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Partial Molar Volumes of Some Aqueous Electrolytes and a Transition Model

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Abstract: An expression has been derived for partial molar volumes and also for apparent molar volumes ϕ_V, from the free-energy equation based on a model which takes explicit accounts of interionic effects and effects due to thermal jostling. The expression suggests that for moderately concentrated solutions ϕ_V varies linearly with $C^{1/3}$ and that the cube root behavior of ϕ_V gives way to $C^{1/2}$ dependence as $C \to 0$. Excellent quantitative agreement is obtained by adopting a value of 60.66×10^{-6} bar^{-1} for $\partial(\ln \epsilon)/\partial P$ of water at 25 °C and 1 atm.

Introduction

Examination of the "lattice" or "cell" theory[1,2] of aqueous strong electrolytes reveals that this model may be a reasonable description for moderate to concentrated solutions while in the limit of infinite dilution the ion-cloud concept of Debye must prevail. A more reasonable formalism appears to be one based on Lietzke, Stoughton, and Fuoss' observations.[3] We have recently proposed a model[4] (henceforth called the transition model) which assumes that ions in solutions (dilute as well as concentrated) have a certain degree of mobility and that it is the time average population density of the ions that corresponds to either the Debye or the "lattice" model. The fundamental equation expressing the mean ionic molal activity coefficient is[4]

$$\log \gamma_\pm = [\log \gamma_\pm]_{\text{Debye}} e^{-15m} + (1 - e^{-15m})[\log \gamma_\pm]_{\text{"cell"}}$$
$$- \log (1 + \nu mM/1000)$$

$$= e^{-15m}\left[\frac{-A_\gamma Z_+ Z_- \sqrt{\frac{1}{2}\sum C_i Z_i^2}}{1 + 1.4 \sqrt{\frac{1}{2}\sum C_i Z_i^2}} \right]$$

$$+ (1 - e^{-15m})(-A\sqrt[3]{C} + BC + \delta)$$
$$- \log (1 + \nu mM/1000) \quad (1)$$

where $A = [A''Z_+Z_-N/2.303\nu RT\epsilon]\, a_{A''}(N/1000)^{1/3}$, $\nu = \nu_+ + \nu_-$, A'' is the cell model analogue of the Madelung constant, ϵ is the bulk dielectric constant, $a_{A''}$ converts a particular

structure to the distance of ionic separation, and δ corrects all activity coefficients calculated according to the "lattice" model[1] to the standard state where Debye-Hückel limiting laws are obeyed at infinite dilution. The parameter, e^{-15m}, describes the probability[4] that an ion behaves as a "Debye" ion. (This probability, which is determined primarily by ion-solvent interactions, has been shown[4] to be dependent upon the number of solute particles and not on the distance between them. Further nuclear magnetic relaxation studies[5] and recent model calculations[6] indicate that even in the first hydration sphere the solvent is not permanently attached to the ions. This would then mean that so long as the number of solute and solvent particles are constant the probability that an ion behaves as a "Debye" ion is fixed and consequently molality should be used in the parameter e^{-15m}). All other quantities have their usual meanings.[1,2]

While expression 1 describes[4] well the activity coefficients of a number of electrolytes in water at 25 °C, ϕ_L (apparent relative molar heat content) calculated according to it also reproduces[4] well the corresponding experimental values for dilute NaCl solution at 25 °C. This paper shows that the pressure derivative of expression 1 yields partial molar volume data in excellent agreement with the experimental data for 1:1 and 1:2 electrolytes and is another confirmation of the general applicability of the two-structure concept.[3]

Results and Discussion

The partial molar Gibbs free energy for an electrolyte in solution is expressed as

$$\bar{G}_2 = \bar{G}_2{}^0 + RT \ln f_\pm{}^\nu X_\pm{}^\nu \tag{2}$$

where $f_\pm$ is the mean ionic mole fraction activity coefficient and $X_\pm$ is the mean ionic mole fraction of the electrolyte in solution. Further $f_\pm$ is related to the mean molal activity coefficient, $\gamma_\pm$, by the expression

$$\log f_\pm = \log \gamma_\pm - \log (1 + \nu mM/1000) \tag{3}$$

and this transforms eq 1 to

$$\log f_\pm = e^{-15m}(\log f_\pm)_{\text{Debye}} + (1 - e^{-15m})(\log f_\pm)_{\text{"cell"}} \tag{4}$$

Differentiation of eq 2 with respect to pressure yields

$$\bar{V}_2 = \bar{V}_2{}^0 + \nu RT \left[\frac{\partial}{\partial P} (\ln f_\pm) \right]_{T,n's} \tag{5}$$

which in view of eq 4 reduces to

$$\bar{V}_2 = \bar{V}_2{}^0 + \nu RT \left[e^{-15m} \frac{\partial}{\partial P} \{\ln f_\pm\}_{\text{Debye}} + (1 - e^{-15m}) \frac{\partial}{\partial P} (\ln f_\pm)_{\text{"cell"}} \right] \tag{6}$$

But

$$\nu RT \frac{\partial}{\partial P} (\ln f_\pm)_{\text{Debye}}{}^7 = \frac{S_V \sqrt{\frac{1}{2} \sum C_i Z_i{}^2}}{1 + ab \sqrt{\frac{1}{2} \sum C_i Z_i{}^2}} \tag{7}$$

and

$$\frac{\nu RT}{\ln (10)} \frac{\partial}{\partial P} (\ln f_\pm)_{\text{"cell"}8} = A_P C^{1/3} + B_P C \tag{8}$$

so that expression 6 then reduces to

$$\bar{V}_2 - \bar{V}_2{}^0 = e^{-15m} \left[\frac{S_V \sqrt{\frac{1}{2} \sum C_i Z_i{}^2}}{1 + 1.4 \sqrt{\frac{1}{2} \sum C_i Z_i{}^2}} \right] + (1 - e^{-15m})[A_P C^{1/3} + B_P C]$$

$$= e^{-15m}[\bar{V}_2 - \bar{V}_2{}^0]_{\text{Debye}} + (1 - e^{-15m})[\bar{V}_2 - \bar{V}_2{}^0]_{\text{"cell"}} \tag{9}$$

where

$$S_V = \nu RT \ln (10) S_f \frac{1}{2} [3(\partial \ln \epsilon/\partial P)_{T,n's} - \beta] \tag{10}$$

$$S_f = \frac{1}{\nu} \sum_i^P \nu_j Z_j{}^2 (kT)^{-3/2}(1.29 \times 10^6) \tag{11}$$

$$A_P = \nu RT \ln (10) A[(\partial \ln \epsilon/\partial P)_{T,n's} - \beta/3] \tag{12}$$

$$B_P = \nu RT \ln (10)[\beta B + (\partial B/\partial P)_{T,n's}] \tag{13}$$

$$\beta = -\frac{1}{V} (\partial V/\partial P)_{T,n's}$$

$$= \text{isothermal compressibility of water} \tag{14}$$

and the various symbols have their usual meanings.[1,7] The quantity ab in Debye's expression for $\log f_\pm$ has values[9] between 1.3 and 1.5 and for the present calculations we have taken $ab = 1.4$.

However, it is common to report results in terms of apparent molar volumes, ϕ_V, rather than in terms of partial molar volumes $\bar{V}$, as the former are usually determined experimentally from density data. Nevertheless, these two quantities are related by

$$\phi_V = (V - n\bar{V}_1{}^0)/n_2 \tag{15}$$

where V is the volume of the solution, $\bar{V}_1{}^0$ is the molar volume of the pure solvent, and n_1 and n_2 are the number of moles of the solvent and solute, respectively. From eq 15 it follows that

$$(\partial V/\partial n_2)_{T,P,n_1} = \bar{V}_2 = \frac{\partial}{\partial m} (m\phi_V) \tag{16}$$

Consequently $\bar{V}_2$ for Debye and "cell" models are expressed by eq 17 and 18, respectively.

$$\frac{\partial}{\partial m} (m\phi_V) = \bar{V}_2{}^0(\equiv \phi_V{}^0) + \left\{ S_V \sqrt{\frac{1}{2} \sum C_i Z_i{}^2} \bigg/ \left(1 + 1.4 \sqrt{\frac{1}{2} \sum C_i Z_i{}^2} \right) \right\} \tag{17}$$

$$\frac{\partial}{\partial m} (m\phi_V) = \bar{V}_2{}^0 + (A_P C^{1/3} + B_P C) \tag{18}$$

If we now express concentration C in terms of the molality m of the solution by

$$C = \rho^0 m + B' m^2 \tag{19}$$

where ρ^0 is the density of water, then for very dilute solutions, for which $C = \rho^0 m$ and for which the ion-cloud concept is valid, expression 17 yields

$$\phi_V = \phi_V{}^0 + \frac{2}{3} S_V C^{1/2} \tag{20}$$

On the other hand, expression 18 now becomes

$$\frac{\partial}{\partial m} (m\phi_V) = \bar{V}_2{}^0 + A_P[\rho^0 m + B' m^2]^{1/3} + B_P[\rho^0 m + B' m^2] \tag{21}$$

Integration of eq 21 yields

Table I. Difference between the Calculated and the Experimental ϕ_V Values Expressed as $\sigma_\phi{}^2 = \sum(\phi_{V(obsd)} - \phi_{V(calcd)})^2/q$ for Various Electrolytes at 25 °C

	$\partial B/\partial P$, mL mol^{-1} bar^{-1}	$\phi_V{}^0$, mL mol^{-1}	$\sigma_\phi{}^2$, $\partial B/\partial P = 0$		$\sigma_\phi{}^2$, $\partial B/\partial P \neq 0$
			$C = 5 \times 10^{-4}$ to 0.3 M	$C = 5 \times 10^{-4}$ to 1.0 M	$C = 5 \times 10^{-4}$ to 1.0 M
NaCl	1.257×10^{-5}	16.61^{18}	0.005	0.018	0.004
NaBr	5.301×10^{-6}	23.48^{a}	0.010	0.056	0.004
NaI	5.393×10^{-6}	34.98^{23}	0.012	0.020	0.005
KCl	1.828×10^{-5}	26.81^{18}	0.030	0.080	0.008
KBr	8.316×10^{-6}	33.75^{18}	0.016	0.109	0.005
KI	7.837×10^{-6}	45.21^{18}	0.014	0.091	0.004
LiCl	4.260×10^{-6}	17.06^{28}	0.003	0.031	0.005
HCl	-4.615×10^{-6}	17.82^{26}	0.065	0.120	0.009
BaCl$_2$	2.219×10^{-5}	23.24^{26}	0.126	1.256	0.085
CaCl$_2$	3.313×10^{-5}	17.78^{26}	0.119	0.166	0.056

^{a} A. W. Geffcken and D. Price, *Z. Phys. Chem., Abt. A,* **155**, 1 (1931).

$$\phi_V = \bar{V}_2{}^0 + A_P\left[\frac{1}{m}\int_0^m (\rho^0 m + B'm^2)^{1/3}dm\right]$$

$$+ B_P\left[\frac{1}{m}\int_0^m (\rho^0 m + B'm^2)dm\right]$$

$$= \bar{V}_2{}^0 + \tfrac{3}{4}A_P C^{1/3} + B_P C/2$$

$$+ \tfrac{3}{5}A_P m^{2/3}B'^{1/3} + (B_P/3)B'm \quad (22)$$

But

$$\phi_V(\text{solution}) = e^{-15m}[\phi_V]_{\text{Debye}} + (1 - e^{-15m})[\phi_V]_{\text{"cell"}}$$

Therefore

$$\phi_V(\text{solution}) = e^{-15m}[\phi_V{}^0 + \tfrac{2}{3}S_V/C^{1/2}]$$
$$+ (1 - e^{-15m})[\bar{V}_2{}^0 + B_P C/2$$
$$+ \tfrac{3}{4}A_P C^{1/3} + \tfrac{3}{5}A_P B'^{1/3}m^{2/3} + B'mB_P/3] \quad (23)$$

where $\bar{V}_2$ is the value that ϕ_V would have at $C = 0$ according to the "cell" model.

Assuming that $\bar{V}_2{}^0 \approx \phi_V{}^0$, eq 23 reduces to

$$\phi_V = \phi_V{}^0 + e^{-15m}(\tfrac{2}{3})S_V C^{1/2}$$
$$+ (1 - e^{-15m})[\tfrac{3}{4}A_P C^{1/3} + B_P C/2$$
$$+ \tfrac{3}{5}A_P m^{2/3}B'^{1/3} + (B'mB_P)/3] \quad (24)$$

The coefficient S_V in this equation depends on $(\partial \ln \epsilon/\partial P)_{T,n's}$ and on the isothermal compressibility of water and as such has a common value for salts of the same valence type.

However, it was observed[10] that although ϕ_V varies linearly with $C^{1/2}$ in dilute solutions, the slope, which is $\tfrac{2}{3}S_V$, shows considerable individuality[11] within a series of similar valence type electrolytes. This slope has been variously estimated as 1.9–2.5[12] for 1:1 electrolytes depending upon the value of $(\partial \ln \epsilon/\partial P)_{T,n's}$ employed. Moreover, while $(\partial \ln \epsilon/\partial P)_{T=25°C,n's,P=1\text{atm}}$ have been determined from direct measurement on pure water,[13–16] considerable variation[17] exists among reported values and it has been suggested[8,17] that $(\partial \ln \epsilon/\partial P)_{T,n's}$ be found from partial molar volume data.

Redlich and Bigeleisen[18] made precise density determination on very dilute solutions of hydrochloric acid and observed that the ϕ_V against $C^{1/2}$ plot has a limiting slope of 1.86. Subsequent studies[17,19,20] on other 1:1 electrolytic solutions also showed that the limiting slope for 1:1 electrolytes is 1.868. This corresponds to a value of 2.802 for S_V and hence of 60.66 × 10^{-6} bar^{-1} for $(\partial \ln \epsilon/\partial P)_{T=25°C,n's,P=1\text{atm}}$ with $\beta^{21} = 45.24$ × 10^{-6} bar^{-1}. The $(\partial \ln \epsilon/\partial P)_{T=25°C,n's,P=1\text{atm}}$ value thus obtained must apply to all strong salts in order to be truly consistent. We shall use the above value of $(\partial \ln \epsilon/\partial P)_{T=25°C,P=1\text{atm}}$ in our further consideration of expression 24.

For very dilute solutions ($C < 0.01$ M) lattice contributions to ϕ_V would be negligibly small as compared to Debye's so that ϕ_V would be linear in $C^{1/2}$ as has indeed been observed.[22] In comparatively more concentrated solutions ($C > 0.03$ M), the lattice contributions (with $C^{1/3}$ term only) outweigh those due to Debye so that ϕ_V would be linear in $C^{1/3}$. Since Bahe[8] always considered solutions more concentrated than $C = 0.03$ M the linear relationship between ϕ_V and $C^{1/3}$ is not unexpected. Further, since lattice theory[1,2] is valid only for concentrated solutions, linear extrapolation of $\phi_V - A_P C^{1/3}$ vs. C to yield $\phi_V{}^0$ is not realistic. Expression 24 takes care of this problem.

We now examine the effectiveness of eq 24 to predict ϕ_V of various electrolytes at various concentrations. This requires values of B, A, B', β, and $\partial B/\partial P$ in addition to the value of $(\partial \ln \epsilon/\partial P)_{T,n's,P=1\text{atm}}$. While values of A, B, and β are known,[4,19,21] there is no direct method to evaluate $\partial B/\partial P$ and for the present purpose we have taken $\partial B/\partial P = 0$. The data necessary to convert molalities to molarities were taken from the literature.[23] ϕ_V values of various 1:1 electrolytes at 25 °C were then calculated for different concentrations of the electrolytes ($C = 0.0005, 0.0001, 0.0002, 0.005, 0.01, 0.02, 0.05, 0.01, 0.2, 0.05, 0.01, 0.2, 0.4, 0.5, 0.6, 0.8,$ and 1.0 M). Except for sodium chloride, potassium chloride, potassium bromide, and potassium iodide, for which Dunn[20] has determined ϕ_V values at 25 °C for very dilute solutions (10^{-3}–10^{-4}) to about 1.0 M, ϕ_V data for other electrolytes are available[24,25] for $C > 0.05$ M solutions only. The ϕ_V data at 25 °C for these electrolytes at $C < 0.05$ (to $C = 0.0005$) were then calculated from Scott's formula.[26] The reliability of Scott's formula[26] to evaluate ϕ_V for $C < 0.05$ was tested by comparing the ϕ_V values so obtained (at 25 °C) for sodium chloride, potassium chloride, potassium bromide, and potassium iodide with their corresponding experimental values as determined by Dunn.[20] The two agreed well within the experimental uncertainty. It is assumed that ϕ_V values calculated from Scott's formula for $C < 0.05$ for other electrolytes should also bear the same good agreement with their corresponding experimental values. The ϕ_V data at 25 °C for dilute solutions of hydrochloric acid were taken from Redlich and Bigeleisen[18] while those for $C > 0.2$ were evaluated from Young and Smith's formula.[27] These calculated ϕ_V values compared excellently with those of Fortier et al.[28]

The ϕ_V values calculated from expression 24 in the manner discussed above agreed well with their corresponding observed ϕ_V values at 25 °C ($C = 5 \times 10^{-4}$ to 0.3 M). The difference between the calculated and the observed ϕ_V values at 25 °C was expressed as

$$\sigma_\phi{}^2 = \sum(\phi_{V(obsd)} - \phi_{V(calcd)})^2/q$$

where q is the number of experimental points. These $\sigma_\phi{}^2$ values

are recorded in Table I (column 4). The universality of the $(\partial \ln \epsilon/\partial P)_{T,n\text{'s}}$ value at 25 °C was next checked by evaluating ϕ_V at 25 °C for barium chloride and calcium chloride, the necessary data for both of which are available.[4,29-31] The calculated and the experimental ϕ_V values (for $C = 5 \times 10^{-4}$ to 0.3 M) again are in good agreement (Table I, column 4). However, for $C > 0.3$ M the agreement between the calculated and the experimental ϕ_V values is not so good and it affected the overall σ_ϕ^2 ($C = 5 \times 10^{-4}$ to 1 M) (Table I, column 5). This failure may be due either to (1) evaluation of $(\partial \ln \epsilon/\partial P)_{25°C,p=1\text{atm},n\text{'s}}$ in the manner suggested above or to (2) the assumption that $(\partial B/\partial P) = 0$. It was, however, observed that if $(\partial \ln \epsilon/\partial P)_{25°C,P=1\text{atm},n\text{'s}}$ has the value 88.84×10^{-6} bar^{-1}, the overall agreement between the observed and the calculated ϕ_V values is improved somewhat but it would yield 2.993 and 15.55 as the limiting slope for the ϕ_V data of 1:1 and 2:1 electrolytes. These slopes are evidently not consistent with the experimental[19,20,28] and theoretical values.[17] The probable failure for $C > 0.3$ M may therefore lie with the assumption that $(\partial B/\partial P) = 0$. Since $(\partial B/\partial P)$ is a quantity characteristic of an electrolyte and as it involves additional contributions to ϕ_V according to a theory[1,2] which is applicable to concentrated solutions, we evaluated it by fitting the observed ϕ_V data for 1 M solution to eq 24. This value of $\partial B/\partial P$ was next used to calculate ϕ_V values for the electrolyte at all concentrations from expression 24. The agreement between the observed and the calculated ϕ_V values at 25 °C has now improved considerably (Table I, column 6).

The $(\partial \ln \epsilon/\partial P)_{25°C,P=1\text{atm},n\text{'s}}$ value of 60.66×10^{-6} bar^{-1} obtained from our analysis of ϕ_V data is greater than the recent value[13] of 47.10×10^{-6} bar^{-1} but is less than the value 76×10^{-6} bar^{-1} which Bahe and Jung[8] obtained from their analysis of ϕ_V data in terms of their lattice model.[1,2] Nevertheless, in view of Bahe and Jung's observations,[8] our value of $[\partial \ln \epsilon/\partial P]$ at 25 °C and at 1 atm does not seem impossible.

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Photocurrent Spectroscopy of Semiconductor Electrodes in Liquid Junction Solar Cells

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Abstract: Photocurrent spectra obtained by a two-beam (one pump-one probe) spectroscopic method on the semiconductor electrode of liquid junction solar cells can vary with the pump irradiance. In cells with n-type CdS, CdSe, CdTe, and GaAs photoanodes and chalogenide anion solutions this irradiance dependence results from and sensitively detects the presence of carrier recombination centers. With semiconductors showing no detectable recombination centers by this technique, cells with external solar to electrical conversion efficiences of 8–9% have been made. Classical single beam photocurrent spectroscopy reveals that poor short-wavelength response in semiconductor liquid junction solar cells is due to surface or near surface recombination centers and resembles p–n junction solar cells in this respect. Lowered long-wavelength response is associated with shrinkage of the depletion region of imperfect and overdoped semiconductors.

Introduction

The analysis of efficiency losses in photovoltaic solar cells requires the identification of carrier recombination centers and other mechanisms leading to photocurrent decrease.[1] Photocurrent spectra for semiconductor–liquid junction cells[2] have been used to determine band gaps and redox solution absorb-ance[2,3] but also contain many other features which relate directly to cell operation such as short- and long-wavelength defects and dependence on incident light intensity. This latter dependence may account for cell efficiency deterioration observed by others at light levels corresponding to only 0.01–0.1 of typical solar irradiance.[3,4]

We have recently introduced a method of two-beam spec-