Research Article

Dielectric, Thermodynamic, and Computational Studies of Hydrogen Bonded Binary Mixtures of N-Methylaniline with Propan-1-ol and Isopropyl Alcohol

T. Vijaya Krishna,[1] S. Sreehari Sastry,[2] Sie Tiong Ha,[3] and V. R. K. Murthy[4]

[1] *Department of Physics, Vasireddy Venkatadri Institute of Technology, Nambur 522508, India*
[2] *Department of Physics, Acharya Nagarjuna University, Nagarjunanagar 522510, India*
[3] *Department of Chemical Science, Faculty of Science, University Tunku Abdul Rahman, Jalan University, Bandar Barat, 31900 Kampar, Malaysia*
[4] *Department of Physics, Indian Institute of Technology, Chennai 600036, India*

Correspondence should be addressed to S. Sreehari Sastry; sreeharisastry@yahoo.com

The molecular interactions between the polar systems N-methylaniline with alcohols, propan-1-ol, and isopropyl alcohol for various mole fractions at different temperatures are studied by determining the dielectric permittivity using LF impedance analyzer, microwave bench, and Abbe's refractometer in radio, microwave, and optic frequency regions, respectively. Dipole moment, excess dipole moment, excess Helmholtz free energy, excess permittivity, excess inverse relaxation time, and excess thermodynamical values are calculated using experimental data. Hamiltonian quantum mechanical calculations are performed using PC Spartan and ArgusLab modeling softwares for both pure and equimolar binary systems of N-methyl aniline with alcohols.

1. Introduction

Dielectric relaxation spectroscopy is a powerful tool for examining the underlying physics of solvent systems [1, 2] and for exploring the molecular dynamics of liquids, which are characterized by inter- and intramolecular structures that vary rapidly with time. Historically, such studies have focused separately on long-range and short-range molecular forces [3]. At one extreme, long-range, nonspecific dispersion forces produce weakly bonded van der Waals complexes, while at the other, short-range, highly directional hydrogen bonding generates molecular networks. In reactions, where the solvent is directly involved in the process (as in solvolytic reactions), the reaction rate can be markedly sensitive to the solvent structure and dynamics [4]. In chemical processing applications, the availability of quantitative data on dielectric properties of solvent systems or methods for their prediction are essential for the design and implementation of microwave heated processes.

There is an increased interest in the study of liquid mixtures leading to formation of hydrogen bonding in the system due to solute-solvent interactions during the recent times [5]. Hydrogen bonding is complex in liquid state because of the uncertainty in identifying the particular bonds and the number of molecules involved. The presence of hydrogen bond brings a considerable change in the dielectric properties of liquid mixtures [6]. The component liquids taken in course of this investigation are amines and alcohols. Aromatic amines, which are nonassociative, are very important in biology, in the production of dyes, pesticides, and antioxidants [7, 8]. Alcohols are industrially and scientifically important organic compounds and their physical and chemical properties are largely determined by the –OH group. Alcohols are strongly associated in solution because of dipole-dipole interaction and hydrogen bonding. The nature of interaction between –NH and –OH groups plays an important role in biological systems and drug synthesis [9, 10].

The present work aims at studying the dielectric behavior of pure and binary mixtures of N-methylaniline with propan-1-ol (system 1) and N-methylaniline with isopropyl alcohol (system 2) in different frequency ranges for various mole fractions at different temperatures. From the experimental data, the dielectric parameters dipole moment, excess dipole moment, excess Helmholtz free energy, excess permittivity, excess inverse relaxation time, and excess thermo dynamical values are calculated for the pure and binary mixtures [11–14]. Hamiltonian quantum mechanical calculations [15, 16] such as semiempirical and *ab initio* calculations are performed by optimized converged geometry operation using PC Spartan and ArgusLab modeling softwares [17, 18]. The obtained theoretical values are further compared with the experimental values.

2. Experimental

The compounds N-methylaniline (NMA), propan-1-ol (1PN), and isopropyl alcohol (IPA) of AR grade are purchased from E. Merck, Germany, and are purified by standard methods. The binary mixtures are prepared for different mole fractions, that is, mole fraction (x_2) of N-methylaniline is varied from 0 to 1 in alcohols 1PN and IPA (with a step increment of 0.1). The temperature controller system with a water bath, supplied by M/s Sakti scientific instruments company, India, has been used to maintain the constant temperature within the accuracy limit of ± 1 K. Densities at different temperatures are measured by using a 10 ml specific gravity bottle and METTLER TOLEDO balance (Model no: AB135-S/FACT) whose accuracy is 0.01 mg.

The static permittivity values at the spot frequencies 1 kHz ($\varepsilon_{\text{static}}$), 10 kHz, 100 kHz, 1 MHz, and 10 MHz for the above systems are measured using HP-LF impedance analyzer (Model no: 4192 A) at different temperatures. The real (ε') and imaginary (ε'') parts of the complex dielectric permittivity ($\varepsilon^* = \varepsilon' - j\varepsilon''$) are determined with microwave bench (X-Band-8.60 GHz) using Plunger technique [19] for the above temperatures. The high frequency dielectric permittivity ($\varepsilon_\infty = n^2$) is obtained from the refractometer measurements using M/s ASCO make Abbe's refractometer with sodium D light as source at different temperatures. The error in the estimation of $\varepsilon_{\text{static}}, \varepsilon', \varepsilon_\infty$ and density is 1% and the error in the estimation of ε'', τ is 2%. Dipole moments of the liquids in gaseous state are taken from literature [20].

2.1. Theory. The dipole moments for the pure and equimolar systems (system 1 and 2) are measured experimentally, by diluting them in nonpolar solvent benzene, using Higasi's method [11].

$$\mu^2 = \frac{27kTM_2\left(a_0 - a_\infty\right)}{4\pi N d_1 \left(\varepsilon_1 + 2\right)^2}, \tag{1}$$

where M_2 is molecular weight of solute, a_0, and a_∞ are, respectively, the slopes of $\varepsilon_{\text{static}}$ and ε_∞ with respect to the weight fraction of the solute, d_1 is density of solvent, and ε_1 is the static dielectric permittivity of solvent (Benzene).

The excess dipole moments ($\Delta\mu$) of the systems are determined [12, 21, 22] by (2) as follows:

$$\Delta\mu = \mu_{12} - \mu_1 - \mu_2, \tag{2}$$

where μ_1 is the dipole moment of NMA, μ_2 is the dipole moment of either 1PN or IPA, and μ_{12} is the dipole moment of the equimolar solute mixtures NMA + 1PN or NMA + IPA.

The excess Helmholtz free energy (ΔF^E) is a good dielectric parameter to evaluate the interaction between the components in the mixture through breaking mechanism of hydrogen bond and is expressed [23] as

$$\Delta F^E = \Delta F_{or}^E + \Delta F_{rr}^E + \Delta F_{12}^E, \tag{3}$$

where ΔF_{or}^E represents the excess dipolar energy due to long range electrostatic interaction, ΔF_{rr}^E represents the excess dipolar energy due to the short range interaction between identical molecules, and ΔF_{12}^E represents the excess free energy due to short-range interaction between dissimilar molecules.

The above terms are given in detail in (4) as

$$\Delta F^E = \frac{-N_A}{2}\left\{ \sum_{r=1,2} x_r^2 \mu_r^2 \left[R_{fr} - R_{fr}^0\right] \right.$$
$$+ \sum_{r=1,2} x_r^2 \mu_r^2 \left[g_{rr} - 1\right]\left[R_{fr} - R_{fr}^0\right]$$
$$\left. + x_1 x_2 \mu_1 \mu_2 \left[R_{f_1} + R_{f_2} - R_{f_1}^0 - R_{f_2}^0\right]\right\}, \tag{4}$$

where, $R_{fr}^0 = (8\pi N_A/9V_r)((\varepsilon_r - 1)(\varepsilon_{\infty r} + 2)/(2\varepsilon_r + \varepsilon_{\infty r}))$, $R_{fr} = (8\pi N_A/9V_r)((\varepsilon_m - 1)(\varepsilon_{\infty r} + 2)/(2\varepsilon_m + \varepsilon_{\infty r}))$, $g_{12} = g_f$, V_r is the molar volume of the components, and $\varepsilon_r, \varepsilon_{\infty r}$ are the dielectric permittivity values at static and optic frequencies of the pure liquids, respectively. The error in the estimation of excess Helmholtz free energy is 0.001 J-mol^{-1}.

The contribution of hydrogen bonds to the dielectric properties of the mixtures can be studied in terms of excess permittivity (ε^E). The excess permittivity, ε^E, which provides qualitative information about formation of multimers in the mixture, can be computed as [24]

$$\varepsilon^E = \left(\varepsilon_m - \varepsilon_{\infty m}\right) - \left[\left(\varepsilon_1 - \varepsilon_{\infty m}\right)x_1 + \left(\varepsilon_2 - \varepsilon_{\infty m}\right)x_2\right], \tag{5}$$

where x is mole fraction and suffix 1, 2, and m represents liquid 1, liquid 2, and mixture, respectively.

The qualitative information provided by excess permittivity about the mixtures is as follows.

$\varepsilon^E = 0$ indicates that there is no interaction between the components in the mixture.

$\varepsilon^E < 0$ indicates that the components in the mixture interact in such a way that the effective dipolar polarization gets reduced and the components may form multimers leading to less effective dipoles.

$\varepsilon^E > 0$ indicates that the components in the mixture interact in such a way that the effective dipolar polarization gets increased and the components may form multimers leading to more effective dipoles.

The excess inverse relaxation time $(1/\tau)^E$ which gives information regarding the dynamics of solute-solvent interaction and represents the average broadening of dielectric spectra can be defined [25] as

$$\left(\frac{1}{\tau}\right)^E = \left(\frac{1}{\tau}\right)_m - \left[\left(\frac{1}{\tau}\right)_1 x_1 + \left(\frac{1}{\tau}\right)_2 x_2\right]. \qquad (6)$$

The thermodynamic parameters excess Gibb's energy of activation $(\Delta G^*)^E$, excess molar enthalpy of activation $(\Delta H^*)^E$, and excess molar entropy of activation $(\Delta S^*)^E$ at different mole fractions can be determined by fitting the Eyring rate equation [26, 27] as

$$\tau = \frac{h}{kT} \exp\left(\frac{\Delta G^*}{RT}\right) = \frac{h}{kT} \exp\left(\frac{\Delta H^* - T\Delta S^*}{RT}\right), \qquad (7)$$

where h is the Planck's constant, k is the Boltzmann constant, T is the temperature in Kelvin, and R is the gas constant.

Minimum energy structures of the monomers NMA, 1PN, IPA, and the equimolar hydrogen bonded complexes are obtained from semiempirical Hamiltonian quantum mechanical calculations such as Austin Model 1 (AM1), Parameterized Model number 3 (PM3), and Modified Neglect of Differential Overlap (MNDO) converged geometry optimization procedure using PC Spartan and ArgusLab modeling softwares. *Ab initio* calculations have been carried out using PC Spartan modeling software and the geometry optimizations are done at the Hartree-Fock (HF) level using 6-31G* basis set.

3. Results and Discussion

We studied the temperature dependence on dielectric relaxation in pure and binary mixtures of N-methylaniline (NMA), propan-1-ol (1PN), and isopropyl alcohol (IPA) at different frequencies to understand the nature of molecular orientation processes [28]. The dielectric data is used to calculate Kirkwood effective correlation factor, corrective Kirkwood correlation factor, Bruggeman parameter, relaxation time and the thermodynamic parameters-Gibb's energy of activation, molar enthalpy, and molar entropy of activation. Conformational analysis of the formation of hydrogen bond between equimolar mixtures of propan-1-ol with benzoates is studied from FT-IR spectra. The theoretical vibrational frequencies of the pure and equimolar hydrogen bonded systems are obtained from Hamiltonian quantum mechanical calculations using Spartan modeling software. The same data is used to study excess dielectric parameters and reporting in this communication.

The dipole moment (μ) values for pure and equimolar systems (system 1 and system 2) at room temperature are determined experimentally with Higasi's method and theoretically with Hamiltonian quantum mechanical calculations (*ab initio* and semiempirical) and the corresponding values are given in Table 1.

The dipole moments for these systems are measured experimentally by diluting them in nonpolar solvent benzene. It is very clear from the experimental dipole moment values that there is an increase in the dipole moment of equimolar mixture when compared to the individual systems. This may be due to the formation of hydrogen bonding between the mixture systems [29]. The theoretical dipole moment values, mainly Hartree-Fock calculations, are in good agreement with the experimental values. The small deviation between the theoretical and experimental values may be due to the model dependency in theoretical case and due to the π electron cloud of nonpolar solvent benzene affecting the dipole moment value of the solute systems in experimental case [30]. The dipole moment values, measured for the pure and equimolar systems, are significantly affected by the variation in temperature as shown in Table 2.

The excess dipole moment ($\Delta\mu$) values obtained theoretically and experimentally (at different temperatures) are given in Tables 1 and 2. It is observed that in all cases the values of $\Delta\mu$ are negative which indicates the absence of any contribution from ionic structure of the binary system to the total dipole moment since the formation of an ionic structure involves a very high positive value for $\Delta\mu$ [31]. The excess dipole moment value is a qualitative index for the presence of hydrogen bonding in system 1 and system 2.

This shows that the strength of dipole-dipole interaction depends on the concentration and temperature of the mixture. The values of ΔF_{or}^E for system 1 are greater than system 2. This may be due to the interaction of the compounds in the mixture which produces structural changes.

The values of ΔF_{rr}^E predict the information on the short range interaction between similar molecules. In both systems the values of ΔF_{rr}^E are highly positive at all mole fractions, as shown in Table 4, indicating the existence of short range interaction through hydrogen bonding. The values of ΔF_{rr}^E for system 1 are greater than system 2 predicting the strong short range interaction between the components of similar molecules.

The values of ΔF_{12}^E predict the information on the strength of interaction between unlike molecules. In both systems, the values of ΔF_{12}^E have appreciable change with respect to concentration and temperature. This reveals that hetero association involves between the compounds varying with concentration and temperatures as shown in Table 5.

Finally the high positive values of ΔF^E for system 1 and system 2, Table 6, indicate the formation of β-clusters with antiparallel alignment [12]. Due to the formation of these β-clusters, the effective dipole moment will be decreased when compared to the sum of individual systems and thereby it destructs the angular correlation between nonideal molecules which may decrease its internal energy [33].

The long-range and short-range interactions between dipoles can be studied from the thermodynamical parameter excess Helmholtz free energy (ΔF^E) and its constituent parameters ΔF_{or}^E, ΔF_{rr}^E, ΔF_{12}^E [32].

The value of ΔF_{or}^E represents the long-range interaction between the dipoles in the mixture. In system 1 and system 2,

Table 1: Experimental and theoretical dipole moment (μ) and excess dipole moment ($\Delta\mu$) values in Debye for pure systems—NMA, 1PN, IPA, and equimolar systems—NMA + 1PN, NMA + IPA at room temperature (PCS: PC Spartan, AGS: ArgusLab).

Compound	Experimental		HF 6-31G* PCS		Theoretical											
					AM1				PM3				MNDO			
					PCS		AGS		PCS		AGS		PCS		AGS	
	μ	$\Delta\mu$	μ	$\Delta\mu$	μ	$\Delta\mu$	μ	$\Delta\mu$	μ	$\Delta\mu$	μ	$\Delta\mu$	μ	$\Delta\mu$	μ	$\Delta\mu$
NMA	1.87	—	1.48	—	1.48	—	1.48	—	1.24	—	1.24	—	1.11	—	1.13	—
1PN	1.57	—	1.67	—	1.47	—	1.54	—	1.40	—	1.43	—	1.35	—	1.39	—
IPA	1.63	—	1.71	—	1.61	—	1.62	—	1.52	—	1.53	—	1.43	—	1.44	—
NMA + 1PN	3.12	−0.32	3.02	−0.13	2.55	−0.40	2.75	−0.27	2.39	−0.25	2.02	−0.65	2.24	−0.22	2.27	−0.25
NMA + IPA	3.21	−0.29	3.10	−0.09	2.75	−0.34	2.38	−0.72	2.52	−0.24	2.12	−0.65	1.96	−0.58	1.93	−0.64

Table 2: Experimental dipole moment (μ) and excess dipole moment ($\Delta\mu$) values in Debye for pure systems—NMA, 1PN, IPA, and equimolar systems—NMA + 1PN, NMA + IPA at different temperatures.

| Temperature/K | NMA (μ) | 1PN (μ) | IPA (μ) | NMA + 1PN | | NMA + IPA | |
				(μ)	($\Delta\mu$)	(μ)	($\Delta\mu$)
303	1.87	1.57	1.63	3.12	−0.32	3.21	−0.29
308	1.83	1.59	1.69	3.17	−0.25	3.28	−0.24
313	1.89	1.60	1.68	3.31	−0.18	3.34	−0.23
318	1.88	1.58	1.69	3.25	−0.21	3.27	−0.30
323	1.91	1.62	1.74	3.43	−0.10	3.38	−0.27

Table 3: Variation of ΔF_{or}^{E} with mole fraction (x_2) of NMA in 1PN and IPA at different temperatures.

| X_2 | $T = 303$K | | $T = 308$K | | $T = 313$K | | $T = 318$K | | $T = 323$K | |
	NMA + 1PN	NMA + IPA	NMA + 1PN	NMA + IPA	NMA + 1PN	NMA + IPA	NMA + 1PN	NMA + IPA	NMA + 1PN	NMA + IPA
0	00.0000	00.0000	00.0000	00.0000	00.0000	00.0000	00.0000	00.0000	00.0000	00.0000
0.1	32.2230	27.7058	34.6322	26.8023	34.6322	21.0805	35.2345	17.4667	25.5977	19.2736
0.2	44.2690	43.3656	46.9794	40.6552	42.4621	36.7403	44.8713	32.8253	39.4506	29.5127
0.3	36.4391	29.5127	39.7518	26.2000	36.4391	24.2460	36.7403	14.7563	39.1495	12.3471
0.4	07.2276	−02.7103	06.0230	−06.3241	−01.8069	−13.2506	−2.7103	−18.9724	−01.8069	−15.6598
0.5	−32.8253	−32.5242	−36.7403	−40.3541	−46.0759	−48.7863	−42.4621	−49.9909	−39.4506	−47.2805
0.6	−69.2645	−65.6507	−73.1794	−78.9013	−86.7312	−85.8277	−80.7082	−81.3105	−78.6001	−75.8898
0.7	−98.7772	−91.2484	−106.3059	−109.6186	−116.5450	−117.4485	−106.3059	−115.6416	−108.7151	−108.414
0.8	−101.7887	−92.1519	−113.8347	−103.5956	−126.483	−99.6806	−111.1243	−96.0668	−106.6071	−99.0783
0.9	−77.9978	−55.7127	−85.8277	−71.3725	−78.6001	−76.4921	−75.8898	−73.1794	−76.4921	−71.3725
1	00.0000	00.0000	00.0000	00.0000	00.0000	00.0000	00.0000	00.0000	00.0000	00.0000

Table 4: Variation of ΔF_{rr}^{E} with mole fraction (x_2) of NMA in 1PN and IPA at different temperatures.

| X_2 | $T = 303$K | | $T = 308$K | | $T = 313$K | | $T = 318$K | | $T = 323$K | |
	NMA + 1PN	NMA + IPA	NMA + 1PN	NMA + IPA	NMA + 1PN	NMA + IPA	NMA + 1PN	NMA + IPA	NMA + 1PN	NMA + IPA
0	00.0000	00.0000	00.0000	00.0000	00.0000	00.0000	00.0000	00.0000	00.0000	00.0000
0.1	93.2360	72.5771	98.1749	69.2645	96.3680	56.0139	95.7657	46.0759	72.2760	48.4851
0.2	166.3552	143.6485	173.4624	136.1198	162.0187	125.8807	163.5244	113.2324	148.7681	104.1979
0.3	210.3231	169.2463	220.7429	162.9221	215.0211	151.7796	210.805	136.1198	205.8050	128.5910
0.4	215.1415	168.6440	220.4418	166.5359	213.2142	158.7060	206.2877	143.6485	203.7820	144.5520
0.5	198.0061	166.5359	203.2762	164.1267	201.4693	160.2118	200.5659	151.4784	201.4693	151.4784
0.6	171.8361	146.0577	180.0877	145.7566	180.9911	147.8646	179.7865	143.3474	180.9911	144.2508
0.7	132.4758	114.1358	140.6370	117.7496	147.2623	123.1703	145.7566	118.9542	145.7566	118.9542
0.8	85.8578	74.0829	93.6576	80.4070	102.3910	84.3220	98.1749	80.4070	98.1749	82.2139
0.9	38.3062	29.5127	43.9679	36.138	44.8713	40.6552	43.6667	38.8483	44.8713	39.1495
1	00.0000	00.0000	00.0000	00.0000	00.0000	00.0000	00.0000	00.0000	00.0000	00.0000

TABLE 5: Variation of ΔF_{12}^E with mole fraction (x_2) of NMA in 1PN and IPA at different temperatures.

X_2	$T = 303K$		$T = 308K$		$T = 313K$		$T = 318K$		$T = 323K$	
	NMA + 1PN	NMA + IPA	NMA + 1PN	NMA + IPA	NMA + 1PN	NMA + IPA	NMA + 1PN	NMA + IPA	NMA + 1PN	NMA + IPA
0	00.0000	00.0000	00.0000	00.0000	00.0000	00.0000	00.0000	00.0000	00.0000	00.0000
0.1	04.5660	03.5571	04.7283	03.3878	04.5556	02.2125	04.5433	01.4001	02.6182	01.6316
0.2	12.7254	11.1322	13.1707	10.5485	12.4053	09.5581	12.3508	08.2157	10.8613	07.2089
0.3	17.9897	15.0014	18.7276	14.9589	19.1441	14.0558	18.5466	12.3544	18.1683	11.1860
0.4	15.8424	13.7909	16.6357	14.0691	17.5316	13.8111	16.9762	12.0862	16.5832	12.0029
0.5	09.3078	08.0868	10.1822	09.2444	11.7528	09.9796	10.9800	09.3189	10.2016	09.0461
0.6	−00.7338	−00.4287	−0.4216	02.0523	02.4032	02.9171	01.0159	02.1709	00.3387	01.3464
0.7	−10.4347	−08.6805	−9.6881	−04.9768	−08.3641	−04.0990	−10.9610	−03.8869	−10.2385	−05.1880
0.8	−16.4193	−13.5920	−14.8587	−08.5288	−13.5373	−14.4807	−16.9548	−14.4175	−18.1462	−12.9819
0.9	−10.8746	−10.4485	−10.0267	−09.1445	−12.5144	−09.1620	−12.3988	−09.0969	−12.0188	−09.1149
1	00.0000	00.0000	00.0000	00.0000	00.0000	00.0000	00.0000	00.0000	00.0000	00.0000
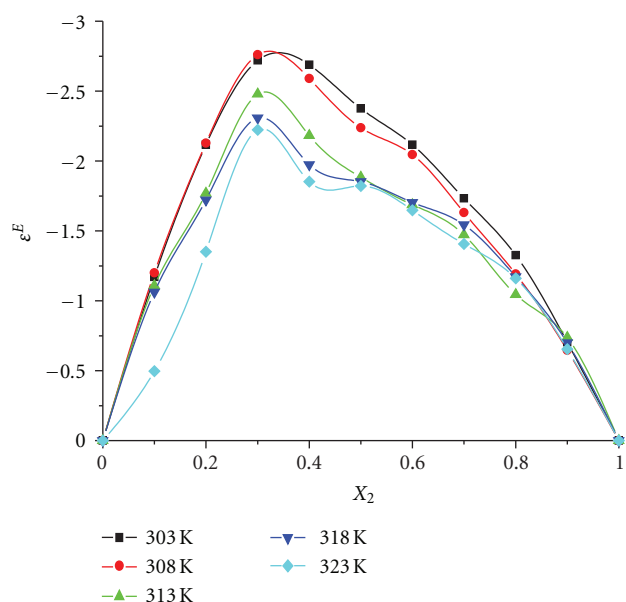
FIGURE 1: Plot of excess permittivity (ε^E) with mole fraction (x_2) of NMA in IPA at different temperatures.
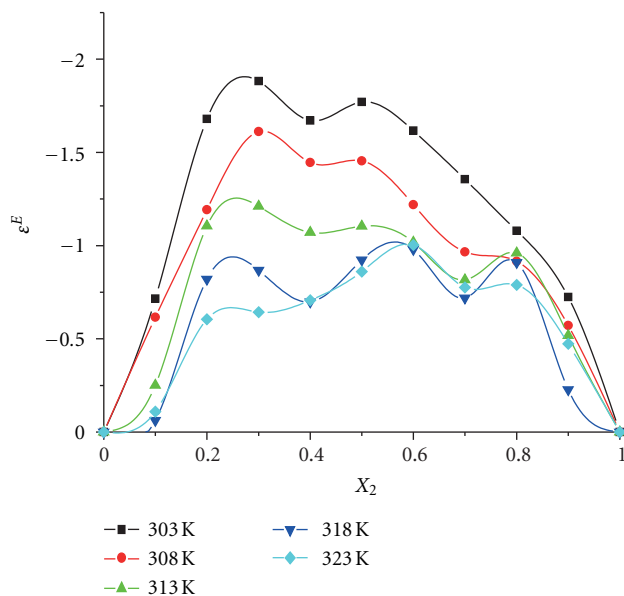
FIGURE 2: Plot of excess permittivity (ε^E) with mole fraction (x_2) of NMA in 1PN at different temperatures.

the positive values of ΔF_{or}^E indicate the existence of attractive forces between the dipoles and larger separation between the interacting molecules. Negative values of ΔF_{or}^E indicate the repulsive force between dipoles and interacting molecules are at closer distance. In both systems, values of ΔF_{or}^E are positive up to equimolar concentration and negative for remaining concentrations. The values of ΔF_{or}^E are decreasing for all the mole fractions, in both systems, as the temperature is increasing and are given in Table 3.

The decrement in the internal energy of molecule leads to the increment in the excess free energy value. The negative values of ΔF^E indicate the formation of α-clusters. Due to the formation of these α-clusters, the effective dipole moment will be increased which increases the internal energy.

The excess permittivity (ε^E) is another dielectric parameter, which gives information about the interaction between the components of the mixture. Rana et al. [34] had pointed out that the change in the value of ε^E with concentration is due to the interaction between dissimilar molecules which may produce structural changes. In system 1 and system 2, negative values of ε^E are obtained for all concentrations at different temperatures as shown in Figures 1 and 2, respectively. These negative values indicate that the molecules in the mixture form multimers through hydrogen bonding in such a way that the effective dipole moment gets reduced [35, 36]. The more negative deviations in ε^E values of system 1 compared to system 2 indicate that the strength of hydrogen bond formation is more in system 1 than in system 2.
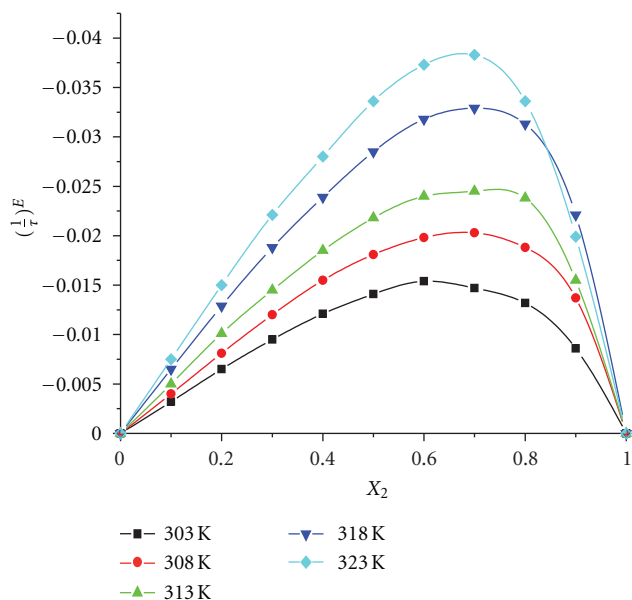
FIGURE 3: Plot of excess inverse relaxation time $((1/\tau)^E)$ with mole fraction (x_2) of NMA in 1PN at different temperatures.
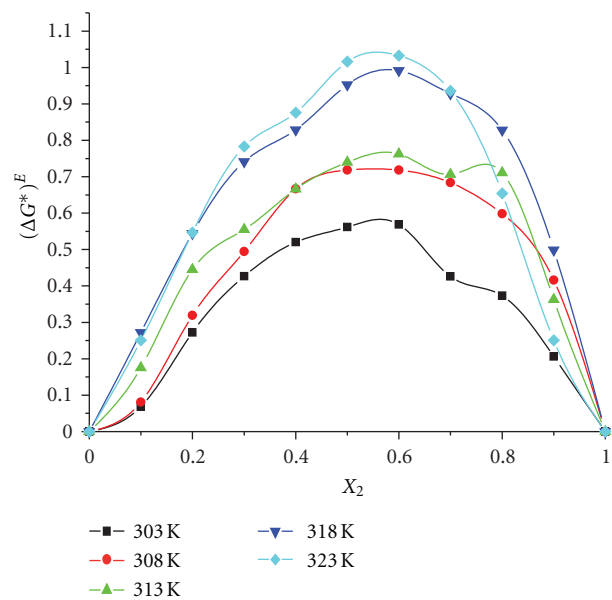

FIGURE 4: Plot of excess inverse relaxation time $((1/\tau)^E)$ with mole fraction (x_2) of NMA in IPA at different temperatures.

FIGURE 5: Variation of excess Gibb's energy of activation $(\Delta G^*)^E$ with mole fraction (x_2) of NMA in 1PN at different temperatures.
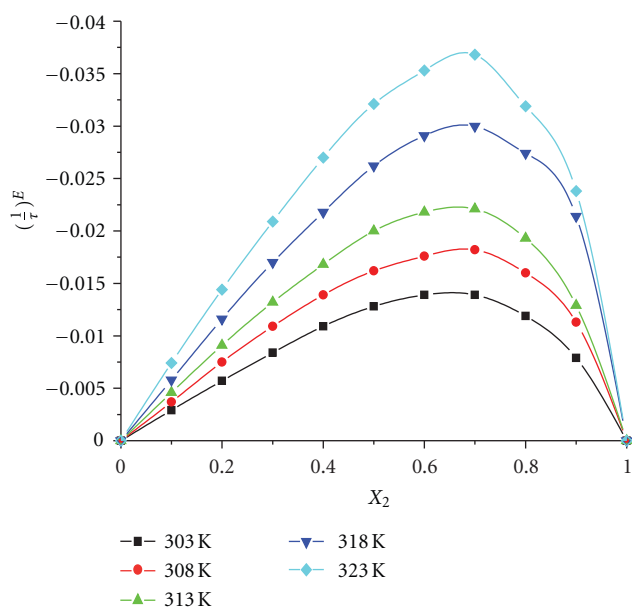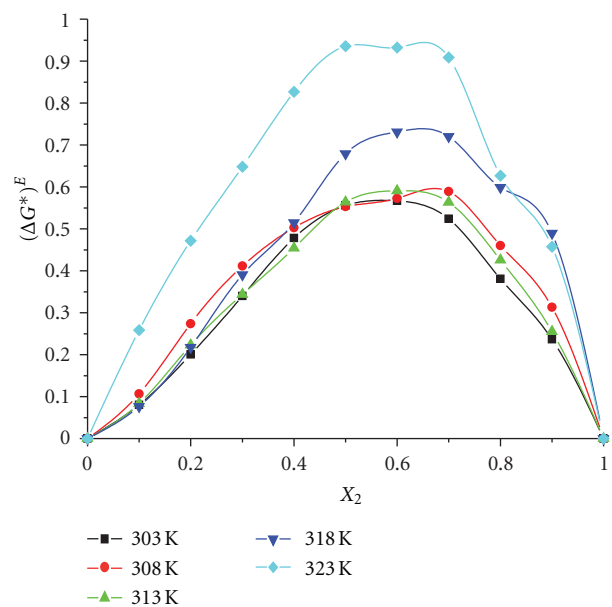

FIGURE 6: Variation of excess Gibb's energy of activation $(\Delta G^*)^E$ with mole fraction (x_2) of NMA in IPA at different temperatures.

The calculated values of excess inverse relaxation time $(1/\tau)^E$, for both systems, are negative and are presented in Figures 3 and 4 for the systems 1 and 2, respectively.

These negative values indicate the slower rotation of dipoles due to the formation of hydrogen-bonded structures producing a field, which hinders the effective dipole rotation [14, 25]. Further, it is observed that the negative deviations are more in case of system 1 than in system 2 which shows greater strength of intermolecular hetero interaction in system 1.

The variation of excess Gibb's energy of activation $(\Delta G^*)^E$ values, with mole fraction and temperature, for system 1 and system 2 are shown in Figures 5 and 6, respectively.

The values of $(\Delta G^*)^E$ are positive, in both systems, which indicates the presence of interaction between the molecules of the mixtures. The magnitude of $(\Delta G^*)^E$ is an excellent indicator of the strength of interaction between unlike molecules in liquid mixtures [37]. Ali and Nain [38] attributed the increasing positive values of $(\Delta G^*)^E$ in few binary liquid mixtures to hydrogen bond formation between

TABLE 6: Variation of ΔF^E with mole fraction (x_2) of NMA in 1PN and IPA at different temperatures.

X_2	T = 303K		T = 308K		T = 313K		T = 318K		T = 323K	
	NMA + 1PN	NMA + IPA	NMA + 1PN	NMA + IPA	NMA + 1PN	NMA + IPA	NMA + 1PN	NMA + IPA	NMA + 1PN	NMA + IPA
0	00.0000	00.0000	00.0000	00.0000	00.0000	00.0000	00.0000	00.0000	00.0000	00.0000
0.1	130.0250	103.8400	137.5354	99.4546	135.5558	79.3069	135.5435	64.9427	100.4919	69.3903
0.2	223.3496	198.1463	233.6125	187.3235	216.8861	172.1791	220.7465	154.2734	199.0800	140.9195
0.3	264.7519	213.7604	279.2223	204.0810	270.6043	204.1814	266.0919	163.2305	263.1228	152.1241
0.4	238.2115	179.7246	243.4016	174.2809	228.9389	159.2665	220.5536	136.7623	218.5583	140.8951
0.5	174.4886	142.0985	176.7181	133.0170	167.1462	121.4051	169.0838	110.8064	172.2203	113.2440
0.6	101.8378	79.9783	106.4867	68.9076	96.6631	64.9540	100.0942	64.2078	102.7297	69.7074
0.7	23.2639	14.2069	24.6430	03.1542	22.3532	01.6228	28.4897	−00.5743	26.8030	05.3522
0.8	−32.3502	−31.6610	−35.0358	−31.7174	−37.6293	−29.8393	−29.9042	−30.0773	−26.5784	−29.8463
0.9	−50.5662	−36.6485	−51.8865	−44.3790	−46.2432	−44.9989	−44.6219	−43.4280	−43.6396	−41.3379
1	00.0000	00.0000	00.0000	00.0000	00.0000	00.0000	00.0000	00.0000	00.0000	00.0000

TABLE 7: Heat of formation (E) and hydrogen bonding energy (ΔE) values in kcal mol^{-1} (PCS: PC Spartan, AGS: ArgusLab).

| Compound | AM1 | | | | PM3 | | | | MNDO | | | |
| | PCS | | AGS | | PCS | | AGS | | PCS | | AGS | |
	E	ΔE	E	ΔE	E	ΔE	E	ΔE	E	ΔE	E	ΔE
NMA	24.21	—	25.43	—	20.67	—	21.44	—	24.26	—	25.46	—
1PN	−68.92	—	−68.15	—	−61.57	—	−61.44	—	−67.71	—	−65.68	—
IPA	−68.03	—	−66.59	—	−63.94	—	−63.20	—	−65.41	—	−63.68	—
NMA + 1PN	−49.35	−4.64	−45.32	−2.60	−46.11	−5.21	−46.07	−6.07	−43.51	−0.06	−40.25	−0.03
NMA + IPA	−48.19	−4.37	−44.07	−2.91	−45.93	−2.66	−46.65	−4.89	−48.20	−7.06	−38.40	−0.19
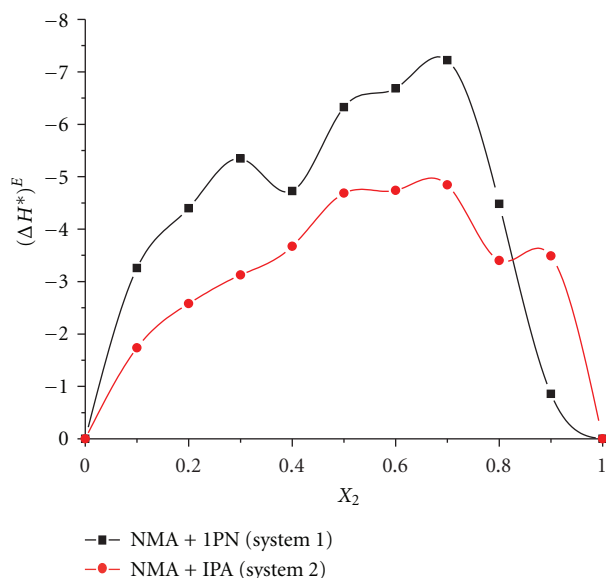
FIGURE 7: Variation of excess molar enthalpy $(\Delta H^*)^E$ with mole fraction (x_2) of NMA in 1PN and IPA.
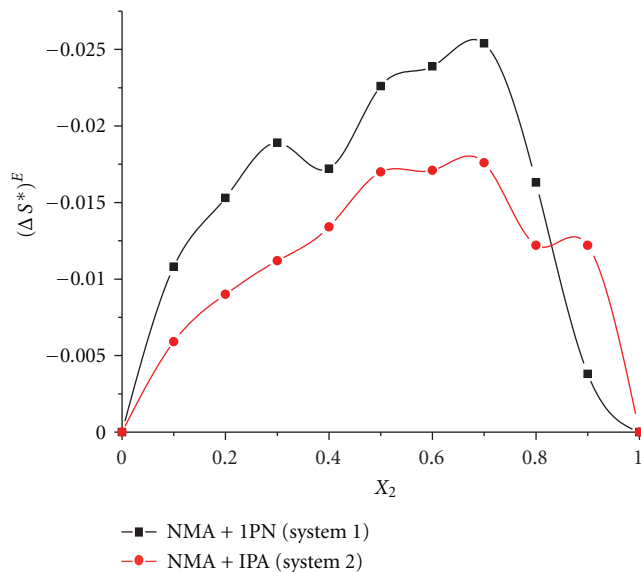
FIGURE 8: Variation of excess molar entropy $(\Delta S^*)^E$ with mole fraction (x_2) of NMA in 1PN and IPA.

unlike molecules, which supports the present investigation. Further, it is observed that $(\Delta G^*)^E$ values of system 1 are greater than that of system 2 indicating a stronger bond formation in system 1. The excess molar enthalpy $(\Delta H^*)^E$ and excess molar entropy $(\Delta S^*)^E$ values are shown in Figures 7 and 8, respectively. The negative values of $(\Delta H^*)^E$, for both the systems, show that strong attractive interactions are present between unlike molecules of the mixtures [39]. The formation of hydrogen bonding between the components in
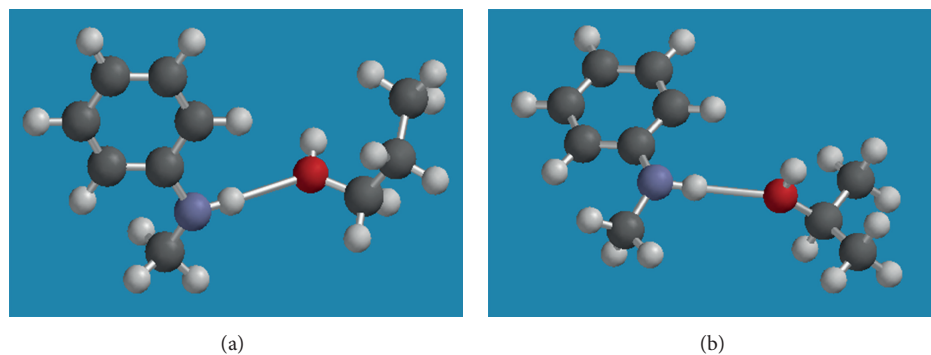
(a)

(b)

FIGURE 9: Optimized converged geometrical structures of hydrogen bonded (a) NMA AND 1PN and (b) NMA AND IPA (red: oxygen, blue: nitrogen, black: carbon, white: hydrogen).

system 1 and system 2 is also justified by the negative values of excess molar entropy [14].

The hydrogen bonding energy or the interaction energy (ΔE) values are calculated, for both systems, using Hamiltonian quantum mechanical calculations and are given in Table 7.

The interaction energy between the components of a mixture should be negative if that mixture is stabilized by the presence of hydrogen bonds. Moreover, the magnitude of the interaction energy would be a measure of the hydrogen-bonding stabilization. The hydrogen bonding energies in the present study are found to be negative in both the binary complexes, in all theoretical models, indicating the formation of hydrogen bonding [30]. The optimized converged geometrical structures of hydrogen bonded systems 1 and 2, which are obtained from Hamiltonian quantum mechanical calculations, are shown in Figures 9(a) and 9(b), respectively.

Studying the variations in the above dielectric and thermodynamical parameters, one can observe some sort of correlation among them leading to structural changes in mixture. For instance, the high positive values of ΔF^E, for the present systems, indicate the formation of β-clusters with antiparallel alignment. Due to this, the effective dipole moment will be decreased when compared to the sum of individual systems, which gives negative values of excess dipole moment and excess permittivity. Further, the formation of β-clusters destructs the angular correlation between nonideal molecules which may decrease the internal energy and thus giving negative values of interaction energy (ΔE). Another observation in the present study is that the relaxation time decreases as the temperature increases, which gives negative values of excess inverse relaxation time. This may be due to the decreasing viscosity of medium. With increase in the temperature, the thermal agitation increases and the dipole requires more energy in order to attain the equilibrium with the applied field and results in negative excess molar entropy values. This indicates that the activated state is more ordered than the normal state, which is true because in the activated state the dipoles try to align with the applied field. Thus the parameters determined in the paper correlate one another

and at the same time each parameter supports the formation of hydrogen bonding between the mixture systems.

4. Conclusion

The dielectric and thermodynamic parameters, dipole moment, excess dipole moment, excess Helmholtz free energy, excess permittivity, excess inverse relaxation, and excess thermodynamical values, are computed for the pure and binary mixtures of the systems N-methylaniline with propan-1-ol (system 1) and N-methylaniline with isopropyl alcohol (system 2) for various mole fractions at different temperatures. The formation of hydrogen bonding between the mixture systems is identified by studying the variations in the parameters determined. Using quantum mechanical calculations, the values of dipole moment and excess dipole moment are determined theoretically and they are in good agreement with the experimental values.
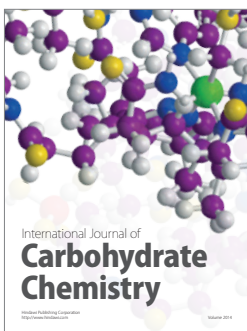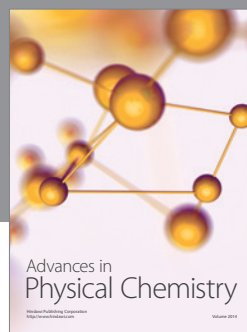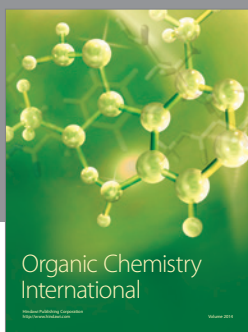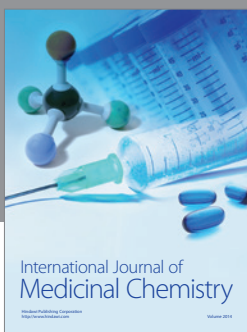
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