

Influence of molecules with chloro group on the associative liquid methanol: A dielectric relaxation approach

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Abstract. The dielectric relaxation parameters, viz., static dielectric constant, ϵ , and relaxation times, τ , have been determined for chlorobenzene–methanol (CB–MET), 1,2 dichloro ethane–methanol (DE–MET) and dimethylene chloride–methanol (DC–MET) mixtures with thirteen different concentrations at three temperatures, viz., 15, 25 and 45°C. The experimental technique used for this work was the time domain reflectometry (TDR) in the frequency range of 10 MHz to 20 GHz using the Hewlett Packard HP 54750 sampling oscilloscope. The information regarding hydrogen bonding structural behavior in MET due to CB, DE and DC are obtained by using the theoretical models based on the excess properties. The data suggest that CB and DE are not influenced by hydrogen bonding in MET whereas DC is influenced by the hydrogen bonding mechanism in MET. It appears that the behavior of DC on MET is different from CB and DE in MET.

Keywords. Time domain reflectometry; excess parameters; chloro group molecules; dielectric relaxation time; dielectric constant.

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1. Introduction

The main objective of the dielectric relaxation study is to understand intermolecular interactions in a molecular system. Extensive studies have been done to understand these interactions on different types of binary polar mixtures having different molecular groups. As molecules with –OH groups form associative liquid due to hydrogen bonding, the effect of molecules with other groups on these molecules is very important to understand the behavior of hydrogen bonding in the presence of other groups. Earlier, molecules with amino groups [1–3], nitrile group [4,5] have been reported. The objective of the present work is to report the influence of chloro group molecules on the associative liquid systems. The associative liquid is selected to be methanol, whereas three types of molecules with chloro groups are taken for the study, viz., chlorobenzene (CB), 1,2 dichloro ethane (DE) and dimethylene chloride (DC). In the first system only one chloro group is attached to benzene, whereas there are two chloro groups in the second and third types of molecules

attached to linear chain of carbon atoms. The study provides dielectric parameters, viz., dielectric constant and relaxation times. Different excess parameters are determined for understanding the nonlinear behavior.

2. Experimental and results

All the chemicals used in the present investigation were obtained commercially and used without purification. The solutions were prepared at thirteen different volume percentage of MET in CB, DE and DC from 0 to 100%.

The complex permittivity spectra were studied using the time domain reflectometry [6,7] method. The Hewlett Packard HP 54750 sampling oscilloscope with HP 54754A TDR plug in module has been used. A fast rising step voltage pulse of about 40 ps rise time was propagated through a coaxial line system. Transmission line system under test was placed at the end of the coaxial line in the standard military applications (SMA) coaxial connector with 3.5 mm outer diameter and 1.35 mm effective pin length. All measurements were done under open load conditions. The change in the pulse after reflection from the sample placed in the cell was monitored by the sampling oscilloscope. In the experiment, time window of 5 ns was used.

A temperature controller system with water bath and a thermostat has been used to maintain constant temperature within the accuracy limit of $\pm 0.1^\circ\text{C}$. The sample cell is surrounded by a heat insulating container through which water of constant temperature is circulated using a temperature controller system. The temperature at the cell is checked using the electronic thermometer.

The time dependent data were processed to obtain complex reflection coefficient spectra $\rho^*(\omega)$ over the frequency range from 10 MHz to 20 GHz using Fourier transformation as

$$\rho^*(\omega) = (c/j\omega d)[p(\omega)/q(\omega)] \quad (1)$$

where $p(\omega)$ and $q(\omega)$ are Fourier transforms of $[R_1(t) - R_x(t)]$ and $[R_1(t) + R_x(t)]$ respectively, c the velocity of light, ω the angular frequency, d the effective pin length and $j = \sqrt{-1}$.

The complex permittivity spectra $\epsilon^*(\omega)$ were obtained from reflection coefficient spectra $\rho^*(\omega)$ by applying bilinear calibration method [6]. Chloro group molecules and methanol were used as calibrating liquids.

The experimental values of ϵ^* are fitted with the Debye expression [8–10]

$$\epsilon^*(\omega) = \epsilon_\infty + \frac{\epsilon_0 - \epsilon_\infty}{1 + j\omega\tau} \quad (2)$$

where ϵ_0 and τ are the fitting parameters. A nonlinear least-squares fit method [11] was used to determine the values of dielectric parameters. The values of ϵ_0 and τ obtained are given in table 1 for the systems studied.

3. Discussion

There is no appropriate molecular theory available in the literature, which correlates dielectric relaxation parameters to solute–solvent interaction. In the absence of such a theory, the

Table 1. Dielectric parameters for chloro group molecule+MET mixtures.

Volume % of MET	15° C	25° C	45° C
CB+MET			
ϵ_0			
100	34.64(0)	32.55(0)	30.91(0)
98	34.63(4)	32.52(6)	30.66(2)
95	34.02(5)	31.77(7)	30.04(3)
90	33.08(5)	30.89(8)	28.93(4)
80	31.22(3)	28.89(9)	27.17(5)
70	28.36(8)	26.59(10)	25.06(7)
50	23.6(12)	21.78(12)	20.13(7)
40	19.54(13)	18.6(13)	16.84(8)
20	14.23(12)	13.19(12)	12.22(6)
10	10.35(9)	9.77(8)	9.69(5)
8	8.24(5)	7.98(4)	7.86(4)
5	7.01(2)	6.98(2)	6.72(1)
0	6.26(0)	5.91(0)	5.07(0)
τ (ps)			
100	47.17(0)	43.92(0)	39.44(0)
98	46.56(9)	43.73(8)	39.06(6)
95	46.24(13)	43.1(11)	38.56(9)
90	45.59(13)	42.74(11)	38.24(9)
80	44.61(17)	42.07(14)	38.08(10)
70	44.13(30)	41.77(25)	37.75(19)
50	43.68(42)	41.24(31)	37.23(28)
40	43.2(70)	40.66(62)	36.22(54)
20	35.55(88)	33.24(74)	31.52(63)
10	28.82(51)	26.73(38)	25.44(29)
8	23.07(17)	21.54(14)	19.88(11)
5	18.58(12)	17.24(9)	16.39(7)
0	16.45(0)	15.14(0)	14.97(0)
DE+MET			
ϵ_0			
100	34.64(0)	32.55(0)	30.91(0)
98	33.62(1)	32.52(1)	30.79(1)
95	33.5(5)	32.07(2)	30.56(1)
90	32.68(5)	31.6(3)	30.4(2)
80	31.11(6)	29.76(5)	28.84(3)
70	28.82(9)	27.88(6)	28.81(7)
50	24.92(13)	24.21(0)	23.44(8)
40	21.65(13)	21.11(11)	20.42(10)
20	17.65(11)	17.08(9)	16.49(9)
10	14.63(7)	14.14(6)	13.67(5)
8	12.91(3)	12.54(3)	12.06(3)
5	11.9(1)	11.56(1)	11.03(1)
0	11.12(0)	10.81(0)	9.92(0)
τ (ps)			
100	47.17(0)	43.92(0)	39.44(0)
98	48.96(4)	43.89(3)	39.31(3)
95	47.92(14)	43.73(6)	39.19(4)

Table 1. Continued.

Volume % of MET	15° C	25° C	45° C
90	47.48(16)	43.61(9)	39.07(6)
80	46.06(18)	43.49(17)	38.34(11)
70	43.85(28)	41.28(22)	36.73(21)
50	38.5(44)	36.1(36)	32.31(28)
40	34.02(47)	30.72(40)	27.81(34)
20	24.89(45)	22.3(34)	20.42(33)
10	17.79(31)	15.48(24)	14.1(21)
8	13.46(15)	12.77(15)	11.42(12)
5	11.73(6)	10.85(5)	9.97(5)
0	10.91(0)	10.34(0)	9.62(0)
DC+MET			
ϵ_0			
100	34.64(0)	32.55(0)	30.91(0)
98	33.95(1)	32.25(3)	30.78(3)
95	33.93(1)	32.13(4)	30.41(4)
90	33.16(1)	31.53(5)	30.29(5)
80	31.5(5)	30.41(6)	29.07(5)
70	29.51(7)	28.43(9)	27.59(6)
50	25.51(12)	24.81(13)	23.8(6)
40	21.75(15)	21.21(14)	20.66(8)
20	16.93(13)	16.29(13)	15.77(8)
10	13.48(8)	12.7(8)	11.43(3)
8	11.59(4)	10.78(4)	9.98(1)
5	10.42(1)	9.76(1)	9.39(1)
0	10.07(0)	9.00(0)	8.89(0)
τ (ps)			
100	47.17(0)	43.92(0)	39.44(0)
98	47.11(4)	42.85(10)	39.32(12)
95	47.04(4)	42.82(12)	39.23(12)
90	46.78(5)	42.32(14)	39.11(14)
80	46.23(16)	42.24(17)	39.03(18)
70	45.4(23)	41.02(27)	38.57(18)
50	40.25(44)	37.52(44)	35.62(19)
40	33.35(51)	31.66(48)	30.18(30)
20	22.58(49)	20.8(44)	18.83(38)
10	14.11(26)	12.96(31)	10.81(18)
8	9.19(20)	8.69(17)	6.43(11)
5	6.71(7)	6.6(7)	6.26(6)
0	5.44(0)	5.41(0)	5.18(0)

Number in parenthesis indicates uncertainty; e.g., 13.5(3) means 13.5 ± 0.3 .

excess parameters or other mixture formulae may provide some trend regarding the interactions. The excess parameter approach seems to be very useful.

Let p be the measurable macroscopic property of any molecular system. If two molecular systems, A and B are considered, the corresponding macroscopic properties for pure systems, A and B, are p_A and p_B . If we prepare a mixture of A and B having x_A and $x_B (= 1 - x_A)$ mole fractions of the systems A and B, respectively, the excess property [12] p^E corresponding to the mixed system is defined as

$$p^E = p_{AB} - (x_A p_A + x_B p_B) \quad (3)$$

where p_{AB} is the value of the property p corresponding to the mixture system, A–B. The value p^E can be determined for the system, if one can measure p_A , p_B and p_{AB} and this provides information regarding interactions between A and B. $p^E = 0$ indicates no significant interaction between A and B. $p^E > 0$ indicates that interaction between A and B leads to increase in the value of the property p . Similarly, $p^E < 0$ indicates the reverse trend.

To get a quantitative picture, p^E can be fitted to the Redlich–Kister equation [13,14]

$$p^E = x_A x_B \sum_{n=0}^{\infty} B_n (x_A - x_B)^n. \quad (4)$$

The coefficients B_n 's provide information regarding molecular picture of interactions, e.g., B_0 corresponds the effective interaction between A and B. B_1 corresponds to two of A with one of B and so on.

For the work presented here, the excess properties may be computed corresponding to the static dielectric constant and inverse of the relaxation time. The inverse of relaxation time is taken instead of the relaxation time, as the inverse corresponds to the broadening of a spectral line in resonant spectroscopy. The broadening of two levels are additive for two energy levels. The analogy is taken here in dielectric relaxation time [15]. The excess permittivity ϵ^E may provide qualitative information in the mixture as follows:

- (1) $\epsilon^E = 0$ indicates that liquids 1 and 2 do not interact at all.
- (2) $\epsilon^E < 0$ indicates that liquids 1 and 2 interaction is in such a way that the total effective dipolar polarization get reduced. Liquids 1 and 2 may form multimers leading to the less effective dipoles.
- (3) $\epsilon^E > 0$ indicates that liquids 1 and 2 interaction is in such a way that the total effective dipole moment increases. There is a tendency to form multimers, leading to alignment of dipoles in parallel direction.

The information regarding the dynamics of liquids 1 and 2 interaction from this excess property of $(1/\tau)^E$ is as follows:

- (1) $(1/\tau)^E = 0$: there is no change in the dynamics of liquids 1 and 2 interaction.
- (2) $(1/\tau)^E < 0$: liquids 1 and 2 interaction produces a field such that the effective dipoles rotate slowly.
- (3) $(1/\tau)^E > 0$: liquids 1 and 2 interaction produces a field such that the effective dipoles rotate faster, i.e., the field co-operate in the rotation of dipoles.

The variation of ϵ^E and $(1/\tau)^E$ with mole fraction of methanol at temperatures 15, 25, and 45°C are shown in figures 1 and 2 respectively.

The excess permittivity plots for all the system studied show that, with the addition of MET, the values of excess permittivity become negative in CB and DE while it is positive for DC molecule. Therefore, in CB–MET and DE–MET, multimers are formed in the mixture for all temperatures except for mole fraction 0.9461 to 0.9896 at temperature 25 °C and 0.9737 to 0.9896 at 45 °C of MET in DE. The variation of excess inverse relaxation time is found to be negative for all the systems. The negative value of $(1/\tau)^E$ indicates slower rotation of multimers. CB system influences MET system the least, whereas DC influences the most.

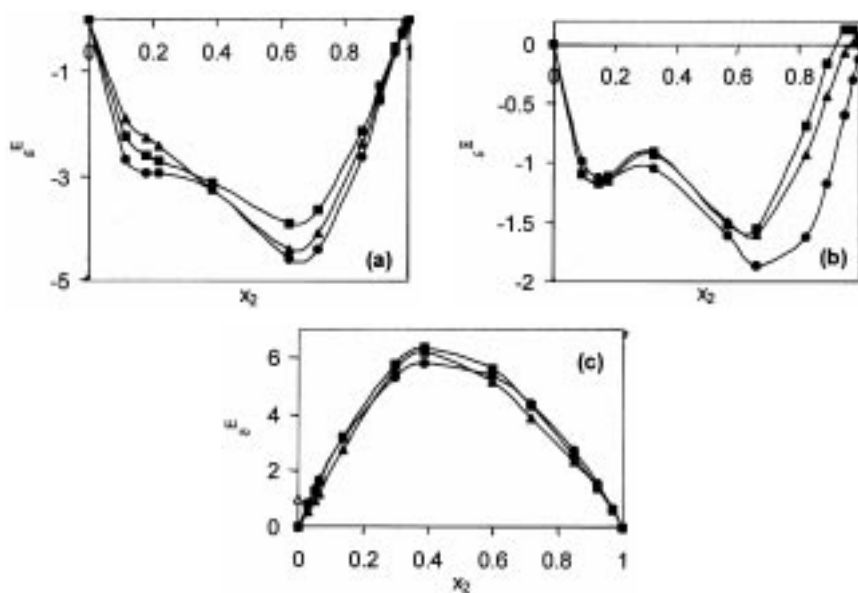


Figure 1. The permittivity ϵ^E vs. mole fraction of MET, x_2 , at 15°C (●), 25°C (■) and 45°C (▲) for (a) CB–MET, (b) DE–MET and (c) DC–MET.

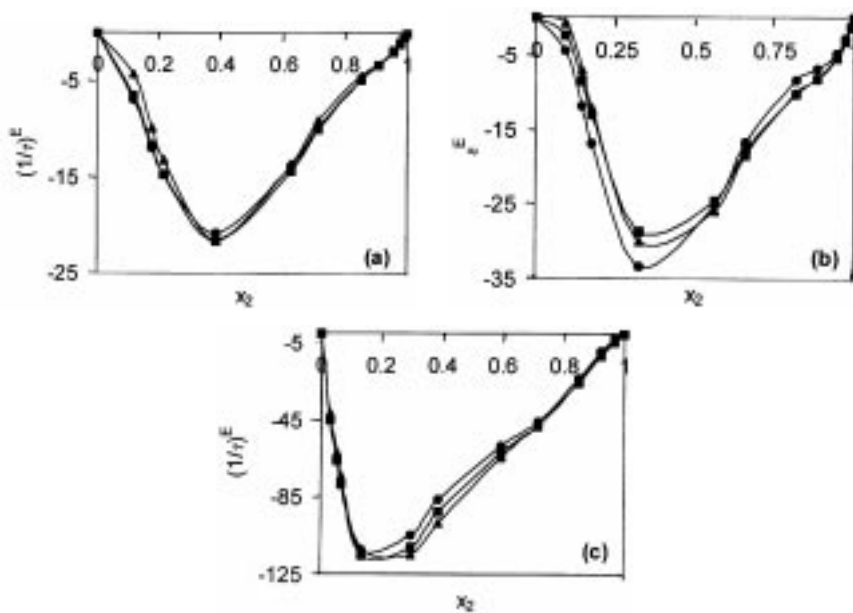


Figure 2. Excess inverse relaxation time $(1/\tau)^E$ vs. mole fraction of MET, x_2 , at 15°C (●), 25°C (■) and 45°C (▲) for (a) CB–MET, (b) DE–MET and (c) DC–MET.

4. Conclusion

Excess properties corresponding to dielectric relaxation parameters for chloro group molecule–methanol systems are reported at various temperatures. The interaction of the chloro group molecules with methanol as hydrogen bonded liquid is discussed. The DC molecules interact with methanol in such a way that the effective polarization gets enhanced, whereas they get reduced in the other two systems.

References

- [1] S M Puranik, A C Kumbharkhane and S C Mehrotra, *J. Mol. Liq.* **50**, 143 (1991)
- [2] A C Kumbharkhane, S M Puranik and S C Mehrotra, *J. Mol. Liq.* **51**, 261 (1992)
- [3] S Ahire, A Chaudhari, M Lokhande and S C Mehrotra, *J. Sol. Chem.* **27**, 993 (1998)
- [4] S N Helembe, M P Lokhande, A C Kumbharkhane, S C Mehrotra and S Doraiswamy, *Pramana – J. Phys.* **44**, 410 (1995)
- [5] S N Helembe, M P Lokhande, A C Kumbharkhane and S C Mehrotra, *Pramana – J. Phys.* **45**, 19 (1995)
- [6] R H Cole, J G Berbarian, S Mashimo, G Chryssikos, A Burns and E Tombari, *J. Appl. Phys.* **66**, 793 (1989)
- [7] S M Puranik, A C Kumbharkhane and S C Mehrotra, *J. Chem. Soc. Faraday Trans.* **87**, 1569 (1991)
- [8] S Havriliak and S A Negami, *J. Polym. Sci. Polym. Symp.* **99**, 117 (1966)
- [9] K S Cole and R H Cole, *J. Chem. Phys.* **9**, 341 (1941)
- [10] D W Davidson and R H Cole, *J. Chem. Phys.* **18**, 1417 (1950)
- [11] P R Bevington, *Data reduction and error analysis for the physical sciences* (McGraw Hill, New York, 1969)
- [12] M Tabellout, P Lanceleur, J R Emery, D Hayward and R A Pethrick, *J. Chem. Soc. Faraday Trans.* **86**, 1453 (1990)
- [13] S F Al-Azzawl, A M Awwad, A M Al-Dujaili and M K Al-Noori, *J. Chem. Engg. Data* **35**, 463 (1990)
- [14] M I Aralaguppi, T M Aminabhavi, R H Balundgi and S S Joshi, *J. Phys. Chem.* **95**, 5299 (1991)
- [15] S C Mehrotra and J E Boggs, *J. Chem. Phys.* **66**, 5306 (1977)