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Thermodynamic, ultrasonic and FT-IR studies on binary liquid mixtures of anisaldehyde and alkoxyethanols at different temperatures

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ABSTRACT

The experimental density, viscosity, and ultrasonic speeds of anisaldehyde (AA) and alkoxyethanols namely 2-methoxy ethanol (MOE), 2-ethoxy ethanol (EOE) and 2-butoxy ethanol (BOE) have been measured over the full range of compositions at atmospheric pressure and at different temperatures (303.15, 308.15, 313.15 and 318.15 K). From these experimental values the molar volume (Vm), adiabatic compressibility (βad) and intermolecular free length (L_f), are computed and their excess properties along with deviation in viscosity ($\Delta\eta$) are fitted to Redlich–Kister type equation, a multi parametric nonlinear regression analysis technique to derive the binary coefficients and to estimate the standard deviation between experimental and calculated data. The experimental data of viscosity is also used to test the applicability of empirical relations of Grunberg–Nissan, Katti–Chaudhri, Heric–Brewer and Hind et al. for the systems studied. Further, FT IR analysis of these binary mixtures at different concentrations, confirms the presence of hydrogen bonding, and supported the results as observed in thermodynamic analysis with respect to forces of association/dispersion between unlike molecules. The interaction of AA with alkoxyethanol is found to decrease with increase in alkyl chain length of the alkoxy group.

1. Introduction

Chemical thermodynamics is used to predict whether a mixture of reactants has a spontaneous tendency to change into products, to predict the composition of the reaction mixture at equilibrium, and to predict how that composition will be modified by changing the conditions. Physico-chemical and thermodynamic investigations play an important role in understanding the nature and extent of the patterns of molecular aggregation that exist in binary liquid mixtures due to their sensitivities to variations in composition and the molecular structure of the pure components [1,2]. The experimental data of excess thermodynamic properties of liquid mixtures provide useful information about molecular interactions and can be used to test thermodynamic models [3–5]. Interactions of the type: ion–ion, ion–solvent, and solvent–solvent within the liquid system are understood by the interpretation of data obtained from thermo-chemical, electrochemical, biochemical, and kinetic studies. The physical properties, such as density, viscosity, surface tension, refractive index, dielectric constant, molar polarization, group frequency shift in IR spectra, etc. give important information about the overall changes resulting from various interactions that occur when liquids are mixed together.

Alkoxyethanols are a very interesting class of substances from a practical point of view, as oxygenated compounds are increasingly used as additives to gasoline due to their octane enhancing and pollution-reducing properties [6,7]. They have wide use as monomers in the production of polymers and emulsion formulations. Alkoxyethanols are considered as constituted of two different functional subgroups viz., an ether subgroup (R-O-), which includes an oxygen atom attached to a methylene group, and a primary alcohol sub group (–OH). From a theoretical point of view, mixtures containing alkoxy alcohols are very important, not only because of their self association but also due to the strong intra-molecular effects which is produced by the presence of –O and –OH groups in the same molecule [8]. In particular, the formation of the intra-molecular H-bonds leads to enhanced dipole–dipole interactions in solutions containing oxy-ethanols and alkanes relative to those present in mixtures with homomorphic alkanols [9]. There has been a recent upsurge of interest in the study of thermodynamic properties of binary liquid mixtures [10,11]. Different spectroscopic techniques like IR and NMR have been used to investigate the existence of intra-molecular hydrogen bonds [12], even in vapor phase. For molecules of the type $CH_3-(CH_2)n-O-(CH_2)n-OH$, 5 or 6 or 7 membered rings are formed (for $n=2$, 3 and 4 respectively). It is reported that, alkoxyethanols with two ether groups and $n=1$ form 5-membered rings similar to those previously cited; but can also form 8-membered rings of quite different properties [13].

P-anisaldehyde ($CH_3OC_6H_4CHO$) — an aromatic pale clear liquid, with a methoxy group in para-position of the benzene ring. Chemically

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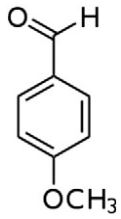
it is 4-methoxy-benzaldehyde, which is soluble in alcohol and ether and insoluble in water.



Detailed research has shown that research work has been done on the binary mixtures of anisaldehyde with a variety of compounds. Less amount of work is done with anisaldehyde as common compound. It's been studied with acetonitrile [14]; cresols [15] halobenzenes [16] benzenes [17]. It is evident from the existing available data that no work is yet done on the binary mixtures of alkoxyethanols and anisaldehyde.

The present work reports the density (ρ) and viscosity (η) for binary mixtures of anisaldehyde (AA) with 2-methoxyethanol (MOE), 2-ethoxyethanol (EOE), and 2-butoxyethanol (BOE) over the entire range of composition at 303.15 K, 313.15 K, and 323.15 K, and the derived thermodynamic properties of the above mentioned binary mixtures. It is also aimed to study the molecular interactions between AA and alkoxyethanols, giving a stress on dipole induced interactions and hydrogen bonding. The infrared spectroscopic studies (FT-IR) further support/reveal the existence of specific interactions through their bond stretching vibrations/change in intensity in specific wave lengths. Further, the empirical relations of viscosity like Katti–Chaudhry, Grunberg–Nissan Heric Brewer and Hind et al. are tested for the applicability on the experimental viscosity data of all systems studied.

2. Experimental

2.1. Materials and method

2-methoxyethanol (MOE); 2-ethoxyethanol (EOE) and 2-butoxyethanol (BOE) and anisaldehyde (AA) were purchased from S.D Fine Chemicals India and were purified as described in the literature [18]. The pure chemicals were stored over activated 4 Å molecular sieves to reduce water content before use. The chemicals after purification were 99.8% pure, and their purity was ascertained by GLC and also by comparing experimental values of density, viscosity, and ultrasound velocity with those reported in the literature when available, as presented in Table 1.

The binary mixtures are prepared gravimetrically using an electronic balance (Shimadzu AY120) with an uncertainty of $\pm 1\times10^{-7}$ kg and stored in airtight bottles. The uncertainty on mole fraction is estimated to be 1×10^{-4}. It is ensured that the mixtures are properly mixed and the measurement of the required parameters was done within one day of preparation.

The viscosity, η, of the pure liquids and liquid mixtures is determined using an Ubbelohde suspended-level viscometer. The viscometer is suspended in a thermostatted water bath in which the temperature is maintained constant to ±0.01 K. Three sets of readings for the flow time are taken by using a Racer stop watch that can register time to ±0.01 s, and the arithmetic mean is taken for the calculation of the viscosity. Because the flow times are greater than 200 s and the capillary diameter is 0.55 mm, which is much less than the tube length of 100 mm, both kinetic energy and tube end corrections are negligible. The viscometer is calibrated with triple distilled water and dry cyclohexane.

It is estimated using the following formula:

$$\eta/\eta_w = \rho\, t/\rho_w t_w. \quad (1)$$

The estimated uncertainty in the viscosity measurements is found to be less than 1%.

The densities, ρ, of pure liquids and their mixtures are determined using a 10^{-5} m^3 double-arm pycnometer, and the values from triplicate replication at each temperature are reproducible within 2×10–1 kg m^3. The pycnometer is calibrated using conductivity water with 995.61 kg m^{-3} as its density at 303.15 K. The position of the liquid levels, in the two arms of the pycnometer (which is made sure that it is air bubble-free), is recorded with the help of a traveling microscope that could be read to 0.01 mm, and the uncertainty in the measurement of density is found to be 2 parts in 10^4 parts. The reproducibility in mole fractions was within ±0.0002.

Temperature control for the measurement of viscosity and density is achieved by using a microprocessor assisted circulating water bath, (supplied by Mac, New Delhi) regulated to ±0.01 K, using a proportional temperature controller. Adequate precautions were taken to minimize evaporation losses during the actual measurements.

Ultrasonic velocity of sound (u) were determined by a multifrequency ultrasonic Interferometer (Mittal Enterprise, New Delhi, M-81) working at 1 MHz, The uncertainty of the ultrasonic velocity measurements was 0.8 m s^{-1}.

IR measurements for all the three binary mixtures of AA over the entire composition range are recorded through Nicolet nexus 670 spectrometer (Germany), using KBr pellet in the region (400 to 4000) cm^{-1} with 4.0 cm^{-1} resolution. The uncertainty in the measurement of wave number is within ±0.1 cm^{-1}.

2.2. Calculations

Following are the equations adopted for calculating the parameters from the measured parameters mentioned above.

$$\text{Adiabatic compressibility } \beta ad = \left(\rho\ U^2\right)^{-1} \quad (2)$$

Table 1
Comparison of density ρ, viscosity η and ultrasonic velocity U, of the pure liquids with literature data at 303.15 K.

Compound	Experimental $\rho\times10^{-3}$ kg/m^3	Literature $\rho\times10^{-3}$ kg/m^3	Experimental η/m·pas	Literature η/m.pas	Experimental u/m·s^{-1}	Literature u/m·s^{-1}
Anisaldehyde	1.1204	1.1200[a]	3.5783	3.5783[a]	1543.0	1542.0[a]
M.O.E	0.9527	0.9558[b]	1.5476	1.544[d]	1354.0	1359.2[c]
E.O.E	0.9186	0.9212[b]	1.6315	1.643[b]	1314.4	1319.2[c]
B.O.E	0.8921	0.8923[b]	2.4031	2.408[b]	1321.4	1322.0[c]

[a] [38].
[b] [39].
[c] [40].
[d] [41].