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THE MOLECULAR CORRELATION OF 2-PENTENENITRILE AND CHLOROBENZENE MIXTURE AT 15^0C TEMPERATURE

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ABSTRACT

The dielectric study of 2-pentenenitrile (PN) with chlorobenzene (CBZ) mixture has been carried out at temperature 15^0C in the frequency range of 10 MHz to 20 GHz using time domain reflectometry (TDR) for 11 different concentrations of the system. The dielectric parameters such as static dielectric constant (ε_0) and relaxation time (τ) have been obtained by Fourier transform and the least squares fit method and these are fitted in Kirkwood model. The Kirkwood correlation factor (g_f) and effective Kirkwood correlation factor (g^{eff}) of the mixtures have been determined. In the mixtures the values of g^{eff} are less than one and it shows that; the antiparallel alignment of dipoles and the values of g_f are less deviated from one it represents that; weaker interaction between the constituent molecules of the system.

Key words: Dielectric permittivity, Kirkwood parameters, Time domain reflectometer, Nitrile group, Chlorine group.

INTRODUCTION

The information about formation of monomers and multimers as well as interaction between the molecules of the mixture can be obtained by the study of dielectric spectra of the mixture of bipolar liquids at microwave frequencies[1,2]. Pentenenitrile (PN) is non-associative liquids and chlorobenzene (CBZ) is associative liquid. One is of nitrile group and other with 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 detailed study of molecular correlation between pentenenitrile and chlorobenzene mixture using time domain technique at 15^0C temperature.

EXPERIMENTAL

Material and apparatus

A spectrograde 2-pentenenitrile (Fluka cheme Gmbh-9471 Buchs, Steinheim, Switzerland) and AR grade chlorobenzene (E-Merck) were used without further purification. The density and molecular weight of the liquids are as follows:

2-Pentenenitrile-density: 0.795 gm cm^{-3}; mol.wt.-81.12.

Chlorobenzene-density: 1.105 gm cm^{-3}; mol.wt.-112.56

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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 The change in the pulse after reflection from the sample placed in the cell was monitored by the sampling oscilloscope. The reflected pulse without sample $R_l(t)$ 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.

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-

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

Where $p(\omega)$ and $q(\omega)$ are Fourier transforms of $[R_1(t)\text{-}R_x(t)])$ 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 $\varepsilon^*(\omega$ 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].

$$\varepsilon^*(\omega.\ \varepsilon_\infty \frac{\varepsilon_0-\varepsilon_\infty}{1+j\omega\tau} \qquad \ldots(2)$$

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.

$$\frac{4\Pi N\mu^2\rho}{9kTM}g_f=\frac{(\varepsilon_0-\varepsilon_\infty)(2\varepsilon_0+\varepsilon_\infty)}{\varepsilon_0(\varepsilon_\infty+2)^2} \qquad \ldots(3)$$

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 PN and CBZ in gas phase are taken as 4.12D and 1.69 D[10], respectively.

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

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 -

$$\frac{4\Pi N}{9kT}\left(\frac{\mu_1^2\rho_1}{M_1}\varphi_1+\frac{\mu_2^2\rho_2}{M_2}\varphi_2\right)g^{eff}=\frac{(\varepsilon_{0m}-\varepsilon_{\infty m})(2\varepsilon_{0m}+\varepsilon_{\infty m})}{\varepsilon_{0m}(\varepsilon_{\infty m}+2)^2} \qquad \ldots(4)$$

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

$$\frac{4\Pi N}{9kT}\left(\frac{\mu_1^2\rho_1 g_1}{M_1}\varphi_1+\frac{\mu_2^2\rho_2 g_2}{M_2}\varphi_2\right)g_f=\frac{(\varepsilon_{0m}-\varepsilon_{\infty m})(2\varepsilon_{0m}+\varepsilon_{\infty m})}{\varepsilon_{0m}(\varepsilon_{\infty m}+2)^2} \quad \ldots(5)$$

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.

The static dielectric constant (ε_0) and relaxation time (τ) obtained by fitting experimental data with the Debye equation for 15^0C temperature is listed in Table 1. The values of static dielectric constant (ε_0) increases with the increase of concentration of PN in CBZ and relaxation time (τ) values have no trend.

Table 1: Static dielectric constant (ε_0) and relaxation time (τ) for 15°C temperature

Volume % of PN in CBZ	ε_0	τ (ps)
0	5.93 (0)	13.84 (0)
10	9.64 (2)	16.72 (11)
20	11.07 (1)	15.62 (13)
30	12.68 (6)	16.65 (35)
40	14.01 (4)	16.62 (35)
50	14.84 (4)	17.53 (24)
60	16.26 (5)	15.36 (28)
70	17.17 (4)	15.70 (26)
80	18.39 (4)	15.18 (25)
90	19.10 (2)	14.61 (12)
100	21.52 (2)	13.96 (1)

Number in bracket represent error in the corresponding value, e.g. means 14.61 (12) means 14.61 ± 0.12

In equation (5), 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. Temperature dependent g^{eff} and g_f for the system is shown in Fig. 1.

The values of g^{eff} are very less than one and it indicates that; there is antiparallel alignment of dipoles. The deviation of g_f values from unity is large in CBZ region but little in PN rich region. The large deviation of g_f values in CBZ region shows that stronger interaction but the little deviation in PN rich region shows weaker interaction between the constituent molecules in the system. The values of g^{eff} and g_f are calculated from equation (4) and (5) for the mixtures of the system.

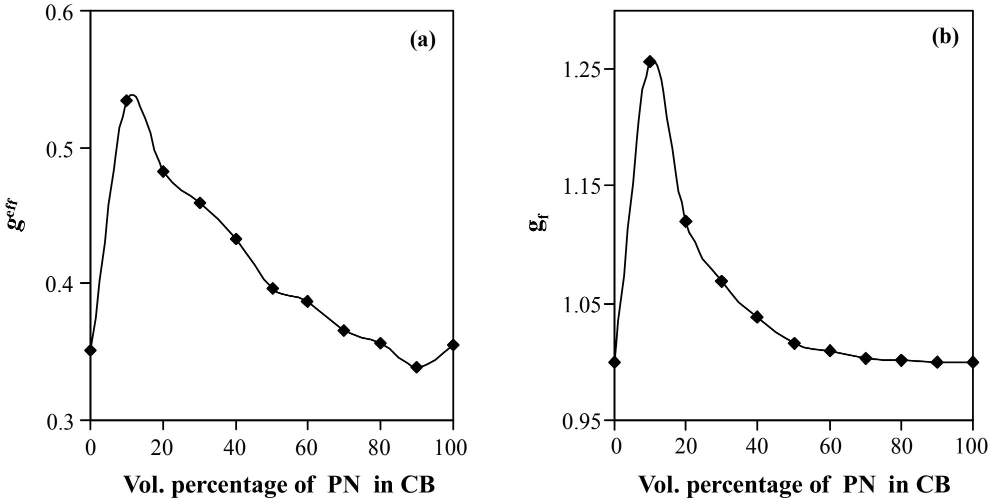

Fig. 1: (a) Kirkwood effective correlation factor g^{eff} and (b) Kirkwood correlation factor g_f, versus volume fraction (ϕ_2 of PN in CBZ)

CONCLUSION

The dielectric spectra analysis gives the dielectric parameters. The dielectric parameters were used to obtain the Kirkwood parameters. The Kirkwood correlation factors have been reported for PN-CBZ mixtures for 15^0C temperature and different 11-concentrations. The correlation of the chlorine group CBZ with the C≡N bonded liquid PN is discussed. From the above investigation it shows that; the stronger interaction between the PN and CBZ molecules in CBZ region and weaker interaction in PN rich region. It also shows that; the antiparallel alignment of the dipoles in the system one observes significant deviation from the various models.

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REFERENCES

1. S. N. Helambe, A. S. Chaudhary and S. C. Mehrotra, J. Mol. Liq., **84**, 235 (2000).
2. V. P. Pawar, S. C. Mehrotra, J. Mol. Liq., **95**, 63 (2002).
3. R. H. Cole, J. G. Berbarian, S. Mashimo, G. Chryssikos, A. Burns and E. Tombari, J. Appl. Phys., **66**, 793 (1989).
4. S. M. Puranik, A. C. Kumbharkhane and S. C. Mehrotra, J. Chem. Soc. Faraday Trans., **87**, 1569 (1991).
5. C. E. Shannon, Proc. IRE, **37**, 10 (1949).
6. H. A. Samulan, Proc. IRE, **39**, 175 (1951).
7. P. Debye, Polar molecules, Chemical Catalog, New York (1929).
8. P. R. Bevington, Data Reduction and Error Analysis for the Physical Sciences, Mc-Graw Hill, New York (1969).

9. H. Frolhich, Theory of Dielectrics, Oxford University Press, London (1949).
10. R. C. Weast, Handbook of Chemistry and Physics, 64th Ed. CRC Press Boca Raton, Florida (1983-84).
11. A. C. Kumbharkhane, S. M. Puranik and S. C. Mehrotra, J. Sol. Chem., **22**, 219 (1993).