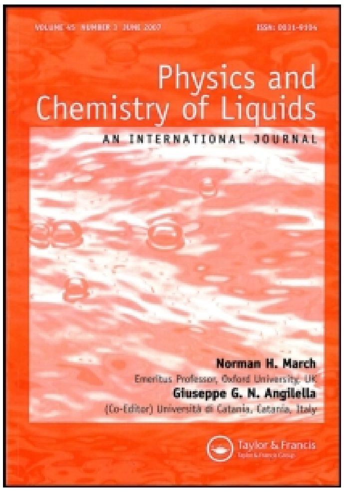


Physics and Chemistry of Liquids
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713646857

Studies on Intermolecular Interactions in Liquid Butane-1,2-Diol-Water Mixtures

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

To cite this Article Kinart, Cezary M. and Kinart, Wojciech J.(1995) 'Studies on Intermolecular Interactions in Liquid Butane-1,2-Diol-Water Mixtures', Physics and Chemistry of Liquids, 30: 4, 243 — 249
To link to this Article: DOI: 10.1080/00319109508030671
URL: http://dx.doi.org/10.1080/00319109508030671

Phys. Chem. Liq., 1995, Vol. 30, pp. 243–249
Reprints available directly from the publisher
Photocopying permitted by license only

STUDIES ON INTERMOLECULAR INTERACTIONS IN LIQUID BUTANE-1,2-DIOL–WATER MIXTURES

CEZARY M. KINART

Department of Chemical Education, University of Lodz,
90-136 Lodz, Lindleya 3, Poland

WOJCIECH J. KINART**

Department of Organic Chemistry, University of Lodz,
90-136 Lodz, Narutowicza 68, Poland

(Received 5 April 1995)

The ^{1}H-NMR spectra of butane-1,2-diol (BD-1,2) – water mixtures as function of concentration were recorded at 298 K and the spectral parameters, $\Delta\delta$(BD-1,2 – H_2O) were evaluated. The surface tensions (σ_{12}) were measured at 298.15 K. From literature values of density (d_{12}), viscosity (η_{12}), dielectric permittivity (ε_{12}) and the measured surface tensions the molar volumes (V_{12}) and their deviations from "ideality", at 298.15 K, were calculated. Further on the temperature coefficients of dielectric permittivity, α_{12}, were evaluated. These structural parameters as functions of concentration suggest the formation of the "complexes" (sub-units) of the BD-1,2 · $2H_2O$, BD-1,2 · $4H_2O$ and 2BD-1,2 · H_2O types.

KEY WORDS: Intermolecular interactions in liquid mixtures, ^{1}H-NMR spectra, surface tensions.

INTRODUCTION

Previously the mutual intermolecular interactions in liquid mixtures of butane-1,4-diol – water were studied[1]. The present paper includes the results of studies on butane-1,2-diol – water system.

It was intended to determine the effect of the hydrophobic radical length in isomeric butanediols on the water structure in these water–diol systems which are not fully understood as yet. The structure of all the isomeric butanediols in the form of vapour, liquid and their diluted solution in organic solvents has been thoroughly investigated by Kuhn[2] and Fishman and Chen[3]. It follows from the work of the latter authors that all the isomeric butanediols can form both intra- and intermolecular hydrogen bonds. The intermolecular bonds in liquid BD-1,2 and BD-1,4 are 0.76 Å and 0.75 Å in length, respectively, while those of intermolecular bonds are 2.1 Å and 1.2 Å, respectively. Differences in the intermolecular bond length result in the formation of five-membered rings in BD-1,2 and seven-membered ones in BD-1,4. These conclusions are confirmed by the values of the intermolecular hydrogen bonding energy[3]. Taking into consideration all the aforementioned literature data it seemed of interest to extend studies on intermolecular interactions in liquid BD-1,2 – water mixtures, using ^{1}H-MR spectra and physicochemical methods.

EXPERIMENTAL

Butane-1,2-diol (Merc, Schuchard) was stored over molecular sieves for a few days following which it was distilled under vacuum. Fractions of BD-1,2 were collected at 102 °C and 5 mm Hg. The water content in the solvent was determined by the Carl Fischer method and was found not to exceed 0.01 wt%. Water was prepared for measurements as previously[1]. The ^{1}H-NMR spectra were recorded using a Tesla BS 467 (60 MHz) spectrometer, at 298 ± 1 K. The chemical shift values for proton signals of BD-1,2 and H_2O were measured with an accuracy of about ± 0.2 Hz in respect to an external HMDS (hexamethyldisiloxane). The surface tensions measurements were performed with an accuracy ± 0.1% using a stalagmometer. All the solutions were prepared by weight.

RESULTS AND DISCUSSION

Only Bald *et al.*,[4] have measured physicochemical properties (density, viscosity and dielectric permittivity) of the BD-1,2 – H_2O mixtures. They have measured the electric conductivity of NaI in this mixtures. They have postulated on the basis of results obtained by them that the strongest intermolecular interactions between components of butane-1,2-diol – water liquid binary mixtures are present within the composition range corresponding to ca. 30 mol. % of BD-1,2. However, no conclusion can be derived on the basis of their work regarding the number or stoichiometry of intermolecular "complexes" (sub-units) composed from molecules of butane-1,2-diol and water, which may be formed.

In the present work, in order to achieve more conclusive results, the chemical shift differences, δ(BD-1,2 – H_2O) were measured at 298 K, between the centre of the ^{1}H-NMR signals of the multiplet corresponding to two methylene protons of the —CH_2—OH group of BD-1,2 molecules and the centre ^{1}H-NMR signal of water molecules over a wide range of solvent compositions, i.e., from 0.47 to 98.11 mol. % of butane-1,2-diol. From these new spectral data the spectral parameter $\Delta\delta$(BD-1,2 – H_2O) has been found (using the same method as previously [1,4]). We have shown in our previous papers[1,5] that the maximum values of this parameter are located at the composition with the strongest intermolecular interactions between the components whereby hydrogen bonding is involved. Values of the chemical shift differences δ(BD-1,2 – H_2O) measured over the whole range of compositions are listed in Table 1. The changes of parameter $\Delta\delta$(BD-1,2 – H_2O) shown in Figure 1 exhibit maximum at ca. 67 mol. % of BD-1,2. Thus, the conclusion can be drawn that at this composition the strongest hydrogen bond interactions between components are displayed, and that the most stable "complex" (sub-unit) is of the 2BD-1,2 · H_2O type.

Table 1 Relative ^{1}H-NMR chemical shifts, δ(BD-1,2 – H_2O), and surface tensions for binary liquid mixtures BD-1,2 – H_2O, measured at 298.15K.

mol.% of BD-1,2	*δ(BD-1,2 – H_2O) [Hz]*	*$\sigma \cdot 10^3$ [$N \cdot m^{-1}$]*
0.00	–	71.89
0.47	72.90	70.48
2.18	73.30	66.12
4.78	73.80	60.35
7.91	74.10	55.08
11.79	74.70	50.05
16.69	75.40	45.56
23.11	76.10	43.31
31.86	76.40	41.90
44.49	78.20	40.85
64.33	79.50	39.19
67.56	79.80	38.93
73.24	77.20	38.42
79.20	74.80	37.98
85.48	71.70	37.72
98.11	64.10	36.01
100.00	–	35.84

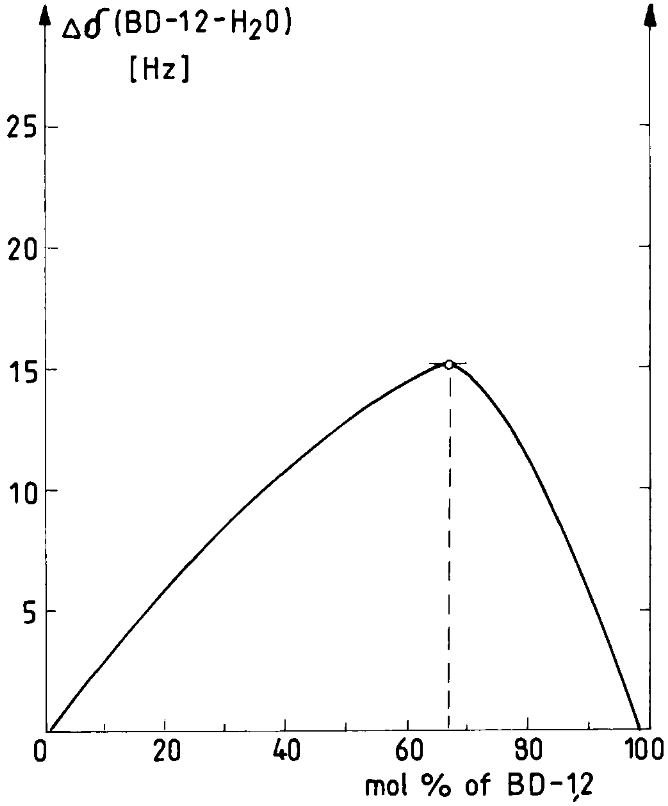


Figure 1 Changes in the function $\Delta\delta$(BD-1,2 – H_2O) = f(mol. %) for the liquid BD-1,2 – H_2O mixtures, at 298 K.

From the dielectric permittivity values (see paper[4]) the temperature coefficients of the dielectric 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's *et al.*,[6] thermodynamic consideration) as a region characterized by maximal intermolecular interactions between two different components of given liquid mixture. Conclusions drawn from analysis of changes in $\Delta\delta$ and α_{12} are fully consistent[1-4]. Changes in α_{12} vs. composition of liquid BD-1,2 – H_2O mixtures are shown in Figure 2.

The maximum of α_{12} is found at ca. 67 mol. % BD-1,2. This confirms the conclusion drawn from ^{1}H-NMR spectral data regarding the formation of a "complex" (sub-unit) of the $2BD\text{-}1{,}2 \cdot H_2O$.

Further interesting results can be obtained by detailed analysis of the function $\alpha_{12} = f(\text{mol.\% BD-1,2})$. This indicates that the increasing addition of BD-1,2 to

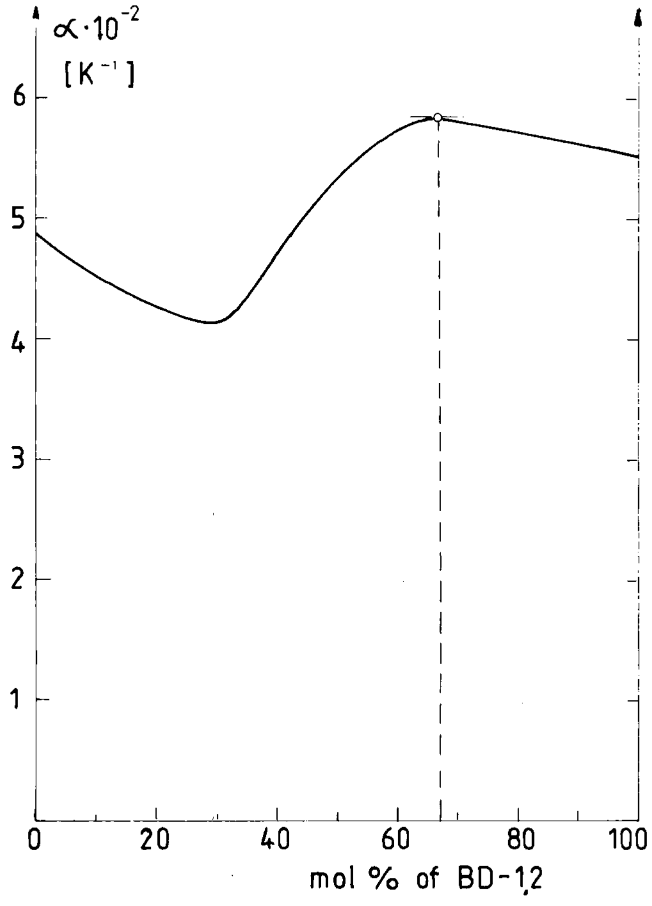


Figure 2 Changes in the temperature coefficient of dielectric permittivity drawn as a function of composition for the liquid BD-1,2 – H_2O mixtures, at 298.15 K.

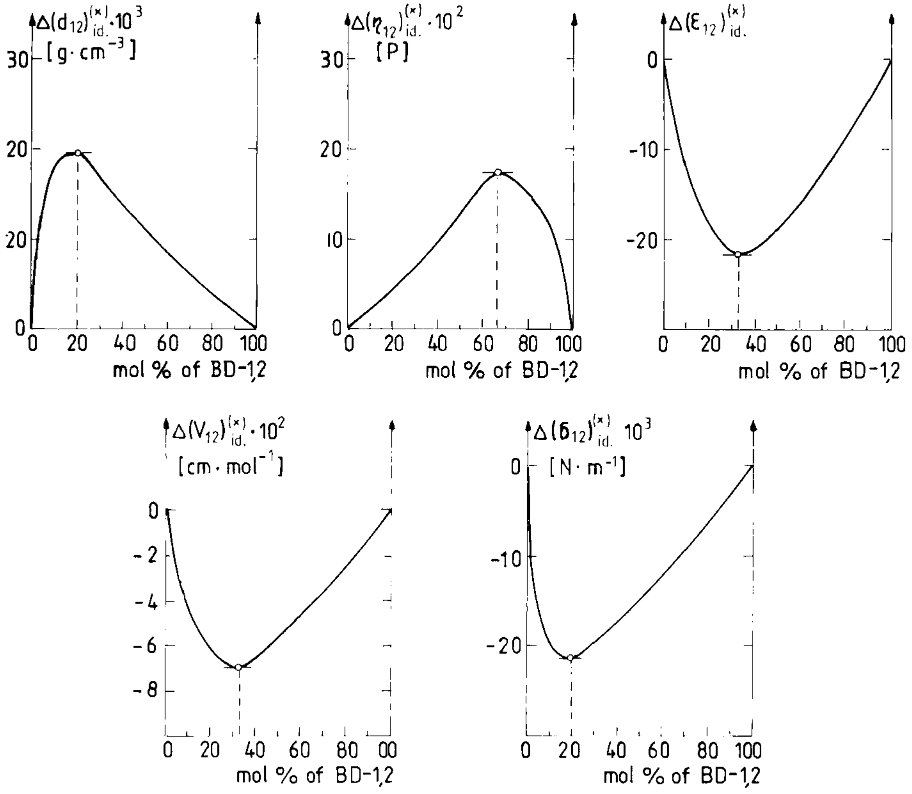
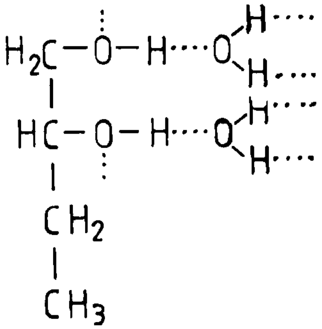


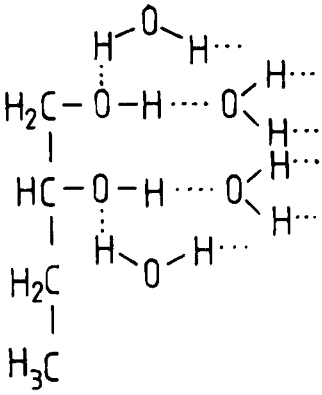
Figure 3 The course of changes of deviations from "ideality" of density, viscosity, dielectric permittivity, molar volume and surface tension as a function of composition for the liquid BD-1,2 – H_2O mixtures, at 298.15 K.

water up to ca. 30 mol. % BD-1,2, where a minimum is reached, causes a rapid drop in α_{12}. Further addition of BD-1,2 to the mixtures causes an increase in α_{12}, which results in a maximum at ca. 67 mol. % BD-1,2. Therefore, it is possible to assume that the internal structure of H_2O is disrupted by the addition of small amounts of BD-1,2 (up to 30 mol. %), whereas further addition of BD-1,2, up to ca. 67 mol.%, stabilizes the internal structure of mixed solvent increasingly by hydrogen bonding between the component molecules. The same analysis made for the butane-1,2-diol-rich composition region shows a continuous increase in α_{12} down to ca.6 mol. % of BD-1,2. Therefore, it seems that the molecules of H_2O, within the composition range 100–67 mol. % BD-1,2, act as "structure-makers" with respect to molecules of BD-1,2 in the neat solvent.

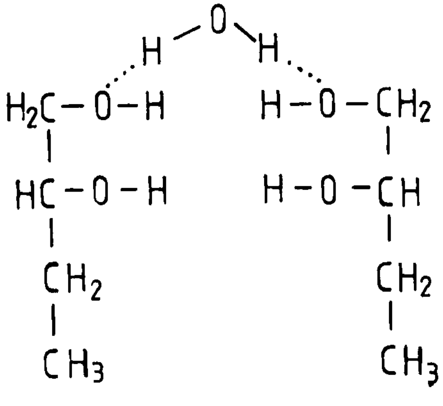
Additional information about intermolecular interactions in liquid binary mixtures is provided by the analysis of deviations from "ideality" of basic physicochemical properties of these mixtures, i.e., density (d_{12}), viscosity (η_{12}), dielectric permittivity (ε_{12}), surface tension (σ_{12}) and molar volumes (V_{12})[1,5,7]. A thorough review of the literature justifies the correctness of using these parameters in the



sub-unit: BD-1,2·$2H_2O$



sub-unit: BD-1,2·$4H_2O$



sub-unit: 2BD-1,2·H_2O

Figure 4

analysis of intermolecular interactions[7]. In this paper, using experimental values of surface tensionat 298.15 K (see Tab. 1) and literature values of density, viscosity and dielectric permittivity[4] the deviations from "ideality" of the functions involved have been calculated from the following equations.

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

where: M-molecular weight

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

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

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

where:

$$V = \frac{M}{d}$$

$$\Delta(\sigma_{12})^{(x)}_{\text{ideal}} = \Delta(\sigma_{12})^{(x)}_{\text{add}} = \sigma_{12} - (x_1 \cdot \sigma_1 + x_2 \cdot \sigma_2)$$

Values calculated from above equations over a wide range of BD-1,2 – H_2O mixtures (at 298.15 K) are shown in Figure 3.

The value of $\Delta(\eta_{12})^{(x)}_{\text{ideal}}$ exhibits the largest deviation from "ideality" at the compositions ca. 67 mol. % of BD-1,2 what suggests the formation of a "complex" (sub-unit) of the 2BD-1,2 · H_2O type. This confirms the conclusion drawn from ^{1}H-NMR spectral data and dielectric measurements. The values of $\Delta(V_{12})^{(x)}_{\text{ideal}}$ and $\Delta(\varepsilon_{12})^{(x)}_{\text{ideal}}$ have a minimum at the composition ca. 33 mol. % of BD-1,2 whereas the values of $\Delta(d_{12})^{(x)}_{\text{ideal}}$ and $\Delta(\sigma_{12})^{(x)}_{\text{ideal}}$ have a maximum at the composition ca. 20 mol.% of BD-1,2 what suggests the formation of the "complexes" (sub-units) of BD-1, 2 · $2H_2O$ and BD-1,2 · $4H_2O$ types.

Therefore, due to all aforementioned literature data[2,3], concerning the structure of liquid BD-1,2 and H_2O and the present studies, the structure of the mentioned above "complexes" (sub-units) of the BD-1,2 · $2H_2O$, BD-1,2·$4H_2O$ and 2BD-1, 2·H_2O types can be suggested as given in Figure 4.

References

1. C. M. Kinart, *Phys. Chem. Liq.*, **26**, 209 (1993).
2. L. P. Kuhn and R. E. Bowman, *Spectrochim. Acta*, **17**, 650 (1961).
3. E. Fishman and T. L. Chen, *Spectrochim. Acta*, **25 A**, 1231 (1969).
4. A. Bald, A. Szejgis, J. Woźnicka and M. Jóźwiak, *J. Chem. Research* (s), 249 (1992); (**M**), 2201 (1992).
5. S. Romanowski, C. M. Kinart and W. J. Kinart, *J. Chem. Soc. Faraday Trans.*, **91**, 65, (1995).
6. M. T. Räetzsch, H. Kehlen and H. Rosner, *Z. Phys. Chem.* (Leipzig), **255**, 115 (1974).
7. L. Skulski and C. M. Kinart, *Pol. J. Chem.*, **66**, 287 (1992).