Monatshefte für Chemie 119, 699—702 (1988)

Monatshefte für Chemie
Chemical Monthly

An Alternate Method to Estimate the *Pitzer* Coefficients of Apparent Molal Expansibility of Aqueous Electrolytes

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(Received 9 May 1987. Accepted 3 June 1987)

An alternate method to estimate the *Pitzer* coefficients of the ion-interaction model for apparent molal expansibility from the temperature dependence of the *Pitzer* coefficients for apparent molal volume is described. The calculated coefficients are in excellent agreement with those obtained using a least squares technique to experimental data.

(Keywords: Ion-interaction model; Electrolytes; Apparent molal volumes; Apparent molal expansibility)

Eine alternative Methode zur Abschätzung der Pitzer-Koeffizienten der effektiven molalen Expansibilitäten von wäßrigen Elektrolyten

Es wird ein alternativer Weg zur Abschätzung der *Pitzer*-Koeffizienten nach dem ionischen Wechselwirkungsmodell für die effektiven molalen Expansibilitäten aus der Temperaturabhängigkeit der *Pitzer*-Koeffizienten für das effektive molale Volumen beschrieben. Die berechneten Koeffizienten sind in ausgezeichneter Übereinstimmung mit Werten, die nach einer Methode der kleinsten Fehlerquadrate aus experimentellen Daten erhalten wurden.

Introduction

Very recently, we [1, 2] demonstrated the utility of the ion-interaction theory of *Pitzer* [3] in describing the volume properties of aqueous single and mixed electrolyte solutions. We fitted the volumetric data to appropriate individual *Pitzer* equations for apparent molal volume, Φ_V, compressibility Φ_K and expansibility Φ_E of numerous aqueous single electrolytes and presented temperature and pressure dependences of the *Pitzer* ion-interaction coefficients. These coefficients for each of the properties of an electrolyte were evaluated employing a nonlinear least squares technique. This note describes an alternative method to estimate Φ_E using the temperature dependent equations for the *Pitzer* coefficients of Φ_V.

Results and Discussion

The *Pitzer* equations relating Φ_V and molality, m (mol kg^{-1}) for a single electrolyte type $M\nu_{M^+} X\nu_{X^-}$ is

$$\Phi_V = \Phi_V^0 + \nu |Z_M Z_X| (A_V/2b) \ln(1 + bI^{1/2}) + 2\nu_M \nu_X RT [m B_{MX}^V + m^2 (\nu_M \nu_X)^{1/2} C_{MX}^V] \quad (1)$$

with

$$B_{MX}^V = (\partial \beta^{(0)}/\partial P)_T + (\partial \beta^{(1)}/\partial P)_T (2/\alpha^2 I) [1 - (1 + I^{1/2}) \exp(-\alpha I^{1/2})] \quad (2)$$

and

$$C_{MX}^V = (\partial C^\Phi/\partial P)_T/2 \quad (3)$$

Φ_V^0 is the value of Φ_V at infinite dilution; ν, stoichiometry of an electrolyte is $\nu_M + \nu_X$; A_V, *Pitzer-Debye-Hückel* slope; α and b are 2 and 1.2 respectively. I is the ionic strength on molal basis and R and T have their usual significance. $(\partial \beta^{(0)}/\partial P)_T$, $(\partial \beta^{(1)}/\partial P)_T$ and $(\partial C^\Phi/\partial P)_T$ are the ion-interaction coefficients; we observed $(\partial \beta^{(1)}/\partial P)_T$ to be negligible in all the electrolytes.

The apparent molal expansibility Φ_E is given by

$$\Phi_E = (\partial \Phi_V/\partial T)_P \quad (4)$$

The pertinent ion-interaction coefficients for Φ_E are $(\partial^2 \beta^{(0)}/\partial P\, \partial T)$ and $(\partial^2 C^\Phi/\partial P\, \partial T)$ with $(\partial^2 \beta^{(1)}/\partial P\, \partial T)$ being zero. Earlier these coefficients were determined with a least squares routine [1, 2].

The temperature dependence of $(\partial \beta^{(0)}/\partial P)_T$ and $(\partial C^\Phi/\partial P)_T$ for Φ_V was noted to fit with the expression

$$Y = a + bT + cT^2 \quad (5)$$

Thus the differentiation of Eq. (5) with respect to T should yield the ion-interaction coefficients for Φ_E. So one has

$$(\partial Y/\partial T) = b + 2CT \quad (6)$$

Eq. (6) can be used for calculating $(\partial^2 \beta^{(0)}/\partial P\, \partial T)$ and $(\partial^2 C^\Phi/\partial P\, \partial T)$

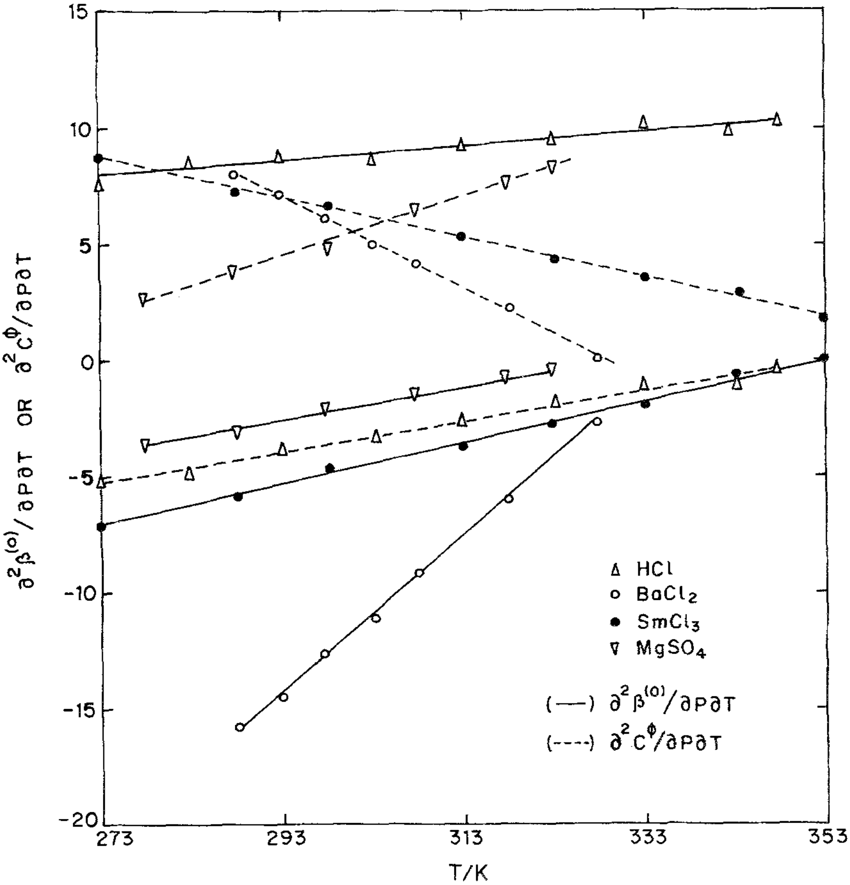

Fig. 1. $\partial^2\beta^{(0)}/\partial P\,\partial T$ and $\partial^2 C^{\Phi}/\partial P\,\partial T$ as a function of T for single electrolyte solutions. Values of $\partial^2 C^{\Phi}/\partial P\,\partial T$ to be multiplied by 10^{-8} for HCl and $SmCl_3$; both coefficients to be multiplied by 10^{-6} for $MgSO_4$. Remaining values to be multiplied by 10^{-7}

from the values of b and c parameters in the Table 2 of our earlier work [1].

The values of $(\partial^2\beta^{(0)}/\partial P\,\partial T)$ and $(\partial^2 C^{\Phi}/\partial P\,\partial T)$ thus obtained agree closely to those obtained from the experimental data for reported 23 electrolytes of different charge type using a least squares routine. In Fig. 1 the calculated values of these coefficients are plotted for selected electrolyte solutions HCl, $BaCl_2$, $MgSO_4$, $SmCl_3$ along with those obtained through a direct Φ_E fit, showing excellent agreement. The average standard deviation of fit for 23 electrolyte solutions is 0.9%.

These coefficients can be easily substituted in the appropriate Φ_E equation in order to estimate Φ_E at various concentrations and temperatures without a least squares program.

References

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[3] *Pitzer KS* (1973) J Phys Chem 77: 268