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Conductance and solvation behaviour of sulfacetamide sodium in water–dimethyl sulfoxide mixtures at different temperatures

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ABSTRACT

The ion solvation behaviour of Sulfacetamide sodium in water and effect of dielectric constant on it by varying the compositions (v/v) of water + DMSO mixtures in the range of 283 to 313 K, using electrical conductivity principle have been studied. Kraus-Bray and Shedlovsky models of conductivity were used for analyzing conductance data. The limiting molar conductance (λ_m^0), Association constant K_a, Energy of activation of the rate process (E_a), and related thermodynamic parameters has been determined. Using viscosity of the solvent, Walden product $\lambda_m^o \eta_0$ and Stoke's molecular radius have been determined. Standard thermodynamic parameters of association (ΔG_A, ΔH_A, ΔS_A) were calculated and discussed. The results show the decrease in limiting molar conductance with decrease in dielectric constant and the K_a was found to increase. These computed values have been used to discuss the solvation behaviour of Sulfacetamide sodium in water + DMSO.

KEYWORDS

Sulfacetamide sodium;
Electrical conductivity;
Limiting molar conductance;
Association constant;
Ion solvation;
Born model.

INTRODUCTION

Mixed solvent systems are used in a wide range of applications, and understanding the effect of changes in solvent composition remains a central problem in physical chemistry. The electrical conductivity study of electrolyte in solvent mixtures is of great importance as it gives wealthy information's especially behaviour of ions in solution, ion solvent interaction and solvent structural effects[1-4]. The study of electrolytes in solvent mixtures is found to be useful for various electrochemical and technical investigations[5-8]. Study of solvation behaviour of medicinal compounds under varying biological conditions is an important field of studies reveals a great deal of information to medicinal chemist[9,10]. Moreover, these studies would enable us to derive useful informations regarding the ion-solvent interactions of the drug molecules. Ion-solvent interactions are the controlling forces in dilute solutions where ion-ion interaction is minimum and these studies may be of great importance in determining the pharmacological properties of the drug molecules. The conductance values may be useful to have an appropriate idea regarding drug diffusion and change in the values of hydrophobic interactions of drug cations in going from water to non aqueous solvents[11]

Sulfonamide is a drug, extensively used for the treatment of infections caused by gram- positive and gram–negative microorganisms, some fungi, and certain protozoa. The therapeutic uses of sulfonamides are also found on diuretic and hypoglycemic agents. Sulfacetamide sodium is a sulfonamide[12] antibacterial and is applied in infections or injuries of the eyes. It is also used in the topical treatment of acne vulgaris, seborrheic dermatitis and various bacterial infections caused by susceptible organisms. The electrical conductivity of Sulfacetamide sodium or dielectric effect on it in aqueous, non aqueous and partial aqueous media is not available in literature. This has prompted us to investigate the solvation behaviour of Sulfacetamide sodium in water + DMSO in the temperature range of 283 to 313 K.

MATERIALS AND METHODS

Sulfacetamide sodium (Sigma-Aldrich make) was used as such, without further purification while preparing solution. Triply distilled water and purified[13] solvent-dimethyl sulphoxide of conductivity ($10^{-6}S^{-1}cm^{-1}$) were used in the entire work. Conductance measurements were made with a digital conductivity meter (CM 180 Elico make) and a calibrated dip type conductivity cell (cell constant = 0.999 cm^{-1}). The instrument was calibrated as reported[14]. The solution of known concentration was taken in a double walled vessel and kept in a thermostat / cryostat maintained at desired temperature ± 0.1°C for approximately 20-30 minutes and its specific conductivity was noted.

RESULTS AND DISCUSSION

Limiting molar conductance

Measured specific conductance of solutions of the electrolyte under investigation in water, 10, 20, 40, 60 and 80 % DMSO at 283, 293, 303 and 313K has been corrected[15] for solvent conductance and used to calculate molar conductance, λ_m using equation (1).

$$\lambda_m = \frac{1000k}{C} \qquad (1)$$

where C is the concentration and k is the specific conductance of Sulfacetamide sodium solution. The molar conductance, λ_m of the electrolyte was analyzed initially by using Kraus –Bray equation[16].

$$\frac{1}{\lambda_m} = \frac{1}{\lambda_m^o} + \frac{\lambda_m C}{{\lambda_m^o}^2 K_c} \qquad (2)$$

where a plot of $1/\lambda_m$ vs λ_m was linear, proposing that the electrolyte forms ion-pairs in equilibrium with ions. The values of λ_m^o and K_c obtained from the intercept and slope of the above plot. However, this model does not include any correction for inter-ionic effects or for the activities of the ions. We, therefore, preferred to adopt Shedlovsky[17] relation, which not only solve above limitation but also enables one to evaluate the absolute limiting molar conductance and association constant K_a.

$$\frac{1}{S\lambda_m} = \frac{1}{\lambda_m^o} + \frac{C\lambda_m S f_\pm^2 K_a}{{\lambda_m^o}^2} \qquad (3)$$

Required relative permittivity (ε) and viscosity (η) values were obtained from the literature[18-20]. K_a is the association constant and $f_\pm$ 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. $C\lambda_m Sf\pm^2$. The calculated values of limiting molar conductance's using Kraus-Bray and Shedlovsky models are presented in TABLE 1.

TABLE 1 : Limiting molar conductance λ_m^o for sulfacetamide sodium in water + DMSO from T = 283 to 313 K

Property	0 % DMSO	10 % DMSO	20 % DMSO	40 % DMSO	60 % DMSO	80 % DMSO
T = 283 K	λ_m^o /($S\cdot cm^2\cdot mol^{-1}$)					
λ_m^o (Kraus-Bray)	52.07	42.80	39.21	22.22	14.20	11.12
λ_m^o (Shedlovsky)	53.47	43.01	40.19	24.82	15.72	13.31
T = 293 K						
λ_m^o (Kraus-Bray)	64.51	51.81	46.94	28.74	18.56	14.11
λ_m^o (Shedlovsky)	65.78	51.98	48.06	30.95	20.09	16.09
T = 303 K						
λ_m^o (Kraus-Bray)	78.12	62.89	57.14	35.58	23.69	17.86
λ_m^o (Shedlovsky)	80.00	64.00	59.00	38.40	26.41	20.04
T = 313 K						
λ_m^o (Kraus-Bray)	92.59	76.05	68.96	43.48	29.24	22.87
λ_m^o (Shedlovsky)	95.20	77.80	69.71	46.60	31.27	25.71

Limiting molar conductance is found to be higher in water and decreased sharply with the decrease in dielectric constant on adding DMSO solvent to it irrespective of the solvent specific property. The addition of DMSO to water results in decrease in the limiting molar conductance, due to the diminishment of hydrogen bonds with increasing DMSO concentration, indicating that the water hydrogen bonding sites are becoming increasingly less hydrogen bonded with increasing concentration of DMSO[21]. In particular, in the mixing process, hydrogen bonding is simply transferred from water-water interactions to water-DMSO interactions, and so reduces the ions mobility. The limiting molar conductance of the solute under investigation increased with an increase in temperature from (283 to 313) K for all compositions of DMSO 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.

Association constant

The computed values of association constant K_a are presented in TABLE 2. The extent of ion association depends on the nature of ion-solvent interaction in the solution rather than being dependent on the relative permittivity of the medium[22]. Greater hydrogen bonding of water-DMSO mixtures probably facilitates the ion association[23]. This suggests the fact that the values of K_a increased with the proportion of DMSO in water. With increasing temperature, increased thermal motion probably destroys the solvent structure and hence the mobility if ions should increase. This may account for the fact that the values of K_a decreased as the temperature increased.

TABLE 2 : Association constant K_a for sulfacetamide sodium in water + DMSO from T = 283 to 313 K

T/K	0 %	10 %	20 %	40 %	60 %	80 %
283	3.35	6.51	12.16	21.16	35.81	54.18
293	3.27	5.28	10.83	10.82	26.36	45.60
303	3.15	4.42	9.40	9.40	21.18	35.30
313	3.11	3.62	6.07	6.07	16.27	22.35

Walden product

The Walden product $\lambda^o_m\eta_o$ [24,25] were calculated for Sulfacetamide sodium for all compositions of water + DMSO from 283 to 313 K, and the results are depicted in Figure 1. Walden product values decreased with increasing temperature. These negative temperature coefficients of Walden product may be due to the increase in size of solvated ions in the mixtures as the temperature increase. This is because of the variation in the volume of organic solvent and aqueous molecules in the sheath of solvation at that temperature[26]. The two effective factors on the Walden product are the limiting molar conductance and viscosity, in which limiting molar conductance λ^o_m is directly proportional with T, while η is inversely proportional to temperature. This observation leads us to say that the contribution of the η values is the most effective factor on the inverse proportional behaviour of Walden product with temperature. The variation of the Walden product with increase in the amount of DMSO reflects the change of solvation[27]. The maximum values of Walden product near volume 40 % DMSO may be due to the preferential solvation of the ions by both the solvent mixtures.

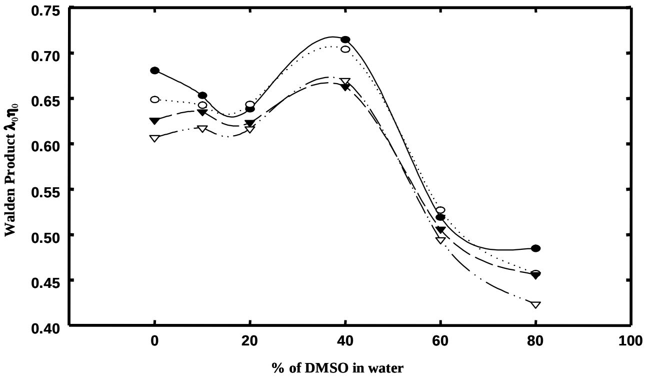

Figure 1 : Plots of Walden product $\lambda^o_m\eta_o$/(S·cm^2·mol^{-1}·kg·m^{-1}·s^{-1}) against percentage of DMSO for Sulfacetamide sodium in water + DMSO at different temperatures (●, for 283 K; ○, for 293 K; ▲, for 303 K; Δ, for 313 K).

Thermodynamic parameters

Since the conductance can be correlated to the rate process[15], the variation of λ^o_m with temperature is given by the equation $\lambda^o_m = Ae^{-E_a/RT}$. where E_a is the activation energy, R is the gas constant, A is the Arrhenius factor and T is the absolute temperature. E_a was calculated from the slope of the plot of $\log \lambda^o_m$ vs. $1/T$. E_a increased with decrease in dielectric constant of the solvent mixture. Increase in the value of E_a is an indication of the decrease in the value of λ^o_m.

From the slope of plot log K_a vs. 1/T, which was linear, (ΔH_a) was calculated. Change in free energy was calculated from the equation ΔG_a = -RT ln K_a and ΔS_a

from (ΔH_a - ΔG_a) / T. The calculated values of these thermodynamic parameters are presented in TABLE 3. ΔH_a and ΔG_a was found to be negative for the system and both increased with increase in the amount of co- solvents. ΔG_a was negative in all the studied cases proposing the spontaneity and feasibility of the exothermic (ΔH_a is negative) behaviour in water + DMSO system. Therefore it can be proposed that the association process is favored in the system by the negative value of ΔG_a. The minimum value of enthalpy of association may be due to the preferential hydration of ions[24] or it may also be referred to as the formation of some complexes from molecules of organic co-solvents and water with a cation or with both cation and anion. The small ΔS_a value has been considered due to the decreased orientation of water molecule and also for the formation of ion pairs.

TABLE 3 : The computed E_a and thermodynamic parameters of association for sulfacetamide sodium in different compositions of solvent mixture at different temperature.

T(K)	Parameters	0 %	10 %	20 %	40 %	60 %	80%
	E_a(kJ/mol)	13.98	14.48	15.72	16.43	17.77	19.78
	ΔH_a (kJ/mol)	-1.98	-14.25	-16.2	-17.07	-24.27	-25.44
283	ΔG_a (kJ/mol)	-2.85	-4.41	-5.88	-7.18	-8.67	-9.40
	ΔS_a(kJK^{-1} /mol)	0.003	-0.035	-0.036	-0.035	-0.055	-0.053
293	ΔG_a (kJ/mol)	-2.89	-4.06	-5.80	-6.89	-7.97	-9.31
	ΔS_a(kJK^{-1}/ mol)	0.004	-0.035	-0.035	-0.035	-0.056	-0.052
303	ΔG_a (kJ/mol)	-2.89	-3.75	-5.65	-6.38	-7.69	-8.97
	ΔS_a (kJK^{-1}/ mol)	0.003	-0.035	-0.035	-0.035	-0.055	-0.051
313	ΔG_a (kJ/mol)	-2.95	-3.35	-4.69	-6.19	-6.92	-7.18
	ΔS_a (kJK^{-1}/mol)	0.004	-0.035	-0.367	-0.035	-0.055	-0.053

Thermodynamics of solvation

The change in free energy ($\Delta G_{s\text{-}s}$), enthalpy ($\Delta H_{s\text{-}s}$) and entropy ($\Delta S_{s\text{-}s}$) of solute-solvent interaction resulting from the transfer of species from one solvent to another or from composition to other were calculated using Born[28] equation and the result obtained for all the cases are given in the TABLE 4.

The change in free energy was calculated using,

$$\Delta G_{S-S} = -\frac{N_A (Z_i e_0)^2}{r_i}\left(1-\frac{1}{\varepsilon}\right) \tag{4}$$

The change in entropy $\Delta S_{s\text{-}s}$ of the system was calculated using the following relation,

$$\Delta S_{S-S} = \frac{N_A (Z_i e_0)^2}{2r_i}\,\frac{1}{\varepsilon^2}\,\frac{\delta\varepsilon}{\delta T} \tag{5}$$

$$\Delta H_{s\text{-}s} = \Delta G_{s\text{-}s} + T\Delta S_{s\text{-}s} \tag{6}$$

The free energy change arising from solute–solvent interaction is a measure of stability of the species in a solution. The observed large negative $\Delta G_{s\text{-}s}$ value is an indication of higher stability of the species in solvent media than in vacuum and which is supported by the exothermic character of the reaction indicated by negative $\Delta H_{s\text{-}s.}$ The negative sign of $\Delta G_{s\text{-}s}$ also indicates the spontaneity of the process. The $\Delta S_{s\text{-}s}$ values are very small and suggest the requirement of steric restriction for the formation of ion pairs or ion-association.

TABLE 4 : Computed thermodynamic parameters of solvation for sulfacetamide sodium in water + DMSO from *T* = 283 to 313 K mixture at different temperature

Property	0 %	10 %	20 %	40 %	60 %	80%
			T = 283 K			
$\Delta G_{S\text{-}S}$ (kJ/mol)	-221.26	-214.08	-215.25	-207.08	-195.64	-199.55
$\Delta S_{S\text{-}S}$(kJK^{-1} /mol)	0.0127	0.0100	0.0098	0.0107	0.0110	0.0138
$\Delta H_{S\text{-}S}$ (kJ/mol)	-217.67	-211.26	-212.48	-204.05	-192.51	-195.65
			T = 293K			
$\Delta G_{S\text{-}S}$ (kJ/mol)	-219.94	-218.18	-228.00	-219.56	-210.67	-213.61
$\Delta S_{S\text{-}S}$(kJK^{-1} /mol)	0.0126	0.0110	0.0114	0.0186	0.0161	0.0206
$\Delta H_{S\text{-}S}$ (kJ/mol)	-216.25	-214.96	-224.67	-214.11	-205.96	-207.58
			T = 303K			
$\Delta G_{S\text{-}S}$ (kJ/mol)	-219.28	-220.93	-224.36	-212.97	-203.72	-204.61
$\Delta S_{S\text{-}S}$(kJK^{-1} /mol)	0.0138	0.0133	0.0133	0.0066	0.0109	0.0115
$\Delta H_{S\text{-}S}$ (kJ/mol)	-215.10	-216.91	-220.33	-210.98	-200.42	-201.12
			T = 313K			
$\Delta G_{S\text{-}S}$ (kJ/mol)	-218.88	-230.14	-231.99	-210.79	-206.35	-228.23
$\Delta S_{S\text{-}S}$(kJK^{-1} /mol)	0.0152	0.0172	0.0151	0.0138	0.0153	0.0195
$\Delta H_{S\text{-}S}$ (kJ/mol)	-214.13	-224.76	-227.27	-206.48	-201.57	-222.14

Solvation number (S_n)

Solvation number of an ion is the number of solvent molecules that surrounds its translational degree of freedom and get associated to that central ion. Solvation number reflects the magnitude of ion-solvent interaction of the system. Solvation number was calculated using the relation.

$$S_n = \frac{d_{AB} - r_i}{r_{sol/sol\,mix}} \tag{7}$$

where r_i is the corrected Stoke's radius of the ion calculated using the following equation,

$$r_i = \frac{0.820Z}{\lambda^{o}_{m}\eta_{o}} + 0.0103\varepsilon + r_y \tag{8}$$

where $r_y = 0.85$ A°, for dipolar unassociated solvents and $\lambda^{o}_{m}\eta_{o}$ is the Walden product. The calculated values of corrected Stoke's Molecular radius r_i are presented in TABLE 5.

TABLE 5 : Corrected Stoke's molecular radius r_i/A° for Sulfacetamide sodium in water + DMSO from T = 283 to 313 K

T/K	0 %	10 %	20 %	40 %	60 %	80 %
283 K	3.205	3.239	3.258	3.111	3.509	3.545
293 K	3.224	3.227	3.216	3.09	3.450	3.612
303 K	3.231	3.209	3.225	3.113	3.472	3.574
313 K	3.234	3.210	3.205	3.084	3.483	3.688

The calculated values of solvation number are presented in TABLE 6. The solvation number was found to be in between 2.1 to 2.9 in pure water. The values increased with increase in temperature for all compositions of water + DMSO. At a given temperature, it remained almost the same within the experimental error irrespective of variation in the amount of DMSO.

TABLE 6 : Solvation number S_n for ion-pair formation of sulfacetamide sodium in water + DMSO from T = 283 to 313 K

T/K	0 %	10 %	20 %	40 %	60 %	80 %
283 K	2.1	1.2	1.2	1.2	1.1	1.1
293 K	2.0	1.2	1.2	1.2	1.1	1.2
303 K	2.3	1.4	1.4	1.3	1.3	1.3
313 K	2.9	1.8	1.8	1.7	1.7	1.8

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