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Evaluation of limiting molar conductance, Walden product, association constant and thermodynamic properties of sulfacetamide sodium in water + EtOH mixtures

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ABSTRACT

The ion solvation behavior of sulfacetamide sodium in water and various volume fractions of ethanol (EtOH) in water in the range of 283 to 313 K, using electrical conductivity principle have been studied. The conductance data were analyzed according to Kraus–Bray and Shedlovsky models of conductivity. The limiting molar conductance λ_m^o, association constant K_a, energy of activation of the rate process (E_a), and related thermodynamic parameters have been determined. Using viscosity of the solvent, Walden product ($\lambda_m^o \eta_0$) and Stokes molecular radius have been determined. Standard thermodynamic parameters of association (ΔG_a, ΔH_a,) were calculated and discussed. The limiting molar conductance sharply decreased for the increased amount of ethanol suggesting the increased ion–solvent and solvent–solvent interactions.

1. Introduction

The electrical conductivity study of electrolytes in mixed solvents is known to be influenced by a number of factors like viscosity, temperature, relative permittivity, hydrogen bonding, ion-solvation and solvent–solvent interactions [1–8]. Literature reveals that nature of the ion–solvent interactions and ion–ion interactions or the behavior of the electrolytes in a solvent of different relative permittivity can be informative depending on the conductance and ionic mobility of these electrolytes in solutions [9–14].

Water + EtOH mixtures at different temperatures exhibit a wide range of relative permittivity (ε), viscosity (η) and a high degree of hydrogen bonding effect. Varied interaction between water and ethanol because of mixing them at different quantities may be studied by the measurement of conductivity over that composition range. Appropriate conductivity measurements provide useful indications of ion–solvent interaction, proton–anion and proton–solvent association, and solvent structure.

In continuation with our earlier report [15] on ion association and solvation of sulfonamide drug; sulfathiazole sodium in aqueous and partial aqueous media, we report herein the solvation behavior of another sulfonamide drug sulfacetamide sodium in water + ethanol in view of evaluation of limiting molar conductance, Walden product, association constant and thermodynamic properties.

Study of solvation behavior of medicinal compounds under varying biological conditions is an important field of studies which revealed much information to medicinal chemist [16]. The conductivity values may be useful to have an appropriate idea regarding drug diffusion and change in the nature of hydrophobic interactions of drug with the change in free energy involved while moving from water to non-aqueous solvents [17].

The sulfonamides constitute an important class of drugs and have extensively been documented for their wide variety of pharmacological activities such as antimicrobial, insulin releasing antibiotic, diuretic, ant carbonic anhydrase, anti-thyroid, hypoglycemic, anti HIV and antitumor activity. Sulfacetamide sodium is a sulfonamide [18] antibacterial and is applied in infections or injuries of the eyes. The structure of sulfacetamide sodium is given in Fig. 1. We report in this communication the electrical conductivity of sulfacetamide sodium in partial aqueous media by varying the compositions (v/v) of water + ethanol at four different temperatures.

2. Materials

Sodium acetyl[(4-aminophenyl)sulfonyl]azanide (Sigma-Aldrich, USA, 99%, <0.05% H_2O) was used as such, without further purification. The purity was checked from the melting point. (Melting point obtained in the lab: (531–533) K; Literature value [18]: 530 K). The conductivity of water used in this study was obtained by deionization and triple distillation with specific conductance in the range of $(1 \text{ to } 3)\cdot 10^{-7}\ \mathrm{S\cdot cm^{-1}}$. Ethanol conductivity $10^{-7}\ \mathrm{S^{-1}\cdot cm^{-1}}$ was used.

3. Solutions

Mixed solvents, $\phi_2 = 0.1$, $\phi_2 = 0.2$, $\phi_2 = 0.4$, and $\phi_2 = 0.6$ were prepared by mixing known quantities of water and EtOH in volume ratio at laboratory temperature. The calculated values of mass fractions

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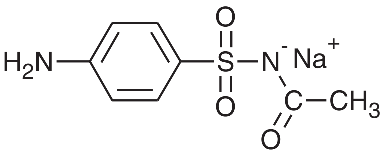

Fig. 1. The structural formula of sodium acetyl[(4-aminophenyl)sulfonyl]azanide.

of ethanol in water at studied temperatures are given in Table 1. Solutions of sulfacetamide sodium with a concentration range of (0.001 to 0.01) mol·L^{-1} were prepared in water or water + EtOH as and when needed. Taking into account the sources of error, we estimate the uncertainty in molar concentration to be within $\pm 5.0 \cdot 10^{-4}$ mol·L^{-1}. Work could not be carried out beyond $\phi_2 = 0.6$ and pure ethanol due to solubility problem.

4. Instrument and methods

For measurement of electrical conductivity, the digital conductivity meter (CM-180, Elico India) and immersion type cells (cell constant = 0.998 cm^{-1}) were used. Cell constant was determined to be within 0.01% precision at various times by calibration with aqueous potassium chloride [19] solutions. The solution of known concentration was taken in a double walled vessel and kept in a thermally stabilized water bath with good thermal regulation (±0.1 °C) for approximately 20 to 30 min and its specific conductivity was noted. All conductivity measurements were repeated thrice and it was found to be reproducible to 0.1%.

5. Results and discussion

5.1. Limiting molar conductance

The specific conductances of solutions of sulfacetamide sodium with a concentration range of (0.001–0.01) mol·L^{-1} in$\phi_2 = 0.0$, $\phi_2 = 0.1$, $\phi_2 = 0.2$, $\phi_2 = 0.4$, and $\phi_2 = 0.6$ EtOH in water at 283, 293, 303 and 313 K were measured. The molar conductance for all the studied systems was calculated using Eq. (1).

$$\lambda = \frac{\kappa}{C} \tag{1}$$

where C is the molar concentration, κ is the specific conductance of sulfacetamide sodium solution from which the specific conductance of the used solvent was subtracted. The experimental molar conductivities were analyzed as per Kraus–Bray conductivity equation [20].

$$\frac{1}{\lambda_m} = \frac{1}{\lambda_m^o} + \frac{\lambda_m C}{\lambda_m^{o\,2} K_c}. \tag{2}$$

The limiting molar conductances, λ_m^o and dissociation constant, K_c were obtained from the intercept and slope of the plot $1/\lambda_m vs \lambda_m C$.

Table 1
Calculated values of mass fractions (W_2) of ethanol in water from $T = 283$ K to 313 K.

T/K	W_2			
	$\phi_2 = 0.10$ EtOH	$\phi_2 = 0.20$ EtOH	$\phi_2 = 0.40$ EtOH	$\phi_2 = 0.60$ EtOH
T/K = 283	0.0988	0.1963	0.3889	0.5790
T/K = 293	0.0987	0.1960	0.3877	0.5773
T/K = 303	0.0987	0.1958	0.3866	0.5759
T/K = 313	0.0987	0.1956	0.3857	0.5745

However, this model does not include any correction for inter-ionic effects or for the activities of the ions. Therefore, Shedlovsky [21] relation was used to evaluate the absolute limiting molar conductance and association constant K_a.

$$\frac{1}{S\lambda_m} = \frac{1}{\lambda_m^o} + \frac{C\lambda_m S f_{\pm}^2 K_a}{\lambda_m^{o\,2}} \tag{3}$$

Required relative permittivity (ε) and viscosity (η) values were obtained from the literature [22–24]. The $f_{\pm}$ is the mean ionic activity coefficient of the electrolyte. λ_m^o and K_a were obtained from the intercept and slopes of the plot of $1/S\lambda_m$ vs $C\lambda_m S f_{\pm}^2$. The values of limiting molar conductance evaluated using Kraus–Bray and Shedlovsky models at different temperatures having uncertainty of ±0.5% are presented in Table 2.

Limiting molar conductance (λ_m^o) was found to be higher in water and then decreased sharply on adding ethanol to it, despite the maximum in viscosity near $\phi_2 = 0.5$ ethanol. This behavior may be due to the formation of hydrogen bond between ethanol and water molecules resulting in the association of ethanol and water molecules, which in turn reduces the solvated ionic mobility and decreases the limiting molar conductance values with higher percentage of ethanol in the solvent mixture. The variation in viscosity (η) is not only the factor controlling the ionic mobility, which is evidenced by the Walden product. The limiting molar conductance of sulfacetamide sodium increased with increase in temperature from 283 K to 313 K for all volume fractions of co-solvent due to the increase in ionic mobility. Increase in thermal energy breaks more number of hydrogen bonding that of water decreasing the solvated ionic size and hence increases the mobility of the species.

5.2. Association constant

The calculated values of association constant having uncertainty of ±2% were presented in Table 3. The values of K_a of the studied system at the same temperature were found to increase as the proportions of solvent ethanol increase with water. The extent of ion association depends on the nature of ion–ion interaction in the solution, relative permittivity of the medium and also intermolecular hydrogen bonding between the solvent molecules. This suggests the fact that the values of K_a increased with the increase of EtOH in water. The association constant for the studied salt was found to decrease with the increase in temperature; increased thermal motion probably breaks more bonds between ions and makes them to move away from each other, where it gets solvated. Hence the mobility if ions should increase. This may account for the decrease in K_a for the increased temperature.

To identify the association Fuoss [25] suggested the following equation

$$C\lambda_m = K_C\left(\lambda_m^0\right)^2 \tag{4}$$

According to Fuoss, the slope of the plot log λ_m vs log C is around −0.5, it is an indication of the presence of ion-pairs in equilibrium with the salt. In the present case, the slope was found to be −0.11. The higher value of the slope hints the absence or minor amount of ion-pair formation. Moreover it also supports the fact that higher ion aggregates (ion–ion and triplet ion pair) from 1:1 salts cannot occur in higher permittivity media [26,27] ($\varepsilon > 10$).

5.3. Variation of Walden products with solvent composition

If ionic mobility depends on bulk viscosity as per the Stokes' law, the Walden products [28] would appear reciprocal to the ionic radius. The variations in Walden product with solvent composition and