The Volume Change on Ion-Pairing of Symmetrical Electrolytes *

Y. Marcus

Department of Inorganic and Analytical Chemistry, The Hebrew University,
Jerusalem 91904, Israel

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Dedicated to Professor Alfred Klemm on the occasion of his 70th birthday

The increase in the standard partial molar volume of a symmetrical electrolyte on ion-pairing, $\Delta \bar{V}^{\infty}$, calculated from the experimental association constant at ambient pressure, the isothermal compressibility, the dielectric constant of the solvent and its pressure coefficient, is as good a measure of this quantity as values calculated from more elaborate experimental procedures, such as the pressure coefficient of the association constant or high precision density determinations in dilute solutions.

Introduction

When symmetrical electrolytes associate in solution to ion pairs, the electrostriction caused by the ions disappears. The association is, therefore, accompanied by an increase in volume, $\Delta \bar{V}^{\infty}$, which is the difference between the standard partial molar volumes of the ion pairs and of the completely dissociated electrolyte. Two experimental procedures have commonly been used for obtaining this quantity. In one of them, the pressure derivative of the association constant, obtained generally from conductivity measurements, is calculated:

$$\Delta \bar{V}^{\infty} = -RT(\partial \ln K_{\mathrm{m}}(p)/\partial p)_T , \qquad (1)$$

where $K_{\mathrm{m}}(p)$ is the association constant on the molal scale at pressure p. This procedure requires K_{m} data at several pressures up to quite high ones, typically to 100 MPa, which are not easy to obtain with high precision. The differentiation reduces the accuracy of $\Delta \bar{V}^{\infty}$ obtained by this procedure even further [1, 2]. The other procedure is to obtain apparent molar volumes Φ_V from density measurements over the range of concentrations in which the electrolyte is only partly associated, and calculate:

$$\Delta \bar{V}^{\infty} = (\lim_{c \to \infty} \Phi_V - \Phi_V(c))/\alpha + k\,\alpha^{1/2} c^{1/2} , \qquad (2)$$

where α is the degree of dissociation of the electrolyte, c is its molar concentration, and k is the Debye-Hückel limiting law slope. In (2) $\lim_{c \to \infty} \Phi_V$ represents the apparent molar volume of the completely associated electrolyte, i.e., of the ion pair. Linear terms in c have been omitted for the sake of simplicity; they have to be included in accurate calculations. Again, it is difficult to obtain densities to sufficiently high precisions in the dilute solution range, where α is appreciably different from both 0 and 1 [3, 4].

The concept of association of an electrolyte to ion pairs inherently implies some model, and the Bjerrum approach [5], according to which oppositely charged ions are associated if their electrostatic interaction energy exceeds kT, is adopted. The model considers the ions as point charges, capable of approaching each other in the continuous dielectric medium of relative permittivity ε no nearer than the characteristic distance a. The general applicability of this model has been recently confirmed [6]. Acceptance of this model requires the experimental association constant obtained at ambient conditions and expressed on the molar scale to be given by the equation [5]:

$$K_{\mathrm{exptl}}/\mathrm{dm}^3\,\mathrm{mol}^{-1} = 4 \cdot 10^{-24} \pi N_{\mathrm{Av}} (a/\mathrm{nm})^3 \cdot b^3 Q(b) = K , \qquad (3)$$

where

$$b = (z^2 e^2 / 4 \pi \varepsilon_0 k_{\mathrm{B}})\, T^{-1} \varepsilon^{-1} a^{-1} = 16710.3\, (T/\mathrm{K})^{-1} \varepsilon^{-1} (a/\mathrm{nm})^{-1} , \qquad (4)$$

$$Q(b) = \int_2^b t^{-4} \exp(t)\, \mathrm{d}t . \qquad (5)$$

N_{Av} is Avogadro's number, z is the charge number of the ions, and t is an auxiliary variable. For a

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Reprint requests to Y. Marcus, Department of Inorganic and Analytical Chemistry, The Hebrew University, Jerusalem 91904, Israel.

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given temperature T and solvent (characterized by ε), K is an implicit function of a (which characterizes the electrolyte) only.

If (1) is to be applied to (3), K must first be converted to the molal scale by multiplication with the density of the solvent, $\varrho/\text{kg dm}^{-3}$. On the assumption that the distance parameter a is pressure independent, the result is:

$$\begin{aligned}\Delta\bar{V}^{\infty} &= -RT(\partial\ln(K\cdot\varrho)/\partial p)_T\\ &= RT\varkappa_T[([3+\exp(b-\ln Q(b))\,b^{-3}]\\ &\quad\cdot[\varkappa_T^{-1}(\partial\ln\varepsilon/\partial p)_T])-1]\end{aligned}\tag{6}$$

where $\varkappa_T$ is the isothermal compressibility of the solvent, $(\partial\ln\varrho/\partial p)_T$. It should be noted that (6) applies at all pressures, including ambient pressure. Such an equation has been derived previously, e.g. [3, 7].

The main purpose of the present paper is the demonstration that (6) can be the basis of determinations of $\Delta\bar{V}^{\infty}$ that are as good as, if not superior to, the more tedious methods mentioned above, i.e. $K_m(p)$ or $\Phi_V(\alpha)$, and the advocacy of its universal employment in their stead.

Method

The calculation requires as input data the experimental association constant of the electrolyte, $K_{\text{exptl}}/\text{dm}^3\,\text{mol}^{-1}$, and the isothermal compressibility $\varkappa_T$, the dielectric constant ε, and its pressure derivative $(\partial\ln\varepsilon/\partial p)_T$, all obtained at a given temperature T and pressure, usually ambient.

The quantities T/K and ε are inserted into (4) and b values are obtained for a series of a values around the expected one. Equation (5) is now integrated numerically for these b values to obtain corresponding $Q(b)$ values. These, in turn, are inserted into (3) and (6), together with the $\varkappa_T$ and $(\partial\ln\varepsilon/\partial p)_T$ data, to obtain related K and $\Delta\bar{V}^{\infty}$ values, which have a as the variable parameter. Whereas $\log K$ has been found to be non-linear with a, the functional dependence of the related $\Delta\bar{V}^{\infty}$ and $\log K$ is very closely linear. This permits an accurate interpolation to find the $\Delta\bar{V}^{\infty}$ corresponding to the experimental $K = K_{\text{exptl}}$.

Alternatively, $Q(b)$ can be obtained from (4) and K_{exptl} as:

$$Q(b) = 2.8318\cdot 10^{-14}(T/\text{K})^3\,\varepsilon^3\,K_{\text{exptl}}\,. \tag{7}$$

Numerical integrations of (5) are again carried out for a series of b values, and a value of b is interpolated in these for the corresponding experimental $Q(b)$. This corresponding set is then used in (6) to give $\Delta\bar{V}^{\infty}$. At high values of the experimental $Q(b)$, the approximation [7] $Q(b)\approx\exp(b)\cdot b^{-4}$ may serve in the numerical calculations.

If RT is taken in Jmol^{-1} and $\varkappa_T$ and $(\partial\ln\varepsilon/\partial p)_T$ in bar^{-1} (1 bar = 0.1 MPa), then the right hand side of (6) must be multiplied by 10 to give $\Delta\bar{V}^{\infty}$ in $\text{cm}^3\,\text{mol}^{-1}$.

The accuracy of the numerical integration depends on the number of steps used, and ± 0.1% can readily be achieved with 100 steps in a reasonably short time on a microcomputer. This compares favorably with the series expansions employed previously [8]. The accuracy determining factors are the experimental values of $\varkappa_T$ and $(\partial\ln\varepsilon/\partial p)_T$ that are used for the solvent at the given T and p, together with the accuracy of the value K_{exptl} of the particular electrolyte studied. The contribution of the latter factor is $\pm 1\,\text{cm}^3\text{mol}^{-1}$ in $\Delta\bar{V}^{\infty}$ for an uncertainty of ± 20% in K_{exptl}.

Applications

The method can be applied whenever the input data: K_{exptl}, ε, $\varkappa_T$ and $(\partial\ln\varepsilon/\partial p)_T$ are known or can be estimated for the given T and p and the electrolyte/solvent system of interest. Here only a few cases will be dealt with, where $\Delta\bar{V}^{\infty}$ values have already been estimated by the experimentally more elaborate $K_m(p)$ or $\Phi_V(\alpha)$ methods, as found in the literature.

The data for the lithium halides in alcohols have been discussed previously [3] and need not be repeated here. Corresponding values of $\varkappa_T$ and $(\partial\ln\varepsilon/\partial p)_T$ have been selected from the literature for primary, secondary, straight-chain and branched alcohols, and have been reported [3]. A semiempirical relationship between these two quantities has been found to hold (see Appendix):

$$(\partial\ln\varepsilon/\partial p)_T = [(\varepsilon-1)(2.974 + 0.0257\,\varepsilon)/3.81\,\varepsilon]\cdot\varkappa_T\,. \tag{8}$$

For an accuracy of $\pm 0.5\cdot 10^{-6}\,\text{bar}^{-1}$ in $\varkappa_T$ the corresponding accuracy in $(\partial\ln\varepsilon/\partial p)_T$ is $\pm 2.0\cdot 10^{-6}\,\text{bar}^{-1}$. This relationship should prove useful also for other cases of association of symmetrical electrolytes in alcohols.

The case of the alkali metal iodides in acetone, where $K(p)$ has been obtained from conductivity

Table 1. Comparison of $\Delta \bar{V}^{\infty}/\mathrm{cm}^3\,\mathrm{mol}^{-1}$ for the association of alkali metal iodides in acetone at 30 °C.

Salt	Ambient pressure		1.53 kbar	
	Inada [1]	present work	Inada [1]	present work
LiI	21	15.9 ± 0.8	12	8.0 ± 0.5
NaI	25	16.8 ± 0.8	12	8.0 ± 0.5
KI	23	17.7 ± 0.9	12	8.0 ± 0.5
CsI	24	20.6 ± 1.0	12	10.0 ± 0.5

measurements to 2 kbar [1], is a good illustration of the use of the present method. The data quoted for $V(p)/V(1)$ and $\varepsilon(p)$ [1] and others from standard Tables [9] yield $\varkappa_T = 1.19 \cdot 10^{-6}\,\mathrm{bar}^{-1}$ and $\varkappa_T^{-1}(\partial \ln \varepsilon/\partial p)_T = 1.31 \pm 0.02$ at ambient pressure and $\varkappa_T = 0.51 \cdot 10^{-6}\,\mathrm{bar}^{-1}$ and $\varkappa_T^{-1}(\partial \ln \varepsilon/\partial p)_T = 1.23 \pm 0.02$ at 1.53 kbar. The values of $\Delta \bar{V}^{\infty}$ calculated by the author [1] and by the present method are compared in Table 1. The former have been obtained from the slopes of small-scale curves of $\ln K$ vs. p, and are not very accurate. The unexplained non-monotonous sequence of values at ambient pressure illustrates this point. In the present calculation the quantity that limits the accuracy seems to be the uncertainty in $\varkappa_T$, estimated to be ± 5%, which produces a corresponding uncertainty in $\Delta \bar{V}^{\infty}$, in addition to any uncertainties that accrue from the K values, the errors of which have not been given [1].

Another case that can illustrate the use of the present method is that of the association of cadmium and sulfate ions in aqueous acetonitrile solutions [4]. The authors have made highly precise density determinations in dilute solutions (in the range from 0.004 to 0.040 mol dm^{-3}) of cadmium sulfate in water and in 3 and 21 mol% aqueous acetonitrile, and also conductivity measurements, from which they have calculated association constants. The Debye-Hückel limiting slope k of (2), or as used in [4], requires the knowledge of $\varkappa_T$ and $(\partial \ln \varepsilon/\partial p)_T$ for its calculation. These have been obtained from a previous work of two of the authors [10] by interpolation. The results for $\Delta \bar{V}^{\infty}$ obtained by the authors [4] and by the present method are compared in Table 2.

If the uncertainty of K given by the authors [4] for aqueous cadmium sulfate, ± 1.6%, applies also for the mixtures, the resulting error of $\Delta \bar{V}^{\infty}$ from the present method is ± 0.1 cm^3 mol^{-1}. To this must be added any errors in $\varkappa_T$ and $(\partial \ln \varepsilon/\partial p)_T/\varkappa_T$ the uncertainty of the interpolated values of the former [10] is ± 2.5%, that of the latter is relatively negligible. Errors of ± 0.5 to ± 0.8 cm^3 mol^{-1} therefore arise from these sources. Hence the estimates of the uncertainty in the values obtained by the present method. In spite of the high precision attained for the density measurements [4], their conversion to estimates of $\Delta \bar{V}^{\infty}$ lead to the result that a 2% relative increase of the mol% of acetonitrile from 20.92 to 21.32 produces a relative increase of 57 ± 31% in $\Delta \bar{V}^{\infty}$ (from 61 to 96 cm^3 mol^{-1})! No comment on this was provided, however in [4], and this may reflect inherent inaccuracies in their method. The present procedure, of course, provides a smooth dependence of $\Delta \bar{V}^{\infty}$ on the mol% of acetonitrile.

A final case to be discussed here is the association of tetrabutylammonium picrate in mixtures of benzene and chlorobenzene [2], where, again, K_m has been obtained from conductivity measurements at various pressures, up to 0.65 kbar. The pressure derivative of K_m has then been used to calculate $\Delta \bar{V}^{\infty}$ but the K_m values themselves have not been presented in the paper. Instead, distance parameters a, obtained by means of the Fuoss theory of ion pairing, have been reported. The use of these a values in (4) gave the required b, and this, in turn, in (5) the required $Q(b)$, for the calculation of

Table 2. Comparison of $\Delta \bar{V}^{\infty}$ values for the association of cadmium sulfate in aqueous acetonitrile at 25 °C.

Mol% CH_3CN	$10^5 \cdot \varkappa_T/\mathrm{bar}^{-1}$	$(\partial \ln \varepsilon/\partial p)_T/\varkappa_T$	K dm^3 mol^{-1}	$\Delta \bar{V}^{\infty}/\mathrm{cm}^3\,\mathrm{mol}^{-1}$	
				authors [4]	present
0.00	4.51	1.054	248 ± 4	9.3 ± 1.0	20.6 ± 0.6
3.00	4.55	1.096	354	7.2 ± 1.2	22.3 ± 0.6
20.92	5.43	1.173	2960	61 ± 6	31.5 ± 0.9
21.32	5.46	1.173	3100	96 ± 13	31.8 ± 0.9

Table 3. Comparison of $\Delta \bar{V}^\infty$ values for the association of tetrabutylammonium picrate in benzene + chlorobenzene mixtures at 25 °C.

Vol% C_6H_5Cl	ε	a/nm	$\Delta \bar{V}^\infty/\mathrm{cm^3\,mol^{-1}}$	
			authors [2]	present work
0	2.27	0.622	61.6 ± 5.1	59 ± 2
11	2.62	0.615	54.5 ± 3.3	55 ± 2
16	2.78	0.603	57.3 ± 1.0	54 ± 1
30	3.22	0.594	51.8 ± 1.3	49 ± 1
40	3.55	0.585	48.5 ± 0.8	47 ± 1
50	3.87	0.575	50.8 ± 1.0	44 ± 1

$\Delta \bar{V}^\infty$ by the present method. These are compared with the values reported in [2] in Table 3. The necessary $(\partial \ln \varepsilon/\partial p)_T$ data for the benzene + chlorobenzene mixtures have been given in the paper, the $\varkappa_T$ data have been estimated from data in the sources quoted there [2].

The nonmonotonous change of $\Delta \bar{V}^\infty$ with the composition of the solvent, reported by the authors [2], should be noted. This feature has not been commented on in [2], and the limits of error given by the authors are therefore not realistic. The values obtained in the present work agree with their general trend and also with their absolute magnitude, but do not suffer from these fluctuations. Their accuracy is limited by the uncertainties in a (not given), those of $\varkappa_T$ (± 3%), and those of $(\partial \ln \varepsilon/\partial p)_T$ (± 2%).

Discussion

The examples discussed in this paper show that the calculated $\Delta \bar{V}^\infty$ values are of the correct magnitude (Tables 1 and 3), have the correct pressure dependence (Table 1), and do not suffer from unexplained inconsistencies (Tables 2 and 3), compared with the experimental values. Since, however, ion pairs are in fact defined only operationally, it is to be expected that the present method of obtaining the volume change on ion-pairing applies only to such cases where the association has been measured by a method compatible with the underlying concept of association, e.g. by conductivity measurements.

Cases are abundant in the literature, where agreement of the association constants expected from the Bjerrum theory of association [5] with experimental values is poor. Such cases include those of mixed solvents having dielectric constants ε equal to that of a given solvent, but showing widely different values of K for a given electrolyte. Such discrepancies have been explained in terms of preferential solvation. A short discussion of this has been given in [11].

A corollary of the acceptance of the Bjerrum expression (3) for the association constant K, and its derivative with respect to the pressure, to give $\Delta \bar{V}^\infty$ in (6), is the derivation with respect to the temperature to give the standard molar heat of ion-pairing, $\Delta \bar{H}^\infty$. Again, many cases of discrepancies between the values of the derived expression (see, e.g., [12]):

$$\Delta \bar{H}^\infty = -RT[(b-1)(1 + T\,\mathrm{d}\ln\varepsilon/\mathrm{d}T) + \alpha T], \qquad (9)$$

where α is the isobaric thermal expansivity of the solvent, and experimental calorimetric values have been noted. The question arises whether the calorimetric determination of the heat of association applies to the same process to which the calculation

Table 4. The ratios of the pressure derivative of the dielectric constant and the isothermal compressibility of alcohols at 298.15 K and 1 bar.

Alcohol	$(\partial \ln \varepsilon/\partial P)_T/\varkappa_T$	
	experimental [a]	Eq. (8)
methanol	0.96	0.97
ethanol	0.87	0.90
1-propanol	0.89	0.87
1-butanol	0.83	0.84
1-pentanol	0.87	0.82
1-hexanol	0.80	0.80
1-heptanol		0.78
1-octanol		0.76
1-nonanol		0.75
1-decanol		0.73
2-propanol		0.86
2-butanol	1.21 (?)	0.84
2-methyl-1-propanol	0.99	0.85
3-methyl-1-butanol	0.85	0.82
2-ethyl-1-hexanol		0.76

[a] Estimated accuracy: ± 2%. Values calculated from data in the following sources: T. Chen, W. Dannhauser, and J. Johari, J. Chem. Phys. **50,** 2046 (1969): PrOH, 2-BuOH; W. E. Danforth, Phys. Rev. **38,** 1224 (1931): EtOH, i-BuOH, HxOH; H. Hartmann, A. Neumann, and G. Rinck, Z. Phys. Chem. **44,** 204 (1965): MeOH; F. E. E. Harris, E. W. Haycock, and B. J. Alder, J. Chem. Phys. **21,** 1943 (1953): BuOH; J. S. Jacobs and A. W. Lawson, ibid. **20,** 1161 (1952): MeOH, EtOH, HxOH; S. Kyropoulus, Z. Phys. **40,** 507 (1927): MeOH, EtOH; B. B. Owen and S. R. Brinckley, Phys. Rev. **64,** 32 (1943): MeOH, EtOH, i-BuOH, HxOH; R. G. Bennet, G. H. Hall, and J. H. Calderwood, J. Phys. D **6,** 781 (1973): PnOH, i-PnOH; Ref. [14] for $(\partial \ln \varepsilon/\partial P)_T$. Also Landoldt-Börnstein, New Series (1967), Vol. II/5, p. 41, and G. W. Marcks, J. Acoust. Soc. Amer. **41,** 103 (1967) for $\varkappa_T$.

applies, and if not, what adjustments are appropriate.

It is suggested that the examples treated in the present paper, where the $\Delta \bar{V}^{\infty}$ from (6) is seen to agree with experimentally determined values, be taken also for the experimental determination of $\Delta \bar{H}^{\infty}$. This would test the applicability of the calorimetric determination to the cases of ion-pairing that fall within the range of validity of the Bjerrum treatment.

Appendix

The dielectric constant of a liquid at a given temperature and pressure has been expressed as [13, 14]:

$$\begin{aligned}\varepsilon(T,P) = \{&D[\varrho(T,P)-\varrho(T,P_0)]+2\varrho(T,P)\\ &+2\varrho(T,P_0)[\varepsilon(T,P_0)+2]/[\varepsilon(T,P_0)-1]\}/\\ &\cdot\{D[\varrho(T,P)-\varrho(T,P_0)]-\varrho(T,P)\\ &+\varrho(T,P)[\varepsilon(T,P_0)+2]/[\varepsilon(T,P_0)+1]\} \qquad (10)\end{aligned}$$

with a single, temperature, pressure, and solvent independent parameter, D. It requires density data $\varrho(T, P)$ at the given pressure, but dielectric constant data only at ambient pressure, $P_0 = 1$ bar. The pressure derivative of (10) is:

$$\begin{aligned}(\partial \ln \varepsilon/\partial\, \mathrm{d}P)_{T,P_0} = \{&[\varepsilon(T,P_0)-1]/\varepsilon(T,P_0)\} \qquad (11)\\ &\cdot[D+2+(1-D)\,\varepsilon(T,P_0)]\,(1/3)\,\varkappa_T\,.\end{aligned}$$

A fit of this theoretically based equation to data for straight-chain alcohols (Table 4) shows the factor (1/3) to be too large, and that is should be replaced by (1/3.8) in order to obtain a good fit with the parameter $D = 0.9743$, that has been found to be solvent-independent [14]. This change converts (11) to the empirical (8).

[1] E. Inada, Rev. Phys. Chem. Japan **48,** 72 (1978).
[2] J. Everaert and A. Persoons, J. Phys. Chem. **86,** 546 (1982).
[3] Y. Marcus, N. Ben-Zwi, and I. Shiloh, J. Soln. Chem. **5,** 87 (1976).
[4] G. Schwitzgebel, C. Lührs, and J. Barthel, Ber. Bunsenges. Phys. Chem. **84,** 1220 (1980).
[5] N. Bjerrum, Kgl. Dan. Vidensk. Selsk. Mat.-Fys. Medd. **7,** No. 9 (1926).
[6] J. C. Justice, J. Phys. Chem. **79,** 454 (1975).
[7] P. Hemmes, J. Phys. Chem. **76,** 895 (1972).
[8] H. S. Harned and B. B. Owen, Physical Chemistry of Electrolyte Solutions, Reinhold, New York, 3rd Ed., 1958.
[9] Landolt-Börnstein, Zahlenwerte und Funktionen, Springer, Berlin 1971, Vol. II/1, p. 665.
[10] C. Lührs and G. Schwitzgebel, Ber. Bunsenges. Phys. Chem. **83,** 623 (1979).
[11] Y. Marcus and A. S. Kertes, Ion Exchange and Solvent Extraction of Metal Complexes, Wiley-Intersci., London 1969, pp. 148–150.
[12] Y. Marcus, J. Phys. Chem. **80,** 2451 (1976).
[13] W. E. Danforth Jr., Phys. Rev. **38,** 1224 (1931).
[14] E. Schadow and R. Steiner, Z. Phys. Chem. **66,** 105 (1969).