymmetrical methods. All ternary  $V^E$  values are negative. The correlative equations give better results comparing with the predictive methods. The symmetrical predictive methods give better results than asymmetrical methods.

The systems present important deviations from ideality, as consequence of their structures and interactions.

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