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Structural study of methanol-water mixture from dielectric parameters

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Abstract : Binary mixtures of water and methanol over entire range of composition have been studied by hydrogen-bonded model suggested by Luzar. The Luzar theory is applied to determine the molecular parameters and correlation terms for the mixture. The theoretical and experimental values of static dielectric constant and excess permittivity are reported. The shape of theoretical curve matches with the experimental ones over the whole concentration of the water in methanol. The negative values of excess dielectric parameter suggests that the addition of methanol to water may create multimeric structure.

Keywords : Dielectric permittivity, Kirkwood correlation factor, methanol-water mixtures, hydrogen-bonded model.

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1. Introduction

Methanol is one of the hydrogenbonded primary alcohols and is widely used as an industrial solvent. Methanol is an associating liquid that can donate and accept the hydrogen bonds in the water mixture. Since solution properties of methanol particularly in aqueous solution are of considerable interest due to their non-ideal nature and hydrogen bonding network [1–5], extensive experimental and theoretical dielectric studies have been carried out on methanol-water mixtures in order to investigate the hydrogen bond structure and intermolecular rotation in these mixtures [1–11]. The static and dynamic dielectric properties of methanol-water mixtures have also been studied [12–15]. Palinkas *et al* [16] have found that the librational frequencies are higher for methanol molecules with a greater number of hydrogen bonds, and that the line width of librational bond are narrower in methanol-rich mixtures.

The dielectric properties of methanol-water mixtures are structure sensitive [17] that is, they depend upon correlation and interaction between the electric dipoles. To understand the dielectric behaviour of the associating molecules, it is necessary to determine the various molecular parameters such as dielectric polarization, Kirkwood correlation factor, dipole moment *etc.* which are related with inter- and intra-molecular association. The Kirkwood correlation factor is determined from the dielectric constant. The calculation of Kirkwood correlation factor provides the information of hydrogen bonding and the hindrance of molecular orientation by neighboring molecules [17–19]. The calculation of the theoretical dielectric constant using Kirkwood correlation factor provides more precise theoretical model for the mixture. Luzar [20–22] has suggested the theoretical model for the binary mixtures. The model gives a qualitative agreement with the experimental results for dimethyl-sulphoxide-water mixtures. However, no study has been done so far on the methanol-water system using hydrogen bonded Luzar model.

In the present work, methanol-water mixtures with

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various concentrations are investigated by Time Domain Reflectometry (TDR) technique in the frequency range of 10 MHz to 10 GHz at different temperatures. The dielectric behavior of methanol-water mixtures is discussed on the basis of the hydrogen-bonded theory. Furthermore, we report an application of Luzar model to the excess permittivity results for methanol-water mixtures.

2. Experimental

Methanol was obtained commercially and used without purification. However, water used in the preparation of solutions was distilled and ion-exchanged before use. The dielectric permittivity of methanol-water mixtures was measured by TDR in the frequency range between 10 MHz to 10 GHz. Details of the apparatus and procedure of the TDR have been reported previously [6,18,19].

A Tektronix 7854 sampling oscilloscope with 7S12 TDR unit has been used. The experiments were performed with an 'open ended' SMA cell (dia 3.5 mm outer, 1.52 mm inner, length of inner conductor or pin length 1.28 mm). Effective pin length was found to be 1.35 mm. The time window chosen for the measurements was kept at 5 n sec. In our experiment, a fast rising voltage step with a rise time of 25 ps was allowed to propagate through a coaxial line section filled with the sample under study. Change in the reflected pulse shape due to the sample, were monitored by the sampling oscilloscope. These reflected pulses were added and subtracted and transferred to PC/XT for Fourier transformation as well as data processing [6,18,19].

3. Results and discussion

The Kirkwood correlation as determined from the dielectric constant gives information about collective orientation correlation between molecules [17–19]. The calculation of Kirkwood correlation factor 'g' provides information regarding the hindrance of molecular orientation by neighboring molecules. The deviation of 'g' from unity is a measure of degree of hindered relative molecular motion arising from short range intermolecular forces. When the molecules tend to direct themselves with parallel dipole moments, 'g' will be greater than unity. If the molecules prefer an ordering with antiparallel dipoles, 'g' will be smaller than unity.

For a mixture, the Kirkwood correlation factor g_i can be expressed as [17] as follows :

$$\left[(\varepsilon_{0i}-\varepsilon_{\infty i})(2\varepsilon_{0i}+\varepsilon_{\infty i})/9\varepsilon_{0i}\right]=4\pi/9kT\sum^{2}g_i\mu_i^2, \quad (1)$$

where i = 1, 2 represent water and methanol, respectively; μ_i is their dipole moment in gas phase, ρ_i is the density, k is the Boltzmann constant, T is the temperature, ε_{0i} and $\varepsilon_{\infty i}$ are the static dielectric constant and dielectric constant at high frequency. g_i is the Kirkwood correlation factor for the i-th liquid system.

The interpretation of the dielectric phenomena in terms of the Kirkwood correlation factor is very difficult for mixtures of associating compound. We have considered two models as follows :

(i) In the first model, we have assumed that the mixture can be represented by one correlation factor g^{eff} as follows :

$$[(\varepsilon_{0m}-\varepsilon_{\infty m})\ (2\varepsilon_{0m}+\varepsilon_{\infty m})/9\varepsilon_{0m}]$$
$$=[4\pi/9kT]g^{eff}[\rho_m\mu_m^2]. \quad (2)$$

To calculate g^{eff} values, we have taken dipole moment of methanol and water as 1.70 D and 1.84 D, respectively. The value $\varepsilon_{\infty m}$ is taken as the square of the refractive index data. We believe that g^{eff} defined by eq. (2) is a reasonable measure of the molecular correlation. The observed value of greater than unity in water-methanol mixtures, leads to the conclusion that the molecules associate to form multimer with parallel dipole moment. The high values of g^{eff} indicate average parallel orientation of electric dipoles in a molecule. It can be seen that as water is added in methanol at regular steps in the mixture, the values of g^{eff} increase. The increase of correlation in methanol and methanol-water mixtures may be due to the association effect. The correlation factor is essentially connected to the total orientation polarization and the dominating contribution to it is embodied in (ε_{0m} – $\varepsilon_{\infty m}$). The calculating the Kirkwood correlation factor (g^{eff}) from eq. (2) is not fully legitimate since in the investigating binary system, the water-water, water-methanol and methanol-methanol correlation exit.

(ii) It is impossible to determine g_1 and g_2 from a single value of the static dielectric constant without some assumption. In the second model, the Kirkwood correlation factors for individual species i = 1, 2 are modified by assumed for methanol-water mixture that two kinds of intermolecular hydrogen bonds exist. One is the hydrogen bond between the water molecules, another is the hydrogen bond between the methanol and water molecules. These new correlations (g_1 and g_2) are described by the relation as follows [22–25] :

$$g_1 = 1 + Z_{11}\cos\varphi_{11} + Z_{12}\cos\varphi_{12}(\mu_2/\mu_1), \tag{3}$$

$$g_2 = 1 + Z_{21}\cos\varphi_{21}(\mu_1/\mu_2), \tag{4}$$

where $Z_{11} = 2 < n_{HB}^{11} >$; $Z_{12} = <n_{HB}^{12}>$; and $Z_{21} = <n_{HB}^{12}>X_1/(1 - X_1)$ are the average number of particles forming the hydrogen bond with water-water, water-methanol and methanol-water pairs, respectively. X_1 is the mole fraction of water; φ_{11}, φ_{12} and φ_{21} are the angles between the neighbouring dipoles of water and methanol molecules. The average number of hydrogen bonds [$<n^{11}HB>$, $<n^{12}HB>$ and $<n^{21}HB>$] per water molecule for 1*i* pairs (i = 1, 2) have been determined according to the following relation [22] :

$$<n^{1i}HB> = n_{1i}\omega^{1i}/n_1, \tag{5}$$

where $\omega^{1i} = 1/(1 + \alpha^{1i} e^{\beta E11})$ is the probability of bond formation between water and methanol. n_1 is the number density of water molecule. The value of $\beta = 1/kT$ and α^{1i} is the ratio of the two sub-volume of the phase space, related to the non-hydrogen-bonded and hydrogen-bonded pairs. The values of $<n^{11}HB>$ and $<n^{12}HB>$ depend on the number of densities of hydrogen bonding pair between water and methanol, (n_{12}) and those between water molecules $n_{11} = 2n_1 - n_{12}$. This can be calculated, during which water-water (11 pairs) and water-methanol (12 pairs) are formed [22]. Figure 1 shows plot of the average number of hydrogen bonds between water-water molecules (11 pairs) and water-methanol (12 pairs) against mole fraction of water. The values of $<n^{12}HB>$ decrease and those of $<n^{11}HB>$ increase with mole fraction of water.

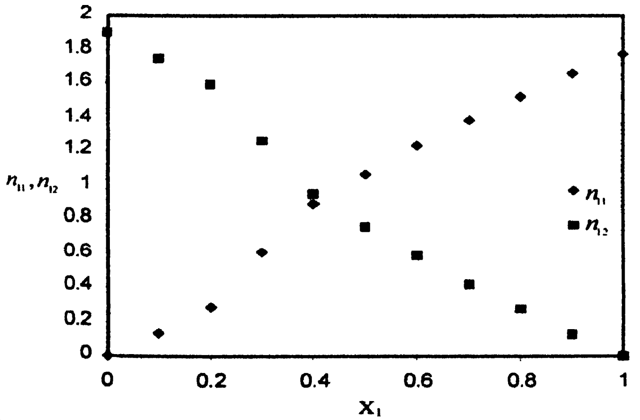

Figure 1. The average number of hydrogen bonds between water-water molecule (n_{11} pair) and water-methanol (n_{12} pair) against mole fraction of water X_1.

The different parameters required in the Luzar model, are dipole moments, polarizabilities, possible number of hydrogen bonds and angles between dipoles $\cos\varphi_{11}$ and $\cos\varphi_{12}$ for the water and methanol. In our analysis, the best possible values of molecular parameters for which static dielectric constant values are in reasonable agreement with the experimental values are given in Table 1. As can be seen from Figure 2, the Luzar model gives a good qualitative account of the dielectric constant for water-methanol mixtures at 25°C. The values of static dielectric constant obtained from the Luzar model along with the experimental values obtained from TDR technique in our laboratory are given in Table 2. It should be noted that the Luzar applied the model to the water-dimethyl sulfoxide (DMSO) system and found that the experimental data can be explained by using larger values of dipole moments in the liquid phase. We have also used the model to explain the static dielectric constant of the mixtures. We found that our experimental data can be explained by the theory, provided values of the dipole

Table 1. Molecular parameters used in computation of the static dielectric constant

Molecular parameters		
Dipole moment of water in Debye	(μ_1^0)	1.98
Dipole moment of methanol in Debye	(μ_2^0)	2.84
Polarizability for water in A^{03}	(α_1)	1.78
Polarizability for methanol in A^{03}	(α_2)	4.00
Bonding energy for water-water[a]	(E_{11})	−13.40
Bonding energy for water-methanol[a]	(E_{12})	−16.25
Statistical volume ratio for water-water	(α_{11})	28.00
Statistical volume ratio for water-methanol	(α_{12})	40.00
Number of hydrogen bonds	(m)	3.00

[a]Units : kJ mol^{-1}.

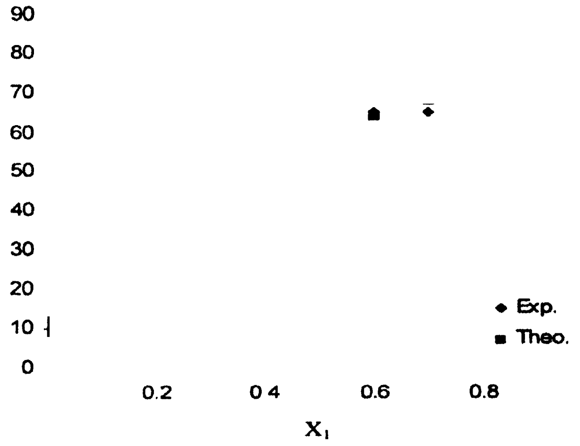

Figure 2. Theoretical and experimental static dielectric constant for water-methanol mixtures, as function of mole fraction of water (X_1) at 25°C.

Table 2. Theoretical values of the static dielectric constants as calculated by the model suggested by Luzar [22] along with the experimental values for methanol water mixtures.

	0°C		10°C		25°C		40°C	
X_1	Exp[a]	Theo[b]	Exp[a]	Theo[b]	Exp[a]	Theo[b]	Exp[a]	Theo[b]
0.0	38.40	36.54	36.00	35.29	33.77	33.56	29.61	32.01
0.1	43.59	43.85	42.54	42.27	40.37	40.08	39.36	38.09
0.2	49.83	50.62	48.23	48.85	45.94	46.24	39.60	43.79
0.3	58.21	56.20	56.75	54.05	51.27	51.40	43.78	48.96
0.4	61.57	61.73	59.42	59.32	56.16	55.94	48.44	52.82
0.5	64.83	66.85	63.61	64.18	60.84	60.44	52.90	56.98
0.6	67.66	71.61	65.29	68.70	65.60	64.61	61.80	60.82
0.7	71.18	76.04	65.29	72.90	65.60	68.47	61.80	64.36
0.8	75.11	80.19	73.46	76.81	72.13	72.06	65.98	67.65
0.9	78.14	84.07	77.82	80.48	76.47	75.41	67.10	70.71
1.0	86.20	87.72	85.60	83.91	79.50	78.55	70.50	73.55

[a]Experimental values determined from TDR. [b]Calculated by the model suggested by Luzar [22].

moments of water and methanol are taken as 1.98 Debye and 2.84 Debye respectively, which are larger than the corresponding values of dipole moments in the gas phase. It can be seen from Figure 2 that the experimental values are in general, smaller than the corresponding experimental values. It is because of the fact that the Luzar theory neglected formation of hydrogen bond interaction between methanol-methanol (22 pairs). There is no theory yet available to consider the formation of solute-solute 22 pair interaction. All other parameters used in the calculations are same as those given in Ref. [22]. The values of g^{eff}, g_1 and g_2 are given in Table 3.

The excess dielectric constant :

There is no appropriate molecular theory available in the literature, which correlates the dielectric parameters to solute-solvent interaction. The solute-solvent interaction may provide the structural information of binary liquids. In the absence of such a theory, excess dielectric constant parameters or other mixture formulae may provide some trend regarding the interactions. The excess parameter approach seems to be very useful.

The contribution of hydrogen bonds to the dielectric properties of mixtures is studied in terms of the excess static dielectric constant [22]. The excess permittivity (ε^E) may also provide structural information. This is determined for the methanol-water solutions as follows

$$(\varepsilon_0^E) = (\varepsilon_0)_M - [(\varepsilon_0)_\omega X_1 + (\varepsilon_0)_{MTH}(1 - X_1)], \quad (6)$$

where $(\varepsilon_0)_M$, $(\varepsilon_0)\omega$, and $(\varepsilon_0)_{MTH}$ represent values static dielectric constant (ε_0) corresponding to mixture, water and methanol, respectively and X_1 is the mole fraction of water.

The excess permittivity (ε_0^E) may provide qualitative information in the mixture as follows :

(i) (ε_0^E) = 0 indicates that water and methanol do not interact at all.

(ii) (ε_0^E) < 0 indicates that water and methanol interaction is such that the total effective dipolar polarization get reduced. Water and methanol may form multimers leading to the less effective dipoles

The resulting excess dielectric constants (experimentally and theoretical) are shown in Figure 3. The negative values of excess permittivity were observed. The negative values of excess parameter suggests that the addition of methanol to water may create multimeric structure leading to decrease in the total permittivity. The hydrogen-bonded model gives quantitative agreement with the experimental data of excess dielectric constant of the mixture. The shape of the theoretical curve of the excess dielectric

Table 3. Kirkwood correlation factor g^{eff} and values of g_1, g_2 at different temperatures.

X	0°C			10°C			25°C			40°C		
	g^{eff}	g_1	g_2	g^{eff}	g_1	g_2	g^{eff}	g_1	g_2	g^{eff}	g_1	g_2
0.0	2.86	–	1.00	2.98	–	1.00	2.88	–	1.00	2.68	–	1.00
0.1	2.76	1.60	1.04	2.85	1.55	1.04	2.95	1.49	1.04	2.72	1.44	1.04
0.2	2.85	1.75	1.07	2.88	1.71	1.07	2.98	1.64	1.07	2.86	1.59	1.06
0.3	2.90	1.85	1.09	2.76	1.81	1.09	2.92	1.75	1.09	2.88	1.69	1.09
0.4	2.99	1.92	1.11	2.98	1.88	1.11	3.16	1.81	1.11	3.12	1.76	1.11
0.5	3.12	1.97	1.13	3.17	1.93	1.13	3.19	1.87	1.13	2.91	1.82	1.12
0.6	3.25	2.02	1.14	3.25	1.98	1.15	3.23	1.92	1.14	2.92	1.87	1.14
0.7	3.41	2.06	1.16	3.45	2.02	1.17	3.27	1.97	1.16	2.92	1.91	1.16
0.8	3.27	2.09	1.20	3.28	2.05	1.20	3.29	2.00	1.19	2.97	1.95	1.19
0.9	3.26	2.11	1.32	3.29	2.08	1.27	3.29	2.03	1.25	3.36	1.98	1.24
1.0	3.33	2.16	–	3.23	2.13	–	3.18	2.08	–	2.92	2.03	–

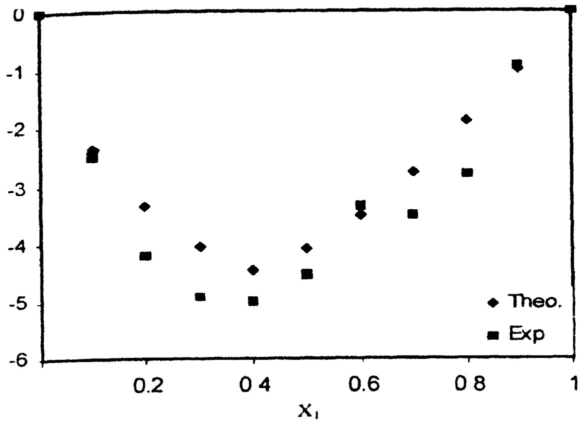

Figure 3. Theoretical and experimental excess dielectric constant for water-methanol mixtures, as function of mole fraction of water (X_1).

constant matches with the experimental ones over the whole concentration of the water in methanol. The maxima of theoretical curves also exactly match with the maxima of the experimental curve.

4. Conclusions

The contribution of hydrogen bonds to dielectric properties of water-methanol mixtures has been studied. The values of the Kirkwood correlation factors have been evaluated for different concentrations of water in methanol. The hydrogen-bonded model gives quantitative agreement with the experimental static dielectric constant and excess parameter of the mixture, if the values of dipole moments of water and methanol are assumed to be larger than the corresponding values in the gas phase.

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