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Volumetric, isentropic compressibility and viscosity coefficient studies of binary solutions involving amides as a solute in aqueous and CCl_4 solvent systems at 298.15 K

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ABSTRACT

The experimental measurements of the density, speed of sound and viscosity coefficient in binary solutions involving water and CCl_4 as solvents and formamide, *N*-methylformamide, *N*, *N*-dimethylformamide, *N*-methylacetamide and *N*, *N*-dimethylacetamide as solute in the concentration range (0.00992 mol·kg^{-1} to 1.07890 mol·kg^{-1}) at 298.15 K are reported. The data are used to obtain the isentropic compressibility (β_s) of solutions and Jones-Dole viscosity B and D coefficients for solutes. The derived properties like apparent molar volume (V_ϕ) and apparent molar isentropic compressibility (K_ϕ) of amides at different concentrations are evaluated. The data of limiting apparent molar volume (V_ϕ^0) and apparent molar isentropic compressibility (K_ϕ^0) for amides in both solvent systems (H_2O and CCl_4) and their concentration variation are examined to study the effect of intermolecular H-bond formation (for the amide molecules), hydrophobic interaction effect in water and amide-CCl_4 interactions. It has been observed that there is loss of volume and compressibility of amide molecules in transferring them from pure liquid state to water and gain in transferring to CCl_4 solutions (non-aqueous solvent) except for dimethylacetamide. The transfer volumes and compressibilities from CCl_4 to water are negative and are attributed to —H bond formation between solute molecules. The viscosity B coefficients for the amides are found to be high positive in water while they are of small magnitude in CCl_4 medium. All these results are discussed on the basis of solute-solvent interaction, hydrophobic interaction in water and H-bond formation possibilities in CCl_4. It is proposed that, the dissolution of dimethylformamide in water takes place substitutionally in water cavities with very little volume change.

1. Introduction

The primary step of many biochemical reactions can be thought of as a process in which the reactant is transferred from pure liquid state to one medium or from one medium to another. These provide subtle information about the binding sites, specific non-covalent bonds interactions, solvation and hydrophobic interaction effects. The importance of such medium effects are now well recognized and proved to shed light on phenomena related to protein denaturation, water structural effects and many results are now available on solute-solvent interactions for simple model systems [1–7].

Monosubstituted amides have been observed to be associated in chains both in the pure state and in certain solvents. The chain like structure is caused by hydrogen bonding of the amide proton on one amide molecule to the carbonyl oxygen on another amide molecule. Klotz and Franzen [8] studied the thermodynamics of the interamide hydrogen bond formation of *N*-methylacetamide at 298.15 K in CCl_4, dioxane and water. A comparison of the thermodynamic quantities among the three solvents studied lead to the conclusion that the value of the free energy and hence stability is largely determined by the enthalpy of the system. Water can form —H bonds with the amides and hence there is disruption of interamide hydrogen bonds. Hinton and Amis [9] have studied PMR of aqueous *N*-methylacetamide solutions and concluded that this amide causes structure breaking and making effect on water constitutes opposing effects which cause a periodicity in the water chemical shift-water mole-fraction curve.

Enthalpies of solutions in water, CCl_4 and MeOH for *N*-alkylamides were reported by Wadsö et al. [10] at 298.15 K. Using the data these workers reported values for association constants and enthalpies of association for alkyl amides in CCl_4 solutions. They noted that, the significant heat-capacity effects can be found for transfer processes, where no water is involved. For the alcohol solutions, the specific heat capacity of solute at infinite dilution ($C_{P_2}^0$) values are nearly identical to that of pure amide whereas a significant excess value is found for the CCl_4 solution.

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Viscosity coefficient studies of aqueous solutions of amides in water at 298.15 K have been reported by Herskovits and Kelly [11]. They observed a positive viscosity B coefficient values. The observed effect is attributed to the water structure-forming and structure breaking influence of the non-polar hydrocarbon portion and the polar $-CONH_2$ portion of these compounds. They noted that the hydrophobic influence of the solute on the structure of water should contribute to the viscosity increment of aqueous solutions, which is most noticeable in case of the higher homologs of the amides.

Patil and co-workers [12] using a volume and compressibility data for solutions of amides in H_2O and D_2O studied the energy volume coefficient (internal pressure) variation as a function of amide concentration. The examined trends in limiting transfer properties (for volume and compressibility) and the results have been interpreted in terms of effects of amides on the water structure through H-bonding and hydrophobic interactions.

For the studies of solute-solvent interactions, transfer functions especially in H_2O and D_2O or H_2O and CCl_4 for solutes have been proved to be very useful tool, since they eliminate the solid or gaseous state as a reference for the thermodynamic functions [13,14]. In this communication, we report the experimentally obtained density, sound velocity and viscosity coefficient data for aqueous solutions and CCl_4 solutions for rationally chosen amides, namely formamide (FA), *N*-methylformamide (NMF), *N*, *N*-Dimethylformamide (DMF), *N*-methylacetamide (NMA) and *N*, *N*-dimethylacetamide (DMA) at 298.15 K and at ambient pressure. The binary solutions of formamide could not be studied in carbon tetrachloride (CCl_4) due to solubility problems. The data of sound velocity and density have been used to calculate adiabatic compressibility (β_{ad}) of solutions. Further the derived properties like apparent molar volume and apparent molar compressibility of amides as a function of molality were calculated and used to obtain limiting, that is, infinite dilution values for volume and compressibility of amide molecules. Subsequently, these data were used to obtain the transfer functions related to volume of transfer and compressibility of transfer for amides from CCl_4 to water solutions. The viscosity coefficient data are subjected to analysis by applying Jones-Dole equation, the viscosity B and D coefficients along with the Einstein-Simha factor were calculated. The details about all these are presented and discussed.

2. Experimental procedure

2.1. Materials

The name of chemicals, abbreviation, source, purity and molecular weight of studied compounds are tabulated in Table 1. All chemicals were used without any purification. The basic data of density, sound velocity and compressibility for studied solutes (amides) as well as solvents (water and CCl_4) are summarized in Table 2. The water used for preparation of solutions was freshly prepared quartz double distilled water. The solvent CCl_4 of HPLC grade (MERCK) was used after distillation. The binary solutions were prepared fresh on molality basis in stoppered flasks. The high precision balance used for weighing was Shimadzu AUW220D and weights were made with an accuracy of ± 0.1 mg.

2.2. Density measurement

The experimental density measurements of all pure liquids and solutions were determined by using an Anton Paar Digital Densitometer (DMA-5000) at 298.15 K ± 0.001 K. The densitometer was calibrated using water and air as standards. Appropriate humidity and lab pressure corrections were applied and the uncertainty in density measurements was found to be of the order of $\pm 3 \cdot 10^{-3}$ kg·m^{-3}. The details of density measurements and reliability of the measurements have been reported earlier [15].

2.3. Speed of sound

Sound velocity (u) measurements were carried out for pure studied amides, for amides in water and in CCl_4 at 298.15 ± 0.05 K using a Mittal ultrasonic interferometer at a fixed frequency of 2 MHz. The reliability of the measurements was checked by obtaining sound velocity data for H_2O and CCl_4 and other liquids at 298.15 K. The sound velocity data were found to be reproducible within ± 0.5 m·s^{-1}. The u values for H_2O and CCl_4 are found to be 1497.70 m·s^{-1} and 921.26 m·s^{-1} which compare well with literature values [14,16].

2.4. Viscosity measurement

The viscosity coefficient measurements for aqueous solutions were made by using Ubbelohde viscometer with flow time of 487.1 ± 0.1 s (for H_2O at 298.15 K). Care was taken in cleaning of the viscometer. The viscometer was suspended vertically, with good reproducibility, in the water bath of 60 l capacity, using specially leveled stand. The temperature of the well-insulated, stirred water bath was maintained constant at 298.15 ± 0.005 K by circulating water from cryostat (Julabo F25MP) through circulating coil suspended in the bath. The flow times for water and solutions were measured several times with the electric timer having an accuracy of ±0.1 s.

The time of flow measurements for binary solutions of amides in CCl_4 were measured by the Tuan-Fuoss [17] type viscometer so that evaporation of CCl_4 can be avoided. The flow time for CCl_4 at 298.15 K was measured as 537.8 s. The viscosities were calculated from the average flow times 't' and densities ρ, based on the equation:

$$\eta = \alpha\rho t - \frac{\beta\rho}{t} \quad (1)$$

where, α and β are the capillary constants which were determined by making time of flow measurements at different temperatures.

Table 1
List of chemicals, abbreviation, source, purity and molecular weight of studied amides.

Chemical	Abbreviation	Source	Mass fraction purity	Molecular weight (kg·mol^{-1})
Formamide	FA	Sigma-Aldrich	0.995	0.04504
N-methylformamide	MFA	Sigma-Aldrich	0.99	0.05907
N, *N*-dimethylformamide	DMF	Sigma-Aldrich	0.998	0.07309
N-methylacetamide	NMA	Sigma-Aldrich	0.99	0.07309
N, *N*-dimethylacetamide	DMA	Sigma-Aldrich	0.998	0.08712