Comments on “Retention of Ionizable Compounds on HPLC. pH Scale in Methanol–Water and the pK and pH Values of Buffers”

SIR: In a recent paper appearing in this journal, Bosch et al.¹ proposed a relatively simple interactional model for interpreting molar refractivities and volumetric properties of binary water–methanol mixtures. The basic model assumes that the two mixed solvents, denoted as S1 and S2 (water and methanol, respectively), form a mixed water–methanol structure, S12, according to the equilibrium

where K_{S12}^f represents the mole fraction-based formation constant for the mixed structure, and X_1 , X_2 , and X_{12} are mole fractions of the three solvents that may coexist in the mixture. A water–methanol mixture is regarded as a system in which two types of molecules (water and methanol) interact to form three different structures (S1, S2, and S12). The solvent is thus composed of water clusters (S1), methanol clusters (S2), and mixed methanol–water clusters (S12) which are in thermodynamic equilibrium.

Mass balance constraints,

$$X_1^o = X_1 + 0.5X_{12} \quad (2)$$

$$X_2^o = X_2 + 0.5X_{12} \quad (3)$$

and

$$X_1^o + X_2^o = X_1 + X_2 + X_{12} = 1 \quad (4)$$

relate equilibrium mole fractions (X_1 , X_2 , and X_{12}) to stoichiometric mole fractions (X_1^o and X_2^o). Molar volume and molar refractivity were assumed to be mixture additive properties (Y),

$$Y_{\text{mix}} = X_1 Y_1 + X_2 Y_2 + X_{12} Y_{S12} \quad (5)$$

where Y_1 and Y_2 refer to the molar volumes (or molar refractivities) of pure water and methanol, respectively, and Y_{S12} is the molar volume (or molar refractivity) of the mixed cluster. Combination of eqs 1–5, after suitable algebraic manipulations, yields the following mathematical expression,

$$Y_{\text{mix}} = Y_1 + (Y_2 - Y_1)X_2^o + Y_{S12}\{k - [k^2 - 4kX_2^o(1 - X_2^o)]^{0.5}\} \quad (6)$$

$$k = K_{S12}^f / (K_{S12}^f - 4) \quad (7)$$

which was used in calculating the numerical values of K_{S12}^f and Y_{S12} via a nonlinear least-squares regression analysis. The numerical value of K_{S12}^f was required in subsequent equations pertaining to acid dissociation constants and preferential solvation around carboxylic acids dissolved in water–methanol solvent mixtures. The authors further stated that computations become much more complicated for an alternative reactional scheme,

that had a different number of moles on each side of the equilibrium reaction.

The purpose of this communication is not to criticize the excellent work of Bosch and co-workers but rather to suggest an alternative method for computing K_{S12}^f based on a linearized form of the authors' model. From a historical and thermodynamic standpoint, the interactional model proposed by Bosch et al. is nearly identical in concept to the ideal associated solution (IAS) model when applied to systems containing two dimeric carboxylic acids. Equation 1 would describe the formation of the “mixed” carboxylic acid dimer. To date, the IAS model has been successfully applied to excess Gibbs energies, excess molar enthalpies, excess molar volumes, and viscosities of select binary nonelectrolyte solutions. The IAS model, which has been developed thoroughly by Prigogine and DeFay² and reviewed in monographs by Acree³ and Prausnitz et al.,⁴ can be traced to Dolezalek.⁵ An extensive analysis of this model for the triethylamine and chloroform system was presented by Hepler and co-workers.⁶

To derive a linear expression from the Bosch et al. interactional model, one uses eqs 2, 3, and 5 to define ΔY_{mix} as

$$Y_{\text{mix}} = (X_1^o - 0.5X_{12})Y_1 + (X_2^o - 0.5X_{12})Y_2 + X_{12}Y_{S12} \quad (9)$$

$$\Delta Y_{\text{mix}} = Y_{\text{mix}} - X_1^o Y_1 - X_2^o Y_2 = X_{12}(Y_{S12} - 0.5Y_1 - 0.5Y_2) \quad (10)$$

$$\Delta Y_{\text{mix}} = X_{12}\Delta Y_{S12} \quad (11)$$

the difference between the measured value of Y for the binary mixture and an *idealized* value calculated as the stoichiometric

(2) Prigogine, I.; DeFay, R. *Chemical Thermodynamics*; Longmans: London, 1954; Chapter XXVI (translated by D. H. Everett).

(3) Acree, W. E., Jr. *Thermodynamic Properties of Nonelectrolyte Solutions*; Academic Press Inc.: Orlando, FL, 1984; Chapters 7 and 8.

(4) Prausnitz, J. M.; Lichtenthaler, R. N.; Gomes de Azevedo, E. *Molecular Thermodynamics of Fluid-Phase Equilibria*, 2nd ed.; Prentice-Hall Inc.: Englewood Cliffs, NJ, 1986; Chapter 7.

(5) Dolezalek, F. Z. *Phys. Chem.* **1908**, 64, 727–747.

(6) Hepler, L. G.; Kooner, Z. S.; Roux-Desgranges, G.; Grolier, J.-P. E. *J. Solution Chem.* **1985**, 14, 579–594.

(1) Bosch, E.; Bou, P.; Allemann, H.; Rosés, P. *Anal. Chem.* **1996**, 68, 3651–3657.

mole fraction average of the known pure solvent properties (Y_1 and Y_2). For notational simplicity, ΔY_{S12} is defined as $\Delta Y_{S12} = Y_{S12} - 0.5 Y_1 - 0.5 Y_2$. Equations 1–3 are combined to give

$$K_{S12}^f = X_{12}^2 / [(X_1^o - 0.5 X_{12}) (X_2^o - 0.5 X_{12})] \quad (12)$$

$$X_1^o X_2^o = X_{12}^2 [(1 - 0.25 K_{S12}^f) / K_{S12}^f] + 0.5 X_{12} \quad (13)$$

Substitution of $X_{12} = \Delta Y_{\text{mix}} / \Delta Y_{S12}$ into eq 13, followed by suitable mathematical rearrangement, gives the following linear relationship between $X_1^o X_2^o / \Delta Y_{\text{mix}}$ and ΔY_{mix} , with the formation constant and ΔY_{S12} calculated from the slope and intercept:

$$X_1^o X_2^o / \Delta Y_{\text{mix}} = [(1 - 0.25 K_{S12}^f) / (K_{S12}^f \Delta Y_{S12}^2)] \Delta Y_{\text{mix}} + 0.5 / \Delta Y_{S12} \quad (14)$$

The above linear expression facilitates computation of K_{S12}^f and eliminates the much more complex nonlinear regression analysis required by eq 6. For select systems considered by this author, the numerical values of K_{S12}^f calculated from eq 14 were nearly identical to values reported by Bosch et al.¹ Details for linearizing the second reaction scheme (eq 8) are described in detail elsewhere.³

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