Thermodynamic Properties of Electrolytes in n-Butanol - E.M.F.Measurements on Cells with Transference

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EMF of the cells with transference

Ag,AgX / MX (C_1) // MX (C_2) / AgX.Ag

(MX = LiCl, Me_4NCl, Et_4NCl, Bu_4NCl, Bu_4NBr and Bu_4NI) have been measured in n-butanol. Mean activity coefficients calculated using the data along with reported association constant values from conductance data are found to be anomalous. So a method has been devised to calculate mean activity coefficients using only EMF data. These values in n-butanol are comparable with the values in DMF, DMSO and tetramethylurea in spite of a large difference in the dielectric constant of the solvents. This agreement is explained on the basis of very high solvation of the ions in n-butanol.

Determination of mean activity coefficients of electrolytes using concentration cell methods have proven to be superior to other methods [1]. This method is employed extensively in aqueous solutions [2]. But, such information for non-aqueous solvents is scarce because, most of the electrodes exhibit irreversible behaviour in these solvents. However, it has been observed that Ag/AgX electrodes behave reversibly in alcoholic solvents; in fact, some results on concentration cells without transference have been reported for methanol and ethanol [3]. However, cells without transference cannot be used at low concentrations [1] because the flowing amalgam electrodes show erratic behaviour. In solvents like n-butanol (which have low dielectric constant), the study need be conducted particularly at low concentrations in order to avoid the complications of high ion - ion interactions occuring at high concentrations. Electromotive force (EMF) measurements of the cells with transference have been carried out in n-butanol at quite low concentrations using lithium chloride, tetramethylammonium chloride, tetraethyla-mmonium chloride, tetrabutylammonium chloride, tetrabutylammonium bromide and tetrabutylammonium iodide as solutes. Measurements are repeated at three different temperatures. The results have been used to evaluate association constants and the mean activity coefficients of the electrolytes.

EXPERIMENTAL

n-Butanol was purified essentially by the method reported earlier [4]. Freshly distilled solvent was checked for its purity by

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measurements of physical properties like conductivity and density before EMF measurement [5]. All the electrolytes used in these studies (BDH AnalaR or Reidel Pure) were recrystallysed from conductivity water and dried under reduced pressure at 373.15°K before use [6].

Silver - silver halide electrodes were prepared essentially by the same method as reported by Ives and Janz [7]. The cell designed by Hornibrook [8] was used with slight modifications. The concentration cell was equipped with two pairs of electrodes. Potential was measured twice for each pair of electrodes. The polarity was then reversed and measurement was repeated. In case the potentials in the two positions differed by more than 0.02 mV, the whole set of measurements was rejected.

Method of Calculation

Hornibrook [8] suggested the following equation for the evaluation of mean activity coefficients of the electrolytes from the EMF values.

$$\Delta \log \gamma_{\pm} = -\left\{\frac{E}{kt_R}\right\} - \{\log C_1 - \log C_2\}$$

$$- t_R^{-1} \int_{C_2}^{C_1} \Delta t \; d \log C \; - t_R^{-1} \int_{(\gamma_\pm)_2}^{(\gamma_\pm)_1} \Delta t \; d \log \gamma_{\pm} \quad \ldots (1)$$

where E = the EMF of the cell, k = 4.606 RT/F, C_1 and C_2 are the concentrations of the free ions in the two solutions, t_R = transference number of the cation at the reference concentration and all other symbols have their usual meaning [8].

Conductance measurements of various uni-univalent electrolyte solutions in n-butanol reveal that all the electrolytes form ion - pair in this solvent [5,9,10]. So, to calculate the concentration of free ions, a knowledge of degree of dissociation of the electrolytes at various concentrations or the dissociation / association constant of the electrolyte is required. The method suggested by Nanez and Day [11] has been employed in the present case to evaluate the degree of dissociation at a given concentration of the electrolyte using the following steps.

A first order approximate value of the mean activity coefficient $(\gamma_{\pm})_1$ was evaluated using the extended Debye-Huckel equation [12]. An approximate value of the degree of dissociation (α_1) is evaluated using this value of $(\gamma_{\pm})_1$ in the following equation:

$$\alpha = 1/2 \left\{\frac{K}{\gamma_{\pm}^2 C}\right\} \pm \left\{\frac{K^2}{\gamma_{\pm}^4 C^2} + \frac{4K}{\gamma_{\pm}^3 C}\right\}^{1/2} \quad \ldots (2)$$

where K is the dissociation constant $(= 1/K_A)$.

Marshall and Grunwald [13] showed that dissociation constant K from EMF measurements might be identical with the ion-pair dissociation constant from conductance measurements. Evans and Gardam [5] have reported the values of association constants of some

tetraalkylammonium salts from conductivity measurements in n-butanol at 298.15°K. These K_A values are used in equation 2 to evaluate $(\alpha)_1$.

With this value of $(\alpha)_1$, a second approximate value of $(\gamma_\pm)_2$ is calculated using new concentration value of $\alpha_1 C$ in the Debye-Huckel equation. This value of $(\gamma_\pm)_2$ is used in equation 2 to calculate a second approximate value of degree of dissociation $(\alpha)_2$. This process of successive approximations was repeated until $(\alpha_n - \alpha_{n-1}) < 0.0001$.

The final values of α at various concentrations were used to evaluate $\Delta \log \gamma_\pm$ from the EMF values in n-butanol using equation 1. $\Delta \log \gamma_\pm$ can thus be evaluated from EMF data, transference number and dissociation constant of the salt. The procedure is essentially the same as described by Harned and Owen [12].

The values of $\Delta \log \gamma_\pm$ is empirically related to the mean activity coefficient of the electrolyte $\log \gamma_\pm$ by the relationship [12]:

$$\log \gamma_\pm = A' - \Delta \log \gamma_\pm \quad \ldots (3)$$

The Debye-Huckel equation can be written in the form [14]:

$$-\log \gamma_\pm = AC^{1/2} - B'C \quad \ldots (4)$$

Combining equations 3 and 4 and rearranging, the following equation is obtained:

$$\Delta \log \gamma_\pm - AC^{1/2} = A' - B'C \quad \ldots (5)$$

A is the Debye Huckel constant which can be evaluated using relevent physical constants. Using $\Delta \log \gamma_\pm$ calculated above, the left hand side of equation 5 can be evaluated for different values of C. The plot of this *vs* C is expected to be a straight line from which A' and B' can be evaluated; hence, $\log \gamma_\pm$ from equation 4.

RESULTS AND DISCUSSION

EMF values of cells with transference of all the electrolytes at different concentrations are given in Table 1.

Association constant values are not available for all the salts. The values from conductance data are available in literature [5] for tetrabutylammonium chloride, tetrabutylammonium bromide and tetrabutylammonium iodide and have been used here. Transference number data are reported from our laboratory [15]. Using these values and the EMF data from the present work, plots of $\Delta \log \gamma_\pm - AC^{1/2}$ *vs* C are made for these salts. It is found that the plots are not linear as expected; they show a distinct curvature over the entire concentration range studied, thus making an accurate extrapolation (to obtain A') very difficult.

The mean activity coefficients were evaluated by combining B' obtained from the slope of the tangent of the above plot at the given concentration with equation 4. All the relevent values for these electrolytes are

Table 1

EMF Values of Cells with Transference for Some Electrolytes

Solvent n-Butanol; Temperature varying;
Varying concentrations of salt in the cell is C_1;
concentration in reference solution is C_2;

C_1 mol/dm³	EMF values in mV 298.15°	308.15°	318.15°
Electrolyte LiCl; C_2 mol/dm³ = 0.000050			
0.000709	51.81	52.63	53.58
0.001110	63.08	64.72	65.74
0.001432	69.51	71.45	72.62
0.001981	77.81	80.00	81.57
0.002580	84.59	87.18	89.03
Electrolyte Me_4NCl; C_2 mol/dm³ = 0.000049			
0.000630	43.82	45.97	46.34
0.001109	56.68	59.33	60.34
0.001880	68.08	70.63	72.94
0.002629	75.75	78.20	80.02
0.003350	81.16	83.86	85.61
Electrolyte Et_4NCl; C_2 mol/dm³ = 0.000050			
0.000691	48.22	48.78	49.00
0.001312	62.86	64.00	65.10
0.001889	71.56	72.82	74.54
0.002279	76.14	77.26	79.04
0.002871	81.52	82.80	85.02
Electrolyte Bu_4NCl; C_2 mol/dm³ = 0.000051			
0.000619	49.71	50.66	51.59
0.001021	61.19	62.75	64.36
0.001501	70.39	72.37	74.33
0.002139	79.06	81.36	83.47
0.002780	85.14	97.89	90.33
Electrolyte Bu_4NBr; C_2 mol/dm³ = 0.000049			
0.000390	38.18	39.24	40.28
0.001081	61.98	63.56	65.32
0.001269	65.72	67.47	69.40
0.001992	76.08	77.72	79.62
0.002701	83.18	85.12	87.00
0.003297	87.92	90.00	92.08
Electrolyte Bu_4NI; C_2 mol/dm³ = 0.000050			
0.000580	47.05	48.22	49.53
0.000961	57.18	59.18	61.64
0.001423	65.06	67.61	70.49
0.001965	71.67	74.59	78.08
0.002435	76.18	79.25	83.01

recorded in Table 2. With the mean activity coefficients so obtained and the final values of α, the values of association constants were calculated at all the concentrations for the above three electrolytes with the help of the following equation:

$$K_A = \frac{(1 - \alpha)}{\alpha^2 \gamma_\pm^2 (C)} \quad \ldots\ (6)$$

Activity coefficients of the ion-pairs were assumed to be unity [12]. The values of the association constants at various concentrations of these electrolytes are also recorded in Table 2.

Table 2 reveals that the K_A values calculated from equation 6 are different from those reported in ref 5 (from conductometry). Further, the value is not a constant; it varies with concentration.

The EMF value is calculated from the above values of $\gamma_\pm$ and α in Table 2 using the equation:

$$E = -(2RT/F) \int_{C_2}^{C_1} t_+ \, d \ln(\gamma_\pm \alpha C) \quad \ldots\ (7)$$

The calculated value of E differs from the experimental value. The non-constancy of K_A and the disagreement between the experimental & calculated EMF values may be due to the incorrect values of the association constant used in the analysis of the EMF results. Therefore a method is

Table 2

Mean Activity Coefficients ($\gamma_\pm$) and Degree of Dissociation (α) of Some Electrolytes calculated from Conductometric Association Constants (K_A)

C/mol.dm^{-3}	α	$\gamma_\pm$	K_A from eq 6
Bu_4NCl K_A from ref 5 is 640			
0.000051	0.9740	0.9261	645
0.000619	0.8290	0.7452	722
0.001021	0.7769	0.6853	771
0.001501	0.7328	0.6321	830
0.002139	0.6910	0.5779	905
0.002780	0.6599	0.5350	981
Bu_4NBr K_A from ref 5 is 860			
0.000049	0.9668	0.9199	874
0.000390	0.8562	0.7815	961
0.001081	0.7661	0.6529	1130
0.001269	0.7505	0.6275	1180
0.001992	0.7081	0.5495	1368
0.002701	0.6796	0.4905	1571
0.003297	0.6608	0.4481	1763
Bu_4NI K_A from ref 5 is 1180			
0.000050	0.9546	0.9214	1197
0.000580	0.7498	0.7529	1353
0.000961	0.6047	0.6943	1453
0.001423	0.6325	0.6428	1565
0.001965	0.5887	0.5958	1695
0.002435	0.5617	0.5628	1804

devised to evaluate the association constants of the electrolytes only from the EMF results.

Analysis of Data without using K_A from Conductometry

The calculation is initiated with an approximate value of K_A. The association constant reported [5] is taken as the initial value wherever it is available. Otherwise it is calculated using the equation

$$K_A = 4\ \pi\ Na^3e^b/3000 \qquad \ldots (8)$$

where a is the distance of closest approach (taken from ref 5), b = 16.708 x 10^{-4}/DTa; D the dielectric constant of n-butanol is taken as 17.1 at 298.15, 15.8 at 308.15 and 14.6 at 318.15 [16]; all other symbols have their usual meaning [12].

EMF values and the initial K_A values obtained above are used to evaluate the values of α_1 and $(\gamma_\pm)_1$ at various concentrations using equation (1) and (2) respectively. These values are again used to evaluate K_A at different concentrations and their mean value is chosen; the calculation is repeated to get a second approximate value {α_2 and $(\gamma_\pm)_2$}. This whole process is repeated until the calculated values of K_A are independent of concentration. Now the last set of α, $\gamma_\pm$ and K_A value are used in equation 7 to calculate EMF value. This is found to agree with the experimental EMF value.

A computer programme was used for this evaluation.

The association constants so obtained for various electrolytes at different temperatures are recorded in Table 3.

Table 3 shows that the association constant increases with temperature for all electrolytes. This is in accordance with the findings for various solvents at low temperatures [17]. In

Table 3

Association Constant K_A of Some Electrolytes at Different Temperatures

Electrolyte	K_A At		
	298.15°K	308.15°K	318.15°K
LiCl	1217	1320	1647
Me_4NCl	4432	5753	7289
Et_4NCl	2912	3621	4026
Bu_4NCl	1763	1892	2306
Bu_4NBr	1875	2293	3061
Bu_4NI	3201	3249	3482

solution, two opposite forces are operative on the ions which affect association in opposite ways.

(i) The thermal forces tend to give random orientations to the ions and thus enhance the dissociation of the electrolytes;

(ii) The dielectric constant of the solvent decreases with increase in temperature and thus enhance the electrostatic interactions, which might increase the association of the ions in solution.

It has been observed that at low / moderate temperatures, the contribution from thermal forces are much less than the electrostatic forces; with the result, the association increases with the increase in temperature for almost all electrolytes [12,18]. At higher temperatures, however, association starts to decrease with increase in temperature [12,17,18].

Table 3 further reveals that the association constants of tetraalkylammonium salts decrease with the increase in the size of the cations. The probability of ion-pair formation in solution is more for small ions because of comparatively high charge density on the surface of these ions as compared with that on the surface of the larger ions. However, the association constant of lithium chloride is much less than that of tetraalkylammonium salts (even though the lithium ion is several times smaller than tetraalkylammonium ions). This is because tetraalkylammonium ions are is not solvated in solution due to its large size but lithium ion is heavily solvated in all the solvents. The size of the solvated lithium ions is more than that of tetraalkylammonium ions in various solvents including n-butanol [4,19,20].

Association constants of tetrabutylammonim halides increase with the size of the anions as could be expected [4,20].

Mean Activity Coefficients

The mean activity coefficients evaluated from EMF measurements are recorded in Table 4.

The values in the Table show that mean activity coefficients decrease with increase in concentration of electrolytes. This is as expected from theoretical relationships between $\gamma_\pm$ and C [11,12] and also in line with earlier reports in both aqueous and some nonaqueous solvents [21]. The values are found to decrease with increase in temperature and this is also as expected [21,22].

Table 4

Degree of Dissociation (α) and mean Activity Coefficients ($\gamma_\pm$) in n-Butanol at Various Temperatures

C	T = 298.15°K		T = 308.15°K		T = 318.15°K	
mol.dm^{-3}	α	$\gamma_\pm$	α	$\gamma_\pm$	α	$\gamma_\pm$
LiCl						
0.000050	0.8527	0.9254	0.9431	0.9253	0.9397	0.9101
0.000709	0.7267	0.7724	0.7067	0.7625	0.6876	0.7508
0.001110	0.6695	0.7376	0.6495	0.7278	0.6297	0.7140
0.001432	0.6366	0.7168	0.6166	0.7068	0.5972	0.6920
0.001981	0.5947	0.6890	0.5747	0.6791	0.5564	0.6629
0.002580	0.5614	0.6658	0.5414	0.6588	0.5245	0.6384
Me_4NCl						
0.000049	0.8587	0.9289	0.8300	0.9253	0.8027	0.9165
0.000630	0.5084	0.8239	0.4671	0.8183	0.4362	0.8027
0.001109	0.4291	0.7923	0.3912	0.7877	0.3643	0.7689
0.001880	0.3630	0.7603	0.3291	0.7554	0.3062	0.7344
0.002629	0.3253	0.7385	0.2940	0.7335	0.2736	0.7109
0.003550	0.2945	0.7180	0.2656	0/7130	0.2475	0.6889
Et_4NCl						
0.000050	0.8989	0.9275	0.8804	0.9232	0.8722	0.9132
0.000691	0.5714	0.8080	0.5369	0.8013	0.5287	0.7787
0.001312	0.4804	0.7680	0.4481	0.7607	0.4427	0.7338
0.001889	0.4322	0.7333	0.4017	0.7336	0.3481	0.7063
0.002279	0.4088	0.7101	0.3795	0.7229	0.3767	0.6917
0.002871	0.3815	0.7136	0.3536	0.7055	0.3519	0.6733
Bu_4NCl						
0.000051	0.9338	0.9259	0.9337	0.9210	0.9192	0.9110
0.000619	0.6767	0.8030	0.6792	0.7904	0.6459	0.7697
0.001021	0.6071	0.7693	0.6108	0.7549	0.5782	0.7319
0.001501	0.5538	0.7415	0.5584	0.7255	0.5274	0.7006
0.002139	0.5063	0.7146	0.5119	0.6971	0.4830	0.6704
0.002780	0.4729	0.6940	0.4792	0.6753	0.4520	0.6474
Bu_4NBr						
0.000049	0.9304	0.9262	0.9179	0.9218	0.8974	0.9120
0.000390	0.7297	0.8326	0.7007	0.8250	0.6600	0.8080
0.001081	0.5878	0.7671	0.5572	0.7582	0.5176	0.7374
0.001269	0.5692	0.7556	0.5349	0.7460	0.4962	0.7251
0.001992	0.5044	0.7224	0.4755	0.7128	0.4398	0.6874
0.002701	0.4653	0.6988	0.4377	0.6888	0.4044	0.6641
0.003297	0.4400	0.6823	0.4135	0.6720	0.3820	0.6464
Bu_4NI						
0.000050	0.8907	0.9277	0.8903	0.9228	0.8861	0.9125
0.000580	0.5796	0.8204	0.5819	0.8088	0.5800	0.7856
0.000962	0.5065	0.7908	0.5096	0.7774	0.5097	0.7508
0.001423	0.4527	0.7660	0.4566	0.7512	0.4583	0.7219
0.001965	0.4113	0.7445	0.4156	0.7285	0.4188	0.6968
0.002435	0.3852	0.7297	0.3899	0.7129	0.3940	0.6795

Table 5

Activity coefficients ($\gamma_\pm$) of the Electrolytes at Specific Concentrations and Temperature

Concentra.	298.15°K			308.15°K			318.15°K		
mol/dm³ =	0.001	0.002	0.003	0.001	0.002	0.003	0.001	0.002	0.003
LiCl	0.749	0.681	0.652	0.736	0.673	0.641	0.723	0.662	0.629
Me_4NCl	0.801	0.758	0.728	0.797	0.750	0.723	0.775	0.732	0.702
Et_4NCl	0.783	0.739	0.711	0.775	0.727	0.708	0.752	0.701	0.670
Bu_4NCl	0.770	0.719	0.690	0.755	0.708	0.670	0.732	0.683	0.640
Bu_4NBr	0.772	0.720	0.691	0.750	0.710	0.674	0.739	0.684	0.657
Bu_4NI	0.789	0.742	0.720	0.777	0.727	0.711	0.749	0.696	0.670

In order to compare the data in n-butanol with those in other solvents, the values of mean activity coefficients at specific concentrations (of 0.001, 0.002 and 0.003 mol.dm^{-3}) are evaluated by intrapolation in the activity coefficient - concentration plots. The relevant results are recorded in Table 5.

Comparison of the values in Table 5 with reported values in other solvents reveals that the values in n-butanol are less than those in solvents like methanol [23], N-methylformamide [24], formamide [25] and water [26]; but they are comparable with those in N,N-dimethylformamide [27], dimethylsulphoxide [21,28], propylene carbonate [29] and tetramethylurea [30]. The dielectric constant of the latter solvents are very high as compared to that of n-butanol. The comparable values of the mean activity coefficients in these solvents may be attributed to the heavy solvation of both the cations and the anions in n-butanol [4,20]. In case of N,N-dimethylformamide, dimethylsulphoxide, propylene carbonate and tetramethylurea [19,31], the cations are heavily solvated but there is practically no primary solvation of the anions in these solvents.

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