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Dielectric and thermodynamic properties in a binary mixture of dimethylene chloride with formamide

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ABSTRACT

The dielectric and thermodynamic properties of dimethylene chloride with formamide have been determined at 10, 15, 20 and 25 °C using time domain reflectometry (TDR) for 11 different concentrations of the system. The dielectric properties viz. static dielectric constant (ε_0) and relaxation time (τ) have been obtained by the least squares fit method with Debye model. The dielectric constant and relaxation time increase with increasing the mole fraction of formamide in dimethylene chloride of the system. The excess inverse relaxation time is found to be negative in the system and excess permittivities are found to be negative in dimethylene chloride and positive in the formamide rich region for all temperatures. The thermodynamic parameters such as free activation energy (ΔG), molar enthalpy of activation (ΔH) and molar entropy of activation (ΔS) have been determined.

1. Introduction

In this work, we report the qualitative study of dielectric and thermodynamic properties in a binary mixture of dimethylene chloride with formamide by using time domain reflectometry technique. The dimethylene chloride (DCM) is a non-associative liquid and formamide (FA) is an associative liquid, one with the chloro-group and other with the C═O group.

The dielectric relaxation study provides useful information regarding solute–solvent interactions in liquid mixtures. The extensive studies have been done to understand these interactions on different types of binary mixtures having different or same molecular groups [1–11]. Recently, the dielectric relaxation study has done the work on the binary mixtures of various liquids such as glycerol-amides and amines [12], N-dimethylethanolamine-alcohols and amides [13], formamide-dipolar solvents [14], ethanolamine-alcohols and amides [15], amides — dimethylsulfoxide and 1,4-dioxane [16], amides — ethyl alcohol and ethylene glycol [17] and formamide–acetamide [18].

The objective of the present work is to report the dielectric and thermodynamic properties in a binary mixture of ($-CH_2$-Cl) functional group of DCM with ($-NH_2$-C═O) functional group of FA. These functional groups are industrially important solvents used in the chemistry, biochemistry, pharmaceutical and material science.

2. Experimental

2.1. Materials

DCM and FA (AR grade, Qualigens Fine Chemicals Pvt. Ltd., Bombay, India) were used without further purification. The solutions were prepared at 11 different volume percentages of DCM from 0% to 100%. Using these volume percents the mole fraction is calculated as

$$x_1 = \left(v_1\rho_{1/}m_1\right) \Big/ \left[\left(v_1\rho_{1/}m_1\right) + \left(v_2\rho_{2/}m_2\right)\right] \quad (1)$$

where m_1, v_1, ρ_1 and m_2, v_2, ρ_2 represent the molecular weight, volume percent and density of liquids 1 and 2, respectively.

2.2. Apparatus

The complex permittivity spectra were studied using time domain reflectometry (TDR) method [19,20] over the frequency range 10 MHz to 30 GHz [21,22]. The basic TDR setup consists of a broadband sampling oscilloscope, TDR module and coaxial transmission line. The Tektronix DSA8200 sampling oscilloscope and TDR module 80E08 with the step generator unit were used. A 200 mV step pulse with 18 ps incident pulse and 20 ps reflected pulse time and 200 kHz repetition rate passes through coaxial 50 Ω lines. All measurements are carried out in open load condition. Sampling oscilloscope monitors changes in step pulse after reflection from the sample. Reflected pulse without sample $R_1(t)$ and with sample $R_X(t)$ was recorded in time window of 5 ns and

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digitized in 2000 points. The temperature of the sample was controlled electronically within ±0.5 °C.

3. Results and discussion

3.1. Dielectric parameters

The experimental values of $\varepsilon^*(\omega)$ are fitted with the Debye equation [23]

$$\varepsilon^*(\omega) = \varepsilon_\infty + \frac{\varepsilon_0 - \varepsilon_\infty}{1 + j\omega\tau} \quad (2)$$

with ε_0 and τ as fitting parameters. A nonlinear least-squares fit method [24] was used to determine the values of dielectric parameters. The value of ε_∞ was taken to be 3 for all the systems studied since for the frequency range considered here, ε^* is not sensitive to ε_∞. The measurements in the frequency range 10 MHz to 30 GHz are interesting because the dielectric dispersion of these molecules occurs in the same frequency range. Figs. 1(a) and 2(a) show the frequency dependence of dielectric dispersion (ε') of pure DCM and pure FA respectively, at various temperatures. Dielectric dispersion decreases with increasing the frequency. In the low frequency region, the dielectric constant is high and in the high frequency region, the dielectric constant is low at all temperatures. The dielectric absorption (ε'') curves for pure DCM and pure FA at various temperatures are depicted in Figs. 1(b) and 2(b) respectively.

The values of static dielectric constant (ε_0), relaxation time (τ) and effective Kirkwood correlation factor (g^{eff}) of pure DCM and FA at 25 °C along with literature values [25–28] are listed in Table 1. The experimental ε_0, τ (ps) and g^{eff} values of this study are in good agreement

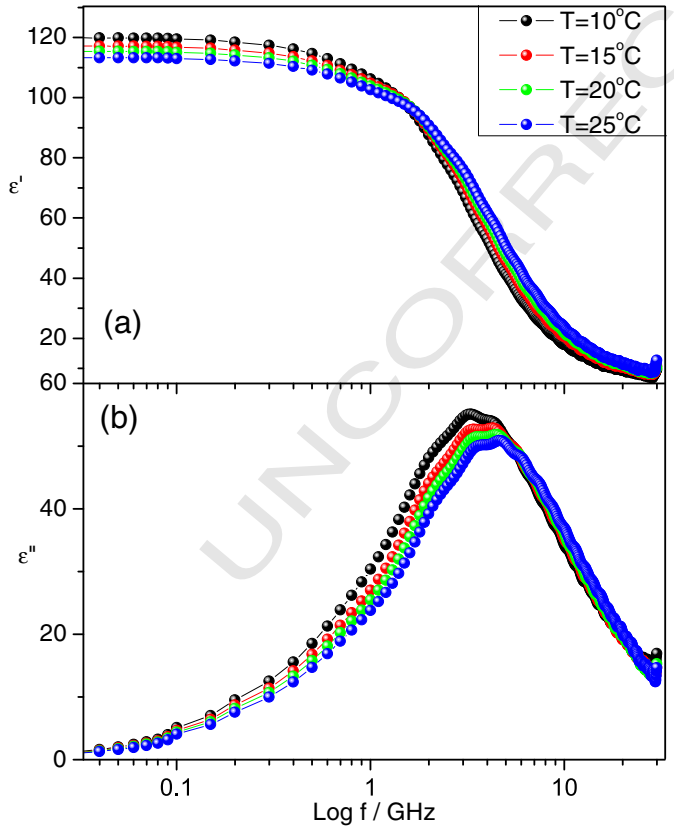

Fig. 1. (a): Frequency dependence of dielectric permittivity (ε') for pure FA at T = 10, 15, 20 and 25 °C. (b): Frequency dependence of dielectric loss (ε'') for pure FA at T = 10, 15, 20 and 25 °C.

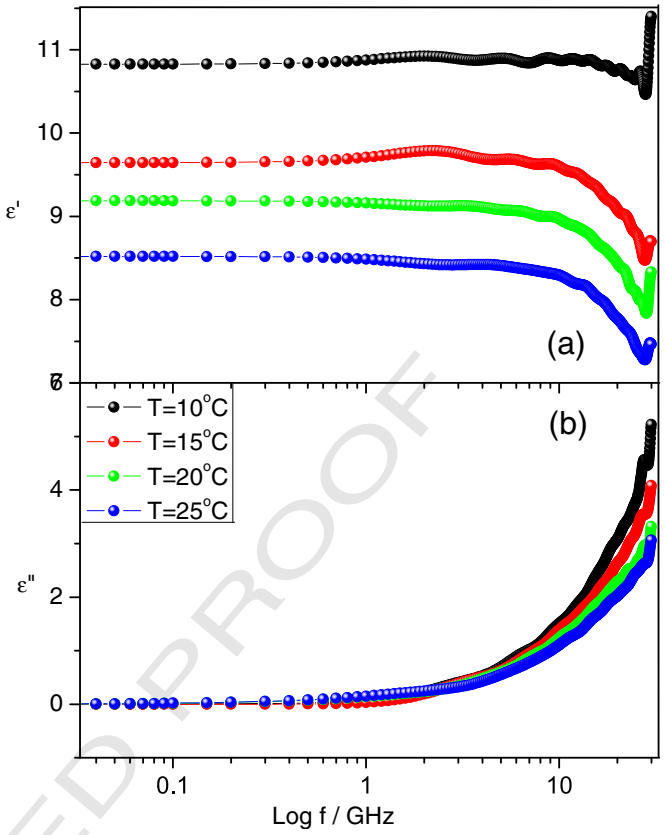

Fig. 2. (a): Frequency dependence of dielectric permittivity (ε') for pure DCM at T = 10, 15, 20 and 25 °C. (b): Frequency dependence of dielectric loss (ε'') for pure DCM at T = 10, 15, 20 and 25 °C.

with the literature values. The values of the static dielectric constant (ε_0) and relaxation time (τ) obtained by fitting experimental data to the Debye equation are presented in Table 2. It is clear from Table 2 that as the concentration of FA increases in DCM mixture the static dielectric constant of a mixture increases. The values of static dielectric constant are rapid and substantially increase at $x_2 = 0.7079$ for all temperatures in the system. Similarly, the values of relaxation time are large in the FA rich region as compared to the DCM rich region for all temperatures. This gives the formation of large structure due to the chain like structure of FA in the mixture. The average values of static dielectric constant and relaxation time for the FA are higher than DCM. The larger values of static dielectric constant and relaxation time of the FA are due to the presence of a C═O group in the molecular structure.

3.2. Excess parameters

The information related to liquids 1 and 2 interaction may be obtained by excess properties [29] related to the permittivity and relaxation

Table 1
Comparison of data for the pure liquids used with literature values at 25 °C.

Liquids	ε_0		τ (ps)		g^{eff}	
	This work	Lit.	This work	Lit.	This work	Lit.
DCM	8.52	8.80[a]	5.71	5.71[a]	0.63	0.64[a]
FA	108.18	109.56[b]	38.10	37.80[c]	1.96	2.09[d] (30 °C)

[a] Ref. [25].
[b] Ref. [26].
[c] Ref. [27].
[d] Ref. [28].