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

[M. Nakahara and J. Osugi, *Rev. Phys. Chem. Japan*, **45**, 69 (1975)]

BY BORIS S. EL'YANOV

In a very interesting review by Nakahara and Osugi1) and in the following "Comments" by Hamann2) 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 Linton3) proposed a simple formula for describing the pressure effect on activity coefficients of ions, which is convenient to present here as follows:

$$\log\gamma^{(p)}/\log\gamma^{(1)}=1+F(P-1)/[1+b(P-1)], \qquad \text{(a)*}$$

where F and b are constants. Since the validity of this formula has not been proved in Ref. (3), Nakahara and Osugi1) attempted to check its accordance with the limiting equation of the Debye-Hückel theory

$$\log\gamma^{(p)}/\log\gamma^{(1)}=(\rho^{(p)}/\rho^{(1)})^{1/2}(\varepsilon^{(1)}/\varepsilon^{(p)})^{3/2}, \qquad \text{(b)}$$

where ρ and ε are the density and the dielectric constant of the solvent respectively. It is worth regreting, 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

$$\frac{\partial\ln\gamma}{\partial p}=\frac{\bar{v}-\bar{v}^{\circ}}{RT}, \qquad \text{(c)}$$

where $\bar{v}$ and $\bar{v}^{\circ}$ are the partial molal volumes of the ion in the solution at a finite concentration and in infinitely diluted solution respectively, then this formula characterises expressed in terms of volume the difference between two interactions of the ion-water type in the solutions, which differ by the ion-

---

(*Received August 13, 1976*)

* Formula (5) of Ref. (1)

1) M. Nakahara and J. Osugi, *This Journal*, 45, 69 (1975)

2) S. D. Hamann, *ibid.*, 46, (1976)

3) S. D. Hamann and M. Linton, *J. C. S. Faraday Trans. 1*, 70, 2239 (1974)

ion type interaction. It is quite reasonable, therefore, to accept as a first approximation, that $\bar{v}$ and $\bar{v}^\circ$ 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 γ 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[4]: 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 Values of ε/ρ for various fluids[a)]

P, kbar	ρ	ε	ε/ρ	P, kbar	ρ	ε	ε/ρ
	a) Water (25°C)				d) Ethanol (30°C)		
0	0.9970	78.39	78.63	0	0.781	23.2	29.7
1.0	1.0380	81.87	78.87	0.5	0.816	24.5	30.0
2.0	1.0722	85.00	79.28	1.0	0.844	25.3	24.0
3.0	1.1014	87.88	79.79	2.0	0.884	26.4	29.9
4.0	1.1270	90.91	80.66	4.0	0.943	28.7	30.4
5.0	1.1501	93.47	81.27	6.0	0.980	30.3	30.9
6.0	1.1710	95.85	81.85	8.0	1.019	31.7	31.1
7.0	1.1902	98.06	82.39	12.0	1.073	33.7	31.4
8.0	1.2079	100.13	82.89				
	b) Carbon disulfide (30°C)				e) *n*-Pentane (30°C)		
0	1.241	2.61	2.10	0	0.613	1.82	2.97
0.5	1.291	2.74	2.12	0.5	0.664	1.90	2.86
1.0	1.332	2.82	2.12	1.0	0.701	1.96	2.80
2.0	1.394	2.94	2.11	2.0	0.743	2.03	2.73
4.0	1.487	3.11	2.09	4.0	0.796	2.12	2.66
6.0	1.550	3.23	2.08	6.0	0.835	2.19	2.62
8.0	1.601	3.33	2.08	8.0	0.865	2.24	2.59
12.0	1.689	3.52	2.08	12.0	0.907	2.33	2.57
	c) Diethyl ether (30°C)						
0	0.720	4.15	5.76				
0.5	0.771	4.53	5.87				
1.0	0.801	4.88	6.09				
2.0	0.847	5.39	6.36				
4.0	0.911	6.05	6.64				
6.0	0.952	6.53	6.86				
8.0	0.988	6.93	7.01				
12.0	1.047	7.68	7.33				

a) Experimental values of ρ and ε are from Refs. (5)~(7)

---

[4] B. S. El'yanov, *Austr. J. Chem.*, **28**, 933 (1975)

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

$$\varepsilon^{(p)}/\rho^{(p)}=\varepsilon^{(1)}/\rho^{(1)}[1+\alpha(P)]. \qquad \text{(d)}$$

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

$$\log\gamma^{(p)}/\log\gamma^{(1)}=\left(\frac{\rho^{(p)}}{\varepsilon^{(p)}}\bigg/\frac{\rho^{(1)}}{\varepsilon^{(1)}}\right)^{1/2}\frac{\varepsilon^{(1)}}{\varepsilon^{(p)}}=\frac{1}{[1+\alpha(P)]^{1/2}}\times\frac{\varepsilon^{(1)}}{\varepsilon^{(p)}}. \qquad \text{(e)}$$

As it has been shown[8]

$$1/\varepsilon^{(p)}=1/\varepsilon^{(1)}-k^*(P-1)/[1+b(P-1)], \qquad \text{(f)}$$

where $k^*=\frac{1}{\varepsilon^{(1)}}\left(\frac{\partial\ln\varepsilon}{\partial P}\right)_1$ and $b=9.20\times10^{-5}\,\text{bar}^{-1}$.
Then

$$\varepsilon^{(1)}/\varepsilon^{(p)}=1-(\partial\ln\varepsilon/\partial P)_1\times(P-1)/[1+b(P-1)]. \qquad \text{(g)}$$

From (e) and (g) we shall get

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

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 (h) the formula (a).

If instead of (f) to use another dependence of ε on P, then it will be replaced in (a) the factor, characterizing the pressure effect. Thus, for the Owen-Brinkley equation[9]

$$1/\varepsilon^{(p)}=1/\varepsilon^{(1)}-\mathrm{A}\ln[(B+P)/(B+1)], \qquad \text{(i)}$$

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 cell[13], which has

---

5) T. Grindley and J. E. Lind, *J. Chem. Phys.*, **54**, 3983 (1971)

6) W. L. Lees, Dissertation. Harvard University (1949)

7) W. E. Danforth, *Phys. Rev.*, **38**, 1224 (1931)

8) B. S. El'yanov and S. D. Hamann, *Austr. J. Chem.*, **28**, 945 (1975)

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)

11) S. D. Hamann, in "Modern Aspects of Electrochemistry", Vol. 9, Chap. 2, p. 66, Ed. B. E. Conway and J. O'M. Bockris, Plenum, New York (1974)

12) J. Buchanan and S. D. Hamann, *Trans. Faraday Soc.*, **49**, 1425 (1953)

13) M. Nakahara, K. Shimizu and J. Osugi, *This Journal*, **40**, 1 (1970)

been used in Ref. (10) as being chemically inert and protecting the water solution from the impurities, permited 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.

N. D. Zelinsky Institute of Organic Chemistry
Academy of Sciences of the USSR
Leninsky Prosp. 47
Moscow, USSR

---

14) A. J. Ellis, *J. Chem. Soc.*, **1959**, 3689
15) A. B. Gancy and S. B. Brummer, *J. Electrochem. Soc.*, **115**, 804 (1968)