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Some Observations of the Water Activity in Uni-uni Valent Electrolyte Solutions

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The association or dissociation of various ionic species has sometimes been determined in aqueous electrolyte solutions at high concentrations. In such experiments, the constant ionic medium method has usually been employed for the control of the activity coefficients. The validities and the limitations of this method have been discussed by Rossotti and Rossotti.[1]

As the association or the dissociation of ions in aqueous solutions is accompanied by hydration or dehydration, the activity of water as well as the activity coefficients of the ionic species should be controlled in order to obtain reasonable chemical constants; information about the water activity in various constant ionic media is desirable for this purpose.

For the present study, the water activity in some very common uni-uni valent electrolyte solutions has been determined by a Karl Fischer titration method based on the principle that the water concentration in a benzene phase in an equilibrium with an aqueous phase is approximately proportional to the water activity in the latter.[2] The results thus obtained were then compared with the values calculated from the previous osmotic data,[3] and some consideration was done of the validities of the constant ionic media from this point of view.

Experimental

All of the reagents used were of a reagent grade. The concentrations of thiocyanate solutions were determined by argentometry, but the other concentrations were determined by gravimetry.

All of the procedures were carried out in the manner described in a previous paper.[2]

Results and Discussion

As has been described,[2] the water activity, A_w, of an aqueous solution can be calculated from the water concentration in a benzene phase in an equilibrium with the sample solution (which will be denoted by C_w), and that in an equilibrium with pure water (which will be denoted by C_{wo}), by using the following equation:

$$A_w = C_w/C_{wo}$$

The value of C_{wo} experimentally determined at 25°C is 0.034M.[2]

Table 1 shows the water activities determined by the titration method in the present study and those calculated from the molal osmotic coefficients by using the following equation:[3]

$$\ln A_w = -\frac{mW_w\nu\phi}{1000}$$

Here, ν is the number of ions formed from one mole of electrolyte; m is the concentration of electrolytes in the molality unit; W_w is the molecular weight of water, and ϕ is the molal osmotic coefficient.

In most salt solutions, the values calculated from the osmotic coefficients on the assumption that the salts are completely dissociated in the

TABLE 1. WATER ACTIVITIES OBTAINED FROM THIS WORK AND FROM THE OSMOTIC COEFFICIENTS[3]

Solute	mol/kg water	$A_{w_{\text{obs}}}$	A_{w_ϕ}
NaSCN	1.0	0.97	0.966
	2.0	0.94	0.927
	3.0	0.91	0.889
	4.0	0.87	0.847
$NaClO_4$	1.0	0.97	0.968
	2.0	0.93	0.935
	3.0	0.90	0.901
	4.0	0.87	0.867

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[1] F. J. C. Rossotti and H. Rossotti, "The Determination of Stability Constants," McGraw-Hill Co., Inc., New York (1961).

[2] Y. Hasegawa and T. Sekine, This Bulletin, **38**, 1713 (1965).

[3] R. A. Robinson and R. H. Stokes, "Electrolyte Solutions," Butterworths, London (1959).

aqueous solutions agree with the values determined by the present titration method. However, in a few solutions (for example, in the thiocyanate solution, as we can see from Table 1), the values are rather larger than the values from the osmotic coefficient method. From these results, the following conclusions may be drawn:

As the values obtained by these two independent methods are consistent, many strong electrolytes may be considered to be dissociated completely, and both of these methods are applicable for the determination of water activities, even when the electrolyte concentration is very high. The difference between the values obtained by these two methods could be explained by that the ν in the equation is smaller than the values calculated by assuming complete dissociation; that is, sodium ions and thiocyanate ions might be associated to some extent.

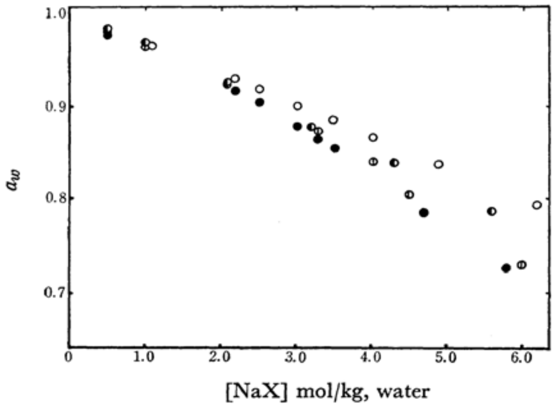

Fig. 1. Change in the water activity of four sodium salt solutions as a function of concentration of NaX.

○ Sodium perchlorate
◐ Sodium chloride
⦶ Sodium bromide
● Sodium iodide

Figure 1 shows the water activities in solutions of four salts as a function of the salt concentration (molal units). We can see from Fig. 1 that, although the differences at a certain concentration are rather small, still the following decreasing order of the values of the water activity can be estimated in these sodium salt solutions:

$$A_{w_{\mathrm{NaClO_4}}} > A_{w_{\mathrm{NaCl}}} > A_{w_{\mathrm{NaBr}}} > A_{w\mathrm{NaI}}$$

The water activity in aqueous salt solutions may be influenced by many factors. Robinson and Stokes[3] pointed out that the hydration of univalent anions decreases with an increase in the ionic radius. As the ionic radii of these anions decrease in the following order;

$$r_{\mathrm{ClO_4^-}} > r_{\mathrm{I^-}} > r_{\mathrm{Br^-}} > r_{\mathrm{Cl^-}}$$

the water activity in the solutions should decrease in the same order as long as we consider this problem in terms of hydration.

On the other hand, the following *"destroying-order"* of the water structure by solute anions was proposed, on the basis of IR measurements of various aqueous solutions, by Yamatera and Gordon[4] and Choppin and Buijs:[5]

$$\mathrm{ClO_4^-} > \mathrm{I^-} > \mathrm{Br^-} > \mathrm{NO_3^-} > \mathrm{Cl^-}$$

If the water structure of these solutions is destroyed in this order, the water activity should decrease in the same order. However, the experimental observations gave just the reverse order except that the perchlorate solutions gave the largest values of water activity. Thus, factors other than the hydration or the destruction of the structure of water must be taken into account in formulating a reasonable explanation of these results.

Some more data on the water activities which will be useful in various discussions of solution chemistry are given in Table 2 by molarity and molality.

TABLE 2. WATER ACTIVITIES IN SOME ELECTROLYTE SOLUTIONS

Solute	mol/l	mol/kg water	A_w
NaCl	0.50	0.51	0.98_4
	1.0	1.0	0.96_9
	2.0	2.1	0.92_6
	3.0	3.2	0.87_8
	4.0	4.4	0.83_9
	5.0	5.6	0.78_7
NaBr	0.50	0.51	0.98_4
	1.0	1.0	0.96_6
	2.0	2.1	0.92_6
	3.0	3.3	0.87_3
	4.0	4.5	0.80_6
	5.0	6.0	0.73_0
NaI	0.50	0.51	0.97_6
	1.0	1.0	0.96_4
	2.0	2.2	0.91_7
	3.0	3.3	0.86_4
	4.0	4.7	0.78_6
	4.8	5.8	0.72_6
$\mathrm{NaClO_4}$	0.50	0.51	0.98_4
	1.0	1.1	0.96_6
	2.0	2.2	0.92_9
	3.0	3.5	0.88_6
	4.0	4.9	0.83_7
	4.8	6.2	0.79_4
	7.0	10.6	0.62_5

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[4] H. Yamatera and G. Gordon, The Xth Colloquium Spectroscopium Internationale (1962, Maryland, U. S. A.).

[5] G. R. Choppin and K. Buijs, *J. Chem. Phys.*, **39**, 2042 (1963).

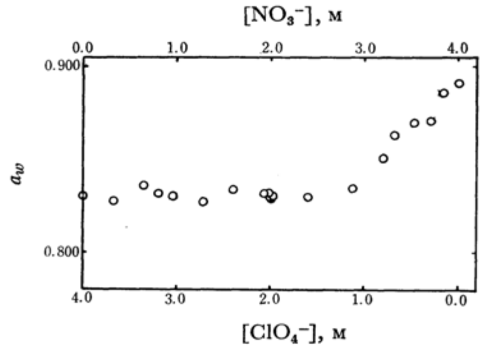

Fig. 2. Water activity in 4M Na (NO_3, ClO_4) solutions as a function of perchlorate or nitrate concentration.

Further study was carried out in mixed salt solutions in order to ascertain the ability of the constant ionic method to control the water activity. Mixtures of sodium perchlorate and nitrate were chosen as the representatives of the mixed electrolyte solutions because the difference in the water activity at 4M, for example, is largest between perchlorate and nitrate solutions.

Figure 2 shows the water activity in solutions containing sodium perchlorate and nitrate mixtures. We can seen from Fig. 2 that even when the sodium ion concentration is kept at 4M, the water activity changes continuously from 0.83 in 4M sodium perchlorate to 0.89 in 4M sodium nitrate; the water activity is almost constant until the nitrate concentration reaches 2.8M, but it increases abruptly beyond 2.8M. For the determination of very weak metal complexes, it is necessary to add a very large amount of ligand anions to the ionic media; that is, a large portion of the perchlorate ions should be replaced by the ligand anions. For example, when we examined europium(III) nitrate complexes ($K_1=1.3$ and $\beta_2=0.30$ in 4M Na(ClO_4, NO_3)),[6] it was necessary to replace almost 70% of the perchlorate ions in 4M sodium perchlorate media with nitrate ions in order to determine the second stability constants accurately. The present results indicate that even when such a large alternation of the medium is made the change in the water activity is still not very large; in view of this, the author regards the nature of the medium as still being kept constant.

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6) T. Sekine, I. Sakamoto, T. Sato, T. Taira and Y. Hasegawa, This Bulletin, **40**, 251 (1967).