

Molecular Dynamics of Acetonitrile And 1, 2 Dichloroethane Mixtures At 35^oc Temperature

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Abstract

The dielectric permittivity spectra of acetonitrile (ACN) with 1,2 Dichloroethane (DCE) mixture has been studied at temperature 35^oC in the frequency range of 10 MHz to 20 GHz using time domain reflectometry (TDR) for 11 different concentrations of the system. The Kirkwood correlation factor of the mixtures has been determined. The static dielectric constants for the mixtures have been fitted with the modified Bruggeman model. The investigation shows that there is antiparallel alignment of the dipoles of the mixture. The interaction between the acetonitrile and 1, 2 dichloroethane is weaker.

Keywords: Dielectric, Chlorine, Nitrile, Kirkwood parameters, Bruggeman parameters.

Introduction

The dielectric relaxation study of solute-solvent mixture at microwave frequencies gives information about formation of monomers and multimers as well as interaction between the molecules of the mixture [1-2]. Acetonitrile (ACN) is non-associative liquids and 1, 2 Dichloroethane (DCE) is associative liquid. ACN is C≡N group and DCE is of chlorine group. It is interesting to see the effect of nitrile group with chlorine-group. The objective of the present paper is to report the molecular interaction of acetonitrile and 1, 2 Dichloroethane mixture at 35^oC temperature using TDR.

Experimental

Material

A spectrograde acetonitrile and AR grade 1, 2 Dichloroethane (E-Merck) were used without further purification. The solutions were prepared at 11 different volume percentages of ACN in DE from 0 % to 100 % just before the measurements. The density and molecular weight of the liquids are as follows:

Acetonitrile-density - 0.7857 gm cm⁻³; mol. wt. - 41.05

1, 2 Dichloroethane -density: 1.256 gm cm⁻³; mol.wt.-98.96

Apparatus

The complex permittivity spectra were studied using the time domain reflectometry [3,4] 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 39 ps rise time generated by a pulse generator was propagated through a coaxial line system of characteristic impedance 50 Ohm. Transmission line system under test was placed at the end of 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 carried out 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. The reflected pulse without sample $R_1(t)$ and with sample $R_x(t)$ were digitized in 1024 points in the memory of the oscilloscope and transferred to a PC through 1.44 MB floppy diskette drive.

The temperature controller system with water bath and a thermostat has been used to maintain the constant temperature within the accuracy limit of $\pm 1^\circ\text{C}$.

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 [5, 6] 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 is the velocity of light, ω is angular frequency, 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 bilinear calibration method [3].

The experimental values of ϵ^* are fitted with the Debye equation [7]

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

with ϵ_0 , ϵ_∞ , and τ as fitting parameters. A nonlinear least-squares fit method [8] was used to determine the values of dielectric parameters. In Eq.(2), ϵ_0 is the static dielectric constant, ϵ_∞ is the limiting high-frequency dielectric constant and τ is the relaxation time

Results And Discussion

The Kirkwood correlation factor g_f [9] is also a parameter for getting information regarding orientation of electric dipoles in polar liquids. The g_f for pure liquid may be obtained by the expression

$$\frac{4\pi N\mu^2\rho}{9kTM} g_f = \frac{(\epsilon_0 - \epsilon_\infty)(2\epsilon_0 + \epsilon_\infty)}{\epsilon_0(\epsilon_\infty + 2)^2} \quad (3)$$

Where μ is dipole moment in gas phase, ρ is density at temperature T , M is molecular weight, k is Boltzman constant, N is Avogadro’s number. The dipole moments for ACN and DCE in gas phase are taken as 3.95D and 2.06 D [10] respectively.

For the mixture of two polar liquids 1, 2 Eq. (3) is modified by ref.[11] with the following assumptions:

1. Assume that g for the binary mixture is expressed by an effective averaged correlation factor g^{eff} such that the Kirkwood equation for the mixture can be expressed by

$$\frac{4\pi N}{9kT} \left(\frac{\mu_1^2\rho_1}{M_1} \phi_1 + \frac{\mu_2^2\rho_2}{M_2} \phi_2 \right) g^{eff} = \frac{(\epsilon_{0m} - \epsilon_{\infty m})(2\epsilon_{0m} + \epsilon_{\infty m})}{\epsilon_{0m}(\epsilon_{\infty m} + 2)^2} \quad (4)$$

with ϕ_1 and ϕ_2 as volume fractions of liquids 1 and 2 respectively.

2. Assume that the correlation factors for molecules 1 and 2 in the mixture contribute to the effective g proportionality to their pure-liquid values g_1 , g_2 . Under this assumption the Kirkwood equation for the mixture can be written

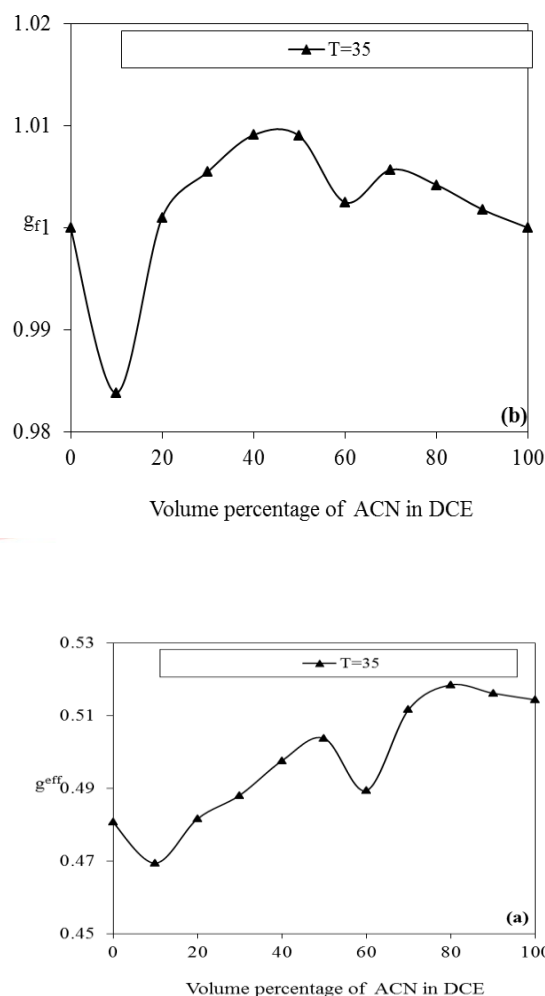
$$\frac{4\pi N}{9kT} \left(\frac{\mu_1^2\rho_1g_1}{M_1} \phi_1 + \frac{\mu_2^2\rho_2g_2}{M_2} \phi_2 \right) g_f = \frac{(\epsilon_{0m} - \epsilon_{\infty m})(2\epsilon_{0m} + \epsilon_{\infty m})}{\epsilon_{0m}(\epsilon_{\infty m} + 2)^2} \quad (5)$$

where g^{eff} is the effective Kirkwood correlation factor for a binary mixture, with ϕ_1 and ϕ_2 as volume fractions of liquids 1 and 2 respectively.

In equation (4), the values of g^{eff} will change from g_1 to g_2 as concentration of molecule 2 will decrease from 100% to 0%. The Kirkwood correlation factor (g_f) which gives angular correlation between the molecules of the system studied. The values of g^{eff} are less than one and it shows that there is a antiparallel alignment of dipoles. The values of g_f are near to unity and it indicates that weaker interaction between the constituent molecules.

The values of g^{eff} and g_f are calculated from equation (4) and (5) for the mixtures of the system. Temperature dependent g^{eff} and g_f for the system is given in Figure 1

Figure 1 The Kirkwood effective correlation factor g^{eff} and correlation factor g_f for ACN – DCE mixture:



The modified Bruggeman equation [12] is another parameter, which may be used an indicator of liquid 1 and 2 interaction. The Bruggeman factor f_B is given by,

$$f_B = \left(\frac{\epsilon_{0m} - \epsilon_{02}}{\epsilon_{01} - \epsilon_{02}} \right) \left(\frac{\epsilon_{01}}{\epsilon_{0m}} \right)^{1/3} = (1 - \phi_2) \quad (6)$$

According to equation (6), a linear relationship is expected which will give a straight line when plotted f_B against ϕ_2 . However, here the experimental values of f_B were found to deviate

from the linear relationship. The Bruggeman dielectric factor f_B versus volume fraction ϕ_2 of ACN at 35°C is given in Figure 2.

To fit the experimental data, Eq.(6) has been modified [13]

$$f_B = 1 - [a - (a-1)\phi_2]\phi_2 \quad (7)$$

where 'a' is numerical fitting parameter.

The parameters 'a' has been determined by the least squares fit method and it is found to be 0.745. The value of 'a' = 1 corresponds to the ideal Bruggeman mixture formula. The deviation from 1 relates to interaction between corresponding liquids 1 and 2. The small deviation of "a" suggest that weaker interaction between ACN and DCE.

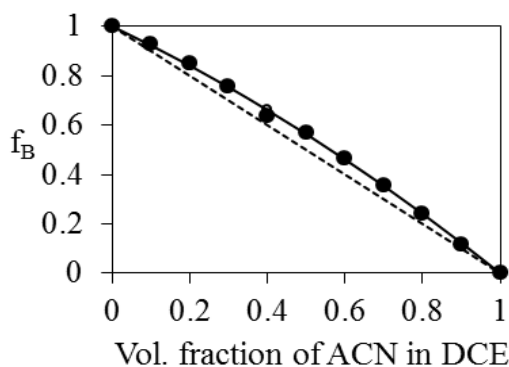


Figure 2. The Bruggeman plot for ACN-DCE mixture at 35°C. Dashed line denote original model (equation 6). Continuous line is the theoretical curve obtained from equation (7). Experimental points are shown by the symbol ●.

Conclusion

The Kirkwood correlation factors have been reported for ACN-DCE mixtures at 35°C temperature for 11 different concentrations. The interaction of the

chlorine group with the nitrile group liquids is discussed. One observes significant deviation from the various models. The Kirkwood effective correlation factors g^{eff} are less than one, it indicates that the dipoles of constituent molecules are antiparallel alignment. The values of Kirkwood parameter g_f are near to unity and it shows that the weaker interaction between the constituent molecules. The deviation of Bruggeman parameter 'a' from unity is small and it indicates that weaker interaction between the molecules of the ACN-DCE mixture.

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