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INVESTIGATIONS OF INTERMOLECULAR INTERACTIONS BETWEEN 2-METHOXYETHANOL AND NITROBENZENE THROUGH DIELECTRIC RELAXATION STUDY

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Complex dielectric spectra $\varepsilon^*(\omega) = \varepsilon' - \mathrm{i}\varepsilon''$ of binary mixture of 2-methoxyethanol with nitrobenzene were obtained in the frequency range of 10 MHz to 20 GHz over the volume fraction range $0 < v < 1$ and at different temperatures of 288, 298, 308, and 318 K using the time domain reflectometry (TDR) technique. The static dielectric constant ε_s and relaxation time τ have been obtained. These values are used to obtain the excess permittivity $\varepsilon_\mathrm{s}^\mathrm{E}$, excess inverse relaxation time $(1/\tau)^\mathrm{E}$, Kirkwood correlation factor g^eff, Bruggeman factor f_B, and thermodynamic parameters. On the basis of above parameters, intermolecular interaction and dynamics of molecules at molecular level are predicated.

Keywords: dielectric relaxation, excess parameters, Kirkwood correlation factor, thermodynamic parameters, time domain reflectometry

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1. Introduction

Extensive dielectric study has been done to understand molecular interactions in water and associative liquids such as ketone [1], amino acid [2, 3], amide [4], and with carbon dioxide [5]. Alcohols with ketone [6], nitriles [7, 8], p-fluorophenylacetonitrile [9], phenolic group [10, 11], alkyl halids [12, 13] were studied. Chlorobenzene with dimethylsulphoxide [14, 15], heterocyclic and phenyl rings of 2,6-daryl-4-piperidones [16], phenols with 2,6-diphenyl piperidons [17], alkanols with sodium dodecyl sulphate [18], propylene carbonate with acetonitrile [19] were studied.

Patil et al. [20] obtained the complex dielectric spectra for alcohols and aniline binary mixtures (i. e. ethanol, propanol, butanol, hexanol, heptanol with aniline) and reported that ε_s and τ decrease with increasing concentration of aniline in the alcohol. Rana et al. [21] carried out the dielectric relaxation study of propanol–2-chloroaniline and 3-chloroanilines over the entire range of concentration at frequency ranging from 10 MHz to 10 GHz using time domain reflectometry (TDR) technique at four different temperatures and found strong interactive association between aniline and propanol. Ahire et al. [22] studied the complex dielectric spectra for pyridine with three different formamides at four different temperatures using TDR. They calculated various parameters like Bruggeman factor, effective Kirkwood correlation factor, excess dielectric properties like excess permittivity and excess inverse relaxation time. Lou et al. [23] carried out the dielectric relaxation measurement in nitrobenzene–toluene over the temperature range 10–70 °C and frequency range from 50 MHz to 13.5 GHz, in which the effectiveness of ideal free energy relations for describing the process of dipolar relaxation was examined.

No attempt, so far, seems to have been made to study the dielectric behaviour of 2-methoxyethanol–nitrobenzene (ME–NB) molecular interactions in the microwave region. It is appropriate to report the present work on the dielectric behaviour of ME and NB liquid molecules, and also their conformations, because the dielectric behaviour and molecular dynamics of the ME–NB binary system can be explored more clearly only by comparing the dielectric data of the mixture system

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with the dielectric data of the individual molecules and their dynamics.

In NB molecules the charge distribution is shielded and H-bonds do not appear, whereas in ME molecules the charge distribution is exposed. In pure NB spatial correlation between molecules may appear only by means of dipole–dipole interactions. When there is an exposed distribution of charges, there may be very strong intermolecular interaction, however, in shielded distribution relative contribution to neighbour molecules is absent and hence there may be weak intermolecular interaction between the molecules of the liquids. Because of this disparity we have chosen these liquids for present study. Here the picosecond TDR [24] in reflection mode has been used to obtain dielectric parameters. The objective of this paper is to report dielectric relaxation study of the above system using TDR at temperatures of 288, 298, 308, and 318 K. From the dielectric parameters, excess permittivity, excess inverse relaxation time, Kirkwood correlation factor, Bruggeman factor, and thermodynamic parameters are obtained. On the basis of these parameters, intermolecular interaction and dynamics of molecules at molecular level are discussed.

2. Experiment

2.1. Chemicals

Spectroscopic grade ME and NB obtained from ACROS ORGANICS and MERK respectively are used without further purification. The solutions were prepared at different volume percentage of NB in ME in the step of 10% at room temperature. The concentrations were prepared for 5 ml solution at room temperature assuming ideal mixing behaviour, within 0.02% error limit.

2.2. TDR set-up and data acquisition

The Hewlett Packard HP54750A sampling oscilloscope with HP54754A TDR plug-in module has been used. After observing TDR response for sample under study, the time window was kept to 5 ns. Also by observing TDR response for sample under study, the SMA (standard military applications) sample cell with 1.35 mm effective pin length has been used. The sample cell holds the liquid under consideration. The physical dimensions of the cell are very important, so one must be careful while designing the sample cell. The impedance of the cell should be matched with coaxial transmission line to which cell is connected. If there is impedance mismatch then unwanted reflections may disturb the wave thereby causing some errors in the measurements. The proper design of cell includes the inner conductor and outer conductor diameters. The length of the inner conductor is called as ‘pin length’ of the cell and is very important factor in analysis. The sample length must be enough to avoid unwanted reflections.

In total reflection method, the sample length must be long enough to produce an adequate difference signal but short enough to keep less complication of resonance effects at frequencies above the range of interest.

The characteristics impedance of a coaxial line is given by

$$Z = \frac{138.2}{\sqrt{\varepsilon}} \log_{10} \frac{b}{a} \,. \tag{1}$$

This impedance for our transmission line is frequently 50 Ω. Here a is the diameter of inner conductor and b is the inner diameter of outer conductor, ε is the relative permittivity of the dielectric between the conductors. Using Teflon and air and taking appropriate a, b, a cell can be designed to have a matching impedance of $Z = 50\ \Omega$ (for air $\varepsilon = 1$ and for Teflon $\varepsilon = 2.2$). The SMA type cell has $b = 3.5$ mm. The inner conductor of SMA connector itself is considered as ‘inner conductor’ and hex-nut acts as an outer conductor. Since these SMA connectors have already been designed for precise 50 Ω impedance, a special design when used with high frequency is not required. The physical length of inner conductor can be changed. When cell is filled with sample above the physical length of inner conductor, the fringing effect [25, 26] takes place. Due to the fringing field the effective pin length [27] will not be equal to physical pin length. The effective electrical pin length will be more than the physical pin length. The accurate determination of effective pin length d is very important for the accurate evaluation of dielectric parameters. It is found that for SMA type cell effective pin length [27] is greater than actual physical length by 0.1–0.2 mm.

To reduce noise, time dependent response curve was averaged over 64 measurements taken and then stored in TDR oscilloscope memory with 1024 points per waveform. Firstly, the response waveform for empty cell is acquired and stored in memory, and then secondly, the response waveform for sample is acquired and stored in other memory. The empty cell waveform is used as reference waveform. Both the response waveforms are the reflected waveforms from the sample cell with open termination transmission line.

The data acquisition is carried out for 11 concentrations at 288, 298, 308, and 318 K. The temperature of sample was maintained at desired value, within accuracy limit of ± 1.15 K, by circulating constant temperature water through heat insulating jacket surrounding sample cell.

At each time the response waveforms without sample and with sample were recorded. The time dependent response waveform without sample is referred to as $R_1(t)$ and with sample referred as $R_x(t)$.

2.3. Data analysis

The time dependent data were processed to obtain complex reflection coefficient spectra $\rho^*(\omega)$ over the frequency range from 10 MHz to 10 GHz using Fourier transformation as in [28, 29],

$$\rho^*(\omega) = \frac{c}{\mathrm{i}\omega d} \frac{p(\omega)}{q(\omega)}\,, \tag{2}$$

where $p(\omega)$ and $q(\omega)$ are Fourier transformations of $R_1(t) - R_x(t)$ and $R_1(t) + R_x(t)$, respectively, c is the velocity of light, ω is angular frequency, d is effective pin length.

The complex permittivity spectra $\varepsilon^*(\omega)$ [30] were obtained from reflection coefficient spectra $\rho^*(\omega)$ by applying bilinear calibration method [24].

The complex permittivity spectra measured using TDR are fitted by the nonlinear least squares fit method to the Havriliak–Negami expression [31] to obtain various dielectric parameters:

$$\varepsilon^*(\omega) = \varepsilon_\infty + \frac{\varepsilon_\mathrm{s} - \varepsilon_\infty}{[1 + (\mathrm{i}\omega\tau)^{1-\alpha}]^\beta}\,, \tag{3}$$

where $\varepsilon^*(\omega)$ is the complex permittivity at an angular frequency ω, ε_∞ is the permittivity at high frequency, ε_s is the static permittivity, τ is the relaxation time of the system, α is the shape parameter representing symmetrical distribution of relaxation time, and β is the shape parameter of an asymmetric relaxation curve. The value of ε_∞ was taken to be 3.2; for the frequency range considered here, ε^* is not sensitive to ε_∞.

Equation (3) includes Cole–Cole ($\beta = 1$) [32], Davidson–Cole ($\alpha = 0$) [33], and Debye ($\alpha = 0$, $\beta = 1$) [34] relaxation models. The dielectric model for fitting dielectric parameters suitable for present system is Davidson–Cole model. Therefore, the complex permittivity spectra has been fitted in Davidson–Cole model with $\alpha = 0$ and β ($0 < \beta \le 1$) as one of the fitting parameters along with ε_s and τ. The value of fitting parameter β in Havriliak–Negami equation obtained is in the range of 0.7 to 0.82 for different concentrations.

3. Theory

3.1. Excess permittivity and excess inverse relaxation time

The information regarding interaction of liquids 1 and 2 may be obtained from excess dielectric properties [15, 35] like excess permittivity and excess relaxation time in the mixture. In the present work excess dielectric properties are determined corresponding to static permittivity and inverse relaxation time. The inverse relaxation time analogy is taken from spectral line broadening (which is the inverse of relaxation time) from the resonant spectroscopy [36].

The excess permittivity $\varepsilon_\mathrm{s}^\mathrm{E}$ is defined as

$$\varepsilon_\mathrm{s}^\mathrm{E} = (\varepsilon_\mathrm{s})_\mathrm{m} - [(\varepsilon_\mathrm{s})_1 x_1 + (\varepsilon_\mathrm{s})_2 x_2]\,, \tag{4}$$

where x is mole fraction and suffixes m, 1, 2 represent mixture, liquid 1 (ME), and liquid 2 (NB), respectively.

The excess permittivity may provide qualitative information about structure formation in the mixture as follows:

(i) $\varepsilon_\mathrm{s}^\mathrm{E} = 0$: indicates the liquids 1 and 2 do not interact and do not change their individual structural properties in the presence of other liquid.

(ii) $\varepsilon_\mathrm{s}^\mathrm{E} < 0$: indicates the liquids 1 and 2 interact in such a way that the total effective dipoles get reduced. The liquids 1 and 2 may form multimers leading to the less effective dipoles. In general, the negative excess permittivity indicates the formation of multimers in the binary mixtures.

(iii) $\varepsilon_\mathrm{s}^\mathrm{E} > 0$: indicates the liquids 1 and 2 interact in such a way that the total effective dipole moment increases. This may be due to breaking of multimer structure into monomer structure in the presence of other molecule.

Similarly, the excess inverse relaxation time $(1/\tau)^\mathrm{E}$ may be defined as

$$(1/\tau)^\mathrm{E} = (1/\tau)_\mathrm{m} - [(1/\tau)_1 x_1 + 1/\tau)_2 x_2]\,. \tag{5}$$

Information regarding the dynamics of liquids 1 and 2 can be retrieved from this excess inverse relaxation time $(1/\tau)^\mathrm{E}$ as follows:

(i) $(1/\tau)^\mathrm{E} = 0$: there is no change in the dynamics of liquids 1 and 2.

(ii) $(1/\tau)^\mathrm{E} < 0$: the interaction of liquids 1 and 2 produces a field such that the effective dipoles rotate slowly.

(iii) $(1/\tau)^\mathrm{E} > 0$: the interaction of liquids 1 and 2 produces a field such that the effective dipoles rotate rapidly, i. e. the field will co-operate in rotation of dipoles.

The experimental values of both the excess parameters were fitted to the Redlich–Kister equation [37]:

$$A^{\mathrm{E}} = x_1\,x_2 \sum_{j=0}^{n} B_j\,(x_1 - x_2)^j\,, \tag{6}$$

where A^{E} is either $\varepsilon_{\mathrm{s}}^{\mathrm{E}}$ or $(1/\tau)^{\mathrm{E}}$, x_1 and x_2 are mole fractions of ME and NB respectively. Using these B_j, values of excess parameters at various concentrations were calculated and used to draw the smooth curves.

3.2. The Bruggeman factor

The static permittivity of two-component mixture must lie somewhere between two extremes corresponding to static permittivity of two liquids. In order to understand the dipole interaction in the mixture of two liquids, the Bruggeman mixture formulae [38] have been proposed. The Bruggeman mixture formulae can be used as first evidence of molecular interactions in binary mixture. This formula states that static permittivity of binary mixture $(\varepsilon_{\mathrm{s}})_{\mathrm{m}}$, solute $(\varepsilon_{\mathrm{s}})_1$, and solvent $(\varepsilon_{\mathrm{s}})_2$ can be related to volume fraction of NB (v_2) in mixture as

$$f_{\mathrm{B}} = \frac{(\varepsilon_{\mathrm{s}})_{\mathrm{m}} - (\varepsilon_{\mathrm{s}})_2}{(\varepsilon_{\mathrm{s}})_1 - (\varepsilon_{\mathrm{s}})_2} \left[\frac{(\varepsilon_{\mathrm{s}})_1}{(\varepsilon_{\mathrm{s}})_{\mathrm{m}}}\right]^{1/3} = 1 - v_2\,. \tag{7}$$

3.3. The Kirkwood correlation factor

The Kirkwood correlation factor g [4] is also a parameter containing information regarding orientation of electric dipoles in polar liquids. The g for the pure liquid is given by the following expression:

$$g = \frac{\varepsilon_0(\varepsilon_{\mathrm{s}} - \varepsilon_\infty)(2\varepsilon_{\mathrm{s}} + \varepsilon_\infty)\,9\,k\,T\,M}{\varepsilon_{\mathrm{s}}(\varepsilon_\infty + 2)^2 \mu^2\,N\,\rho}\,, \tag{8}$$

where μ is dipole moment in gas phase, ρ is density at temperature T, ε_0 is free space permittivity, M is molecular weight, k is the Boltzmann constant, and N is Avogadro's number.

We assume that the Kirkwood factor g for mixtures can be expressed by an effective averaged correlation factor g^{eff} such that Kirkwood equation for the mixture can be approximated as

$$g^{\mathrm{eff}} = \frac{\varepsilon_0((\varepsilon_{\mathrm{s}})_{\mathrm{m}} - \varepsilon_{\infty m})(2(\varepsilon_{\mathrm{s}})_{\mathrm{m}} + \varepsilon_{\infty m})\,9\,k\,T}{N\,(\varepsilon_{\mathrm{s}})_{\mathrm{m}}(\varepsilon_{\infty m} + 2)^2 \left(\dfrac{\mu_1^2\,\rho_1}{M_1} v_1 + \dfrac{\mu_2^2\,\rho_2}{M_2} v_2\right)}\,, \tag{9}$$

where v_1 and v_2 are the volume fractions of liquids 1 and 2, $\varepsilon_{\infty m}$ is high frequency dielectric constant of mixture.

The other way to visualize variation in the Kirkwood correlation factor is to assume that correlation factors for molecules 1 and 2 in mixture contribute to effective g in equal proportion to their values corresponding to pure liquids, i. e., g_1 and g_2. Under this assumption the Kirkwood equation for the mixture can be approximated as

$$g_{\mathrm{f}} = \frac{\varepsilon_0((\varepsilon_{\mathrm{s}})_{\mathrm{m}} - \varepsilon_{\infty m})(2(\varepsilon_{\mathrm{s}})_{\mathrm{m}} + \varepsilon_{\infty m})\,9\,k\,T}{N\,(\varepsilon_{\mathrm{s}})_{\mathrm{m}}(\varepsilon_{\infty m}+2)^2 \left(\dfrac{\mu_1^2\,\rho_1\,g_1}{M_1} v_1 + \dfrac{\mu_2^2\,\rho_2\,g_2}{M_2} v_2\right)}\,, \tag{10}$$

where g_{f} is a fractional change in correlation factor for mixture. The values of g^{eff} in Eq. (10) will change from g_1 (ME) to g_2 (NB) as concentration of NB varies from 0 to 100%. In Eq. (10), g_{f} is unity for pure liquids and will remain close to unity if there is no interaction between 1 and 2.

3.4. Thermodynamic parameters

According to Eyring rate equation [39] the relation between activation enthalpy and entropy and relaxation time τ is given by

$$\tau = \frac{h}{kT} \exp \frac{\Delta H - T\,\Delta S}{RT}\,, \tag{11}$$

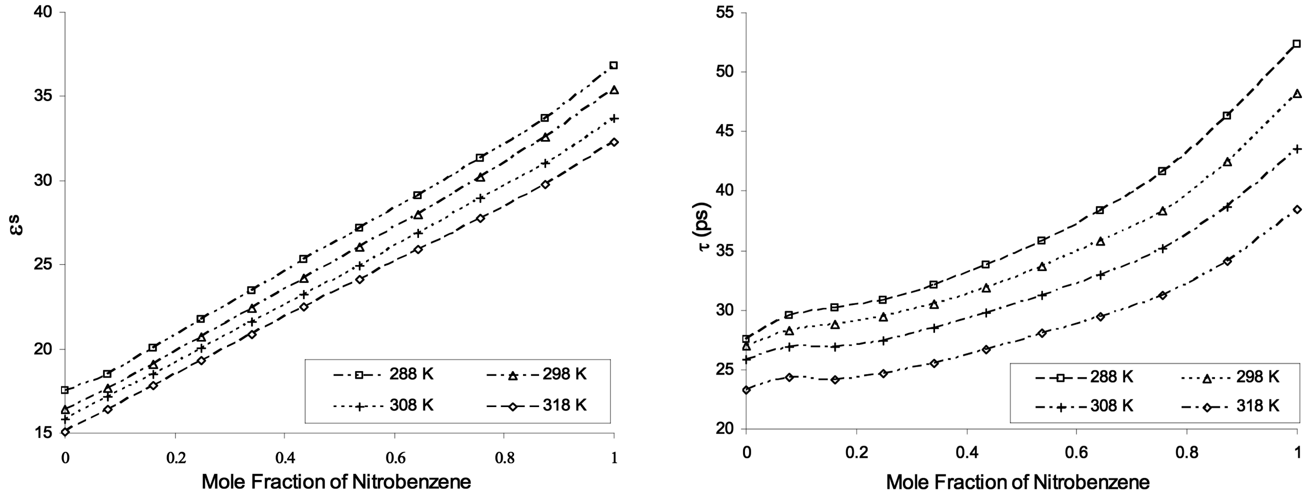
where ΔH is the molar enthalpy of activation and ΔS is the molar entropy of activation for the dipole reorientation process. ΔH is obtained from the slope of $\ln(\tau\,T)$ versus $1/T$. It follows from this equation that, if ΔH and ΔS are independent of the temperature, the plot of $\ln(\tau\,T)$ versus $1/T$ is linear,

$$\Delta H - T\,\Delta S = RT\,\ln \tau) - RT\,\ln \frac{h}{kT}\,. \tag{12}$$

The order of magnitude of the enthalpy of activation and entropy of activation can give some clue to the molecular energy and order of molecules in the relaxation process.

4. Results and discussion

The experimental and the literature values of ε_{s} for pure liquids are given in Table 1 and are in good agreement [40]. The values of the dielectric parameters ε_{s} and τ obtained from Eq. (3) for NB, ME, and NB–ME with the mole fraction of NB at four different temperatures are represented in Figs. 1(a) and 1(b), respectively.



(a) (b)

Fig. 1. Variation of (a) static dielectric constant ε_s and (b) relaxation time τ as a function of mole fraction of NB (x_2) at 288, 298, 308, and 318 K.

Table 1. Comparison of estimated and literature values of ε_s for pure liquids at 298 K.

Liquid	ε_s	
	This work 298 K	Literature 298.2 K
Nitrobenzene	35.42	34.82 [19]
2-methoxyethanol	16.42	17.58 [19]

From Fig. 1(a), it can be observed that ε_s values increase with the increase in mole fraction of NB in ME. Same type of change in ε_s values has been observed at four temperatures under study. The τ values (Fig. 1(b)) gradually increase with the increase in mole fraction of NB in ME. With the increase in temperature, the relaxation time values are decreasing by maintaining same type of variation with the change in concentration. In ME-rich region, τ values are not so much sensitive with the change in temperature. The ε_s as well as τ increases with the increase in volume fraction of NB in ME, indicating that with an increase in number of dipoles in the solution, the intermediate structures formed rotate slowly thereby giving the increase in the values of τ in the solution.

It is also seen from Fig. 1(a, b) that the ε_s value of NB–ME mixtures increases almost linearly with the increase in concentration of NB whereas τ value increases linearly with the increase in concentration of NB only in the 20–80% volume region. Below 20% and above 80% volume concentration of NB the τ value curvedly increases. The nonlinear increase in τ is due to the strong intermolecular hydrogen bonding in NB and ME molecules, whereas the linear behaviour suggests weak intermolecular interaction due to shielded charge distribution in NB molecules and exposed charge distribution in ME molecules [41].

The obtained excess permittivity and excess inverse relaxation data for the binary mixture of NB–ME are presented in Figs. 2(a) and 2(b), respectively. Both ε^E and $(1/\tau)^E$ were fitted by Redlich–Kister equation [37]. The estimated values of B_j coefficients along with their standard error and 95% confidence interval are given in Table 2.

The observed ε^E is found to be negative for all concentrations and temperatures (Fig. 2(a)), indicating that the total number of dipoles in NB–ME decreases, which is due to the opposite alignment of the dipoles of the interacting NB and ME molecules. It is interesting to see that the deviation in $(\varepsilon_s)^E$ uniformly decreases with the increase of temperature. The values of $(1/\tau)^E$ (Fig. 2(b)) are positive at NB-rich region, whereas they are negative below 0.2 mole fraction of NB at all temperatures. The negative values of $(1/\tau)^E$ indicate the formation of linear structures, probably dimeric, and these rotate slowly under the influence of an external varying field. At higher concentration of NB the molecular interaction produces a cooperative field and the effective dipoles have more freedom of rotation.

The information about the interaction can also be obtained by the Bruggeman factor as shown in Fig. 3. It can be seen from these plots that f_B shows a small deviation from the ideal Bruggeman behaviour. This again confirms the weak intermolecular interaction in the mixture. It is interesting to observe the similar temperature dependent behaviour as in the excess permittivity.

Table 2. Estimated values of B_j coefficients in Redlich–Kister equation along with their standard error of coefficient and 95% confidence interval for 2-methoxyethanol–nitrobenzene mixture at different temperatures.

Excess parameter	Temperature	B_j coefficient	Value	Standard error of coefficient	95% confidence interval
$(\varepsilon_s)^E$	288 K	B_0	−2.5596	0.1111	−2.8224, −2.2967
		B_1	−1.812	0.4361	(−2.8431, −0.7809)
		B_2	−5.0334	0.5158	(−6.2532, −3.8136)
		B_3	2.7071	1.1426	(0.0054, 5.4089)
	298 K	B_0	−2.1781	0.0787	(−2.3642, −1.9921)
		B_1	−1.4877	0.3087	(−2.2177, −0.7578)
		B_2	−2.5191	0.3652	(−3.3827, −1.6556)
		B_3	1.8327	0.8089	(−0.08, 3.7454)
	308 K	B_0	−1.636	0.0768	(−1.8176, −1.4544)
		B_1	−1.0764	0.3013	(−1.7889, −0.3638)
		B_2	−1.6133	0.3565	(−2.4562, −0.7703)
		B_3	−0.501	0.7896	(−2.3681, 1.366)
	318 K	B_0	−0.5759	0.0419	(−0.675, −0.4767)
		B_1	−0.9763	0.1645	(−1.3654, −0.5873)
		B_2	−1.6722	0.1946	(−2.1324, −1.212)
		B_3	−1.2172	0.4311	(−2.2366, −0.1978)
$(1/\tau)^E$	288 K	B_0	0.0041	0.0005	(0.0028, 0.0054)
		B_1	−0.0019	0.0021	(−0.0069, 0.003)
		B_2	−0.0082	0.0025	(−0.0141, −0.0023)
		B_3	0.0163	0.0055	(0.0033, 0.0294)
	298 K	B_0	0.006	0.0004	(0.0051, 0.007)
		B_1	−0.0008	0.0016	(−0.0046, 0.003)
		B_2	−0.0039	0.0019	(−0.0084, 0.0007)
		B_3	0.012	0.0042	(0.002, 0.022)
	308 K	B_0	0.0076	0.0006	(0.0063, 0.009)
		B_1	−0.0022	0.0023	(−0.0076, 0.0031)
		B_2	−0.0001	0.0027	(−0.0064, 0.0063)
		B_3	0.0107	0.0059	(−0.0033, 0.0247)
	318 K	B_0	0.0082	0.0009	(0.0061, 0.0104)
		B_1	−0.0042	0.0036	(−0.0126, 0.0043)
		B_2	0.001	0.0042	(−0.0089, 0.011)
		B_3	0.0182	0.0093	(−0.0039, 0.0403)

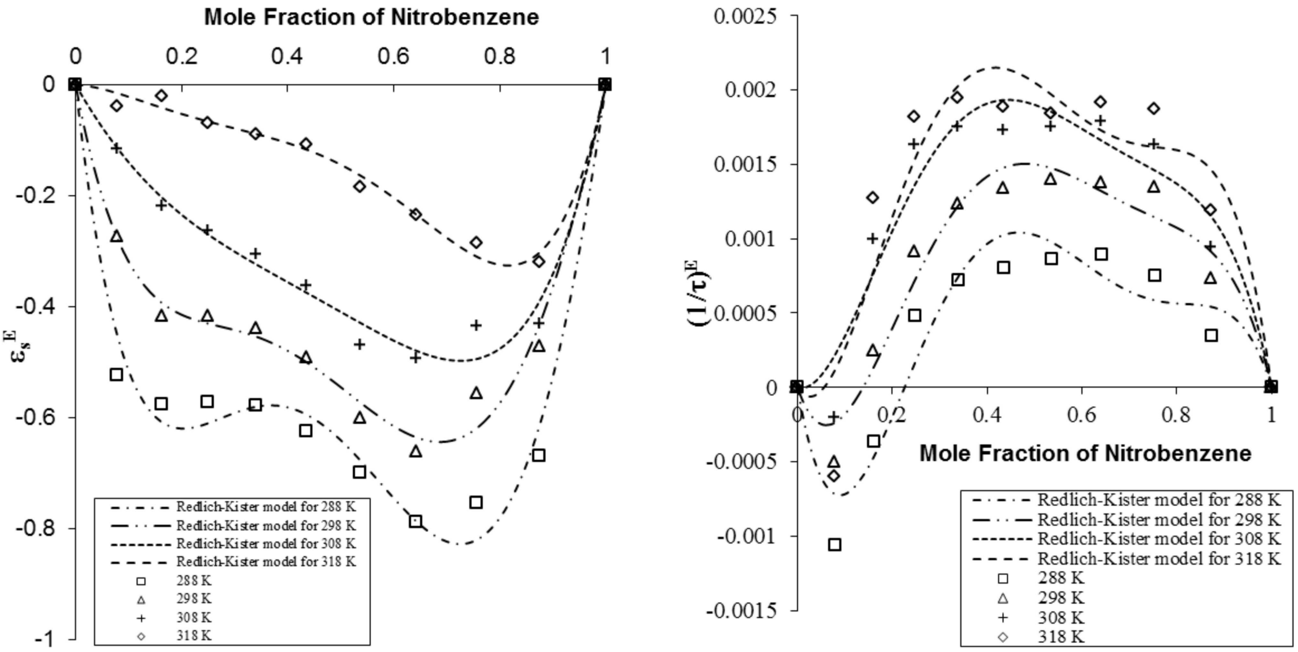
Table 3. Variation of g^{eff} for the mixture of 2-methoxyethanol–nitrobenzene as a function of volume fraction v_2 of nitrobenzene at different temperatures.

v_2	288 K	298 K	308 K	318 K
0	1.42	1.37	1.36	1.33
0.1	1.28	1.25	1.25	1.24
0.2	1.20	1.18	1.18	1.17
0.3	1.14	1.12	1.12	1.11
0.4	1.10	1.08	1.07	1.07
0.5	1.06	1.05	1.04	1.03
0.6	1.03	1.02	1.01	1.00
0.7	1.00	0.99	0.98	0.98
0.8	0.98	0.98	0.97	0.96
0.9	0.97	0.97	0.95	0.94
1	0.98	0.98	0.96	0.94

Table 4. Variation of g_f for the mixture of 2-methoxyethanol–nitrobenzene as a function of volume fraction v_2 of nitrobenzene at different temperatures.

v_2	288 K	298 K	308 K	318 K
0	1	1	1	1
0.1	0.96	0.98	0.99	0.99
0.2	0.96	0.97	0.98	0.99
0.3	0.96	0.97	0.97	0.98
0.4	0.96	0.96	0.97	0.98
0.5	0.96	0.96	0.97	0.98
0.6	0.96	0.96	0.97	0.98
0.7	0.96	0.96	0.97	0.98
0.8	0.97	0.97	0.97	0.98
0.9	0.97	0.98	0.98	0.98
1	1	1	1	1

The values of g^{eff} calculated from Eq. (9) are given in Table 3 for the mixtures. The value of g^{eff} is 1.42 for ME at 288 K which decreases to 1.33 at 318 K. These values confirm the formation of hydrogen bonding in pure ME system. The corresponding values for NB are 0.98 and 0.94 respectively, indicating weak dipole–



(a) (b)

Fig. 2. Variation of (a) excess permittivity ε^E and (b) excess inverse relaxation time $(1/\tau)^E$ as a function of mole fraction x_2 of nitrobenzene at 288, 298, 308, and 318 K.

Table 5. Estimated values of enthalpy ΔH and entropy ΔS as a function of volume fraction of nitrobenzene.

v_2	ΔH (kJ/mol)	ΔS (kJ/mol)
0	1.64	−0.037
0.1	2.26	−0.035
0.2	3.12	−0.033
0.3	3.07	−0.033
0.4	3.19	−0.033
0.5	3.37	−0.033
0.6	3.64	−0.032
0.7	4.09	−0.031
0.8	4.65	−0.030
0.9	5.15	−0.029
1	5.26	−0.030

dipole interaction resulting in the formation of antiparallel dipoles in the pure system. The g_f values are less than unity (Table 4), which suggest that the addition of small amount of NB breaks large amount of H-bonded long-range ordered ME structures.

The estimated values of energy parameters are given in Table 5. It can be seen there that the enthalpy of activation ΔH increases with the increase in concentration of NB in the mixtures. This means that more energy is needed for group dipole reorientation with the increase in volume fraction of NB in the mixture. The variation of ΔS with the volume fraction of NB indicates that disorder of the system is increasing with addition of NB.

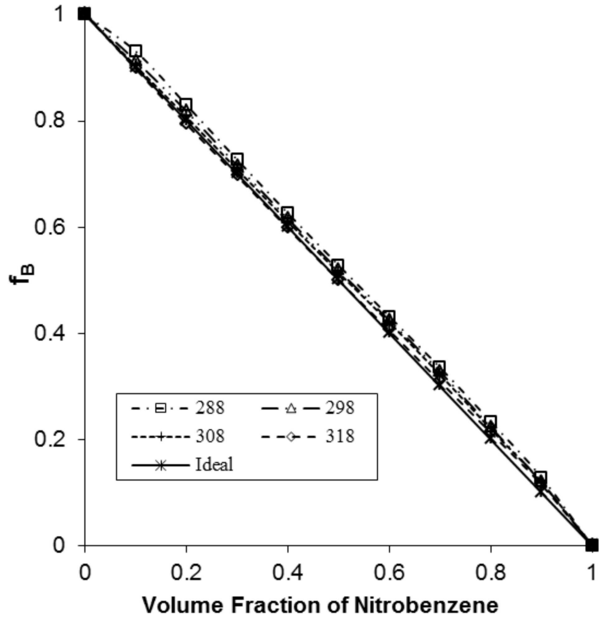


Fig. 3. Bruggeman plot for 2-methoxyethanol–nitrobenzene. Solid line denotes the ideal line, Eq. (7).

5. Conclusions

The dielectric study of binary mixtures of nitrobenzene with 2-methoxyethanol confirms the formation of heteromolecular H-bond interactions over the entire concentration and temperature. The dielectric parameters show systematic change with concentration and temperature. The negative value of ε^E indicates that the total numbers of dipoles in NB–ME decrease which may be due to the opposite alignment of the dipoles of the interacting NB and ME molecules. This is also concluded from g^{eff} values. The excess inverse relaxation time values are negative at ME-rich region indicating that the solute–solvent interaction hinders the rotation of dipoles of the system. The studied system shows Arrhenius behaviour. The negative value of ΔS indicates that there is a highly ordered group dipole reorientation in NB–ME, as is evident from the excess permittivity data.

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TARPMOLEKULINIŲ 2-METOKSIETANOLIO IR NITROBENZENO SĄVEIKŲ TYRIMAS, MATUOJANT DIELEKTRINĘ RELAKSACIJĄ

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Santrauka

Dvinario 2-metoksietanolio ir nitrobenzeno mišinio kompleksiniai spektrai $\varepsilon^*(\omega) = \varepsilon' - \mathrm{i}\varepsilon''$ gauti $0 < v < 1$ tūrio daliai dažnių srityje nuo 10 MHz iki 20 GHz 288, 298, 308 ir 318 K temperatūroje, naudojant laikinę reflektometriją. Gautos statinė dielektrinė konstanta ε_s ir relaksacijos trukmė τ. Šios vertės naudojamos viršijančiajai skvarbai $\varepsilon_\mathrm{s}^\mathrm{E}$, viršijančiajai atvirkštinei relaksacijos trukmei $(1/\tau)^\mathrm{E}$, Kirkvudo koreliacijos koeficientui g^eff, Brugemano koeficientui f_B ir termodinaminiams parametrams nustatyti. Remiantis gautais parametrais, molekuliniu lygmeniu aiškinama tarpmolekulinė sąveika ir molekulių dinamika.