

Heteromolecular Structure Formation in Aqueous Solutions of Ethanol, Tetrahydrofuran and Dimethylformamide

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II. THEORY AND EXPERIMENT

Abstract—The refractometric method has been used to determine optical properties of concentration features of aqueous solutions of ethanol, tetrahydrofuran and dimethylformamide at the room temperature. Changes in dielectric permittivity of aqueous solutions of ethanol, tetrahydrofuran and dimethylformamide in a wide range of concentrations (0÷1.0 molar fraction) have been studied using molecular dynamics method. The curves depending on the concentration of experimental data on excess refractive indices and excess dielectric permittivity were compared. It has been shown that stable heteromolecular complexes in binary solutions are formed in the concentration range of 0.3÷0.4 mole fractions. The real and complex part of dielectric permittivity was obtained from dipole-dipole autocorrelation functions of molecules. At the concentrations of $C = 0.3 \div 0.4$ m.f. the heteromolecular structures with hydrogen bonds are formed. This is confirmed by the extremum values of excessive dielectric permittivity and excessive refractive index of aqueous solutions.

Keywords—Refractometric method, dielectric constant, molecular dynamics, aqueous solution.

I. INTRODUCTION

DIELECTRIC spectroscopy is very sensitive technique to investigate structural and relaxation changes in media and identify the formation of molecular associates that affect the macroscopic properties of solutions [1]-[3].

This work is aimed to demonstrate that refractometric method is a powerful tool to observe formation of molecular associates in water. To determine dielectric properties of concentration dependences of aqueous solutions of tetrahydrofuran (THF), dimethylformamide (DMF) and ethanol (ETH), the refractometric method was used. Refractive indices of aqueous solutions over the entire range of concentration (0÷1.0 mole fraction) at a room temperature were measured. The excess dielectric permittivity of mixture was calculated using molecular dynamics method described in [4]. The comparisons of curves of excess dielectric permittivity depending on the concentration and experimental data on excess refractive indices have been used.

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A. Materials:

THF, DMF, ETH (99.9%, Sigma-Aldrich, USA) and double-distilled water were used.

B. Preparation of Solutions

Aqueous solutions of THF, DMF and ETH were prepared by gravimetric method described in [5].

C. Molecular Dynamics

In our calculation we have used the GROMACS 4.5.5 software package [6] for six different systems, with pure THF, DMF, ETH and water molecules, and their aqueous solutions. The force fields of structures of THF and DMF molecules were taken from [4]. The method of All Atom Optimized Potentials for Liquid Solvents (OPLS-AA) of ETH molecule was used. It has been shown that the OPLS describes structural and thermodynamic properties [7], [8] of liquid ETH fairly well. The SPC/E model has been chosen. Compared to other models, SPC/E better describes both the radial distribution function of the atoms of water and its dielectric permittivity [9].

A box with a certain number of solute - ETH, DMF, and THF, and solvent - water molecules was created, which corresponds to experimental values of refractive indices measured at different concentrations, which are given in Tables I and II. The calculations were performed at a fixed pressure and temperature over the entire range of concentrations using the Nose-Hoover barostat and thermostat algorithms in a cubic box filled with THF/DMF/ETH and water molecules (Table I).

The long range Coulomb forces between the solute and solvent molecules were applied using the Ewald method with an accuracy of $1 \cdot 10^{-6}$ kJ/mol. The equilibrium state for each system was reached within 15 ns, with a time step of 1.0 fs. This procedure was repeated in the entire range of concentrations (0÷1 mole fraction), at a room temperature (300 K) in THF–water, DMF–water and ETH–water systems. No constrains on angles and bonds were used. The cut-off distance of 0.9 nm for THF and water, 1.0 nm for ETH, 1.2 nm for DMF was used for Lennard-Jones potential. The value of isothermal compressibility of water in our calculations is $4.5 \cdot 10^{-6}$ Pa⁻¹.

The short-range forces were applied at half of the box length and the Mesh Ewald summation [10] was used. Periodic boundary conditions for each system were applied in

all directions. The intermolecular interactions were calculated using pair potential assigned with partial charges and written as the sum of the Coulomb and Lennard-Jones potentials [4].

TABLE I
DIELECTRIC CONSTANT AT DIFFERENT MOLE FRACTION OF THF, DMF AND ETH IN WATER WITH THE CORRESPONDING NUMBER OF MOLECULES

| C, mole frac. | $N_{\text{THF/DMF/ETH}}$ | N_{WATER} | ϵ^E , THF-water | ϵ^E , DMF-water | ϵ^E , ETH-water |
|---------------|--------------------------|--------------------|--------------------------|--------------------------|--------------------------|
| 0.0 | 0 | 516 | 0 | 0 | 0 |
| 0.1 | 51 | 465 | 16.78 | 6.76 | 2.413 |
| 0.2 | 103 | 413 | 23.86 | 11.19 | 9.5475 |
| 0.3 | 172 | 344 | 24.82 | 16.53 | 24.137 |
| 0.4 | 206 | 310 | 20.102 | 12.87 | 22 |
| 0.5 | 258 | 258 | 14.16 | 10.35 | 19.33 |
| 0.6 | 310 | 206 | 18.302 | 7.92 | 18.38 |
| 0.7 | 361 | 155 | 11.756 | 6.78 | 15.176 |
| 0.8 | 413 | 103 | 9.93 | 5.99 | 9.423 |
| 0.9 | 464 | 52 | 4.51 | 2.7 | 5.789 |
| 1.0 | 516 | 0 | 0 | 0 | 0 |

$N_{\text{THF/DMF/ETH}}$ is the number of THF/DMF/ETH molecules; N_{WATER} is the number of water molecules; $(\epsilon^E)_{\text{THF-water}}$, $(\epsilon^E)_{\text{DMF-water}}$ and $(\epsilon^E)_{\text{ETH-water}}$ are the dielectric constants for DMF-water, THF-water, ETH-water, respectively,

TABLE II
EXCESS REFRACTIVE INDEX VALUES OF THF-WATER, DMF-WATER AND ETH-WATER MIXTURES AT 25 °C

| C, mole frac. | n^E THF-water | C, mole frac. | n^E DMF-water | C, mole frac. | n^E ETH-water |
|---------------|-----------------|---------------|-----------------|---------------|-----------------|
| 1.0000 | 0.0000 | 1.0000 | 0.0000 | 1.0000 | 0.0000 |
| 0.7864 | 0.0119 | 0.8080 | 0.0161 | 0.8613 | 0.0042 |
| 0.6664 | 0.0185 | 0.6767 | 0.0247 | 0.735 | 0.0083 |
| 0.4703 | 0.0270 | 0.4819 | 0.0362 | 0.5521 | 0.0133 |
| 0.3412 | 0.0302 | 0.3518 | 0.0433 | 0.4183 | 0.0163 |
| 0.2497 | 0.0350 | 0.2586 | 0.042 | 0.3161 | 0.0176 |
| 0.1816 | 0.0289 | 0.1887 | 0.0390 | 0.2356 | 0.0174 |
| 0.1289 | 0.0256 | 0.1342 | 0.0308 | 0.1704 | 0.0158 |
| 0.0868 | 0.0172 | 0.0906 | 0.0231 | 0.1167 | 0.0121 |
| 0.0525 | 0.0145 | 0.0549 | 0.0162 | 0.0715 | 0.0085 |
| 0.0240 | 0.0080 | 0.0251 | 0.0099 | 0.0331 | 0.0044 |
| 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 |

The excess dielectric permittivity of the aqueous solution has been calculated using the technique described in [4].

D. Experimental Section

Refractive indices of pure components (water, THF, DMF and ETH) were measured using high-sensitivity digital refractometer PAL-BX/RI (ATAGO, Japan).

For the refractive index measurements, aqueous solutions of THF, DMF, and ETH with the concentration of 0÷1.0 mole fraction were prepared. Each mixture corresponding to a specific concentration was recorded five times at a fixed temperature of 25±0.05 °C and the average value was calculated.

III. RESULTS AND DISCUSSION

The investigations of dielectric properties can be used to characterize structural properties of liquids, to determine their concentration and detect the formation of clusters and associates. We have used computer simulations to determine dielectric properties of aqueous solutions of weak bonded solute molecules, such as THF, DMF, and solutions of ETH, in which hydrogen bonds are formed. The dielectric properties of THF and DMF in aqueous solutions are different from those of their pure liquids.

Figs. 1-3 show plots of experimental values of the excess refractive index (curve 1) and calculated values of the excess dielectric constant (curve 2) of freshly prepared aqueous solutions of THF, DMF, and ETH over the entire range of component concentrations. From Figs. 1-3, we can see that maximum values of refractive indices and dielectric permittivity are observed at component concentrations of $C = 0.3 \div 0.4$ m.f., which correspond to the maximum number of hydrogen bonds in the system. The ratio of solvent molecules to solute molecules is two times more, and at this state, the maximum number of hydrogen bonds is realised in the systems. So, at the concentration of $C = 0.3 \div 0.4$ m.f., the heteromolecular structures with H-bond in the binary mixture are formed by insertion of the solute molecule between water molecules. The maximum value of refractive indices and modulus of dielectric permittivity at the concentration of $C = 0.3 \div 0.4$ m.f. indicates the formation of heteromolecular structures with hydrogen bonds as shown in Figs. 7-9.

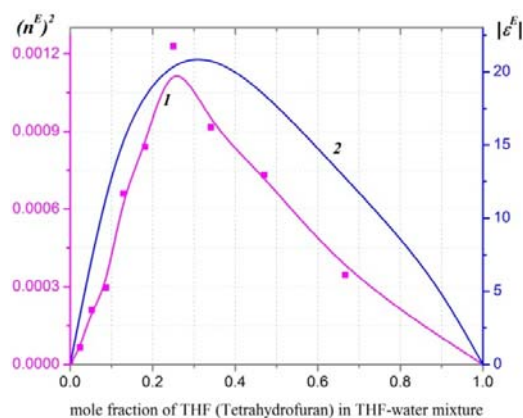


Fig. 1 Changes of the absolute values of excess refractive index of freshly prepared aqueous solutions of THF (curve 1) and excess dielectric constant at different initial concentrations of components (curve 2)

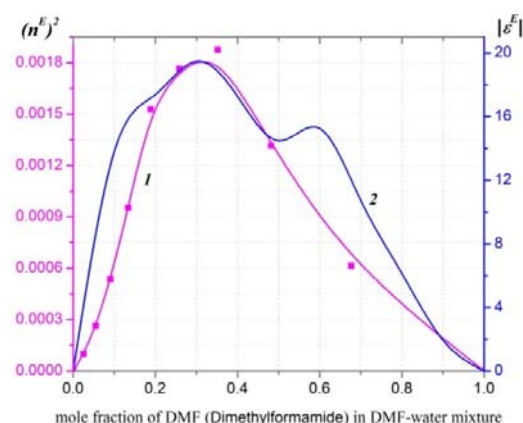


Fig. 2 Changes of the absolute values of excess refractive index of freshly prepared aqueous solutions of DMF (curve 1) and excess dielectric constant at different initial concentrations of components (curve 2)

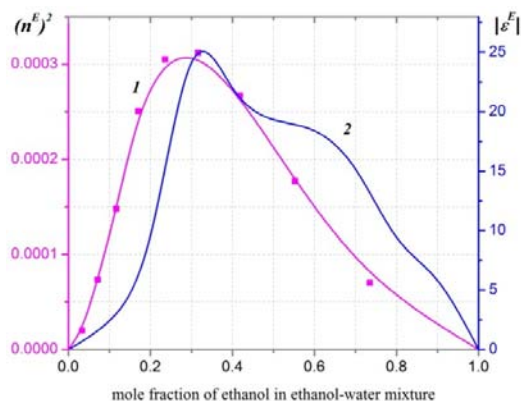


Fig. 3 Changes of the absolute values of excess refractive index of freshly prepared aqueous solutions of ETH (curve 1) and excess dielectric constant at different initial concentrations of components (curve 2)

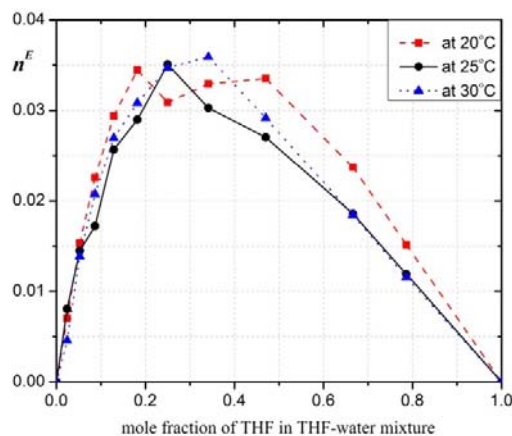


Fig. 4 The temperature dependence of changes of the absolute values of excess refractive index of freshly prepared aqueous solutions of THF at different initial concentrations of components

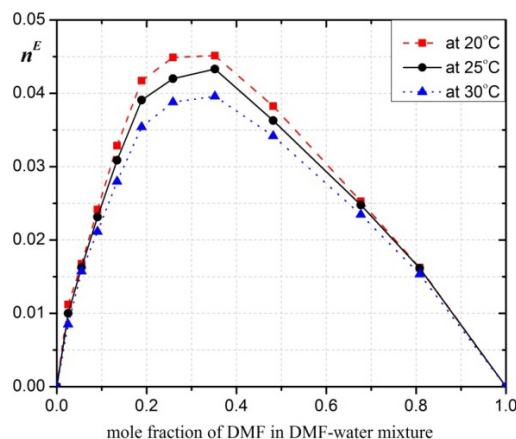


Fig. 5 The temperature dependence of changes of the absolute values of excess refractive index of freshly prepared aqueous solutions of DMF at different initial concentrations of components

Figs. 4-6 show curves of experimental values of the excess refractive index of freshly prepared aqueous solutions of THF, DMF and ETH depending on temperatures over the entire

range of component concentrations.

In Fig. 4, it is seen that, with the increase in temperature, the maximum value of excess refractive indices shifts towards the increasing concentration. The intensity of excess refractive index grows with the increase of temperature. Such fact is connected with a benzene ring of THF molecule.

As shown in Fig. 5, with the increase in temperature, the maximum value of excess refractive indices shifts to decreasing concentrations.

The behaviour of $n^E(x)$ indicates that changes in the concentration of solute molecules in aqueous solution over the entire investigated interval C are accompanied by changes in the structure of the solution. THF, DMF, and ETH create weak bonds in their pure solution.

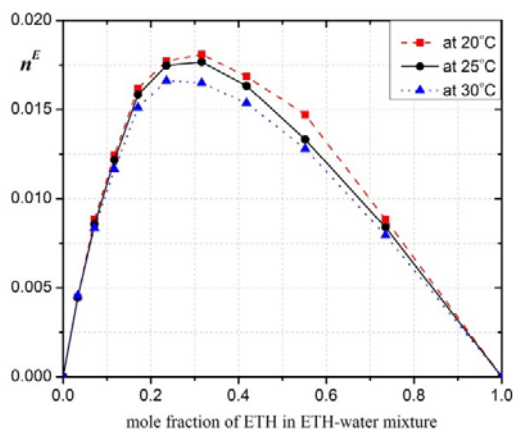


Fig. 6 The temperature dependence of changes of the absolute values of excess refractive index of freshly prepared aqueous solutions of ETH at different initial concentrations of components

From Fig. 5, we can see that with the increase in temperature, the maximum value of excess refractive indices shift towards decreasing concentrations. Furthermore, ETH molecule can act not only as a donor, but also as a proton acceptor (by oxygen in $C=O$), i.e. simultaneously form two hydrogen bonds, which apparently leads to strong self-association of molecules in a pure ETH. The ETH molecule consists of a non-polar hydrophobic part (CH_3) and a polar hydrophilic group ($C-O-H$), and refers to diphilic (heterofunctional) molecules capable of participating in both hydrophobic and hydrophilic interactions with water molecules. The intensity of excess refractive index decreases with the increase in temperature. For this fact, changes in the structure are caused by processes of competition for the formation of hydrogen bonds between water molecules and ETH, depending on temperature and the ratio of components in the solution.

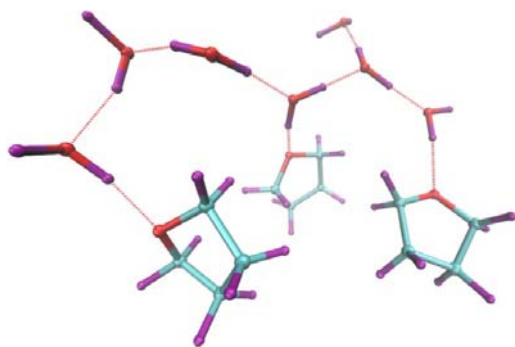


Fig. 7 Heterocluster formation of “THF-water” at the concentration of 0.3 mole fraction of THF

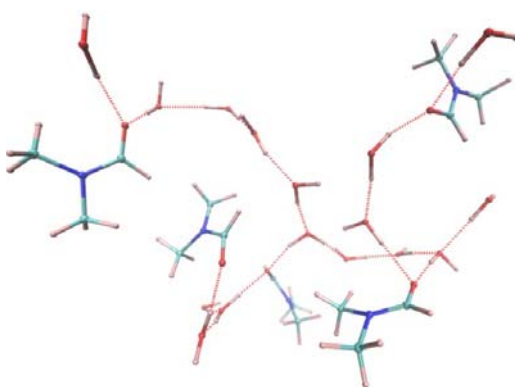


Fig. 8 Heterocluster formation of “DMF-water” at the concentration of 0.3 mole fraction of THF



Fig. 9 Heterocluster formation of “ETH-water” at the concentration of 0.3 mole fraction of THF

IV. CONCLUSION

Based on our experimental and simulation studies and analysis, it can be concluded that i) all solvents are completely soluble in water and; ii) THF and DMF tend to create hydrogen bonds between their and water molecules; iii) increasing the concentration of water molecules up to 0.6÷0.7 mole fraction also increases the number of hydrogen bonds between water and solute molecules, and leads to formation of hydrogen bonds.

The comparison of experimentally observed refractive indices with calculated dielectric permittivity of aqueous solutions of THF, DMF, and ETH over a wide range of concentrations and temperatures revealed the following: molecules of these liquids incorporate in the structure of the hydrogen network of water and form heteromolecular

hydrogen bonds. The temperature dependences of excess refractive indices of THF and DMF require more detailed analysis. They will be considered in our next investigations.

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