Commentary on “Correlation of solubility of hexamethylene-1,6-bisthiosulphate disodium salt dihydrate versus dielectric constants of water + ethanol mixtures”

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Abstract

Apelblat model equation coefficients reported by Song and coworkers [Fluid Phase Equilib. 384 (2014) 143-149] are found to give calculated mole fractions that exceed unity for the solubility of hexamethylene-1,6-bisthiosulphate disodium salt dihydrate dissolved in binary aqueous-ethanol solvent mixtures. The calculated mole fraction solubilities are approximate ten thousand times the experimental values. A polemic is also given regarding the authors' interpretation of an observed mathematical relationship between the experimental mole fraction solubility data and the dielectric constant of the binary solvent mixture. The authors' interpreted one of the curve-fit equation coefficients as the free energy of solute at the thermodynamic equilibrium state. An unit analysis examination shows that the unit of the curve-fit equation coefficient must be J/(mol K) which is inconsistent with free energy.

KEY WORDS AND PHRASES

Hexamethylene-1,6-bisthiosulphate disodium salt dihydrate solubility, modified Apelblat model, mathematical representation

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In a paper appearing in *This Journal* Song and coworkers [1] reported the solubility of hexamethylene-1,6-bisthiosulphate disodium salt dihydrate in five binary aqueous-ethanol solvent mixtures in the temperature range from 278.45 K to 327.55 K. The variation in the mole fraction solubility, x_0 with temperature, T , was described in terms of the modified Apelblat equation:

$$\ln x_0 = A + \frac{B}{T} + C \ln T \quad (1)$$

where the A, B and C denote the equation coefficients determined by curve-fitting the measured mole fraction solubilities in accordance to Eqn. 1. The authors provided a set of curve-fit equation coefficients for each of the five binary solvent mixtures studied. Readers should note that the equation coefficients given in Table 3 of the published paper [1], when substituted into Eqn. 1 above, do not back-calculate the observed mole fraction solubilities. For example, when we substitute the numerical values of $A = -0.77892$, $B = -5231.5$, and $C = 3.8187$ from Table 3 of the authors' paper [1] into Eqn. 1

$$\ln x_0 = -0.77892 - \frac{5231.5}{T} + 3.8187 \ln T \quad (2)$$

we calculate a mole fraction of $x_0 = 30.716$ for the solubility of hexamethylene-1,6-bisthiosulphate disodium salt dihydrate in the binary aqueous-ethanol solvent mixture with water mole fraction composition of 0.5 mole fraction at $T = 298.05$ K. Mole fraction solubilities cannot exceed unity.

There is clearly a problem with the tabulated equation coefficients for the modified Apelblat equation. What the authors' equation coefficients back-calculate is $10^4 x_0$, which is how the solubility data is given in Table 2 of the published paper [1]. The experimental value of $10^4 x_0 = 31.13$ is in good agreement with the value back-calculated using the authors' curve-fit equation coefficients. The problem is that the back-calculated value is $10^4 x_0$, and not x_0 as implied by the

left-hand side of Eqn. 1. To calculate the mole fraction solubility one would have to subtract $4 \ln 10$ from each of the five A coefficients given in Table 3 of reference [1].

There is also a problem in the manuscript which pertains to the authors' mathematical description of how the mole fraction solubility varies with the dielectric constant of the binary solvent mixtures. The authors described the variation of the mole fraction solubility with dielectric constant by a model outwardly like the Arrhenius equation

$$x_T = k \exp\left(-\frac{E_T}{R D_T}\right) \quad (3)$$

where x_T is the solubility of hexamethylene-1,6-bisthiosulphate disodium salt dihydrate, E_T is the free energy, D_T corresponds to the dielectric constant of the binary solvent at a certain temperature T , k is the pre-exponential factor and R refers to the universal gas constant. The authors went on to state the pre-exponential factor k represents the frequency of molecular collision, and the free energy E_T represents the energy of solute at the thermodynamic equilibrium state. The problem with this interpretation is two-fold. First a simple unit analysis of the exponential term reveals that E_T must have the same units as R . The dielectric constant must be dimensionless because it is defined the ratio of the permittivity of a substance to that of free space or a vacuum. The numerical values of E_T that the authors give in Table 9 of their published paper have units of kJ mol^{-1} , which is incorrect based on a simple unit analysis. A quantity with a unit of $\text{kJ mol}^{-1} \text{T}^{-1}$, which is the unit E_T must have, cannot be called a free energy. The unit is inconsistent with that of a free energy.

Second the authors state that k represents the frequency of molecular collision, but tabulated its calculated numerical value in Table 9 as a unitless quantity. We found no information in the manuscript regarding the type of molecular collision(s). Are the collisions solute-solute

collisions, solute-water collisions, solute-ethanol collisions, water-ethanol collisions, water-water collisions, ethanol-ethanol collisions, or all molecular collisions? Frequency is generally defined as the rate at which something occurs, which in the current case would be the rate at which molecular collisions occur. This should have units of something like number of molecular collisions per unit time. The time dependence could be removed by redefining k as perhaps fraction of the molecular collisions involving the solute molecule; however, this definition would impose the mathematical restriction that k must be less than unity. The authors did report values of k greater than unity in Table 9 of their paper [1].

The authors should have described the observed mathematical relationship between the mole fraction solubility and dielectric constant of the binary solvent mixture in more generalized terms as:

$$x_T = \text{constant}_1 \exp\left(-\frac{\text{constant}_2}{D_T}\right) \quad (4)$$

without trying to rationalize the meaning for the curve-fit equation coefficients as the frequency of molecular collisions and the free energy of the solute at the thermodynamic equilibrium state. There is no theoretical justification that we are aware of for expressing the solubility in terms of Eqn. 3. The units do not work out for the E_T value to be free energy and for k to be a frequency.

There are a couple of other very minor typographical errors in the published paper by Song and coworkers [1]. The third, fifth, seventh, ninth and eleventh column headings in Table 7 of reference [1] should be $10^4 x_0$ (not x_0). The x-axis labeling in Figure 8 of reference [1] is inconsistent with the figure caption. The labeling indicates the binary solvent composition in mole fraction, while the figure caption states that the graph represents the variation of the dielectric

constants of ethanol +water mixtures with the weight fraction of water at 293.15 K. The authors use the symbol of φ_1 for the mass fraction of water.

Reference

- [1] L. Song, H. Guo, Y. Xu, Z. Wei, X. Zhang, J. Ji, C. Yang, Correlation of solubility of hexamethylene-1,6-bisthiosulphate disodium salt dihydrate versus dielectric constants of water + ethanol mixtures, *Fluid Phase Equilib.* 384 (2014) 143-149.

Table of Contents Highlights

- Published Apelblat model coefficients give mole fractions that exceed unity
- Published Apelblat model coefficients calculate 10^4 times observed solubilities
- Polemic given regarding authors' mole fraction versus dielectric constant model