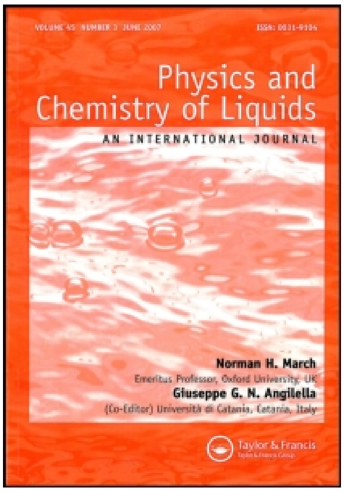

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Cezary M. Kinart[a]; Wojciech J. Kinart[b]; Adam Bald[a]; Adam Szepgis[a]
[a] Department of Chemical Education, University of Lodz, Lodz, Poland [b] Department of Organic Chemistry, University of Lodz, Lodz, Poland

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STUDIES ON INTERMOLECULAR INTERACTIONS IN LIQUID WATER–BUTANE-1,3-DIOL MIXTURES

CEZARY M. KINART [a,*], WOJCIECH J. KINART [b],
ADAM BALD [a] and ADAM SZEJGIS [a]

[a] *Department of Chemical Education, University of Lodz, 90-236 Lodz, Pomorska 163, Poland;*
[b] *Department of Organic Chemistry, University of Lodz, 90-136 Lodz, Narutowicza 68, Poland*

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^{1}H-NMR spectral and physicochemical studies of liquid mixtures of butane-1,3-diol–water suggest the formation of the intermolecular "complexes" of the $H_2O \bullet$ BD-1,3, $2H_2O \bullet$ BD-1,3, $4H_2O \bullet$ BD-1,3, $H_2O \bullet$ 2 BD-1,3 and $3H_2O \bullet$ 2BD-1,3 types.

Keywords: ^{1}H-NMR spectra; physicochemical properties; intermolecular complexes

INTRODUCTION

This paper is a continuation of our earlier studies on the analysis of intermolecular interactions in the liquid mixtures of water with different butane-diols, based on the correlation existing between the ^{1}H-NMR spectral results and some physicochemical intensive properties of the same binary mixtures [1]. The internal structure of liquid butane-1,3-diol (BD-1,3) and water have already been reviewed [1]. Taking into account all available data [2] concerning the structure of liquid BD-1,3 and water it seemed appropriate to extend these studies to the H_2O–BD-1,3 binary mixtures.

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* Corresponding author.

EXPERIMENTAL

For the present ^{1}H-NMR spectral studies and the measurements of relative permittivities chemical pure BD-1,3 (Fluka) was used. The ^{1}H-NMR spectra were recorded using a Tesla BS 467 (60 MHz) spectrometer, at 298 ± 1 K. The proton chemical shifts of water and BD-1,3 were measured with an accuracy of ca. ± 0.2 Hz with respect to an external standard HMDS (hexamethyldisiloxane). The relative permittivity measurements were performed with an accuracy of ± 0.1%, using a bridge of the type OH – 301(made in Hungary). All the solutions were prepared by weight.

RESULTS AND DISCUSSION

The review through the literature data shows that only Piekarski *et al.* [3] in their work attempted to estimate and analyse intermolecular interactions in the liquid mixtures of butane-1,3-diol and water. However, they did not interpret their results in terms of stoichiometry and internal structure of intermolecular "complexes" formed by molecules of BD-1,3 and H_2O. In this work, with the aim of analysing the intermolecular interactions between the components in the binary liquid H_2O – BD-1,3 mixtures, we measured the values of chemical shift differences $\delta(H_2O - \text{BD-1,3})$ at 298 K, between the centre of the ^{1}H-NMR signal of H_2O and the centre of multiplet of two overlaping signals corresponding to two protons linked with C(1) and the second signal corresponding to one proton linked with the C(3) carbon atom of BD-1,3 molecules over a wide range of solvent compositions i.e., from 2.00 mol. % to 99.00 mol. % of BD-1,3 (see Tab. I). Subsequently, using the same method as previously [1, 2] from these new spectral data the spectral parameter $\Delta\delta(H_2O - \text{BD-1,3})$ has been found. The values of these parameter or, more precisely, the location of its maximum values, are located at the composition with the strongest intermolecular interactions between the components, where hydrogen bonds are involved [1, 2]. The $\Delta\delta(H_2O - \text{BD-1,3})$ values are visualized in Figure 1 as a function of the mixture compositions.

The analysis of the data indicates the presence of a maximum $\Delta\delta(H_2O - \text{BD-1,3})$ at ca. 50 mol. % of BD-1,3. Thus, at this

TABLE I Relative ^{1}H-NMR chemical shifts, $\delta(H_2O-BD\text{-}1,3)$, measured at 298 K and relative permittivities for binary liquid mixtures, H_2O-BD-1,3, measured at 288.15, 293.15, 298.15, 303.15 and 308.15 K

BD-1,3	$\delta(H_2O-BD\text{-}1,3)$	ε_{12}				
mol. %	[*Hz*]	288.15 *K*	293.15 *K*	298.15 *K*	303.15 *K*	308.15 *K*
0.00	–	82.20	80.30	78.53	77.76	75.01
0.50	–	81.34	79.27	77.44	75.71	74.03
1.00	–	80.32	78.26	76.41	74.72	73.04
2.00	67.50	78.38	76.34	74.47	72.83	71.15
5.00	68.30	73.10	71.12	69.36	67.72	66.06
7.00	–	69.27	67.35	65.65	64.02	62.39
10.00	69.80	65.91	64.02	62.35	60.75	59.18
15.00	71.40	60.26	58.46	56.80	55.31	53.86
20.00	73.20	55.76	54.02	52.39	51.01	49.67
30.00	76.80	49.06	47.44	45.94	44.67	43.52
40.00	80.20	44.28	42.76	41.46	40.23	39.20
48.00	83.60	–	–	–	–	–
50.00	84.10	40.67	39.28	38.11	36.95	35.98
55.00	84.70	–	–	–	–	–
60.00	85.30	37.85	36.60	35.47	34.43	33.52
70.00	86.90	35.56	34.43	33.30	32.40	31.56
80.00	88.70	33.55	32.53	31.46	30.63	29.86
90.00	90.70	31.69	30.74	29.87	29.00	28.27
95.00	91.60	30.86	29.95	29.15	28.27	27.56
99.00	92.60	–	–	–	–	–
100.00	–	30.20	29.37	28.48	27.69	26.98

composition the strongest interactions between components involving hydrogen bonds, are observed, and the most stable "complex" is $H_2O \bullet$ BD-1,3.

From the relative permittivity (Tab. I), the temperature coefficient of the relative permittivity, denoted α_{12}, viz. $\alpha_{12} = (1/\varepsilon_{12})\cdot[d\varepsilon_{12}/d(1/T)]$, were calculated. The composition range of binary liquid mixtures within which α_{12} attains its highest value should be interpreted (as shown in Räetzsch *et al.*'s thermodynamic considerations [4]) as a region characterized by maximal intermolecular interactions between two different components of the given liquid mixture. Conclusions drawn from the analysis of changes $\Delta\delta$ and α_{12} are fully consistent [1, 4]. Changes in the α_{12} vs. composition of liquid H_2O-BD-1,3 mixtures are shown in Figure 1.

The maximum of α_{12} is found at ca. 50 mol. % of BD-1,3. This confirms the conclusion from ^{1}H-NMR spectral data concerning the formation of a "complex" of $H_2O \bullet$ BD-1,3.

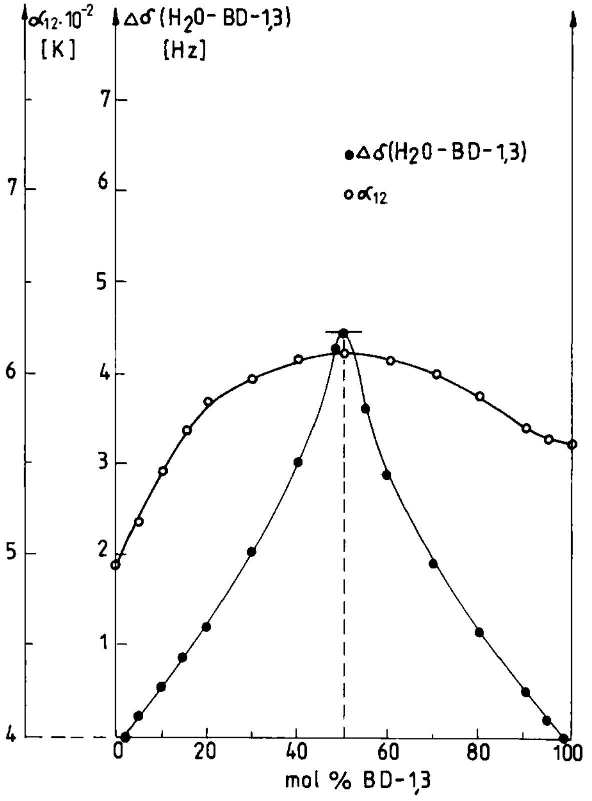

FIGURE 1 Changes in $\Delta\delta(H_2O - BD\text{-}1,3)$ at 298 K and changes in the temperature coefficient of relative permittivity (α_{12}) as a function of composition for the liquid H_2O–BD-1,3 mixtures, at 298.15 K.

Additional information about intermolecular interactions in liquid binary mixtures is provided by the analysis of deviations from "ideality" of basic physicochemical properties of these mixtures, i.e., density (d_{12}), viscosity (η_{12}), relative permittivity (ε_{12}) and molar volumes (V_{12}) [1, 4]. A thorough review of the literature data justifies the correctness of using these parameters in the analysis of intermolecular interactions [5]. In this study, using experimental values of relative permittivity (see Tab. I) and literature values [2] of viscosity and density at 298.15 K, the deviations from "ideality" of the functions involved have been calculated from the following equations:

$$\Delta(d_{12})^{(x)}_{\text{ideal.}} \approx \Delta(d_{12})^{(x)}_{\text{add.}} = d_{12} - \frac{x_1 \cdot M_1 + x_2 \cdot M_2}{x_1 \cdot \frac{M_1}{d_1} + x_2 \cdot \frac{M_2}{d_2}}$$

$$\Delta(\eta_{12})^{(x)}_{\text{ideal.}} = \Delta(\eta_{12})^{(x)}_{\text{add.}} = \eta_{12} - (\eta_1)^{x_1} \cdot (\eta_2)^{x_2}$$

$$\Delta(\varepsilon_{12})^{(x)}_{\text{ideal.}} \cong \Delta(\varepsilon_{12})^{(x)}_{\text{add.}} = \varepsilon_{12} - (x_1 \cdot \varepsilon_1 + x_2 \cdot \varepsilon_2)$$

$$\Delta(V_{12})^{(x)}_{\text{ideal.}} = \Delta(V_{12})^{(x)}_{\text{add.}} = V_{12} - (x_1 \cdot V_1 + x_2 \cdot V_2)$$

where M is the molecular weight.

Values calculated from the above equations over a range of H_2O – BD-1,3 mixtures (at 298.15 K) are shown in Table II.

Deviations from "ideality" in densities, viscosities, relative permittivities and molar volumes attain their highest values at ca.: 20 mol. %, 70 mol. %, 33 mol. % and 40 mol. % BD-1,3 which suggest the formation of stable intermolecular "complexes" of the types $4H_2O$ • BD-1,3, H_2O • 2BD-1,3, $2H_2O$ • BD-1,3 and $3H_2O$ • 2BD-1,3. It follows from the work of Piekarski [3] dealing with changes of Kirkwood's correlation factor as function of the composition of the mixed solvent H_2O–BD-1,3 and literature data [6] regarding the structure of liquid BD-1,3 that formed in the studied liquid system intermolecular "complexes" have the linear internal structure.

TABLE II The deviations from "ideality" of density, viscosity, relative permittivity and molar volume as a function of concentration for the liquid H_2O – BD-1,3 mixtures at 298.15 K

BD-1,3 (*mol.* %)	$\Delta(d_{12})^{x}_{\text{ideal.}}$ [$g \cdot cm^{-3}$]	$\Delta(\eta_{12})^{x}_{\text{ideal.}}$ [cP]	$\Delta(\varepsilon_{12})^{x}_{\text{ideal.}}$	$\Delta(V_{12})^{x}_{\text{ideal.}}$ [$cm^3 \cdot mol^{-1}$]
0.00	0.00000	0.00	0.00	0.0000
5.00	0.00710	0.80	−6.66	−0.1529
10.00	0.01387	2.16	−11.18	−0.3462
15.00	0.01766	–	–	−0.5012
20.00	0.01885	6.08	−16.13	−0.6008
22.00	0.01868	–	–	−0.6285
25.50	0.01852	–	–	−0.6559
30.00	0.01821	12.03	−17.57	−0.7092
40.00	0.01595	18.86	−17.05	−0.7353
50.00	0.01314	25.45	−15.40	−0.7010
60.00	0.01021	32.22	−13.02	−0.6187
70.00	0.00741	36.43	−10.20	−0.5030
80.00	0.00474	35.54	−7.03	−0.3565
90.00	0.00231	25.31	−3.61	−0.1906
95.00	0.00114	13.51	−1.84	−0.0985
100.00	0.00000	0.00	0.00	0.0000

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