Commentary on “Thermodynamic equilibrium of hydroxyacetic acid in pure and binary solvent systems”

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Abstract

Problems are discussed regarding published mathematical representations by Huang and coworkers [J. Chem. Thermodyn. 108 (2017) 76-83] for describing how the measured mole fraction solubility varies with solvent composition in the binary (ethanol + ethyl acetate) and binary (acetone + ethanol) solvent systems. Several sets of published equation coefficients were found to give back-calculated mole fraction solubilities that exceeded unity. The published solubility data for hydroxyacetic acid dissolved in binary (ethanol + ethyl acetate) was reanalyzed and new curve-fit equation coefficients were calculated for the simplified form of the Combined Nearly Ideal Binary Solvent (NIBS)/Redlich-Kister Model. Two simple methods for identifying possible errors in curve-fit equation coefficients were also presented.

Key Words and Phrases: Hydroxyacetic acid solubilities; mathematical representations; binary solvent mixtures

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In a recent paper appearing in *This Journal* Huang and coworkers [1] reported the solubility of hydroxyacetic acid in five neat organic mono-solvents, in binary (ethanol + ethyl acetate) and binary (acetone + ethanol) solvent mixtures in the temperature from 273.15 K to 313.15 K. The solubility was determined with a synthetic method that involved incremental solute addition until no more solute dissolved. Solute dissolution was followed with a laser monitoring method. The authors described the temperature dependence of the mole fraction solubility using the Modified Apelblat, Wilson and NRTL models. The Combined Nearly Ideal Binary Solvent/Redlich-Kister and Combined Apelblat-Jouyban-Acree models were used to describe how the mole fraction solubility of hydroxyacetic acid varied binary solvent composition and with both solvent composition and temperature, respectively.

The purpose of this brief commentary is to point out an error in the authors' mathematical representation regarding the simplified version of the Combined Nearly Ideal Binary Solvent/Redlich-Kister equation:

$$\ln x_1 = B_0 + B_1 x_2^o + B_2 x_2^{o2} + B_3 x_2^{o3} + B_4 x_2^{o4} \quad (1)$$

that journal readers may not have noticed in hopes that future mistakes can be avoided. For information purposes the above expression is Eqn. 12 in the published paper by Huang and coworkers. The simplified equation is derived from Combined Nearly Ideal Binary Solvent (NIBS)/Redlich-Kister (CNIBS/R-K) equation [2]:

$$\ln x_1 = x_2^o \ln (x_1)_2 + x_3^o \ln (x_1)_3 + x_2 x_3 \sum_{i=0}^N S_i (x_2^o - x_3^o)^i \quad (2)$$

by replacing the initial mole fraction composition of component 3 in the binary solvent mixture, x_3^o , with $1 - x_2^o$ and then expanding the summation term for $N = 2$ [2]. Mole fraction solubilities of the binary mixtures and in the neat organic mono-solvents are denoted as $\ln x_1$ and as $\ln (x_1)_2$

and $\ln(x_1)_3$, respectively. Numerical values of B_i are obtained by regression analysis by curve-fitting the experimental mole fraction solubility data in accordance to Eqn 1.

It is very easy to check a set of curve-fitted equation coefficients for possible errors. Eqn. (1) above should describe the experimental mole fraction solubility in both mono-solvents that comprise the binary solvent mixture. Mole fraction solubilities must be less than unity, which requires that the numerical value of B_0 be negative. The sum of all five B_i coefficients must also be negative, otherwise one calculates a mole fraction solubility that exceeds unity in one of the organic mono-solvents. These are two very simple checks that can be made on any set of curve-fit equation coefficients for Eqn. 1 above. If the fore-mentioned conditions are not met, then one needs to carefully exam the computational procedure for possible errors.

Several sets of the curve-fit equation coefficients that Huang and coworkers [1] give in Table 6 of their published paper for the binary (acetone + ethanol) solvent system, when substituted into Eqn. 1 above, yield mole fraction solubilities that exceed unity. For example, if I substitute the numerical values of B_i that the authors reported in Table 6 of their manuscript into Eqn. 1 I obtain the following mathematical expression:

$$\ln x_1 = -2.030 - 0.265 x_2^o + 7.828 x_2^{o2} - 16.13 x_2^{o3} + 11.92 x_2^{o4} \quad (3)$$

for describing the solubility of hydroxyacetic acid in binary (acetone + ethanol) solvent mixtures at $T/K = 313.15$. Careful examination of Eqn. 3 reveals that when $x_2^o = 1$ (neat acetone) one calculates $\ln x_1 = 1.323$, which corresponds to a mole fraction solubility of $x_1 = 3.75$. Clearly there is a problem with using this set of equation coefficients to calculate the solubility of hydroxyacetic acid in acetone. I suspect that the problem results from the fact that the authors performed no solubility measurements in the acetone-rich concentration region for this binary solvent system. Experimental measurements were performed only up to an acetone mole fraction composition of

$x_2^o = 0.499$. There are no experimental values to “anchor” Eqn. 1 at high acetone concentrations. In this case there is really not much that can be done to improve the calculation ability of Eqn. 1. Additional solubility measurements would be needed both in acetone-rich concentration region and in the acetone mono-solvent to obtain curve-fit equation coefficients capable of predicting the solubility of hydroxyacetic acid in acetone. Readers should exercise caution in using the curve-fit equation coefficients in Table 6 of the Huang et al. paper to predict the solubility of hydroxyacetic acid in the acetone-rich concentration region of the binary (acetone + ethanol) solvent system.

The equation coefficients given in Table 6 for the binary (ethanol + ethyl acetate) solvent system also have problems. For this binary solvent system the authors measured the solubility of hydroxyacetic acid in both organic mono-solvents, and at seven binary solvent concentrations that covered a fairly wide range of ethanol mole fraction. Based on the experimental design, one would expect that the calculated curve-fit equation coefficients should provide a reasonably accurate mathematical description of the observed solubility data. If I substitute the numerical values of B_i that the authors reported in Table 6 of their manuscript into Eqn. 1 I obtain the following mathematical expression:

$$\ln x_1 = -2.405 + 2.022 x_2^o + 4.629 x_2^{o2} - 13.92 x_2^{o3} + 9.356 x_2^{o4} \quad (4)$$

for describing the solubility of hydroxyacetic acid in binary (ethanol (2) + ethyl acetate (3)) solvent mixtures at $T/K = 298.15$. The tabulated curve-fit equation coefficients calculate a value of $\ln x_1 = -0.318$ for hydroxacetic acid dissolved in ethanol ($x_2^o = 1.000$). The calculated mole fraction solubility of $x_1 = 0.7276$ differs significantly from the measured mole fraction solubility of $x_1 = 0.319$. One also notes that the calculated mole fraction solubility of hydroxyacetic acid in ethyl acetate would be $x_1 = 0.090$ ($\ln x_1 = -2.405$ for $x_2^o = 0.000$). The experimental mole fraction

solubility of hydroxyacetic acid in ethyl acetate is $x_1 = 0.0580$ at $T/K = 298.15$. The question now becomes why are there such large differences between the calculated and observed mole fractions?

I suspect that the reason for the very large differences between the experimental data and back-calculated values based on the authors' tabulated curve-fit equation coefficients is that the authors did not include the experimental solubility data in the two organic mono-solvents in their regression analysis. I have reanalyzed the authors' experimental data in accordance with Eqn. 1 above. The equation coefficients that I obtained are given in Table 1. The equation coefficients that I obtained for the binary (ethanol + ethyl acetate) solvent system are significantly different than the values that Huang and coworkers report in Table 6 of their published paper [1]. As a quick check of my regression analysis, I substitute the numerical values given in Table 1 into Eqn. 1 above to obtain the following expression:

$$\ln x_1 = -2.823 + 7.291 x_2^o - 16.030 x_2^{o2} + 17.860 x_2^{o3} - 7.433 x_2^{o4} \quad (4)$$

for calculating the solubility of hydroxyacetic acid in binary (ethanol + ethyl acetate) solvent mixtures at $T/K = 298.15$. The back-calculated mole fraction solubilities of hydroxyacetic acid in ethanol and ethyl acetate, $x_1 = 0.321$ and $x_1 = 0.0594$, are in excellent agreement with the experimental values of $x_1 = 0.319$ and $x_1 = 0.0580$ given in Table 2 of the Huang et al. paper [1].

Errors can occur in curve-fitting experimental solubility data in accordance to specific mathematical equations and representations. In the case of the simplified version of the Combined NIBS/Redlick-Kister equation it is possible to check for errors simply by looking at the derived curve-fit equation coefficients. The numerical value of B_0 in Eqn. 1 must be negative, and the sum of the five equation coefficients be negative as well. If not, one calculates a mole fraction solubility that exceeds unity. Once a possible error is detected one needs to carefully examine the data set and regression analysis to learn the cause of the problem. As an additional illustration example, I

will discuss another curve-fitting error that was found in a recently published paper in another *Elsevier* journal. Ji and coworkers [3] reported the solubility of cetilistat in binary solvent mixtures containing water with either acetone, isopropyl alcohol, or acetonitrile. Solubility measurements were performed at several binary solvent compositions in the temperature range from 278.15 K to 323.15 K. The authors used Eqn. 1 above to mathematically describe the variation in the mole fraction solubility of cetilistat with binary solvent composition. When I substituted the numerical values of B_i that Ji and coworkers reported in Table 6 of their manuscript the following mathematical expression was obtained:

$$\ln x_1 = 1.04 - 1.72 x_2^o + 2.23 x_2^{o2} - 4.29 x_2^{o3} + 2.73 x_2^{o4} \quad (5)$$

for calculating the solubility of cetilistat in binary aqueous-acetone solvent mixtures at $T = 323.15$ K. One quickly notes that the B_0 coefficient in Eqn. 5 is a positive value. There is a problem with the reported curve-fit equation coefficients. What the problem was in this particular case was that the authors inadvertently regressed 10 times the mole fraction solubility. The authors' tabulated equation coefficients were back-calculating values of $10 x_1$. Once the problem was spotted and identified it was easy to correct. One simply needed to subtract $\ln 10$ from all of the tabulated B_0 values [4].

One further comment is provided regarding the curve-fit equation coefficients given in the published paper by Huang and coworkers [1]. The curve-fit equation coefficients for the expression based on the Combined Apelblat-Jouyban-Acree model for the binary (acetone + ethanol) will likely have limited predictive ability as the experimental data used in determining the numerical values did not include solubility measurements in the acetone-rich concentration region. This would be Eqn. 13 and the curve-fit coefficients in Table 7 in the paper by Huang et al. Equation coefficients in Table 7 for the binary (ethanol + ethyl acetate) solvent system may give

poor back-calculations for the solubility in the two organic mono-solvents, as was the case with the authors' calculated coefficients for Eqn. 1.

References

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Table 1. Recalculated Coefficients for Eqn. 1 for Describing the Solubility of Hydroxyacetic Acid
in Binary (Ethanol + Ethyl Acetate) Solvent Mixtures

T/K	B_0	B_1	B_2	B_3	B_4
273.15	-3.647	7.560	-13.157	12.217	-4.695
278.15	-3.520	8.306	-16.766	17.560	-7.205
283.15	-3.355	7.993	-16.163	16.843	-6.816
288.15	-3.198	7.881	-16.182	16.951	-6.823
293.15	-3.026	8.016	-18.140	20.631	-8.734
298.15	-2.823	7.291	-16.030	17.860	-7.443
303.15	-2.615	6.570	-13.938	15.029	-6.061
308.15	-2.420	5.980	-12.419	13.265	-5.284
313.15	-2.234	5.691	-12.128	13.362	-5.438

HIGHLIGHTS

- Errors found in published equation coefficients
- Published solubility data reanalyzed
- New coefficients determined for simplified form of CNIBS/R-K model