Dielectric relaxation of 1-nitropropane-ethanol mixtures using pico second time domain technique from 10 MHz to 50 GHz

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Complex dielectric measurements in the frequency range 10 MHz - 50 GHz have been carried out in 1-nitropropane-ethanol mixtures with various concentrations by using a time domain reflectometry (TDR) at 283 K to 298 K. The dielectric relaxation response of 1-nitropropane-ethanol mixtures have been analyzed by using Debye model. The dielectric parameters such as static dielectric constant, relaxation time, excess permittivity, excess inverse relaxation time, Kirkwood correlation factor, enthalpy of activation and Gibbs free energy of activation have been determined for 1-nitropropane-ethanol system. The study confirms that the intermolecular interaction varies significantly with the increase in concentration of 1-nitropropane in ethanol.

1 Introduction

The dielectric studies of nitroalkanes have been investigated extensively to investigate the inter-molecular interaction in the nitroalkanes[1,2]. Dielectric relaxation studies in microwave region on liquid systems are efficient tools to investigate the structure and dynamics of molecular interactions. Time domain dielectric relaxation spectroscopy covers a broad band frequency window and therefore enables the investigation of diverse range of processes. One of the essential problems of molecular physics of the liquid state is to learn the inter-molecular interaction in the dynamics of molecules. Dielectric characterization has great potential in studying the inter-molecular interaction and dipolar alignments in H-bonded liquid systems. The strong H-bond self association and the formation of molecular network structures have a powerful effect at different polar solvents. The desire to understand these properties has triggered a great deal of research concerning the structure of H-bonded systems in polar solvent systems. Therefore, we choose the NTP- ethanol mixtures to study dielectric relaxation of mixtures using a TDR.

The NTP is a nitroalkane in which propane is substituted at C-1 by a nitro group and produced industrially by the reaction of propane and Nitric acid[3]. It is a colorless oily flammable nitroalkane having high value of permittivity, dipole moment and highly associated in their pure liquid state. M.F. Vuks illustrated that 1-nitropropane, nitromethane, nitrobenzene, and other nitro compounds are characterized by a very high dipole moment reaching ~ 4- 4.5 D. Since the energy of dipole interaction is proportional to the fourth power of the dipole moment (U α μ^4), it is expected to assume that association in these compounds is due to the strong dipole interaction of their molecules, forming dimers with the dipole having an anti parallel orientation[4]. They are used as a propellant fuel, gasoline additive, solvent, and in chemical synthesis. Ethanol is a very polar molecule as it contains hydroxyl group with high electro negativity of oxygen allowing hydrogen bonding to take place with other molecules. Ethanol has an extensive use as a solvent of substances intended for human consumption, including scents, flavorings, colorings, and medicines[5]. The excess enthalpies, Gibb's free energy of nitroalkanes with non-polar solvents were reported earlier[2,6,7].

The present paper reports the study of dielectric relaxation of NTP-ethanol binary mixture conducted using time domain reflectormetry (TDR) in the frequency range 10 MHz to 50 GHz at four different temperatures. The dielectric parameters like static dielectric constant, relaxation time were determined. The excess inverse relaxation, excess permittivity, effective Kirkwood correlation factor, thermodynamic parameters like enthalpy, entropy, Gibb's free energy has been determined.

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2 Experimental Details

2.1 Materials

1-nitropropane ($CH_3CH_2CH_2NO_2$ purity 98%) and ethanol (C_2H_5OH, purity 99.9%) were purchased from Merck Life Sciences Pvt. Ltd. Mumbai. The chemicals were used without any further purification.

2.2 Measurement

The complex permittivity and loss spectra for NTP-Ethanol in pure state and their binary mixture was measured in the frequency range of 10 MHz to 50 GHz at 283° to 298° K using time domain reflectometry (TDR) technique[8]. The Tektronix DSA8300 sampling mainframe oscilloscope with dual channel sampling module 80E10B has been used. The block diagram of TDR is shown in Fig. 1 and the actual set up in our laboratory is shown in Fig. 2.

A sampling module provides 12 ps incident and 15 ps reflected rise time pulse was fed through a coaxial line
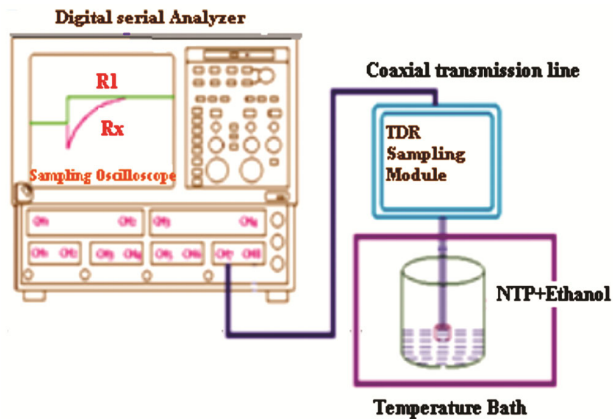
Fig. 1 — Block diagram of time domain dielectric technique

Fig. 2 — Experimental set up of time domain dielectric technique (TDDT).

system having 50 ohm impedance. Sampling oscilloscope monitor changes in 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 5 ns and digitized in 2000 points. The Fourier transformations of the pulse and data analysis were done to determine complex permittivity spectra $\varepsilon^*(\omega)$ using non linear least square fit method[9,10]. The temperature of all samples under test has been maintained using calibrated temperature controller system.

3 Results and Discussion

3.1 Complex permittivity

The frequency dependent complex permittivity spectra for different concentrations of NTP in ethanol mixture are shown in Fig. 3. The loss peak of ethanol observed at lower frequency side and the loss peak of NTP appear on higher frequency side which shows nearly equal value of dielectric loss. Overall it seems that the position of loss peak shifted towards higher frequency side which indicates the decrease of relaxation time and faster ion dynamics[11].

To calculate static dielectric constant (ε_0), relaxation time (τ) and distribution parameters (α and β), complex permittivity $\varepsilon^*(\omega)$ data were fitted by the non-linear least square fit method to the Harviliak-Negami expression[12]:

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

where ε_0, ε_∞, τ, α and β are the fitting parameters. The Havriliak-Negami expression includes the Debye[13] ($\alpha=0$, $\beta=1$), Cole-Cole[14] ($\beta=1$) and Cole-Davidson[15] ($\alpha=0$) relaxation spectral function in limiting form. The molecular motions of the
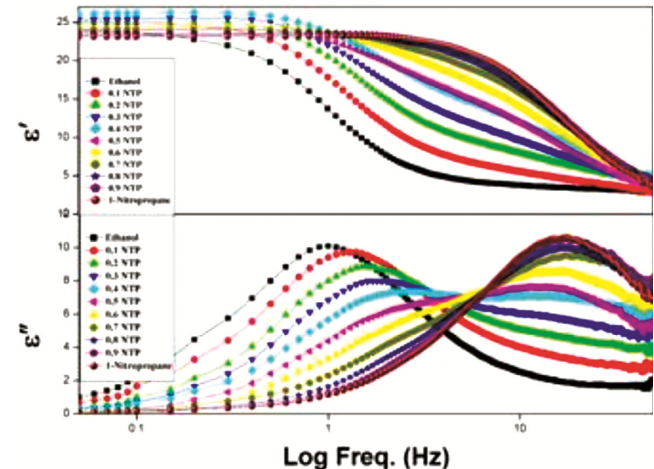

Fig. 3 — Frequency dependent complex permittivity spectra of 1-nitropropane-ethanol at 25 $^\circ$C.

Table 1 — Temperature dependent dielectric parameters of 1-nitropropane-ethanol mixture.

Volume fraction of 1-Nitropropane	10 °C		15 °C		20 °C		25 °C	
	ε_0	τ	ε_0	τ	ε_0	τ	ε_0	τ
0	28.7(2)	168.4(3)	25.7(1)	158.5(1)	25.1(1)	146.1(1)	24.3(2)	133.9(2)
0.1	28.3(8)	146.9(1)	26.4(7)	130.4(8)	24.9(6)	118.8(7)	24.9(6)	114.7(6)
0.2	28.6(1)	109.9(1)	26.8(1)	105.2(9)	25.3(8)	96.2(8)	25.2(7)	88.2(7)
0.3	28.6(1)	87.5(1)	27.5(1)	83.9(1)	25.4(1)	84.1(1)	25.4(9)	72.6(8)
0.4	28.8(1)	69.0(1)	28.1(1)	62.5(9)	26.2(1)	57.8(8)	25.9(5)	57.0(1)
0.5	26.6(1)	51.8(8)	25.8(1)	45.9(8)	24.9(1)	42.7(7)	23.8(1)	41.1(6)
0.6	26.0(1)	35.8(6)	25.5(1)	31.0(5)	24.6(9)	30.4(5)	23.7(1)	26.7(5)
0.7	25.7(8)	27.4(4)	24.7(8)	22.3(4)	24.2(6)	20.1(3)	23.5(7)	17.5(3)
0.8	25.2(4)	18.4(2)	24.5(4)	15.2(1)	23.9(3)	13.4(1)	23.4(3)	12.8(1)
0.9	24.8(2)	13.5(9)	24.1(1)	12.3(6)	23.7(1)	11.2(5)	23.4(1)	10.5(5)
1	24.6(2)	10.8(1)	23.8(2)	10.2(9)	23.3(1)	9.7(7)	23.2(1)	9.9(6)

examined highly polar molecules of NTP and Ethanol are well described with single Debye type rotational relaxation modes which is in line with the results obtained by Naoya and Toshiyuki[16].

It was observed from Table 1 that that the values of static dielectric constant are increasing with the increasing volume fraction of NTP in ethanol up to 0.4 concentrations and thereafter it decreases up to pure NTP. The decrease in the dielectric constant may be due to increase of thermal oscillation of the molecules and increase in degree of disorder of dipoles[17].

Also, the values of relaxation time are decreasing with increasing temperature. The variation of relaxation time with increase in volume fraction of NTP in ethanol solution at 10 °C to 25 °C presents a very fascinating behavior.

Chandra and Nath[1] have reported the relaxation time (τ) value of NTP as 7.8 at 303 K, which are very similar to our value of τ as 9.9 at 298 K. This confirms that as temperature decreases, value of relaxation time increases. Also, the relaxation time of the molecules of the solution decreases exponentially as concentration of NTP is increased.

3.2 Kirkwood factor

Modified form of Kirkwood correlation factor based on volume fraction mixture law to study the orientation of dipoles due to heterogeneous interaction in binary mixtures can be expressed as follows[18];

$$\frac{4\pi N}{9kT}\left[\frac{\mu_E^2 \rho_E}{M_E} v_E + \frac{\mu_{NTP}^2 \rho_{NTP}}{M_{NTP}}(1 - v_E)\right] g^{eff} = \frac{(\varepsilon_{0m} - \varepsilon_{\infty m})(2\varepsilon_{0m} + \varepsilon_{\infty m})}{\varepsilon_{0m}(\varepsilon_{\infty m} + 2)^2} \quad \dots (2)$$

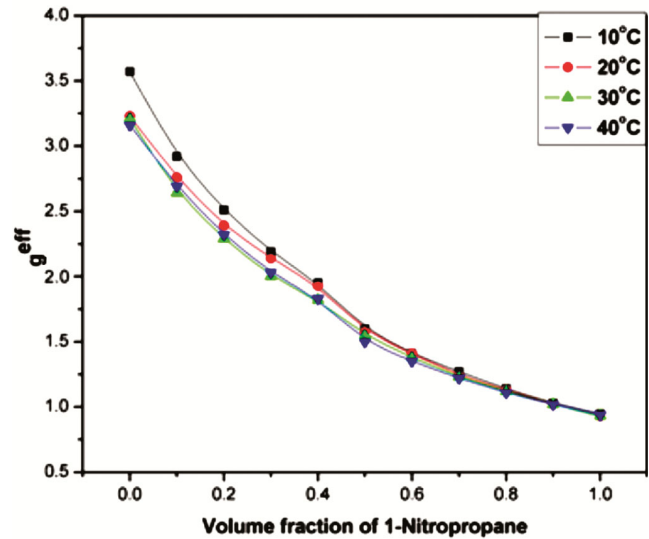

Fig. 4 — Kirkwood correlation factor for 1-nitropropane in ethanol solution.

Where, g^{eff} is the effective Kirkwood correlation factor, μ_E, μ_{NTP} are the dipole moment of ethanol and NTP, ρ_E, ρ_{NTP} are the densities of ethanol and NTP respectively, ε_0 is static dielectric constant, ε_∞ is permittivity at high frequency, N is Avogadro's number, K is Boltzman's constant, T is the temperature. To calculate effective Kirkwood correlation factor we have taken the values of dipole moment of ethanol[19] as 1.69 D, and the dipole moment of NTP[20] as 3.60 D, the value of density of ethanol and density of NTP are 0.789 g/cm³ and 0.998 g/cm³, respectively.

The value of effective Kirkwood correlation factor 'g^{eff}' for ethanol at 25 °C is found to be 3.16 which is greater than the value of 1-nitropropane that is 0.94.

The temperature effect on the values of effective Kirkwood correlation factor at different concentrations is shown in Fig. 4. The values of the effective Kirkwood

correlation factor (g^{eff}) indicate that the parallel alignment of dipoles tends to reduce with rise in temperature and with increase in volume fraction of NTP in ethanol.

The value of pure NTP is less than unity which shows insufficient interaction with anti-parallel orientation of electric dipoles between pure NTP molecules. This has been confirmed with the results obtained by Naoya and Toshiyuki such that the small Kirkwood factor in nitro group molecules has a tendency to align in anti parallel intermolecular configuration due to their strong dipole-dipole interaction[21, 16].

3.3 Excess inverse relaxation

The excess inverse relaxation determined for NTP – Ethanol solution is as follows which is used to provide structural information;

$$\left(\frac{1}{\tau}\right)^{E} = \left(\frac{1}{\tau}\right)_{m} - \left[\left(\frac{1}{\tau}\right)_{E} X_{E} + \left(\frac{1}{\tau}\right)_{NTP} (1 - X_{E})\right] \ldots (3)$$

Where, $\left(\frac{1}{\tau}\right)^{E}$ is the excess inverse relaxation time. The inverse relaxation time analogy is taken from spectral line broadening in the resonant spectroscopy[22]. The inverse relaxation time values are negative for all concentrations for both systems studied which indicate slower rotation of the dipoles that produces a field in such a way that the effective dipole rotation is hindered[23] due to the solute–solvent interaction form the hydrogen bonded structures. The variation of excess relaxation time $(1/\tau)^{E}$ with volume fraction of NTP at 10 °C to 25 °C is shown in Fig. 5.

3.4 Excess dielectric permittivity

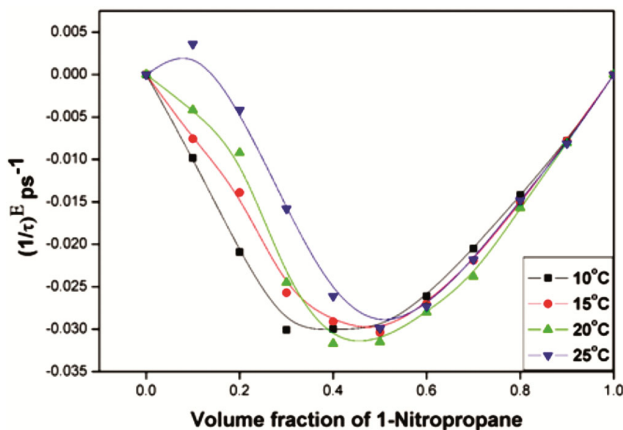The strength and nature of inter-molecular interactions in binary liquid mixtures is specified by excess dielectric constant ε_0^E parameter.

The excess dielectric constants for the above binary liquid mixtures were evaluated using;

$$\varepsilon_0^E = (\varepsilon_0)_m - \left[(\varepsilon_0)_E X_E + (\varepsilon_0)_{NTP} (1 - X_E)\right] \ldots (4)$$

Where, $(\varepsilon_0)_m$ is dielectric constant of the binary liquid mixture. $(\varepsilon_0)_E$ and $(\varepsilon_0)_{NTP}$ are the dielectric constants of Ethanol and Nitropropane respectively and X_E be the volume fractions of ethanol[24].

The excess dielectric constant data provide the following information in relation to the molecular conformation[25]:

(i) $\varepsilon_0^E = 0$ indicates that mixture constituents do not interact and thus have ideal mixing behavior.

(ii) $\varepsilon_0^E < 0$ indicates that mixture constituents interact so as to reduce the total number of effective dipoles that contributed to the mixture dielectric polarization.

(iii) $\varepsilon_0^E > 0$ indicates that the constituents of a mixture interact in such a way that there is an increase in number of effective dipoles contributed in the mixture dielectric polarization.

The positive deviations from ideal behavior (ε_0^E being positive) are qualitatively attributed to a "build-in" of components of the mixture in the structure of respective solvent. In the present study, excess dielectric constant varies as a function of concentration and reaches an optimum measure at 0.6 which is shown in Fig. 6. $\varepsilon_0^E > 0$ which indicates that the binary liquids interact in such a way that the effective dipole increases. There is formation of multimers and a tendency of dipole aligned in parallel direction.
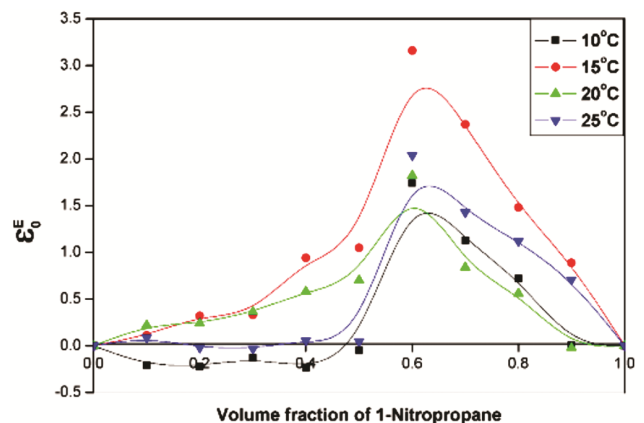

Fig. 5 — Excess inverse relaxation time $(1/\tau)^E$ of NTP-ethanol mixture.

Fig. 6 — Excess dielectric permittivity ε_0^E of NTP-ethanol mixture.
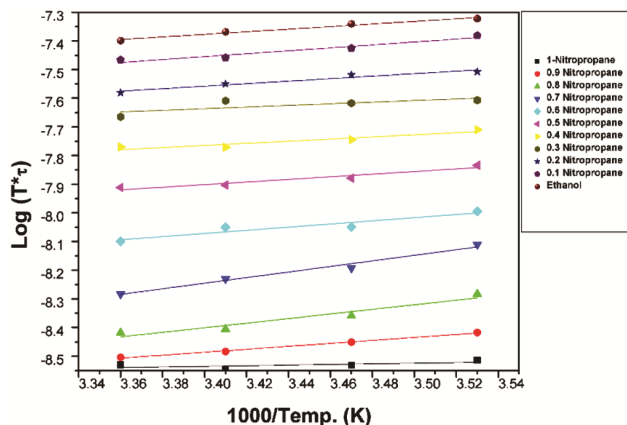
Fig. 7 — Arrhenius behavior of NTP- ethanol.

3.5 Thermodynamic parameters

Eyring[26] was the first one who correlates the dielectric relaxation to the chemical rate theory. According to this theory the following relation was carried out[27, 28];

$$\tau = \frac{h}{KT} \exp\frac{\Delta G}{RT} \qquad \dots (5)$$

where, ΔG is the free energy of activation for dipole relaxation, K is the Boltzman's constant, and h is Plank's constant.

The Gibb's free energy (ΔG) is related to enthalpy of activation (ΔH) and the entropy of activation (ΔS) by following relation;

$$\Delta G = \Delta H - T^* \Delta S \qquad \dots (6)$$

Equations (5) and (6) indicate that the plot of log(τT) versus (1/T) should give approximately a linear relationship with a slope (ΔH/R), from which ΔH can be calculated. Plot of ln(T*τ) versus 1000/T (^{o}K) of NTP–Ethanol for various concentrations are straight line as shown in Fig. 7.

In binary mixture of polar liquids mixed together, there is a change in the energy of the system. This change in energy can be interpreted with thermodynamic parameters such as free energy of activation (ΔG), molar enthalpy of activation (ΔH) and molar entropy of activation (ΔS).

All positive values of ΔH suggest endothermic interaction[29]. Molar enthalpy of activation (ΔH) value for pure 1-Nitropropane is found to be 7.98 KJ/mol, i.e., 1.90 kcal/mol in temperature range 283 K to 298 K. S Chandra and D Nath[1] has got ΔH value for NTP as 2.39 kcal/Mol at 303°K. This confirms that as the temperature of system increases enthalpy also increases, which is reported in Table 2.
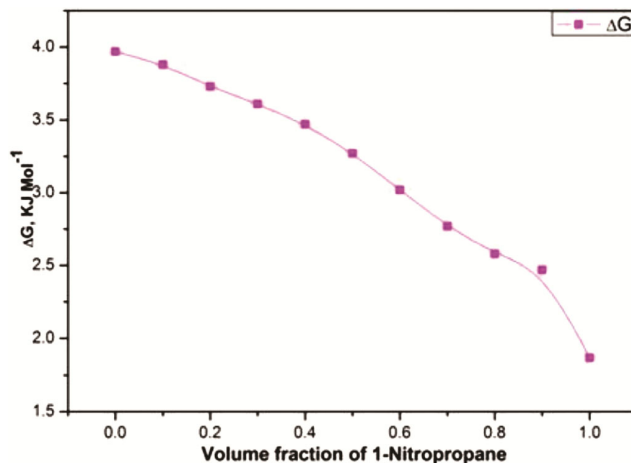

Fig. 8 — Gibb's free energy behavior of NTP + ethanol at 298 K.

Table 2 — Enthalpy, entropy of activation for 1-nitropropane-ethanol mixture.

Concentration of 1-Nitropropane	Enthalpy of activation ΔH (KJ mol^{-1}K^{-1})	Entropy of activation ΔS (KJ mol^{-1})
0	8.35(7)	0.20(2)
0.1	9.33(1)	0.20(6)
0.2	8.07(1)	0.20(4)
0.3	5.35(3)	0.19(1)
0.4	6.75(1)	0.20(6)
0.5	8.37(1)	0.21(5)
0.6	10.2(2)	0.22(8)
0.7	17.9(1)	0.25(6)
0.8	14.6(3)	0.24(1)
0.9	9.48(5)	0.22(2)
1	1.98(1)	0.20(6)

Positive values of entropy point out that the environment is not cooperative for the system and the activated system becomes less ordered than the normal one. Entropies for NTP + Ethanol at different temperatures are found to be positive indicating that the systems are less ordered.

The free energy of activation (ΔG) value is greater for pure ethanol as compared to pure NTP and ΔG value decreases with increase in concentration of NTP at all temperatures which is shown in Fig. 8. This indicates that the ethanol molecules in the mixture dominate over NTP molecules. This dominance of ethanol over NTP is primarily due to its large dipole moment values and presence of C-O. Also, the molecular interaction decreases with increasing concentration of NTP and therefore dipoles require less energy in order to attain equilibrium with applied field.

4 Conclusions

Dielectric relaxation response of NTP - ethanol binary mixture using TDR in the range of 10 MHz to 50 GHz has been determined TDR spectroscopy technique. The dielectric relaxation parameters, i.e., static dielectric constant, relaxation time, variation in excess permittivity and excess inverse relaxation, effective Kirkwood correlation factor, activation enthalpy and entropy have been reported for NTP-ethanol mixture for dissimilar temperatures. The findings are summarized as follows:

(i) The values of static dielectric constant are increasing with the increasing volume fraction of NTP in ethanol up to 0.4 concentrations and thereafter it decreases up to pure NTP.

(ii) The relaxation process taking place in ethanol rich solutions which is relatively slower than in the NTP rich solutions. The relaxation time values confirm that there is a dissociation of ethanol-ethanol network leading to rapid fall in τ values with an increase in NTP concentration.

(iii) Effective Kirkwood correlation factor validates the parallel alignment of dipoles that tends to reduce with rise in temperature and increase in volume fraction of NTP in ethanol.

(iv) The negative excess relaxation values point out that there is slower rotation of dipoles with effective dipole moments which gets reduced.

(iv) The positive values of excess dielectric permittivity confirm the hydrogen bond interaction with an increase in number of effective dipoles contributed in the mixture.

(v) The positive values of enthalpy ensure the endothermic reaction. The positive entropy of activation indicates that the activated state is more disordered. The decreasing Gibb's free energy values specify that the dipoles require less energy in order to attain equilibrium with applied field.

Acknowledgement

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