

Commentary on “Experimental Measurements and Equilibrium Study of Functional D-Sorbitol in Good and Anti-Solvent Binary Mixtures”

William E. Acree, Jr.

Department of Chemistry, University of North Texas, 1155 Union Circle Drive #305070, Denton, TX 76203 (USA)

Abstract

Problems are identified regarding the published equation coefficients of Hu and coworkers [J. Mol. Liq. 238 (2017) 296-302] for mathematically describing the solubility behavior of D-sorbitol in binary acetonitrile + ethanol solvent mixtures using the modified Apelblat, Combined Nearly Ideal Binary Solvent/Redlich-Kister (CNIBS/R-K) and Jouyban-Acree models. The published equation coefficients for the modified Apelblat and CNIBS/R-K model calculate one thousand times the mole fraction solubility of D-sorbitol, rather than the mole fraction solubility as stated in the published paper. More serious errors were found regarding the authors’ analyses using the Jouyban-Acree model.

Key Words and Phrases:

D-Sorbitol solubilities; mathematical representations; modified Apelblat model; Combined Nearly Ideal Binary Solvent/Redlich-Kister model; Jouyban-Acree model

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

In a recent paper appearing in This Journal Hu and coworkers [1] reported the solubility of D-sorbitol in binary ethanol (A) + acetonitrile (B) solvent mixtures in the temperature range from $T = 278.15$ K to $T = 333.15$ K. The variation in the measured mole fraction solubility with solution temperature and/or binary solvent composition was mathematically described in terms of the modified Apelblat equation:

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

a polynomial version of the Combined Nearly Ideal Binary Solvent/Redlich-Kister model:

$$\ln x = B_0 + B_1 x_A + B_2 x_A^2 + B_3 x_A^3 + B_4 x_A^4 \quad (2)$$

and the Jouyban-Acree model:

$$\ln x = x_A \ln (x)_A + x_B \ln (x)_B + x_A x_B \sum_{i=0}^N \frac{J_i (x_A - x_B)^i}{T} \quad (3)$$

where $(x)_A$ and $(x)_B$ are the measured mole fraction solubilities of D-sorbitol in acetonitrile and ethanol, respectively. The various curve-fit coefficients in Eqns. 1 - 3, namely A , B , C , B_i and J_i , were determined by least-squares analysis.

The purpose of the present communication is to point out several errors in the authors' mathematical representations. First, in the case of the modified Apelblat model, one can easily show that the calculated equation coefficients that the authors report in Table 3 of their published paper yield mole fraction solubilities that differ by three orders of magnitude from the observed values. For example, the equation for calculating the mole fraction solubility of D-sorbitol in the acetonitrile mono-solvent:

$$\ln x = -182.23 + \frac{5467}{T} + 28.49 \ln T \quad (4)$$

gives a value of $x = 0.208$ at $T = 298.15$ K. The experimental mole fraction solubility is $x = 0.000209$ at this temperature as listed in Table 2 of the authors' published paper. What the authors have done in **this** case is to develop modified **Apelblat** correlations that calculate 10^3x (and not x) as stated in their published paper.

The calculated coefficients for Eqn. 2 are similarly flawed. If I substitute the numerical B_i values that are given in Table 4 of the authors' published paper for $T = 298.15$ K into Eqn. 2 above:

$$\ln x = -1.61 + 3.56x_A - 0.17x_A^2 - 4.51x_A^3 + 3.11x_A^4 \quad (5)$$

I calculate

$$\ln x = -1.61 \quad (6)$$

$$\ln x = -1.61 + 3.56 - 0.17 - 4.51 + 3.11 \quad (7)$$

mole fraction solubilities of $x = 0.200$ and $x = 1.46$ in acetonitrile ($x_A = 0.0$) and in ethanol ($x_A = 1.0$). Mole fraction solubilities cannot exceed unity. The experimental values are $x = 0.000209$ and $x = 0.001465$, respectively. Again, what the authors are **calculating** are CNIBS/R-K equation coefficients that give 10^3x , rather than x . Readers need to be aware of this in using the authors' tabulated equation coefficients.

The authors' treatment using the Jouyban-Acree model involves both conceptual and curve-fitting errors. The authors stated that when N was set equal to 2 in Eqn. 3 above, by substituting $x_B = (1 - x_A)$, the Jouyban-Acree model could be rewritten as:

$$\begin{aligned} \ln x = \ln(x)_B + [\ln(x)_A - \ln(x)_B]x_A + \frac{(J_0 - J_1 + J_2)x_A}{T} + \frac{(-J_0 + 3J_1 - 5J_2)x_A^2}{T} \\ + \frac{(2J_1 + 8J_2)x_A^3}{T} + \frac{(-4J_2)x_A^4}{T} \end{aligned} \quad (8)$$

which could be further simplified to:

$$T \ln x = A_1 T + A_2 T x_A + A_3 x_A + A_4 x_A^2 + A_5 x_A^3 + A_6 x_A^4 \quad (9)$$

where A_1, A_2, A_3, A_4, A_5 and A_6 are the model constants. The problem with the stated simplification is that the numerical values of the solubility of D-sorbitol in both acetonitrile and in ethanol depend on temperature. The quantities $\ln(x)_A$ and $[\ln(x)_A - \ln(x)_B]$ cannot be treated as simple constants. Treating $\ln(x)_A$ and $[\ln(x)_A - \ln(x)_B]$ as temperature independent quantities is a conceptual error.

One can further show that the numerical values of the coefficients reported in Table 5 of the published paper [1] do not correctly describe the measured solubility data. For example, if one substitutes the numerical values of the coefficients into Eqn. 9 the following expression is obtained:

$$\ln x = -0.96 \quad (10)$$

for the mole fraction solubility of D-sorbitol in acetonitrile (at $x_A = 0.0$). This would give a mole fraction solubility of $x = 0.3829$ at each of the temperatures studied. This is not consistent with the measured solubility data. The experimental mole fraction solubilities that are tabulated in Table 2 of the Hu et al. paper [1] range from $x = 0.000108$ at $T = 278.15$ K to $x = 0.000729$ at $T = 333.15$ K.

There are also numerous errors in the authors' calculated numerical values of ξ_H and ξ_S :

$$\xi_H = \frac{|\Delta_{sol} H_m^o|}{|\Delta_{sol} H_m^o| + |T \Delta_{sol} S_m^o|} \quad (11)$$

$$\xi_S = \frac{|T \Delta_{sol} S_m^o|}{|\Delta_{sol} H_m^o| + |T \Delta_{sol} S_m^o|} \quad (12)$$

that are tabulated in Table 6 of the published manuscript. For example, the authors give numerical values of $\Delta_{sol} H_m^o = 28.44$ kJ/mole and $\Delta_{sol} S_m^o = 18.84$ J/(mole K) for the molar enthalpy and molar

entropy of solution at $x_A = 0.235$ and at the mean temperature. I calculate the mean temperature to $T_m = 305.65$ K, which is the arithmetic average of the 12 temperatures at which the authors performed solubility measurements. Substituting values of $\Delta_{sol}H_m^o = 28.44$ kJ/mole, $\Delta_{sol}S_m^o = 18.84$ J/(mole K) and $T = 305.65$ K into Eqns. 11 and 12, I calculate $\zeta_H = 0.832$ and $\zeta_S = 0.168$. The values that the authors give in Table 6 for this binary solvent composition are $\zeta_H = 0.748$ and $\zeta_S = 0.252$. I also note that the three thermodynamic functions given in Table 6 are not internally consistent. The values do not obey the required thermodynamic relationship that $\Delta G = \Delta H - T \Delta S$. There are clearly errors in the authors' tabulated numerical values.

There are other shortcomings in the paper by Hu and coworkers. The authors stated in the section subsection titled "2.2 Quantification of D-Sorbitol" that "The melting temperature T_m of D-Sorbitol can be found in the literature. However, the fusion enthalpy $\Delta_{fus}H$ of D-sorbitol has not been reported so far. In order to correlate the solubility of D-Sorbitol in binary solvent mixtures, in the present work, the fusion enthalpy $\Delta_{fus}H$ of D-sorbitol was determined by means of a differential scanning calorimetric (DSC) instrument (NETZSCH STA449F3, Germany) under nitrogen atmosphere over the temperature range from (313.15 to 873.15) K and thermogravimetric-analysis (TG) in Fig. 6." While the authors did give the DSC thermogram, there was no numerical value given for enthalpy of fusion of D-sorbitol. Contrary to the authors' claim that the fusion enthalpy of D-sorbitol has not been reported so far, a search of the published chemical literature found that several research groups have reported $\Delta_{fus}H$ values for D-sorbitol. Barone et al. [2] reported a value of $\Delta_{fus}H = 30.2$ kJ/mole, Siniti et al. [3] obtained a value of $\Delta_{fus}H = 31.65$ kJ/mole, Gombas et al. [4] published a value of $\Delta_{fus}H = 39.53$ kJ/mole, and Tong et al. [5] reported a value of $\Delta_{fus}H = 30.66$ kJ/mole. All four research groups determined the enthalpy of fusion of D-sorbitol based on DSC measurements.

References

- [1] Y. Hu, Y. Yu, Y. Zhang, W. Yang, T. Li, R. Deng, M. Jiang, Experimental measurements and equilibrium study of functional d-sorbitol in good and anti-solvent binary mixtures, *J. Mol. Liq.*, 238 (2017) 296-302.
- [2] G. Barone, G. Della Gatta, D. Ferro, V. Piacente, Enthalpies and entropies of sublimation, vaporization and fusion of nine polyhydric alcohols, *J. Chem. Soc., Faraday Trans.* 86 (1990) 75-79.
- [3] M. Siniti, J. Carre, J. M. Letoffe, J. P. Bastide, P. Claudy, The thermal behavior of hexitols. Part 1. Vitrification and crystallization of iditol, mannitol, sorbitol, and dulcitol. *Thermochim. Acta* 224 (1993) 97-104.
- [4] Gombas, A.; Szabo-Revesz, P.; Regdon, G., Jr.; Eroes, I. Study of thermal behaviour of sugar alcohols, *J. Therm. Anal. Calorim.* 73 (2003) 615-621.
- [5] B. Tong, Z. C. Tan, Q. Shi, Y. S. Li, S. X. Wang, Thermodynamic investigation of several natural polyols. (II) Heat capacities and thermodynamic properties of sorbitol, *J. Therm. Anal. Calorim.* 91 (2008) 463-469.

HIGHLIGHTS

- Errors are found in the published equation coefficients for the modified Apelblat model
- Errors are found in the published equation coefficients for the CNIBS/R-K model
- Errors are found in the published equation coefficients for the Jouyban-Acree model
- Errors are found in the published values of ξ_H and ξ_S