COMMUNICATIONS

DE LA FACULTÉ DES SCIENCES
DE L'UNIVERSITÉ D'ANKARA

Série B : Chimie

TOME 16 B ANNÉE 1969

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by

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Faculté des Sciences de l'Université d'Ankara
Ankara, Turquie

Communication de la Faculté des Sciences de l'Université d'Ankara

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On The Dissociation of Strong Electrolytes *

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(Received March 22, 1969)

This work is a study on the dissociation of the strong electrolytes. We have shovn that the degrees of dissociation obtained from the integral heat of dilution as well as from the conductance measurements ensures the obtainment of better results in the computation of the activity coefficient. Therefore, the thought that there are un-dissociated units in the solutions of the mentioned strong electrolytes gains strength.

INTRODUCTION

Characteristic strong electrolytes such as NaCl, KCl, KBr etc. are often supposed as being entirely dissociated in each concentration. But there are signs which indicate that the situation must not be so, as pointed out as early as in 1927 by Nernst, Naude and Orthmann. For instance the course of the integral heat of dilution of many strong electrolytes, specially in the concentrated solutions show that these electrolytes do not completely dissociated. This fact had been taken into account also by Eigen and Wicke after 1951. Eigen and Wicke have calculated also the dissociation constants suitable for the course of the integral heat of dilution for some strong electrolytes. Should the case be so, it would then be right to expect the obtainment of better results by taking into account the effects of the incomplete dissociation when trying to express by an equation the characteristics representing the deviation from the ideal case of the strong electrolytes solutions for instance their activity coefficient

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* This paper is a part of a thesis submitted to the Faculty of Science, University of Ankara in partial fulfillment of the requirments for the degree of "Doctor of Science" by A. Zeren.

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Starting from this idea we have made the necessary changes in an equation based on a solution model completely dissociated, and arranged it in such a way as to suit also an incomplete dissociation. Then using this equation we have calculated the activity coefficients of some strong electrolytes. The calculations we made for NaCl, KCl, KBr, CsCl, CsBr and RbCl have show that the degree of dissociation which can explain the course of the integral heat of dilution of these electrolytes permits the obtainment of results more suitable to experiments in the calculation of the activity coefficient and consequently that the idea that these electrolytes do not undergo a complete dissociation is right.

Solutions Models

The studies carried out so far to find equations linking the activity coefficients to other characteristics are based on a number of different solution models [1–37]. In these models it is noticed that it is desired to explain the deviation from the ideal case mainly through three factor such as (1) interionic electrostatic interaction, (2) hydration caused by ion-solvent effect, (3) association caused by ion-ion effect. The solution models used generally take into account one or two of these factors. It is very reasonable to expect the model comprising the three factors to be more successful than all the other models. But it cannot be said that a model combining these three factors will be a perfect one; it may be necessary to add some other secondary factors to the model. We have dwelt only on an electrolytic solution model which brings together these three factors. In this model the soluted electrolyte, together with free ions, produces units also which are equivalent to non-dissociated molecules in equilibrium with them. The proportion of these units can change between zero and one depending on the existing conditions and the nature of the electrolyte. Furthermore, we admit that free ions with mutual electrostatic action are in a hydratized state caused by water molecules whose number depends on their nature and that the hydration number does not change by con-concentration.

The reason for our thinking on such a model is not simply to bring together the different characteristics in the models used so far. It is possible also to explain by this model the abnormalities noticed in the integral heat of dilution of many strong electrolytes. The deviation from the theoretical slope in the curves of the integral heat of dilution as well as the negative dilution heats noticed in concentrated solutions lead one to think that even some electrolytes which may be considered as model strong electrolytes are not found in an entirely dissociated state [38–40]. Electrolytes the dilution heat of which shows such abnormalities can be represented by a model much closer to reality through their being attributed a dissociation constant capable of explaining the abnormality.

An Equation That Can Also Express The Incomplete Dissociation

In order to be able to test the correctness of the assumption that the dissociation of strong electrolytes whose integral heat of dilution show abnormalities should not be complete, we chose the way of calculating the activity coefficient of these strong electrolytes, by an equation which takes in account also the incomplete dissociation. If the values we shall calculate from this equation would agree with the experimental results up to the higher concentrations than those calculated for the state of complete dissociation, we would than consider this fact as a strong support of the idea which claims that the dissociation is not complete. For this test, we have chosen the Robinson-Stokes equation [24] whose basic model is more or less close to the one we have thought of and which has already given remarkably good results for many electrolytes. We have modified this equation initially conceived for complete dissociation in such a way as to conform to incomplete dissociation. Because of the incomplete dissociation the ion concentration in the solution will be less than the stoichiometric concentration. The mean concentration of the ions produced by an electrolyte which we solved in water to obtain m stoichiometric molality would be not m but about

$m\alpha$. If we show by n the number of the total water molecules which the ions produced by a single electrolyte molecule attach to themselves, the water quantity attached by all the ions in the solution should be about $nm\alpha$. If we deduct this attached water from 55.51 mol which is the total amount of the solvent we get the value of $55.51 - nm\alpha$ as the free water amount in the solution. This means that the water amount which determines the solution molality is not 55.51 mol but $55.51 - nm\alpha$ mol. So, the exact molality of the solution will not be equivalent to m or to $m\alpha$ but to a value like

$$m' = \frac{55.51\ m\alpha}{55.51 - nm\alpha} = \frac{m\alpha}{1 - 0.018\ nm\alpha} \tag{1}$$

For the process of establishing the equation we used this concentration value. As a starting point we used the

$$\log m\gamma = \log m'\gamma' - \frac{n}{\nu} \log a_w \tag{2}$$

equation obtained by Harned [41] from the equilibriums in the aqueous solution of an electrolyte. In this equation m denotes the stoichiometric molality; γ the mean molal activity coefficient of electrolyte; m' the real molality in the case of hydratized ions; γ' the mean molal activity coefficient of hydratized ions. By re-establishing this equation we get the relation of

$$\log\gamma = \log\gamma' - \log \frac{m}{m'} - \frac{n}{\nu} \log a_w \tag{3}$$

Now in this equation let us put the

$$\frac{m}{m'} = \frac{1 - 0.018\ nm\alpha}{\alpha}$$

value:

$$\log\gamma = \log\gamma' - \log \frac{1 - 0.018\ nm\alpha}{\alpha} - \frac{n}{\nu} \log a_w$$

Instead of the molal activity coefficient of the hydratized ions γ' we can put the value

$$\log\gamma' = \log f' - \log(1+0.018\nu m')$$

of the kind of the rational activity coefficient f':

$$\log\gamma = \log f' - \log(1+0.018\nu m') - \log\frac{1-0.018\ nm\alpha}{\alpha} - \frac{n}{\nu}\log a_w$$

If we arrange the equation and instead of m' we put its value from relation (1), we get the equation of

$$\log\gamma = \log f' - \frac{n}{\nu}\log a_w - \log\left[\frac{1}{\alpha} - 0.018\,(n-\nu)m\right]. \qquad (4)$$

Instead of the water activity a_w we find here we can put the value

$$\log a_W = -0{,}007824\nu\ m\Phi$$

which is of the kind of the osmotic coefficient of the solution:

$$\log\gamma = \log f' + 0.007824\ nm\Phi - \log\left[\frac{1}{\alpha} - 0.018\,(n-\nu)m\right].$$

Instead of the term on the right which is the logarithm of the rational activity coefficient of hydratised ions we can put the value

$$\log f' = -\frac{0.5092\ z_1\ z_2\ \sqrt{\mu}}{1+0.3286\ \mathring{a}\ \sqrt{\mu}}$$

as also Stokes and Robinson by admitting that a° parameter is the nearest distance that hydratised ions can reach and thus we can ensure the interionic electrostatic interaction also to be represented in the equation:

$$\log\gamma = -\frac{0.5092\ z_1\ z_2\ \sqrt{\mu}}{1+0.3286\ \mathring{a}\ \sqrt{\mu}} + 0.007824\,nm\Phi - \log\left[\frac{1}{\alpha} - 0{,}018\,(n-\nu)m\right]. \qquad (5)$$

Equation Test

To test the equation (5) which we changed to conform to the solution model we thought of we needed the dissociation degrees of the various concentrations of the different electrolytes. At the same time we vanted that these dissociation degrees could explain the course of the integral heat of dilution. Eigen and Wicke [27] have determined the dissociation constants conform to the course of dilution heats for NaCl, KCl, KBr, CsCl and CsBr. We took these values as they were. We made also use, for CsCl and RbCl, of dissociation degrees given by Davies [42] on the basis of conductance measurements. Thus for CsCl, we have compared the constant given by Eigen-Wicke with the one given by Davies and in this way we have demonstrated that it is possible to get better results by slightly changing the constants.

We have calculated the α values which we have used in equation (5) with the help of the relation

$$K_c = \frac{cy^2\alpha^2}{1-\alpha}$$

of the dissociation constants we have mentioned. Then putting these α values into the equation we have searched, for the concentrations up to 5 molals, the most convenient å which gives the logγ values conforming to the experimental results as well as the n parametres.

RESULTS

The values we have obtained for six electrolytes are seen in the table and in the graphic. The result is really good. For the five electrolytes outside NaCl, it has been possible to obtain activity coefficients conforming to experimental results in concentrated solutions up to 5 molals. For RbCl to which Stokes-Robinson equation can correspond only up to 1.5 molals, equation (5) has given results suitable to experiments up to 5.0 molals. Again, in the case of CsCl and CsBr to which Stokes-Robinson equation cannot be applied, it has been possible to get

NaCl

($K = 6.0$; $\mathring{a} = 4.06$; $n = 5.20$)

	—log γ		
m	(calcd)	(exp)	Diff.
0.1	0.110	0.109	+0.001
0.5	0.168	0.167	+0.001
1.0	0.181	0.182	—0.001
2.0	0.171	0.175	—0.004
3.0	0.146	0.146	0.000
4.0	0.120	0.106	+0.014
5.0	0.093	0.058	+0.035

KCl

($K = 2.5$; $\mathring{a} = 4.33$; $n = 3.80$)

	—log γ		
m	(Calcd)	(exp)	Diff.
0.1	0.116	0.113	+0.003
0.5	0.189	0.188	+0.001
1.0	0.219	0.219	0.000
2.0	0.240	0.242	—0.002
3.0	0.243	0.245	—0.002
4.0	0.240	0.239	+0.001
4.5	0.238	0.234	+0.004

KBr

($K = 2.5$; $\mathring{a} = 4.62$; $n = 4.20$)

	—log γ		
m	(calcd)	(exp)	Diff.
0.1	0.114	0.112	+0.002
0.5	0.181	0.182	—0.001
1.0	0.207	0.210	—0.003
2.0	2.223	0.227	—0.004
3.0	0.223	0.225	—0.002
4.0	0.219	0.216	+0.003
5.0	0.206	0.203	+0.003

CsCl

($K = 2.0$; $\mathring{a} = 3.21$; $n = 3.20$)

	—log γ		
m	(calcd)	(exp)	Diff.
0.1	0.129	0.121	+0.008
0.5	0.222	0.217	+0.005
1.0	0.265	0.264	+0.001
2.0	0.302	0.304	—0.002
3.0	0.318	0.320	—0.002
4.0	0.325	0.324	+0.001
5.0	0.327	0.323	+0.004

CsCl

(K = 2.97; å = 2.93; n = 3.00)

	—log γ		
m	(calcd)	(exp)	Diff.
0.1	0.127	0.121	+0.006
0.5	0.222	0.217	+0.005
1.0	0.265	0.264	+0.001
2.0	0.303	0.304	—0.001
3.0	0.317	0.320	—0.003
4.0	0.323	0.324	—0.001
5.0	0.325	0.323	+0.002

CsBr

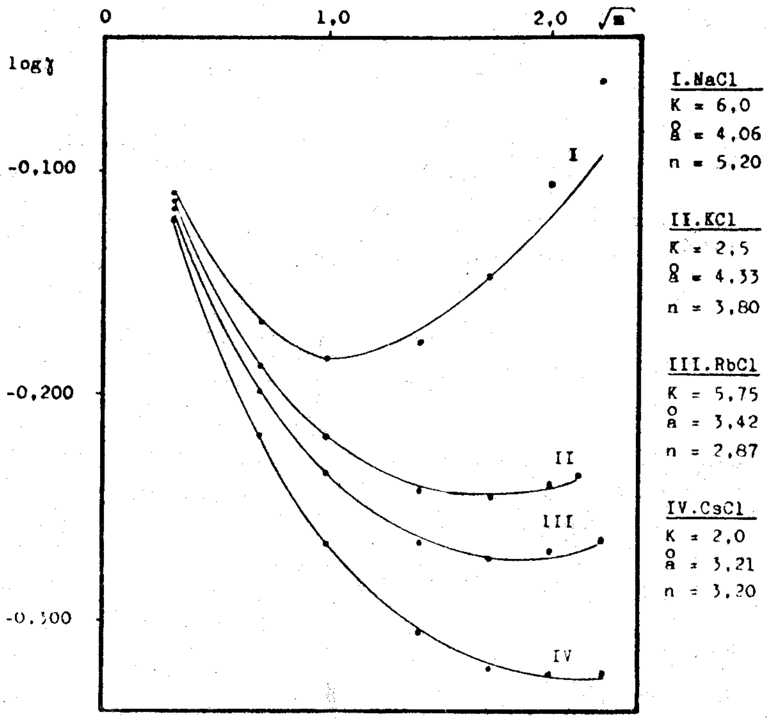
(K = 0.9; å = 4.28; n = 3.40)

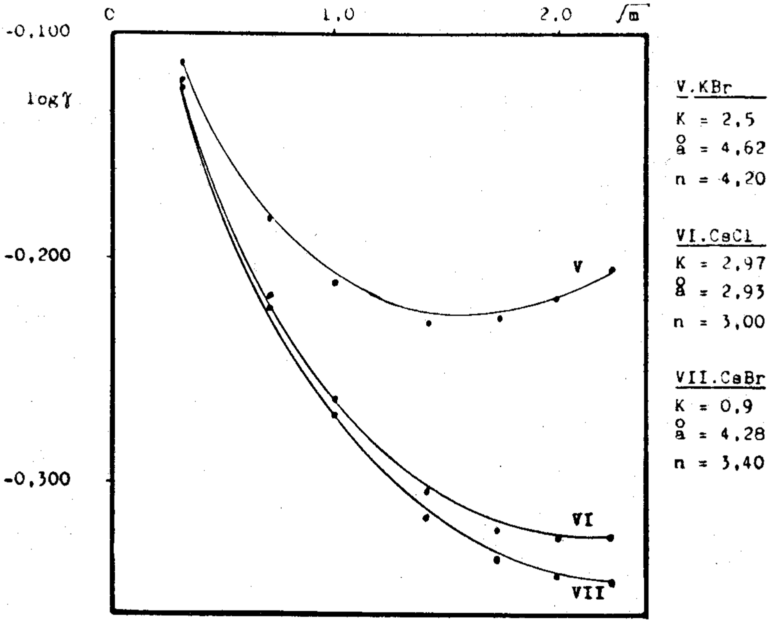
	—log γ		
m	(calcd)	(exp)	Diff.
0.1	0.131	0.123	+0.008
0.5	0.226	0.220	+0.006
1.0	0.271	0.269	+0.002
2.0	0.311	0.313	—0.002
3.0	0.330	0.332	—0.002
4.0	0.341	0.340	+0.001
5.0	0.345	0.344	+0.001

RbCl

(K = 5.75; å = 3.42; n = 2.87)

	—log γ		
m	(calcd)	(exp)	Diff.
0.1	0.119	0.117	+0.002
0.5	0.200	0.198	+0.002
1.0	0.235	0.234	+0.001
2.0	0.261	0.263	—0.002
3.0	0.268	0.271	—0.003
4.0	0.270	0.269	+0.001
5.0	0.265	0.263	+0.002


0
1,0
2,0
$\sqrt{m}$
log γ
-0,100
-0,200
-0,300
I
II
III
IV
I. NaCl
K = 6,0
$\overset{o}{a}$ = 4,06
n = 5,20
II. KCl
K = 2,5
$\overset{o}{a}$ = 4,33
n = 3,80
III. RbCl
K = 5,75
$\overset{o}{a}$ = 3,42
n = 2,87
IV. CsCl
K = 2,0
$\overset{o}{a}$ = 3,21
n = 3,20



results that can be considered as very good up to 5.0 molals. As regard KCl and KBr, while Stokes-Robinson equation has given good results up to 4.0 molals the equation (5) has given good results up to 4.5 and 5.0 molals. Altough Stokes-Robinson equation has given good result up to 5.0 molals only in the case of NaCl equation (5) has shown deviations after 3.5 molals. This result shows that NaCl is dissociated in an amount different from that calculated by Eigen-Wicke.

Comparison of Maximum Concentrations where Stokes-Robinson and (5) equation can be applied

	Stokes-Robinson	Equation (5)
NaCl	5.0	3.5 molals
KCl	4.0	4.5
KBr	4.0	5.0
RbCl	1.5	5.0
CsCl	–	5.0
CsBr	–	5.0

Thus we have shown that the degrees of dissociation obtained from the integral heat of dilution as well as from the conductance measurements ensures the obtainment of better results in the computation of the activity coefficient. Therefore, the thought that there are un-dissociated units in the solutions of the mentioned strong electrolytes gains strength. But have these undissociated units been brought about by incomplete dissociation or by ion association. For 1–1 electrolytes critical Bjerrum distance is 3.57 Å in water (25° C). In exchange, the å values which ensure the equation (5), are greater than this distance for those other than CsCl and RbCl. Then it is more reasonable to speak, not of ion pair formation but of incomplete dissociation.

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ÖZET

Kuvvetli elektrolitlerin aktiflik katsayılarının hesabında, seyrelme ısılarının gidişine uygun disosiasyon dereceleri kullanarak, deneylere daha yüksek konsantrasyonlara kadar uygun değerler elde edilebileceği gösterilmiştir. Dolayısiyle, söz konusu kuvvetli elektrolitlerin çözeltilerinde disosiye olmamış birimlerin bulunduğu düşüncesi kuvvetlenmektedir.

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Ankara Üniversitesi Basımevi - 1969