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Conductance and Ion-Solvation behaviour of Sodium Sulfonates in aqueous-organic mixture

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Abstract: *The solvent corrected conductance of sodium salts of alkane sulphonic acids have be calculated in water, MeOH, DMF and DMSO solvent mixture of diverse composition in the temperature range 298-318K. The limiting molar conductance Λ^0 and the association constant of the ion-pair, $K_{A,}$ encompass be compute by Shedlovsky equation. In DMF and DMSO, the limiting molar conductance decrease with raise in the proportion of organic component of the solvent mixture. Kraus-Bray equation has also been used to correlate the Λ^0 and the dissociation constant of the ion-pair, $K_{C,}$ have be compute. The consequences have been discussed within terms of solvent-solvent and ion-solvent relations.*

Key Words: *Association constant, Dissociation constant, Ion-pair, Limiting molar conductance, Sulphonate.***

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I. Introduction

The conductance behaviour of numerous electrolytes in dual solvent systems is reported to be influenced by number of factors like density, viscosity, dielectric constant of the medium, ion-solvent interactions and solvent-solvent interactions. Ion-solvent interactions stabilize the ion by solvating it. Though literature is replete with such type of information[1-8], conductivity studies have not been carried earlier on these salts. These are soluble in water and find application as commercial electrolyte standards for electroplating[9], of Sn and Pb, which are prepared and analyzed by R. M. Reed and H. V. Tartar[10]. They are also used as effluent components in anion chromatography[11],. Sodium butane sulfonate is known to be a strong structure builder of solvents. Kirilova and group investigated the state of molecular ion equilibria in solutions of sodium methane sulfonate in water and methane sulphonic acid by studying its IR spectrum. Wei and Hingerty studied the structure of sodium methane sulfonate. Sodium butane sulfonate finds application in the analysis of peptides and proteins. In the present communiqué the authors tale their observations taking place the conductance behaviour of SSMS, SSMS and SSPS in binary solvent mixtures of methanol-water, dimethyl formamide-water and dimethyl sulphoxide-water.

II. Experimental Equations

Deionised water was distill and used. N,N-dimethyl formamide, dimethyl sulphoxide (Sd-fine) and methanol was purchase from Chemicals Ltd., Bombay, after purification following literature methods. The densities of solvent mixtures were measured using a double stem pycnometer with a bulb of 10 cm^3 capacity. The viscosities of solvent system used in the present study were determined using Ubbelohde viscometer. This is repeated three times and using the arithmetic mean of the efflux times, the viscosity (η) was calculated using the following equation[12], equation (1)

$$\eta = [at-(b/t)]\ \rho \qquad \ldots(1)$$

Where t is the efflux time, ρ is the density of the liquid, a and b are the constants of the viscometer. These constants are calculated by measuring the flow time of aqueous organic mixture and using the density and viscosity values of solvent mixture at the same temperature and at different temperatures in the range 298-318K presented in Table-1-3.

Sodium salts of alkane sulphonic acids namely sodium methyl sullfonate (SSMS), butyl sulfonate (SSBS) and pentyl sulfonate (SSPS) was ready subsequent the literature technique.

A digital conductivity bridge (ELICO model CM 180) equipped with a dip type conductivity cell having cell constant 1.064 cm^{-1} was used to compute the conductance of the solution. Conductivity cell was calibrated using standard KCl solution. The exactitude of the conductivity bridge used is ±04μS. Temperature was maintain steady in the range 298-318K using a thermostat with an accuracy of ± 0.4^0C. To maintain the temperature below room temperature an ice bath equipped with a mechanical stirrer was used.

The solution of sulfonate was thinned to diverse concentrations in the range 0.05M to 5.0×10^{-3} M using diverse volumes of solvent / solvent system used are water, MeOH, DMF, DMSO and aqueous mixtures of these three organic solvents in different proportions and the conductance values were measured in the temperature range 298-318K as in the series. These values are found to be reproducible with ±0.4% error. The solvent systems used in this study have conductance values in the range 0.012-0.0414mS. The solvent conductance values were subtracted from the conductance of the solution to get the conductance of the solute at each concentration from which the specific conductance was evaluated. Using these values the molar conductance value (Λ) was calculated using the relation, Λ = (1000k)/C where k is the specific conductance and C is the molarity of the solute. The same procedure was followed at diverse compositions of solvent mixtures in the range 0-100 % (v/v) and at different temperatures in the range 298-318K.

The molar conductance (Λ) values thus determined are analyzed using Kraus-Bray equation[13], equation (2) and Shedlovsky equation[14], equation (3)

$$\frac{1}{\Lambda} = \frac{\Lambda C}{K_C {\Lambda^0}^2} + \frac{1}{\Lambda^0} \qquad \dots \qquad (2)$$

$$\frac{1}{S\Lambda} = \frac{S f_{\pm}^2 K_A C \Lambda}{{\Lambda^0}^2} + \frac{1}{\Lambda^0} \qquad \dots \qquad (3)$$

Λ is molar conductance by concentration C; Λ^0 is the limiting molar conductance; K_A is the association constant of the ion-pair; K_C is the dissociation constant; $f_{\pm}$ is the mean ionic activity coefficient, S is a factor given via, equation (4-8)

$$S = \left[\frac{\beta\sqrt{C\Lambda}}{4{\Lambda^0}^{3/2}} + \sqrt{1 + \frac{\beta^2 C\Lambda}{4{\Lambda^0}^3}} \right]^2 \qquad \dots (4)$$

$$\log f_{\pm} = \left[\frac{-1.8246\times10^6 (C\alpha)^{1/2} /(\varepsilon T)^{3/2}}{1 + 50.24\times10^8 R(C\alpha)^{1/2} (\varepsilon T)^{1/2}} \right]^2 \qquad \dots (5)$$

$$\alpha = \frac{S\Lambda}{\Lambda^0} \qquad \dots (6)$$

$$\beta = \frac{8.20\times10^5 \Lambda^0}{(\varepsilon T)^{3/2}} + \frac{82.5}{\eta(\varepsilon T)^{1/2}} \qquad \dots (7)$$

where R is the ion-size parameter which is equal to the Bjerrum critical distance q given by

$$q = R = \frac{e^2}{2\varepsilon kT} \qquad \dots (8)$$

k is the Boltzmann's constant, and T is the temperature in Kelve,

Є is dielectric constant and η is viscosity of the solvent; Presented in Table 1-3. S is calculated using Λ^0 obtained from the Onsager model using the plot of Λ against √C. The least square analysis of the data (Λ and C) using the above two equations (equations 2 and 3) is satisfactory with linear correlation coefficient in the range 0.93-0.94.

III. Results And Discussion Tables

The limiting molar conductance Λ^0 values of binary solvent systems of diverse compositions in the choice 0-100% (v/v) obtained using the two equations (equation 2 and equation 3) are presented in Table 4-9. These indicate that in DMF and DMSO are gradually decrease with increase in proportion of organic component of the solvent mixture and increase with temperature as expected due to increase in the mobility of the ions. The Λ^0 values also depend on the composition of the binary solvent mixture. However, a different behaviour is observed in aqueous-MeOH. The Λ^0 values decrease upto 40-60% MeOH and thereafter they increase slightly. Similar behavior is observed with all the three alkyl sulfonates at all the four temperatures used. This may be due to the change in the viscosity and dielectric constant of the medium to solvent-solvent and ion-solvent interactions. A decrease in mobility of the ion due to solvation shell increases by size and captures more number of conducting ions. The higher value of Λ^0 in 100% water than in 100% organic solvent suggests that the ions are relatively free in water which has higher dielectric constant than the organic solvent and slight variation in aqueous-MeOH.

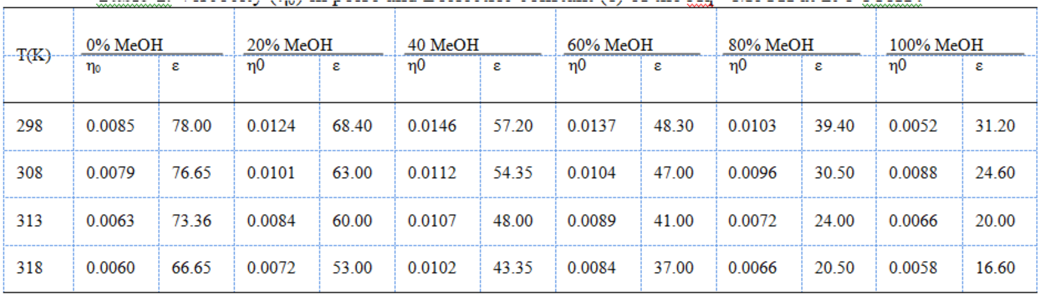
In solution the ions are within equilibrium by means of the ion-pairs. These values are evaluated for the three electrolytes applying linear smallest amount square analysis using Kraus-Bray and Shedlovsky models, the dissociation constant K_C and the association constant K_A of the ion-pair have been evaluate and presented in Table 4-9 along with Λ^0 values. There appears to e good agreement between K_A and Kc (which is K_A^{-1}) which are obtained from different models. This data indicates that for each electrolyte $K_A > 1$ suggesting that the fraction of ions which exist as ion-pairs is higher than the free ions.

The K_A values of each sulfonate in different 100% solvents are in the following order

Methyl sulfonate
DMSO > MeOH > DMF > Water
Butyle sulfonate
DMF > DMSO > MeOH > Water
Pentyl sulfonate
DMSO > DMF > MeOH > Water

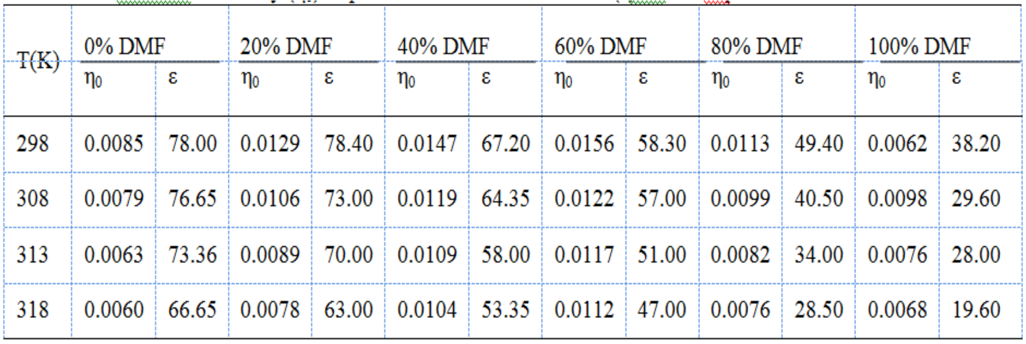
This trend suggests that ion-pair formation is controlled not solely by dielectric constant of the medium but also by viscosity of it.

Table 1. Viscocity (η_0) in poise and Dielectric constant (ε) of the Aq - MeOH at 298-318K .



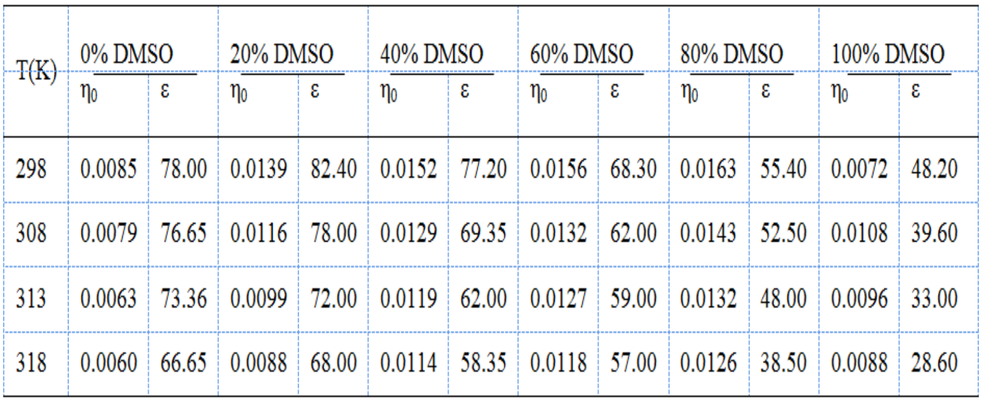
T(K)	0% MeOH		20% MeOH		40 MeOH		60% MeOH		80% MeOH		100% MeOH	
	η_0	ε	η0	ε	η0	ε	η0	ε	η0	ε	η0	ε
298	0.0085	78.00	0.0124	68.40	0.0146	57.20	0.0137	48.30	0.0103	39.40	0.0052	31.20
308	0.0079	76.65	0.0101	63.00	0.0112	54.35	0.0104	47.00	0.0096	30.50	0.0088	24.60
313	0.0063	73.36	0.0084	60.00	0.0107	48.00	0.0089	41.00	0.0072	24.00	0.0066	20.00
318	0.0060	66.65	0.0072	53.00	0.0102	43.35	0.0084	37.00	0.0066	20.50	0.0058	16.60

Table 2. Viscocity (η_0) in poise and Dielectric constant (ε) of the Aq - DMF 308-318K .



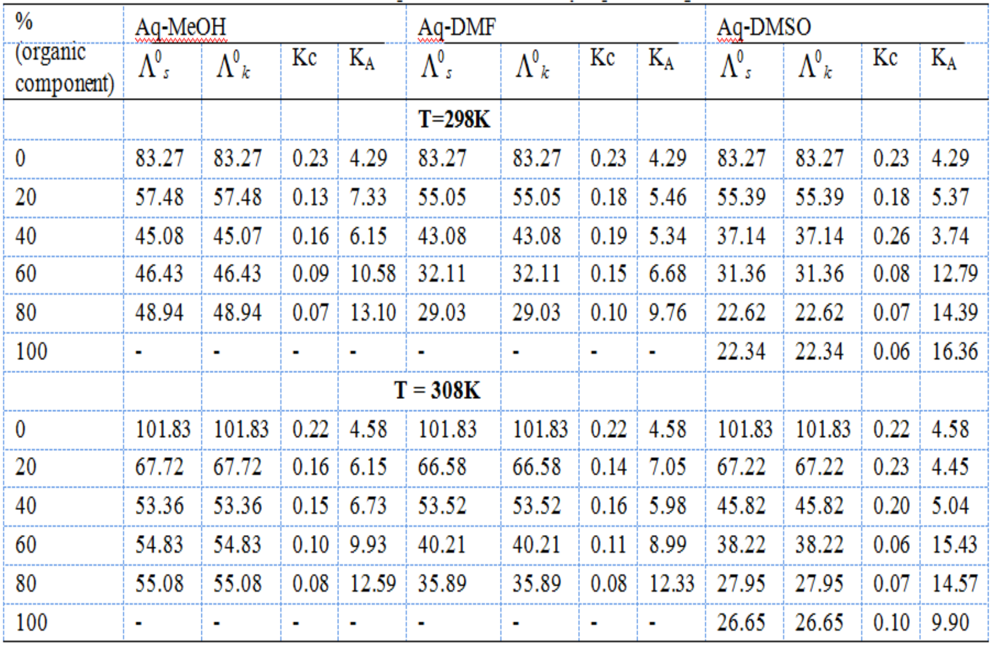
T(K)	0% DMF		20% DMF		40% DMF		60% DMF		80% DMF		100% DMF	
	η_0	ε	η_0	ε	η_0	ε	η_0	ε	η_0	ε	η_0	ε
298	0.0085	78.00	0.0129	78.40	0.0147	67.20	0.0156	58.30	0.0113	49.40	0.0062	38.20
308	0.0079	76.65	0.0106	73.00	0.0119	64.35	0.0122	57.00	0.0099	40.50	0.0098	29.60
313	0.0063	73.36	0.0089	70.00	0.0109	58.00	0.0117	51.00	0.0082	34.00	0.0076	28.00
318	0.0060	66.65	0.0078	63.00	0.0104	53.35	0.0112	47.00	0.0076	28.50	0.0068	19.60

Table 3. Viscocity (η_0) in poise and Dielectric constant (ε) of the Aq- DMSO 308-318K.



T(K)	0% DMSO		20% DMSO		40% DMSO		60% DMSO		80% DMSO		100% DMSO	
	η_0	ε	η_0	ε	η_0	ε	η_0	ε	η_0	ε	η_0	ε
298	0.0085	78.00	0.0139	82.40	0.0152	77.20	0.0156	68.30	0.0163	55.40	0.0072	48.20
308	0.0079	76.65	0.0116	78.00	0.0129	69.35	0.0132	62.00	0.0143	52.50	0.0108	39.60
313	0.0063	73.36	0.0099	72.00	0.0119	62.00	0.0127	59.00	0.0132	48.00	0.0096	33.00
318	0.0060	66.65	0.0088	68.00	0.0114	58.35	0.0118	57.00	0.0126	38.50	0.0088	28.60

Table 4. Molar conductance (mho cm^2 mol^{-1}), Dissociation constant (Kc) and Association constant (K_A) values of Sodium salt of methane sulphonic acid in binary aqueous-organic mixtures.

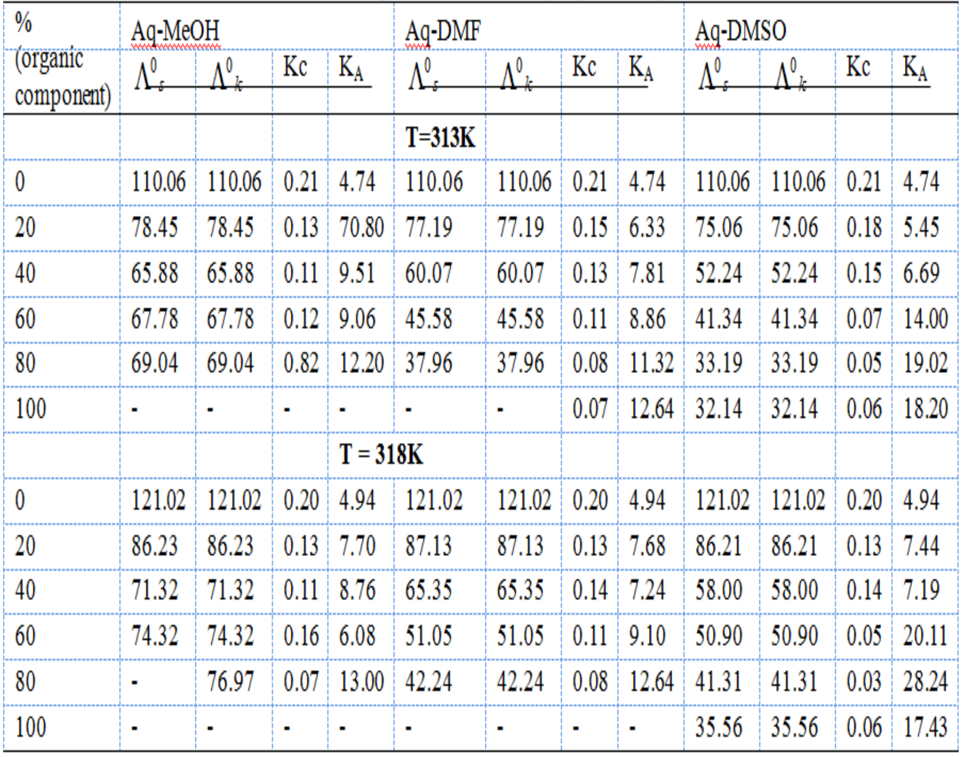


% (organic component)	Aq-MeOH				Aq-DMF				Aq-DMSO			
	Λ^0_s	Λ^0_k	Kc	K_A	Λ^0_s	Λ^0_k	Kc	K_A	Λ^0_s	Λ^0_k	Kc	K_A
					T=298K							
0	83.27	83.27	0.23	4.29	83.27	83.27	0.23	4.29	83.27	83.27	0.23	4.29
20	57.48	57.48	0.13	7.33	55.05	55.05	0.18	5.46	55.39	55.39	0.18	5.37
40	45.08	45.07	0.16	6.15	43.08	43.08	0.19	5.34	37.14	37.14	0.26	3.74
60	46.43	46.43	0.09	10.58	32.11	32.11	0.15	6.68	31.36	31.36	0.08	12.79
80	48.94	48.94	0.07	13.10	29.03	29.03	0.10	9.76	22.62	22.62	0.07	14.39
100	-	-	-	-	-	-	-	-	22.34	22.34	0.06	16.36
					T = 308K							
0	101.83	101.83	0.22	4.58	101.83	101.83	0.22	4.58	101.83	101.83	0.22	4.58
20	67.72	67.72	0.16	6.15	66.58	66.58	0.14	7.05	67.22	67.22	0.23	4.45
40	53.36	53.36	0.15	6.73	53.52	53.52	0.16	5.98	45.82	45.82	0.20	5.04
60	54.83	54.83	0.10	9.93	40.21	40.21	0.11	8.99	38.22	38.22	0.06	15.43
80	55.08	55.08	0.08	12.59	35.89	35.89	0.08	12.33	27.95	27.95	0.07	14.57
100	-	-	-	-	-	-	-	-	26.65	26.65	0.10	9.90

Λ^0_k = Kraus-Bray Model Λ^0_s = Shedlovsky model

K_A = Association constant from Shedlovsky equation K_C =Dissociation constant from Kraus-Bray equation

Table 5. Molar conductance (mho cm^2 mol^{-1}), Dissociation constant (Kc) and Association constant (K_A) values of Sodium salt of methane sulphonic acid in binary aqueous-organic mixtures .

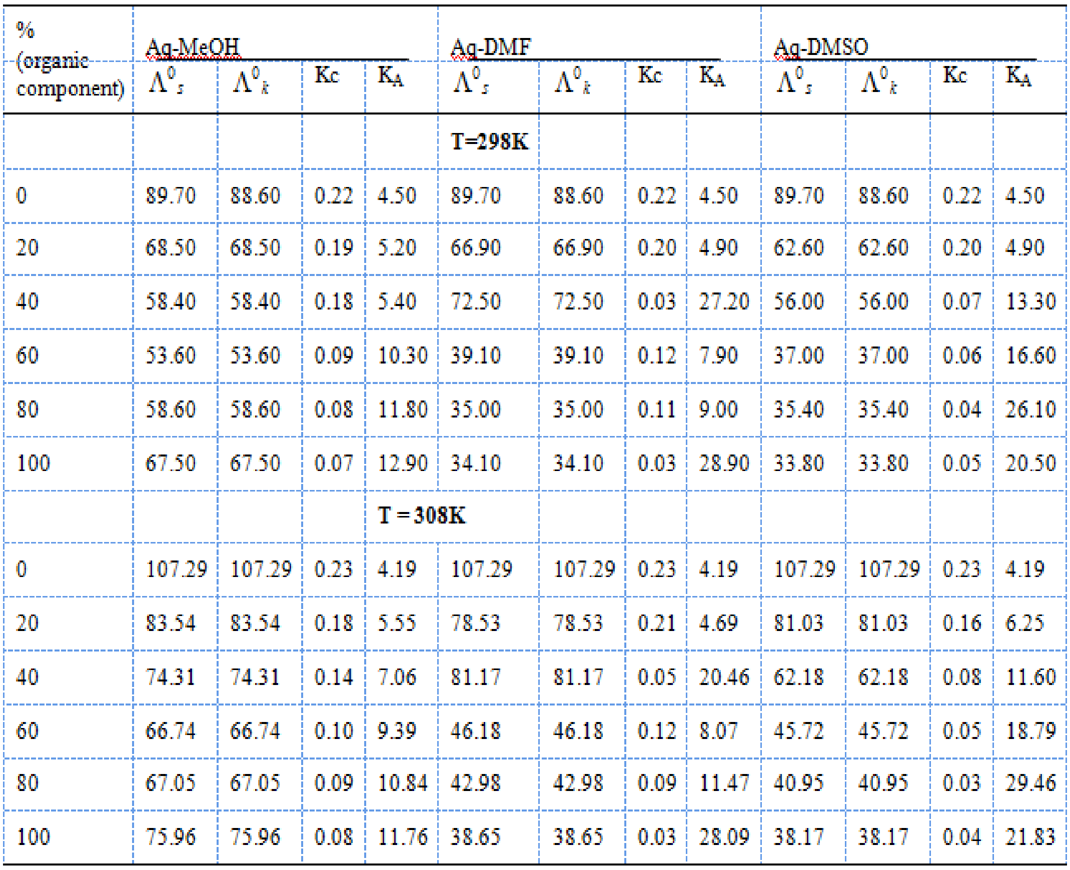


% (organic component)	Aq-MeOH				Aq-DMF				Aq-DMSO			
	Λ^0_s	Λ^0_k	Kc	K_A	Λ^0_s	Λ^0_k	Kc	K_A	Λ^0_s	Λ^0_k	Kc	K_A
					T=313K							
0	110.06	110.06	0.21	4.74	110.06	110.06	0.21	4.74	110.06	110.06	0.21	4.74
20	78.45	78.45	0.13	70.80	77.19	77.19	0.15	6.33	75.06	75.06	0.18	5.45
40	65.88	65.88	0.11	9.51	60.07	60.07	0.13	7.81	52.24	52.24	0.15	6.69
60	67.78	67.78	0.12	9.06	45.58	45.58	0.11	8.86	41.34	41.34	0.07	14.00
80	69.04	69.04	0.82	12.20	37.96	37.96	0.08	11.32	33.19	33.19	0.05	19.02
100	-	-	-	-	-	-	0.07	12.64	32.14	32.14	0.06	18.20
					T = 318K							
0	121.02	121.02	0.20	4.94	121.02	121.02	0.20	4.94	121.02	121.02	0.20	4.94
20	86.23	86.23	0.13	7.70	87.13	87.13	0.13	7.68	86.21	86.21	0.13	7.44
40	71.32	71.32	0.11	8.76	65.35	65.35	0.14	7.24	58.00	58.00	0.14	7.19
60	74.32	74.32	0.16	6.08	51.05	51.05	0.11	9.10	50.90	50.90	0.05	20.11
80	-	76.97	0.07	13.00	42.24	42.24	0.08	12.64	41.31	41.31	0.03	28.24
100	-	-	-	-	-	-	-	-	35.56	35.56	0.06	17.43

Λ^0_k = Kraus-Bray Model Λ^0_s = Shedlovsky model

K_A = Association constant from Shedlovsky equation K_C = Dissociation constant from Kraus-Bray equation

Table 6. Molar conductance (mho cm^2 mol^{-1}), Dissociation constant (Kc) and Association constant (K_A) values of Sodium salt of 1-butane sulphonic acid in binary aqueous-organic mixtures .

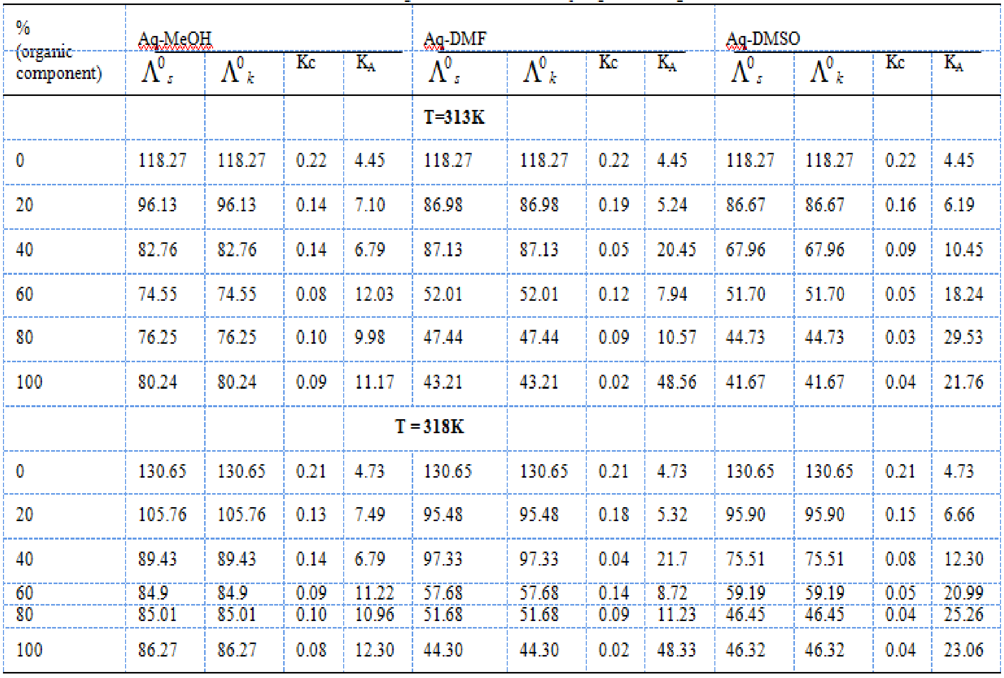


% (organic component)	Aq-MeOH Λ^0_s	Λ^0_k	Kc	K_A	Aq-DMF Λ^0_s	Λ^0_k	Kc	K_A	Aq-DMSO Λ^0_s	Λ^0_k	Kc	K_A
					T=298K							
0	89.70	88.60	0.22	4.50	89.70	88.60	0.22	4.50	89.70	88.60	0.22	4.50
20	68.50	68.50	0.19	5.20	66.90	66.90	0.20	4.90	62.60	62.60	0.20	4.90
40	58.40	58.40	0.18	5.40	72.50	72.50	0.03	27.20	56.00	56.00	0.07	13.30
60	53.60	53.60	0.09	10.30	39.10	39.10	0.12	7.90	37.00	37.00	0.06	16.60
80	58.60	58.60	0.08	11.80	35.00	35.00	0.11	9.00	35.40	35.40	0.04	26.10
100	67.50	67.50	0.07	12.90	34.10	34.10	0.03	28.90	33.80	33.80	0.05	20.50
					T = 308K							
0	107.29	107.29	0.23	4.19	107.29	107.29	0.23	4.19	107.29	107.29	0.23	4.19
20	83.54	83.54	0.18	5.55	78.53	78.53	0.21	4.69	81.03	81.03	0.16	6.25
40	74.31	74.31	0.14	7.06	81.17	81.17	0.05	20.46	62.18	62.18	0.08	11.60
60	66.74	66.74	0.10	9.39	46.18	46.18	0.12	8.07	45.72	45.72	0.05	18.79
80	67.05	67.05	0.09	10.84	42.98	42.98	0.09	11.47	40.95	40.95	0.03	29.46
100	75.96	75.96	0.08	11.76	38.65	38.65	0.03	28.09	38.17	38.17	0.04	21.83

Λ^0_k = Kraus-Bray Model Λ^0_s = Shedlovsky model

K_A = Association constant from Shedlovsky equation K_C = Dissociation constant from Kraus-Bray equation

Table7. Molar conductance (mho cm^2 mol^{-1}), Dissociation constant (Kc) and Association constant (K_A) values of Sodium salt of 1-butane sulphonic acid in binary aqueous-organic mixtures .



% (organic component)	Aq-MeOH Λ^0_s	Λ^0_k	Kc	K_A	Aq-DMF Λ^0_s	Λ^0_k	Kc	K_A	Aq-DMSO Λ^0_s	Λ^0_k	Kc	K_A
					T=313K							
0	118.27	118.27	0.22	4.45	118.27	118.27	0.22	4.45	118.27	118.27	0.22	4.45
20	96.13	96.13	0.14	7.10	86.98	86.98	0.19	5.24	86.67	86.67	0.16	6.19
40	82.76	82.76	0.14	6.79	87.13	87.13	0.05	20.45	67.96	67.96	0.09	10.45
60	74.55	74.55	0.08	12.03	52.01	52.01	0.12	7.94	51.70	51.70	0.05	18.24
80	76.25	76.25	0.10	9.98	47.44	47.44	0.09	10.57	44.73	44.73	0.03	29.53
100	80.24	80.24	0.09	11.17	43.21	43.21	0.02	48.56	41.67	41.67	0.04	21.76
					T = 318K							
0	130.65	130.65	0.21	4.73	130.65	130.65	0.21	4.73	130.65	130.65	0.21	4.73
20	105.76	105.76	0.13	7.49	95.48	95.48	0.18	5.32	95.90	95.90	0.15	6.66
40	89.43	89.43	0.14	6.79	97.33	97.33	0.04	21.7	75.51	75.51	0.08	12.30
60	84.9	84.9	0.09	11.22	57.68	57.68	0.14	8.72	59.19	59.19	0.05	20.99
80	85.01	85.01	0.10	10.96	51.68	51.68	0.09	11.23	46.45	46.45	0.04	25.26
100	86.27	86.27	0.08	12.30	44.30	44.30	0.02	48.33	46.32	46.32	0.04	23.06

Λ^0_k = Kraus-Bray Model Λ^0_s = Shedlovsky model

K_A = Association constant from Shedlovsky equation K_C = Dissociation constant from Kraus-Bray equation

Table 8. Molar conductance (mho cm^2 mol^{-1}), Dissociation constant (Kc) and Association constant (K_A) values of Sodium salt of pentane sulphonic acid in binary aqueous-organic mixtures .

% (organic component)	Aq-MeOH				Aq-DMF				Aq-DMSO			
	Λ^0_s	Λ^0_k	Kc	K_A	Λ^0_s	Λ^0_k	Kc	K_A	Λ^0_s	Λ^0_k	Kc	K_A
					T=298K							
0	76.09	77.15	0.18	5.53	76.09	77.15	0.18	5.53	76.09	77.15	0.18	5.53
20	54.09	56.01	0.19	5.12	56.07	56.07	0.15	6.47	67.62	67.62	0.13	7.41
40	46.90	48.12	0.14	6.81	39.88	39.88	0.14	7.02	39.86	39.86	0.15	6.44
60	45.41	46.86	0.11	8.71	33.93	33.93	-	-	27.96	27.96	0.09	10.48
80	57.97	59.00	0.05	19.06	36.55	36.55	0.04	22.26	26.88	26.88	0.05	21.06
100	64.24	65.15	0.08	12.17	44.29	44.29	0.12	8.21	34.81	34.81	0.03	28.00
				T = 308K								
0	91.41	91.41	0.19	5.17	91.41	91.41	0.19	5.17	91.41	91.41	0.19	5.17
20	69.84	69.84	0.16	6.00	64.21	64.21	0.16	6.29	78.69	78.69	0.12	8.39
40	56.35	56.35	0.15	6.34	49.99	49.99	0.10	9.55	47.02	47.02	0.15	6.72
60	55.61	55.61	0.12	7.99	38.69	38.69	0.09	10.77	32.19	32.19	0.01	10.19
80	65.55	65.55	0.06	17.22	39.99	39.99	0.06	17.04	30.06	30.06	0.05	19.46
100	77.11	77.11	0.08	11.86	62.77	62.77	0.02	60.70	38.08	38.08	0.04	25.74

$\Lambda^0{}_k$ = Kraus-Bray Model $\Lambda^0{}_s$ = Shedlovsky model

K_A = Association constant from Shedlovsky equation K_C = Dissociation constant from Kraus-Bray equation

Table 9. Molar conductance (mho cm^2 mol^{-1}), Dissociation constant (Kc) and Association constant (K_A) values of Sodium salt of pentane sulphonic acid in binary aqueous-organic mixtures .

% (organic component)	Aq-MeOH				Aq-DMF				Aq-DMSO			
	Λ^0_s	Λ^0_k	Kc	K_A	Λ^0_s	Λ^0_k	Kc	K_A	Λ^0_s	Λ^0_k	Kc	K_A
					T=313K							
0	101.49	101.49	0.19	5.27	101.49	101.49	0.19	5.27	101.49	101.49	0.19	5.27
20	78.53	78.53	0.16	6.28	74.19	74.19	0.17	5.74	89.37	88.69	0.11	9.13
40	62.65	62.65	0.15	6.47	57.34	57.34	0.09	11.21	53.63	53.63	0.23	4.36
60	61.16	61.16	0.14	7.46	44.69	44.69	0.08	11.27	38.37	38.37	0.07	13.60
80	69.55	69.55	0.07	13.23	46.52	46.52	0.05	20.74	35.68	35.68	0.04	22.15
100	77.11	77.11	0.06	14.34	65.61	65.61	0.02	54.14	41.78	41.78	0.03	27.59
				T = 318K								
0	106.44	106.44	0.18	5.37	106.44	106.44	0.18	5.37	106.44	106.44	0.18	5.37
20	87.75	87.75	0.17	5.91	85.80	85.80	0.12	8.14	91.87	90.79	0.13	7.79
40	68.51	68.51	0.16	6.21	62.32	62.32	0.10	9.99	58.48	58.48	0.12	7.84
60	66.36	66.36	0.15	6.49	48.63	48.63	0.09	10.66	46.35	46.35	0.07	13.66
80	76.71	76.71	0.07	13.40	52.56	52.56	0.04	24.11	42.49	42.49	0.04	27.05
100	81.52	81.52	0.06	14.54	74.52	74.52	0.02	55.97	46.99	46.99	0.03	32.37

$\Lambda^0{}_k$ = Kraus-Bray Model $\Lambda^0{}_s$ = Shedlovsky model

K_A = Association constant from Shedlovsky equation K_C = Dissociation constant from Kraus-Bray equation

IV. ConclusioN

We can conclude from these experimental observations that ion-ion interactions are strong in DMSO while ion-solvent interactions are weaker in DMSO compared to other solvents in the case of sodium alkyl sulfonates.

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