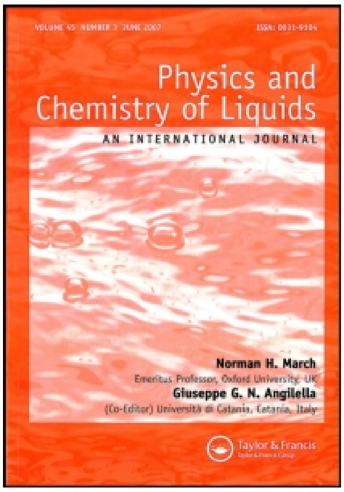

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STUDY OF INTERMOLECULAR INTERACTIONS IN LIQUID BUTANE-1,4-DIOL-WATER MIXTURES BY MEANS OF MEASURING THEIR ^{1}H-NMR SPECTRA AND ANALYSIS OF THEIR PHYSICOCHEMICAL PROPERTIES

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The ^{1}H-NMR spectra of butane-1,4-diol (BD-1,4)–water (H_2O) mixtures as function of concentration were recorded at 298 K and the spectral parameter, $\Delta\delta$(BD-1,4–H_2O) data were evaluated. From literature values of density (d_{12}), viscosity (η_{12}) and dielectric permittivities (ε_{12}), molar volumes (V_{12}), kinematic viscosities (η_{12}/d_{12}) and their deviations from "ideality" were calculated. Further on, the temperature coefficients of the dielectric permittivity, $\alpha_{12} = (1/\varepsilon_{12})\cdot[d\varepsilon_{12}/d(1/T)]$, were found. These structural parameters as functions of concentration suggest the formation of the "complexes" (sub-units) of the BD-1,4·2 H_2O, 2 BD-1,4·3 H_2O and 2 BD- 1,4·H_2O types.

KEY WORDS: ^{1}H-NMR spectra, intermolecular interactions, binary mixtures.

INTRODUCTION

Previous studies on the internal structure of various liquid binary mixtures are continued in this paper[1–5]. Now the intermolecular interactions in the mixtures of butane- 1,4-diol (BD-1,4) and water (H_2O) will be analysed. The ^{1}H-NMR spectra of liquid BD-1,4-H_2O mixtures (at 298 K) within nearly the whole range of compositions (i.e. from 2.21 to 64.65 mol.% of BD-1,4) were recorded. The same graphical method as used previously[1–5] has been applied to determine the relative differences in the chemical shift values δ(BD-1,4-H_2O) of the centre of the multiplet corresponding to two methylene protons of the $-CH_2OH$ group of BD-1,4 and the centre of the H_2O protons signal. Subsequently, the spectral parameters $\Delta\delta$(BD-1,4-H_2O) have been evaluated. Furthermore, literature values[6] of densities (d_{12}), viscosities (η_{12}) and dielectric permittivities (ε_{12}) were applied for analysis of interactions in the solutions considered. From all these data, using the method[3] previously described, the molar volumes (V_{12}), kinematic viscosities (η_{12}/d_{12}), their deviations from "ideality" and temperature coefficients of dielectric permittivities have been determined and analysed.

In recent years aqueous solutions of different polyhydroxy compounds, especially those connected with biological systems, have been the object of research[7,8]. According to literature data[9–11], butane-1,4-diol can form both intra- and intermolecular hydrogen bonds. Water is obviously a strongly associated liquid. Thus, there is a possibility that different association equilibria in BD-1,4 water mixtures can occur. Taking into consideration all the aforementioned literature data it seemed of interest to extend those studies using ^{1}H-NMR spectra and physicochemical methods.

EXPERIMENTAL

For the present ^{1}H-NMR studies chemical pure butane-1,4-diol (P.P.H. POCH Gliwice) were used. It was stored over 4 Å molecular sieves for a few days following which BD-1,4 was distilled under vacuum in a dry nitrogen atmosphere. Fractions of BD-1,4 were collected at 112°C and 5 mm. The water content in the solvent was determined by the Karl Fisher method and it was found not to exceed 0.03 wt%. The refractive index of the dial had the value $n_D^{20} = 1.4468$, in good agreement with the literature data[12]. Water was deconized, distilled over alkaline $KMnO_4$ and finally distilled twice in an argon atmosphere. ^{1}H-NMR spectra were recorded on the Tesla spectrometer of the type BS 467 (60 MHz), at 298 ± 1 K. The chemical shift values for proton signals of butane-1,4-diol and water were measured with an accuracy of about ± 0.2 Hz in respect to an external standard HMDS (hexamethyldisiloxane). All the binary solutions made of BD-1,4 and H_2O were prepared by weight.

RESULTS AND DISCUSSION

There are a limited number of studies on the structure of liquid binary mixtures BD-1,4-H_2O. Nakomishi *et al.*[13] have listed values of densities and partial volumes (V^E). They have suggested, that the large negative ΔV^E value observed in the liquid BD-1,4-H_2O mixture containing 60 mol.% of H_2O can be well explained by the occupation of the free volume, or cavities, in the open BD-1,4 structure with water. The same position was taken by Krestov[14], who has presented thermodynamic functions of the viscous flow of BD-1,4-H_2O mixtures. Bald *et al.*[6] have measured the electric conductance of NaI in the BD-1,4-H_2O mixtures. They have also analysed changes in viscosities, relative dielectric permittivities, densities and calculated them from molar volumes, polarizabilities and their excess values (i.e. V^E and ε^E) as functions of compositions of the same binary mixtures. They have postulated on the basis of results obtained that the strongest intermolecular interactions between

Table 1 Relative chemical shifts, δ(BD-1,4-H_2O), measured at 298 K.

mol. % of BD-1,4	δ(BD-1,4-H_2O) [Hz]
2.21	72.75
4.83	74.25
8.01	75.75
11.93	77.75
16.89	79.25
23.36	81.50
32.16	83.75
37.48	85.25
40.75	86.25
44.84	89.00
52.51	94.50
64.65	105.00

In the present work, in order to achieve more conclusive results, the chemical shift differences, δ(BD-1,4-H_2O) (in Hz) were measured at 298 K, between the centre of the ^{1}H-NMR signals of the multiplet corresponding to two methylene protons of the $-CH_2OH$ group of BD-1,4 molecules and the centre of the ^{1}H-NMR signals of water molecules over a wide range of solvent compositions, i.e. from 2.21 mol.% to 64.65 mol.% of butane-1,4-diol. Subsequently, using the same method as previously[1-5], from these new spectral data the spectral parameter $\Delta\delta$(BD-1,4-H_2O) has been found. The maximum values of this parameter, as has been shown in my previous papers[1-5], 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-1,4-H_2O) measured over the whole range of concentrations are listed in Table 1. The changes of parameter $\Delta\delta$(BD-1,4-H_2O) shown in Figure 1 exhibit maximum at ca. 40 mol.% of BD-1,4. 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 2 BD-1,4 $\cdot$ 3 H_2O type.

Using values of dielectric permittivities[6], the temperature coefficient of ε_{12}, denoted α_{12}, viz. $\alpha_{12} = (1/\varepsilon_{12}) \cdot [d\varepsilon_{12}/d(1/T)]$ was calculated. It was established[15] that this coefficient can be used as a good criterion for estimating the mutual interactions between components of the solution with hydrogen bonds involved. In my previous works[1-5] it has been shown that there is a fairly good agreement in conclusions drawn from the behaviour of the spectral parameter $\Delta\delta$ and for the α_{12} property. The changes of the coefficient α_{12} as a function of the composition at 298.15 K are shown in Figure 2.

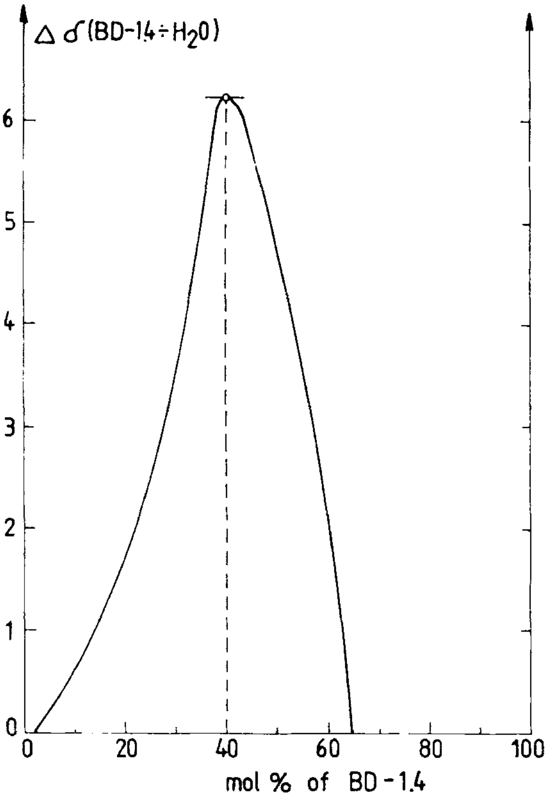

Figure 1 Changes in the function $\Delta\delta(\text{BD-1,4-H}_2\text{O}) = f(\text{mol.\%})$ for the liquid butane-1,4-diol–water mixtures, at 298 K.

structure of various liquid binary mixtures. Using the literature[6] values of densities (d_{12}), viscosities (η_{12}), and dielectric permittivities (ε_{12}) at 298.15 K the deviations from "ideality" of these functions were evaluated using the following equations:

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

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

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

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

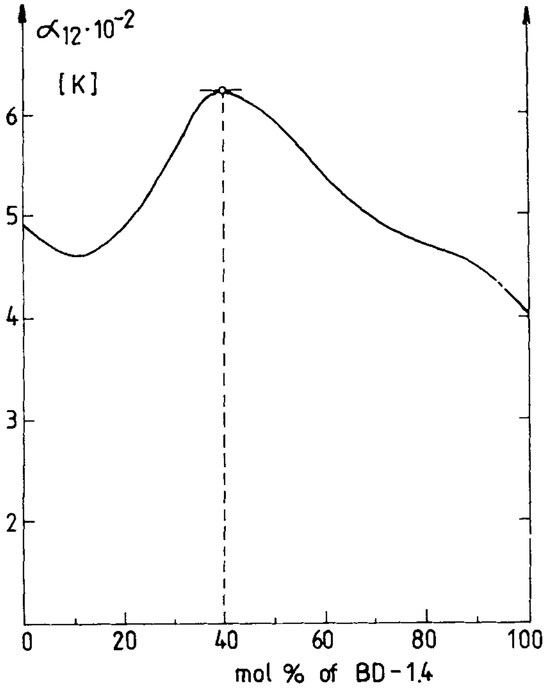

Figure 2 Changes in the temperature coefficient of dielectric permittivity drawn as a function of composition for the liquid butane-1,4-diol–water mixtures at 298.15 K.

where

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

$$\Delta\left(\frac{\eta_{12}}{d_{12}}\right)^{(x)}_{\text{ideal.}} \cong \Delta\left(\frac{\eta_{12}}{d_{12}}\right)^{(x)}_{\text{add.}} = \frac{\eta_{12}}{d_{12}} - \left(\frac{\eta_1}{d_1}\right)^{x_1}\left(\frac{\eta_2}{d_2}\right)^{x_2}$$

These changes as functions of the composition are shown in Figure 3. The values of $\Delta(\varepsilon_{12})^{(x)}_{\text{ideal.}}$ and $\Delta(V_{12})^{(x)}_{\text{ideal.}}$ exhibit the largest deviations from "ideality" at the composition ca. 40 mol.% of BD-1,4 which suggest the formation of a "complex" (sub-unit) of the 2 BD-1,4 · 3 H_2O type. This confirms the conclusion drawn ^{1}H-NMR spectral data and dielectric measurements. The value of $\Delta(d_{12})^{(x)}_{\text{ideal.}}$ has a maximum at the composition ca. 33 mol.% of BD-1,4, whereas the values of $\Delta(\eta_{12})^{(x)}_{\text{ideal.}}$ and $\Delta(\eta_{12}/d_{12})^{(x)}_{\text{ideal.}}$ have maximum at the composition ca. 68–70 mol.% of BD-1,4 which confirms the formation of the "complexes" (sub-units) of the BD-1,4 · 2 H_2O and 2 BD-1,4 · 2 H_2O types. The analysis of the Walden's product ($\Lambda_0 \cdot \eta_{12}$) or more precisely its logarithm ($\log \Lambda_0 \cdot \eta_{12}$) plotted in the function of the reciprocal of dielectric

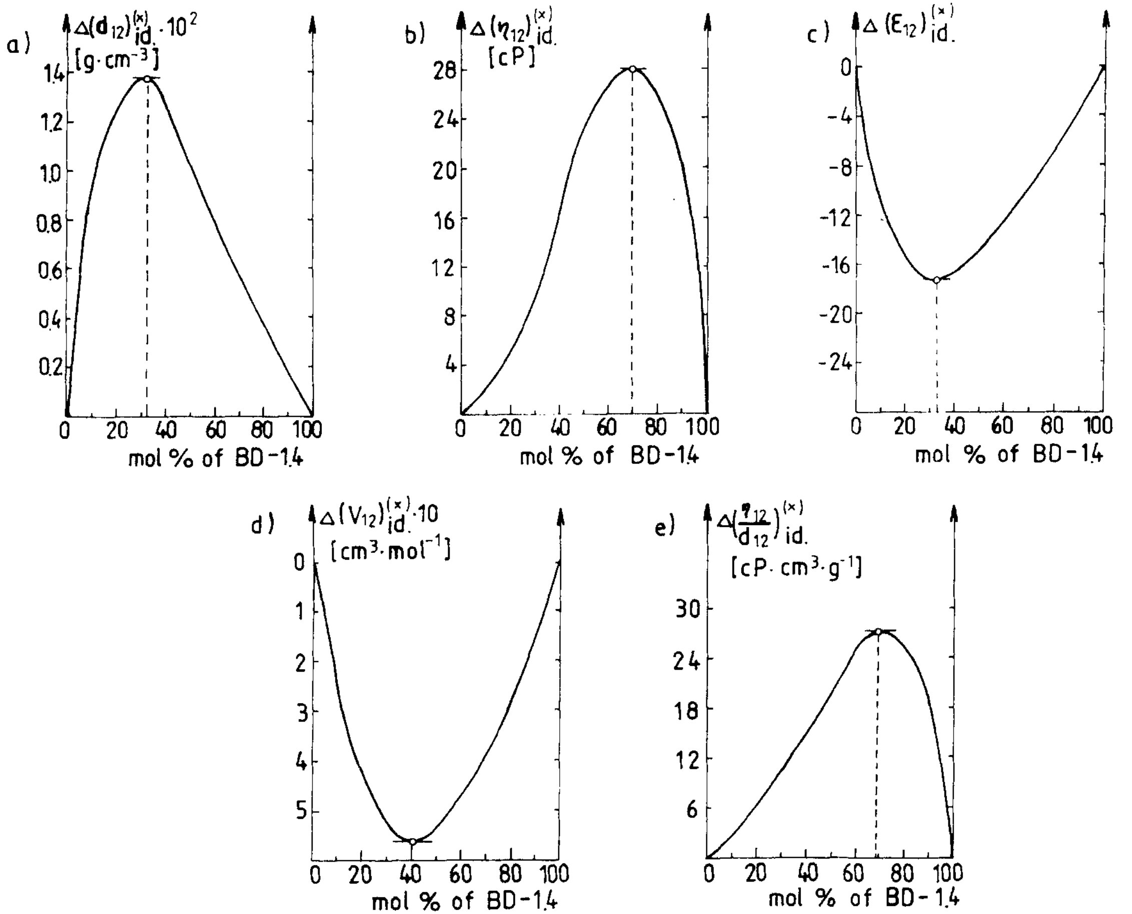

Figure 3 The course of changes of deviations from "ideality" of density, viscosity, dielectric permittivity, molar volume and kinematic viscosity as a function of composition for the liquid butane-1,4-diol–water mixtures at 298.15 K.

permittivity of the studied liquid mixture has been applied previously by other authors[16,17] to estimate the occurrence in the system studied of intermolecular interactions. The linear behaviour of this dependence indicates that the system studied has properties close to the ideal system. In case of the presence of intermolecular interactions in the mixture under investigation the plot of function $\log \Lambda_0 \cdot \eta_{12} = f(1/\varepsilon_{12})$ is represented by two lines intersecting at the point which corresponds to the composition characterized by the maximum value of intermolecular interactions. In the present study, using literature values[6] of the molar limiting conductance (Λ_0) of NaI and viscosity in the wide composition range of BD-1,4-H_2O mixtures, I have carried out the above analysis. The graph of the function $\log \Lambda_0 \cdot \eta_{12} = f(1/\varepsilon_{12})$ consists of two lines intersecting at the point corresponding to the value of the reciprocal of delectric permittivity equal approximately to $1/\varepsilon_{12} = 0.0245$, which corresponds to ca. 40 mol.% of BD-1,4 in the studied liquid butane-1,4-diol-water mixture (see Figure 4). It fully confirms the conclusions drawn from my ^{1}H-NMR spectroscopic studies and analysis of all studied physicochemical parameters characterizing this liquid solvent mixtures. It seems that the most stable intermolecular "complexes" (sub-units) are built from molecules of BD-1,4 and H_2O corresponding to the following stoichiometry: 2 BD-1,4$\cdot$3 H_2O.

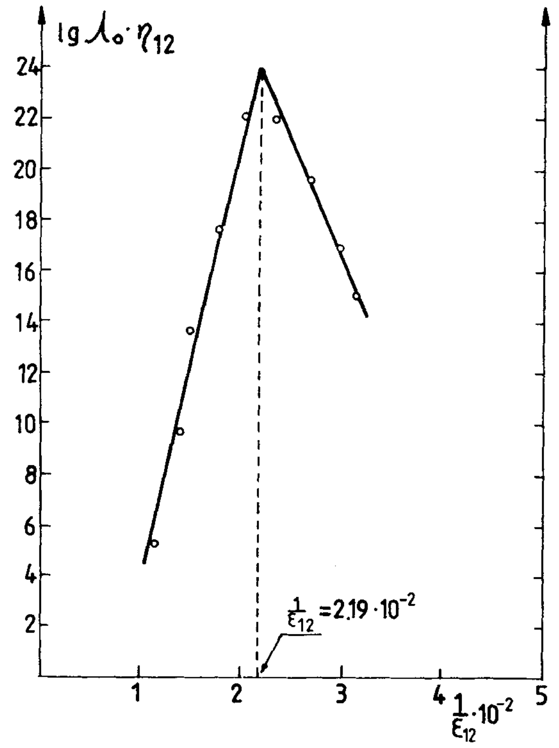

Figure 4 Changes in the function $\log \Lambda_0 \cdot \eta_{12} = f(1/\varepsilon_{12})$ for the liquid butane-1,4-diol-water mixtures at 298.15 K.

The complexes (sub-units) of the BD-1,4·2 H_2O, 2 BD-1,4·3 H_2O and 2 BD-1,4·H_2O types which are internally H-bonded form subsequently "flickering" internal structures of types (BD-1,4·2 $H_2O)_n$, (2 BD-1,4·2 $H_2O)_m$ and (2 BD-1,4·$H_2O)_p$ which can mutually convert from one to another. At the present moment it does not seem possible to construct a model of such internal structure: this will require further studies.

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