ABSTRACT

In this study binary and ternary solutions are prepared by using the sodium acetate concentrations (0.1, 0.125, 0.2, 0.25, 0.4, 0.5, 0.8, 1 M) in water and acetone –water mixtures. The important parameters such as apparent molal molar volume, free energy of activation of viscous flow and thermodynamic activation parameter (enthalpy and entropy) determined of sodium acetate in water, 20%, 40%, 60% and 80% V/V acetone –water mixtures at 298.15K, 303.15K and 308.15 K from density and viscosity measurements respectively. The limiting apparent molal volumes and experimental slopes were derived from the Masson equation, have been interpreted in terms of solute–solvent and solute–solute interactions respectively. The viscosity data were analyzed using the Jones–Dole equation and the derived parameter B - coefficient has also been interpreted in terms of solute–solute interactions in the solutions.

INTRODUCTION

The studies on viscosities and densities of electrolyte solutions are usually done to obtain information about structure and properties of solutions. Different types of interactions exist between the ions in the electrolytic solutions and of these, ion – ion and ion – solvent interactions are of current interest. These interactions help in understanding the nature of the solvent as it has been found by number of researchers that the addition of an electrolyte either breaks or makes the structure of the liquid. The making and breaking of the liquids structure have been considered as a measure of solute – solute and solute – solvent interactions [1,2].

The volumetric and viscous behavior of solutes has been proven to be very useful in elucidating the various interactions occurring in solutions and it is an important key thermodynamic properties, so these properties (viscosity and density) of electrolyte solutions were among the earliest studies in the field of solution chemistry and have influenced the developments of our view of the solution process [3,4].

Many recent articles have been written concerning the effect of the salt ions on transport properties of aqueous non-aqueous mixtures [5,6]. Thus, the present paper reports acoustical properties of sodium acetate in water and acetone mixtures over a wide concentration range at temperatures under study. The results are interpreted in terms of molecular interactions occurring in the solution.

MATERIALS AND METHODS

Sodium acetate anhydrous of high purity was obtained from Thomas Baker Company, acetone was obtained from Sigma-Aldrich Company. Triply distilled water with a specific conductance of < 10^{-6} S.cm^{-1} was used for the preparation of different sodium acetate solutions at room temperature (25ºC). The precision of balance used was ±1×10^{-5} g.

Density and Viscosity measurements:

The water –acetone mixtures (20%, 40%, 60%and 80% V/V) were prepared by mixing known volume of solutions in airtight-stoppered bottles. Adequate precautions were taken to minimize evaporation losses during the actual measurements. Mass measurements for stock solutions were done on a kern sohn Gmbh electronic balance with a precision of ±0.0001. The
The conversion of molarity into molality was accomplished using experimental density values. The uncertainty in molality of solution is estimated to be ±0.0001 mol. kg⁻¹.

\[
C = \frac{1000 m \rho}{1000 + mM_2} - \quad (1)
\]

where (C) is the molarity, (m) is the molality and (M₂) is the molar mass of sodium acetate.

The density was determined by using specific gravity bottle by relative measurement method with accuracy ±1x10⁻⁴ gm/cm³. The temperature was automatically kept constant within ±0.01 K.

The viscosity, was measured by means of a suspended Ubbelohde type viscometer, calibrated at the experimental temperatures with doubly distilled water. After attainment of thermal equilibrium, efflux times of flow were recorded with a stop watch. At least three repetitions of each data point were taken to average the flow time. The viscosity of solution (η) is given by the following equation:

\[
\eta = c \frac{1}{\rho} - \quad (2)
\]

where (c) is the viscometer constant and (t) and (ρ) are the efflux time of flow in seconds and the density of the experimental liquid respectively.

RESULTS AND DISCUSSION

The experimental values of densities of sodium acetate in water and 20%, 40%, 60% and 80% Water-acetone mixtures at 298.15 K, 303.15 K, and 308.15 K are reported in Table (1).

From Table (1) we observed that overall densities of sodium acetate in water and 20%, 40%, 60%, 80% (V/V%) Water-acetone mixtures increased with the increase in concentration of sodium acetate which is attributed to presence of strong ion-solvent interactions. Whereas we can be observed that density decrease with increasing temperatures and from water to water-acetone mixtures in the same concentration and temperature.

Apparent molar volumes (ϕᵥ) were determined from the solution densities using the following equation [7]:

\[
\phi_v = \frac{M}{\rho} - 1000 (\rho - \rho_o) \quad (3)
\]

Where M is the molar mass of the sodium acetate salt, ρ₀ and ρ are the densities of solvent mixture and solution respectively and m is the molality of the solution. The result of (ϕᵥ) of sodium acetate are reported in Table (1).

The apparent molar volume (ϕᵥ) values increases with increase in concentration of sodium acetate in binary mixtures. The (ϕᵥ) values increased with increase ratio of acetone in mixtures which suggests strengthening of solute-solute interactions in mixtures. Upon addition of the solute, resultant change in apparent molal volume becomes more due to weak approach of solute to solvent molecules. These volumes are move in water-acetone than in water. This represents strong and variable interactions between solute and solutes. And we were observed the same behavior for apparent molar volume which increases with increase in temperature in all system indicates at higher concentrations the existence of weak ion-solvent interaction.

Masson found that the apparent molar volumes (ϕᵥ) vary with the square root of the molal concentration by the linear equation [8]:

\[
\phi_v = \phi_v^* + S_v^* \sqrt{m} - \quad (4)
\]

Where (ϕᵥ∗) is the limiting apparent molal volume and (S_v∗) is the experimental slope. The plots of (ϕᵥ) against (m) of sodium acetate in water and 20%, 40%, 60% and 80% water-acetone at 298.15 K, 303.15 K and 308.15 K are reported in Figure (1).

The values of (ϕᵥ∗) and (S_v∗) of sodium acetate in water and 20%, 40%, 60% and 80% water-acetone at 298.15 K, 303.15 K and 308.15 K are reported in Table (2).
Figure (1): a plot of apparent molal volume ($\phi_v$) against ($\sqrt{\eta}$) for sodium acetate in A) water B) 20% Water+Acetone C) 40% Water+Acetone D) 60% Water+Acetone E) 80% Water+Acetone mixtures at different temperatures.

Table (2): values of ($\phi_v^0 (\text{cm}^3 \text{mol}^{-1})$) and ($S_v^\bullet (\text{cm}^3 \text{mol}^{-3/2} \text{kg}^{1/2})$) of sodium acetate in water and 20%, 40%, 60% and 80% Acetone-water mixtures at different temperatures.

The parameter ($S_v^\bullet$) is the volumetric virial coefficient that characterizes the pair-wise interaction of solvated species in solution. The sign of ($S_v^\bullet$) is determined by the interaction between the solute species. In the present study ($S_v^\bullet$) values were found to be positive and increase with increase in temperature in 20%, 40%, 60% and 80% water-acetone mixtures which may be due to less solvation of sodium acetate with rise in temperature.[10-12]

The volume of transfer ($\Delta \phi_v^\bullet (\text{cm}^3 \text{mol}^{-1})$) of sodium acetate from water to water-acetone mixtures was calculated by using given relation at different temperatures and is summarized in Table (3).

$$
\Delta \phi_v^\bullet = \phi_v^\bullet_{(\text{water-acetone})} - \phi_v^\bullet_{(\text{water})}
$$

The limiting apparent molar expansibilities ($\phi_E$) can be obtained by the following equation and figure (2):

$$
\phi_2 = \left(\frac{\partial \phi_v^\bullet}{\partial I}\right)_p = a_1 + 2a_2 I
gn(6)
$$
It is found that value of \( \Delta \phi_E \) for sodium acetate for all most water-acetone mixtures are negative at 298 K, 303 K and positive at 308 K in system negative values of \( \Delta \phi_E \) (Table 3) decrease with increasing Percentage of acetone and temperature, suggests that the electrostriction first increase and then decrease with increasing temperature. It brings about decrease in volume of the solvent thereby increasing the strong interaction between acetone and water. In sodium acetate-watersystem, hydrophobic interactions are leading at lower percentage, while at higher percentage hydrophilic interactions are leading. The electrostriction of the neighboring water will be decrease at higher temperature this will lead to decrease in reduction of shrinkage. It brings about increase in volume of the solvent thereby decreasing the strong interaction between acetone and water. This will lead to positive volume transfer or in other words it may be say that there is an increase inelectrostriction. In sodium acetate with acetone-water system hydrophilic interactions are dominating over hydrophobic interactions at higher percentage of acetone. Both negative and positive transfer volume has behavior similar with earliststudy[13].

The values of \( \phi_E \) of the sodium acetate solutions study at all temperatures are determined and reported in table (4).

From table (5) the viscosity of a sodium acetate solutions under study decrease markedly as temperature is raised [14]. As the temperature increased, more molecules are able to escape from the potential wells provided by their neighbors and so the solution becomes more fluid.

The observed value of viscosity increased with increasing sodium acetate concentration due to the increase of the intermolecular forces which cause to resist in flow process.[15] The viscosity data has been analyzed using the Jones–Dole equation[16]:

\[
\eta = \frac{1}{\eta_0} \sqrt{\frac{A}{C}} + \frac{B}{C} \tag{7}
\]
A perusal of table (6) shows that the values of the (A) coefficient decrease with the increase in percentage of acetone in the mixtures under study and decrease with the increase in temperature for water and increase with the increase in temperature for almost water-acetone mixtures. This may be interpreted as more solvation of sodium acetate takes place at higher temperature for water and at lower temperature for almost water-acetone mixtures. The effect of solute–solvent interaction on the solution viscosity can be inferred from the B-coefficient. The viscosity B-coefficient is also a valuable tool to provide information concerning the solvation of the solute in solution. Viscosity coefficient (B), the ion–solvent parameter represents the higher terms of the long–range columbic forces, hydrodynamic or size and shape effect, solvation effect and chemical structural effects. From table(6) and figure(3) it is evident that the values of the B coefficient are positive, thereby suggesting the presence of strong solute–solvent interactions which are strengthened with the increase temperature for water whereas the (B) values decrease with the increase temperature thereby suggesting the presence of weak solute–solvent interactions. On other hand the (B) values decrease with the increase in percentage of acetone in its aqueous solution. These indicates the structure making nature of sodium acetate for water and the structure breaking nature of sodium acetate for almost water-acetone mixtures. This is in agreement with the results obtained from density measurements.[17,18]

using the following relations for calculating $\Delta G_2$ contribution per mole of solute to free energy of activation for viscous flow of the solution[19]

$$\Delta G_2 = \Delta G_1^* + \frac{RT}{\phi_T^*}[1000B - (V_1^* - \phi_T^*)]$$

where $\Delta G_1^*$ the free energy of activation of viscous flow per mole of pure solvent which calculated from relation (9), $R$ is gas constant, $h$ is Planck’s and $N$ is Avogadro Constant respectively, $T$ is the absolute temperature, $V_1^{10}$ molar volume which calculated from relation (10).

The enthalpy $\Delta H$ and entropy $\Delta S$ of activation of viscous flow were computed using the equation:

$$\Delta G_2 = \Delta H^* - T\Delta S^*$$

The values, $\Delta H^*$ and, $\Delta S^*$ are obtained from the intercept and slope of $\Delta G_2$ versus $T$ figure (4). The $\Delta H^*$ and, $\Delta S^*$ are summarized in Table (7).

![Figure 3: Plots of (V-1)-√(V-1) vs (V-1) for sodium acetate in A) water B)20% Water-Acetone C) 40% Water-Acetone D) 60% Water-Acetone E) 80% Water-Acetone mixtures at different temperatures](image)

![Figure 4: Plots of (V-1)-√(V-1) vs (T) for sodium acetate in A) water B)20% Water-Acetone C) 40% Water-Acetone D) 60% Water-Acetone E) 80% Water-Acetone mixtures at different temperatures](image)
The data of densities and viscosities increases as function of concentration. Due to the values of the limiting apparent molal volume, viscosity, B-coefficient and other parameters indicate the presence of strong solute–solute interactions and weak solute–solute interactions with increasing of sodium acetate concentration in water whereas indicate the absence of strong solute–solute interactions presence of strong solute–solute interactions for sodium acetate in almost water-acetone and solute–solute interactions decreases with increase in percentage of acetone in its aqueous solution and predominates at higher temperature for water whereas the solute-solute interaction intensifies at higher temperature for almost water-acetone mixtures.

**REFERENCES**


