

Short communication

Comments on “Solubility and solution thermodynamics of 2,3,4,5-tetrabromothiophene in (ethanol + trichloromethane) binary solvent mixtures”



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ABSTRACT

Several mathematical errors and shortcomings in the paper by Yang and coworkers [Fluid Phase Equilib. 363 (2014) 276–281] are discussed. The solubility data for 2,3,4,5-tetrabromothiophene dissolved in binary ethanol + trichloromethane solvent mixtures is used to describe the preferential solvation around the dissolved solute.

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In a recent paper appeared in this journal, Yang and coworkers [1] reported the experimental solubility of 2,3,4,5-tetrabromothiophene (Fig. 1) in ethanol + trichloromethane mixtures at 12 different temperatures ranging from 278.15 to 323.15 K along with some thermodynamic parameters derived from solubility data. The experimental data were correlated using the general cosolvency model (GCM) reported as Eq. (5), the CNIBS/R-K model reported as Eq. (6) and the Jouyban-Acree model reported as Eq. (9) in the original paper [1]. The accuracy of the computations was evaluated using mean deviations (*MD*) defined as:

$$MD = 100 \frac{\sum \left(\frac{|x_1 - x_1^{cal}|}{x_1} \right)}{N} \quad (1)$$

where *N* is the number of experimental points, x_1 is the experimental solubility and x_1^{cal} is the calculated solubility.

The aim of this communication is to report the results of our

back-calculations based on the correlations presented in the manuscript and to derive additional thermodynamic data based on the inverse Kirkwood-Buff integrals (IKBI), which we use to evaluate the preferential solvation of 2,3,4,5-tetrabromothiophene by the solvent components in the saturated mixtures [2].

Regarding the computations using GCM model, we obtained a different set of model constants in re-training the model at 278.15 K, and even different *MD* value using the reported *B* values in Table 3 [1]. Our computations resulted in $B_0 = -3.925$, $B_1 = -0.966$, $B_2 = -5.154$, $B_3 = 3.363$, and B_4 value was not statistically significant ($p > 0.10$). When these constants were used to back-calculate the solubility values, the resulted *MD* was 2.0. When the reported *B* values for 278.15 K in Table 3 in original paper [1] were used in the back-calculation process, the obtained *MD* was 1.46, which is considerably different than the reported *MD* value of 0.014. According to the original work of GCM [3], the model constants could be computed using regressing $\ln x_1$ against x_2 , x_2^2 , x_2^3 , and x_2^4 . In this process, the partial coefficients with the probability of >0.05 (or 0.10) do not improve the correlation and should be excluded from the model. It should be noted that Yang et al. [1] reported the derivation of GCM from CNIBS/R-K model as a new derivation, whereas, this has been reported in 1997 [3] and authors listed this

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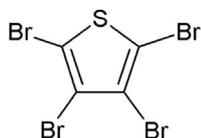


Fig. 1. Molecular structure of 2,3,4,5-tetrabromothiophene.

reference in their article.

Regarding the computations of CNIBS/R-K model, we again found different model constants at 278.15 K, i.e. $S_0 = 0.192$, $S_1 = -1.437$, $S_2 = -0.966$, and MD of 1.4, which is completely different from the reported value of 0.013. The calculated deviations that Yang and coworkers reported in the last column of both Tables 3 and 4 of their paper appear to be off by a factor of 100.

Regarding the computations of Jouyban-Acree (see Eq. (2) below) and combined Jouyban-Acree-van't Hoff (see Eq. (3) below) models, we note that the authors trained their predictive expressions:

$$\ln X_{mT} = m_1 \ln X_{1,T} + m_2 \ln X_{2,T} + \frac{165.504 m_1 m_2}{T} - \frac{284.978 m_1 m_2 (m_1 - m_2)}{T} - \frac{418.23 m_1 m_2 (m_1 - m_2)^2}{T} \quad (2)$$

$$\ln X_{mT} = m_1 [4.609 - (3171.614/T)] + m_2 [6.923 - (3023.460/T)] + \frac{165.504 m_1 m_2}{T} - \frac{284.978 m_1 m_2 (m_1 - m_2)}{T} - \frac{418.23 m_1 m_2 (m_1 - m_2)^2}{T} \quad (3)$$

in terms of the mass fraction compositions of ethanol (m_1) and chloroform (m_2) of the initial binary solvent mixtures. We thought this was very unusual as the authors had reported the initial binary solvent compositions in Table 2 of their manuscript in terms of mole fractions. We decided to check the trained expressions that the authors had given in their manuscript to see if the solvent compositions were truly mass fractions. We performed our calculations assuming both mass fraction and mole fraction compositions. The results of our computations are summarized in Table 1 for Eq. (3) at 278.15 K and 282.15 K. We obtained very large deviations (as large as 136%) between the observed and back-calculated mole fraction 2,3,4,5-tetrabromothiophene solubilities whenever mass fractions were used. Much smaller deviations were found whenever mole fraction compositions were used. We suspect that the solvent compositions in the trained versions of the Jouyban-Acree and combined Jouyban-Acree-van't Hoff models should be mole fractions rather than mass fractions as the authors stated in their manuscript. Readers should exercise caution when using the predictive equations given in the paper by Yang and coworkers pertaining to the Jouyban-Acree models. For the readers convenience we summarize in Table 2 the errors that we found in the paper by Yang and coworkers [1].

It is possible to obtain valuable information regarding the interactions of 2,3,4,5-tetrabromothiophene with both solvent components through preferential solvation computations as illustrated below. The preferential solvation parameter of 2,3,4,5-tetrabromothiophene (compound 3) by trichloromethane (compound 1) in trichloromethane (1) + ethanol (2) mixtures is defined

as [2,4]:

$$\delta x_{1,3} = x_{1,3}^I - x_1 = -\delta x_{2,3} \quad (4)$$

where, $x_{1,3}^I$ is the local mole fraction of trichloromethane (1) in the environment near to the 2,3,4,5-tetrabromothiophene solute. The solute is preferentially solvated by trichloromethane (1) whenever the numerical value of $\delta x_{1,3}$ is greater than zero. If this parameter is negative 2,3,4,5-tetrabromothiophene is preferentially solvated by ethanol (2). Numerical values of $\delta x_{1,3}$ are determined from the inverse Kirkwood-Buff integrals for the individual solvent components as shown in Eqs. (5) and (6):

$$G_{1,3} = RT\kappa_T - V_3 + x_2 V_2 D/Q \quad (5)$$

$$G_{2,3} = RT\kappa_T - V_3 + x_1 V_1 D/Q \quad (6)$$

where κ_T is the isothermal compressibility of the solvent mixtures (expressed in units of GPa^{-1}), V_1 and V_2 are the partial molar volumes of the two co-solvents trichloromethane (1) and ethanol (2), respectively, and V_3 is the partial molar volume of 2,3,4,5-tetrabromothiophene. The function D is the derivative of the standard molar Gibbs energies of transfer of 2,3,4,5-tetrabromothiophene (3) from neat ethanol (2) to the trichloromethane (1) + ethanol (2) mixtures, with respect to the mole fraction of trichloromethane (1) in the mixtures. The second terms in the function Q contains the second derivative of the excess molar Gibbs energy of mixing of the two solvents with respect to the mole fraction of ethanol (2) in the mixtures:

$$D = \left(\frac{\partial \Delta_{\text{tr}} G_{3,2 \rightarrow 1+2}^0}{\partial x_1} \right)_{T,p} \quad (7)$$

$$Q = RT + x_1 x_2 \left(\frac{\partial^2 G_{1+2}^{\text{Exc}}}{\partial x_2^2} \right)_{T,p} \quad (8)$$

The numerical values of the preferential solvation parameter of 2,3,4,5-tetrabromothiophene by trichloromethane (1) were calculated at each solvent composition from the inverse Kirkwood-Buff integrals as follows:

$$\delta x_{1,3} = \frac{x_1 x_2 (G_{1,3} - G_{2,3})}{x_1 G_{1,3} + x_2 G_{2,3} + V_{\text{cor}}} \quad (9)$$

The correlation volume (V_{cor}) used in Eq. (9) was obtained by means of the following expression:

$$V_{\text{cor}} = 2522.5 \left(r_3 + 0.1363 (x_{1,3}^I V_1 + x_{2,3}^I V_2)^{1/3} - 0.085 \right)^3 \quad (10)$$

where r_3 denotes the molecular radius of the solute (in nm) calculated by using Eq. (11) and N_{Av} refers to Avogadro's number.

$$r_3 = \left(\frac{3 \cdot 10^{21} V_3}{4\pi N_{\text{Av}}} \right)^{1/3} \quad (11)$$

Several interactions were required to obtain the final numerical value of the definitive correlation volume. The interactions were accomplished by replacing $\delta x_{1,3}$ in the Eq. (4) to calculate $x_{1,3}^I$ until a non-variant value of V_{cor} was obtained.

Fig. 2 depicts the Gibbs energy of transfer behavior of 2,3,4,5-tetrabromothiophene (3) from neat ethanol (2) to the various trichloromethane (1) + ethanol (2) mixtures at 298.15 K. These values

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