

Simple equations for predicting volume properties of aqueous concentrated electrolyte mixtures*

ANIL KUMAR

Chemical Engineering Division, National Chemical Laboratory, Poona 411 008, India

Present address: Institute of Physical Chemistry & Electrochemistry, University of Karlsruhe, D7500 Karlsruhe, West Germany.

MS received 13 May 1985

Abstract. Simple equations are presented for predicting density, compressibility and expansivity of aqueous mixed electrolyte solutions. These equations do not require any empirical parameter. Equations are tested upto very concentrated solutions and at various temperatures. It is essential to know the properties of single electrolyte solutions for predicting properties in mixtures. Predicted properties are in excellent agreement with experimental data.

Keywords. Volume properties; density; compressibility; expansivity; aqueous mixed electrolytes.

1. Introduction

Recently, there has been a continuous growing interest in the pvt properties of aqueous mixed electrolytes. The specific interaction theory of Pitzer (1973) was recently applied (Kumar *et al* 1982; Kumar and Atkinson 1983; Kumar 1985a, b) for estimating volume properties of aqueous electrolyte mixtures in the high ionic strength range. In addition, the Brønsted-Guggenheim theory (Guggenheim and Turgeon 1955) was used to develop suitable expressions (Kumar 1984a, b, 1985c) for evaluating pvt properties in dilute mixtures of electrolytes. These methods needed adjustable parameters mostly derived from constituent electrolyte solutions and a few derived from the mixtures.

In the following, equations are derived for estimating densities, compressibilities and expansivities of aqueous concentrated mixed electrolyte systems using the properties of single electrolyte solutions.

2. Equations

2.1 Density

Apparent molal volume ϕ_v of single electrolyte in water is given by (Millero 1972)

$$\phi_v = [1000(d_0 - d)/mdd_0] + (M/d). \quad (1)$$

where d and d_0 are densities of solution and pure water. M is molecular weight of electrolyte and m is molality.

* NCL communication No. 3825.

Similarly, mean apparent molal volumes of mixture of J salts is written as (Kumar 1984a):

$$\phi_V^* = \left[1000 (d_0 - d_m) / \sum_j m_j d_m d_0 \right] + \left[\sum_j m_j M_j / d_m \sum_j m_j \right]. \quad (2)$$

As shown recently (Kumar *et al* 1982) ϕ_V^* can be defined as

$$\phi_V^* = \left(\sum_j m_j \phi_{Vj} \right) / \left(\sum_j m_j \right), \quad (3)$$

where m_j is molality of an electrolyte in mixture and ϕ_{Vj}^0 is apparent molal volume of a single electrolyte at the ionic strength of mixture. Ionic strength I of mixture can be given as

$$I (\text{mol} \cdot \text{kg}^{-1}) = \frac{1}{2} \sum m_i z_i^2, \quad (4)$$

where z is charge on ion of electrolyte.

Equation (1) can be rewritten for the J th electrolyte as

$$\phi_{Vj}^0 = [1000 (d_0 - d_j^0)] / [m_j^0 d_j^0 d_0] + (M_j / d_j^0), \quad (5)$$

where m_j^0 is the molality of the J th electrolyte alone at the ionic strength of mixture and d_j^0 is the density of the J th electrolyte alone at the ionic strength of mixture.

Substituting (5) into (3), equating with (2) and solving for d_m gives

$$d_m = \left(1000 + \sum_j m_j M_j \right) / \left\{ (1000/d_0) \left[\sum_j y_j ((d_0/d_j^0) - 1) + 1 \right] + \sum_j (m_j M_j / d_j^0) \right\}. \quad (6)$$

In (6), y_j is ionic strength fraction of the J th salt and can be written as,

$$y_j = m_j / m_j^0. \quad (7)$$

Equation (6) can be used to estimate the density of the mixture. d_0 , density of pure water can be taken from any reliable compilation (e.g. Kell 1975). d_j^0 , density of a single electrolyte solution at the ionic strength of mixture is available in literature.

2.2 Compressibility

Apparent molal compressibility ϕ_K of a single electrolyte solution is given by (Kumar 1984b).

$$\phi_K = [1000 (\beta d_0 - \beta_0 d)] / (m d d_0) + (M/d). \quad (8)$$

where β and β_0 are the adiabatic compressibilities of electrolyte solution and water respectively. Similar to (2), one can write an equation for the mean apparent molal compressibility ϕ_K^* as (Kumar 1984b):

$$\phi_K^* = [1000 (\beta_m d_0 - \beta_0 d_m)] / \left(\sum_j m_j d_m d_0 \right) + \left(\sum_j m_j M_j \right) / \left(\sum_j m_j d \right), \quad (9)$$

where β_m is the adiabatic compressibility of aqueous mixed electrolytes. Using an identical relationship for ϕ_k^* as done in (3) and (5) and solving for β_m yields

$$\beta_m = \left[d_m (1000 \sum_j y_j \beta_j^0 / d_j^0 + \sum_j \beta_j^0 m_j M_j / d_j^0) \right] / \left(1000 + \sum_j m_j M_j \right). \quad (10)$$

One can use (10) to estimate the adiabatic compressibility of aqueous mixed electrolyte solutions of J th electrolytes. The sound velocity, U , can then be obtained using Newton's relation as,

$$u = (1/\beta_m d_m)^{1/2}. \quad (11)$$

Analogous to (10), which is derived on a molal basis, one can easily derive the expression for calculating adiabatic compressibility from apparent molar compressibility, β_{cm} which is given as

$$\beta_{cm} = \sum_j (y'_j [d_0 \beta_{c_j}^0 - d_{c_j}^0 \beta_0]) + (d_m \beta_0 / d_0). \quad (12)$$

Equation (12) has y'_j as ionic strength fraction on molar basis, where I_c is defined as $\frac{1}{2} \sum c_i z_i^2$. $\beta_{c_j}^0$ is adiabatic molar compressibility of individual electrolyte solution at the ionic strength of mixture. $d_{c_j}^0$ is the density of a single electrolyte solution at the molar ionic strength of mixture.

2.3 Expansivity

Expansivity α of an electrolyte solution is given by (Millero 1979):

$$\alpha = -(1/d) (\partial d / \partial T)_p. \quad (13)$$

Following the derivation of compressibility, one can easily derive

$$\alpha_m = \left[d_m \left(1000 \sum_j y_j \alpha_j^0 / d_j^0 + \sum_j \alpha_j^0 m_j M_j / d_j^0 \right) \right] / \left(1000 + \sum_j m_j M_j \right), \quad (14)$$

where the symbols have usual meanings and α_m is the expansivity of an aqueous mixed electrolyte solution.

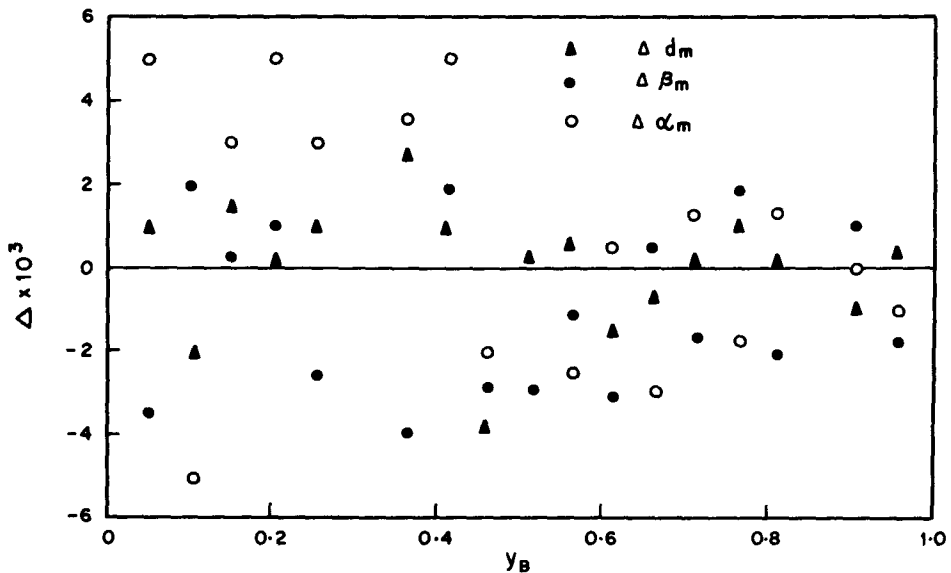
3. Results and discussion

Equations (6), (10) and (14) can easily be used to estimate density, compressibility and expansivity respectively of aqueous mixed electrolyte solutions, provided the respective properties of single electrolyte solutions are known. Table 1 lists the various ternary, quaternary and multi-component systems analysed at various temperatures. Mixtures analysed contain systems with two different cations with a common anion, three different cations with a common anion, four different cations with a common anion, different cations and different anions, and associated electrolytes like sulphates and nitrates. Densities and compressibilities of pure electrolyte solutions were taken either from the references cited by Millero (1972) or from the present author's earlier work (Kumar *et al* 1982; Kumar and Atkinson 1983). Table 1 also lists the standard deviation of fit obtained between experimental and predicted values.

For the sake of clarity, figure 1 demonstrates the difference between experimental

Table 1. Summary of experimental data used for testing (6), (10) and (14).

Systems (aqueous)	t (°C)	σ Standard deviation (%)	References
<i>Density</i>			
NaCl-CaCl ₂	5-35	0.04	Kumar <i>et al</i> (1982)
			Kumar and Atkinson (1983)
CaCl ₂ -MgCl ₂	25	0.03	Kumar and Atkinson (1985a)
NaCl-MgCl ₂	25	0.015	Kumar and Atkinson (1985a)
NaCl-KBr	25	0.04	Kumar (1985b)
CaCl ₂ -ZnCl ₂	15	0.03	Huggins (1964)
KCl-KClO ₃	25, 50	0.04	Turnetskaya and Lepeshkov (1965)
CuSO ₄ -MgSO ₄	25	0.07	Turnetskaya and Lepeshkov (1965)
NaNO ₃ -Co(NO ₃) ₂	25	0.04	Avesina and Shevchuk (1967)
CsNO ₃ -Al(NO ₃) ₃	25	0.010	Aikhipov (1976)
Ca(NO ₃) ₂ -AgNO ₃	25	0.025	Khutsistova <i>et al</i> (1979)
NaCl-CaCl ₂ -MgCl ₂	25	0.029	Kumar and Atkinson (1985b)
NaCl-KCl-CaCl ₂ -MgCl ₂	25	0.035	Krumgalz and Millero (1982)
<i>Compressibility</i>			
NaCl-CaCl ₂	5-35	5.35×10^{-3}	Kumar <i>et al</i> (1982)
		σ in sound speed = 0.12	Kumar and Atkinson (1983)
<i>Expansivity</i>			
NaCl-CaCl ₂	25	6.75×10^{-3}	Kumar and Atkinson (1983)

Figure 1. Experimental-calculated (Δ) density (d_m), compressibility (β_m) and expansivity (α_m) for NaCl-CaCl₂-H₂O at $t = 2$ and 25°C.

and calculated quantities (d_m , β_m and α_m) for a typical system aq. NaCl-CaCl₂ at ionic strength 2 and at 25°C. Experimental values were taken from the references listed in table 1. As clear from this figure, the difference Δ is random for all the properties. Statistically speaking, one can estimate the density, compressibility and expansivity to ± 0.03 , ± 0.005 and $\pm 0.006\%$ respectively which is good for most practical uses.

4. Conclusions

In the above approach, one can see that no empirical constants are used for prediction but yet the predictions are excellent. One can certainly estimate these properties with much higher accuracy though that is achieved by including various adjustable parameters as shown elsewhere (Kumar and Atkinson 1983).

References

- Aikhipov S M 1976 *Zh. Neorg. Khim.* **21** 275
Averina R A and Shevchuk V G 1967 *Zh. Neorg. Khim.* **12** 3138
Guggenheim E A and Turgeon J C 1955 *Trans. Faraday Soc.* **51** 747
Huggins C M 1964 *J. Chem. Eng. Data* **9** 434
Kell G S 1975 *J. Chem. Eng. Data* **20** 97
Khutsistova F M, Protsenko P I and Berdynkova V A 1979 *Zh. Neorg. Khim.* **24** 2815
Krumgalz B S and Millero F J 1982 *Mar. Chem.* **11** 477
Kumar A 1984a *Indian J. Chem.* **A23** 633
Kumar A 1984b *Indian J. Chem.* **A23** 987
Kumar A 1985a *J. Chem. Eng. Data* **30**
Kumar A 1985b *Can. J. Chem.* (accepted)
Kumar A 1985c *Indian J. Chem.* (accepted)
Kumar A and Atkinson G 1983 *J. Phys. Chem.* **87** 5504
Kumar A and Atkinson G 1985a *J. Chem. Eng. Data* (submitted)
Kumar A and Atkinson G 1985b *J. Solution Chem.* (submitted)
Kumar A, Atkinson G and Howell R D 1982 *J. Solution Chem.* **11** 857
Millero F J 1972 *The partial molal volumes of electrolytes in aqueous solution in structure and transport processes in water and aqueous solutions* (ed.) R A Horne (New York: John Wiley & Sons)
Millero F J 1979 *Activity coefficients in electrolyte solutions* (ed.) R M Pytkowicz (Boca Raton: CRC)
Pitzer K S 1973 *J. Phys. Chem.* **77** 268
Turnetskaya A F and Lepeshkov I N 1965 *Zh. Neorg. Khim.* **10** 2163