

Study of Dielectric Relaxation of Allyl Chloride with Acetone Binary Mixtures Using Time Domain Reflectometry Technique

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Static dielectric constant and relaxation time of allyl chloride, acetone and their mixtures over wide range of concentration were obtained using the time domain reflectometry in microwave frequency range at 313.15 K. The intermolecular interaction in allyl chloride + acetone binary system is discussed with the help of excess parameters *viz.*, excess static dielectric constant (ϵ_s^E), excess inverse relaxation time ($1/\tau)^E$ and effective Kirkwood correlation factor. The effective Kirkwood correlation factor show that the allyl chloride posses antiparallel dipole tendency and acetone posses parallel dipole tendency. The excess parameters are fitted to Redlich-Kister equation.

Key Words: Static dielectric constant, Relaxation time, Effective Kirkwood correlation factor.

INTRODUCTION

The dielectric properties of polar liquids and their mixtures becomes highly interdisciplinary field of physics, chemistry, biochemistry, pharmaceutical, materials science and engineering¹. The intra and intermolecular interaction has significant effects on the dielectric properties of polar liquids while their measurements provide the path to understand molecular structures and unlike molecular interactions in mixed solvents^{1,2}. Allyl chloride is a highly versatile product due to its dual reactive sites at the double bond and the chlorine atom having dipole moment 1.94 D³. It is used as a chemical intermediate in many industries including the preparation of polymers, resins *etc.*⁴. Acetone is an interesting dipolar and aprotic solvent having dipole moment 2.88 D³. Use of acetone start from house, laboratory as cleaning agent to solvent as in plastic, synthetic fibers, production of methyl methacrylate and bisphenol A. Both allyl chloride and acetone exhibit dipole-dipole interaction. So study of intermolecular interaction between allyl chloride and acetone is very challenging and interesting because hydrogen bonding is less possible.

Very few researchers attempt study of allyl chloride and acetone. Maharolkar *et al.*⁵, reported the dielectric constant of mixtures decreases in addition of allyl chloride in *n*-butanol due to decrease in hydrogen bonding. Johari⁶ reported the addition of acetone in 1-propanal was a considerable structure breaking and consequently dielectric constant decreases. Mohsen-Nia *et al.*⁷ was studied the dielectric constant of acetone by using low-pass filter method. Dharne *et al.*⁸

determined the dielectric constant of allyl chloride with dimethyl formamide by using time domain reflectometry method. Dielectric relaxation studies have been carried out extensively to understand intermolecular interactions and dynamics of liquid mixtures^{9,10}. The objective of this paper is to report the dielectric relaxation study of allyl chloride + acetone binary mixtures. Time domain reflectometry in reflection mode has been used to obtain the dielectric parameters over a wide range of frequency^{8,11}.

EXPERIMENTAL

The chemicals used in the present work are allyl chloride and acetone of AR grade and are used without further purification. The 5 mL solutions were prepared at eleven different volume percentages by adding acetone in allyl chloride starting from 0-100 % in steps of 10 %, by micropipette with an accuracy of ± 0.0006 mL.

The complex permittivity spectra were studied using the time domain reflectometry on the Hewlett-Packard HP 54750A sampling oscilloscope with the HP 54754A time domain reflectometry plug-in module. A fast rising step voltage pulse of about 39 ps rise time generated by a tunnel diode was propagated through a flexible coaxial cable of characteristics impedance of 50 Ω . The sample was placed at the end of the coaxial line in the standard military application (SMA) coaxial cell. The experimental detail is same as explained earlier⁸⁻¹⁰.

A temperature controller system with a water bath and thermostat was used to maintain a constant sample temperature within the accuracy limit of ± 1 °C.

Data analysis: The time dependent data were processed to obtain complex reflection coefficient spectra $\rho^*(\omega)$ over a frequency range of 10 MHz to 10 GHz by using Fourier transform^{12,13}

$$\rho^*(\omega) = \left[\frac{c}{j\omega d} \right] \left[\frac{p(\omega)}{q(\omega)} \right] \quad (1)$$

where $p(\omega)$ and $q(\omega)$ are Fourier transforms of $[R_i(t) - R_s(t)]$ and $[R_i(t) + R_s(t)]$, respectively, c is the speed of light, ω is the angular frequency, d is effective pin length and $j = \sqrt{-1}$. The time dependent response waveform without sample is referred to as $R_i(t)$ and with sample referred as $R_s(t)$.

The complex permittivity spectra $\epsilon^*(\omega)$ is obtained from reflection coefficient spectra $\rho^*(\omega)$ by applying a bilinear calibration method¹⁴. The complex permittivity spectra are fitted by the nonlinear least squares fit method¹⁵ to the Debye equation¹⁶ to obtain various dielectric parameters.

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

where ϵ_s is the static dielectric constant, $\epsilon_\infty = n_D^2$ is high frequency limiting dielectric constant which is determined from refractive index at optical frequency, ω is the angular frequency and τ is the relaxation time of the system.

Theory: The excess parameters can be determined as,

$$A^E = A_m - [A_1X_1 + A_2X_2] \quad (3)$$

where A^E is excess parameters, A_m , A_1 and A_2 are parameters [static dielectric constant (ϵ_s), inverse relaxation time ($1/\tau$)] of allyl chloride and acetone mixture, respectively. X_1 and X_2 are mole fraction of allyl chloride and acetone, respectively. The excess inverse relaxation time which represent the average broadening of dielectric spectra. The inverse relaxation time analogy is taken from spectral line broadening (which is the inverse of relaxation time) in resonant spectroscopy¹⁷. The excess or deviation parameters were fitted to the Redlich-Kister equation¹⁸.

The Kirkwood correlation factor (g)¹⁹ of polar liquid is determined by

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

where ' μ ' is dipole moment in gas phase, ' ρ ' is density at temperature T , ' M ' is molecular weight, ' k ' is Boltzmann constant and ' N ' is Avogadro's number. In eqn. 5, dipole moment (μ) of allyl chloride and acetone is 1.94 and 2.88 D, respectively³. The determined ' g ' value of allyl chloride and acetone is 0.86 and 1.09 at 313.15 K.

The effective Kirkwood correlation factor (g^{eff})²⁰ of mixed components were evaluated by the eqn. 5

$$\frac{4\pi N}{9KT} \left(\frac{\mu_A^2\rho_A}{M_A} \Phi_A + \frac{\mu_B^2\rho_B}{M_B} \Phi_B \right) g^{\text{eff}} = \frac{(\epsilon_{sm} - \epsilon_{\infty sm})(2\epsilon_{sm} + \epsilon_{\infty sm})}{\epsilon_{sm}(\epsilon_{\infty sm} + 2)^2} \quad (5)$$

where ' Φ_1 ' and ' Φ_2 ' is the volume fractions of liquid first and second, respectively.

RESULTS AND DISCUSSION

In general, ideal binary mixtures follow linear behaviour of static dielectric constant (ϵ_s), high frequency limiting dielectric constant (ϵ_∞) and relaxation time with one of mixture constituent mole fraction. The non-linear variation of these parameters of allyl chloride + acetone binary system represented in Table-1 confirms the formation of dipole-dipole molecular complexes in the mixtures. The static dielectric constant reveals that interaction between unlike molecule increasing the effective dipole moments in the mixtures²¹. It is also noticed that relaxation time increases as mole fraction of X_2 (acetone) increases. Increase in relaxation time may be due to increase in molecular size and viscosity of medium²². This non-linearity nature of variation of these parameters indicates intermolecular association take place between allyl chloride and acetone molecules. The π electron which is loosely held in carbonyl group (C=O) of acetone are strongly pulled towards oxygen atom, so carbonyl oxygen atom acts as nucleophilic with carbonyl carbon is electrophilic centre. In allyl chloride, due to inductive effect chlorine atom is more electronegative than carbon. Thus, allyl chloride form dipole-dipole association through its chlorine (-Cl) atom with carbonyl group (C=O) of acetone.

TABLE-1
STATIC DIELECTRIC CONSTANT, HIGH FREQUENCY
LIMITING DIELECTRIC CONSTANT AND RELAXATION
TIME OF ALC + ACE SYSTEM

Mole fraction of ACE	313.15 K		
	ϵ_s	ϵ_∞	τ (ps)
0	7.47(2)	1.980	11.44(2)
0.1093	9.47(4)	1.960	13.69(3)
0.2164	11.29(3)	1.938	16.22(2)
0.3213	11.97(5)	1.921	17.57(6)
0.4241	12.66(7)	1.907	18.58(4)
0.5248	13.47(2)	1.896	19.36(3)
0.6236	13.99(4)	1.885	20.28(7)
0.7204	14.61(6)	1.871	21.91(5)
0.8154	15.58(3)	1.855	24.17(2)
0.9086	16.89(5)	1.836	26.25(3)
1.0000	18.77(2)	1.817	28.91(2)

The excess properties are play an important rule to extract the intermolecular interaction in polar liquids. The variations of excess static dielectric constant of present system are shown in Fig. 1. The positive value of excess static dielectric constant in allyl chloride rich region ($X_2 < 0.6$) indicates that effective dipole moment per unit volume increases with parallel alignment. In acetone rich region complex shows opposite behaviour which indicates dipole moment per unit volume decreases with antiparallel alignment^{9,23,24}. There is negative excess inverse relaxation time over entire range of concentration of X_2 as shown in Fig. 2. It indicates slower rotation of dipole due to steric hindrance increases to rotation of dipoles²⁵. The determined a_j coefficient (Redlich-Kister) and standard deviation (σ) of excess dielectric constant and excess inverse relaxation time are listed in Table-2.

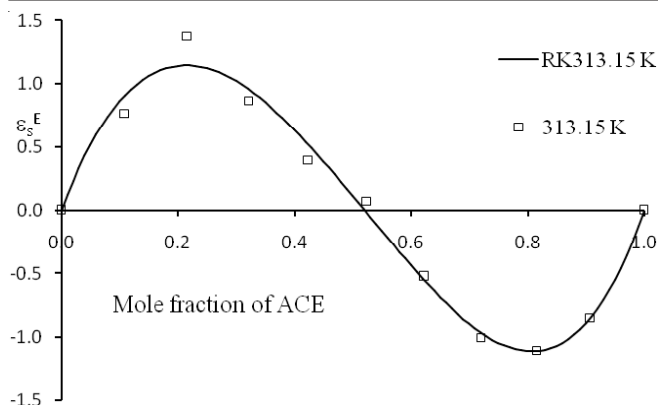


Fig. 1. Excess static dielectric constant of allyl chloride + acetone binary system

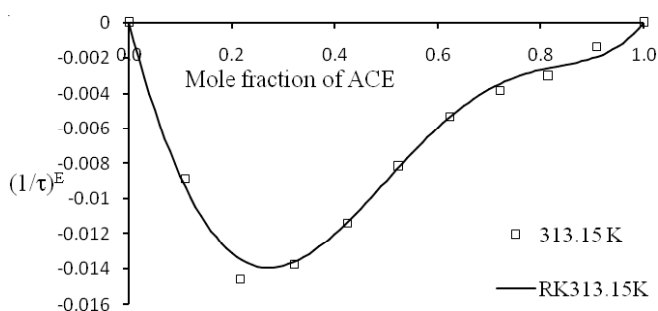


Fig. 2. Excess inverse relaxation time of allyl chloride+acetone binary system

	a ₀	a ₁	a ₂	a ₃	σ
ε _s ^E	0.4565	-11.1452	-0.9723	-1.5880	0.1238
(1/τ) ^E	-0.0360	0.0646	-0.0370	-0.0281	0.0005

The effective Kirkwood correlation factor (g^{eff}) provides valuable information about ordering of the electric dipoles in the polar liquid state *i.e.*, it quantifies the extent of polarization of the medium²⁶. The value of g^{eff} of present system is depicted in Fig. 3. The values of g^{eff} for pure allyl chloride are less than unity indicate the antiparallel orientation of the electric dipoles and the g^{eff} values for pure acetone is greater than unity indicate a high degree of coordinated chain like structures with parallel orientation of electric dipoles^{26,27}. This indicates strength of dipole-dipole interaction in acetone is greater than allyl chloride molecule. For mixtures of allyl chloride with acetone, values

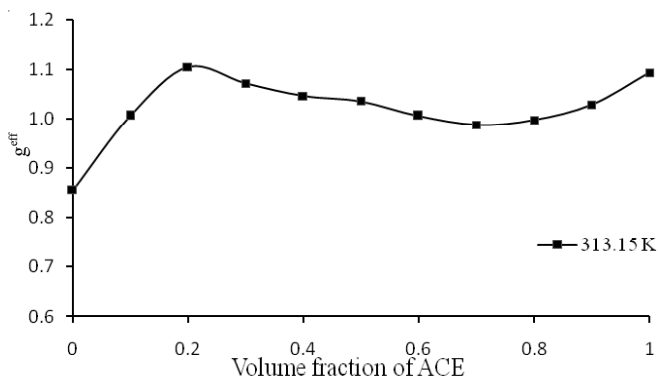


Fig. 3. Effective Kirkwood correlation factor of allyl chloride + acetone binary system

of g^{eff} greater in allyl chloride rich region is resemblance to positive excess dielectric constant in same region. In acetone rich region decreases in g^{eff} values is resemblance to negative excess dielectric constant in same region. The variation of g^{eff} value of the mixed components confirms the change in orientation of dipoles of allyl chloride due to their dipole-dipole interaction with acetone molecules.

Conclusion

The non-linear nature of determined static dielectric constant, high frequency limiting dielectric constant and relaxation time confirm dipole-dipole association present between allyl chloride and acetone molecule. The effective Kirkwood correlation factor indicates allyl chloride possess antiparallel tendency of dipoles and acetone possess parallel tendency of dipoles. On mixing this opposite tendency, excess dielectric constant and effective Kirkwood correlation factor of mixtures suggest increases in parallel orientation of dipole in allyl chloride rich region while in acetone rich decrease in parallel orientation of dipoles. The negative excess inverse relaxation time indicate dipole rotate slowly.

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