Dielectric relaxation properties of aqueous dimethylamine, trimethylamine and ethylamine using time domain reflectometry technique

A R Deshmukh[a], S A Ingole[a], R V Shinde[b], M P Lokhande[c] & A C Kumbharkhane[a*]

[a]School of Physical Sciences, Swami Ramanand Teerth Marathwada University, Nanded 431 606, India

[b]College of Agriculture Engineering and Technology, VNMKV, Parbhani 431 402, India

[c]Department of Physics, Government Vidarbha Institute of Science & Humanities, Amravati 444 604, India

The complex permittivity spectra of dimethylamine (40 wt. % in water), trimethylamine (30 wt. % in water) and ethylamine (70 wt. % in water) have been obtained at different temperature using time domain reflectometry technique in the frequency range of 10 MHz-50 GHz. The relaxation mechanism for these systems is described by using Cole-Davidson model. The temperature dependant dielectric relaxation parameters such as static dielectric constant (ε_0), relaxation time (τ) and distribution parameter (β) have been obtained by using non-linear least square fit method. The extracted static dielectric constant (ε_0) and relaxation time (τ) values have been used to calculate thermodynamic parameter and Kirkwood correlation factor (g^{eff}). The enthalpy of activation $\Delta_{act}H$ suggests that chemical kinetic is exothermic. Entropy of activation $\Delta_{act}S$ suggests that the system is less ordered and Gibbs free energy of activation $\Delta_{act}G$ reveals the molecular reorientation for all the three systems. Kirkwood factor for DMA40, TMA30 and EA70 is greater than unity which confirms the hydrogen bond interaction and parallel orientation of dipoles in molecules.

Keywords: Time domain reflectometry, Complex permittivity, Dielectric relaxation, Thermodynamic parameter, Kirkwood factor

1 Introduction

Amines have structure resembling of ammonia where one or more hydrogen atoms are replaced by alkyl or other group. The basic building block of amines are neutral (NH_2) or charged ($-NH_3^+$) group found in many biological systems[1-3]. Moreover, it has many industrial and commercial uses. The presence of NH_2 group in amine plays an effective role in the inter-molecular hydrogen bonding. The strength of this hydrogen bond gets reduced from primary to tertiary amine due to reduction in the number of hydrogen atoms attached to nitrogen. For this reason, we are interested to perform its dielectric relaxation study. The lower aliphatic amines such as methylamine, dimethylamine, trimethylamine and ethylamine amines were found in gas phase at standard atmospheric condition due to its lower boiling points. The literature survey shows the hydrogen bonding for such gas phase amines was well studied[4-6]. Also the previous experimental interpretation on amines gives an enlightenment regarding relaxation time and solute solvent interactions[7-10]. The radical study of aqueous amines with electron spin resonance has been reported earlier[11].

There are various spectroscopic techniques such as neutron scattering, nuclear magnetic resonance (NMR) and broadband dielectric spectroscopy which give the structural and dynamical information about the system under test[7-12]. In dielectric spectroscopy, the time domain reflectometry (TDR) technique has its own importance for study the materials, especially liquid systems. It gives knowledge about variation of permittivity as a function of frequency in microwave region along with the dipolar arrangement and hydrogen bonding in the liquid system.

The aim of present paper is to understand the structural and dynamical behavior of amines such as dimethylamine (40 wt. % in water), trimethylamine (30 wt. % in water) and ethylamine (70 wt. % in water). We performed the dielectric permittivity measurements by using time domain reflectometry (TDR) in frequency range 10 MHz to 50 GHz at different temperatures. The dielectric parameters such as static dielectric constant, relaxation time, thermodynamic parameter and Kirkwood correlation factor have also been discussed using nonlinear least square fit method.

2 Experimental Details

2.1 Materials

The raw chemicals of all three amines, i.e., dimethylamine (40 wt. % in water) (DMA40),

---

trimethylamine (30 wt. % in water) (TMA30) and ethylamine (70 wt. % in water) (EA70) were readily purchased from SDFC Limited and used without any further purification.

2.2 Measurements

The block diagram for experimental setup of TDR is shown in Fig. 1. 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 12 ps incident and 15 ps 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 5 ns 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 as described earlier[13, 14].

3 Results and Discussion

3.1 Complex permittivity

Figure 2(a - d) respectively shows the frequency dependant complex permittivity spectra for DMA40, TMA30, EA70 and water from 25 °C to 5 °C. From
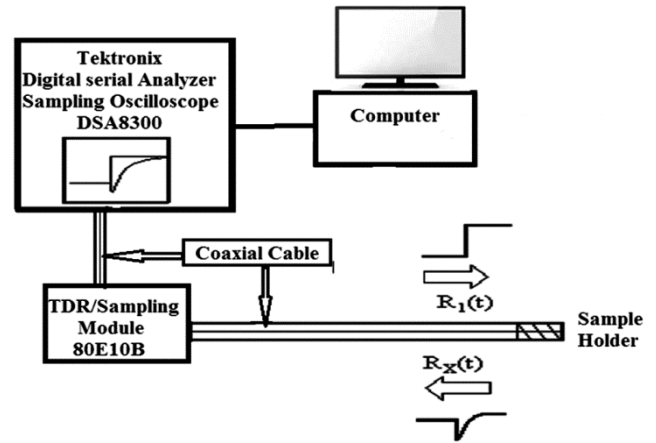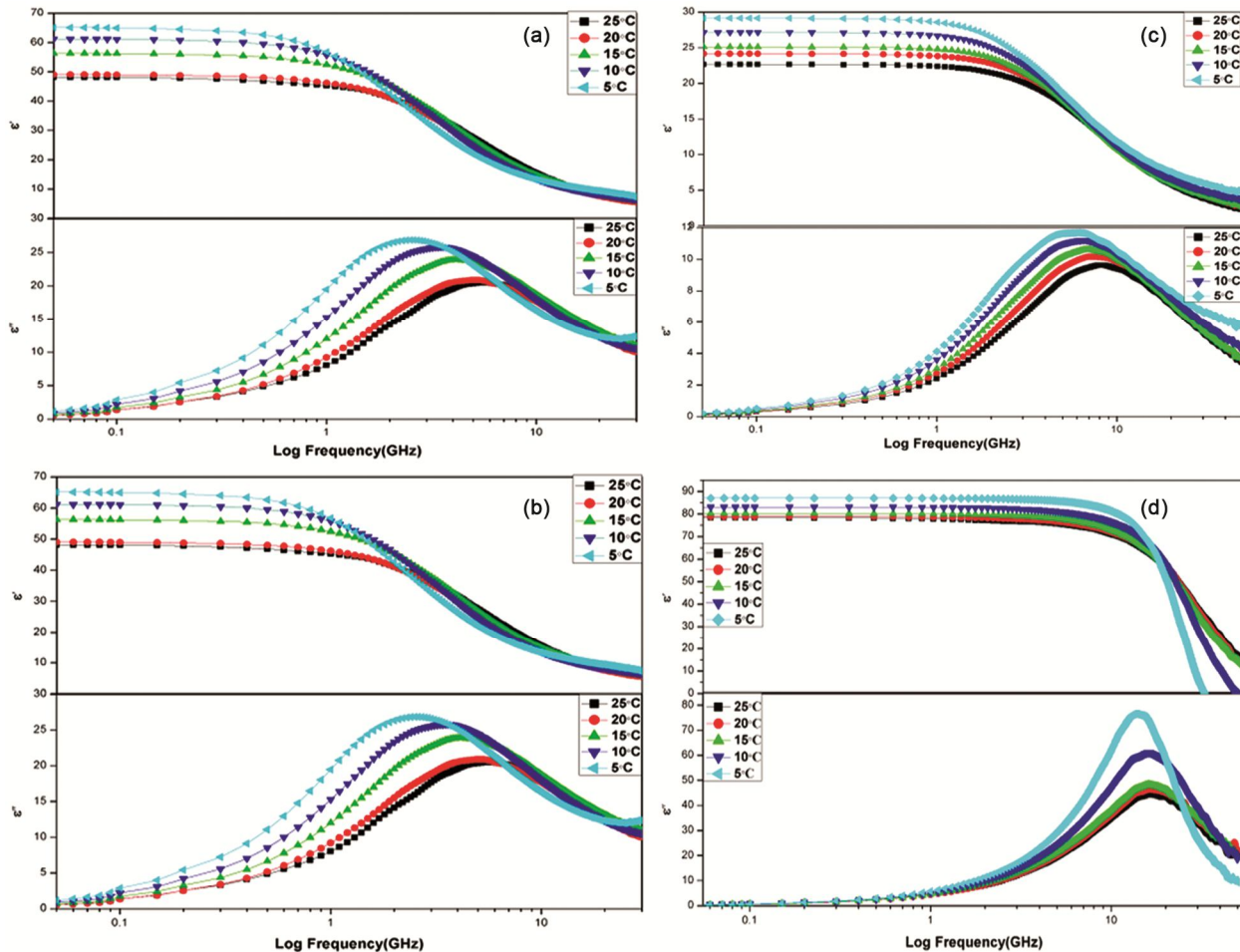

Fig. 1— TDR block diagram.

Fig. 2 — Complex dielectric spectra for (a) DMA40, (b) TMA30, (c) EA70 and (d) Water at different temperatures.

Fig. 2 it has been observed that value of permittivity (ε') and loss (ε'') decrease in high frequency region. The effect of temperature change reflects in complex permittivity spectra which show increasing permittivity and loss with decreasing temperature for all the systems. In addition, the loss peak shifted toward the lower frequency side with decreasing temperature marks the increase in relaxation time, which may happen due to increase in viscosity and decreasing inter-molecular distance between molecules.

The complex permittivity spectrum for DMA40, TMA30 and EA70 shows asymmetric Cole-Davidson type relaxation process and has been fitted using nonlinear least squares fit method[15]:

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

where, ε_0 is the static dielectric constant, ε_∞ is permittivity at high frequency, ω is frequency, τ is relaxation time and β is empirical parameter for distribution of relaxation times having value in between 0 and 1. The values of dielectric parameters (ε_0, ε_∞, τ and β) are determined using least squares fit method which is reported in Table 1. It is interesting to note from Table 1 that, the relaxation parameter β decreases with decreasing temperature; a cause behind this mechanism is increasing asymmetric distribution of relaxation time along the molecules with decreasing temperature.

It is observed from Figs 3 and 4 that the static dielectric constant and dielectric relaxation time decrease as temperature increases for all systems. There are two reasons for this phenomena (i) rapid fall in orientation polarization, because increased thermal agitation reduces well ordering of dipoles (ii) decrease in H-bond strength and size of complex system with increasing temperature[16, 17].

3.2 Thermodynamic properties

The thermodynamic parameters like $\Delta_{act}H$, $\Delta_{act}S$ and $\Delta_{act}G$ have been obtained from Eyring's rate equation[18]:

$$\tau = (\ /kT)exp(\Delta_{act}H/RT)exp(-\Delta_{act}S/R) \ ... (2)$$

and

$$\Delta_{act}G = \Delta_{act}H - T\Delta_{act}S \qquad ... (3)$$

where, $\Delta_{act}H$ is enthalpy of activation in kJ/mol, $\Delta_{act}S$ is the entropy of activation in J/mol/K and $\Delta_{act}G$ is the Gibbs free energy of activation in kJ mol^{-1}. The values of these parameters are reported in Table 2. The molecular relaxation time depends on many

factors such as chain length of molecule, viscosity, temperature; etc[19, 20]. The positive values of activation energy $\Delta_{act}H$ reveal that heat was released in molecular reorientation process. The positive values of entropy of activation indicate that system

Table 1 — Dielectric relaxation parameters for Amines at different temperatures.

Temp.	ε_0	τ(ps)	β
DMA40			
25°C	46.32(6)	33.25(8)	0.909(1)
20°C	48.48(9)	35.62(14)	0.886(1)
15°C	52.90(15)	41.72(27)	0.861(3)
10°C	58.13(25)	53.40(54)	0.831(3)
5°C	62.74(41)	66.24(111)	0.779(4)
TMA30			
25°C	48.29(4)	27.65(4)	0.917(1)
20°C	49.60(5)	30.78(6)	0.908(1)
15°C	57.44(9)	35.71(11)	0.889(1)
10°C	62.94(14)	44.14(21)	0.870(1)
5°C	68.18(27)	56.76(54)	0.822(2)
EA70			
25°C	22.80(1)	18.73(2)	0.969(1)
20°C	24.50(2)	18.78(3)	0.960(1)
15°C	25.61(1)	21.61(4)	0.922(1)
10°C	27.97(4)	23.22(7)	0.888(1)
5°C	30.46(7)	24.49(13)	0.847(1)
Water			
25°C	79.03(8)	8.74(3)	1.000
20°C	80.08(10)	8.91(4)	1.000
15°C	81.68(12)	9.30(5)	1.000
10°C	86.75(30)	10.12(11)	1.000
5°C	94.49(62)	11.60(23)	1.000

Numbers given in parentheses denote uncertainties in the least significant digits obtained by the least square fit method, e.g. 46.32(6) means 46.32 ± 0.06 and 0.909(1) means 0.909 ± 0.001.
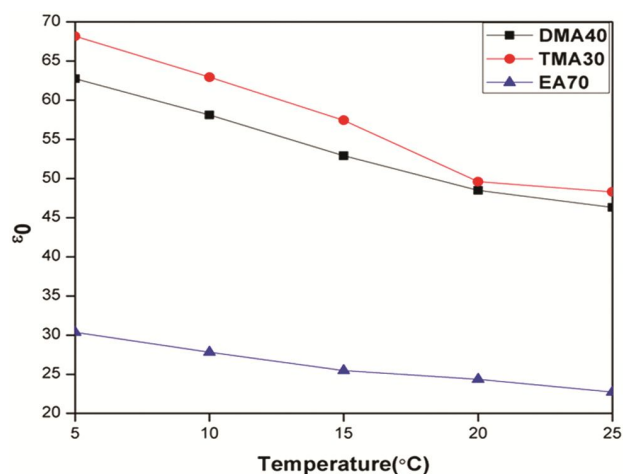

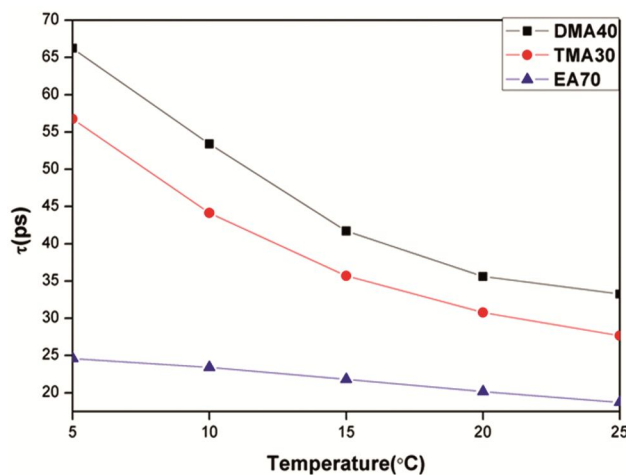Fig. 3 — Static dielectric constant for DMA40, TMA30 and EA70 at different temperatures.

Fig. 4 — Relaxation time for DMA40, TMA30 and EA70 at different temperatures.

Fig. 5 — Arrhenius plot for DMA40, TMA30 and EA70.

Table 2 — Thermodynamic parameters for Amines.

System	$\Delta_{act}H(kJ\ mol^{-1})$	$\Delta_{act}S(J\ mol^{-1}\ K^{-1})$	$\Delta_{act}G(kJ\ mol^{-1})$
DMA40	22.25(25)	0.260(8)	3.19
TMA30	22.46(20)	0.262(7)	3.09
EA70	7.16(5)	0.214(1)	2.77
Water[21]	7.22(17)	0.221(6)	2.32

Numbers given in parentheses denote uncertainties in the least significant digits, e.g. 22.25 (25) means 22.25 ± 0.25 and 0.260(8) means 0.260 ± 0.008.

environment is less ordered than normal system. The average Gibbs free energy of activation was found to be 3.19, 3.09 and 2.77 kJ/mol for DMA40, TMA30 and EA70 respectively in the temperature range 25-5 °C. The reported values suggest the molecular reorientation in the liquid state. The temperature dependant relaxation time behavior is described by Arrhenius plot as shown in Fig. 5.

3.3 Kirkwood factor

The Kirkwood Frohlich equation provides useful information regarding the orientation correlation of dipoles in the case of pure liquids[22]:

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

where ε_0, is the static dielectric constant, ε_∞ is the dielectric constant at high frequency, g is the Kirkwood correlation factor, μ is the dipole moment of liquid, N is the Avogadro number, ρ is the density of liquid and k, T have their usual meanings[23]. The effective Kirkwood correlation factor (g^{eff}) gives information about dipole-dipole interaction in binary mixtures of liquid by the modified Kirkwood correlation equation[24]:
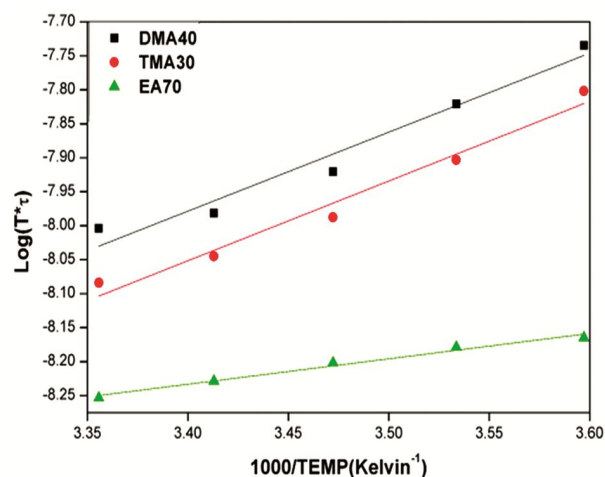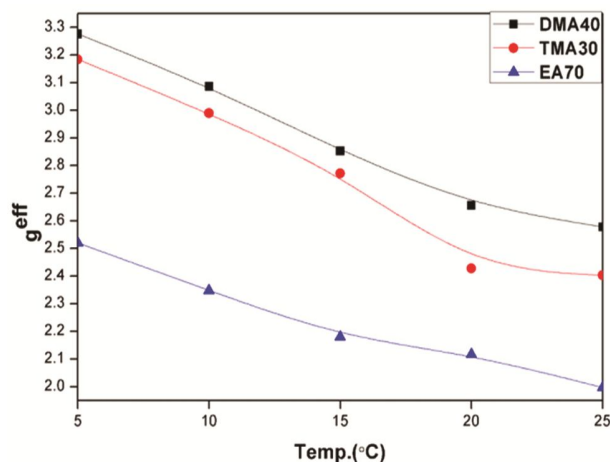

Fig. 6 — Kirkwood correlation factor for DMA40, TMA30 and EA70 at different temperatures.

$$\frac{4\pi N}{9kT}\left[\frac{\mu_w^2 \rho_w}{M_w}V_w + \frac{\mu_A^2 \rho_A}{M_A}(1 - V_w)\right]g^{eff} = \frac{(\varepsilon_{0m} - \varepsilon_{\infty m})(2\varepsilon_{0m} + \varepsilon_{\infty m})}{\varepsilon_{0m}(\varepsilon_{\infty m} + 2)^2} \qquad ... (5)$$

where μ_w, ρ_w, M_w be the dipole moment, density and molecular weight of solvent(water) and μ_A, ρ_A, M_A be the dipole moment, density and molecular weight of solute(DMA, TAM and EA). V_w is the volume fraction of water, N is the Avogadro number, ρ is the density of liquid and k, T has their usual meanings[22]. The departure of g^{eff} from unity measures the extent of inter-molecular hydrogen bonding. For molecule with parallel orientation of dipole g^{eff} will be greater than unity and for anti-parallel orientation of dipole g^{eff} will be less than unity. The experimental values of g^{eff} for DMA40, TMA30, and EA70, are found to be 2.58, 2.40 and 1.99, respectively at 25 °C. These values indicates that the parallel orientation of DMA40, TMA30 and EA70 molecules. From Fig. 6 it has been

observed that as temperature increases value of effective Kirkwood correlation factor decreases which gives the confirmation to decreasing dielectric constant and relaxation time with increasing temperature due to reducing well ordering of dipoles and decreasing H-bond strength.

4 Conclusions

The temperature dependant complex permittivity spectra of DMA40, TMA30, EA70 and water have been studied using TDR technique in the frequency range from 10 MHz to 50 GHz. The dielectric permittivity spectra are well studied by Cole-Davidson model. The hydrogen bonding dynamics is discussed using thermodynamic parameter and Kirkwood factor. The thermodynamic parameter suggests the molecular reorientation process in amines. The Kirkwood factor for DMA40, TMA30 and EA70 is greater than unity which confirms the hydrogen bond interaction and parallel orientation of dipole in system under test.

Acknowledgement

References

1   Gugliucci A, *Clin Chim Acta,* 344 (2004) 23.
2   Casero R A & Marton L J, *Nat Rev Drug Discov,* 6 (2007) 373.
3   Moinard C, Cynober L & Bandt J P, *Clin Nutr,* 24 (2005) 184.
4   Aue D H, Webb H M & Bowers M T,J *Am Chem Soc*, 95:8 (1973) 2699.
5   Tubergen M J & Kuczkowski R L, *J Am Chem Soc*, 115 (1993) 9263.
6   David H, *J Am Chem Soc*, 102 (1980) 5316.
7   Kumar S & Guganathan L, *J Adv Chem Sci*, 2 (2016) 198.
8   Arcega Solsona F J & Fornies-Marquina J M, *J Phys D: Appl Phys*, 15 (1982) 1783.
9   Gilchrist J, *Chem Phys*, 65 (1982) 1.
10 Ramana V V, Kiran Kumar A B V, Ashok Kumar M & Moodley M K, *J Chem*, 2013 (2013) 1.
11 Neta P & Fessenden R W, *J Phys Chem*, 75 (1971) 738.
12 Mel'nichenko Y B, Schüller J, Richer R & Ewen B, *J Chem Phys,* 103 (1995) 2016.
13 Cole R H, Berberian J G, Mashimo S, *J Appl Phys,* 66 (1989) 793.
14 Kumbharkhane A C, Puranik S M & Mehrotra S C, *J Chem Soc Faraday Trans*, 87 (1991) 1569.
15 Davidson D W & Cole R H, *J Chem Phys*, 18 (1950) 1417.
16 Mohan A, Malathi M, Shaikh S S & Kumbharkhane A C, *J Sol Chem*, 45 (2016) 221.
17 Navarkhele V V & Bhanarkar M K, *Molecul Phys*, 107 (2009) 1823.
18 Hill N E, Vaughan W E, Priceand A H & Davies M, *Dielectric properties and molecular behavior*, (Van Nostrand Reinhold Company- London), (1969) 480.
19 Sengwa R J, *Indian J Pure Appl Phys*, 41 (2003) 295.
20 Lide D R, CRC Handbook of Chemistry and Physics (Taylor and Francis- Boca Raton) 87th Edn, (2007) 2388.
21 Chalikwar P A, Deshmukh A R & Kumbharkhane A C, *Phys Chem Liq*, 55 (2017) 410.
22 Mehrotra S C, Kumbharkhane A C & Chaudhari A S, *Binary Polar Liquids: structural and dynamical characterization using spectroscopic methods* (Elsevier- Netherlands) 1st Edn, 2017.
23 Hasted J B, *Aqueous Dielectrics* (Chapman and Hal, London) 1973.
24 Kirkwood J G, *J Chem Phys*, 7 (1939) 911.