Response to “Comments on ‘Thermodynamic Models for Correlation of Solubility of Hexaquocobalt(II) Bis(*p*-toluenesulfonate) in Liquid Mixtures of Water and Ethanol from 288.15 to 333.15 K’”

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The comments from Acree et al. [1], which are focused on “Thermodynamic Models for Correlation of Solubility of Hexaquocobalt(II) Bis(*p*-toluenesulfonate) in Liquid Mixtures of Water and Ethanol from 288.15 to 333.15 K” are appreciated. We have read it carefully and are particularly grateful to you for your hard work on this topic. In order to let other researchers and readers know better about our work, our explanations for the questions proposed by these comments are also given.

In our recent paper [2] we reported the solubilities of hexaquocobalt(II) bis(*p*-toluenesulfonate) [Co(OTs)₂·6H₂O] in water and ethanol mixtures containing molar fractions of 0–0.342 ethanol from 288.15 to 333.15 K using a synthetic method. The experimental data were correlated by the modified Apelblat equation, the Combined Nearly Ideal Binary Solvent Redlich–Kister (CNIBS/R–K) model, and a hybrid model that was a combination of the Jouyban–Acree and modified Apelblat models. The parameters of the above models were listed in Tables 3–5 in [2].

Before the experiments, we did some pre-experiments that measured the solubility of Co(OTs)₂·6H₂O in ethanol and found the solubility of Co(OTs)₂·6H₂O increased little with increasing temperature. Therefore, we thought ethanol might not be a better choice as an antisolvent for crystallization of Co(OTs)₂·6H₂O in industry, and we decided to measure the solubilities of Co(OTs)₂·6H₂O in water rich binary solvents. Based on the experimental data, we found that the solubility tends to level out when the molar fraction of ethanol (*x*₂) is in the range of 0.228–0.342. According to Liu et al. [3], some of the ethanol and water molecules in the mixture will form (water)₂–ethanol clusters. Therefore, the addition of ethanol leads to the formation of more clusters. Combined with our research, we held the idea that these new clusters (formed by ethanol and water molecules, the molar fraction of ethanol is ~ 0.333, which is quite close to 0.342) were adverse to the increase of the

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solubility of $\text{Co}(\text{OTs})_2 \cdot 6\text{H}_2\text{O}$. Thus the molar fraction of ethanol in the water and ethanol mixtures was only up to 0.342, and the aim of that work was to report the solubility data of $\text{Co}(\text{OTs})_2 \cdot 6\text{H}_2\text{O}$ at different temperatures and explain the leveling out phenomenon.

Through further analysis of this study we found that the variation tendency of the solubility of $\text{Co}(\text{OTs})_2 \cdot 6\text{H}_2\text{O}$ was complicated when $x_2 > 0.342$. Moreover, different water/ethanol complexations would induce the solubility variation of $\text{Co}(\text{OTs})_2 \cdot 6\text{H}_2\text{O}$ in water and ethanol mixtures, and the solubility of $\text{Co}(\text{OTs})_2 \cdot 6\text{H}_2\text{O}$ increased with the increasing x_2 when $x_2 < \sim 0.348$ and $x_2 > \sim 0.741$; while it decreased with the increasing x_2 in the range ~ 0.348 – 0.741 . This phenomenon and the explanation were reported in our recent paper [4]. The experimental solubilities of $\text{Co}(\text{OTs})_2 \cdot 6\text{H}_2\text{O}$ in water and ethanol mixtures at $T = 298.15$ K and $p = 0.1$ MPa were reported in Table 2 and Fig. 4 in [4]. Meanwhile, the solubility data of $\text{Co}(\text{OTs})_2 \cdot 6\text{H}_2\text{O}$ were correlated by the CNIBS/R–K model and the following mathematical representation was obtained:

$$\ln x_1 = -5.87426 + 4.64751x_2^B - 2.85424(x_2^B)^2 - 13.46155(x_2^B)^3 + 13.51918(x_2^B)^4 \quad (1)$$

The comparisons between experimental data and the calculated ones are evaluated by the average relative deviations (ARD) as:

$$\text{ARD} = \frac{1}{n} \sum_{i=1}^n \frac{|x_{1,i}^{\text{exp}} - x_{1,i}^{\text{cal}}|}{x_{1,i}^{\text{exp}}} \quad (2)$$

where n refers to the number of data points for each solvent, $x_{1,i}^{\text{exp}}$ is the experimental solubility value and $x_{1,i}^{\text{cal}}$ is the calculated solubility value obtained from the model.

The overall ARD are less than 3.03%, indicating that the solubility data calculated by the CNIBS/R–K model are in good agreement with the experimental values. The above parameters can be used to make predictions of the solubilities of $\text{Co}(\text{OTs})_2 \cdot 6\text{H}_2\text{O}$ at other water and ethanol solvent compositions at $T = 298.15$ K by the CNIBS/R–K model, no matter in ethanol-rich binary solvent or in water-rich binary solvent.

We agree with Acree's point of view that one of the goals for developing mathematical representations is to be able to make predictions at other solvent compositions and at other temperatures. The parameters of the CNIBS/R–K model and hybrid model published in this journal could predict the solubilities of $\text{Co}(\text{OTs})_2 \cdot 6\text{H}_2\text{O}$ at other solvent compositions when $x_2 < 0.342$, in other words, it is suitable to obtain the solubilities of $\text{Co}(\text{OTs})_2 \cdot 6\text{H}_2\text{O}$ in water-rich binary solvent. The predictive power of the model was validated when $T = 288.15$ K at this time, and the procedure and method to measure the solubility data of $\text{Co}(\text{OTs})_2 \cdot 6\text{H}_2\text{O}$ was similar to our previous work [2, 4]. The experimental results are listed in Table 1.

Table 1 Experimental and calculated solubilities of $\text{Co}(\text{OTs})_2 \cdot 6\text{H}_2\text{O}$ in water and ethanol mixed solvents at $T = 288.15$ K and $p = 0.1$ MPa

x_2	$10^3 x_1^{\text{exp}}$	CNIBS/R–K model ($(x_1^{\text{exp}} - x_1^{\text{cal}})/x_1^{\text{exp}}$ (%))	Hybrid model ($(x_1^{\text{exp}} - x_1^{\text{cal}})/x_1^{\text{exp}}$ (%))
0.300	5.167	−0.433	4.266

x_2 is the mole fraction of ethanol in water and ethanol binary solvents; x_1^{exp} is the experimental solubility; x_1^{cal} is the calculated solubility. The standard uncertainty of T is $u(T) = 0.05$ K. The relative standard uncertainty of the solubility measurement is $u_r(x_1) = 0.02$. The relative standard uncertainty of the mole fraction of ethanol is $u_r(x_2) = 0.02$. The relative uncertainty of pressure is $u_r(p) = 0.05$

However, it is undeniable that our results reported in this journal are limited in terms of predictive ability since it can only predict the solubilities of $\text{Co}(\text{OTs})_2 \cdot 6\text{H}_2\text{O}$ within the investigate molar fraction of ethanol, and it may be not suitable to predict the solubilities of $\text{Co}(\text{OTs})_2 \cdot 6\text{H}_2\text{O}$ when $x_2 > 0.342$, especially in the ethanol rich binary solvent. This will limit the application of experimental results and the parameters which derived from the experiment data may lead to a misunderstanding of the readers. It is true that the derived mathematical representations cannot be expected to provide meaningful predictions at experimental conditions where no measurements were made. We also accept Acree's opinions that the measurements of solubilities of any solute need to be performed over a broad range of solvent composition, and if possible include both co-solvents.

Additionally, we very much appreciate the comments from Acree et al.

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