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Study of molecular interactions in the polar binary mixtures of N-methyl aniline and alcohols, using excess dielectric and thermodynamic parameters

T. Vijaya Krishna [a,*], T. Madhu Mohan [b]

[a] Department of Physics, Vasireddy Venkatadri Institute of Technology, Nambur 522 508, India
[b] Department of Physics, Hindu College Techno Campus, Amaravathi Road, Guntur 522 002, India

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ABSTRACT

Molecular interactions between the polar systems N-methyl aniline and alcohols (propan-1-ol/propan-2-ol) 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. The dipole moment, excess dipole moment, excess Helmholtz energy, excess permittivity, excess inverse relaxation time and excess thermodynamic values are calculated using experimental results. The optimized geometry, harmonic vibrational wave numbers and dipole moments of pure and equimolar binary mixtures have been calculated theoretically from the *ab initio* Hartree–Fock (HF) and Density Functional Theory (DFT – B3LYP) methods with 6-31+G* and 6-311+G** basis sets using Spartan 08 modelling software. Conformational analysis of the formation of hydrogen bond in the equimolar binary mixture systems of N-methyl aniline and alcohols (propan-1-ol/propan-2-ol) is supported by experimental FT-IR spectra. The calculated wave numbers and dipole moments agree well with the experimental values. Further, the correlations among the parameters are discussed in detail.

1. Introduction

Molecular interaction studies play an important role in understanding the structure and properties of liquids and liquid mixtures. Hydrogen bonding plays an important role in governing the structure and the dynamics of chemical and biological systems [1]. Hydrogen bonding is complex in the liquid state because of the uncertainty in identifying the particular bonds and the number of molecules involved. The local structures of hydrogen bonded liquids are complicated due to molecular clusters and network structures. Dielectric and thermodynamic investigations of solutions containing varying amounts of interacting molecules help to detect the formation and composition of hydrogen bonded complexes, since the presence of hydrogen bond brings a considerable change in the dielectric and thermodynamic properties of liquid mixtures [2]. In particular, the excess dielectric and thermodynamic properties of mixtures are more useful in the study of molecular interactions and arrangements [3].

The component liquids taken for the present investigation are amine and alcohols. Aromatic amines, which are non-associative, are very important in the production of dyes, pesticides and antioxidants [4]. 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 (amine) and –OH (alcohol) groups plays an important role in biological systems and drug synthesis [5]. The dielectric relaxation and spectroscopic studies on the binary mixture systems of propan-1-ol with benzoates and propan-2-ol with aniline have been carried out to understand the nature of molecular interactions [6,7].

The present work aims at studying the dielectric and thermodynamic behavior of pure and binary mixtures of N-methyl aniline with propan-1-ol (system 1) and N-methyl aniline with propan-2-ol (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 energy, excess permittivity, excess inverse relaxation time and excess thermo dynamical values are calculated for the pure and binary mixtures [8–11]. The theoretical vibration frequencies and dipole moments of the pure and equimolar hydrogen bonded systems are obtained from the Hamiltonian quantum mechanical calculations [12,13] *i.e.*, *ab initio* Hartree–Fock (HF) and Density Functional Theory (DFT – B3LYP) methods with 6-31+G* and 6-311+G** basis sets using Spartan 08 modelling software [14]. Conformational analysis of the formation of hydrogen bond in the equimolar binary mixture systems of N-methyl aniline with propan-1-ol/propan-2-ol is supported by the experimental

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* Corresponding author. Tel.: +91 9490743400.
E-mail address: tvijayakrishna1980@gmail.com (T. Vijaya Krishna).

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FT-IR spectra. The derived theoretical values are compared with the experimental values.

2. Experimental

2.1. Materials

The compounds N-methyl aniline (NMA), propan-1-ol (1PN), propan-2-ol (2PN), and benzene of AR grade are procured from Merck, Germany. All the liquids used were further purified by standard procedure [15]. The specifications of the purity of samples and the comparison of the experimental and literature values [16,17] of some basic parameters are given in tables 1a and 1b.

2.2. Procedure

The binary mixtures are prepared for different mole fractions *i.e.*, mole fraction (x_2) of alcohols (1PN/2PN) is varied from 0 to 1 for both system 1 and system 2 (with a step increment of 0.1). The permittivity values at spot frequencies 1 kHz ($\varepsilon_{\text{static}}$), 10 kHz, 100 kHz, 1 MHz, and 10 MHz for the above systems are measured using a HP-LF impedance analyzer (Model No: 4192 A) at temperatures, T = (303.15, 308.15, 313.15, 318.15, and 323.15) K. The real (ε') and imaginary (ε'') parts of the complex dielectric permittivity ($\varepsilon^* = \varepsilon' - \varepsilon''$) are determined with Microwave bench (X-Band, 8.60 GHz) using the Plunger method [18] at different 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 temperature controller system with a water bath, supplied by M/s Sakti Scientific Instruments Company-India, has been used to maintain the constant temperature with an uncertainty ±0.1 K. The mass measurements are performed on a digital electronic balance (Mettler Toledo AB 135, Switzerland) with an uncertainty of ±0.00001 g. The densities of the pure liquids are measured at the corresponding temperatures by using a 10 cm^3 specific gravity bottle. The average uncertainties in the measurement of $\varepsilon_{\text{static}}$, ε_∞, ε', ε'' and density are ±0.002, ±0.0002, ±0.01, ±0.03, and ±0.0001 $\text{g} \cdot \text{cm}^{-3}$ respectively [8]. The average uncertainties in the measurement of dipole moment, Helmholtz energy and relaxation time are ±0.02 D, ±0.001 $\text{J} \cdot \text{mol}^{-1}$ and ±0.02 ps respectively [8,10]. The FT-IR-spectra of pure and equimolar binary mixture systems are recorded in the 400 to 4000 cm^{-1} region on Perkin–Elmer (spectrum bX) series.

3. Theory

Higasi's method [9] is used to measure the dipole moments for the pure and equimolar systems (system 1 and system 2), by diluting them in non-polar solvent benzene.

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

where M_2 is molar mass 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, ε_1 is the static dielectric permittivity of solvent (benzene).

The excess dipole moments ($\Delta\mu$) [8] of the systems are determined by equation (2)

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

where μ_1 is the dipole moment of NMA, μ_2 is the dipole moment of either 1PN or 2PN and μ_{12} is the dipole moment of the equimolar solute mixtures (NMA + 1PN) or (NMA + 2PN).

The excess Helmholtz energy (ΔA^{E}) is a dielectric parameter to evaluate the interaction between the components in the mixture through breaking mechanism of hydrogen bond [19] and is expressed as

$$\Delta A^{\text{E}} = \Delta A^{\text{E}_{\text{or}}} + \Delta A^{\text{E}_{\text{rr}}} + \Delta A^{\text{E}_{12}}, \tag{3}$$

where $\Delta A^{\text{E}_{\text{or}}}$ represents the excess dipolar energy due to long range electrostatic interaction, $\Delta A^{\text{E}_{\text{rr}}}$ represents the excess dipolar energy due to the short range interaction between identical molecules, $\Delta A^{\text{E}_{12}}$ represents the excess free energy due to short-range interaction between dissimilar molecules.

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

$$\Delta A^{\text{E}} = \frac{-N_{\text{A}}}{2}\left\{\sum_{r=1,2} x_r^2\mu_r^2\left[R_{\text{fr}} - R_{\text{fr}}^0\right] + \sum_{r=1,2} x_r^2\mu_r^2[g_{rr} - 1]\left[R_{\text{fr}} - R_{\text{fr}}^0\right]\right.$$
$$\left. + x_1x_2\mu_1\mu_2\left[R_{f_1} + R_{f_2} - R_{f_1}^0 - R_{f_2}^0\right]\right\}, \tag{4}$$

where, $R_{\text{fr}}^0 = (\frac{8\pi N_{\text{A}}}{9V_{\text{r}}})\frac{(\varepsilon_{\text{r}}-1)(\varepsilon_{\infty\text{r}}+2)}{(2\varepsilon_{\text{r}}+\varepsilon_{\infty\text{r}})}, R_{fr} = (\frac{8\pi N_{\text{A}}}{9V_{\text{r}}})\frac{(\varepsilon_{\text{m}}-1)(\varepsilon_{\infty\text{r}}+2)}{(2\varepsilon_{\text{m}}+\varepsilon_{\infty\text{r}})}$, $g_{12} = g_f$ and V_{r} is the molar volume of the components. ε_r, $\varepsilon_{\infty\text{r}}$ are the dielectric permittivity values at static and optic frequencies of the pure liquids respectively.

The contribution of hydrogen bonds to the dielectric properties of the mixtures can be studied in terms of excess permittivity (ε^{E}).

TABLE 1a
Specifications of the chemical samples.

Chemical name	Source	Initial mole fraction purity	Purification method	Final mole fraction purity	Analysis method
N-methyl aniline (NMA)	Merck	0.990	Distillation	0.994	GC[a]
Propan-1-ol (1PN)	Merck	0.990	Distillation	0.992	GC[a]
Propan-2-ol (2PN)	Merck	0.990	Distillation	0.996	GC[a]

[a] Gas–liquid chromatography.

TABLE 1b
Comparison of experimental values of ε_{static}, refractive index, density and dipole moment values at room temperature (T = 300.15 K) with literature [16,17].[a]

Compound	$\varepsilon_{\text{static}}$		Refractive index		Density/($\text{g} \cdot \text{cm}^{-3}$)		Dipole moment/D	
	Experimental 300.15 K	Literature 293.15 K	Experimental 300.15 K	Literature 293.15 K	Experimental 300.15 K	Literature 298.15 K	Experimental 300.15 K	Literature 293.15 K
NMA	05.878	06.061	1.566	1.568	0.9798	0.9891	1.87	1.73
1PN	20.678	20.451	1.391	1.385	0.7985	0.7997	1.57	1.66
2PN	18.562	18.528	1.383	1.377	0.7792	0.7809	1.63	1.66

[a] Standard uncertainties u are u (ε_{static}) = 0.002, u (refractive index) = 0.0002, u (density) = 0.0001 $\text{g} \cdot \text{cm}^{-3}$ and u (dipole moment) = 0.02 D.