Dielectric spectroscopy and hydrogen bonding studies of 1-chloropropane–ethanol mixture using TDR technique

Ravindra V. Shinde*, Avadhut R. Deshmukh[†], Shital A. Ingole[†]
and Ashok C. Kumbharkhane^{†,‡}

*College of Agriculture Engineering and Technology
Vasantrao Naik Marathwada Krishi Vidyapeeth Basmat Road
Parbhani 431402, Maharashtra, India

[†]School of Physical Sciences
Swami Ramanand Teerth Marathwada University
Vishnupuri, Nanded 431606, Maharashtra, India

[‡]akumbharkhane@yahoo.co.in

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The time-domain reflectometry technique was exercised to assess the complex permittivities of 1-chloropropane and ethanol along with their binary mixture in the frequency range of 10 MHz–50 GHz and in the temperature range of 10–25°C. Dielectric parameters like static dielectric permittivity (ϵ_0) and relaxation time (τ) have been acquired by the least-square-fit method. The obtained assessments of static permittivity and relaxation time were used to compute various dielectric parameters like excess dielectric constant, excess relaxation time, Kirkwood correlation factor and thermodynamic parameters. The experimental outcome illustrates the nonlinear variations in dielectric permittivity, relaxation time and authenticates the structural formation due to intermolecular interaction between 1-chloropropane and ethanol. Molecular rotary motion and dipole reorientation movements of these complex systems are presented in agreement with the molar entropy and enthalpy.

Keywords: Time-domain reflectometry; complex permittivity; dielectric relaxation; thermodynamic parameter; Kirkwood factor.

1. Introduction

An exploration to learn the hydrogen bond reorganization dynamics of solvent–solvent as well as pure solvent–mixtures has been extensively made with the help of dielectric relaxation spectroscopy. To identify hydrogen bonding and intermolecular interactions in the mixture, dielectric relaxation studies on binary mixtures play a chief role.

Structurally, 1-chloropropane (CAS No. 540-54-5) is an organochlorine compound as well as a secondary haloalkane, the concluding label recognizes the two C–C bonds seen around the carbon atom. 1-Chloropropane is a flammable, colorless liquid with chloroform odor and is prepared by the reaction of *n*-propyl alcohol with hydrochloric acid in the presence of zinc chloride as a catalyst.¹ It is an organic compound with chemical formula $\text{CH}_3\text{CH}_2\text{CH}_2\text{Cl}$ and a vapor pressure of 345 mm-Hg at 25°C. The inhalation exposure of 1-chloropropane in humans causes central nervous system-related effects characterized by nausea, headache, dizziness, unconsciousness, coma and even respiratory irritation. Also, liquid form of 1-chloropropane can cause eye, skin and digestive irritations.^{2,3} Ethanol ($\text{C}_2\text{H}_5\text{OH}$) is a nonaqueous protic solvent.⁴ It has a dielectric constant (ϵ) of 25.07 and a dipole moment (μ) of 1.70 D.⁵ It is a colorless, inflammable liquid having a low boiling point (78°C).⁶ It is

miscible with water in all proportions and is also miscible with most organic solvents.^{7,8} Ethanol is important as an industrial and pharmaceutical solvent.

Numerous researchers have studied the temperature-dependent dielectric relaxation parameters of assorted associating molecule mixtures. Cavity formation and dipolar contribution to the *Gauche-trans* isomerization of 1-chloropropane and 1,2-dichloroethane have been reported by Melendez-Pagan *et al.*⁹ Conformational and structural studies of 1-chloropropane and 1-bromopropane from temperature-dependent FT-IR spectra of rare gas solutions and *ab initio* calculations are reported by Durig *et al.*¹⁰

In the present investigation, the dielectric relaxation of 1-chloropropane in ethanol solution at different temperatures (10°C, 15°C, 20°C and 25°C) is undertaken. A regular microwave technique and the solution methods have been used for this study. Dielectric relaxation of polar liquids in polar solvents by microwave absorption study gives valuable information about various types of molecular associations present in the solutions. It is because microwaves can detect weak molecular interactions.^{11–15} A solute–solvent type of molecular association has been proposed. This aspect motivated us to undertake an extensive study to understand the associative nature of 1-chloropropane in polar ethanol

environment. The study is projected to present a better perception of the nature of molecular involvement in the mixture.

2. Experimental

2.1. Materials

1-Chloropropane ($\text{CH}_3\text{CH}_2\text{CH}_2\text{Cl}$; CAS No. 540-54-5; purity 98%) and ethanol ($\text{C}_2\text{H}_5\text{OH}$; purity 99.9%) were purchased from Merck Life Sciences Pvt. Ltd., Mumbai, and used without purification.

2.2. Measurements

The complex permittivity of the solution was measured in the frequency range of 10 MHz–50 GHz at 10–25°C using time-domain reflectometry (TDR) technique.^{16,17} The temperature of the samples under test has been maintained using a calibrated temperature controller system with an accuracy of $\pm 0.1^\circ\text{C}$. The Tektronix DSA8300 sampling mainframe oscilloscope with dual-channel sampling module 80E10B has been used. To feed the pulse, a coaxial cable having 50- Ω impedance, an inner diameter of 0.28 mm and an outer diameter of 1.19 mm is used. Sampling oscilloscope monitors changes in pulse after reflection from the end of line. Reflected pulses without sample $R_1(t)$ and with sample $R_x(t)$ were recorded in a time window of 0.5 ns and digitized in 2000 points. To determine the complex permittivity spectra $\varepsilon^*(\omega)$, the Fourier transformations of the pulse and data analysis were performed using nonlinear least-square-fit

method,^{18,19} with 50-GHz bandwidth and TDR module with step generator unit was used.

3. Results and Discussion

3.1. Complex permittivity

The complex permittivity spectra for different concentrations of 1-chloropropane in ethanol at 25°C are shown in Fig. 1. To calculate the static dielectric constant (ε_0), relaxation time (τ) and distribution parameters (α and β), complex permittivity $\varepsilon^*(\omega)$ data were fitted by the nonlinear least-square-fit method to the Havriliak–Negami expression,²⁰

$$\varepsilon^*(\omega) = \varepsilon_\infty + \frac{\varepsilon_0 - \varepsilon_\infty}{[1 + (j\omega\tau)^{1-\alpha}]^\beta}, \quad (1)$$

where ε_0 , ε_∞ , τ , α and β are the fitting parameters. The Havriliak–Negami expression includes the Debye ($\alpha = 0$, $\beta = 1$),²¹ Cole–Cole ($\beta = 1$)²² and Cole–Davidson ($\alpha = 0$)²³ and relaxation spectral functions in limiting form.

In this investigation, the binary mixture of 1-chloropropane and ethanol confirms Debye-type dispersion. So, the complex permittivity spectra have been fitted in Debye-type model using the nonlinear least-square-fit method to determine the dielectric relaxation parameters. The static dielectric constant and relaxation time for the binary mixture of 1-chloropropane and ethanol at 25°C reported in Table 1 agree well with the standards reported in literature.

In the binary liquid systems such as 1-chloropropane–ethanol mixture, it has been observed that static dielectric constant ε_0 and relaxation time (τ_0) decrease with the

Fig. 1. Frequency-dependent complex dielectric permittivity spectra of 1-chloropropane–ethanol system at 25°C.

Table 1. Temperature-dependent dielectric parameters for the binary mixture of 1-chloropropane and ethanol.

Volume fraction of 1-chloropropane	10°C		15°C		20°C		25°C	
	ϵ_0	τ (ps)	ϵ_0	τ (ps)	ϵ_0	τ (ps)	ϵ_0	τ (ps)
0.0	28.7 (2)	168.4 (3)	25.7 (1)	158.5 (1)	25.1 (1)	146.1 (1)	24.3 (2)	133.9 (2)
0.1	24.1 (3)	138.9 (4)	22.7 (2)	125.6 (2)	22.2 (3)	102.7 (3)	21.9 (3)	99.0 (3)
0.2	23.3 (6)	75.5 (4)	21.6 (6)	61.0 (3)	20.1 (6)	49.3 (2)	18.5 (5)	54.1 (3)
0.3	19.3 (5)	62.9 (3)	18.9 (4)	58.6 (3)	18.2 (4)	42.8 (2)	17.0 (3)	48.9 (2)
0.4	18.9 (4)	49.9 (2)	17.4 (3)	44.8 (2)	16.8 (3)	35.5 (1)	14.8 (3)	44.2 (2)
0.5	17.7 (3)	46.5 (2)	16.1 (2)	38.8 (1)	15.8 (2)	34.2 (1)	13.9 (2)	20.2 (1)
0.6	16.3 (1)	30.8 (1)	14.4 (1)	25.8 (1)	13.3 (1)	22.6 (9)	12.6 (1)	16.8 (7)
0.7	14.1 (1)	18.2 (6)	12.5 (1)	15.5 (5)	11.8 (1)	13.3 (5)	10.7 (9)	11.9 (4)
0.8	12.0 (6)	11.5 (3)	10.9 (5)	11.1 (2)	10.9 (6)	8.7 (2)	10.4 (5)	8.1 (2)
0.9	11.6 (1)	9.8 (9)	10.7 (1)	8.9 (7)	9.9 (1)	8.3 (7)	9.5 (1)	6.8 (7)
1.0	11.2 (1)	7.7 (8)	9.0 (6)	6.1 (3)	8.9 (5)	5.8 (2)	8.3 (4)	5.7 (2)

increase in the volume fraction of 1-chloropropane in ethanol. Decrease of dielectric constant is due to the transition of spherical molecular aggregates into elongated aggregates giving rise to parallel orientation of the dipoles.²⁴ Shirke *et al.* drew similar conclusions for ethyl acetate–alcohol systems.²⁵ For all the molecules under investigation, the relaxation time decreases with increase in the temperature from 10°C to 25°C. This may possibly be due to that the increase in temperature causes alteration in molar volume, molecules to reorient with faster rate and increase in the rate of loss of energy due to large number of collisions. Analogous sorts of results are presented by Rewar and Bhatnagar.²⁶ Other causes for the decrease in relaxation time are increase in the molar volume and the increase in the effective length of the dipole with increase in temperature. This is in agreement with other works in the literature.²⁷

3.2. Excess dielectric permittivity

For dielectric properties of the mixture, the contribution of intermolecular bonds is studied in terms of the excess static dielectric permittivity. The excess dielectric permittivity can be written as^{17,28,29}

$$\epsilon_0^E = (\epsilon_0)_M - [(\epsilon_0)_E X_E + (\epsilon_0)_C (1 - X_E)], \quad (2)$$

where the subscripts M , E and C represents mixture, ethanol and 1-chloropropane, respectively, and X_E represents the volume fraction of ethanol in mixture.

The plot of excess dielectric permittivity ϵ_0^E of the mixture versus volume fraction of ethanol is shown in Fig. 2. The excess dielectric permittivity provides qualitative information about the multimer formation in the mixture as follows:

- $\epsilon^E = 0$ signifies that the liquids E and C do not interact at all.
- $\epsilon^E < 0$ signifies that the liquids E and C interact in such a way that the total effective dipole gets reduced. The liquids E and C may form multimers leading to the less effective dipole.

Fig. 2. Excess dielectric permittivities for 1-chloropropane–ethanol mixture from 10°C to 25°C.

- $\epsilon^E > 0$ signifies that the liquids E and C interact in such a way that the total effective dipole moment increases. There is a tendency to form multimers.

The peak value of minima for the excess permittivity at different temperatures is found at around $X_E \approx 0.7$. In this system, the negative values of the excess permittivity indicate weak hydrogen interface between ethanol and 1-chloropropane molecules. In addition, it points out that there is a multimer prototype.

3.3. Excess inverse relaxation time

The information related to dynamics of the solute–solvent interaction may be obtained by the excess properties related to the relaxation time in the mixture. The excess inverse relaxation time is defined as^{30,31}

$$\left(\frac{1}{\tau}\right)^E = \left(\frac{1}{\tau}\right)_M - \left[\left(\frac{1}{\tau}\right)_E X_E + \left(\frac{1}{\tau}\right)_C (1 - X_E)\right], \quad (3)$$

Fig. 3. Excess inverse relaxation times for 1-chloropropane–ethanol mixture from 10°C to 25°C.

where $(1/\tau)^E$ is the excess inverse relaxation time which represents the average broadening of dielectric spectra. M , E and C correspond to mixture, ethanol and 1-chloropropane, respectively. 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 E and C interaction.
- (ii) $(1/\tau)^E < 0$: The interaction of E and C produces a field such that the effective dipoles rotate slowly.
- (iii) $(1/\tau)^E > 0$: The interaction of E and C produces a field such that the effective dipoles rotate quickly, i.e., the field cooperate in the rotation of the dipoles.

The variations of excess inverse relaxation time $(1/\tau)^E$ with volume fraction of 1-chloropropane in ethanol are shown in Fig. 3. The negative peak value of $(1/\tau)^E$ has been found at around $X_E = 0.4$. The value of $(1/\tau)^E$ is less than zero, i.e., negative, for all the concentrations at all temperatures. This behavior suggests that there is slower rotation of the dipoles in the system.

3.4. The Kirkwood correlation

The structural information about the liquids from the dielectric relaxation parameter may be obtained by means of the Kirkwood correlation parameter g . This factor is also useful for obtaining information regarding orientation of electric dipoles in polar liquids. The g for the pure liquid may be obtained using the following expression from Ref. 32:

$$g\mu^2 \frac{4\pi N\rho}{9KTM} = \frac{(\epsilon\epsilon_{0m} - \epsilon\epsilon_{\infty m})(2\epsilon\epsilon_{0m} + \epsilon\epsilon_{\infty m})}{\epsilon\epsilon_{0m}(\epsilon\epsilon_{\infty m} + 2)^2}, \quad (4)$$

where μ is the dipole moment in the gas phase, ρ is the density at temperature T , M is the molecular weight, K is the Boltzmann constant and N is Avogadro's number; also ϵ_0 and

ϵ_{∞} are the static dielectric constant and dielectric constant at high frequency and g is the Kirkwood correlation factor for the i th liquid system.

Modified form of the above equation can be used to estimate the Kirkwood correlation factor and to study the orientation of dipoles due to heterogeneous interaction in binary mixtures, which is expressed as follows:

$$\frac{4\pi N}{9KT} \left[\frac{\mu_E^2 \rho_E V_E}{M_E} + \frac{\mu_C^2 \rho_C (1 - V_E)}{M_C} \right] \times g^{\text{eff}} = \frac{(\epsilon_{0m} - \epsilon_{\infty m})(2\epsilon_{0m} + \epsilon_{\infty m})}{\epsilon_{0m}(\epsilon_{\infty m} + 2)^2}, \quad (5)$$

where g^{eff} is the Kirkwood effective correlation factor, μ_E is the dipole moment of ethanol, μ_C is the dipole moment of 1-chloropropane and ρ_E and ρ_C are the densities of ethanol and 1-chloropropane, respectively. V_E represents the volume fraction of ethanol in 1-chloropropane. The value of g^{eff} for ethanol is found to be 3.16 at 25°C which is greater than unity. This indicates the formation of H-bonded molecular multimers of binary mixture of 1-chloropropane and ethanol and favors parallel orientation.

It is also observed that g^{eff} values vary with change in temperature, indicating that temperature change produces appreciable structural change. Determined values of Kirkwood correlation factor are plotted against volume fraction of 1-chloropropane, as shown in Fig. 4.

3.5. Thermodynamic parameters

The activation parameters namely enthalpy ΔH and entropy ΔS for dielectric relaxation process were calculated using the Eyring rate equation,³³

$$\tau = \frac{h}{KT} \exp \frac{\Delta H - T\Delta S}{RT}, \quad (6)$$

Fig. 4. Plot of Kirkwood effective correlation factor g^{eff} versus volume fraction for 1-chloropropane–ethanol mixture at the temperatures of 10–25°C.

Table 2. Thermodynamic parameters for the 1-chloropropane–ethanol binary mixture.

Volume fraction of 1-chloropropane	Enthalpy of activation ΔH (kJ · mol ⁻¹)	Entropy of activation ΔS (J · mol ⁻¹ · K ⁻¹)
0.0	8.35 (7)	0.20 (2)
0.1	14.6 (2)	0.22 (1)
0.2	14.7 (7)	0.23 (2)
0.3	12.6 (8)	0.22 (2)
0.4	6.10 (9)	0.20 (3)
0.5	34.2 (9)	0.30 (3)
0.6	24.8 (3)	0.27 (1)
0.7	17.6 (9)	0.25 (3)
0.8	15.7 (3)	0.24 (1)
0.9	13.8 (2)	0.24 (9)
1.0	11.0 (4)	0.23 (1)

where τ is relaxation time, h is Planck's constant, K is Boltzmann constant, T is the temperature in K and R is gas constant.

The molar activation enthalpy ΔH and entropy ΔS for pure and nine unusual concentrations were gauged and the values are reported in Table 2. The positive values of activation enthalpy ΔH substantiate that heat is absorbed in the molecular reorientation process. The positive values of entropy indicate that activated system is less structured than the standard system.⁵

4. Conclusion

The complex permittivity spectra of 1-chloropropane–ethanol mixture are determined using TDR spectroscopy method in the frequency range of 10 MHz–50 GHz. The dielectric relaxation parameters, i.e., static dielectric constant (ϵ_0), relaxation time (τ), variation in excess permittivity, Kirkwood effective correlation factor (g^{eff}), activation enthalpy (ΔH) and entropy (ΔS), have been reported for 1-chloropropane–ethanol mixture for dissimilar temperatures. We summarize our findings as follows:

- The static dielectric constant of mixtures is found to be in the range of 24.3–8.3. In the 1-chloropropane–ethanol mixture, the dielectric permittivity decreases with increase in the concentration of 1-chloropropane.
- The relaxation time decreases with the addition of 1-chloropropane in ethanol, which may be due to the following reasons: (i) smaller size and fast rotation of 1-chloropropane molecules; and (ii) low viscosity of 1-chloropropane.
- Kirkwood effective correlation factor (g^{eff}) values are greater than unity, indicating the formation of H-bonded molecular multimers of binary mixture of 1-chloropropane and ethanol and favoring parallel orientation.
- The positive values of enthalpy ensure endothermic reaction. The positive entropy of activation indicates that the activated state is more disordered.

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