Dielectric relaxation studies of binary mixture of β -picoline and methanol using time domain reflectometry at different temperatures

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Complex permittivity spectra of binary mixtures of varying concentrations of β -picoline and Methanol (MeOH) have been obtained using time domain reflectometry (TDR) technique over frequency range 10 MHz to 25 GHz at 283.15, 288.15, 293.15 and 298.15 K temperatures. The dielectric relaxation parameters namely static permittivity (ϵ_0), high frequency limit permittivity ($\epsilon_{\infty 1}$) and the relaxation time (τ) were determined by fitting complex permittivity data to the single Debye/Cole-Davidson model. Complex nonlinear least square (CNLS) fitting procedure was carried out using LEVMW software. The excess permittivity (ϵ_0^E) and the excess inverse relaxation time $(1/\tau)^E$ which contain information regarding molecular structure and interaction between polar-polar liquids were also determined. From the experimental data, parameters such as effective Kirkwood correlation factor (g^{eff}), Bruggeman factor (f_B) and some thermo dynamical parameters have been calculated. Excess parameters were fitted to the Redlich-Kister polynomial equation. The values of static permittivity and relaxation time increase nonlinearly with increase in the mol-fraction of MeOH at all temperatures. The values of excess static permittivity (ϵ_0^E) and the excess inverse relaxation time $(1/\tau)^E$ are negative for the studied β -picoline — MeOH system at all temperatures.

Keywords: Complex permittivity; relaxation time; time domain reflectometry; CNLS fitting; Redlich-Kister equation; β -picoline.

1. Introduction

Dielectric relaxation studies of polar liquids involve measurements of complex permittivity (dielectric constant and dielectric loss) over a range of frequency and temperature. Measured complex permittivity data can be used to find dielectric relaxation time, distribution parameter, static permittivity and thermodynamical parameters. These parameters provide useful information about the molecular size, shape, inter and intramolecular interactions and molecular structures. Time Domain Reflectometry (TDR) has widely been used by many researchers to measure the complex permittivity of polar liquids and their binary mixtures.¹⁻⁶

Recently we reported results of our study of dielectric relaxation in the binary mixtures of α -picoline and Methanol (MeOH) at different temperatures using Time Domain Reflectometry (TDR) technique.⁷ In continuation of this work, study of dielectric relaxation behavior of binary mixtures of β -picoline and methanol (MeOH) at different temperatures using TDR technique was undertaken and the results are reported in this paper. α -picoline and β -picoline are the isomers of methyl pyridine with formula C_6H_7N . At room temperature they are colorless liquids. They are used

as precursor to pyridine derivatives and have wide range of applications in pharmaceutical and agricultural industries. The other component considered for the binary mixture system is the lower primary alcohol MeOH. Alcohols play an important role in many chemical reactions on account of their ability to undergo self-association with manifold internal structures.⁸ They are widely used in industries and science as reagents, solvents and fuels.

Due to the presence of lone pair of electron on the nitrogen atom site of picoline and proton donor sites in the alcohol molecules an O—H—N type of proton donor-acceptor linkage is expected in the mixtures of picoline and MeOH. Dielectric relaxation parameters of the like and unlike molecules are considerably affected by the H-bond interaction. Thus it is thought that this study will provide a good scope to analyze dielectric data obtained using TDR technique for binary mixture system of β -picoline and MeOH. Not only that but it will also provide information about the molecular interaction taking place between the components of the binary mixture system. Literature survey suggests that very few researchers have studied dielectric behavior of picoline in its pure state or in a mixed state with other

Fig. 1. Block diagram of TDR.

polar/nonpolar solvents, through physical^{9–11} or dielectric methods.^{12,13}

Aim of the present investigation is to work out a relaxation model for describing the broadband complex permittivity spectra $\varepsilon^*(\omega) = \varepsilon'(\omega) - j\varepsilon''(\omega)$ of β -picoline-MeOH mixtures with various compositions over the frequency range 10 MHz to 25 GHz at four different temperatures: 283.15 K, 288.15 K, 293.15 K, 298.15 K and to gain information about the orientational dynamics and molecular interaction among the molecules of the binary liquid mixture system.

2. Experimental Procedure

MeOH (AR grade) and β -picoline (AR grade) with 99% purity were procured from S. d. Fine chem Limited (India). Binary mixtures of β -picoline and MeOH were prepared at nine concentrations by volume at room temperature. Using following formula these concentrations were converted into the mol fraction of MeOH in β -picoline.

$$X_1 = \frac{\rho_1 \times \frac{v_1}{M_1}}{\rho_1 \times \frac{v_1}{M_1} + \rho_2 \times \frac{v_2}{M_2}}, \quad (1)$$

where M is molecular weight, v is volume and ρ is literature value of density. 1 represents MeOH and 2 represent β -picoline. The maximum error in mole fraction is $\pm 0.1\%$.

The complex permittivity spectra of β -picoline, MeOH and their mixtures were obtained by TDR technique. The Tektronics model no. DSA8200 Digital serial analyzer sampling oscilloscope along with the sampling module 80E08 has been used and this module provides accurate oscilloscope measurement with user selectable bandwidth of 20 or 30 GHz. The block diagram and experimental setup of TDR is shown in Fig. 1. The coaxial cable semi rigid, copper, EZ.86/M17 (Huber+ Suhner Electronics pvt. Ltd.) with flat end was used. The outer diameter of cable is 2.2 mm. Sampling

oscilloscope monitors changes in step pulse after reflection from the end of line. Reflected pulse without sample $R_1(t)$ and with sample $R_X(t)$ were recorded in time window of 2 ns and digitized in 2000 points in the memory of the oscilloscope and transferred to the computer. These recorded pulses are added [$q(t) = R_1(t) + R_X(t)$] and subtracted [$p(t) = R_1(t) - R_X(t)$]. Further the Fourier transformation of $p(t)$ and $q(t)$ was obtained by Shannon¹⁴ and Samulon¹⁵ methods respectively, for the frequency range 10 MHz to 25 GHz.

Figure 2 shows the complex permittivity spectra of β -picoline, MeOH and their mixtures at 283.15 K temperature, which shows a systematic variation of ε' and ε'' with frequency. Permittivity at optical frequency, ε_∞ for pure liquids and $\varepsilon_{\infty m}$ for the binary mixtures were taken as square of the refractive index, n_D , which was measured with an Abbe refractometer at wavelength of sodium-D light. The standard uncertainty of measurement of the refractometer is 0.001%.

Fig. 2. Complex permittivity spectra [$\varepsilon^*(\omega) = \varepsilon'(\omega) - j\varepsilon''(\omega)$] for β -picoline + MeOH at 283.15 K.

3. Data Analysis

The dielectric constant and loss were initially plotted in complex plane. Spectra for the samples were found to display a single dispersion in the considered frequency range. It was observed that the first dispersion encountered was quantitatively described by a semicircle with intercepts on the real axis at $\varepsilon' = \varepsilon_0$ and $\varepsilon' = \varepsilon_{\infty 1}$, representing the limiting low and high frequency permittivity for this dispersion. The choice of the relaxation model depends on the frequency range of measurement and on the quality of the data.¹⁶ Since the complex permittivity measurements in the present study are in the frequency range of 10 MHz–25 GHz, we have applied Cole–Davidson/Debye function,^{17,18}

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

to obtain relaxation parameters for the main relaxation process. In this equation, ε_0 and $\varepsilon_{\infty 1}$ represent the limiting low and high frequency permittivity, τ is the relaxation time due to main relaxation process and β is the asymmetric distribution parameter. Equation (2) reaches to Debye function when β equals to one. CNLS (Complex Non linear Least Square) fitting procedure was carried out using LEVMW.¹⁹ CNLS fitting takes both the real and imaginary parts of the complex permittivity into the objective function simultaneously to ensure the complete fit.²⁰

The Kirkwood correlation factor (g) is a parameter that supplies information regarding the orientation of the electric dipoles in polar liquids. For pure liquids it is given by^{21,22}

$$\frac{4\pi N_A \mu^2 d}{9kTM} g = \frac{(\varepsilon_0 - \varepsilon_{\infty})(2\varepsilon_0 - \varepsilon_{\infty})}{\varepsilon_0(\varepsilon_{\infty} + 2)^2}, \quad (3)$$

where ρ is the density of liquid, M is the molecular weight, k is the Boltzmann constant, N is the Avogadro's number and μ is the dipole moment of polar molecule in gas phase. ε_{∞} is taken as square of the refractive index.

For the mixtures of two polar liquids the effective averaged angular Kirkwood correlation factor (g^{eff}) of two different molecules were evaluated from the modified Kirkwood equation for the binary mixture^{21,22}

$$\begin{aligned} \frac{4\pi N}{9kT} \left(\frac{\mu_1^2 d_1}{M_1} x_1 + \frac{\mu_2^2 d_2}{M_2} x_2 \right) g^{\text{eff}} \\ = \frac{(\varepsilon_m - \varepsilon_{\infty m})(2\varepsilon_m - \varepsilon_{\infty m})}{\varepsilon_m(\varepsilon_{\infty m} + 2)^2}, \end{aligned} \quad (4)$$

where X is the mole fraction of the liquid and subscripts m , 1 and 2 represent the mixture, MeOH and β -Picoline respectively. ε_m is the static permittivity of the mixture, $\varepsilon_{\infty m}$ is the permittivity at optical frequency of the mixtures.

Excess static permittivity (ε_0^E) was calculated using the relation²³,

$$\varepsilon_0^E = \varepsilon_{0m} - (\varepsilon_1 X_1 + \varepsilon_2 X_2). \quad (5)$$

Here ε_1 , ε_2 are relative permittivity and x_1 and x_2 are mole fractions of components 1 and 2, respectively, and ε_m is the static permittivity of mixture.

Excess inverse relaxation time of $(\frac{1}{\tau})^E$ was calculated using the relation,²⁴

$$\left(\frac{1}{\tau}\right)^E = \left(\frac{1}{\tau}\right)_m - \left[\left(\frac{1}{\tau}\right)_1 X_1 + \left(\frac{1}{\tau}\right)_2 X_2\right], \quad (6)$$

where, $(\frac{1}{\tau})_m$ is inverse relaxation time of mixture, and $(\frac{1}{\tau})_1$ and $(\frac{1}{\tau})_2$ are inverse relaxation time of components 1 and 2.

The hetero (A–B) interaction between the components of the mixture can also be obtained from the Bruggeman equation.^{25,26} The Bruggeman factor f_B is related to the volume fraction of one of the components as:

$$f_B = \left(\frac{\varepsilon_m - \varepsilon_2}{\varepsilon_1 - \varepsilon_2}\right) \left(\frac{\varepsilon_1}{\varepsilon_m}\right)^{\frac{1}{3}} = (1 - \phi_2). \quad (7)$$

f_B may vary from one to zero as ϕ_2 varies from zero to one. If there is no interaction between the components in the mixture, then f_B should have a linear relationship with ϕ_2 . If there is interaction between the components in the mixture, then Eq. (7) is modified as

$$\left(\frac{\varepsilon_m - \varepsilon_2}{\varepsilon_1 - \varepsilon_2}\right) \left(\frac{\varepsilon_1}{\varepsilon_m}\right)^{\frac{1}{3}} = 1 - [a - (a - 1)\phi_2]\phi_2, \quad (8)$$

where 'a' is the Bruggeman parameter, which gives valuable information about heterogeneous interaction between the molecules. Using least square fitting method, the value of 'a' was determined. It is assumed that the volume fraction of the solute in the mixture is modified by a factor of $[a - (a - 1)\phi_2]\phi_2$.

The energy parameters for dielectric relaxation process (ΔF_E , ΔH_E and ΔS_E) have been evaluated employing Eyring's equation,²⁷

$$\tau = \frac{h}{kT} \exp\left(\frac{\Delta F_E}{RT}\right), \quad (9)$$

$$\Delta F_E = \Delta H_E - T\Delta S_E, \quad (10)$$

where h is plank's constant, k is Boltzmann constant, R is the gas constant, T is temperature, ΔF_E is the molar free energy of activation, ΔH_E is the molar free enthalpy of activation and ΔS_E is the molar free entropy of activation for dielectric relaxation.

The variations of, excess static permittivity and excess inverse relaxation time with composition are expressed by Redlich–Kister²⁸ polynomial equation,

$$Q = x_1 x_2 \sum_{r=0}^n a_r (x_2 - x_1)^r, \quad (11)$$

where Q refers all excess parameters.

The standard deviations $\sigma(Q)$ were defined as

$$\sigma(Q) = \left| \frac{\Phi_{\min}}{P - n} \right|^{0.5}, \quad (12)$$

where P and n are the experimental points and parameters, respectively. $\Phi_{\min}$ is the minimum value of the objective function Φ defined as,

$$\Phi = \sum_{k=1}^N (n_k)^2, \quad (13)$$

where $n_k = Q_{\text{cal}} - Q$ is the experimental value and Q_{cal} is evaluated using Eq. (11).

4. Results and Discussion

Typical complex plane plots for pure β -picoline, MeOH and their binary mixtures of 30–70%, 50–50% and 40–60% concentrations at 288.15 K temperature are shown in Fig. 3. From the Figure, it can be seen that all the spectra display a single dispersion due to main relaxation process in the considered frequency range. The plot of β -picoline exhibits the principle dispersion of Debye type, whereas its mixture with MeOH and pure MeOH exhibit Cole–Davidson (C–D) type of relaxation behavior. Therefore we have determined dispersion parameters for β -picoline using Debye function, and for MeOH and its mixture with β -picoline at all the concentrations using C–D function. Complex plane plots of α -picoline–MeOH mixtures exhibited similar behavior.⁷

Static permittivity values obtained using the fitting procedures are plotted as a function of mole fraction of MeOH in Fig. 4. As can be seen from Fig. 4, with increasing fraction of MeOH, static permittivity increases non-linearly. This confirms that intermolecular association is taking place in the system and possibly O–H—N type of hydrogen bonded structures between β -picoline and MeOH molecules are formed. The observed value of static permittivity of pure β -picoline in present investigation is higher than our earlier reported value of pure α -picoline at all temperatures.⁷ The larger value of static permittivity of β -picoline is may be due

Fig. 3. Complex plane plots for binary mixtures of β -picoline, MeOH and mixture of β -Picoline–MeOH at 288.15 K.

Fig. 4. Plot of static permittivity (ϵ_0) against Mol fr of MeOH. (—) solid line shows the polynomial fitted curve.

to the change of $-\text{CH}_3$ (methyl group) position in the pyridine ring structure from ortho to meta position. Similar behavior was observed by Rana *et al.*¹ in static permittivity values of chloro substituted anilines.

The excess static permittivity value and its variation with mol fraction of MeOH at different temperatures is shown in Fig. 5. From the figure it can be seen that ϵ_0^E is negative for all concentrations of MeOH in the mixture at all temperatures. This indicates that the molecules of the mixtures may form multimer structures via hydrogen bonding in such a way that the effective dipole moment gets reduced. It can also be seen from Fig. 6 that ϵ_0^E is maximum negative at around 0.614 mole fraction of MeOH. Large magnitude values of ϵ_0^E of β -picoline–MeOH mixture confirms that β -picoline molecules acts as structure breakers for hydrogen bonded MeOH molecules with decrease in total number of parallel aligned dipoles. The magnitude values of ϵ_0^E can be ordered with temperature variation as ϵ_0^E (283.15) < ϵ_0^E (288.15) < ϵ_0^E (293.15) < ϵ_0^E (298.15). This clearly suggest that hydrogen bonded molecular networks are more effectively dissociated with increase in temperature.

The plot of refractive index against mole fraction of MeOH at different temperatures is shown in Fig. 6. From

Fig. 5. Plot of excess static permittivity (ϵ_0^E) against Mol fr of MeOH. (—) show the fitted line of Redlich–Kister equation.

Fig. 6. Plot of refractive index n_D against Mol fr of MeOH. (—) solid line shows the polynomial fitted curve.

the figure it can be seen that refractive index of β -picoline + MeOH mixtures decreases nonlinearly with mole fraction of MeOH. For the visible range of frequencies, the electric field component of electromagnetic wave interacts with the electron cloud surrounding each atom or molecule within its path in such a way as to induce electronic polarization. As a consequence of this polarization light waves are retarded in velocity as they pass through the medium. Since the retardation of electromagnetic radiation results from electronic polarization, the size of the constituent atoms or molecules has a considerable influence on the magnitude of this effect—generally, the larger an atom or molecule, the greater will be the electronic polarization and slower the velocity or higher the refractive index.²⁹ Refractive index of pure β -picoline and MeOH are 1.507 and 1.333, respectively at 283.15 K temperature. This clearly suggests that size of β -picoline molecule is larger than MeOH. Furthermore, variation of refractive index as a function of mole fraction of MeOH suggests that the electronic polarization of the molecules in the mixed state is influenced by the H-bonded interaction between β -picoline and MeOH. The increase in temperature causes increase in inter-atomic spacing and this result in the decrease in refractive index with rise in temperatures at all mixture concentrations. High frequency permittivity $\epsilon_{\infty 1}$, obtained by fitting experimental data to Eq. (2) were found to be different than the experimentally determined permittivity at optical frequency ϵ_{∞} . In case of MeOH, $\epsilon_{\infty 1}$ is markedly different from ϵ_{∞} value ($\epsilon_{\infty 1} - \epsilon_{\infty} = 2.48$ at 298.15 K), which confirms the presence of further absorption in the millimeter and infrared region.⁷ In case of pure β -picoline, a small difference in the values of $\epsilon_{\infty 1}$ and ϵ_{∞} (0.65 at 298.15 K) is found. This indicates the presence of further absorption of very small amplitude in the mm/infrared region and it can be due to the rotational orientation of the $-\text{CH}_3$ group. When MeOH is mixed with β -picoline, main relaxation process of component molecules fuse in to one relaxation process and overlapping of relaxation processes seems to take place. Degree of overlapping varies with variation in the concentration of the constituents of the mixtures, causing increase in the difference $\epsilon_{\infty 1} - \epsilon_{\infty}$ values with increase in concentration of MeOH.

The relaxation time value for pure β -picoline is 11.61 ps at 293.15 K, while the relaxation time of pure α -picoline is

10.61 ps at the same temperature.⁷ Higher value of relaxation time of β -picoline than α -picoline is in agreement with the higher value of viscosity of β -picoline (0.9459 mPa.s at 293.15 K)³⁰ than α -picoline (0.8102 mPa.s at 293.15 K).³¹ Smaller the viscosity of a liquid more is the ease of rotational orientation of the molecule and smaller is the relaxation time. The τ value of β -picoline is much smaller than MeOH, which clearly suggests the associative and nonassociative nature of MeOH and β -picoline, respectively. The relaxation time decreases with increase in temperature at all concentrations. This is may be due to the increase in the thermal agitation and partly due to decrease in the viscosity with rise in temperature.

The variation of $(1/\tau)^E$ with mole fraction of MeOH at 283.15, 288.15, 293.15 and 298.15 K temperatures is shown in Fig. 7. From the figure, it can be seen that $(1/\tau)^E$ is negative for the entire concentration range of the mixture. The negative $(1/\tau)^E$ indicating formation of slowly rotating structures. The evaluated values of excess static permittivity and excess inverse relaxation time were fitted to Redlich–Kister polynomial.²⁸ The coefficient a_j for $j = 0$ to 4 are listed in Table 1.

Figure 8 shows the variation of g^{eff} for the β -picoline + MeOH mixture at different temperatures. For pure β -picoline, MeOH and entire concentration range of their mixtures, g^{eff} values are greater than unity, which indicates that dipolar alignment favor parallel orientations. It can also be seen from Figure that, the g^{eff} vary with change in temperature, indicating that temperature change produces appreciable structural change. The determined values of Bruggeman factor (f_B) are shown in Fig. 9, which shows a nonlinear relation between f_B and volume fraction of MeOH at all temperatures. The Bruggemann parameter ' a ' is a dielectric parameter, which provides information about the interaction between components in the mixture in terms of volume changes. The values of fitting parameter ' a ' for β -picoline–MeOH mixtures along with standard error and correction coefficients are presented in Table 2. At temperatures 283.15

Fig. 7. Plot of excess inverse relaxation time $(1/\tau)^E$ against Mol fr of MeOH. (—) show the fitted line of Redlich–Kister equation.

Table 1. Parameters of Redlich–Kister equation for the mathematical representation of deviation in excess functions for β -picoline + MeOH.

Excess properties	Temp.	a_0	a_1	a_2	a_3	a_4	σ	δ
ϵ_0^E	283.15 K	-24.731	28.869	1.992	-24.361	-4.227	0.153	0.999
	288.15 K	-25.143	29.064	1.423	-24.141	-8.508	0.154	0.999
	293.15 K	-25.652	29.491	2.147	-25.319	-14.064	0.154	0.999
	298.15 K	-26.532	28.920	6.184	-22.564	-27.210	0.238	0.997
$(1/\tau)^E$	283.15 K	-0.088	-0.027	0.034	-0.082	-0.111	0.000	1.000
	288.15 K	-0.085	-0.016	0.055	-0.104	-0.161	0.001	0.998
	293.15 K	-0.080	-0.002	0.075	-0.128	-0.184	0.001	0.998
	298.15 K	-0.079	0.012	0.091	-0.136	-0.195	0.000	0.999

Fig. 8. Plot of effective Kirkwood correlation factor (g^{eff}) against Mol fr of MeOH. (—) solid line shows the polynomial fitted curve.

and 288.15 K the value of fitting parameter ' a ' is positive and greater than unity, which indicate that the effective volume of the components of the binary mixtures increases on mixing, whereas less than unity values of the fitting parameter ' a ' at the temperatures 293.15 and 298.15 K indicate that the effective volume of the components of the binary mixtures decreases on mixing. The values of fitting parameter ' a ' is

Fig. 9. Plot of Bruggeman factor (f_B) against Vol fr of MeOH. (—) solid line shows the Bruggeman equation fitted curve.

higher for β -picoline + MeOH mixture system (Table 2) as compared to α -picoline + MeOH mixture system⁷ at corresponding temperature, this suggests that the molecular interaction of MeOH is stronger with β -picoline than with α -picoline.

Determined values of thermo dynamical parameters: molar free energy of activation (ΔF_E), molar enthalpy of activation (ΔH_E) and molar entropy of activation (ΔS_E) are presented in Table 3. ΔH_E values were determined from the slopes of the plots of $\ln(\tau T)$ versus $1000/T$, which are shown in Fig. 10, while ΔF_E and ΔH_E are calculated using Eyring's rate equations. From Table 3, it can be seen that the value of free energy of activation is least for β -picoline and it increases with increase in concentration of MeOH at all temperatures. Higher value of ΔF_E of MeOH is due to the formation of hydrogen bonded networks in MeOH that tend to increase the effective size of rotating dipole and the dielectric frictional force between the rotating dipole and neighboring molecule. Furthermore, it can be seen that as the temperature increases, the molar free energy of activation for the dipole relaxation process increases for MeOH, β -picoline and their mixtures. This can be attributed to the fact that as the temperature increases, thermal agitation increases and the molecules require more energy to overcome the energy barrier separating the two mean equilibrium positions. In the present study the entropy of activation (ΔS_E) is found to be negative for all concentrations, at all temperatures, suggesting that the orientation in the system becomes co-operative resulting in the activated state, which is less disordered than the normal state.

Table 2. Values of fitting parameter ' a ' of Bruggeman factor for β -picoline + MeOH.

Temperature	Fitting parameter ^a	Standard error	Correction coefficient
283.15 K	1.065	0.031	0.995
288.15 K	1.026	0.031	0.995
293.15 K	0.911	0.027	0.997
298.15 K	0.826	0.03	0.996

Table 3. Values of thermo dynamical parameters of binary mixtures of β -picoline + MeOH at different temperatures.

Mol fr of MeOH	ΔF_E (kJ/mol)				ΔS_E (J/mol K)				ΔH_E (kJ/mol)
	283.15 K	288.15 K	293.15 K	298.15 K	283.15 K	288.15 K	293.15 K	298.15 K	
0.000	10.045	10.166	10.303	10.322	-0.028	-0.028	-0.028	-0.028	2.112
0.209	11.241	11.306	11.365	11.272	-0.012	-0.012	-0.012	-0.011	7.907
0.374	11.931	11.948	11.962	11.895	-0.007	-0.007	-0.007	-0.006	10.01
0.505	12.584	12.618	12.683	12.605	-0.011	-0.011	-0.011	-0.011	9.378
0.614	12.892	12.891	12.935	12.990	-0.015	-0.015	-0.015	-0.015	8.547
0.705	12.999	13.032	13.119	13.117	-0.018	-0.017	-0.017	-0.017	8.040
0.782	13.145	13.147	13.235	13.246	-0.016	-0.016	-0.016	-0.016	8.489
0.848	13.24	13.28	13.34	13.377	-0.018	-0.018	-0.018	-0.018	8.131
0.905	13.337	13.405	13.438	13.459	-0.017	-0.017	-0.016	-0.016	8.622
0.955	13.483	13.573	13.629	13.660	-0.02	-0.02	-0.02	-0.02	7.707
1.000	13.553	13.644	13.771	13.819	-0.023	-0.023	-0.023	-0.022	7.133

Fig. 10. Plot of $\ln(\tau T)$ versus $1000/T \text{ K}^{-1}$. (—) solid line shows trend line.

5. Conclusion

Complex permittivity spectra of β -picoline, MeOH and their mixtures display single dispersion due to main relaxation process in the frequency range of measurement at all temperatures. The plot of β -picoline exhibit the principle dispersion of Debye type where as its mixture with MeOH and pure MeOH exhibit C-D type of relaxation behavior. The presence of additional dispersion regions is confirmed for β -picoline, MeOH and their mixtures by the difference in the $\epsilon_{\infty 1}$ and ϵ_{∞} values. Static permittivity, permittivity at optical frequency, permittivity at high frequency, relaxation time, Kirkwood correlation factor, and Bruggeman factor and thermo dynamical parameters for β -picoline, MeOH and their mixtures over the entire concentration range has been determined and are reported. A nonlinear variation in static permittivity confirms that intermolecular association is taking place in the system. Hydrogen bonded molecular networks are more effectively dissociated with increase in temperature. Molecules of mixture may form multimer structures via hydrogen bonding in such a way that the effective dipole gets reduced. $(1/\tau)^E$ is negative for the entire mole fraction range of MeOH. Parallel orientation of electric dipoles has been observed in the mixture solutions of β -picoline and MeOH.

Comparative study of binary mixtures of MeOH with α -picoline and β -picoline suggests that molecular interaction of MeOH is stronger with β -picoline than with α -picoline.

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