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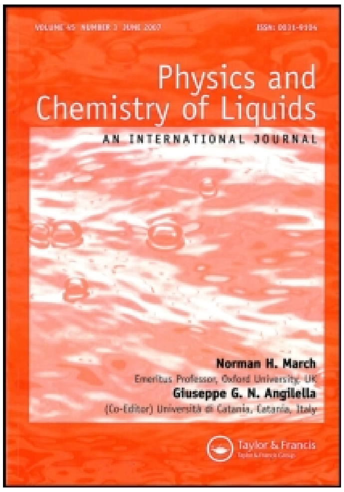

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# Study on the Internal Structures of Liquid N,N-Dimethylformamide-Benzyl Alcohol Mixtures

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# STUDY ON THE INTERNAL STRUCTURES OF LIQUID N,N-DIMETHYLFORMAMIDE–BENZYL ALCOHOL MIXTURES

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The $^1$H-NMR spectra of liquid binary mixtures, N,N-dimethylformamide (DMF)-benzyl alcohol ($PhCH_2OH$), were recorded at 298 K within whole range of the mixed solvent compositions. From these data were found the values of the spectral parameter, $\Delta\delta$(DMF-$PhCH_2OH$). The densities ($d_{12}$) and viscosities ($\eta_{12}$) of the mixed solvents were measured at 298.15 K, as well as the dielectric permittivities ($\varepsilon_{12}$) at 293.15 K, 298.15 K, 303.15 K, 308.15 K, 313.15 K and 318.15 K. From all these new parent data, the values of molar volumes ($V_{12}$), kinematic viscosities ($\eta_{12}/d_{12}$) and their deviations from "ideality" were calculated. Additionally, the values of the temperature coefficients of dielectric permittivity ($\alpha_{12}$), were found. The molar limiting conductances ($\Lambda_0$) of NaCl were measured at 298.15 K within whole range of mixed solvent compositions. From these data were found the values of the association constants ($K_A$) and the Walden products ($\Lambda_0 \cdot \eta$). The scrutiny of all these structural parameters as functions of the mixture composition points at a formation of the "complexes" (sub-units) of the DMF · $PhCH_2OH$ and DMF · 2 $PhCH_2OH$ types in the bulk of the mixed solvents.

KEY WORDS: $^1$H-NMR spectra, intermolecular interactions, molar limiting conductances.

## INTRODUCTION

This work is a continuation of our earlier studies on the analysis of intermolecular interactions in the liquid mixtures of N,N-dimethylformamide with different alcohols[1,3]. In this paper, using the $^1$H-NMR examinations of liquid N,N-dimethylformamide (DMF)-benzyl alcohol ($PhCH_2OH$) binary mixtures and changes in their main physicochemical properties of these mixtures (density, viscosity, dielectric permittivity, temperature coefficient of dielectric permittivity as well as their deviations from "ideality") and the analysis of molar limiting conductance of NaCl, the intermolecular interactions in the DMF-$PhCH_2OH$ binary mixtures will be analysed. Taking into consideration the literature data, discussed in our previous works[1,3], concerning the internal structure of DMF and different alcohols as well as the results of our own studies on the analysis of the intermolecular interactions in liquid binary mixtures of DMF with several aliphatic alcohols, it seemed quite interesting to examine the influence of phenyl ring in the molecule of benxyl alcohol on its interactions with N, N-dimethylformamide.

## EXPERIMENTAL

Benzyl alcohol (P.P.H.POCH Gliwice) was stored over type 4A molecular sieves for a few days following which it was distilled under vacuum in a dry nitrogen atmosphere. N,N-dimethylformamide (Fluka) was dried and purified according to the known procedure[4]. NaCl, Merck suprapur, was dried and purified according to the known procedure[5]. $^1$H-NMR spectra were recorded on the Tesla spectrometer of the type BS 467 (60 MHz), at $298 \pm 1$ K. The chemical shift values for proton signals of N,N-dimethylformamide and benzyl alcohol were measured with an accuracy of about $\pm 0.2$ Hz in respect to an external standard HMDS (hexamethyldisiloxane). The dielectric permittivity measurements were performed with an accuracy of $\pm 0.1\%$, using a bridge of the type OH-301 (made in Hungary), at 293.15 K, 298.15 K, 303.15 K, 308.15 K, 313.15 K and 318.15 K. The viscosities were measured with an accuracy $\pm 0.1\%$, at 298.15 K, using the Höppler viscosimeter. Solvent densities were measured at 298.15 K, using a glass pycnometer of the Lipkin type. The maximum error in the density measurements was $1 \cdot 10^{-4}$ g·cm$^{-3}$. Measurements of the conductivity, at 298.15 K, were performed by means of an E-315A type bridge produced by Mera-Tronic (Poland). A cell similar to that described by Dagett[6] was used. Molar conductance were calculated after correction for solvent conductance. The acccuracy of the temperature control was $\pm 0.01$ K. The uncertainty of the measured values of the conductivity was 0.03 – 0.08 per cent. All the solutions were prepared by weight.

## RESULTS AND DISCUSSION

There is no literature data concerning the analysis of intermolecular interactions in liquid mixtures of N,N-dimethylformamide with benzyl alcohol. In the present paper the chemical shift differences, $\delta$ (DMF-PhCH$_2$OH) (in Hz) were measured at 298 K, between the center of the $^1$H-NMR signal of the formyl proton of N,N-dimethylformamide molecules and the center of the $^1$H-NMR signal of –OH groups of benzyl alcohol molecules over a wide range of solvent compositions, i.e. from 1.25 to 99.15 mol. % of DMF. Subsequently, using the same method as previously[1-3], from these new spectral data the spectral parameter $\Delta\delta$(DMF-PhCH$_2$OH) has been found. This parameter, or more precisely, its maximum values as has been shown in our previous papers[1-3], are lacated at the composition with the strongest intermolecular interactions between the components whereby hydrogen bonds are involved. The $\delta$(DMF-PhCH$_2$OH) values are shown in Table 1, whereas the $\Delta\delta$(DMF-PhCH$_2$OH) values are visualized in Figure 1 as a function of the mixture compositions.

The analysis of the obtained data indicates the presence of a maximum $\Delta\delta$ (DMF-PhCH$_2$OH) at ca. 33 mol. % of DMF. Thus, the conclusion would be drawn that at this composition the strongest interactions between components with involving hydrogen bonds are displayed, and that the most stable "complex" (sub-unit) is of the DMF·2 PhCH$_2$OH type.

In addition to spectral examinations, the dielectric permittivities of the liquid DMF-PhCH$_2$OH mixtures under investigation were measured within full composition range at 293.15 K, 298.15 K, 303.15 K, 308.15 K, 313.15 K and

**Table 1** Relative $^1$H-NMR chemical shifts, $\delta$(DMF-PhCH$_2$OH), measured at 298 K.

| *mol. % of DMF* | *$\delta$ (DMF-PhCH$_2$OH) [Hz]* |
|---|---|
| 1.25 | 134.50 |
| 6.35 | 134.00 |
| 18.65 | 132.80 |
| 22.51 | 130.30 |
| 33.17 | 125.50 |
| 36.50 | 126.80 |
| 42.52 | 131.30 |
| 46.59 | 135.80 |
| 51.58 | 141.00 |
| 57.31 | 145.80 |
| 61.50 | 149.50 |
| 66.11 | 152.80 |
| 75.80 | 159.00 |
| 96.25 | 169.30 |
| 99.15 | 171.00 |

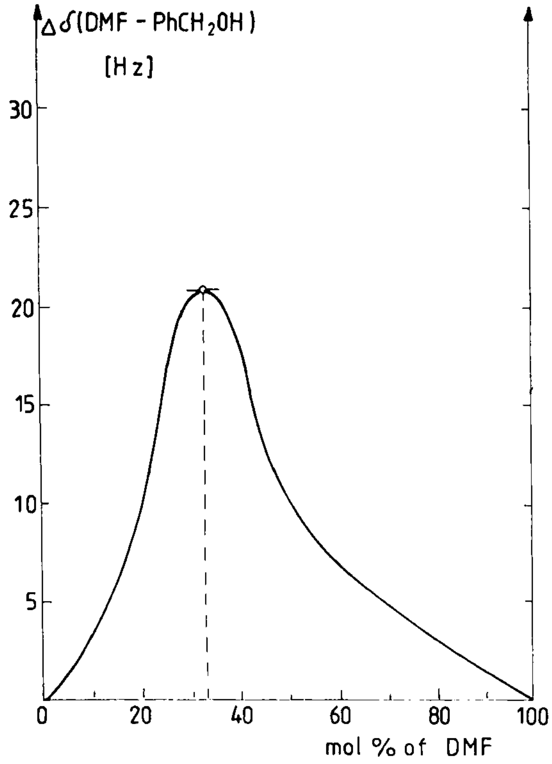

**Figure 1** Changes in the function $\Delta\delta$(DMF - PhCH$_2$OH) = $f$(mol. %) for the liquid N, N-dimethylformamide-benzyl mixtures, at 298 K.

318.15 K (see Tab. 2). This made possible for us to determine the temperature coefficient of dielectric permittivity $\alpha_{12}$, viz. $\alpha_{12} = (1/\varepsilon_{12}) \cdot [d\varepsilon_{12}/d(1/T)]$. The composition range of liquid binary mixtures, within which coefficient $\alpha_{12}$ attains the highest value, should be interpreted (as shown in Räetzsch's thermodynamic considerations[7]) as a region characterized by maximal intermolecular interactions between two different components of the given liquid mixture. It has been shown in our previous papers that there is a full consistence of conclusions drawn from the analysis of changes in spectral parameter $\Delta\delta$ and coefficient $\alpha_{12}$. Changes in the $\alpha_{12}$ value versus compositions of liquid DMF-$PhCH_2OH$ mixtures are shown in Fig. 2.

At it is seen in Figure 2, values of $\alpha_{12}$ reach their maximum at the composition having ca. 33 mol. % of DMF. This confirms the aforementioned conclusion draw from $^1H$-NMR spectral data concerning the possibility of formation of a stable "complex" (sub-unit) of the DMF$\cdot PhCH_2OH$ type.

As has been shown in our previous papers[1-3], 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 ($\eta_{12}$), dielectric permittivity ($\varepsilon_{12}$) and calculated from these data molar volumes ($V_{12}$) and kinematic viscosities ($\eta_{12}/d_{12}$). A thorough review of the literature data justifying the correctness of using these parameters in the analysis of intermolecular interactions has been given previously[8]. In this study, the deviations from "ideality" of these functions have been calculated from experimental values of dielectric permittivity (see Tab. 2), viscosity and density at 298.15 K (see Tab. 3). The course of changes of the calculated values as functions of the mixture compositions (at 298.15 K) are visualized in Figure 3.

All the functions $[\Delta(d_{12})^x_{\mathrm{ideal.}}, \Delta(\eta_{12})^x_{\mathrm{ideal.}}, \Delta(\varepsilon_{12})^x_{\mathrm{ideal.}}, \Delta(V_{12})^x_{\mathrm{ideal.}}$ and $\Delta(\eta_{12}/d_{12})^x_{\mathrm{ideal.}}]$ show the greatest deviations from "ideality" at the composition having ca. 50 mol. % of DMF which corresponds to the formation of a "complex" (sub-unit) of the DMF$\cdot PhCH_2OH$ type in the studied binary mixtures.

The conductivity of solutions of NaCl in DMF-$PhCH_2OH$ mixtures was measured at 298.15 K over the range of salt concentration equal to $1 \cdot 10^{-4} - 2 \cdot 10^{-3}$ mol$\cdot$ dm$^{-3}$. The obtained data allowed us to calculate, using the Fuoss–Justice equations[9-11], the

**Table 2** Dielectric permittivities for liquid binary mixtures DMF-$PhCH_2OH$.

| *mol. % of DMF* | $\varepsilon_{12}$ | | | | | |
|---|---|---|---|---|---|---|
| | *293.15 K* | *298.15 K* | *303.15 K* | *308.15 K* | *313.15 K* | *318.15 K* |
| 0.00 | 13.51 | 13.19 | 12.70 | 12.15 | 11.25 | 10.95 |
| 6.50 | 14.75 | 14.49 | 13.86 | 13.40 | 12.78 | 12.22 |
| 12.94 | 16.10 | 15.91 | 15.35 | 14.75 | 14.26 | 13.75 |
| 25.80 | 19.61 | 18.81 | 18.42 | 17.94 | 17.37 | 16.72 |
| 31.42 | 20.98 | 20.32 | 19.75 | 19.18 | 18.36 | 17.91 |
| 36.50 | 21.95 | 21.55 | 20.85 | 20.21 | 19.49 | 19.05 |
| 47.24 | 25.93 | 23.68 | 22.91 | 22.39 | 21.60 | 21.15 |
| 57.31 | 26.05 | 25.68 | 25.21 | 24.60 | 23.71 | 23.35 |
| 75.80 | 29.98 | 30.35 | 29.32 | 28.91 | 28.60 | 27.58 |
| 92.35 | 34.92 | 34.55 | 33.75 | 33.44 | 32.76 | 31.80 |
| 100.00 | 38.30 | 37.70 | 36.87 | 36.01 | 35.14 | 34.29 |

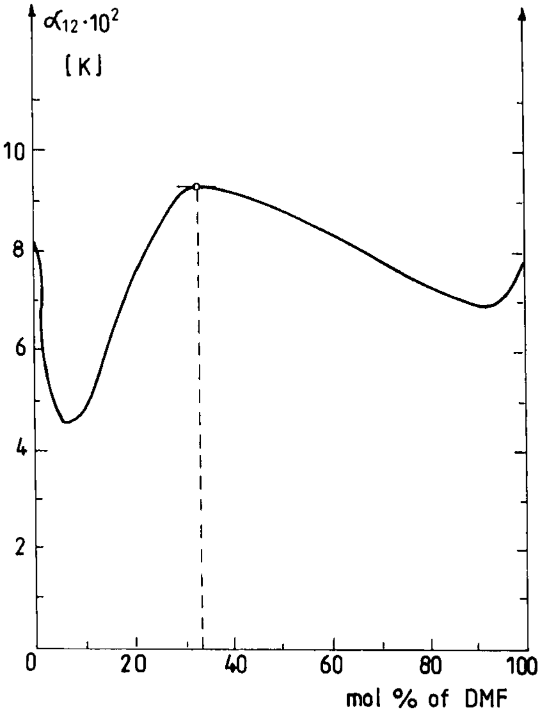

**Figure 2** Changes in the temperature coefficient of dielectric permittivity drawn as a function of composition for the liquid DMF-PhCH$_2$OH mixtures at 298.15 K.

**Table 3** Densities ($d_{12}$) and viscosities ($\eta_{12}$) for liquid binary mixtures DMF-PhCH$_2$OH, measured at 298.15 K.

| *mol. % of DMF* | $d_{12}$ [$g \cdot cm^{-3}$] | $\eta_{12}$ [$cP$] |
|---|---|---|
| 0.00 | 1.0416 | 5.8140 |
| 6.50 | 1.0379 | 5.1400 |
| 12.94 | 1.0329 | 4.5580 |
| 25.80 | 1.0223 | 3.5890 |
| 31.42 | 1.0180 | 3.2060 |
| 36.50 | 1.0136 | 2.8930 |
| 47.24 | 1.0048 | 2.4160 |
| 57.31 | 0.9963 | 2.0360 |
| 75.80 | 0.9762 | 1.4370 |
| 92.35 | 0.9554 | 1.0100 |
| 100.00 | 0.9438 | 0.8024 |

values of molar limiting conductances ($\Lambda_0$), association constants of NaCl ($K_A$) and the Walden products ($\Lambda_0 \cdot \eta$) in the whole range of compositions of the DMF-PhCH$_2$OH mixtures, at 298.15 K. Values of molar limiting conductances and association constants are listed in Table 4.

The analysis of the Walden's product ($\Lambda_0 \cdot \eta$) or more precisely its logarithm plotted in the function of the reciprocal of dielectric permittivity of the studied liquid

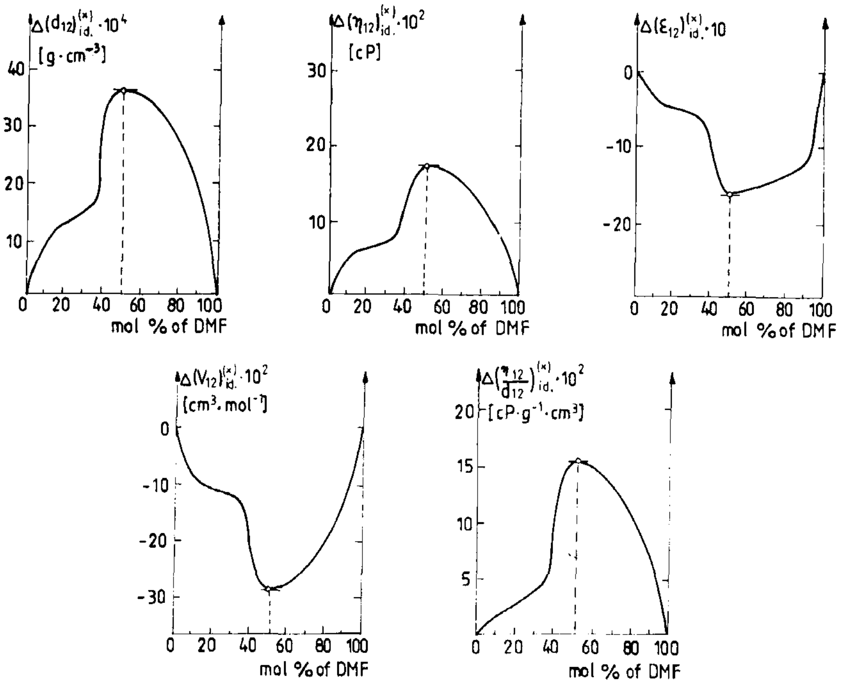

**Figure 3** The course of changes of deviations from "ideality" of density, viscosity, dielectric permittivity, molar volume and kinematic viscosity of composition for the liquid DMF-PhCH$_2$OH mixtures at 298.15 K.

**Table 4** Limiting molar conductances ($\Lambda_0$), Walden products ($\Lambda_0 \cdot \eta$), ionic association constants ($K_A$), standard errors ($\sigma\Lambda_0$ and $\sigma K_A$) for NaCl in N,N-dimethylformamide-benzyl alcohol mixtures at 298.15 K.

| *mol. % of DMF* | $\Lambda_0$ *[cm$^2$ · mol$^{-1}$ · ohm$^{-1}$]* | $\sigma\Lambda_0$ *[cm$^2$ · mol$^{-1}$ · ohm$^{-1}$]* | $\Lambda_0 \cdot \eta_{12}$ *[cm$^2$ · mol$^{-1}$ ohm$^{-1}$ . cP]* | $K_A$ *[dm$^3$ · mol$^{-1}$]* | $\sigma K_A$ *[dm$^3$ . mol$^{-1}$]* |
|---|---|---|---|---|---|
| 0.00 | 8.37 | ±0.02 | 48.663 | 6071.7 | ±1.1 |
| 12.94 | 14.79 | ±0.03 | 67.412 | 1099.8 | ±0.9 |
| 36.50 | 31.29 | ±0.03 | 90.522 | 491.1 | ±0.8 |
| 57.31 | 37.80 | ±0.03 | 76.961 | 317.1 | ±0.7 |
| 75.80 | 47.93 | ±0.03 | 68.875 | 216.7 | ±0.7 |
| 92.35 | 63.33 | ±0.02 | 63.963 | 62.2 | ±0.6 |
| 100.00* | | | | | |

* We haven't measured the value of the molar limiting conductance in pure DMF due to the experimental difficulties associated with considerably low solubility of NaCl in DMF.

mixture has been applied previously by the other authors[12,13] to prove the occurrence in the studied system intermolecular interactions. The linear course of this dependence indicates that it approaches with its properties to the "ideal" system. Whereas, in case of the presence of intermolecular interactions in the studied mixture the plot of the function lg $\Lambda_0 \cdot \eta_{12} = f(1/\varepsilon_{12})$ is represented by two lines

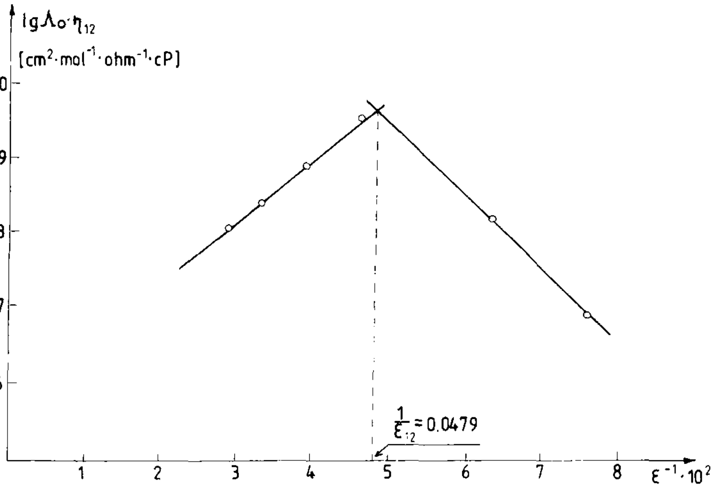

**Figure 4** Changes in the function $\lg(\Lambda_0 \cdot \eta_{12}) = f(1/\varepsilon_{12})$ for the liquid DMF-PhCH$_2$OH mixtures, at 298.15 K.

intersecting at the point which corresponds to the composition characterized by the maximum value of intermolecular interactions. In the present study, using measured by us values of the molar limiting conductance and viscosity in the wide composition range of DMF-PhCH$_2$OH mixtures, we have carried out the mentioned above analysis. The graph of the function $\lg \Lambda_0 \cdot \eta_{12} = f(1/\varepsilon_{12})$ consists of two lines intersecting at the point corresponding to the value of the reciprocal of dielectric permittivity equal approximately to $1/\varepsilon_{12} = 0.0479$, which corresponds to ca. 33 mol. % of DMF in the studied liquid mixtures (see Fig. 4).

It fully confirms the conclusions drawn from $^1$H-NMR spectroscopic studies and analysis of the temperature coefficient of dielectric permittivity.

The character of the dependence of the ionic association constant, $K_A$, on the mixed solvent composition is quite typical for mixtures such as water-non-aqueous solvents and can be easily explained in terms of the decreasing relative permittivity of the mixed solvent when DMF is replaced by PhCH$_2$OH (see Tab. 4).

All these structural parameters, studied in this paper, suggest the formation the stable "complexes" (sub-units) of the DMF·2PhCH$_2$OH and DMF · PhCH$_2$OH types in liquid mixtures of DMF-PhCH$_2$OH. The intermolecular "complex" (sub-unit) in which there are two benzyl alcohol molecules per one DMF molecule is characterized probably by the highest stability.

The comparison of the present results with our earlier works devoted to the analysis of the intermolecular interactions in the liquid mixtures of DMF with aliphatic alcohols[1–3], leads to the conclusion that the appearance of phenyl ring in the molecule of alcohol additionally supports of the intermolecular "complex" of the stoichiometry corresponding to one molecule of DMF and two molecules of alcohol. Such complex is also more stable, in the presently studied mixtures, than its analogue corresponding to the stoichiometry DMF · alcohol. This type of the "complex" was characteristic for mixtures of DMF with aliphatic alcohols.

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