THE DISSOCIATION CONSTANTS OF HALIDES AND NITRATES OF SODIUM AND POTASSIUM IN WATER - ACETONE MIXTURES

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From the conductance measurements the pK values of halides and nitrates of sodium and potassium in 10, 20 and 30 wt% acetone mixtures have been evaluated at 25°C. The results have been discussed in terms of preferential solvation of ions.

As a continuation of our previous investigation [1] in aqueo-organic solvents, dissociation behaviour of halides and nitrates have been examined in water acetone mixtures.

EXPERIMENTAL

Acetone (BDH, AnalaR) was refluxed with potassium permanganate (BDH Analar) and distilled. The middle fraction was subsequently distilled over anhydrous potassium carbonate. Solvents of various compositions were made up by weight in conductivity water.

Nitrates and halides of sodium and potassium were either of G.R., E. Merck or BDH (AnalaR) grade. The salts were dried at 100-120°C for 2 hrs and stored in vacuum desiccator over calcium chloride until required. 0.1 N stock solutions of each of the electrolytes were prepared in various mixed solvents. Solutions of the required concentration were prepared from the stock solutions by double dilution method using the corresponding mixed solvent.

The ionic strength of the solutions were kept as low as possible. The experiment was repeated several times with different concentrations of the salts (ranging from 2.5×10^{-2} to 3.0×10^{-3} N) in various mixed solvents. Conductance measurements were made several times on a digital direct reading conductivity meter (Systronics, Type 304) with a sensitivity of 0.1%. A. dipping type conductivity cell with platinised electrodes (cell constant 1 ohm^{-1} cm^{-1}) was used. The measurements were carried out at 25 ± 0.05°C. The specific and equivalent conductances are expresed in ohm^{-1} cm^{-1} and ohm^{-1} cm^2 $equiv^{-1}$, respectively.

RESULTS AND DISCUSSION

The conductances of different concentrations [8-10] of electrolyte solutions were measured and corrections for the conductances of the solvents were applied. The values of the equivalent conductance, at any concentration have been computed from the corrected conductance data. An auxiliary function, Λ'_o is calculated using the formula [1]

$$\Lambda'_c = \frac{\Lambda + A\sqrt{C}}{1 - B\sqrt{C}} \qquad ..(1)$$

where Λ is the equivalent conductance of the solution at the concentration, c; A and B are the Onsagar constants, and were calculated from the values of viscosities and dielectric constants of water + acetone mixtures at 25°C. These values are 49.88, 58.56 and 70.06 and 0.2555, 0.2908 and 0.3343, respectively, for 10, 20 and 30 wt% acetone mixtures at 25°C. The values of the equivalent conductance at infinite dilution, Λ_o were obtained by linear extrapolation of the auxiliary functions, Λ'_o.

The initial value of α, the degree of dissociation of the electrolyte, at a concentration c of the experimental solution was evaluated from the relation:

$$\alpha = \frac{\Lambda}{\Lambda_o}$$

This value of α was used in the Onsagar equation,

$$\Lambda = \alpha[\Lambda_o - (A + B\Lambda_o)\sqrt{\alpha C}] \qquad ...(2)$$

to get a new value of Λ. This new value of Λ was further used in equation (1) to get a corrected value of Λ'_o. Extrapolation of these corrected Λ'_o values as a function of c to infinite dilution yielded a better value of Λ_o. This process of iteration is repeated several times till the value of α does not change further on reiteration. This final value of α, therefore, represents the degree of disso-

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ciation of the electrolyte at the actual ionic concentration. The values of Λ_o so obtained are recorded in Table 1 along with those available in water[2] at 25°C for the sake of comparison.

As observed in the more dilute solutions, the experimental results are in good agreement with the Debye-Huckel-Onsager conductance theory, but at higher concentrations, deviations become evident. The experimental slope, of the lines in the curves of the plots of Λ_c' vs $\sqrt{c}$ agrees well with the theoretical slope value ($A + B\Lambda_o$) calculated from the Onsager constants A and B and the Λ_o value. This agreement is very much satisfactory in dilute solutions ($c < 0.08$ equiv/l) but at higher concentrations slight deviation occures. However, in the present work, for a few electrolytes such higher concentrations have been studied. The Λ_o values as given in Table 1 seem to be quite in order. Λ_o values decrease as the percentage of acetone increases-similar to that in water + sugar solutions for these electrolytes [1]. It is also seen that Λ_o values are lower in the mixed solvents compared to those in water [2] as expected.

A comparison of the Λ_o values for these electrolytes in water + acetone mixtures with that in water + sugar solutions [1] shows that the Λ_o values are less in water + acetone mixed solvents than in water + d-glucose or water + d-fructose mixtures. This points to the fact that the conductivities of the electrolytes decrease with decrease in dielectric constant of the medium.

The conductivities of the nitrates and halides of sodium and potassium at any given concentration are found to decrease in the order : $Br^- > I^- > Cl^- > NO_3^-$. The difference in the conductivities of the electrolytes may be attributed to an increase in the extent of solvation of the anions in the series: $Br^- < I^- < Cl^- < NO_3^-$.

The dissociation constant for the reaction,

$$MX \rightleftharpoons M^+ + X^- \qquad \ldots(3)$$

can be written as

$$K = \frac{(\alpha C_{M^+} \cdot \alpha C_{X^-}) f_\pm^2}{(1-\alpha) C_{MX}} = \frac{\alpha^2 c f_\pm^2}{(1-\alpha)} \qquad \ldots(4)$$

where the terms have their usual significance. The $\log f_\pm$ values were calculated from the equation

$$-\log f_\pm = S\sqrt{\alpha c} \qquad \ldots(5)$$

using the appropriate values of the Debye-Huckel constant, S in the mixed solvents.

The values of K for different electrolytes obtained by means of equation (4) at various concentations in the mixed solvents were designated as K' and the linear extrapolation of the values of log K' to zero ionic strength (ionic strength, $\mu = \alpha c$) gave the true dissociation constant, pK (Table 2). The results show a good linearity when pK is plotted against the reciprocal of the dielectric constant of the solvent. This agrees reasonably well with the fact that pK values increase with decrease in dielectric constant. The lowering of pK values in water + acetone mixtures as compared to that in water shows that the electrolytes are less dissociated in the mixed solvents.

TABLE 1

Λ_o VALUES OF 1:1 ELECTROLYTES IN WATER AND WATER + ACETONE MIXTURES AT 25°C.

Electrolytes	mass % acetone			
	0	10	20	30
KNO_3	144.96	127.5	113.58	101.34
KCl	149.86	131.46	114.8	101.7
KBr	151.9	137.92	120.5	103.6
KI	158.38	132.9	118.3	102.4
$NaNO_3$	121.6	103.13	87.3	74.9
NaCl	126.45	109.16	91.8	86.71
NaBr	128.51	112.3	96.36	89.78
NaI	126.94	110.25	92.78	87.79

TABLE 2

pK_a VALUES OF 1:1 ELECTROLYTES IN WATER + ACETONE MIXTURES AT 25°C.

Electrolytes	mass % acetone			Electrolytes	mass % acetone		
	10	20	30		10	20	30
KNO_3	1.76	2.53	2.67	$NaNO_3$	1.79	2.65	2.69
KCl	1.70	2.33	2.49	NaCl	1.71	2.56	2.63
KBr	1.66	2.16	2.35	NaBr	1.67	2.47	2.54
KI	1.68	2.18	2.39	NaI	1.69	2.53	2.61

As observed, potassium salts are more dissociated than sodium salts. The pK values of the nitrates and halides of sodium and potassium in any solvent composition are found to decrease in the order: $NO_3^- > Cl^- > I^- > Br^-$ which is reverse to that of their conductivities. In other words, higher the conductivity values greater the dissociation.

REFERRENCES

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THERMODYNAMICS OF DISSOCIATION OF BENZOIC ACIDS IN MIXED SOLVENTS

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Free energies of transfer of ortho-, meta-, and para substituted nitro-, chloro-, hydroxy- and amino benzoic acids from water to binary solvent mixtures have been estimated from pK_a data of the acids obtained from pH measurements. In addition, the effect of substituents of the pK_a value of benzoic acid has been discussed in these binary solvents in terms of qualitative theory of substituent effects. Linear free energy relationships have been examined in the mixed solvents.

Studies on the dissociation constants of acids and especially substituted benzoic acids in aqueous [1] and a few non-aqueous media, eg., formamide [2] ethylene glycol [3] propylene glycol [3], ethanol [3] and tetrahydrofuran [3] have received much attention. Thermodyanamics of dissociation of a number of mono-, and dicarboxylic acids in a wide variety of mixed solvents [4] are reported. However knowledge of the thermodynamic data in mixed solvents is still lacking. Such studies are helpful in understanding the solvent effects, solute-solvent, solvent-solvent interactions on the thermodynamics parameters.

In this communication we report the studies of ortho-, meta-, and para substituted nitro-, chloro-, hydroxy-, and amino benzoic acids in different methanol-, ethanol-, 1-propanol, 2-propanol-, glycerol-, d-glucose-, and d-fructose-water mixtures at 25°C and the corresponding free energy changes calculated from pK_a values.

EXPERIMENTAL

Methanol, ethanol, 1-propanol, 2-propanol and glycerol were B.D.H., Laboratory reagents and purified by methods described in earlier

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