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FT-IR Spectroscopic study of excess thermodynamic properties of liquid mixtures containing N-methylformamide with 2-alkoxyethanols at various temperatures

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ABSTRACT

Densities, speeds of sound and viscosities were measured for the binary mixtures N-methylformamide (NMF) with 2-alkoxyethanols (2-methoxyethanol (ME), 2-ethoxyethanol (EE) and 2-butoxyethanol (BE)) at T = (303.15 to 318.15) K. These experimental data have been used to calculate excess volume (V^E), excess isentropic compressibility (κ_s^E), deviation in viscosity ($\Delta\eta$) and excess Gibbs free energy of activation of viscous flow (G^{*E}). The excess partial molar volumes, $\overline{V}_{m,1}^E$ and $\overline{V}_{m,2}^E$ and excess partial molar volumes $\overline{V}_{m,1}^{\circ E}$, and $\overline{V}_{m,2}^{\circ E}$ at infinite dilution have also been calculated. The variations of these properties with composition of binary mixtures suggest loss of dipolar association, difference in size and shape of the component molecules, dipole–dipole interaction and hydrogen bonding between unlike molecules. The excess parameters have been fitted to the Redlich–Kister equation and the results were analyzed in terms of acid–base interactions, hydrogen bond, and dipole–dipole interaction between unlike molecules. Further, the FTIR spectra have been recorded at 298.15 K and found to be useful for understanding the presence of hydrogen bonding between oxygen atom of carbonyl group of N-methylformamide and hydrogen atom of the –OH group of 2-alkoxyethanols molecules in the present liquid mixtures. A good agreement is obtained between excess quantities and spectroscopic data.

1. Introduction

Molecular properties in liquid state are very useful for design calculations involving separations, heat transfer, mass transfer and fluid flow. Mixing volume effects play a pivotal role in many practical applications that include paints, varnishes and printing ink industries. The present work is in continuation of our earlier studies [1–3] on understanding thermodynamic properties of binary mixtures whose components have relevant industrial applications. The study of physicochemical properties of amide + alkoxyalkanols mixed solvents is interesting because amides are convenient model systems for investigating peptide and protein–solvent interactions. N-methylformamide is chosen for the study, as it is the amide that contains a peptide linkage, the fundamental building block of proteins [4]. N-methylformamide molecules are polar and are self-associated through hydrogen bonds, through its hydrogen bond donors and three acceptors [5,6]. 2-Alkoxyethanols are oxygenated compounds and are increasingly used as additives to gasoline due to their octane enhancing and pollution reducing properties [7,8]. Moreover, 2-alkoxyethanols are polar, non-ionic amphiphile molecule, and very effective as surfactants with a large number of applications [9,10]. On the other hand, the investigation of mixtures involving 2-alkoxyethanols makes possible the study of self-association via inter and intra molecular hydrogen bonds related to the presence of the –OH (Hydroxyl) and –O– (ether) groups in the same molecule [11–14]. Since the components of these binary mixtures have both proton-donating/accepting abilities, significant interaction through hydrogen bonding between unlike molecules is expected. The presence of ethereal oxygen enhances the ability of –OH group of the same molecule to form hydrogen bonds with other unlike molecules.

The present paper reports densities, viscosities and speeds of sound of binary mixtures of N-methylformamide with 2-alkoxyethanols and those of pure liquids at T = (303.15 to 318.15) K, covering the entire composition range, expressed by the mole fraction of N-MFA. The experimental values of density, viscosity and speed of sound were used to calculate excess volume (V^E), excess isentropic compressibility (κ_s^E), deviation in viscosity ($\Delta\eta$) and excess Gibbs free energy of activation of viscous flow (G^{*E}) of N-methylformamide and 2-alkoxyethanols in the mixture over the whole composition ranges at T = (303.15 to 318.15). Further, the present work will provide that, an increasing chain length of 2-alkoxyethanols from methoxy to butoxy, it may

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influence both the sign and magnitude of excess thermodynamic functions. Moreover, FT-IR Spectroscopic data is also collected in the present investigation to know the existence of intermolecular hydrogen bonding between N-methylformamide and 2-alkoxyethanol molecules.

2. Experimental section

2.1. Materials

All the chemicals (A.R. grade) were used in the present work supplied by S.D. Fine Chem. Ltd., India. The purities of all the chemicals are as follows: N-methylformamide (>99%), 2-methoxyethanol (>99%), 2-ethoxyethanol (>98%) and 2-butoxyethanol (99%). 2-Alkoxyethanols were further purified by the methods as described in the literature previously [15–17]. Prior experimental measurements of all liquid samples were stored in dry-box over phosphorous pentoxide to reduce the water content and partially degassed by ultrasound. The mole fraction purities of the purified liquids as determined by gas chromatography are: N-methylformamide (0.997), 2-methoxyethanol (0.993), 2-ethoxyethanol (0.987), and 2-butoxyethanol (0.994). Name of the chemical, source, CAS number, purity in mass fraction and water content of the component liquids are given in Table 1.

2.2. Measurements

All the binary liquid mixtures are prepared by weighing an appropriate amount of pure liquids and electronic balance (Afoset, ER-120A, India) with a precision of ±0.1 mg by syringing each component into airtight stopper bottles to minimize the evaporation and moisture content. The uncertainty of the mole fraction was $\pm 1 \times 10^{-4}$. After mixing the sample, the bubble free homogenous sample is transferred into the U-tube of the densimeter through a syringe. The density measurements were performed with a Rudolph Research Analytical digital densimeter (DDH-2911 Model), equipped with a built-in solid-state thermostat and a resident program with accuracy of temperature of 298.15 K ± 0.03 K. The uncertainty of density measurement liquid mixtures is $\pm 2 \times 10^{-3}$ g·cm^{-3} and the uncertainty of temperature is ±0.01 K. Proper calibrations at each temperature were achieved with doubly distilled, deionized water and with air as standards. A multi frequency ultrasonic interferometer (M-82 Model, Mittal Enterprise, New Delhi, India) operated at 2 MHz, is used to measure the speed of sound, of the binary liquid mixtures at 298.15 K and 308.15 K by using a digital constant temperature water bath. The uncertainty in the measurement of speed of sound is ±0.3% and the uncertainty of temperature is ±0.02 K. The temperature stability is maintained within ±0.01 K by circulating thermostatic water bath around the cell with a circulating pump. In order to minimize the uncertainty of the measurement, several maxima are allowed to pass and their number (50) in the present study is counted. All maxima are recorded with the highest swing of the needle on the micrometer scale. The total distance d (cm) moved by the reflector is given by $d = n\lambda/2$, where λ is the wave length. The frequency, ν, of the crystal being accurately known (2.0 MHz), the speed of sound, u in ms^{-1} is calculated by using the relation $u = \nu\lambda$. The details of its calibration, the experimental setup and measuring procedure have been described previously [18]. The viscosities of pure liquids and their mixtures were determined at atmospheric pressure and at T = 303.15 to 318.15 K by using an Ubbelohde viscometer, which was calibrated with benzene, carbon tetrachloride, acetonitrile, and doubly distilled water. The kinetic energy corrections were calculated from these values and they were found to be negligible. The Ubbelohde viscometer bulb has a capacity of 15 ml and the capillary tube has a length of about 90 mm with 0.5 mm internal diameter. The viscometer was thoroughly cleaned and perfectly dried, and also filled with the sample liquid by fitting the viscometer to about 30° from the vertical and its limbs are closed with Teflon caps to avoid the evaporation. The viscometer was kept in a transparent walled bath with a thermal stability of ±0.01 K for about 20 min to obtain thermal equilibrium. An electronic digital stopwatch with an uncertainty of ±0.01 s was used for flow time measurements. The uncertainty of viscosity thus estimated was found to be ±0.005 mPa/s. The purity of all these solvents is compared with the measured density, speed of sound and viscosity of the pure liquids with the literature [19–28] and these are shown in Table 2. FTIR spectra have been measured by ALPHA FT-IR Spectrometer (Bruker) to study the existence of intermolecular hydrogen bonding between N-methylformamide and 2-alokoxyethanols.

3. Results and discussion

3.1. Excess volumes (V^E)

Table 3 lists the experimental values of densities (ρ), speeds of sound (u) and viscosities (η) of the binary mixtures along with the corresponding mole fractions of N-methylformamide at all experimental temperatures.

The excess volume data of all the liquid mixtures were computed by using the following formula

$$V^E/cm^3.mol^{-1} = [x_1M_1 + x_2M_2]/\rho - [x_1M_1/\rho_1 + x_2M_2/\rho_2] \quad (1)$$

where x_1 and x_2 are the mole fractions of N-methylformamide with 2-alkoxyethanols respectively; M_1 and M_2 and ρ_1 and ρ_2 are the molecular weights and densities of components 1 and 2 respectively and ρ is the density of the mixture.

The V^E data for all the binary systems of N-methylformamide with 2-alkoxyethanols were reported in Table 4 and graphically represented in Figs. 1–4. An examination of V^E data in Figs. 1–4 suggests that excess volume (V^E) data for the mixtures N-methylformamide with 2-alkoxyethanols are negative over the entire composition range at all temperatures. The experimental V^E values can be ascribed qualitatively by considering the factors which influence the excess functions, and these functions depend upon several contributions arising from physical, chemical and structural effects [29,30]. The physical contributions comprising of dispersive forces or weak dipole–dipole interactions lead to positive V^E values. Chemical contributions include breaking up of associates present in pure liquids resulting in positive V^E and specific interactions, like formation of strong hydrogen bonds, charge-transfer complexes and other complex forming interactions including strong dipole–dipole interactions between component molecules, resulting in negative V^E values. The structural contributions include the geometrical fitting of molecules of different molecular sizes into each other's [31] yielding negative V^E values. An examination of V^E data in Table 4 suggests that the factors which are contributing in contraction in volume were dominant in all the liquid mixtures in the investigated temperatures.

Table 1
Provenance and purity of the materials used.

Chemicals	CAS number	Source	Water content in mass fraction	Purity in mass fraction (after purification)
N-methylformamide	123-39-7	Sigma Aldrich, India	0.0005	0.997
2-methoxy ethanol	109-86-4	S.D. Fine Chemicals, India	0.0004	0.993
2-ethoxy ethanol	110-80-5	S.D. Fine Chemicals, India	0.0004	0.987
2-butoxy ethanol	111-76-2	S.D. Fine Chemicals, India	0.0004	0.994