Comments concerning “Measurement of the solubility of the salt of 2-mercaptobenzothiazole with cyclohexylamine and *tert*-butylamine in various solvents at low temperatures: Models and thermodynamic parameters”

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Abstract

Several errors in the published paper by Wongkaew and coworkers [Fluid Phase Equilibria **434** (2017) 141-151] are identified. The errors noted include the failure of the calculated curve-fit parameters for the Modified Apelblat model, the van't Hoff model and the empirical polynomial equation in temperature to correctly back-calculate the measured solubility data for the salts of 2-mercaptobenzothiazole with cyclohexylamine (2-MBT-CHA) and *tert*-butylamine (2-MBT-TBA) dissolved in methyl isobutyl ketone (MIBK), 1,4-dioxane, toluene and water in the temperature range from 303.15 K to 348.15 K. Internal inconsistencies were noted in the reported thermodynamic properties of dissolution, and several errors were noted in the experimental mole fraction solubilities versus temperature graphs.

Key Words and Phrases: Solubility of salt of 2-mercaptobenzothiazole with cyclohexylamine; Solubility of salt of 2-mercaptobenzothiazole with *tert*-butylamine; Mathematical representation of solubility data

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In a recent article published in *This Journal* Wongkaew and coworkers [1] reported the solubility of the salts of 2-mercaptobenzothiazole with cyclohexylamine (2-MBT-CHA) and *tert*-butylamine (2-MBT-TBA) dissolved in methyl isobutyl ketone (MIBK), 1,4-dioxane, toluene and water in the temperature range from 303.15 K to 348.15 K. Solubilities were determined by titrating a known amount of the saturated solution with 0.02 Molar hydrochloric acid to the phenolphthalein end point. Experiments were performed in triplicate and the mean values were used to calculate the mole fraction solubilities, x_1 . The authors mathematically described the variation of the mole fraction solubility of 2-MBT-CHA and 2-MBT-TBA with temperature using the Modified Apelblat model, the van't Hoff equation, the semi-empirical Buchowski-Ksiazczak λh model, an empirical polynomial equation, the Wilson model, and the UNIQUAC model. The purpose of the present commentary is to point out the large number of errors in the authors' calculated curve-fit equation coefficients and back-calculated mole fraction solubilities. The errors that I found are summarized below in bullet format.

- The calculated equation coefficients (A , B , and C) that the authors tabulated in Table 4 for the modified Apelblat equation:

$$\ln x_1 = A + \frac{B}{T} + C \ln T \quad (1)$$

fail to describe the measured experimental solubility data. To illustrate this point I calculate a mole fraction solubility of $x_1 = 0.01129$ for 2-MBT-CHA in MIBK at $T = 303.15$ K by substituting the authors' calculated equation coefficients ($A = 246.981$, $B = -15998.8$ and $C = -34.771$) into Eqn. 1. The mole fraction solubility that the authors report in Table 2 of their manuscript for 2-MBT-CHA dissolved in MIBK at 303.15 K is $10^4 x_1 = 3.8854$. The back-calculated value differs from the experimental mole fraction solubility by more

than 29 times. Similarly large deviations were found for the remaining modified Apelblat model calculations.

- The calculated equation coefficients (A and B) that the authors tabulated in Table 4 for the van't Hoff equation:

$$\ln x_1 = A + \frac{B}{T} \quad (2)$$

fail to describe the measured experimental solubility data. I calculate a mole fraction solubility of $x_1 = 0.0006579$ for 2-MBT-CHA in toluene at $T = 303.15$ K by substituting the authors' calculated equation coefficients ($A = 14.954$ and $B = -6754.32$) into Eqn. 2 above. The mole fraction solubility that the authors report in Table 2 of their manuscript for 2-MBT-CHA dissolved in toluene at 303.15 K is $10^4 x_1 = 0.2002$. The back-calculated value differs from the experimental mole fraction solubility by more than 32 times. Similarly large deviations were found for the remaining van't Hoff model calculations.

- The calculated equation coefficients (A , B , C and D) that the authors tabulated in Table 6 of their manuscript for the empirical temperature polynomial equation:

$$x_1 = A + BT + CT^2 + DT^3 \quad (3)$$

fail to describe the measured experimental solubility data. I calculate a mole fraction solubility of $x_1 = -0.01093$ for 2-MBT-CHA in toluene at $T = 303.15$ K by substituting the authors' calculated equation coefficients ($A = -4.8155$, $B = 0.0463$, $10^5 C = -14.8832$ and $10^6 D = 0.1596$) into Eqn. 3 above. Mole fractions cannot be negative. The mole fraction solubility that the authors report in Table 2 of their manuscript for 2-MBT-CHA dissolved in toluene at 303.15 K is $10^4 x_1 = 0.2002$. I also note that the set of the equation coefficients

that authors tabulate in Table 6 for the solubility of 2-MBT-CHA in water give back-calculated mole fraction solubilities that exceed unity.

- The authors provide insufficient information for calculating their curve-fit equation coefficients for the Wilson model. According to Equations 12 and 13 of the authors' published paper [1] the calculated curve fit equation coefficients are related to the infinite dilution activity coefficients of the solute and solvent. The authors provide no information in the manuscript concerning how the activity coefficients were calculated. Normally for crystalline nonelectrolyte solutes, the activity coefficient of the solute, γ_1 , is calculated by [2,3]:

$$\ln(x_1\gamma_1) = -\frac{\Delta H_f}{RT_t} \left(\frac{T_t}{T} - 1 \right) + \frac{\Delta C_p}{R} \left(\frac{T_t}{T} - 1 \right) - \frac{\Delta C_p}{R} \ln \left(\frac{T_t}{T} \right) \quad (4)$$

where x_1 is the mole fraction solubility of the solute, T_t is the triple point temperature, T is the equilibrium temperature at which the solubility measurement was performed, ΔH_f is the solute's molar enthalpy of fusion at the normal melting point temperature, ΔC_p is the difference in the molar isobaric heat capacity of the liquid and crystalline forms of the solute, and R is the universal gas constant. The melting properties of the two solutes were not reported in the manuscript, so there is no way for one to check the authors' calculated values.

- The calculated thermodynamic properties of dissolution that are reported in Table 11 of the published manuscript do not obey the standard thermodynamic relationship:

$$\Delta G = \Delta H - T \Delta S \quad (5)$$

At the mean temperature of $T = 325,65 \text{ K}$, I calculate a value of $\Delta G = -15,648.11 \text{ J mol}^{-1}$ for the ΔG for the dissolution of 2-MBT-CHA in water by substituting the authors' calculated values of $\Delta H = 6952.00 \text{ J mol}^{-1}$ and $\Delta S = 69.40 \text{ J mol}^{-1} \text{ K}^{-1}$ into Eqn. 5. The value that the authors give in Table 11 is $\Delta G = -28,651.36 \text{ J mol}^{-1}$, which differs significantly from the value calculated from the authors' tabulated ΔH and ΔS values.

- There are inconsistencies in the other sets of thermodynamic dissolution properties as well. In Table 11 the sum of the tabulated $\% \xi_H$ and $\% \xi_S$ for 2-MBT-CHA and 2-MBT-TBA in water exceed the required 100 %.
- The authors correlated the experimental mole fraction solubility with the Buchowski-Ksiazczak (λh) equation:

$$\ln \left(1 + \lambda \frac{(1 - x_1)}{x_1} \right) = \lambda h \left(\frac{1}{T} - \frac{1}{T_{mp}} \right) \quad (6)$$

where T_{mp} is the melting point temperature, and λ and h are the model parameters determined by curve-fitting the experimental x_1 values in accordance with Eqn. 6 above. The authors did not provide the melting point temperatures used to determine the curve-fit parameters. In the absence of melting point temperatures one cannot use the Buchowski-Ksiazczak (λh) equation to make solubility predictions.

- There are several values incorrectly graphed in Figure 3 of the published paper. For example, careful examination of the Figure 3 reveals that the experimental value that is graphed for the mole fraction solubility of 2-MBT-CHA in MIBK (red triangles) at $T = 348.15 \text{ K}$ corresponds approximately to $10^3 x_1 = 84$. The corresponding mole fraction

solubility that is given in Table 2 is $10^4 x_1 = 30.596$. Similar errors were found in Figures 4 - 8.

- There are inconsistencies between the authors' calculated enthalpies of dissolution, ΔH , given in Table 11 of the published paper [1] and the numerical values of van't Hoff B -coefficients. According to the written text the authors calculated the value of ΔH as:

$$\Delta H = -R \frac{\partial \ln x_1}{\partial (1/T)} \quad (7)$$

The van't Hoff B -coefficient corresponds to the slope of the line determined by plotting $\ln x_1$ versus $1/T$ (see Eqn. 2 above). In other words ΔH can be calculated as $\Delta H = -R B$, where R is the universal gas constant. I calculate ΔH for the dissolution of 2-MBT-CHA in MIBK ($B = -4710.22$ from Table 5 of published paper [1]) at the mean temperature of 325.65 K. The numerical value that I obtain is $\Delta H = 39,160.8 \text{ J mol}^{-1}$, which differs significantly from the value of $\Delta H = 22,981.15 \text{ J mol}^{-1}$ that the authors report in Table 11.

- I also have serious reservations regarding the authors' experimental methodology. The authors stated in the paper that the saturated solutions were equilibrated in a stoppered 50-mL flask. A sample of the clear upper liquid was then withdrawn and titrated with a 0.02 M solution of hydrochloric acid using phenolphthalein as indicator. The authors gave a relative uncertainty of $u_r(x_1) = 0.0003$ for the mole fraction solubility in the footnote at the bottom of Tables 2 and 3. This values seems much too small given the experimental method. It is possible to estimate the volume of 0.02 M HCl used in the titration(s) from the measured mole fraction solubility data. In the case of 2-MBT-TBA dissolved in water, the mole fraction solubility at 303.15 K is $x_1 = 0.00000394$, which corresponds to a molar solubility of $c_1 = 0.0002178$, assuming a density of water of $0.99656 \text{ grams cm}^{-3}$ at 303.15

K [4]. The titration reaction between the HCl titrant and the 2-mercaptobenzothiazole-amine salt is likely 1:1, hence

$$\text{moles of HCl} = \text{moles of 2-mercaptobenzothiazole-amine salt} \quad (8)$$

The number of moles of the 2-mercaptobenzothiazole-amine salt would be the molar solubility of analyte times the volume of the saturated solution taken for analysis. The volume taken for analysis cannot exceed 50-mLs as this was the size of the flask used for equilibrating the saturated solution. Assuming the largest possible volume of saturated liquid taken for analysis (e.g. 0.050 liters), this would give:

$$0.02 V_{\text{HCl}} = (0.0002178)(0.050) \quad (9)$$

I calculate a volume of HCl titrate of 0.545 mLs. This assumes that the authors titrated the entire sample that was equilibrated. This seems highly unlikely as I doubt if the authors would fill the flask to the top so that the rubber stopper would be in direct contact with the saturated solution. A relative uncertainty of $u_r(x_1) = 0.0003$ is difficult to achieve using this small of a titrant volume, particularly when titrating to the visual phenolphthalein endpoint. It is not apparent to this reader that phenolphthalein is the appropriate indicator for the titration. The transition range for phenolphthalein is in the pH = 7 to pH = 9 range. I would have thought that an indicator having a color change in the pH = 3 to pH = 5 range would have been more appropriate for this particular acid-base titration.

- There are numerous incorrect statements made in the published paper. For example, in explaining the solubility behavior of 2-MBT-CHA the authors stated “With respect to the solubility of 2-MBT-CHA in toluene, it abruptly decreased and was lower than the solubility of 2-MBT-CHA in MIBK and 1,4-dioxane which has higher polarity than toluene. This indicates that the dissolution of 2-MBT-CHA in toluene is influenced by

factors such as intermolecular interactions and hydrogen bonds between solvent and solute. Hydrogen bonds which occur makes the solubility in this diluent difficult [21]. From Fig. 2, the solubility of 2-MBT-TBA in toluene was also abruptly decreased as similar to 2-MBT-CHA, resulting from intermolecular interactions and hydrogen bonds between 2-MBT-TBA and toluene.” Normally hydrogen-bond formation between the solute and molecule molecules increase solubility. Based on structural considerations, hydrogen-bond formation would be more likely to occur in MIBK and 1,4-dioxane, than in toluene.

In all honesty I am surprised by the large number of errors in the published paper. I would have expected that errors of this nature would have been identified and corrected during the peer-reviewing processes. I point out the errors to inform journal readers that the authors’ calculated curve-fit equation coefficients do not correctly calculate the experimental mole fraction solubilities nor correctly calculate the thermodynamic dissolution properties as shown by the inconsistencies in the enthalpies of dissolution and van’t Hoff *B*-coefficient. Given the large number of mathematical errors that I found in the published paper I must wonder if the authors correctly determined the mole fraction solubilities.

References

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