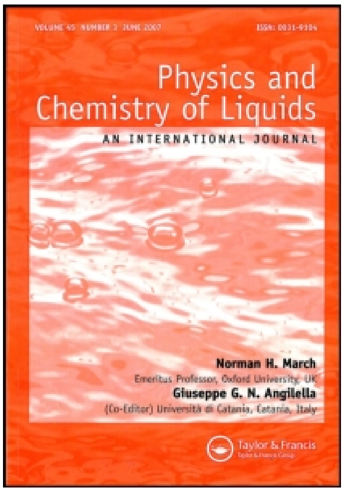

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Some Physicochemical Properties of Aqueous Solutions of Isomeric Butanediols

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SOME PHYSICOCHEMICAL PROPERTIES OF AQUEOUS SOLUTIONS OF ISOMERIC BUTANEDIOLS

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Density, viscosity, electric permittivity and refractive indices for mixtures of water with four isomeric butanediols were measured over the whole composition range at 298.15K. From these data the excess molar volumes, apparent and partial molar volumes of butanediols and water, the excess electric permittivity and Kirkwood's correlation factor for investigated mixtures were calulated.

Analysis of the results obtained showed that although the investigated butanediols exhibit their individual features in the mixtures with water, there is a substantial similarity in the behaviour of butane-1, 2-diol and butane-2,3-diol. The analogous similarity, but to a lower extent, is also observed in the case of the other pair of butanediols, i.e. butane-1,3-diol and butane-1,4-diol which have their apolar fragments shielded by the hydroxyl groups.

KEY WORDS: Water, four isomeric butanediols, kirkwood correlation factor.

INTRODUCTION

Aqueous mixtures of diols are frequently used in chemical and biochemical laboratory practice, as well as in some branches of chemical technology. However, the literature data concerning the physiochemical properties of these systems are rather fragmentary and concern mainly the mixtures of water with ethanediol. In order to fill this gap, at least partly, we have undertaken the physicochemical examinations of the mixtures of water with isomeric butanediols. Recently, we have published some data which refer to the mixtures of water with butane-1,4-diol (BD-1,4)[1] and with butane-1,2-diol (BD-1,2)[2]. Now, we are presenting the results of the density, viscosity, electric permittivity and refractive index measurements for the mixtures of water with two other butanediols, i.e., butane-1,3-diol (BD-1,3) and butane-2,3-diol

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(BD-2,3). In our opinion, these data constitute a valuable experimental material. Some derivative physicochemical functions calculated on this basis such as the apparent and partial molar volumes, Kirkwood correlation factor, etc. give an additional information about the interactions between water and the butanediols and about the structure of the investigated mixtures. It was also expected that the obtained data will enable us to observe variations in the behaviour of isomeric butanediols resulting from the differences in the hydroxyl groups location and in the size of apolar fragments in the molecule. Additionally, having now at our disposal a more precise densimeter we performed supplementary density measurements of the water-butane-1,2-diol and water-butane-1,4-diol mixtures investigated earlier[1,2].

EXPERIMENTAL

Butane-1,3-diol and butane-2,3-diol (Merck, Schuchardt) were stored over type 4A molecular sieves for a few days, and then they were distilled under vacuum in a dry nitrogen atmosphere. Fractions of BD-1,3 were collected at 378K/5 mmHg and of BD-2,3 at 372K/4 mmHg. The water content in the solvents was determined by means of the Karl Fisher method and it was found not to exceed 0.02 wt.%. Water was deionized, distilled over alkaline $KMnO_4$ and finally distilled twice in an argone atmosphere. All solutions were prepared by weight.

Viscosity measurements were performed in Ubbelhode type photo-optic viscosimeter using an electronic time counter similar to that described by Out and Los[3]. The employed counter was standardized by a quartz generator and was accurate to ± 0.001 s.

Densities of the mixtures were measured using a magnetic densimeter as described earlier[1]. It was equipped with an authomatic registration of voltage of the current. The accuracy of the measurements was $\pm 2.10^{-5}$ $g \cdot cm^{-3}$. The densimeter and the viscosimeter were embedded in the thermostat keeping the required temperature to within 5.10^{-4} deg.

The relative permittivities were determined using the apparatus described in our previous paper[1].

The refractive index measurements for sodium light ($\lambda = 589.55$ nm) were performed using the Abbe refractometer thermostated to within ± 0.02 deg.

RESULTS AND DISCUSSION

The measured densities (ρ), viscosities (η), electric permittivities (ε) and refractive indices (n_D) for pure butane-1,3-diol and butane-2,3-diol at 25 °C are presented in Table 1 together with appropriate literature data. Table 1 contains also the analogous data that refer to butane-1,2-diol[2] and butane-1,4-diol[1] examined earlier. As it can be seen our results are generally in a good agreement with the data of other authors.

The ρ, η, ε, and n_D data for the mixtures of water with butane-1,3-diol and butane-2,3-diol within the whole composition range of the binaries determined at 298K are presented in Tables 2 and 3. Table 4 contains supplementary data on

Table 1 *Density, viscosity, electric permittivity and refractive index of pure isometric* butanediols at 298.15 K.

butanediol	ρ $g \cdot cm^{-3}$	η cP	ε	n_D
butane-1,2-diol	0.99945(4) 0.9987 (5) 0.99900(*)	59.61(9) 52.99(*)	22.71(*)	1.4360(9) 1.4359(*)
butane-1,3-diol	1.0000 (8) 1.00241(4) 1.00021(*)	98.3(12) 110.0(11) 96.82(*)	28.48(*)	1.4390(9) 1.4389(*)
butane-1,4-diol	1.01289(6) 1.01316(4) 1.01258(7) 1.01289(*)	71.5 (10) 71.13(11) 71.66 (*)	31.9(14) 30.2(15)30°C 30.33(*)	1.4443(9) 1.4444(*)
butane-2,3-diol	0.99745 (7) 0.9871 (5) 0.99747 (*)	121 (13) 123.94(*)	21.59(*)	1.4366(10) 1.4364(*)

(*) our data

Table 2 Density, viscosity, electric permittivity and refractive index of water-butane-1, 3-diol mixtures at 298.15K.

mol % BD-1,3	ρ $g \cdot cm^{-3}$	η cP	ε	n_D
0.0	0.99707	0.890	78.53	1.3329
0.5	0.99771	–	–	–
1.0	0.99841	–	76.41	–
1.5	0.99919	–	–	–
2.0	0.99998	1.237	74.47	1.3430
2.5	1.00078	–	73.56	–
5.0	1.00486	1.921	69.36	1.3558
7.5	1.00875	–	65.65	–
10.0	1.01210	3.585	62.35	1.3761
15.0	1.01623	–	–	–
20.0	1.01769	8.367	52.39	1.3992
22.5	1.01762	–	–	–
25.0	1.01758	–	–	–
30.0	1.01744	15.69	45.94	1.4119
40.0	1.01545	24.72	41.46	1.4198
50.0	1.01283	34.83	38.11	1.4255
60.0	1.01005	47.24	35.47	1.4288
70.0	1.00737	60.49	33.30	1.4320
80.0	1.00480	74.06	31.46	1.4338
90.0	1.00245	87.00	29.87	1.4367
95.0	1.00132	91.60	29.15	1.4375
100	1.00021	96.82	28.48	1.4389

the refraction index values and “new” density values which refer to the earlier investigated mixtures of water with butane-1,2-diol and butane-1,4-diol. The viscosity and the electric permittivity data for these systems were given in our previous papers[1,2].

The densities of water-butanediol mixtures (Fig. 1) as a function of the mixture composition exhibit a maximum within the range of high water content; its position

Table 3 Density, viscosity, electric permittivity and refractive index of water-butane-2,3-diol mixtures at 298.15K.

mol % BD-2, 3	ρ $g \cdot cm^{-3}$	η *cP*	ε	n_D
0.0	0.99707	0.890	78.53	1.3329
0.5	0.99813	–	–	–
1.0	0.99932	–	77.14	–
1.5	1.00055	–	–	–
2.0	1.00181	1.037	75.52	1.3460
2.5	1.00308	–	74.66	–
5.0	1.00938	2.035	70.18	1.3572
7.5	1.01478	–	65.76	–
10.0	1.01854	3.859	61.67	1.3778
15.0	1.02234	–	54.66	–
20.0	1.02299	8.925	49.08	1.4010
25.0	1.02190	–	–	–
30.0	1.02030	15.13	40.99	1.4112
40.0	1.01619	23.40	35.51	1.4187
50.0	1.01216	33.06	31.58	1.4245
60.0	1.00853	47.21	28.61	1.4286
70.0	1.00529	63.14	26.29	1.4308
80.0	1.00241	81.76	24.42	1.4330
90.0	0.99981	100.6	22.88	1.4350
95.0	0.99861	112.1	22.21	1.4358
100	0.99747	123.9	21.59	1.4364

Table 4 Density and refractive index of water-butane-1,2-diol and water-butane-1,4-diol mixtures at 298.15 K.

	butane-1,2-diol		*butane-1,4-diol*	
mol% BD	ρ $g \cdot cm^{-3}$	n_D	ρ $g \cdot cm^{-3}$	n_D
0	0.99707	1.3329	0.99707	1.3329
0.5	0.99821	–	0.99745	–
1.0	0.99942	–	0.99826	–
1.5	1.00067	–	0.99912	–
2.0	1.00195	1.3430	0.99995	1.3426
2.5	1.00326	–	1.00078	–
5.0	1.00872	1.3580	1.00465	1.3563
7.5	1.01289	–	1.00812	–
10.0	1.01580	1.3782	1.01117	1.3768
15.0	1.01860	–	1.01599	–
20.0	1.01780	1.3980	1.01915	1.3952
25.0	1.01621	–	1.02083	–
30.0	1.01510	1.4098	1.02142	1.4080
40.0	1.01219	1.4180	1.02153	1.4163
50.0	1.00931	1.4228	1.02061	1.4232
60.0	1.00670	1.4272	1.01918	1.4302
70.0	1.00449	1.4302	1.01753	1.4357
80.0	1.00261	1.4325	1.01589	1.4396
90.0	1.00090	1.4338	1.01434	1.4421
95.0	1.00000	1.4349	1.01361	1.4432
100	0.99900	1.4359	1.01289	1.4444

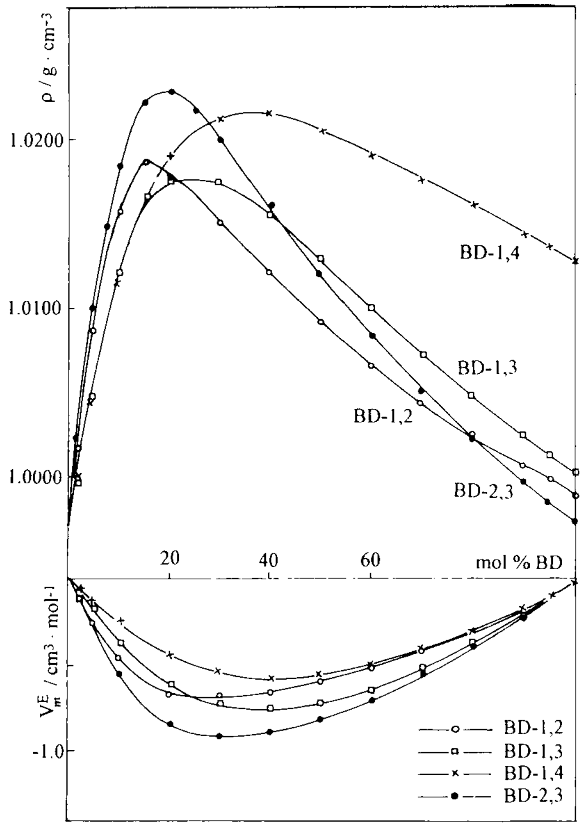

Figure 1 Density ρ and excess volumes V_m^E of water-butanediol mixtures vs. butanediol content at 298.15K.

depends on the kind of diol. It is noteworthy that the densities of water-propanediol mixtures[6] also go through a maximum while those for water-ethanediol and water-glycerol mixtures change monotonously[16]. Therefore, the presence of a hydrophobic group in a diol molecule results in the occurrence of the extremum of the density which is not a thermodynamic property.

As it is seen from Figure 2 the viscosity of each water-buthanediol mixture grows monotonously with an increase of the butanediol content within the whole binary mixture composition range.

The electric permittivity of the water-butanediol mixtures (Fig. 3) decreases rapidly upon addition of a small amount of a diol to water. It seems to point at significant changes in the polarizability of molecules of the mixture components due to the formation of some heteroassociates.

The values of the refractive index, n_D of the investigated mixtures are given in Tables 2-4. They will be used for the Kirkwood correlation parameter, g_k calculation in a further part of this paper.

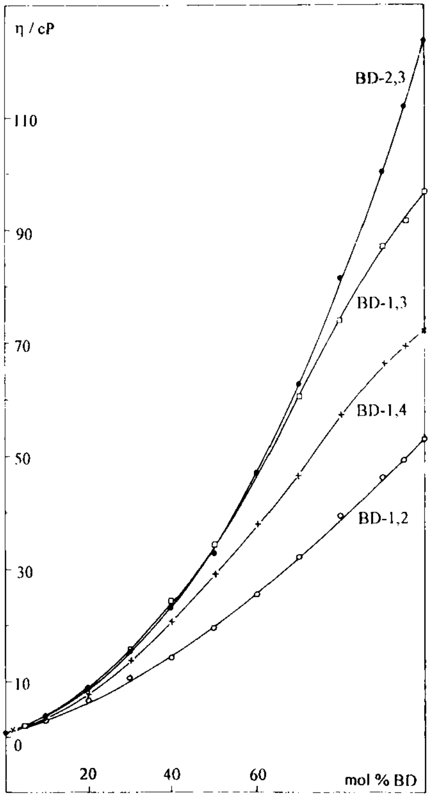

Figure 2 Viscosity η of water-butanediol mixtures vs. butanediol content at 298.15K.

Volumetric properties of the water-butanediol mixtures

From the measured densities the molar excess volumes V_m^E of the mixtures were calculated according to:

$$V_m^E = x_1 M_1 (\rho^{-1} - \rho_1^{-1}) + x_2 M_2 (\rho^{-1} - \rho_2^{-1}) \qquad (1)$$

where M_i, x_i and ρ_i are the molar mass, density and mole fraction of component i with $i = 1$ for water and $i = 2$ for butanediol while ρ is density of the mixture. The values of V_m^E for the investigated systems are presented in Figure 1 as a function of composition.

The apparent molar volumes $V_{i,\varnothing}$ of both components of the mixtures are determined from:

$$V_{i,\varnothing} = V_i^* + V_m^E / x_i \qquad (2)$$

where V_i^* is the molar volume of pure component. The obtained values are given in Table 6. The values of $V_{1,\varnothing}$ and $V_{2,\varnothing}$ as a function of x_i were used to calculate the

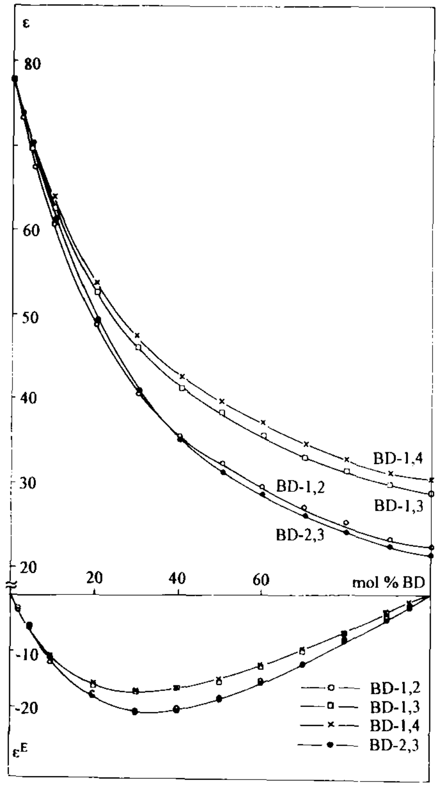

Figure 3 Electric permittivity ε and excess electric permittivity ε^E of water-butanediol mixtures at 298.15K.

partial molar volumes V_i of the components according to:

$$V_i = V_{i,\varnothing} + x_1 x_2 (\delta V_{i,\varnothing} / V_{i,\varnothing} / \delta x_i) \qquad (3)$$

The values of $(\delta V_{i,\varnothing}/\delta x_i)$ were obtained by the local fitting procedure similar to that described by Zegers and Somsen[17]. The partial molar volumes V_1 of water in the mixtures and the corresponding data that refer to the butanediols V_2 are presented in Figure 4. Table 5 summarises the molar V_2^*, the limiting partial molar $V_2^0 = V_{2,\varnothing}^0$ and the excess limiting partial molar volumes $\Delta V_2^E = V_2 - V_2^*$ for the butanediols in their mixtures with water. The V_2^0 values at 298.15 K determined in this work are in a good agreement with the appropriate data from other sources.

As it can be seen in Figure 1, the molar volumes of the mixtures of water with all butanediols deviate significantly from additivity. The excess volume curves show negative values over the whole composition range. A similar behaviour of the V_m^E function for water-diol mixtures was observed earlier by Nakanishi[6] as well as by

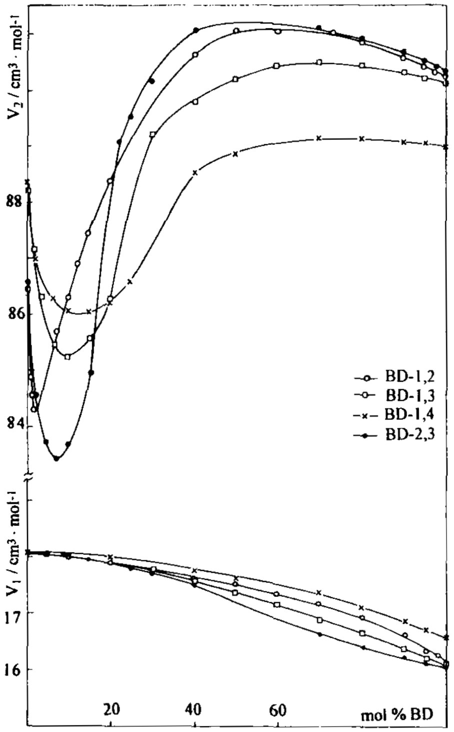

Figure 4 Partial molar volume of water V_1 and of butanediol V_2 in water-butanediol mixtures vs. butanediol content at 298.15K.

Table 5 Some volumetric properties of aqueous solutions of butanediols.

butanediol	$V^0_{2,\varnothing}$ *cm³·mol⁻¹*	$(V^0_{2,\varnothing})_{min}$ *mol% BD*	V^*_2 *cm³·mol⁻¹*	ΔV^E_2 *cm³·mol⁻¹*
butane-1,2,-diol	86.43 (86.19[27])	~3.5	90.21	−3.78
butane-1,3,-diol	88.23 (88.19[27]) (88.32[7])	~10	90.10	−1.87
butane-1,4,-diol	88.30 (88.35[27]) (88.23[24])	~15	88.97	−0.67
butane-2,3,-diol	86.66 (86.47[27]) (86.56[7])	~7.5	90.35	−3.69

Douheret *et al.*,[18], who investigated the mixtures of water with ethanediol, propane-1,2-diol, propane-1,3-diol and butane-1,4-diol. It is known that the negative values of V^E_m connected with the phenomenon of contraction are characteristic for the mixtures of liquids associated by the hydrogen bonds and they reflect an increase in association[19]. According to the authors mentioned above the V^E_m minimum position

Table 6 Apparent molar volume of the butanediols in water at 298.15K.

	$V_{2,\varnothing}$ $cm^3 \cdot mol^{-1}$			
mol% BD	*BD-1,2*	*BD-1,3*	*BD-1,4*	*BD-2,3*
0.5	86.19	88.02	–	86.47
1.0	85.97	87.85	87.96	86.15
1.5	85.78	87.69	87.81	85.95
2.0	85.62	87.55	87.67	85.77
2.5	85.48	87.43	87.54	85.62
3.5	85.27	87.24	87.27	85.36
5.0	85.37	87.02	87.11	85.10
7.5	85.51	86.75	86.96	84.95
10.0	85.74	86.63	86.85	85.05
12.5	86.01	86.64	–	85.32
15.0	86.31	86.74	86.78	85.67
20.0	86.94	87.10	86.86	86.26
25.0	87.62	87.47	87.03	86.85
30.0	88.03	87.74	87.23	87.36
40.0	88.62	88.26	87.57	88.19
50.0	89.07	88.69	87.88	88.77
60.0	89.40	89.07	–	–
70.0	89.66	89.38	88.41	89.58
80.0	89.86	89.65	88.62	89.88
90.0	90.03	89.89	88.81	90.13
95.0	90.12	90.00	88.90	90.24
97.0	90.15	–	88.93	90.29

points at the mixture composition which has the most stable or ordered structure[6,18]. In our case, the position of the V_m^E minimum corresponds to 30 mol% of BD-1,2, 40 mol % of BD-1,3, 40 mol % of BD-1,4 and 30 mol % of BD-2,3. Therefore, it can be concluded that BD-1,2 and BD-2,3 stabilise the structure of water stronger than BD-1,3 and BD-1,4. It is possible that the terminal alkyl groups in the former butanediols are more exposed to water which makes these cosolvents hydrophobically hydrated more strongly than the latter.

An analogous conclusion can be drawn from the analysis of concentration dependencies of the apparent (or partial) molar volumes of the butanediols in water (Fig. 4). The partial molar volumes exhibit a minimum in a water rich region typical of aqueous alkanols and many other non-electrolytes[6,18,20–23]. It was suggested that the decrease of the V_2 or $V_{2,\varnothing}$ of the solute with the increasing of concentration is due to the hydrophobic hydration of the solute[22,24,25]. The position of the minimum (Table 5) and the limiting slope of the V_2 or $V_{2,\varnothing}$ function (Fig. 4) within the high water content composition range depend on the size and shape of the apolar group in the solute molecule[26,27]. Therefore, they can be considered as a measure of the solute hydrophobicity. In the systems investigated here butane-1,2-diol and butane-2,3-diol seem to be more hydrophobic than butane-1,3-diol and butane-1,4-diol. The latter diol, in whose molecule the whole apolar part is shielded by the terminal hydroxyl groups, is hydrophobically hydrated to the smallest extent.

The partial molar volumes of the butanediols in water exhibit a flat maximum within the range of 50–70 mol % of the diol, which can suggest a possibility of a spatial structure formation where one water molecule binds two or three butanediol molecules.

The limiting partial molar volumes of investigated butanediols in water are lower than the molar volumes of pure diols, i.e., the limiting excess partial molar volumes, ΔV_2^E are negative (Table 5). As it was found in the papers of many authors, such volume contraction, connected also with the solute hydrophobic hydration, becomes progressively greater with the size of the apolar residue[28]. Therefore, the ΔV_2^E value can be used as another measure of the solute hydrophobicity. The ΔV_2^E data presented in Table 5 again suggest that butane-1,2-diol and butane-2,3-diol exhibit a similar hydrophobicity and they are hydrated more strongly than butane-1,3-diol and particularly butane-1,4-diol.

The partial molar volumes of water in the mixture with the butanediols are presented in Figure 4. The limiting partial molar volumes, V_1^0 are lower than the molar volume of pure water ($16.08\,\text{cm}^3\cdot\text{mol}^{-1}$ for BD-1,2; $16.03\,\text{cm}^3\cdot\text{mol}^{-1}$ for BD-1,3; $16.52\,\text{cm}^3\cdot\text{mol}^{-1}$ for BD-1,4 and $16.10\,\text{cm}^3\cdot\text{mol}^{-1}$ for BD-2,3). It confirms our suggestions that within the range of small water content, the molecules of water are built in into the pure butanediol structure and they bind several diol molecules.

DIELECTRIC PROPERTIES

1. Excess of electric permittivity ε^E

The excess of electric permittivity, ε^E for water-butanediol mixtures as a function of the mixture composition at 298.15K is presented in Figure 3. The ε^E were calculated from the formula:

$$\varepsilon^E = \varepsilon - (\varepsilon_1 x_1 + \varepsilon_2 x_2) \tag{4}$$

where: ε denotes the electric permittivity of the mixture, ε_1 and ε_2 are the electric permittivities of water and the butanediol respectively, x_1 and x_2 are the mole fractions of water and the butanediol in the mixture. As it is seen from the Figure 3, the excess electric permittivity curves exhibit negative values over the whole composition range with a minimum within 30–40 mol% of butanediol. According to Douheret *et al.*,[18] the ε^E minimum position corresponds to the most ordered or stable structure of the mixture. It is noteworthy that the ε^E values for water-BD-1, 2 and water-BD-2,3 mixtures are the same within the experimental error limits. Similarly, the ε^E values for the other pair of mixtures (i.e. water-BD-1,3 and water-BD-1,4) are also almost identical.

2. Kirkwood correlation factor g_k.

One of the tools for the investigation of molecular interactions in liquids is an analysis of the Kirkwood correlation factor g_k[29]. Its values reflect mutual orientation of neighbouring molecular dipoles and they can inform about the possible kind of associates present in the solution. For monomers $g_k = 1$ and for cyclic dimers $g_k = 0$. In the case of open dimers and multimers the values of $g_k > 1$ suggest parallel dipoles orientation while $0 < g_k < 1$ point at the antiparallel orientation of neighbouring dipoles, hence mixed associated structures[30]. According to Cole[31], the Kirkwood correlation factor for binary liquid mixtures, can be calculated from the equation:

$$g_k = [9kT(M_1x_1/\rho_1 + M_2x_2/\rho_2)/4\pi L(\mu_1^0 x_1 + \mu_2^0 x_2)^2]\cdot$$
$$\cdot[(\varepsilon - \varepsilon_\infty)(2\varepsilon + \varepsilon_\infty)/\varepsilon(\varepsilon_\infty + 2)^2] \quad (5)$$

where: k and L are respectively Boltzmann's and Avogadro's constants, M_i, x_i, ρ_i and μ_i^0 represent respectively, the molar mass, mole fraction, density and gas-phase dipole moment; $i = 1$ denotes water, while $i = 2$ denotes a butanediol. T is a temperature of the mixture, ε-electric permittivity of the solution, while $\varepsilon_\infty = 1{,}1n_D^2$ represents the mixture electric permittivity at high frequency[32]. For water $\mu_i^0 = 1.84$ D.

The experimental values of μ^0 for butanediols are not available. Therefore, the gas phase dipole moments for butanediols were calculated by means of the quantum-mechanical MNDO method as proposed by Dewar and Thiel[33] applying the AMPAC computer programme. As it is known the MNDO method allows to calculate the dipole moments with the accuracy to ca. 0.30D. In order to test this method in application to diols, the gas-phase dipole moment, μ^0 for ethanediol was calculated. We found $\mu^0 = 2{,}29$D, which is very close to the value $\mu^0 = 2{,}24$D[34] determined experimentally.

The calculated values of μ_2^0 for butanediols are set below:

$\mu^0(\text{BD-1,2}) = 2{,}43$D $\mu^0(\text{BD-1,3}) = 2{,}19$D $\mu^0(\text{BD-1,4}) = 2{,}34$D $\mu^0(\text{BD-2,3}) = 2{,}47$D

The Kirkwood correlation factor g_k for water-butanediol mixtures as a function of the mixture composition is presented in Figure 5. The g_k values in all mixtures investigated here are above unity $1{,}5 < g_k < 2{,}6$, which suggests, according to D'Aprano[30] that the water-butanediol open dimers and multimers exist in the system. It is noteworthy that the $g_k = f$ (mol % BD) function for both water-BD-1,3 and water-BD-1,4 mixtures practically does not depend on the mixture composition while for the two other mixtures the g_k values decrease with the increase of the butanediol content.

The above mentioned differences in the behaviour of water-BD-1,3 and water-BD-1,4 mixtures in comparison with that of water-BD-1,2 and water BD-2,3 mixtures result certainly from the differences in molecular structure of the butanediols.

The results of spectroscopic investigations presented by Kuhn[35] and Fishman and Chen[36] suggest that isomeric butanediols form both intermolecular and intramolecular hydrogen bonds. The length and energy of the intermolecular hydrogen bond in the case of BD-1, 2 and BD-2, 3 are almost identical and they differ significantly from the two other butanediols i.e., BD-1, 3 and BD-1, 4. The molecules of butane-1,2-diol and butane-2, 3-diol form five-membered rings which are less stable than seven-membered rings formed by butane-1,3-diol and butane-1,4-diol[36]. Hence,

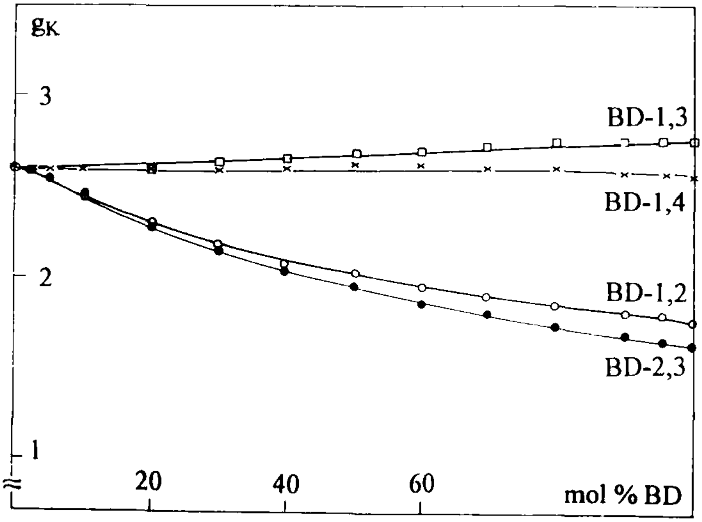

Figure 5 Kirkwood correlation parameter g_k as a function of butanediol content for water-butanediol mixtures at 298.15K.

the water molecules added into the butane-1,2-diol or butane-2,3-diol can influence their intramolecular hydrogen bonds to a large extent which, in turn, is reflected in the changes in g_k parameter values.

CONCLUSIONS

The analysis of obtained results shows that although the investigated butanediols exhibit their individual features in the mixtures with water, there is a substantial similarity in the behaviour of butane-1,2-diol and butane-2,3-diol. It can be so due to the presence in molecules of these butanediols hydrophobic groups exposed to water. The analogous similarity, but to a lower extent, is also observed in the case of the other pair of butanediols, i.e., butane-1,3-diol and butane1,4-diol which, in turn, have their apolar fragments more shielded by the hydroxyl groups.

It is noteworthy that the results obtained from both thermodynamic and relaxational methods lead to similar conclusions.

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