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RESEARCH ARTICLE

Mean distance of closest approach of ions in NaCl (aq.) at 25°C calculated from degrees of association using Bjerrum's theory

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This paper demonstrates, for the first time, the applicability to 1:1 strong electrolytes of Bjerrum's pioneering theory, which relates the degree of ionic association with the mean distance a of closest approach of ions. It can be noted that only recently, strong electrolytes like NaCl were shown to be incompletely dissociated in aqueous solutions. The pre-

sent data on the degrees of dissociation of NaCl (aq.) at 25°C have been used to calculate the values of a for concentrations from zero to saturation, using Bjerrum's theory. It is found that both $Q(b)$, the Bjerrum's integral, and a are simple functions of the molal volume and concentration and that at saturation, a is less than q , the critical distance.

It was generally believed¹⁻³ that 1:1 strong electrolytes like NaCl dissociate completely into ions in aqueous solutions. However, recent X-ray diffraction and mo-

lecular dynamic simulation studies of saturated solutions^{4,5} and investigation of thermodynamic data at all concentrations^{6,7} have shown that even 1:1 strong elec-

trolytes are incompletely dissociated in aqueous solutions as originally supposed^{8,9}.

Taking the dissociation of NaCl (aq.) as a typical example,



the degree of dissociation, α , evaluated^{7a} from osmotic coefficients (φ) decreases with molality m from unity at infinite dilution to a minimum at about 1.5 m (corresponding to mean ionic activity, $a_{\pm} = 1$) and then increases with concentration to a value < 1 at saturation.

The values of α are given in Table 1. With these values of α , it has been possible to give a quantitative and unified explanation for other solution properties like the EMF of concentration cells (which is directly proportional to $\ln(a_{\pm})$) and the densities/molal volumes of solutions, using simple mathematical equations valid for the whole concentration range from very dilute to saturated solutions^{7a-h}.

Therefore, a fresh investigation of the Bjerrum's theory of ionic association was undertaken⁷ⁱ. This theory predicts the degree of association for various distances of closest approach of oppositely charged ions, and it predicts negligible ionic association for 1:1 electrolytes like NaCl (aq.)^{1,2}. Here, with the present knowledge of

the degrees of association^{7a-c}, it has been demonstrated that Bjerrum's theory can be used to calculate the mean distance of closest approach of ions, using NaCl (aq.) as an example.

Bjerrum's integral $Q(b)$ and ionic association

Bjerrum derived the basic relation connecting the degree of association, $(1-\alpha)$, with the distance, a of closest approach of oppositely-charged ions at any concentration, c (refs 1, 2). This relation was obtained by integrating the number of oppositely-charged ions in all the spherical shells around a central ion, from a distance $r = a$, up to the critical distance $r = q (> a)$. For a 1:1 electrolyte, $(1-\alpha)/c$ is proportional to the integral $Q(b)$ as given by¹ (the proportionality constant = $2.755 \text{ cm}^3 \text{ mol}^{-1}$ at 25°C)

$$(1-\alpha)/c = (4\pi N/1000)(e^2/\epsilon kT)^3 Q(b), \quad (2)$$

where e is the electronic charge, ϵ is the dielectric constant of the solvent and N is the Avogadro number. The integral $Q(b)$ depends¹ on r ,

$$Q(b) = \int_2^b x^{-4} e^x dx, \quad (3)$$

where $x (= e^2/\epsilon kTr)$ is the ratio of the mutual electrical potential energy ($e^2/\epsilon r$) to the thermal energy (kT), and has the values $x = 2$ and $x = b$ for $r = q$ and $r = a$ respectively. The critical distance $q = e^2/2\epsilon kT$ for $x = 2$ is the distance at which the probability of finding oppositely-charged ions is minimum. Therefore, eq. (2) gives finite degrees of association for all values of $a \leq q$. At 25°C , $a = 7.14/b \text{ \AA}$ and $q = 3.57 \text{ \AA}$ for a 1:1 electrolyte in aqueous solution. This critical distance was considered too large to form ion pairs^{1,2}.

Linear dependence of $cQ(b)$ on the volume of NaCl (aq.)

For the values of α in Table 1, the corresponding values of $Q(b)$ were calculated as $Q(b) = (1-\alpha)/2.755c$ (see eq. (2)). For calculating the molar concentrations $c (= 1000m/V)$ the molal volumes V were obtained using eqs (4) and (5b) below. For NaCl (aq.) at 25°C , it was demonstrated^{7a,c,d} that the molal volume¹⁰ is the sum of the volumes of solvent (A) and solute (B), as given by the pair of equations,

$$V = V_A + m[(1-\alpha)V_{cr} + \alpha(V_+ + V_- + \delta V_{el})], \quad (4)$$

$$(m < 1.5),$$

Table 1. Degree of dissociation (α), molal volume (V) and molar concentration (c) at molality m and the corresponding values of $Q(b)$, b and a of Bjerrum's eqs (2) and (3), for NaCl (aq.) at 25°C

m mol kg ⁻¹	α	V cm ³	c mol l ⁻¹	$Q(b)$	b	a (Å)
0.000	1.000	1002.86	0.000			
0.100	0.858	1004.63	0.100	0.518	3.85	1.85
0.200	0.832	1006.46	0.199	0.307	2.93	2.44
0.300	0.818	1008.31	0.298	0.222	2.61	2.73
0.400	0.807	1010.17	0.396	0.177	2.47	2.90
0.500	0.801	1012.03	0.494	0.146	2.37	3.01
0.600	0.797	1013.89	0.592	0.125	2.31	3.09
0.700	0.795	1015.75	0.689	0.108	2.26	3.16
0.800	0.792	1017.62	0.786	0.096	2.23	3.20
0.900	0.790	1019.48	0.883	0.086	2.21	3.24
1.000	0.789	1021.34	0.979	0.078	2.18	3.27
1.200	0.788	1025.04	1.171	0.066	2.15	3.32
1.400	0.788	1028.74	1.361	0.057	2.13	3.35
1.600	0.788	1033.57	1.548	0.050	2.11	3.38
1.800	0.791	1037.60	1.735	0.044	2.10	3.40
2.000	0.794	1041.67	1.920	0.039	2.09	3.42
2.500	0.802	1051.98	2.376	0.030	2.07	3.45
3.000	0.812	1062.65	2.823	0.024	2.05	3.48
3.500	0.825	1073.82	3.259	0.019	2.04	3.49
4.000	0.837	1085.21	3.686	0.016	2.04	3.51
4.500	0.847	1096.68	4.103	0.014	2.03	3.52
5.000	0.855	1108.14	4.512	0.012	2.03	3.52
5.500	0.863	1119.81	4.912	0.010	2.02	3.53
6.000	0.865	1130.78	5.306	0.009	2.02	3.53
6.144	0.865	1133.86	5.419	0.009	2.02	3.53

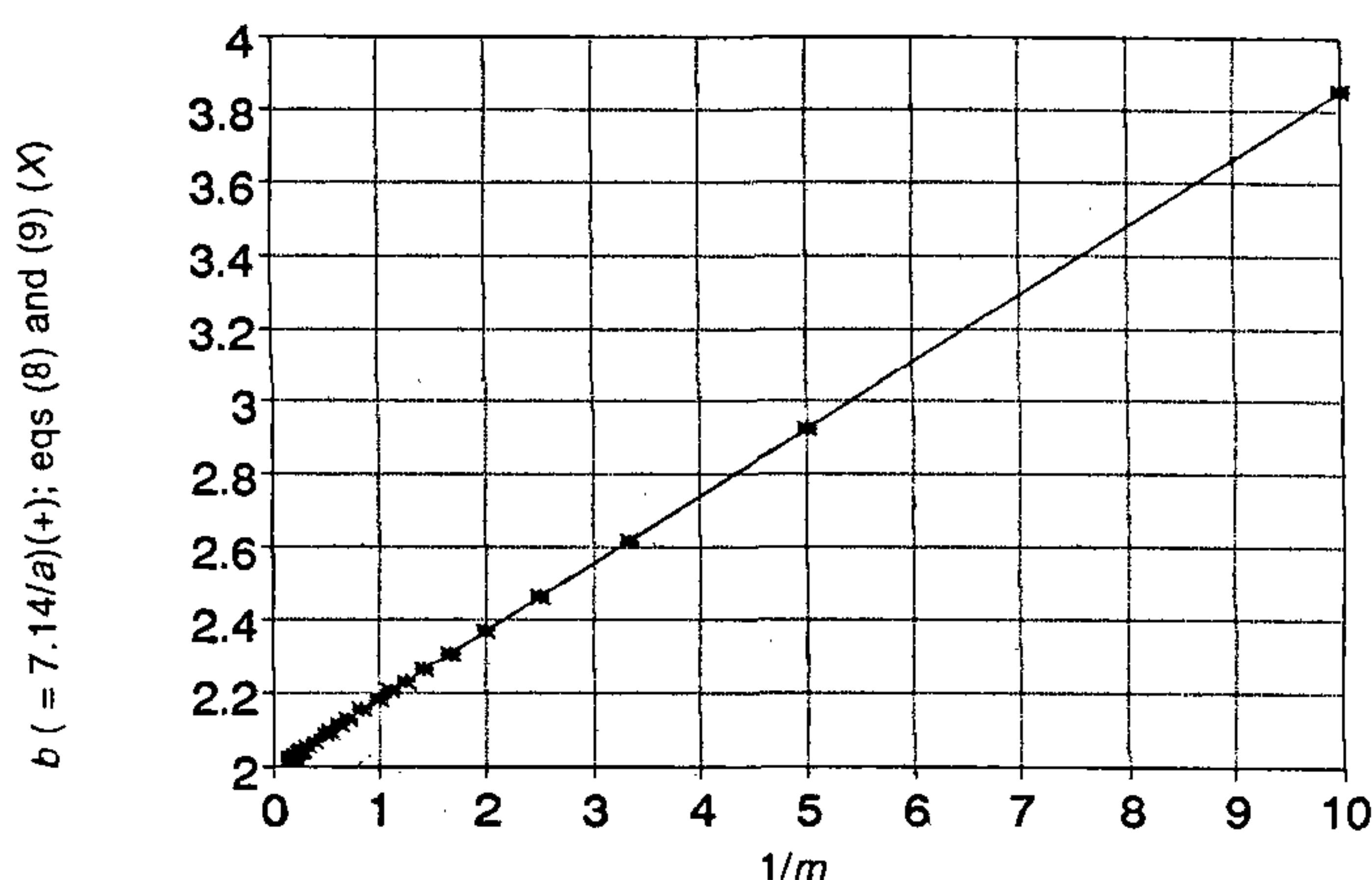


Figure 1. The linear dependence of $b (= 7.14/a)$ on $1/m$ for NaCl (aq.) at 25°C from 0.1 m to saturation ($m = 6.14$), where $a (= 7.14/b)$ is the mean distance of closest approach of oppositely-charged ions (see eqs (8) and (9)).

$$V = V'_A + m\{(1-\alpha)V_{cr} + \alpha(V_+ + V_- + \delta V_{el}) + [\alpha\delta V_d - (1-\alpha)V_{cr}]\} \quad (5a)$$

$$= V'_A + \alpha m(V_{cr} + \delta V_{el}), \quad (m > 1.5 \text{ up to satn.}), \quad (5b)$$

where $V_{cr} = 26.8 \text{ cm}^3 \text{ mol}^{-1}$ is the volume of undissociated NaCl (the same as in the crystal), $V_A = 1002.86 \text{ cm}^3$ and $V'_A = 1002.38 \text{ cm}^3$ are the volumes of 1 kg of water at 25°C in the solution, $(V_+ + V_-) = 18.31 \text{ cm}^3 \text{ mol}^{-1}$ is the volume of ions in the solution, $\delta V_{el} = -2.06 \text{ cm}^3 \text{ mol}^{-1}$ is the change in volume due to electrostriction and $\delta V_d = V_{cr} - (V_+ + V_-) = 8.49 \text{ cm}^3 \text{ mol}^{-1}$ is the volume change accompanying association/dissociation. The last term in eq. (5a) is the volume (due to interionic interaction) shared by the ions and ion pairs.

From eqs (4) and (5b), one finds that $(1-\alpha)$ (and hence $cQ(b)$, see eq. (2)) is directly proportional to the volume of the electrolyte in the solution,

$$(1-\alpha) = 1 - V_{cr}/(\delta V_d - \delta V_{el}) + (V - V_A)/m(\delta V_d - \delta V_{el}) \quad (6a)$$

$$= -0.540 + 0.0948 V_B \quad (m < 1.5). \quad (6b)$$

$$(1-\alpha) = 1 - (V - V'_A)/m(V_{cr} + \delta V_{el}) \quad (7a)$$

$$= 1 - 0.0404 V'_B \quad (m > 1.5 \text{ up to satn.}), \quad (7b)$$

where $V_B = (V - V_A)/m$ and $V'_B = (V - V'_A)/m$ are the volumes per mole of the electrolyte at molality m .

Dependence of $b (= 7.14/a)$ on the molality, m

Table 1 gives the values of b corresponding to the values of $Q(b)$. $Q(b)$ vs b data obtained by numerical integration of eq. (3) was furnished¹¹. The last column gives the values of $a (= 7.14/b)$ (estimated in this way for the first time). Note that Bjerrum's theory gives a definite

value for a at any given concentration. Therefore, in the graph of the degree of association $(1-\alpha)$ vs a , only one value of $a (= 2.44 \text{ \AA})$ is possible at the given concentration ($c = 0.1$). It can be seen from Table 1 that a increases with m until at saturation (6.144 m) it reaches the value 3.53 \AA (corresponding to $b = 2.02$ and $Q(b) = 0.009$). Note that at saturation, a is less than the critical distance $q (= 3.57 \text{ \AA})$!

The relations below show the linear increase of $b (= 7.14/a)$, the ratio of the electrical to thermal energy at the distance a of closest approach, with the amount of solvent per mole of solute, $1/m$ (see Figure 1). For the concentration ranges on the two sides of the α vs m curve^{7a}, linear regressions give the pair of equations,

$$b = (7.14/a) = 2.00 + 0.185/m, \quad (m < 1.5), \quad (8)$$

$$b = (7.14/a) = 1.98 + 0.207/m, \quad (m > 1.5). \quad (9)$$

From eqs (8) and (9), it can be seen that the reciprocal of the distance a varies linearly with $1/m$.

On combining the pairs of eqs (6) and (8) and (7) and (9), one gets,

$$(1-\alpha) = -0.540 + 0.512(V - V_A)(b - 2.00), \quad (m < 1.5), \quad (10)$$

$$(1-\alpha) = 1 - 0.195(V - V'_A)(b - 1.98), \quad (m > 1.5) \quad (11)$$

which shows that $(1-\alpha)$ and hence the Bjerrum's factor $cQ(b)$ (see eq. (2)) are proportional to the product, $V(b - 2.00)$ and $V(b - 1.98)$ for $m < 1.5$ and $m > 1.5$ respectively.

Thus, it is shown here for the first time that Bjerrum's theory can be used for evaluating the mean distance of

closest approach of ions from the available data on the degrees of association.

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