

Dielectric Study of Allyl Chloride with 2-Pentanone and 2-Hexanone in Microwave Frequency Range

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Dielectric measurement on binary mixtures of Allyl chloride (ALC) with 2-Pentanone (2-PE) and 2-Hexanone (2-HE) has been carried out over the entire concentration range using Time Domain Reflectometry (TDR) technique at various temperatures in microwave frequency range of 10 MHz to 10 GHz. The static dielectric constant, excess static dielectric constant (ϵ_s^E), effective Kirkwood correlation factor (g^{eff}) of binary mixtures over entire concentration range were determined to study the effect of increasing alkyl group of ketones on hetero molecular interaction. It was found that magnitude of excess static dielectric constant of mixtures increases with increase of alkyl group of ketones. The study reveals that the dipole moment of Allyl chloride in mixture have antiparallelism tendency where as 2-pentanone and 2-hexanone have parallelism tendency. Excess static dielectric constant is also fitted to Redlich-Kister equation to get information about rates of multimers formation.

Key Words : Static dielectric constant, Effective kirkwood correlation factor, Excess static dielectric constant

Introduction

Study of dielectric relaxation of binary mixtures (polar-polar or polar-nonpolar) in microwave frequencies has become very important tool to get information regarding intermolecular and intramolecular interaction between mixing components, especially when polar liquids are involved.¹⁻³ Allyl chloride has wide application in polymer, resin and many other industries due to its dual reactive sites at the double bond and the chlorine atom. The ketones are among most important organic compound because they are central importance to organic chemistry and biochemistry. The ketones contain carbonyl group (C=O) attached to alkyl group R and R', where R and R' may be same or different alkyl group. It is generally believed that the physical and chemical properties of ketones are largely determined by the carbonyl group, whereas in ALC determined by chlorine atom and double bond in carbon. In pure ALC, 2-PE and 2-HE spatial correlation between molecules may appear through dipole-dipole interaction.

Earlier few researchers reported dielectric properties of ALC with *n*-butanol⁴ and alcohols.⁵ The dielectric properties of some ketones are reported by Buta Singh,⁶ Crossely⁷ and Madhurima.^{8,9} No attempt, so far seems to have been made to study the dielectric behavior of binary mixtures of ALC with 2-PE and 2-HE.

In the present paper, dielectric properties of binary mixtures of polar ALC with polar 2-PE and 2-HE were carried out to confirm complex formation through dipole-dipole interactions of ALC with 2-PE and 2-HE at temperature 283.15, 293.15 and 303.15 K. The objective of the present paper is to report the experimental dielectric para-

eters for ALC+2-PE and ALC+2-HE mixtures, and determine molecules structural properties through the experimental data.

The section 2 of paper provides the experimental details along with data analysis. The theoretical model used to get different molecular parameters is given in section 3. The section 4 provides result and discussion. Conclusion of paper is summarized in section 5.

Experimental

Chemicals. The chemicals used in the present work are AR grade ALC, 2-PE and 2-HE with purity 99% and are used without further purification. The solutions were prepared at eleven different volume percentages of adding 2-PE (or 2-HE) in ALC starting from 0% to 100% in steps of 10%, by micropipette with an accuracy of ± 0.0006 mL.

Experimental Section. The Hewlett Packard HP54750A sampling oscilloscope with HP54754A TDR plug-in module has been used for experimental measurements. A fast rising step voltage pulse of about 39 ps rise time generated by a tunnel diode was propagated through a flexible coaxial cable with 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 data acquisition is carried out for eleven concentrations at three temperatures viz. 283.15, 293.15 and 303.15 K. The experimental details and data analysis are same as explained earlier.^{2-5,10}

The refractive index was determined by using Abbe's Refractometer at same temperature mentioned above and used for determination of high frequency limiting dielectric constant.

Theory

The information regarding intermolecular interaction between two liquid may be obtained from excess static dielectric constant (ϵ_s^E) of mixtures. It is defined as,

$$\epsilon_s^E = \epsilon_{sm} - (\epsilon_{sA}x_A + \epsilon_{sB}x_B) \quad (1)$$

where x is mole fraction and suffixes m , A , B represent mixture, liquid A and liquid B respectively. The excess static dielectric constant was fitted to Redlich-Kister equation¹¹ and determined a_j coefficient.

The Kirkwood correlation factor (g)¹² of polar liquid is determined by,

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

where ' μ ' is dipole moment in gas phase, ' ρ ' is density of liquid at temperature T , ' M ' is molecular weight, ' k ' is Boltzmann constant and ' N ' is Avogadro's number. In Eq. (2) dipole moment (μ) of ALC, 2-PE and 2-HE is 1.94, 2.70 and 2.66 D respectively.¹³ The determined ' g ' value of ALC, 2-PE and 2-HE at 293.15 K are 0.87, 1.33 and 1.43 respectively.

The effective Kirkwood correlation factor (g^{eff})¹⁴ of mixed components were evaluated by the Eq. (3),

$$\frac{4\pi N}{9kT} \left(\frac{\mu_A^2 \rho_A}{M_A} \Phi_A + \frac{\mu_B^2 \rho_B}{M_B} \Phi_B \right) g^{\text{eff}} = \frac{(\epsilon_{sm} - \epsilon_{\infty m})(2\epsilon_{sm} + \epsilon_{\infty m})}{\epsilon_{sm}(\epsilon_{\infty m} + 2)^2} \quad (3)$$

where ' Φ_A ' and ' Φ_B ' be the volume fractions of liquid ' A ' and ' B ' respectively.

The Bruggeman factor (f_B)¹⁵ is another important parameter which may be used as an indicator of solute-solvent interactions and is given by,

$$f_B = \left(\frac{\epsilon_m - \epsilon_B}{\epsilon_A - \epsilon_B} \right) \left(\frac{\epsilon_A}{\epsilon_m} \right)^{(1/3)} = 1 - V \quad (4)$$

where V is volume fraction, which is a qualitative measure of volume of the solute in the mixture. The values of static dielectric constant corresponding to mixture, component A and component B are given by ϵ_m , ϵ_A and ϵ_B respectively.

Result and Discussion

The values of static dielectric constant (ϵ_s) of polar liquids are mainly determined by its dipole moment, the number of dipole moment per unit volume and Kirkwood correlation factor. It is observed that values of Kirkwood correlation factor (g) of ketones are greater than unity and order of ' g ' is 2-HE > 2-PE. The value of ' g ' greater than unity is the representative of self association of molecules with parallel dipole ordering in their dipole-dipole associated structures. The value of ' g ' less than unity for ALC suggest non-associate structure with antiparallel dipolar ordering.^{12,14}

In general, ideal binary mixtures follow linear behavior of

Table 1. Static dielectric constant and high frequency limiting dielectric constant of ALC+2-PE binary system

Mole fraction of 2-PE	283.15 K		293.15 K		303.15 K	
	ϵ_s	ϵ_∞	ϵ_s	ϵ_∞	ϵ_s	ϵ_∞
0	8.32(1)	2.022	7.98(1)	2.005	7.66(3)	1.991
0.0780	9.92(3)	2.014	9.18(3)	1.997	8.78(4)	1.982
0.1598	10.86(5)	2.005	10.15(5)	1.988	9.71(3)	1.974
0.2459	11.64(3)	1.999	10.92(2)	1.982	10.50(2)	1.968
0.3365	12.25(2)	1.994	11.51(3)	1.977	11.04(6)	1.963
0.4321	12.77(4)	1.988	11.97(4)	1.971	11.51(2)	1.957
0.5330	13.28(2)	1.982	12.48(6)	1.966	12.03(2)	1.952
0.6397	13.76(6)	1.977	12.95(1)	1.960	12.57(7)	1.946
0.7527	14.31(2)	1.971	13.46(2)	1.954	13.17(2)	1.940
0.8726	15.17(7)	1.963	14.16(3)	1.946	13.92(4)	1.932
1	16.39(2)	1.946	15.37(1)	1.929	15.1(2)	1.918

ϵ_s values with one of mixture constituent mole fraction. The non-linear variation of static dielectric constant and high frequency limiting dielectric constant of ALC+2-PE and ALC+2-HE mixed components observed in Tables 1 and 2 respectively, confirms the formation of dipole-dipole molecular complexes in the mixtures. The π electron which is loosely held in carbonyl group are pulled towards oxygen atom, so carbonyl oxygen atom acts as nucleophilic with carbonyl carbon is electrophilic centre. In ALC, due to inductive effect chlorine atom is more electronegative than carbon. Thus, ALC form dipole-dipole association through its chlorine (-Cl) atom with carbonyl group (C=O) of ketones. Increase in static dielectric constant of mixtures with increase in mole fraction of 2-PE and 2-HE in respective mixtures confirms the effective dipole moments increases. It is also noticed that static dielectric constant decreases with increase in temperature from 283.15 K to 303.15 K. This is due to thermal agitation, correlation between neighbouring

Table 2. Static dielectric constant and high frequency limiting dielectric constant of ALC+2-HE binary system

Mole fraction of 2-HE	283.15 K		293.15 K		303.15 K	
	ϵ_s	ϵ_∞	ϵ_s	ϵ_∞	ϵ_s	ϵ_∞
0	8.32(2)	2.022	7.98(3)	2.005	7.66(3)	1.991
0.0679	9.61(4)	2.016	9.27(3)	1.997	8.86(4)	1.985
0.1409	10.44(2)	2.011	10.11(1)	1.994	9.69(3)	1.982
0.2194	10.99(3)	2.008	10.66(2)	1.991	10.16(5)	1.980
0.3042	11.46(5)	2.005	11.03(5)	1.988	10.53(3)	1.980
0.3961	11.83(2)	2.002	11.34(2)	1.985	10.86(3)	1.974
0.4959	12.17(6)	1.997	11.69(8)	1.982	11.27(5)	1.971
0.6048	12.56(2)	1.991	12.14(5)	1.977	11.73(4)	1.968
0.7240	12.94(7)	1.985	12.66(7)	1.971	12.21(2)	1.963
0.8551	13.66(3)	1.977	13.36(3)	1.966	12.81(1)	1.957
1	14.70(3)	1.971	14.53(2)	1.960	14.00(3)	1.946

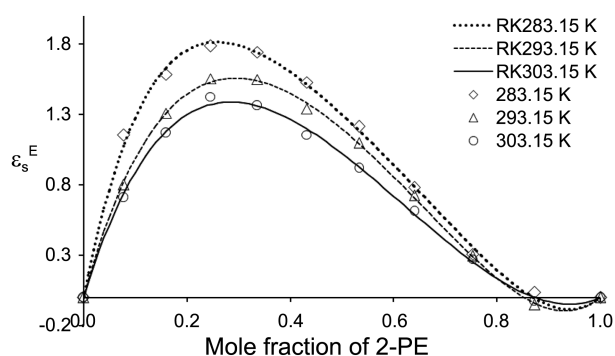


Figure 1. Excess static dielectric constant of ALC+2-PE binary system.

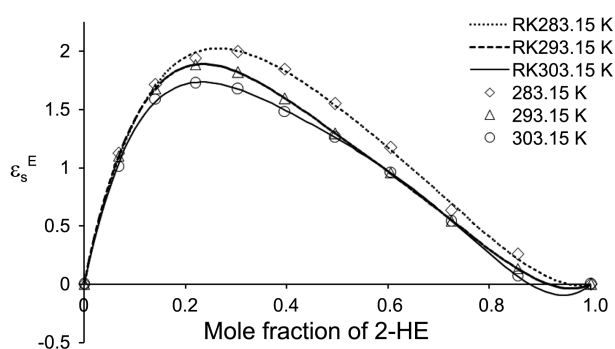


Figure 2. Excess static dielectric constant of ALC+2-HE binary system.

dipole decreases.^{2,16} The static dielectric constant of 2-HE less than 2-PE agrees with statement of static dielectric constant decreases with increase in carbon chain length.^{3,16}

The excess static dielectric constant (ϵ_s^E) of mixed components is function of mole fraction of constituent component are commonly used to extract information on intermolecular interaction and dipole association.^{3,17} The ϵ_s^E values of ALC+2-PE and ALC+2-HE as function of mole fraction of ketones (2-PE, 2-HE) are shown in Figures 1 and 2 respectively. Both the ALC+2-PE and ALC+2-HE have positive values of ϵ_s^E (except 0.9 mole fraction of 2-PE in ALC+2-PE and RK fit line show small negative lobe near pure ketone rich region) which is evidence of 2-PE and 2-HE acts as structure maker ($g > 1$) for non-associated structure of ALC ($g < 1$) during complexation, so dipole moment per unit volume increases with parallel alignment. It increases dielectric polarization of mixtures and lead to formation of monomer and dimer.^{17,18} The magnitude of ϵ_s^E value of ALC+2-HE greater than ALC+2-PE suggest that strength of dipole-dipole interaction of ALC with 2-HE greater than ALC with 2-PE. The maximum magnitude of ϵ_s^E of ALC+2-PE and ALC+2-HE occur at 0.24 mole fraction of 2-PE and at 0.21 mole fraction of 2-HE respectively. Both system shows maximum magnitude corresponding stoichiometric ratio of ALC to ketone is 2:1. The RK coefficient a_j determined by Redlich-Kister equation are given in Table 3 along with error estimate in a_j 's. These parameters indicate significance of multimers formation in the system. The first term (a_0) represent formation of dimers, second

Table 3. a_j coefficients of excess static dielectric constant

Temp. (K)	a_0	a_1	a_2	a_3
ALC+2-PE				
283.15	5.19(25)	-6.71(98)	2.50(116)	-3.95(256)
293.15	4.78(12)	-6.06(47)	0.43(55)	-2.07(123)
303.15	4.09(18)	-5.65(70)	1.08(82)	-1.13(182)
ALC+2-HE				
283.15	6.09(22)	-6.61(87)	3.55(105)	-3.95(231)
293.15	5.13(3)	-6.26(12)	4.52(15)	-5.27(33)
303.15	4.99(8)	-5.08(30)	3.32(37)	-6.98(80)

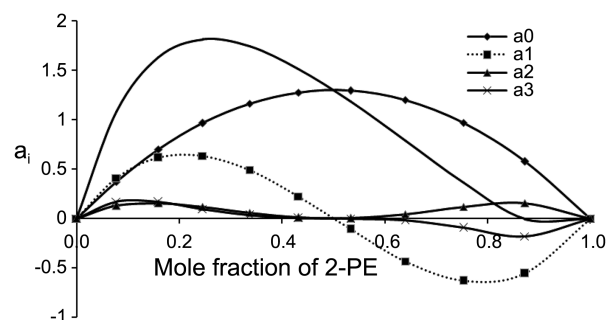


Figure 3. Plot of contribution of a_j versus mole fraction of 2-PE.

term (a_1) represent formation of trimers and so on. The Figure 3 illustrates the contributions of different terms. The evaluation of effective Kirkwood correlation factor (g^{eff}) over entire concentration range of mixtures used to extract information regarding effect of interaction on orientation of dipoles in mixtures.^{14,17} For the present systems, it is represented in Table 4. The g^{eff} values vary from 'g' value of pure ALC to 'g' value of respective ketones with increase in volume fraction of ketones in mixtures. The change in g^{eff} values with increase in temperature is not significant but agreement with variation of ϵ_s with temperature. The concentration dependent non-linear natures of g^{eff} of the mixed components confirm the change in orientation of dipoles of

Table 4. Effective Kirkwood correlation factor (g^{eff}) of ALC+2-PE and ALC+2-HE

Volume fraction of 2-PE	Volume fraction 283.15K 293.15K 303.15K of 2-PE			Volume fraction 283.15K 293.15K 303.15K of 2-HE			
	ALC+2-PE			ALC+2-HE			
0	0.88	0.87	0.85	0	0.88	0.87	0.85
0.1	1.04	0.99	0.97	0.1	1.03	1.02	1.00
0.2	1.11	1.07	1.05	0.2	1.11	1.11	1.09
0.3	1.16	1.12	1.10	0.3	1.15	1.15	1.13
0.4	1.18	1.14	1.13	0.4	1.19	1.18	1.15
0.5	1.20	1.15	1.14	0.5	1.21	1.19	1.17
0.6	1.21	1.17	1.16	0.6	1.22	1.21	1.20
0.7	1.22	1.18	1.18	0.7	1.25	1.24	1.23
0.8	1.23	1.19	1.20	0.8	1.26	1.28	1.27
0.9	1.28	1.22	1.24	0.9	1.32	1.33	1.32
1	1.35	1.33	1.32	1	1.44	1.43	1.42

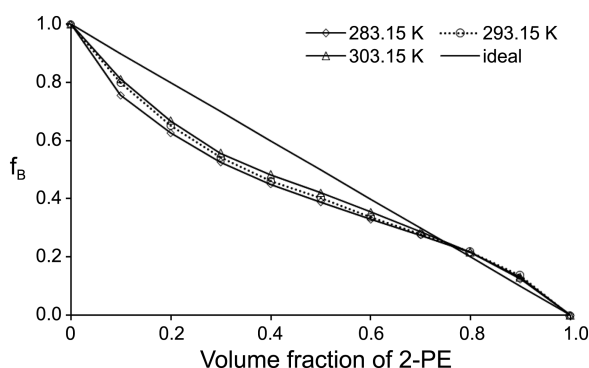


Figure 4. Bruggeman factor of ALC+2-PE binary system.

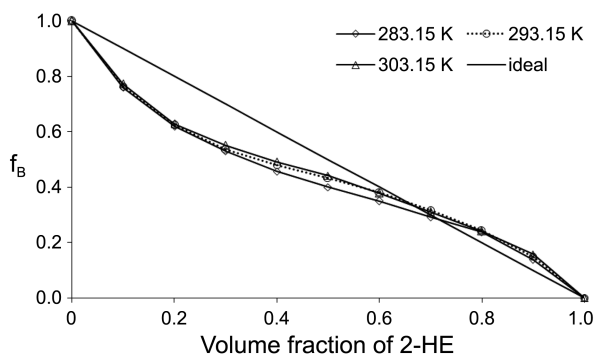


Figure 5. Bruggeman factor of ALC+2-HE binary system.

ALC due to their dipole-dipole interaction with 2-PE and 2-HE molecules. The g^{eff} values of ALC+2-HE greater than ALC+2-PE mixtures is good resemblance with ϵ_s^E values of ALC+2-PE and ALC+2HE as seen in Figures 1 and 2. The g^{eff} values found to be increasing function of size of alkyl group of ketones. This is probably due to the fact that when alkyl group is small polar group is relatively exposed, so that dipolar interaction may occur between associated complexes which tend to counteract the coordination within the complexes. Similar conclusion was made by Dharmalingam¹ for alcohol.

The Bruggeman factor plots of ALC+2-PE and ALC+2-HE as shown in Figures 4 and 5 respectively. The deviation of plots from linearity suggests that formation of complex of ALC with 2-PE and 2-HE.¹⁹ This arises due to dipole-dipole interaction between chlorine (-Cl) group of ALC and carbonyl (C=O) group of ketone (2-PE and 2-HE). The more deviation in ALC region indicates that volume expansion take place in mixture. This is due to small addition of ketones, parallel orientation of dipoles of ALC increases

than the ideal mixture.

Conclusion

The dielectric study of ALC with 2-PE and 2-HE confirm that there is a complex formation between ALC and 2-PE, 2-HE. By considering molecular structure, -Cl group of Allyl chloride interact with carbonyl group (C=O) of ketone. Static dielectric constant decreases with increase in carbon chain length of ketone. Increasing effective Kirkwood correlation factor indicates that the correlation between neighbouring dipoles increases with increase in carbon chain of ketone. The deviation of Bruggeman factor also support to presence of intermolecular interaction of ALC with 2-PE and 2-HE.

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