Commentary on "Solubility and solution thermodynamics of cetilistat in water and (acetone, isopropyl alcohol, acetonitrile) binary solvent mixtures"

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Abstract

Experimental solubility data reported in the recent paper by Ji and coworkers [J. Mol. Liq., 224 (2016) 1380-1387] has been reanalyzed. Several sets of calculated equation coefficients given in the manuscript for the polynomial version of the Combined Nearly Ideal Binary Solvent/Redlich-Kister model and the polynomial version of the van't Hoff-Jouyban-Acree model predict mole fraction solubilities of cetilistat that exceed unity.

Key Words and Phrases:

Cetilistat solubility; binary aqueous-organic solvent mixtures; mathematical representation; solubility prediction

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In a recent article appearing in *This Journal* Ji and coworkers [1] reported the solubility of cetilistat in binary solvent mixtures containing water with either acetone, isopropyl alcohol, or acetonitrile. Solubility measurements were determined at several binary solvent compositions in the temperature range from 278.15 K to 323.15 K. The authors described the temperature dependence of the mole fraction solubility using Modified Apelblat model. The Combined Nearly Ideal Binary Solvent/Redlich-Kister and van't Hoff-Jouyban-Acree models were used to describe how the mole fraction solubility of celitstat 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 polynomial version of the Combined Nearly Ideal Binary Solvent/Redlich-Kister equation:

$$\ln x_1 = B_0 + B_1 x_A + B_2 x_A^2 + B_3 x_A^3 + B_4 x_A^4 \qquad (1)$$

that journal readers may not have noticed. For information purposes the above polynomial expression is Eqn. 7 in the published paper by Ji and coworkers. The polynomial equation is derived from Combined Nearly Ideal Binary Solvent (NIBS)/Redlich-Kister (CNIBS/R-K) equation [2]:

$$\ln x_1 = x_A \ln (x_1)_A + x_B \ln (x_1)_B + x_A x_B \sum_{i=0}^{N} S_i (x_A^o - x_B^o)^i \qquad (2)$$

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

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

Several sets of the curve-fit equation coefficients that the authors give in Tables 6 - 8 of their published paper, 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 I obtain the following mathematical expression:

$$\ln x_1 = 1.04 - 1.72\, x_A + 2.23\, x_A^2 - 4.29\, x_A^3 + 2.73\, x_A^4 \tag{3}$$

for describing the solubility of cetilistat in binary aqueous-acetone solvent mixtures at T = 323.15 K. Careful examination of Eqn. 3 reveals that when $x_A = 0$ (neat acetone) one calculates $\ln x_1 = 1.04$, which corresponds to a mole fraction solubility of $x_1 = 2.83$. I suspect that the problem with the tabulated equation coefficients is that the authors have correlated ten times the mole fraction solubility of cetilistat, rather than the mole fraction solubility. My speculation is based on the fact that the authors have reported the solubility as 10 x_1 in Tables 2 - 4. This would make all of the B_0 coefficients in Tables 6-8 off by ln 10. In other words one would have to subtract 2.303 from each B_0 in order to use the authors tabulated equation coefficients to predict (or back-calculated) the solubility of cetilistat in each of the three binary solvent systems studied.

As an informational note, it is very easy to check a set of equation coefficients for possible errors. In the case of the polynomial version of the Combined Nearly Ideal Binary Solvent/Redlich-Kister equation, the numerical value of B_0 must be less than zero since this would correspond to $\ln x_1$ in pure solvent B, and the sum of the B_i coefficients must also be less than zero since this would correspond to $\ln x_1$ in pure solvent A. If these two conditions are not met, then the mathematical representation will calculate a mole fraction solubility that exceeds unity, which is not possible.

Ji and coworkers [1] also used a mathematical representation:

$$T \ln x_1 = A_0 + A_1 T + A_2 T x_A + A_4 x_A^2 + A_5 x_A^3 + A_6 x_A^4 \qquad (4)$$

which can be obtained by combining the van't Hoff and Jouyban-Acree models (see Eqn. 10 in reference 1]. The correct derivation of the mathematical representation is given elsewhere [3]. Equation describes the variation in the mole fraction solubility with respect to both temperature and binary solvent composition. If I use the A_i equation coefficients in given in Table 9 of the published paper by Ji and coworkers to predict the solubility of cetilistat at T = 323.15 K in the acetone mono-solvent, I obtain:

$323.15 \ln x_1 = -2591.43 + (9.05)(323.15)$

$\ln x_1 = 1.0307$

which also corresponds to a mole fraction solubility that exceeds unity. Again, I suspect that the authors have correlated ten times the mole fraction solubility of cetilistat. Readers should exercise caution in using the equation coefficients that the Ji and coworkers give in Tables 6-11 of their paper.

References

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Highlights

- Errors are identified in paper by Ji and coworkers

- Published correlations yield mole fraction solubilities that exceed unity

- Method presented for quickly checking CNIBS/R-K mathematical representations