

Articles

Static Dielectric Constant and Relaxation Time for the Binary Mixture of Water, Ethanol, *N,N*-Dimethylformamide, Dimethylsulphoxide, and *N,N*-Dimethylacetamide with 2-Methoxyethanol

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Frequency spectra of the complex permittivity of 2-methoxyethanol (2-ME) with water, ethanol, dimethylsulphoxide (DMSO), *N,N*-dimethylformamide (DMF) and *N,N*-dimethylacetamide (DMA) have been determined over the frequency range of 10 MHz to 20 GHz at 25 °C, using the Time domain reflectometry method, for 11 concentrations for each system. The static dielectric constant, dielectric constant at microwave frequency, relaxation time, excess dielectric parameters, and Kirkwood correlation factor have been determined. The relaxation in these systems within the frequency range can be described by a single relaxation time constant, using the Debye model. The parameters show a systematic change with the concentration.

Keywords : Dielectric relaxation, Time domain reflectometry, Kirkwood factor, Excess parameters.

Introduction

Dielectric parameters of ethanol-DMSO, ethanol-Aniline, ethanol-DMF, and ethanol-tetrahydrofuran have been reported earlier.¹⁻⁴ Kumbharkhane *et al.*⁵ have studied the dielectric relaxation in a DMF-water system. Helambe *et al.*⁶ reported the dielectric parameters for a acetonitrile-water binary system. Dielectric study of DMSO-water was done by Puranik *et al.*⁷ All the above systems show a systematic change in dielectric parameters with temperature and concentration.

The aim of the present paper is to report the dielectric relaxation parameters for the following systems at 25 °C.

(a) 2-methoxyethanol-water (b) 2-methoxyethanol-ethanol
(c) 2-methoxyethanol-DMF (d) 2-methoxyethanol-DMSO
and (e) 2-methoxyethanol-DMA.

From the parameters, the excess dielectric permittivity, excess inverse relaxation time, and Kirkwood correlation factor are obtained. The parameters show a systematic change with concentration. Time Domain Reflectometry (TDR)⁸ in reflection mode has been used to obtain the dielectric parameters.

Experimental Section

2-Methoxyethanol, *N,N*-dimethylformamide, dimethylsulphoxide, *N,N*-dimethylacetamide, and ethanol (all AR grade, Spectrochem Chemicals Pvt. Ltd., Bombay, India) were obtained commercially and used without further purification. The water used was obtained by double distillation process. The solutions were prepared at different volume percentages of 2-methoxyethanol in steps of 10%.

The complex permittivity spectra were studied using Time Domain Reflectometry. A Hewlett Packard HP 54750A sampling oscilloscope with HP 54754 A TDR plug-in module was used. A fast rising step voltage pulse of about 39 psec rise time generated by a tunnel diode was propagated through a flexible coaxial cable. The sample was placed at the end of the coaxial line in the standard military application (SMA) coaxial cell of 3.5 mm outer diameter and 1.35 mm effective pin length. All measurements were done under open load condition. The change in the pulse after reflection from the sample placed in the cell was monitored by the sampling oscilloscope. In this experiment, a time window of 5 ns was used. The reflected pulse without sample $R_1(t)$ and with sample $R_s(t)$ were digitised in 1024 points.

The temperature controller system with water bath and a thermostat was used to maintain constant temperature within the accuracy limit of ± 1 °C. The sample cell was surrounded by a heat insulating container through which the water at constant temperature, using a temperature controller system, is circulated. The temperature at the cell was checked using an electronic thermometer.

Data Analysis

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^{9,10} as

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

where ω is angular frequency, $p(\omega)$ and $q(\omega)$ are Fourier transforms of $(R_1(t) - R_s(t))$ and $(R_1(t) + R_s(t))$, respectively, c

is the velocity of light, d is the effective pin length and $j = \sqrt{-1}$.

The complex permittivity spectra $\epsilon^*(\omega)$ were obtained from reflection coefficient spectra $\rho^*(\omega)$ by applying the bilinear calibration method.¹¹ For the calibration process, 2-methoxyethanol and the respective liquid were taken as calibrating liquids.

The experimental values of ϵ^* were fitted with the Debye equation expression¹²⁻¹³

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

with ϵ_0 , ϵ_∞ , and τ as fitting parameters. In Eq. (2), ϵ_0 is the static dielectric constant, ϵ_∞ is the dielectric constant at microwave frequency and τ is the relaxation time. A non-linear least-squares fit method¹⁴ was used to determine the values of dielectric parameters.

Results and Discussion

The density and the dielectric constant of the pure liquids used for the present study are given in Table 1. The static dielectric constant (ϵ_0), dielectric constant at microwave frequency (ϵ_∞) and relaxation time (τ) obtained by fitting experimental data in the Debye equation are listed in Table 2.

The ϵ_0 value decreases with decrease in 2-methoxyethanol content in the binary mixture for all the systems. The relaxation time increases to 40%, 20%, 30% and 30%, respectively, for 2-ME-DMSO, 2-ME-DMA, 2-ME-DMF and 2-ME-water systems, respectively. For the 2-ME-Ethanol system, the relaxation time increases with decreases in the

Table 1. Dielectric constant and density values for the pure liquids used, at 25 °C

| Liquid | ϵ_0 | $\rho/\text{g} \cdot \text{cm}^{-3}$ |
|---------|--------------|--------------------------------------|
| 2-ME | 17.58 | 0.9596 |
| DMSO | 48.75 | 1.0957 |
| DMA | 39.67 | 0.9367 |
| DMF | 40.21 | 0.9445 |
| Water | 79.14 | 0.9970 |
| Ethanol | 25.04 | 0.7850 |

Table 2. Dielectric relaxation parameters for 2-ME-DMSO, 2-ME-DMA, 2-ME-DMF, 2-ME-Water and 2-ME-Ethanol system at 25 °C

| Mol. Frac. of 2-ME | ϵ_0 | ϵ_∞ | τ (ps) |
|--------------------|--------------|-------------------|-------------|
| DMSO-2-ME | | | |
| 0.0000 | 48.75(2) | 2.67(0) | 24.92(2) |
| 0.1099 | 48.05(8) | 3.44(0) | 27.34(12) |
| 0.2174 | 47.33(12) | 3.48(0) | 28.48(17) |
| 0.3226 | 46.10(8) | 3.01(0) | 34.45(16) |
| 0.4256 | 43.28(9) | 2.98(0) | 39.38(22) |
| 0.5264 | 40.64(0) | 3.05(0) | 42.29(0) |
| 0.6250 | 37.50(8) | 2.89(0) | 45.18(24) |

Table 2. Continued

| Mol. Frac. of 2-ME | ϵ_0 | ϵ_∞ | τ (ps) |
|--------------------|--------------|-------------------|-------------|
| 0.7217 | 32.38(12) | 2.95(0) | 44.08(35) |
| 0.8164 | 29.27(8) | 2.84(0) | 43.40(37) |
| 0.9091 | 25.12(0) | 3.00(0) | 42.38(0) |
| 1.0000 | 17.58(0) | 2.94(0) | 30.16(0) |
| DMA-2-ME | | | |
| 0.0000 | 39.67(0) | 2.90(0) | 18.22(0) |
| 0.0865 | 39.24(5) | 2.71(0) | 23.83(10) |
| 0.1757 | 37.45(19) | 2.79(0) | 25.98(33) |
| 0.2676 | 35.49(18) | 2.69(0) | 27.90(36) |
| 0.3624 | 34.58(19) | 2.92(0) | 33.83(50) |
| 0.4602 | 31.44(23) | 2.48(0) | 35.17(57) |
| 0.5612 | 30.62(25) | 2.86(0) | 35.52(65) |
| 0.6655 | 28.82(17) | 3.28(0) | 40.72(47) |
| 0.7733 | 28.73(14) | 2.63(0) | 44.52(48) |
| 0.8847 | 24.62(9) | 2.97(0) | 40.12(35) |
| 1.0000 | 17.58(0) | 2.92(0) | 30.16(0) |
| DMF-2-ME | | | |
| 0.0000 | 40.21(0) | 2.93(0) | 10.51(0) |
| 0.1021 | 39.45(14) | 2.57(0) | 14.79(22) |
| 0.2038 | 39.13(14) | 2.54(0) | 18.62(28) |
| 0.3050 | 36.33(22) | 3.53(0) | 20.87(50) |
| 0.4057 | 35.98(35) | 3.21(0) | 32.40(93) |
| 0.5059 | 35.64(34) | 2.93(0) | 36.94(102) |
| 0.6057 | 32.46(34) | 3.03(0) | 40.08(117) |
| 0.7049 | 30.03(31) | 2.55(0) | 41.99(109) |
| 0.8038 | 25.34(7) | 3.23(0) | 37.37(34) |
| 0.9021 | 21.99(15) | 2.54(0) | 36.89(63) |
| 1.0000 | 17.58(0) | 2.92(0) | 30.16(0) |
| Water-2-ME | | | |
| 0.0000 | 79.14(0) | 4.02(0) | 9.12(0) |
| 0.3274 | 72.81(52) | 4.22(0) | 19.07(56) |
| 0.5227 | 68.34(53) | 3.72(0) | 23.08(64) |
| 0.6525 | 65.03(22) | 4.05(0) | 24.18(32) |
| 0.7449 | 60.31(16) | 4.31(0) | 29.33(28) |
| 0.8142 | 54.12(30) | 4.05(0) | 36.38(56) |
| 0.8679 | 47.78(18) | 3.68(0) | 39.06(40) |
| 0.9109 | 42.18(28) | 3.63(0) | 44.91(72) |
| 0.9460 | 34.75(3) | 3.86(0) | 43.22(12) |
| 0.9753 | 27.66(2) | 3.87(0) | 43.01(11) |
| 1.0000 | 17.58(0) | 4.28(0) | 30.16(00) |
| Ethanol-2-ME | | | |
| 0.0000 | 25.04(0) | 3.40(0) | 136.56(9) |
| 0.1305 | 23.82(2) | 3.55(0) | 114.52(24) |
| 0.2525 | 23.72(3) | 3.47(0) | 108.56(25) |
| 0.3667 | 23.44(3) | 4.04(0) | 105.02(29) |
| 0.4739 | 23.94(4) | 4.00(0) | 103.59(33) |
| 0.5747 | 23.02(4) | 3.81(0) | 67.04(28) |
| 0.6696 | 22.57(4) | 3.79(0) | 65.08(27) |
| 0.7592 | 21.31(4) | 3.45(0) | 52.65(22) |
| 0.8439 | 19.52(4) | 3.33(0) | 42.79(23) |
| 0.9240 | 19.51(3) | 3.21(0) | 42.73(14) |
| 1.0000 | 17.58(2) | 3.49(0) | 30.16(11) |

Number in parentheses represents error. For, e.g. 48.75(2) means 48.75 ± 0.2.

percent of 2-ME in ethanol.

The excess parameters¹⁵ provide the information about the formation of multimers in the mixture. The excess permittivity is defined as

$$\epsilon^E = (\epsilon_0 - \epsilon_\infty)_m - [(\epsilon_0 - \epsilon_\infty)_A x_A + (\epsilon_0 - \epsilon_\infty)_B x_B], \quad (3)$$

where x is the mole fraction and subscripts m, A, B represents mixture, solvent and solute, respectively. The excess permittivity may provide qualitative information about multimer formation in the mixture as follows:

i) $\epsilon^E = 0$ indicates the solute and solvent do not interact at all.

ii) $\epsilon^E < 0$ indicates the solute and solvent interact in such a way that the total effective dipoles is reduced. The solute and solvent may form multimers leading to the less effective dipoles.

iii) $\epsilon^E > 0$ indicates the solute and solvent interact in such a way that the effective dipole moment increases. There is formation of monomers and dimers.

Similarly, the excess inverse relaxation time is defined as

$$(1/\tau)^E = (1/\tau)_m - [(1/\tau)_A x_A + (1/\tau)_B x_B], \quad (4)$$

where $(1/\tau)^E$ is excess inverse relaxation time, which represents average broadening of dielectric spectra. The inverse relaxation time analogy is taken from spectral line broadening (which is the inverse of relaxation time) from the resonant spectroscopy.¹⁶ The information regarding the dynamics of solute-solvent interaction from this excess property is as follows:

i) $(1/\tau)^E = 0$: There is no change in the dynamics of solute-solvent interaction.

ii) $(1/\tau)^E < 0$: The solute-solvent interaction produces a field such that the effective dipoles rotate slower.

iii) $(1/\tau)^E > 0$: The solute-solvent interaction produces a field such that the effective dipoles rotate faster, *i.e.*, the field facilitates rotation of dipoles.

The variations of ϵ^E and $(1/\tau)^E$ with mole fraction of 2-ME are shown in Figures 1-5.

The experimental values of both excess parameters were fitted to the Redlich-Kister³ equation

$$Y^E = (x_A x_B) \sum_k B_k (x_A - x_B)^k, \quad (5)$$

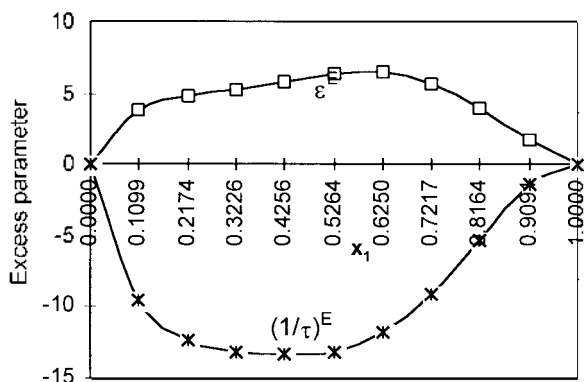


Figure 1. Excess parameters for 2-ME-DMSO system.

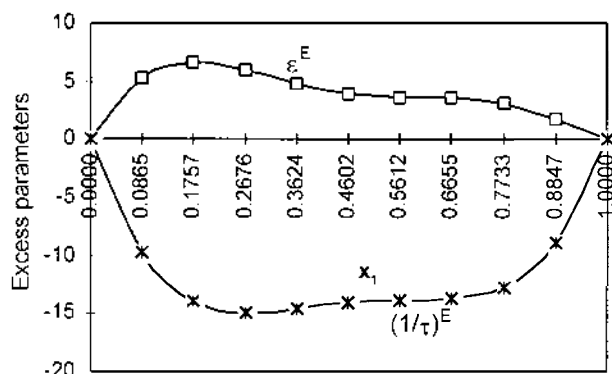


Figure 2. Excess parameters for 2-ME-DMA system.

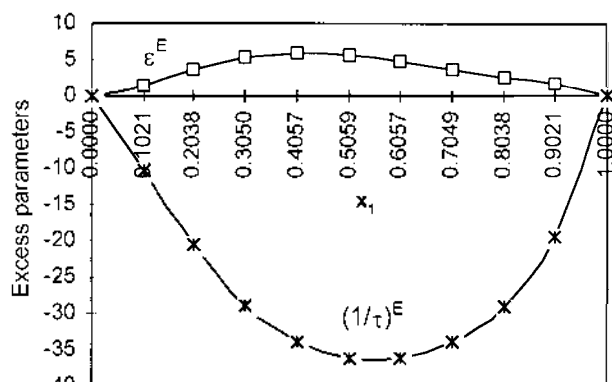


Figure 3. Excess parameters for 2-ME-DMF system.

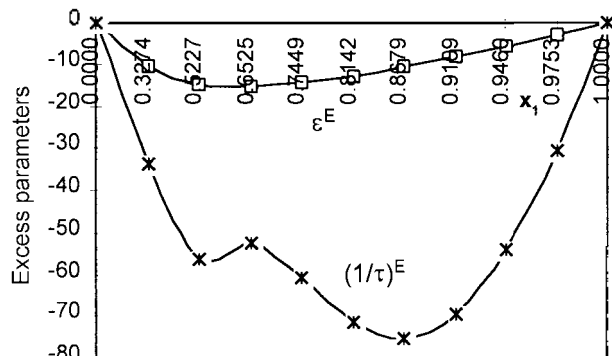


Figure 4. Excess parameters for 2-ME-Water system.

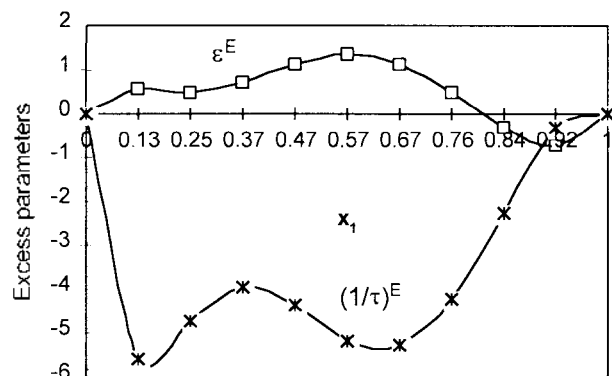


Figure 5. Excess parameters for 2-ME-Ethanol system.

where Y is either ϵ^E or $(1/\tau)^E$. By using the B_k values, Y^E values were calculated and used as guidelines to draw smooth curves in Figures 1-5.

The value of ϵ^E is positive for all the systems studied except for the 2-ME-water system and near the 2-ME rich region for the 2-ME-ethanol system, indicating formation of monomeric or polymeric structures, which increases the total number of dipoles. Negative values indicate the formation of multimer structures, which lead to decrease the total number of dipoles in the system.

The excess inverse relaxation time values are negative for all the systems, indicating the formation of the structures, which rotate slowly, probably due to the dimeric structures.

The Kirkwood correlation factor g^{17} is also a parameter for getting information regarding the orientation of electric dipoles in polar liquids. The g for pure liquid may be obtained by the expression,

$$\frac{4\pi N\mu^2\rho}{9kTM}g = \frac{(\epsilon_0 - \epsilon_\infty)(2\epsilon_0 + \epsilon_\infty)}{\epsilon_0(\epsilon_\infty + 2)^2} \quad (6)$$

where μ is the dipole moment in gas phase, ρ is the density at temperature T , M is the molecular weight, k is the Boltzmann constant, and N is the Avogadro's number.

The corresponding equation for a mixture is not available in the literature. However, for the mixture of two polar liquids, A and B , Eq. (6) is modified,⁵ using different assumptions:

1) Assume that g^{eff} has become an effective correlation factor in the mixture. The Kirkwood equation for the mixture may be expressed as:

$$\frac{4\pi N\left(\frac{\mu_A^2\rho_A}{M_A}X_A + \frac{\mu_B^2\rho_B}{M_B}X_B\right)g^{eff}}{9kT} = \frac{(\epsilon_{0m} - \epsilon_{\infty m})(\epsilon_{0m} + \epsilon_{\infty m})}{\epsilon_{0m}(\epsilon_{\infty m} + 2)^2} \quad (7)$$

where g^{eff} is the effective Kirkwood correlation factor for a binary mixture, with X_A and X_B as volume fractions of liquids A and B , respectively.

2) By assuming that the correlation factor for molecules A and B are affected by the same amount of g_f in the mixture,

the Kirkwood equation for the mixture is

$$\frac{4\pi N\left(\frac{\mu_A^2\rho_A g_A}{M_A}X_A + \frac{\mu_B^2\rho_B g_B}{M_B}X_B\right)g_f}{9kT} = \frac{(\epsilon_{0m} - \epsilon_{\infty m})(\epsilon_{0m} + \epsilon_{\infty m})}{\epsilon_{0m}(\epsilon_{\infty m} + 2)^2} \quad (8)$$

where g_f is the corrective Kirkwood correlation factor.

In Eq. (7), the values of g^{eff} change from g_A to g_B as the concentration of molecule B increases from 0% to 100%. In Eq. (8), the values of g_f remain close to unity if there is no interaction between A and B . The deviation from unity indicates the interaction between A and B .

The calculated values of g_f are tabulated in Table 3. The g_f values deviate sharply from one, indicating stronger intermolecular interaction for all the systems.

The modified Bruggeman equation¹⁸ is another parameter that may be used as an indicator of solute-solvent interaction. The Bruggeman factor f_B is given by

$$f_B = \left(\frac{\epsilon_{0m} - \epsilon_{0B}}{\epsilon_{0A} - \epsilon_{0B}}\right)\left(\frac{\epsilon_{0A}}{\epsilon_{0m}}\right)^{1/3} = (1 - X_B) \quad (9)$$

According to Eq. (9), a linear relationship is expected, which gives a straight line when plotted f_B against X_B . However, here the experimental values of f_B were found to deviate from the linear relationship.

To fit the experimental data, the above equation has been modified as follows

$$f_B = 1 - [a - (a - 1)X_B]X_B, \quad (10)$$

where a is a numerical fitting parameter.

The parameters ' a ' were determined for all systems. The value of ' a ' = 1 corresponds to the ideal Bruggeman mixture formula. The deviation from '1' relates to the corresponding solute-solvent interaction. The values of ' a ' are 2.268, 2.103, 2.221 and 1.972 and 1.751 for 2-ME-DMSO, 2-ME-DMA, 2-ME-DMF, 2-ME-water and 2-ME-ethanol mixture, respectively. The values of ' a ' also indicate the stronger intermolecular interaction for all systems.

Conclusion

The dielectric relaxation parameters, excess parameters and the Kirkwood correlation factor are reported here for 2ME-DMSO, 2ME-DMA, 2ME-DMF, 2ME-water and 2ME-ethanol systems at 25 °C, for 11 different concentrations. These data provide information regarding solute-solvent interaction. From the present study, a strong intermolecular interaction between solute and solvent can be concluded.

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Table 3. Kirkwood correlation factor

| Vol. Frac. of 2-ME | g_f values for 2-ME with | | | | |
|--------------------|----------------------------|-------|-------|-------|---------|
| | DMSO | DMA | DMF | Water | Ethanol |
| 0.0 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 |
| 0.1 | 1.080 | 1.253 | 1.228 | 1.987 | 0.894 |
| 0.2 | 1.104 | 1.287 | 1.343 | 2.053 | 0.912 |
| 0.3 | 1.322 | 1.306 | 1.316 | 1.838 | 0.960 |
| 0.4 | 1.490 | 1.560 | 1.858 | 1.956 | 1.043 |
| 0.5 | 1.572 | 1.491 | 1.904 | 2.150 | 0.748 |
| 0.6 | 1.651 | 1.430 | 1.873 | 2.043 | 0.829 |
| 0.7 | 1.577 | 1.571 | 1.792 | 2.103 | 0.782 |
| 0.8 | 1.522 | 1.644 | 1.458 | 1.807 | 0.769 |
| 0.9 | 1.457 | 1.410 | 1.330 | 1.618 | 0.998 |
| 1.0 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 |

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