

Dielectric study of aqueous solution of acetonitrile

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MS received 2 March 1995

Abstract. Time domain reflectometry method has been used in the frequency range of 10 MHz to 10 GHz to determine dielectric properties of aqueous solutions of acetonitrile in temperature range of 0 °C to 40 °C. The calibration method based on the least squares fit method has been used. The excess permittivity, activation energy, Kirkwood correlation factor and activation energy of acetonitrile-water system have also been determined. The dielectric data show that acetonitrile molecules interact such that the dipoles have a tendency to remain antiparallel.

Keywords. Dielectrics; microwaves; aqueous solutions; acetonitrile; relaxation time; Kirkwood factor.

PACS No. 77·22

1. Introduction

The acetonitrile liquid is a nonhydrogen bonded system with large value of dipole moment. The dielectric data [1–6] show that dipoles of acetonitrile molecules have a tendency to remain antiparallel in liquid state. The system will interact with hydrogen-bonded liquid (such as water) through long-range forces like dipole-dipole interactions. The dielectric relaxation study of acetonitrile-water system should provide information regarding such kind of interactions. Although dielectric studies of the system have been carried out by various groups, they provide information in limited frequency region and temperature. The detailed information about the excess permittivity and thermodynamic properties cannot be obtained by the earlier studies. The objective of the present paper is to report the detailed dielectric work on the system using the time domain technique in temperature range of 0 °C to 40 °C. The Luzar [7] model is also used to get information regarding the interaction in the system.

2. Experimental

Materials:

A spectrograde acetonitrile (MeCN) (E Merc) was used as such without further purification, whereas water was used after double glass distillation and deionization. The solutions were prepared by mixing the MeCN and water in volume. The volume fraction, V_i , of the MeCN was calculated as follows.

$$V_i = \frac{\text{Vol. of MeCN}}{\text{Vol. of MeCN} + \text{Vol. of water}} \quad (1)$$

Apparatus:

The experimental set up used for the study has already been described earlier [8, 9]. In this experimental technique, a 200 mv pulse having rise time 25 ps and repetitive frequency of 1 kHz is generated by tunnel diode pulse generator. The pulse was transmitted through a 3.5 mm coaxial transmission line having characteristic impedance of 50Ω. The cell has inner and outer dimensions of 1.52 mm and 3.5 mm, respectively. The effective pinlength of inner conductor was 0.486 mm. The reflected pulses with and without sample were digitized with 1024 points in the time window of 5 ns. The recorded pulses were added and subtracted in the oscilloscope memory, and were transferred to PC/XT via GPIB for further numerical analysis.

The complex reflection function ρ^* of the sample liquid was determined through Fourier transforming the measured pulses [8–11].

The dielectric parameters were determined by the method as described earlier [12].

3. Results and discussion

The dielectric parameters obtained are summarized in table 1 alongwith literature values wherever available [6] for comparison. In table 1, the numbers in bracket denote the uncertainty in the last significant digit as obtained by the nonlinear least squares fit method described earlier [9]. This does not include instrumental error which is estimated to be about 2%. The static dielectric constant (ϵ_0) and relaxation time (τ) for pure acetonitrile are in good agreement with earlier work [5]. In acetonitrile-water system, it is observed that under experimental error the dielectric relaxation can be described by the Debye model ($\alpha = 0, \beta = 1$).

The structural information about the liquids by dielectric relaxation parameter, can be obtained either by Kirkwood correlation or excess parameters. It is not possible to obtain correlation parameters in the mixture for both solute and solvent from a single value of permittivity. One may assume the existence of the effective correlation factor, g^{eff} defined as [14]

$$\frac{4\pi N}{9KT} \left(\frac{\mu_a^2 \rho_a}{M_a} x_a + \frac{\mu_w^2 \rho_w}{M_w} (1 - x_a) \right) g^{eff} = \frac{(\epsilon_{0m} - \epsilon_{\infty m})(2\epsilon_{0m} - \epsilon_{\infty m})}{\epsilon_{0m}(\epsilon_{\infty m} + 2)^2} \quad (2)$$

where μ_a, μ_w are dipole moments of acetonitrile and water molecules, M_a, M_w are corresponding molecular weights, ρ_a, ρ_w are corresponding densities, x_a is the volume fraction of the acetonitrile molecule in the mixture, ϵ_{0m} and $\epsilon_{\infty m}$ are permittivities at low and high frequency limits, respectively. The values of g^{eff} are given in table 2. The Kirkwood correlation factor g^{eff} decreases as the concentration of acetonitrile increases. It is interesting to note that the values of g^{eff} are less than one in acetonitrile rich region. This indicates that –CN interacts such that the dipoles in the liquid align in antiparallel direction unlike –OH bond in water.

The excess permittivity ϵ^E is defined [9, 15] as

$$\epsilon^E = (\epsilon_0 - \epsilon_{\infty})_m - [(\epsilon_0 - \epsilon_{\infty})_a x_a + (\epsilon_0 - \epsilon_{\infty})_w (1 - x_a)] \quad (3)$$

where subscripts to the brackets m, a, w correspond to mixtures, acetonitrile and water respectively. Excess permittivity gives an idea regarding interaction between solute and water. The plots of excess permittivity vs concentration of water at different temperatures are shown in figure 1.

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Table 1. Dielectric parameters for acetonitrile-water system at different temperatures.

Vol % of MeCN in water V_i	Mole fract. of MeCN	0°C			10°C		
		ϵ_0	ϵ_∞	τ (ps)	ϵ_0	ϵ_∞	τ (ps)
		0°C			10°C		
0**	0.000	87.9	3.0	17.6	83.9	3.0	12.7
10	0.037	83.1(1)	3.0	17.8(3)	78.9(1)	3.0	13.9(2)
20	0.079	83.2(1)	3.0	18.8(2)	76.0(1)	3.0	13.8(1)
30	0.129	74.6(1)	3.0	18.7(2)	74.0(1)	3.0	13.9(2)
40	0.187	74.7(1)	3.0	19.6(2)	67.7(1)	3.0	14.6(2)
50	0.256	71.0(1)	3.0	18.1(1)	61.0(1)	3.0	13.8(2)
60	0.341	64.7(1)	3.0	15.9(1)	58.7(1)	3.0	12.9(1)
70	0.440	56.8(1)	3.0	14.3(2)	50.4(1)	3.0	10.0(2)
80	0.579	53.1(1)	3.0	12.7(1)	47.4(1)	3.0	9.5(2)
90	0.756	44.6(1)	3.0	9.5(1)	40.0(1)	3.0	6.0(1)
100	1.000	42.8(1)	3.0	8.8(2)	39.2(1)	3.0	3.6(1)
		25°C			40°C		
0*	0.000	78.3	3.0	8.2	73.1(1)	3.0	5.8(1)
10	0.037	76.8(1)	3.0	10.9(2)	73.8(1)	3.0	6.5(1)
20	0.079	74.9(1)	3.0	10.6(1)	70.4(1)	3.0	6.6(1)
30	0.129	69.7(1)	3.0	11.2(1)	68.3(1)	3.0	6.7(1)
40	0.187	66.8(1)	3.0	10.8(1)	65.2(1)	3.0	6.6(1)
50	0.256	54.5(1)	3.0	11.2(2)	60.7(1)	3.0	6.5(1)
60	0.341	52.3(1)	3.0	10.6(1)	52.6(1)	3.0	6.1(1)
70	0.440	52.0(1)	3.0	9.6(1)	50.7(1)	3.0	6.0(1)
80	0.579	47.3(1)	3.0	8.8(1)	46.0(1)	3.0	5.5(1)
90	0.756	41.4(1)	3.0	5.4(1)	34.7(1)	3.0	3.2(1)
100	1.000	37.0(1)	3.0	3.4(1)	33.1(1)	3.0	2.5(1)
		35.9*		3.2*			

Number in brackets denote the error obtained from least squares fit method. e.g. 37.0(1) means 37.0 ± 0.1 .

* Reported in ref. [6]

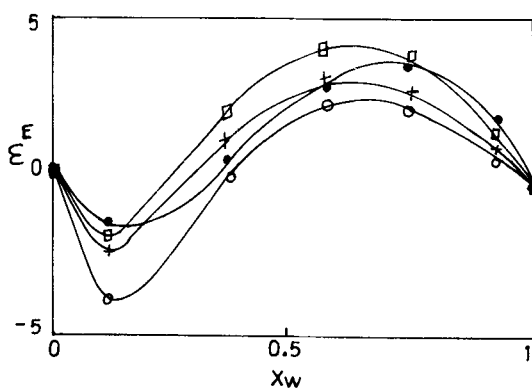
** The values of ϵ_0 and τ are taken from Kaatzte *et al* [13] for pure water to be used as calibrating liquid.

Figure 1 shows the values of excess permittivity which has a tendency to be negative in acetonitrile rich region and tends to be positive in water rich region. This indicates that there is formation of multimer structure at lower concentration of water in acetonitrile. At these lower concentrations of water, there will be creation of new forms of structures which will include a solvated dimer [15], that will have essentially zero dipole moment and hence will lead to decrease in total permittivity. In water rich region there may be a formation of monomeric structures. The monomeric structures will essentially have dipoles due to which total permittivity increases. The behaviour of structural changes with concentration of water in acetonitrile is similar at different temperatures with some change in magnitude.

The values of enthalpy of activation ΔH at different concentrations are also determined [16] and are given in table 3.

Table 2. Values of g^{eff} for acetonitrile-water system at different temperatures.

Mole fract. of MeCN in water	0°C	10°C	25°C	40°C
0.000	2.64(15)	2.67(16)	2.62(15)	2.48(14)
0.037	2.40(14)	2.40(14)	2.47(14)	2.36(14)
0.079	2.29(13)	2.22(13)	2.31(13)	2.18(13)
0.129	1.97(11)	2.11(12)	2.06(12)	2.04(12)
0.187	1.90(11)	1.86(11)	1.88(11)	1.88(11)
0.256	1.74(10)	1.62(9)	1.76(10)	1.69(10)
0.341	1.53(9)	1.55(9)	1.37(8)	1.47(8)
0.440	1.29(7)	1.33(8)	1.29(7)	1.31(7)
0.579	1.17(7)	1.13(6)	1.10(6)	1.10(6)
0.756	0.94(5)	0.91(5)	0.99(6)	0.87(5)
1.000	0.85(5)	0.87(5)	0.86(5)	0.81(4)

**Figure 1.** Variation of ϵ^E vs weight fraction of acetonitrile 40°C; (\square), 25°C; (\bullet), 10°C; (\circ), 0°C; (+).**Table 3.** Activation energy for acetonitrile-water system.

Mole fract. of MeCN in water	Activation energy (ΔH) kJ/mol
0.000	17.38(12)
0.037	14.78(54)
0.079	15.45(39)
0.129	14.91(54)
0.187	16.33(38)
0.256	14.82(63)
0.341	13.77(70)
0.440	11.34(76)
0.579	11.08(67)
0.756	15.12(80)
1.000	17.13(17)

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The contribution of hydrogen bonds to dielectric properties of the mixture can be studied using the model as suggested by Luzar [7]. He applied the model to water-DMSO system. We have used the same model to explain the static permittivity of the mixture. We found that our experimental data cannot be explained well by the theory because of many limitation assumed in the theory. The different parameters required in the Luzar model are dipole moments of molecules 1 (water) and 2 (acetonitrile), polarizabilities of molecules 1 and 2, energy and enthalpies of (1, 1) and (1, 2) pairs and possible number of bondings with molecule 2, average direction cosine angles between dipoles $\cos \Phi_{11}$ and $\cos \Phi_{12}$.

In our analysis, the best possible values of above molecular parameters for which experimental and theoretical static permittivity values give reasonably satisfactory agreement are as follows.

- Dipole moment of molecule 1, $\mu_1 = 20.09 \text{ D}$
- Dipole moment of molecule 2, $\mu_2 = 3.58 \text{ D}$
- Polarizability of molecule 1, $\alpha_1 = 1.47 \text{ \AA}^3$
- Polarizability of molecule 2, $\alpha_2 = 3.2 \text{ \AA}^3$
- Bonding energy for (1, 1) pair, $E_{11} = -13.3 \text{ kJ/mol}$
- Statistical volume ratio for the pair (1, 1) = 28 \AA^3
- Bonding energy for (1, 2) pair, $E_{12} = -10 \text{ kJ/mol}$
- Statistical volume ratio for the pair (1, 2) = 41 \AA^3
- $\cos \Phi_{11} = \cos \Phi_{12} = 1/3$

and number of CH_3CN molecules interacting with H_2O , is taken to be one. The values of permittivity obtained from Luzar model using the above parameters are given in table 4 along with the experimental values. It can be seen from the table that the theoretical values are in general smaller than the corresponding experimental values. It is because of the fact that the Luzar theory neglected formation of solute-solute pair. This causes more number of solute-solvent pair as calculated by the theory. It should also be noted that the value of dipole moment of water molecule is taken to be 14.2% higher than the corresponding gas phase value. The larger values of dipoles as determined by

Table 4. Comparison of experimental values of ϵ_0 with theoretical values obtained from Luzar model.

Mole fraction of MeCN in water	0°C		10°C		25°C		40°C	
	$\epsilon_0^{\text{exp.}}$	$\epsilon_0^{\text{the.}}$	$\epsilon_0^{\text{exp.}}$	$\epsilon_0^{\text{the.}}$	$\epsilon_0^{\text{exp.}}$	$\epsilon_0^{\text{the.}}$	$\epsilon_0^{\text{exp.}}$	$\epsilon_0^{\text{the.}}$
0.000	87.9	88.2	83.9	84.3	78.3	78.6	73.1	73.1
0.037	83.1	83.7	78.9	79.9	76.8	74.6	73.8	69.4
0.079	83.2	79.2	76.0	75.7	74.9	70.6	70.4	65.7
0.129	74.6	74.8	74.0	71.4	69.7	66.7	68.3	62.1
0.187	74.7	70.5	67.0	67.3	66.8	62.8	65.2	58.5
0.256	71.0	66.1	61.0	63.1	54.5	58.7	60.7	54.8
0.341	64.7	61.7	58.7	58.6	52.3	54.8	52.6	51.2
0.440	56.8	56.7	50.4	54.3	52.0	50.8	50.7	47.6
0.579	53.1	52.0	47.4	49.7	47.3	46.7	46.0	43.9
0.756	44.6	46.6	40.0	44.7	41.4	42.2	34.7	39.8
1.000	42.8	40.4	39.2	39.0	37.0	37.1	33.1	35.4

the Luzar theory may be due to the Kirkwood–Fröhlich (KF) model adopted in the theory. The KF model does not include the distortion polarization due to molecules present inside the cavity. This distortion polarization will induce a larger local field at the centre of the cavity.

4. Conclusions

The dielectric relaxation parameters for aqueous acetonitrile have been determined at various temperatures by the time domain reflectometry. The calibration process based on the least squares fit method gives reliable values of dielectric parameters. The dielectric data shows that acetonitrile molecules interact such that they remain antiparallel with respect to dipoles. The activation energy of the acetonitrile system is higher than the corresponding value in water. This is because of strong dipole-dipole interaction in acetonitrile. The relaxation time corresponding to acetonitrile system is much smaller than those of water system. The pair energy of acetonitrile-water system using the Luzar model is found to be -10 kJ/mol.

Acknowledgement

The authors thank Drs P B Patil and G S Raju for discussion and helpful suggestions. The financial assistance from UGC is thankfully acknowledged.

References

- [1] Y P Borado, Dissertation Kharkar State University (1979)
- [2] C Luhrs and G Schiltz, *Phys. Chem.* **83**, 623 (1979)
- [3] G P Gunningham, G A Vidulich and P L Kay, *J. Chem. Engg. Data* **12**, 336 (1967)
- [4] G Dourcheret and M Morenas, *C. R. Hebd. Seances Acad. Sci.* **26UC**, 729 (1967)
- [5] D Decroocq, *Bull. Soc. Chem. France* **1**, 127 (1967)
- [6] J Barthel, K Bachhuber, R Bunchner, J B Gill and M Kleebauer, *Chem. Phys. Lett.* **167**, 63 (1990)
- [7] A Luzar, *J. Mol. Liq. Cryst.* **46**, 221 (1990)
- [8] S M Puranik, A C Kumbharkhane and S C Mehrotra, *J. Microwave Power and Elect. Energy* **26**, 196 (1991)
- [9] A C Kumbharkhane, S M Puranik and S C Mehrotra, *J. Chem. Soc. Faraday Trans.* **87**, 1569 (1991)
- [10] D Bertolini, M Cassettari, G Salvetti, E Tombari and S Veronesi, *Rev. Sci. Instrum.* **61**, 450 (1990)
- [11] R H Cole, J G Barbarian, S Mashimo, G Chryssikos, A Burns and E Tombari, *J. Appl. Phys.* **66**, 793 (1989)
- [12] A C Kumbharkhane, S N Helambe, S Doraiswamy and S C Mehrotra, *J. Chem. Phys.* **99**, 2405 (1993)
- [13] U Kaatz and V Uhlendorf, *Z. Phys. Chem. Neue Folge* **126**, 151 (1981)
- [14] A C Kumbharkhane, S M Puranik and S C Mehrotra, *J. Mol. Liq. Cryst.* **51**, 261 (1992)
- [15] M Tabllout, P Lancelleur and J R Emery, *J. Chem. Soc. Faraday Trans.* **86**, 1493 (1990)
- [16] H Eyring, *J. Chem. Phys.* **4**, 283 (1936)