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Viscometric studies of ternary liquid mixture of thiaocetamide - alkali halide - water system

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ABSTRACT

The relative viscosity measurements have been reported to explain structural interactions of sodium halides and potassium halides (0.125M - 3M) in aqueous thioacetamide solutions at different temperatures. The structural aspects of the alkali halide solutions have been interpreted by the ionic molar volume (V±), ionic B-coefficients (B±) and hydration number of ions (n_B). The change in these data is attributed to the structure making and structure breaking extent of various ions (Na^+ , K^+, Cl^-, Br^- and I^-) present in the aqueous thioacetamide solution.

Key words: Relative viscosities, thioacetamide-alkali halide-water system.

INTRODUCTION

Thermodynamic and physico-chemical studies[1-3] of binary and ternary liquid mixtures are of considerable theoretical and technological importance as they provide a wide range of solvents of varying compositions and properties. In case of electrolyte-solvent system, interactions between components of the binary and ternary mixtures are important in providing a better understanding in many chemical, biological and technological processes in these mixed solvent medium. In the determination of structural behaviour of ions in solution, it is necessary to consider various thermodynamic properties[4-7] to explain various interactions that are likely to occur in the solution. Transport properties such as viscosity and conductance are also important to support the validity of structural concepts in solution. The viscosity of ternary liquid mixtures have been studied by many workers[8,9]. Using these transport properties, we have studied the nature of several non-electrolytes in presence of added electrolytes in aqueous and non-acqueous medium in our laboratory [10-15]. The study of thioacetamide is of considerable interest as a simple peptide analogue having no self association behaviour. Thioacetamide is fairly stable, water soluble, carcinogenic[16,17] in nature and readily absorbed through the skin, causing irritation. Much studies of thioacetamide have been made on rats as their haemoglobin content is very close to human beings.It is a proton donor which can be used for the study of the hydrogen bonding because no self-association is to be expected in the dilute solution. Thioacetamide has been found very suiatable for the study of amide-amide hydrogen bonding in aprotic organic solvents[18,19]. The physico-chemical studies of thioacetamide in ionic liquids have been studied by Forsyth et al20 and has provided some of their current applications as well as an introduction to some of the new cations and anions that have been developed for specific properties. Keeping these facts in mind, the viscosity behaviour of the aqueous thioacetamide in alkali metal halides has been studied in the molar range from 0.125 to 3.00 Mol. L-1 and temperature range from 25 °C to 40 °C.

EXPERIMENTAL

Thioacetamide was Aldritch 99%, dried at room temperature under reduced pressure for 24 hours and stored over P2O5 in a glove box. Sodium halides and potassium halides used in present investigation were E. Merk, GR grade and were used as such without further purification. Water used for the preparation of solutions was of high degree of purity having specific conductivity of the order of 10-6 ohm-1. The density measurements at different temperatures were carried out with Pycnometer in the conventional way. Viscosity measurement at specific temperature was made with the help of modified Tuan-Fuoss Viscometer21. All the measurements were carried out in a water thermostat having controlling capacity within ± 0.05 0C temperature.

RESULTS AND DISCUSSION

The relative viscosity data of thioacetamide-alkali halide-water system at 25 °C, 30 °C, 35 °C and 40 °C were computed using a relation :

$$\eta/\eta_0 = d\,t / d_0\,t_0 \qquad ..(1)$$

where h, d, t and h0, d0, t0 are viscosity, density and flow time for aqueous thioacetamide solution with electrolytes and aqueous thioacetamide solution without electrolytes, respectively. These relative viscosity data obtained for all the six electrolytes in aqueous thioacetamide solution have been utilised to calculate B-coefficient values from the relation:

$$\eta/\eta_0 = 1 + BC \qquad ...(2)$$

where C is concentration ~ 0.1 M. It has been found that this relation holds good for all the six electrolytes in aqueous thioacetamide solution up to the concentration of 0.50 M. The Moulik equation22 which is valid only for concentrated solution (equ. 3), has also been applied to test the relative viscosity data

$$(h/h0)2 = M+KC2 \qquad ...(3)$$

The values of M and K have been calculated from the intercept and slope of the plots of $(\eta / \eta_0)2$ versus C2 (Figs. 1-6) by extrapolating it upto zero concentration. Breslau and Miller equation23. (equ 4) yields average effective rigid molar volume (Ve)

$$Ve = \frac{2.5C+[(2.5C)2 \_ 4\,(10.05C2)(1-h/h0)]1/2}{2(10.05)C2} \qquad ...(4)$$

The B-coefficient value of each ions has been calculated on the separation basis taking BK+ = BCl-. The ionic B-coefficient values (B±) are used to calculate the ionic molar volume (V±) of each ion using equation

$$B\pm = 2.5V\pm \qquad ...(5)$$

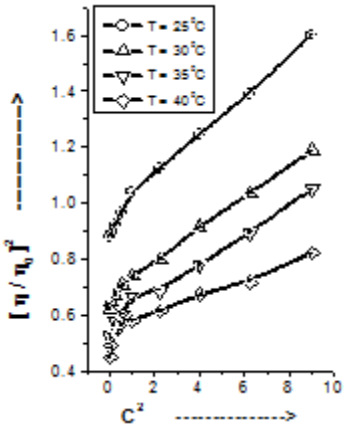

Fig. 1: Plots of $[\eta / \eta_0]^2$ versus c^2 in thioacetamide-NaCl-water system

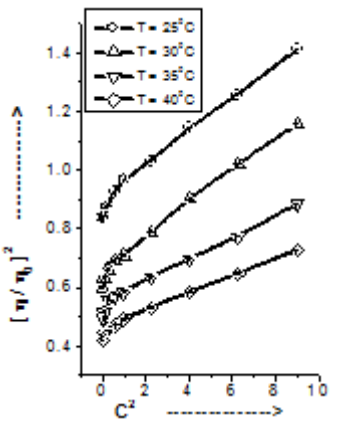

Fig. 2: Plots of $[\eta / \eta_0]^2$ versus c^2 in thioacetamide-NaBr-water system

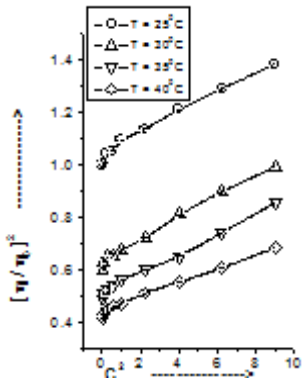

Fig. 3: Plots of $[\eta / \eta_0]^2$ versus c^2 in thioacetamide-NaI-water system

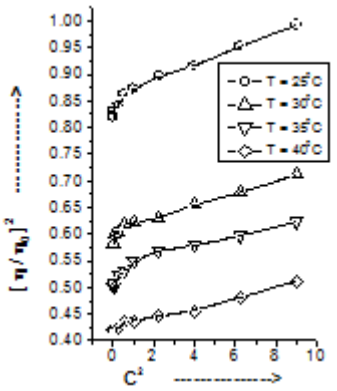

Fig. 4: Plots of $[\eta / \eta_0]^2$ versus c^2 in thioacetamide-KCl-water system

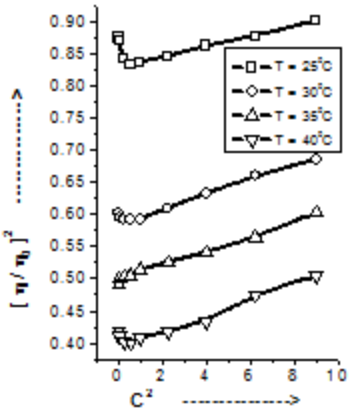

Fig. 5: Plots of $[\eta / \eta_0]^2$ versus c^2 in thioacetamide-KBr-water system

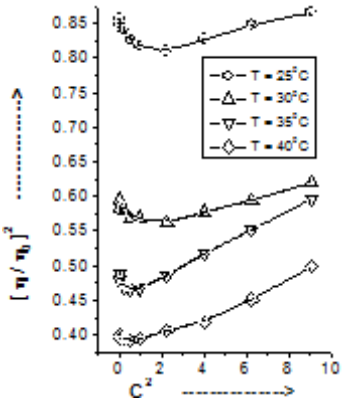

Fig. 6: Plots of $[\eta / \eta_0]^2$ versus c^2 in thioacetamide-KI-water system

The hydration number nB of ions can be calculated from equation :

$$\pm = V^0_{ion} + nB\, V^0_S \qquad ...(6)$$

where V0ion is free ion volume which can be calculated from the relation V0ion = 2.53(r0)3, where r0 is the radius in Å taken from Gourary Adrian radii and V0S is the volume of water equal to 6.62 cm3 mol-1 taking radius of water 1.38 Å. Thus the hydration number of ions are given by the relation

$$nB = \frac{V\pm - V^0_{ion}}{V^0_S} \qquad ...(7)$$

Putting the values of V± from equ. (5) to (7), we get

$$nB = \frac{0.4\, B\pm - V^0_{ion}}{V^0_s} \qquad ...(8)$$

From eq. (8), we calculate hydration number. The positive and negative sign of hydration numbers are assigned to the structure making and structure breaking behaviour of Na+ and K+ ions, respectively. The hydration number and B-coefficient (B±) correlations show that structure making ions have positive ionic molar volume, positive hydration number and positive entropy change while structure breaking ions have reverse values. A perusal of our data reveals that the structure making behaviour of various ions present in the thioacetamide-alkali halide-water system are in the order:

Na+>K+>Cl—>Br—>I—

The experimental result showed the importance of structural modification of thioacetamide in aqueous electrolyte solutions depending upon the hydrogen bond formation capabilities and hydration properties. It is well known that water has unique property to form relatively strong three dimensional hydrogen bond in liquid state24. The presence of non electrolyte like thioacetamide also increased the hydrogen bond formation capabilities between water molecules (N-H—O-H). This has been studied by a variety of techniques such as IR, NMR, and ultrasonic absorption spectroscopy. Due to these facts, thioacetamide has marked influence in the structural behaviour of ions in solution. The straight line behaviour at higher concentration of electrolyte (alkali halides) in aqueous thioacetamide solution showed the validity of Moulik's equation, while at lower concentration region (Einstein region) distorted curves are obtained for all alkali halides which are used in aqueous thioacetamide solution. The trend of curve for sodium halides are different from potassium halides only in the Einstein region. Sodium halides show upward trend whereas potassium halides show slightly downward trend in Einstein region in aqueous thioacetamide solution. This type of variation may be due to different structural behaviour of Na+ and K+ ions in solution at low concentrations.

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