Comments concerning "Solubility and dissolution thermodynamic properties of 1,6-*bis*[3-di-(3,5-di-*tert*-butyl-4-hydroxyphenyl)propionamido]hexane in pure solvents and binary solvent mixtures"

William E. Acree, Jr.

Department of Chemistry, 1155 Union Circle Drive #305070, University of North Texas,

Denton, TX 76203, USA

Abstract

Several mathematical errors in the published paper by Zhang and coworkers are identified. The errors pertain to the published equation coefficients for the modified Apelblat and for the polynomial equation based on the Combined Jouyban-Acree and modified Apelblat models. The published curve-fit equation coefficients do not correctly back-calculate the observed solubility data.

Key Words and Phrases: Irganox 1098 solubility; Mathematical representations; modified Apelblat model; Combined Acree-Jouyban and modified Apelblat models

*To whom correspondence should be addressed. (E-mail: acree@unt.edu); fax: 940-565-4318.

In a recent paper published in This Journal Zhang and coworkers [1] reported the solubility and thermodynamic dissolution properties of 1,6-bis[3-(3,5-di-tert-butyl-4-hydroxyphenyl)-propionamido]hexane (commercial name is Irganox 1098) dissolved in methanol, ethanol, 1-propanol, 2-propanol, acetone, methyl acetate and ethyl formate mono-solvents, and in binary ethanol + acetone and binary ethanol + ethyl solvent mixtures. Solubilities were measured in the temperature range from 283.15 to 323.15 K using a gravimetric analysis method. Aliquots of the equilibrated saturated solutions were transferred into a tared beaker and the solvent was evaporated in a vacuum drying oven at 333.15 K. The concentration of the dissolved Irganox 1098 was calculated from the mass of the residue that remained after solvent evaporation and from the mass of the aliquot of saturated solution taken for analysis.

The authors described the temperature dependence of the measured mole fraction solubility, x_1, in terms of the modified Apelblat equation:

$$\ln x_1 = A + \frac{B}{T} + C \ln T \tag{1}$$

and Buchowski et al. λh model:

$$\ln\left[1 + \lambda\left(\frac{1 - x_1}{x_1}\right)\right] = \lambda h\left(\frac{1}{T} - \frac{1}{T_{mp}}\right) \tag{2}$$

where T_{mp} and T represent the solute's melting point temperature ($T_{mp} = 430.8$ K for Irganox 1098) and solution temperature, respectively. The quantities A, B, C, λ and h are the models' curve-fit parameters whose numerical values were deduced by analyzing the experimental mole fraction solubiilties in accordance to Eqns. 1 and 2.

The authors analyzed the experimental solubility data in the binary solvent mixtures in terms of an equation based on the Combined Jouyban-Acree and modified Apelblat models:

$$\ln x_1 = A_1 + \frac{A_2}{T} + A_3 \ln T + A_4 x_A + A_5 \frac{x_A}{T} + A_6 \frac{x_A^2}{T} + A_7 \frac{x_A^3}{T} + A_8 \frac{x_A^4}{T} + A_9 x_A \ln T \qquad (3)$$

where x_A denotes the initial mole fraction concentration of solvent component A in the binary solvent mixture, and the various A_i values refer to the model's curve-fit parameters. The NRTL model was also used to describe the solubilities of Irganox 1098 in both the neat organic mono-solvents and in the binary solvent mixtures.

The primary objective in using mathematical representations, such as Eqns. 1 - 3, is to enable one to estimate solubilities at other temperatures and at other binary solvent compositions. The mathematical representations become meaningless when the calculated equation coefficients fail to correctly back-calculate the observed solubility data. Unfortunately this is the case with many of the curve-fit equation coefficients provided in the published paper by Zhang and coworkers [1]. To illustrate this point I will calculate the mole fraction solubility of Irganox 1098 in methanol at 298.15 K by substituting the curve-fit equation coefficients from Table S1 ($A = -655$, $B/10^4 = 2.60$, $C = 98.6$) into Eqn. 1 above:

$$\ln x_1 = -655 + \frac{26000}{298.15} + 98.6 \ln 298.15 \qquad (4)$$

$$\ln x_1 = -655 + 87.20 + 561.78 \qquad (5)$$

$$\ln x_1 = -6.02 \qquad (6)$$

I calculate a mole fraction solubility of $x_1 = 0.00243$ for the solubility of Irganox 1098 in methanol at 298.15 K, which differs significantly from the back-calculated value of $x_1 = 0.00320$ that the authors gave in the third column of Table 2 of their published paper [1].

Similarly I calculate the solubility of Irganox 1098 in ethyl acetate at 298.15 K by substituting the curve-fit equation coefficients from Table S1 (A = -195, $B/10^4$ = 0.607, C = 29.8) into Eqn. 1:

$$\ln x_1 = -195 + \frac{6070}{298.15} + 29.8\ln 298.15 \tag{7}$$

$$\ln x_1 = -195 + 20.36 + 169.79 \tag{8}$$

$$\ln x_1 = -4.85 \tag{9}$$

I compute a mole fraction solubility of x_1 = 0.00783 based on the authors' tabulated equation coefficients, which is considerably larger than the back-calculated value of x_1 = 0.00123 that the authors report in the third column of Table 2 of their published paper.

Similarly I calculate the solubility of Irganox 1098 in acetone at 298.15 K by substituting the curve-fit equation coefficients from Table S1 (A = -614, $B/10^4$ = 2.46, C = 92.4) into Eqn. 1:

$$\ln x_1 = -614 + \frac{24600}{298.15} + 92.4\ln 298.15 \tag{10}$$

$$\ln x_1 = -614 + 82.51 + 526.46 \tag{11}$$

$$\ln x_1 = -5.03 \tag{12}$$

I calculate a mole fraction solubility of x_1 = 0.00654, which is approximately two times larger than the back-calculated value of x_1 = 0.00344 that the authors give in Table 2 of their published paper. In the present case there was really no reason for the authors to publish the modified Apelblat parameters. Journal readers will have to re-determine the numerical values if they wish to make predictions at other temperatures.

As one additional example I will calculate the solubility of Irganox 1098 in ethyl acetate (x_A = 0.000) at 298.15 K using Eqn. 3 above. For x_A = 0.00 only the first three terms on the right-hand side of Eqn. 3 contribute to the calculation. The calculated curve-fit equation coefficients from Table S5 (A_1 = -2300, $A_2/10^3$ = 69.0, A_3 = 352) are substituted into Eqn. 3:

$$\ln x_1 = -2300 + \frac{69000}{298.15} + 352 \ln 298.15 \tag{13}$$

$$\ln x_1 = -2300 + 231.43 + 2005.55 \tag{14}$$

$$\ln x_1 = -63.02 \tag{15}$$

to give a back-calculated mole fraction solubility of x_1 = 4.27 x 10^{-28}. The measured mole fraction solubility of Irganox 1098 in ethyl acetate at 298.15 K is x_1 = 0.00123 (from Table 2). For x_A = 1.00 ($A_4/10^3$ = 2.20, $A_5/10^3$ = -53.2, $A_6/10^3$ = -76.1, $A_7/10^3$ = 73.5, $A_8/10^3$ = -30.7, A_9 = -332) the back-calculated solubility would be based on:

$$\ln x_1 = -2300 + \frac{69000}{298.15} + 352 \ln 298.15 + 2200 - \frac{53200}{298.15} - \frac{76100}{298.15} + \frac{73500}{298.15} - \frac{30700}{298.15} - 332 \ln 298.15 \tag{16}$$

$$\ln x_1 - 2300 + 231.43 + 2005.55 + 2200 - 178.43 - 255.24 + 246.52 - 102.97 - 1891.60 \tag{17}$$

$$\ln x_1 = -44.74 \tag{18}$$

I calculate a value of x_1 = 3.71 x 10^{-20} for the mole fraction solubility of ethanol at 298.15. The experimental value given in Table 4 for the solubility of Irganox 1098 in ethanol at 298.15 is x_1 = 0.0110. The authors tabulated curve-fit equation coefficients fail to back-calculate the observed endpoint solubilities of Irganox 1098 in both the ethyl acetate and ethanol mono-solvents at 298.15 K for the binary ethyl acetate + ethanol solvent mixture. It is doubtful if this set of curve-fit

equation coefficients will correctly calculate the solubilities at other solvent mixture compositions for this binary solvent system.

The two calculations that I have spot checked for the Buchowski et al. λh model (Eqn. 2) for the methanol and ethanol mono-solvents indicated that the authors' tabulated curve-fit equation coefficients in Table S2 do correctly back-calculate the observed Irganox 1098 mole fraction solubility in both solvents at 298.15 K. I have not checked all of the authors' calculations. As a precautionary note readers may wish to perform the necessary back-calculations before using the authors' curve-fit parameters to make any solubility predictions as I did find several problems with the parameters for the modified Apelblat model (Eqn. 1 above) and the Combined Jouyban-Acree and modified Apelblat model (Eqn. 3 above).

References

[1]   Y. Zhang, H. Hao, N. Wang, C. Xie, Q. Yin, X. Huang, Solubility and dissolution thermodynamic properties of 1,6-bis[3-(3,5-di-tert-butyl-4-hydroxyphenyl)propion-amido]hexane in pure solvents and binary solvent mixtures. J. Mol. Liq. 252 (2018) 103-111.

HIGHLIGHTS

- Errors found in curve-fit coefficients for mathematical representations

- Apelblat model coefficients fail to back-calculated observed solubilities

- Jouyban-Acree-Apelblat model coefficients give poor back-calculations