Temperature dependent dielectric relaxation studies of halopropane from 10 Mhz to 50 Ghz using a time domain reflectometry (TDR)

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Temperature dependent dielectric relaxation study of halopropane (1-Chloropropane, 1-Bromopropane, 1-Iodopropane) have been carried out in the frequency 10 MHz to 50 GHz using Time domain reflectometry technique. The complex permittivity spectrum has been fitted with single Debye relaxation spectral function. Non-linear square fit method has been used to obtain dielectric parameters such as static dielectric constant (ε_0), relaxation time (τ), Kirkwood Correlation factor (g) and thermodynamic parameters viz. Entropy and enthalpy. The observed properties of Kirkwood correlation and thermodynamic parameters significantly confirm the intermolecular association and hydrogen bonding in halopropanes.

Introduction

Alkyl halides are also called haloalkanes or halogenoalkanes are chemical compounds that are often derived from alkanes that contain one or more halogens. Alkyl halide or haloalkanes are formed by the replacement of hydrogen atoms in an aliphatic hydrocarbon by halogen atoms (Chlorine, Bromine or Iodine). Halopropane plays important role in many chemical reactions. They are clear, colorless, noninflammable liquid which has been found to be clinically useful. In particular, 1-Chloropropane (CLP) is used in organic synthesis, pesticide, pharmaceutical industries. 1-Bromopropane (BMP) was originally used in the production of pesticides, flavors and fragrances.1-Iodopropane (IDP) is used in wide range of medicals industrial applications as well as in human and animal nutrition products, pharmaceutical intermediates, polarizing films for Liquid Crystal Display (LCD) chemicals. Experiences on man and animals indicated that the halopropanes are capable of producing adequate surgical relaxation and reasonably prompt induction and recovery[1].

Dielectric relaxation studies have been carried out for haloalkanes[2-6] to understand inter and intra molecular interactions in the liquid. The aim of present study is to shed light on comparing the influence of the different polar groups in halopropanes and their dielectric relxation parameters like the complex dielectric permittivity spectra, static dielectric constant, relaxation time which was not done previously using a time domain reflectometry (TDR) technique which gives better results in a single measurement.

Experimental Details

Materials

In existing exploration, the liquids CLP ($CH_3CH_2CH_2Cl$, purity 98%), BMP ($CH_3CH_2CH_2Br$, purity 98%) were procured from Merck Life Sciences Pvt. Ltd. Mumbai and IDP ($CH_3CH_2CH_2I$, purity 99%) procured from Sigma Aldrich and used without purification.

The Tektronix Digital Serial Analyzer model no. DSA8300 sampling mainframe along with the sampling module 80E10B has been used for TDR. A sampling module provides 12ps incident and 15ps reflected rise time pulse was fed through a coaxial line system having 50 ohm impedance. Sampling oscilloscope monitors change in step pulse after reflection from the end of line. The reflected pulse without sample $R_1(t)$ and with sample $R_x(t)$ were recorded in the time window of 5ns and digitized in 2000 points. The Fourier transform of the pulse and data analysis was performed to determine complex permittivity spectra $\varepsilon^*(\omega)$ using least square fit method[7].

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Result and discussion

An example of frequency dependence complex permittivity spectra for CLP, BMP and IDP are shown in Fig. 1. Complex permittivity $\varepsilon^*(\omega)$ data were fitted by the non-linear least square fit method to the Harviliak-Negami expression[8].

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

where ε_0 is the static dielectric constant, ε_∞ is the permittivity at high frequency, τ is the dielectric relaxation time, α and β are the fitting parameters.

It can be noticed that the real part of the complex permittivity (ε') decreases with rise in frequency for all halpropanes. The higher values of ε' at lower frequencies may be due to the contribution polarization[8]. The decrease of ε' with increasing frequency means, the response of the permanent dipoles decreases as the frequency increases as well as the contribution of the charge carriers decreases. It can be asserted that the response of permanent dipoles and contribution of charge carriers in halopropanes is established in the order of BMP > CLP >IDP. It is observed that the (ε'') value strongly relies on the frequency of the applied field. Dielectric loss peak is a sign of internal motions, which involve the reorientation of electric dipoles. The dielectric loss of ε'' approaches maximum in the frequency range 25 GHz to 30 GHz for 1-Chloropropane, 20 GHz to 25 GHz for 1-Bromopropane and 10 GHz to 20 GHz for 1-Iodopropane.

The static dielectric constant mainly depends on composition, structure of the material, intermolecular hydrogen bonding and temperature. The temperature dependent study of halopropanes shows that there is decrease in dielectric constant with increase in temperature as shown in Fig. 2. The decrease of dielectric constant with increasing temperature for all halopropanes is due to increase of thermal oscillation of the molecules & increase in degree of disorder of dipoles.

The temperature dependent study of halopropanes shows that there is decrease in relaxation time with increase in temperature as shown in Fig. 3. The dielectric relaxation suggests the change of electric polarization under application of an electric field to sample[9]. The temperature dependent relaxation time values of halopropanes have been established in the order of IDP > BMP > CLP. Decrease in relaxation time with increase in temperature may be due to faster reorientation of molecules and rate of loss of energy
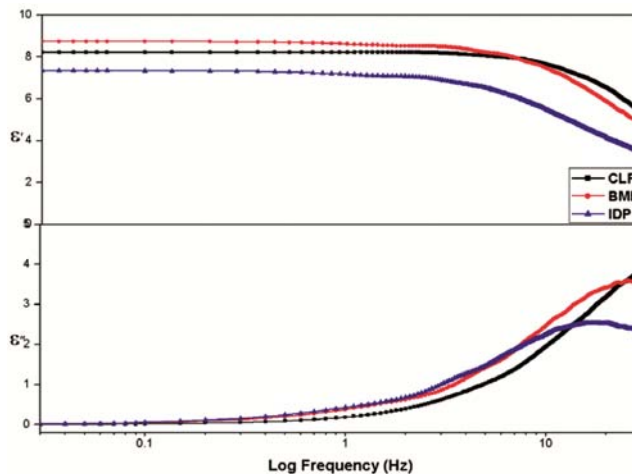

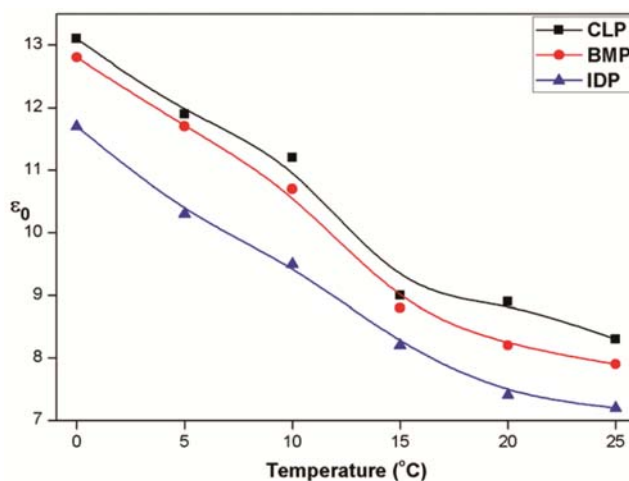Fig. 1 — Complex permittivity spectra for halopropane at 25 °C

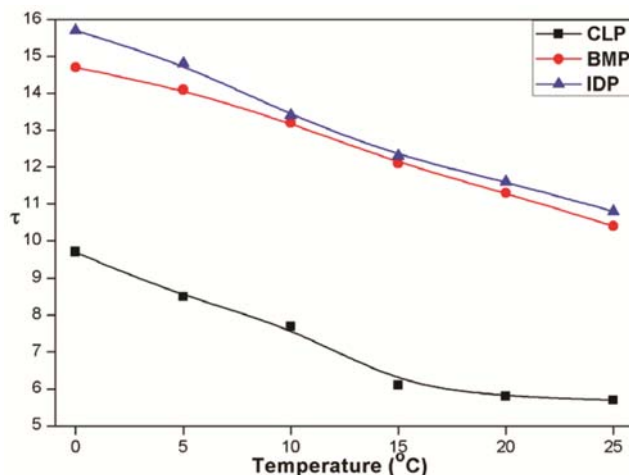Fig. 2 — Plot of static dielectric constant Vs temperature

Fig. 3 — Relaxation time (τ) Vs temperature of halopropane

increases due to large number of collisions. This effect may be due to decrease of hindrance and subsequently increase in molecular reorientation for halopropanes molecules with increase in temperature. Supplementary cause for decrease in relaxation time may be an increase in the effective length of the dipole with increase in temperature.

The Kirkwood-Frohlich equation for pure liquid gives the useful information regarding orientation of electric dipole. The departure of 'g' value from unity is measure of degree of short range dipole ordering due to hydrogen bond interactions. It can be represented as[10]

$$\frac{(\varepsilon\epsilon_0 - \epsilon\varepsilon_\infty)(2\epsilon\varepsilon_0 + \epsilon\varepsilon_\infty)}{\varepsilon\epsilon_0(\epsilon\varepsilon_\infty + 2)^2} = g\mu^2 \frac{4\pi N\rho}{9kTM} \qquad \dots (2)$$

where, μ is the dipole moment, ρ is the density, M is the molecular weight, k is the Boltzmann constant, N is Avogadro's number, ε_0 and ε_∞ are the static dielectric constant and dielectric constant at high frequency, respectively and g is the Kirkwood correlation factor. It is observed that halopropanes (CLP, BMP, IDP) shows anti-parallel alignment of dipoles at room temperature. It can be seen from Fig 4 that the Kirkwood correlation factor 'g' of IDP is lower than CLP and BMP suggest that the hindrance due to intermolecular association in IDP molecules is significantly low in comparison to the intermolecular hindrance in CLP and BMP molecules.

Eyring was the first who explained the dielectric relaxation to the chemical rate theory. According to this theory the following relation was carried out for thermodynamic calculations11-15.
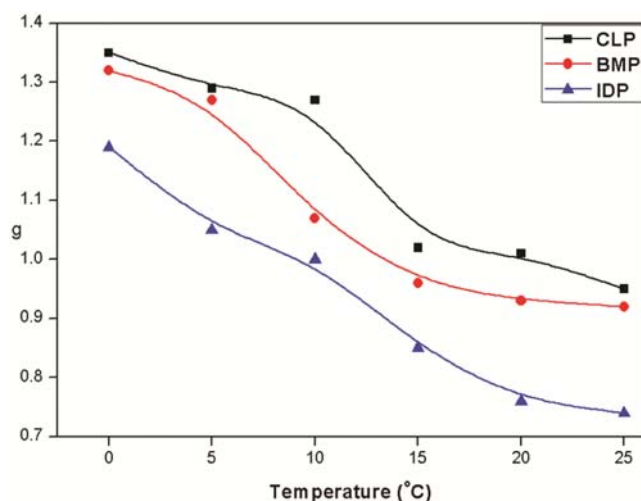
$$\tau = \left(\frac{h}{kT}\right) exp\left(\frac{\Delta H}{RT}\right) exp\left(\frac{-\Delta S}{R}\right) \qquad \dots (3)$$

where, ΔS is the entropy of activation, ΔH is the enthalpy of activation energy in kJ/mole, τ is the relaxation time in ps and T is the temperature in Kelvin, k is the Boltzmann's constant and h is Plank's constant.

The temperature dependence of relaxation time for Halopropanes is described by Arrhenius behavior ($Log(T*\tau)$ Vs. $1000/Temp$ (k) is shown in Fig. 5.

The enthalpy and entropy for pure halopropanes were estimated and values are reported in Table 1.

All positive values of ΔH proposes endothermic interaction and heat is absorbed. The energy is absorbed due to formation of H- bonds. The enthalpy values of halopropanes have been established in the order of CLP > BMP > IDP. In order to achieve group dipole reorientation in the primary relaxation process i.e. to overcome potential barrier, CLP needs more energy than BMP and IDP. Thus, it can be predicted that the bond formation in CLP is stronger than BMP and IDP.

The entropy (ΔS)of a system is a measure of its orderly nature. If the environment of the system is cooperative for a particular process, the activated system becomes more ordered than the normal system and the change in entropy is negative. On the other hand, positive values of entropy indicate that the
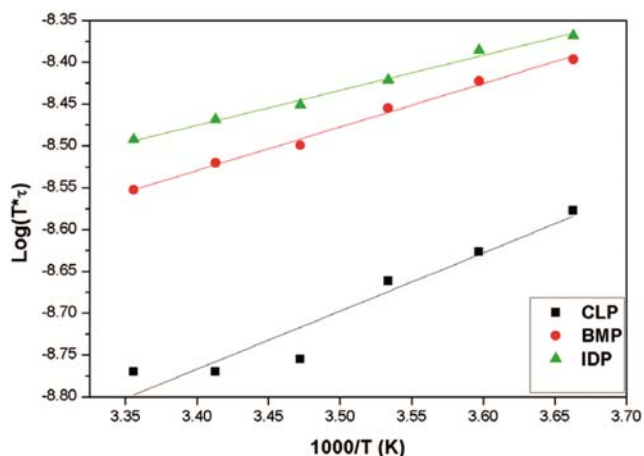

Fig. 5 — Arrhenius behavior of halopropanes

Table 1 — Thermodynamic parameters for Halopropanes

Solute/Solvent	Enthalpy $\Delta H(KJ\ mol^{-1})$	Entropy $\Delta S(J\ mol^{-1}\ K^{-1})$
CLP	11.0	0.237
BMP	9.37	0.226
IDP	7.44	0.221

Fig. 4 — Kirkwood Correlation factor of halopropanes

environment is not cooperative for the system and the activated system becomes less ordered than normal one[16]. Entropies for CLP, BMP and IDP are found to be positive indicating that the systems are less ordered than the normal one.

Conclusions

The complex permittivity spectra of haloprpanes have been studied using TDR in the frequency range of 10 MHz to 50 GHz. It is observed that the pure halopropanes obeys Debye Model. The temperature dependent study of halopropanes shows that there is decrease in static dielectric constant and relaxation time with increase in temperature. The values of Kirkwood correlation factors at room temperature for halopropanes (CLP, BMP and IDP) are less than unity suggests antiparallel alignment of dipoles whereas at low temperature of dipole in the liquid shows parallel alignments. Thermodynamic parameters show the endothermic process and less ordered nature in the system. In this study the calculations for halopropanes are discussed in detail to reveal the effect produced due to the Cl, Br and I group positions attached to the primary Carbon atom.

Acknowledgement

References

1   Stephen C R & North W C, Halopropane-A Clinical evaluation. Anesthesiology, 25 (1964): 600.
2   Durig J R, Zhu X & Shen S, *J Mol struc*, 570 (2001) 1.
3   Kunihiro kasezawa & minoru Kato, *J Phys Chem B*, 113 (2009) 8607.
4   Kato M &Taniguchi Y, *J Chem Phys*, 93(1990) 4345.
5   Melendez-Pagan Y, Taylor B E, Ben-Amotz D, *J Phys Chem B*, 105 (2001) 520.
6   Muñoz Embid José 1 , Fornies-Marquina José , Santos Otin, Bulletin of Chemical Society of Japan 62(1989) 4006.
7   Hasted J, *Aqueous dielectrics*, Chapman and Hall: London (1973). DOI: https://doi.org/10.1002/jobm.19760160714
8   Mehrotra S C, Kumbharkhane A C, Chaudhari A, *Elsevier* (2017) 1.
9   Kao K C, *Dielect Phenom in Solids*, (2004), 41. doi:10.1016/ b978-012396561-5/50012-8
10   Kirkwood J G, *J Chem Phys*, (1939) 7, 911-919
11   Sengwa R J, Khatri Vinita & Sankhla Sonu, *J Solution Chem*, 38(2009) 763.
12   Glasstone S, Laider K J & Eyring H, The Theory of Rate Processes, McGraw Hill, New York, 1941.
13   Hill N E, Vaughan W E, Price A H & Davies M, Dielectric Properties and Molecular Behavior, Van Nostrand Reinhold, Co., London, 1969.
14   Zeberg-Mikkelsen C K & Andersen S I, *J Chem Eng Data*, 50 (2005) 52.
15   Karthick N K, Arivazhagan G, Kumbharkhane A C, Joshi Y S & Kannan P P, *J Mol Structure*, 1108 (2015) 203.
16   Carey F A, Sundberg R J, Advan Org Chem-Part A: Structure and Mechanisms, 3rd ed., Plenum Press, New York, 1990.
17   Chiodelli A & Magistris A, *Solid State Ionics*, 356 (1986) 18.