DERIVATION OF EL'YANOV AND HAMANN'S EMPIRICAL FORMULA

AND ANOTHER NEW FORMULA FOR PRESSURE DEPENDENCE OF

IONIZATION CONSTANTS

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El'yanov and Hamann's empirical formula for the pressure dependence of the ionization constant, $RT \ln (K_p/K_0) = -\Delta \bar{V}_0^0 P/(1+bP)$ has been derived theoretically from the Born model for ionic solvation by taking account of the pressure dependence of the dielectric constant of water. Although b does not depend on temperature and is equal to $9.20 \times 10^{-5} \text{bar}^{-1}$ according to El'yanov and Hamann, the present derivation shows that b depends on temperature, being 8.98, 9.46 and $11.67 \times 10^{-5} \text{bar}^{-1}$ at 15, 25 and 45°C, respectively.

Another new formula for the pressure dependence of the ionization constant has been also obtained, which becomes equal to Owen-Brinkley's formula under some condition. All the formulas proposed by several authors until now have been compared, and their similarities and differences are discussed.

Introduction

In 1941 Owen and Brinkley[1] first derived a quantitative expression for the pressure dependence of ionic equilibria in aqueous solution, which is

$$-RT \ln (K_p/K_0) = \Delta \bar{V}_0^0 P - \Delta \bar{\kappa}_0^0 B\left(P - B \ln \frac{B+P}{B}\right), \qquad (1)$$

where R is the gas constant, T is the absolute temperature, $\Delta \bar{V}_0^0$, K_p and K_0 are the equilibrium constants at pressure P and zero respectively, $\Delta \bar{V}_0^0$ and $\Delta \bar{\kappa}_0^0$ are the changes in the partial molal volume and the partial molal compressibility at infinite dilution at zero pressure and B is a constant characteristic of water in the Tait equation. When they derived the above equation, they started from the empirical Tait-Gibson equation[2] for the partial molal volumes of the ions and assumed that the molal compressibility of a hypothetical pure liquid electrolyte is negligible. Then they could predict how much pressure affects the acid-base equilibria or solubilities of electrolytes in water at various temperaures by using the fundamental values of the partial molal volumes (the values used there were corrected later by Hamann[3]) and compressibilities of the ions at infinite dilution at atmospheric

(Received September 4, 1974)

1) B. B. Owen and S. R. Brinkley, Chem. Rev., 29, 461 (1941)

2) R. E. Gibson, Am. J. Sci., 35A, 49 (1938)

3) S. D. Hamann, "High Pressure Physics and Chemistry", Vol. 2, Chap. 7-ii, ed. by R. S. Bradley, Academic Press, London (1963)

pressure.

In 1968 Lown, Thirsk and Wynne-Jones[4] showed that the accumulated experimental data of the ionization constants of various acids and bases in water could be fitted up to about 2 kbar to a simpler equation

$$-RT \ln (K_p/K_0) = \Delta \bar{V}_0{}^0 P - \frac{1}{2} \Delta \bar{\kappa}_0{}^0 P^2, \qquad (2)$$

which had already been proposed by Owen and Brinkley[1] as an approximate form in the moderate pressure range. But, of course, this form was not successful at the higher pressures.

In 1973 North[5] has given another relationship of the form

$$-RT \ln (K_p/K_0) = \bar{V}_0{}^0 P - hAV_{w,0} \left\{ P - (B+P) \ln \frac{B+P}{B} \right\}, \qquad (3)$$

where h is the hydration number of the electrolyte, $V_{w,0}$ is the molal volume of pure water at zero bar and A and B are the constants characteristic of water in the Tait equation. This equation was derived by assuming the hydration shell to be incompressible and taking account of the pressure dependence of density of solvent water. This formula agreed well with the experimental data of weak acids and bases in water for pressures of up to 12 kbar.

In Russia El'yanov and Gonikberg[6~9] found by means of the correlation analysis used in the Hammett equation that the ionization constants of several weak acids and bases in water could be fitted approximately by the relation

$$RT \ln (K_p/K_0) = -\Delta \bar{V}_0{}^0 \phi, \qquad (4)$$

where ϕ was numerically determined as a function of pressure only and almost (within several per cent) the same for a number of weak electrolytes up to 8 kbar.

Recently El'yanov and Hamann[10, 11] showed ϕ in Eq. (4) can be expressed as an explicit function of pressure: they have given the form

$$RT \ln (K_p/K_0) = -\Delta \bar{V}_0{}^0 \frac{P}{1+bP}. \qquad (5)$$

where the value of b is 9.20×10^{-5} bar^{-1} and independent of temperature. El'yanov and Hamann's formula is merely empirical, so that the author has attempted to derive the formula from a certain model and make clear its physical meaning[12].

4) D. A. Lown, H. R. Thirsk and L. Wynne-Jones, *Trans. Faraday Soc.*, **64**, 2073(1968)

5) N. A. North, *J. Phys. Chem.*, **77**, 931 (1973)

6) B. S. El'yanov and M. G. Gonikberg, *Izv. Acad. Nauk. SSSR, ser. khim.*, 1044 (1967)

7) B. S. El'yanov and M. G. Gonikberg, *Zhur. Fiz. Khim.*, **46**, 1494 (1972)

8) M. G. Gonikberg, "Chemical Equilibria and Reaction Rates at High Pressures", Moscow (1969), Japanese Transtlation by Y. Ogo, Part 2, Chap. 6. 1, Nikkankogyo-Shinbunsha, Tokyo (1972)

9) B. S. El'yanov, *Austr. J. Chem.*, in press

10) S. D. Hamann, Private communication (Aug. 1973)

11) B. S. El'yanov and S. D. Hamann, *Austr. J. Chem.*, in press

12) M. Nakahara, Private communication to Dr. Hamann (Aug. 1973)

### Derivation of El'yanov and Hamann's Formula and Another New One

The fundamental thermodynamic relationship

$$RT\left(\frac{\partial \ln K}{\partial P}\right)_T = -\Delta \overline{V}^0,\qquad(6)$$

can be integrated to give some formula for the pressure dependence of ionization constants when the right-hand side of Eq. (6) is expressed as an explicit function of pressure; for example, $-\Delta \overline{V}^0$ may be formally expanded as a power series of pressure in the following way,

$$-\Delta \overline{V}^0 = -\Delta \overline{V}_0{}^0 - \left(\frac{\partial \Delta \overline{V}^0}{\partial P}\right)_{P=0} P - \frac{1}{2}\left(\frac{\partial^2 \Delta \overline{V}^0}{\partial P^2}\right)_{P=0} P^2 - \frac{1}{6}\left(\frac{\partial^3 \Delta \overline{V}^0}{\partial P^3}\right)_{P=0} P^3 \cdots\cdots$$

$$= -\Delta \overline{V}_0{}^0 + \Delta \bar{\kappa}_0{}^0 P + \frac{1}{2}\Delta \bar{\lambda}_0{}^0 P^2 + \frac{1}{6}\Delta \bar{\mu}_0{}^0 P^3 + \cdots\cdots.\qquad(7)$$

But from a theoretical view-point, such an infinite power series expansion is not useful so far as its convergence is not exactly verified. Then we consider to express $\Delta \overline{V}^0$ as a function of pressure in another way. For the following equilibrium

$$\begin{array}{ccc}\text{associated} & K & \text{ionized} \\ \text{AB} & \rightleftarrows & \text{A}^+ + \text{B}^-. \end{array}\qquad(8)$$
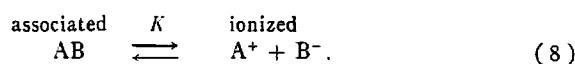
it may be assumed that

$$\overline{V}^0(\text{A}^+) = \overline{V}^0(\text{A}^+)_{\text{int}} + \overline{V}^0(\text{A}^+)_{\text{elect}}.\qquad(9)$$

and

$$\overline{V}^0(\text{B}^-) = \overline{V}^0(\text{B}^-)_{\text{int}} + \overline{V}^0(\text{B}^-)_{\text{elect}},\qquad(10)$$

where the subscripts, int and elect. refer to the intrinsic volume and the electrostrictive volume, respectively. Furthermore, according to the Born equation for solvation,

$$\overline{V}^0{}_{\text{elect}} = -\frac{Ne^2 z^2}{2r}\frac{\partial \varepsilon}{\varepsilon^2 \partial P},\qquad(11)$$

where N, e, z, r and ε are Avogadro's number, protonic charge, the charge number and the radius of the ion, and the dielectric constant of the solvent, respectively. When it could be approximated that

$$\overline{V}^0(\text{A}^+)_{\text{int}} + \overline{V}^0(\text{B}^-)_{\text{int}} - \overline{V}^0(\text{AB})_{\text{int}} = 0,\qquad(12)$$

we have from Eqs. (6), (8), (9), (10), (11) and (12)

$$RT\left(\frac{\partial \ln K}{\partial P}\right)_T = \frac{\alpha}{\varepsilon^2}\frac{\partial \varepsilon}{\partial P},\qquad(13)$$

where

$$\alpha = \frac{Ne^2}{2}\left(\frac{1}{r(\text{A}^+)} + \frac{1}{r(\text{B}^-)}\right).\qquad(14)$$

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Eq. (13) can be integrated with respect to pressure from 0 to P if the pressure dependence of r in Eq. (14) is assumed to be negligible and we have

$$RT \ln (K_p/K_0) = \alpha\left(\frac{1}{\varepsilon_0} - \frac{1}{\varepsilon_p}\right),$$ (15)

which can be also obtained directly from the Denison-Ramsey equation[13] or the Fuoss equation[14] for ion-pair equilibria with some postulates. Here, it is recalled that Dunn and Stokes[15] fitted their experimental data of the dielectric constants of water and formamide in the range of $1\sim2,000$ bar and $5\sim65°C$ to the empirical equation

$$\varepsilon_p = l + \frac{mP}{1+nP},$$ (16)

where l, m and n are the constants dependent on temperature. By combining Eqs. (15) and (16), we have

$$RT \ln (K_p/K_0) = \frac{\alpha}{l^2}\frac{mP}{1+\beta P},$$ (17)

where

$$\beta = \frac{m}{l} + n.$$ (18)

To make Eq. (17) flexible enough to fit experimental data, the theoretical constant, α in Eq. (17) had better be eliminated by introducing one empirical parameter

$$-\Delta \bar{V}_0{}^0 = RT\left(\frac{\partial \ln K}{\partial P}\right)_T \qquad \text{at } P=0.$$ (19)

When Eq. (17) is differentiated with respect to pressure, it follows that

$$-\Delta \bar{V}_0{}^0 = \frac{\alpha m}{l^2}.$$ (20)

In consequence, from Eqs. (17) and (20) we have

$$RT \ln (K_p/K_0) = -\Delta \bar{V}_0{}^0\frac{P}{1+\beta P},$$ (21)

which has just the same functional form as El'yanov and Hamann's formula, Eq. (5). However, although the empirical value of b in Eq. (5) is $9.20 \times 10^{-5} \text{bar}^{-1}$ at any temperature, the value of β cal-

Table 1 The calculated value of β (10^{-5} bar^{-1})

Temp., °C Solvent	10	25	45	65
water	8.98	9.46	11.67	14.24
formamide		4.63	5.64	

13) J. T. Dennison and J. B. Ramsey, *J. Am. Chem. Soc.*, **77**, 2615 (1955)
14) R. M. Fuoss, *ibid.*, **80**, 5059 (1958)

culated by using the data of Dunn and Stokes[15] depends on solvent and temperature as shown in Table 1.

When Eq. (17) is combined with the Owen and Brinkley equation[16,17]

$$\frac{1}{\varepsilon_0} - \frac{1}{\varepsilon_p} = A \ln \frac{B+P}{B}, \tag{22}$$

instead of with the Dunn and Stokes equation, another new formula is obtained with the same procedure as mentioned above. It results that

$$RT \ln (K_p/K_0) = -\Delta \bar{V}_0{}^0 B \ln \frac{B+P}{B}. \tag{23}$$

where B is a constant depending on temperature only and characteristic of the solvent used. Since the numerical values of B in Eq. (23) are available in the literature[17] for many organic solvents, Eq. (23) is very useful to predict the dissociation constants of weak electrolytes in nonaqueous solvents at high pressures if $\Delta \bar{V}_1{}^0$ is known from the density measurement at 1 bar ($\Delta V_0{}^0 \approx \Delta V_1{}^0$).

In the above derivation it is a weak point that the used formulas for the dielectric constant at high pressures are empirical. If the theoretical equation of Kirkwood[18] could be utilized instead of Eq. (16) or (22), we may obtain a more complete formula for the pressure dependence of ionization constants, but such an approach is not easy at present. By the way, it should be considered why the present simple treatment based on the sphere-in-continuum model is successful. 1) Although at first sight this approximate treatment seems too rough indeed because it takes into account of only electrostriction as solute-solvent interaction, it is practically relieved by the cancellation of some volume terms other than the electrostrictive volume between in the associated state and in the ionized state. For example, although for the carboxylic acids in water the so-called hydrophobic hydration around the hydrocarbon chain is involved in addition to the electrostriction, the corresponding volume term would be cancelled in the ionization reaction. 2) There are some uncertain issues with respect to the ionic radius or the effective dielectric constant in the Born equation on which the present derivation is based. However, the introduction of one empirical parameter in Eq. (19) would cover some defects in the Born equation, and further the neglection of the volume increase in the bond breakage which is assumed in Eq. (12).

Temperature Dependence of β

Although β in Eq. (21) really depends on temperature according to the high pressure data of the dielectric constant of water by Dunn and Stokes, El'yanov and Hamann[11] fitted the ionization con-

15) L. A. Dunn and R. H. Stokes, *Trans. Faraday Soc.*, **65**, 2906 (1969)

16) B. B. Owen and S. R. Brinkley, *Phys. Rev.*, **64**, 32 (1943)

17) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions", Chap. 8, Reinhold, New York (1958)

18) J. G. Kirkwood, *J. Chem. Phys.*, **7**, 911 (1939)

stants of ammonium hydroxide[19] in water at 45°C between 0 and 12 kbar and moreover the ionization constants of acetic acid[20] in water between 25 and 225°C at pressures up to 3 kbar to Eq. (5) where b is remarkably independent of temperature. In addition to such an experimental reason, there is another reason why they insist that b is independent of temperature; Eq. (4) or (5) has its basis on the linear free energy relationship[9]. Eq. (4) is a kind of extention of the linear free energy relationship, originally concerned with the substituent effect, to the pressure effect on the free energy change. Eq. (4) can be rewritten in the form

$$\Delta \bar{G}_p{}^0 - \Delta \bar{G}_0{}^0 = f(T)\phi(P), \qquad (24)$$

where $\Delta \bar{G}_p{}^0$ is the standard free energy change and $f(T) = -\Delta \bar{V}_0{}^0$. The differentiation of Eq. (24) with respect to pressure yields

$$\Delta \bar{V}_p{}^0 = f(T)\phi'(P), \qquad (25)$$

which is just equivalent (a necessary and sufficient condition) to Eq. (24). From Eq. (25) we have

$$\Delta \bar{V}_p{}^0 / \Delta \bar{V}_0{}^0 = \phi'(P)/\phi'(0), \qquad (26)$$

which is also equivalent to Eq. (25). The right-hand side of Eq. (26) does not depend on temperature. Accordingly, the variable separability postulate which arises substantially from the approximate nature of the linear free energy relationship and is exhibited in Eq. (24) or (25) means that the pressure effect on the standard partial molal volume change is always the same at any temperature. However, in a general and strict sense, such postulate may be broken in some cases, because for each component of the ionization reaction it can not be expected that $\bar{V}_p{}^0 / \bar{V}_1{}^0$ does not depend at all on temperature over a wide range of pressure.

Comparison of Eqs. (1), (2), (3), (5), (21) and (23)

In order to see the difference between Eqs. (1), (2), (3), (21) and (23), we might use the Maclaurin series expansion; that is

$$RT \ln (K_p/K_0) = D_0{}^{1)}P + D_0{}^{2)}P^2 + D_0{}^{3)}P^3 + \cdots \cdots D_0{}^{n)}P^n + \cdots \cdots, \qquad (27)$$

where

$$D_0{}^{n)} = \frac{RT}{n!}\left(\frac{\partial^n \ln K_p}{\partial P^n}\right)_T \qquad \text{at } P=0. \qquad (28)$$

The above infinite power series is convergent only if the pressure does not exceed its critical value, P_c which is called the radius of convergence defined as

$$P_c = \lim_{n \to \infty} \frac{D_0{}^{n)}}{D_0{}^{n+1)}}. \qquad (29)$$

19) S. D. Hamann and W. Strauss, *Trans. Faraday Soc.*, **51**, 1684 (1955)
20) D. A. Lown, H. R. Thirsk and L. Wynne-Jones, *ibid.*, **66**, 51 (1970)

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Table 2   Comparison of the formulas

	Eq. (1)	Eq. (2)	Eq. (3)	Eq. (21)	Eq. (23)
$D_0^{1)}$	$-\Delta \bar{V}_0^0$	$-\Delta \bar{V}_0^0$	$-\Delta \bar{V}_0^0$	$-\Delta \bar{V}_0^0$	$-\Delta \bar{V}_0^0$
$D_0^{2)}$	$\dfrac{1}{2}\Delta \bar{\kappa}_0^0$	$\dfrac{1}{2}\Delta \bar{\kappa}_0^0$	$-\dfrac{hAV_{w,0}}{2B}$	$\beta\Delta \bar{V}_0^0$	$\dfrac{1}{2B}\Delta \bar{V}_0^0$
$D_p^{2)*}$	$\dfrac{B^2\Delta \bar{\kappa}_0^0}{2(B+P)^2}$	$\dfrac{1}{2}\Delta \bar{\kappa}_0^0$	$-\dfrac{hAV_{w,0}}{2(B+P)}$	$\dfrac{\Delta \bar{V}_0^0}{(1+\beta P)^3}$	$\dfrac{B\Delta \bar{V}_0^0}{2(B+P)^2}$
$D_0^{n)}$ ($n \geq 2$)	$\dfrac{2(-1)^n D_0^{2)}}{nB^{n-2}}$		$\dfrac{2(-1)^n D_0^{2)}}{n(n-1)B^{n-2}}$	$(-1)^n\beta^{n-2}D_0^{2)}$	$\dfrac{2(-1)^n D_0^{2)}}{nB^{n-2}}$
P_c	B		B	β^{-1}	B

$$* \quad D_p^{2)}=\frac{RT}{2!}\left(\frac{\partial^2 \ln K}{\partial P^2}\right)_T$$

As shown in Table 2, P_c is the same for Eqs. (1), (3) and (23) being equal to B ($4\sim4.5$ kbar for water at 25°C), and β^{-1} (ca. 11 kbar) for Eq. (21). Then we can understand that the upper limit pressure beyond which Eq. (2) becomes invalid would be much less than B or β^{-1}. Really, in the paper[20] of Lown et al. it can be seen that the discrepancy between Eq. (2) and the experimental data exists even at the pressure less than 2 kbar.

It is also interesting that the degree with respect to pressure in the denominator of $D_p^{2)}$ is regularly zeroth, first, second and third for Eq. (2), Eq. (3), Eqs. (1) and (23), and Eq. (21), respectively.

Although Eqs. (1) and (23) have different bases, they become equal to each other under the condition that in Eq. (1) $\Delta \bar{\kappa}_0^0=\Delta \bar{V}_0^0/B$: for water at 25°C $\Delta \bar{\kappa}_0^0$ is $3.34\times10^{-4}\Delta \bar{V}_0^0$ bar^{-1} when B is 2,996 bar[17] and, more possibly, $2.19\times10^{-4}\Delta \bar{V}_0^0$ bar^{-1} when B is 4.574 bar[21]. Lown et al.[20] correlated $\Delta \bar{\kappa}_1^0$ with $\Delta \bar{V}_1^0$ and obtained $\Delta \bar{\kappa}_1^0=2.14\times10^{-4}\Delta \bar{V}_1^0$ bar^{-1} for water at 25°C.

In order to compare numerically the new formula, Eq. (23) with Eq. (21), we change them as

Table 3   The value of $P/(1+\beta P)$. 10^3

Pressure, kbar	β, 10^{-5} bar^{-1}	8.98	9.20	9.46	11.67
	Temp., °C	15	25	25	45
2		1.68	1.69	1.68	1.62
4		2.94	2.92	2.90	2.73
6		3.90	3.87	3.83	3.53
8		4.66	4.61	4.55	4.14
10		5.27	5.21	5.14	4.61
12		5.77	5.70	5.62	5.00

21) K. R. Srinivasan and R. L. Kay, J. Chem. Phys., 60, 3645 (1974)

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$$-\frac{RT}{\Delta\bar{V}_0^0}\ln\left(K_p/K_0\right)=\frac{P}{1+\beta P},\qquad(30)$$

and

$$-\frac{RT}{\Delta\bar{V}_0^0}\ln\left(K_p/K_0\right)=B\ln\left(1+P/B\right),\qquad(31)$$

where the right-hand sides have only one parameter. The numerical values of the right-hand sides under various kinds of conditions are listed in Tables 3 and 4.

Table 4   The value of $B\ln(1+P/B)$, 10^3

Pressure, kbar	Solvent	water	water	water	water	water	methanol
	B, bar	2,996	3,081	4,133	4,574	3,672	764
	Temp., °C	25	45	10	25	40	25
	Ref.	(17)	(17)	(21)	(21)	(21)	(17)
	2	1.53	1.54	1.63	1.66	1.60	0.98
	4	2.54	2.56	2.79	2.87	2.70	1.40
	6	3.29	3.33	3.71	3.83	3.56	1.67
	8	3.90	3.94	4.45	4.63	4.25	1.86
	10	4.40	4.46	5.08	5.30	4.83	2.02
	12	4.83	4.89	5.63	5.89	5.33	2.15

Although Eqs. (30) and (31) are considerably different numerically when the values of B tabulated in Ref. (17) are used, the most recent values by Srinivasan and Kay[21] make both Eqs. (30) and (31) quite similar numerically up to 12 kbar. Thus the value of B for the dielectric constant of water at 25°C by Srinivasan and Kay makes the present new formula for the pressure dependence of ionization constants very similar not only to the Owen and Brinkley formula but also to the El'yanov and Hamann formula.

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