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SOME NOTES IN CONNECTION WITH "ION-ION AND ION-WATER INTERACTIONS AT HIGH PRESSURE"


By Boris S. El'yanov

In a very interesting review by Nakahara and Osugi and in the following "Comments" by Hamann there has been discussed some questions on the behavior of electrolyte solutions under high pressure, on which the writer would like to make his notes.

1. Hamann and Linton proposed a simple formula for describing the pressure effect on activity coefficients of ions, which is convenient to present here as follows:

\[ \log \gamma^P(\rho) / \log \gamma^I(\rho) = 1 + F(P - 1) / \left[ 1 + b(P - 1) \right], \]  

(a)

where \( F \) and \( b \) are constants. Since the validity of this formula has not been proved in Ref. (3), Nakahara and Osugi attempted to check its accordance with the limiting equation of the Debye-Hückel theory

\[ \log \gamma^P(\rho) / \log \gamma^I(\rho) = \left( \rho / \rho^I \right)^{1/2} \left( \varepsilon(\rho) / \varepsilon^I(\rho) \right)^{3/2}, \]  

(b)

where \( \rho \) and \( \varepsilon \) are the density and the dielectric constant of the solvent respectively. It is worth regretting, that an error has been made in their calculation, which led the authors to the conclusion of the wrongness of (a).

Furthermore, Nakahara and Osugi criticized the formula (a) on the ground that, in their opinion, the pressure dependence of \( \ln \gamma \) is concerned with the ion-ion interaction, having nothing to do with the ion-water type interaction, which is characteristic for the pressure dependence of \( \ln K \). Here the \( K \) is the ionization constant of electrolyte. Therefore, there are not any grounds for expecting the same type of dependence of both quantities on pressure.

We believe, however, it is not like this. Since

\[ \frac{\partial \ln \gamma}{\partial P} = \frac{\bar{v} - \bar{v}^I}{RT}, \]  

(c)

where \( \bar{v} \) and \( \bar{v}^I \) are the partial molal volumes of the ion in the solution at a finite concentration and in infinitely diluted solution respectively, then this formula characterizes expressed in terms of volume the difference between two interactions of the ion-water type in the solutions, which differ by the ion-
ion type interaction. It is quite reasonable, therefore, to accept as a first approximation, that \( \vartheta \) and \( \delta^* \) depend on the pressure analogously, which leads to the formula (a). Under the concrete circumstances of Hamann and Linton's work\(^3\) this assumption was all the more permissible, that the end purpose of this work was not a precise calculation of \( \varpi \) at the high pressures, but it was necessary only to take into account this quantity, which composed the small part of all the effects at the calculation of the pH of buffer solutions under the pressure. The same assumption has been made by us at the analogous calculation\(^5\): it seems remarkable, that this assumption has been justified to such a great extent\(^2\) and thus a simple formula (a) can be used for practical calculations with a good precision.

It would be interesting to get (a) by the computational way from the limiting equation of the Debye-Hückel theory (b). It states below such a deduction, which is based on the simple assumptions.

<table>
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<th>( P ) kbar</th>
<th>( \rho )</th>
<th>( e )</th>
<th>( e/\rho )</th>
<th>( P ) kbar</th>
<th>( \rho )</th>
<th>( e )</th>
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</table>

a) Experimental values of \( \rho \) and \( e \) are from Refs. (5)—(7)

It may be shown (see the Table), that the quantity $\varepsilon/\rho$ for a lot of fluids including water, depends on the pressure rather little. Let us present this quantity in the following form

$$\varepsilon(\rho)/\rho(\rho)=\varepsilon(1)/\rho(1)[1+\alpha(P)].$$

Then we shall get from (b) and (d)

$$\log \gamma(\rho)/\log \gamma(1)=\frac{\varepsilon(\rho)/\varepsilon(1)^{1/2}}{\varepsilon(1)/\varepsilon(\rho)}=\frac{1}{[1+\alpha(P)]^{1/2}} \times \frac{\varepsilon(1)/\varepsilon(\rho)}{\varepsilon(1)/\varepsilon(\rho)}.$$  

As it has been shown

$$1/\varepsilon(\rho)=1/\varepsilon(1)-k(P-1)/(1+b(P-1)),$$

where $k^*=-\frac{1}{\varepsilon(1)}\left(\frac{\partial \ln \varepsilon}{\partial P}\right)_1$ and $b=9.20 \times 10^{-3} \text{bar}^{-1}$.

Then

$$\varepsilon(1)/\varepsilon(\rho)=1-(\partial \ln \varepsilon/\partial P)_1 \times (P-1)/(1+b(P-1)).$$

From (e) and (g) we shall get

$$\log \gamma(\rho)/\log \gamma(1)=(1+F(P-1))/(1+b(P-1))/[1+\alpha(P)]^{1/2},$$

where $F=-(\partial \ln \varepsilon/\partial P)_1$. The value of $\alpha(P)$ is not large. For water at 5 kbar $\alpha=0.033$ and $(1+\alpha)^{1/2}=1.017$. Therefore, for the majority of practical purposes it can be assumed $(1+\alpha)^{1/2}$ as equal to unity. Then we shall get from (b) the formula (a).

If instead of (f) to use another dependence of $\varepsilon$ on $P$, then it will be replaced in (a) the factor, characterising the pressure effect. Thus, for the Owen-Brinkley equation

$$1/\varepsilon(\rho)=1/\varepsilon(1)-A \ln [(B+P)/(B+1)],$$

it would be replaced the factor $(P-1)/(1+b(P-1))$ in (a) by $(B+1) \ln [(B+P)/(B+1)]$ (with the same value of $F$, convenient to use).

2. The authors of Ref. (10) by means of their high pressure conductivity data for the aqueous solutions of KCl showed the good applicability of the Onsager equation at the high pressures, which had been failed before. At the same time, as it has been noted in Ref. (12), their data for equivalent conductivities exceed to some extent those of Buchanan and Hamann's(12) and of other investigators'.

It seems to us rather possible the following explanation. Teflon conductivity cells(3), which has

6) W. L. Lees, Dissertation, Harvard University (1949)
7) W. E. Danforth, Phys. Rev., 38, 1224 (1931)
9) B. B. Owen and S. R. Brinkley, Phys. Rev., 64, 32 (1943)
10) M. Nakahara, K. Shimizu and J. Osugi, This Journal, 42, 12 (1972)
been used in Ref. (10) as being chemically inert and protecting the water solution from the impurities. Permitted the more accordant data to obtain, than in Ref. (12). At the same time the uncontrolled deformation of teflon at the compression can lead to the change of the cell constant and, therefore, to the regular error at each pressure.

There are some interesting design ideas\(^{13-15}\), which can be used for a subsequent development of the experimental technique in this field.

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