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# Comment regarding the paper "Solubility determination and thermodynamic modelling of 3,5-dimethylpyrazole in nine organic solvents from $T$ = (283.15 to 313.15) K and mixing properties of solutions"

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ABSTRACT

Errors were discovered regarding the published equation coefficients of Yao and co-workers (2017) for mathematically describing the solubility of 3,5-dimethylpyrazole in nine organic solvents using the NRTL model. Larger differences were found between our back-calculated data and those reported in the authors' published paper. The equation parameters were re-regressed based on the reported solubility data.



In a recent paper published in the J. Chem. Thermodynamics, Yao and co-workers [1] reported the solubility of 3,5-dimethylpyrazole in nine organic solvents namely ethanol, isopropanol, *n*-propanol, 1-butanol, methanol, ethyl acetate, toluene, acetone, acetonitrile determined experimentally by using the isothermal saturation method over a temperature range from (283.15 to 313.15) K under 101.3 kPa. As an important part of this work, the authors mathematically described the variation of the determined mole fraction solubility ($x$) in different pure solvents with the modified Apelblat equation:

$$\ln x_1 = A + B/(T/K) + C\ln(T/K) \tag{1}$$

Buchowski-Ksiazcyak $\lambda h$ equation:

$$\ln\left[1+\frac{\lambda(1-x_1)}{x_1}\right] = \lambda h\left(\frac{1}{T/K}-\frac{1}{T_m/K}\right) \tag{2}$$

Wilson model:

$$\ln\gamma_1 = -\ln(x_1+\Lambda_{12}x_2) + x_2\left[\frac{\Lambda_{12}}{x_1+\Lambda_{12}x_2}-\frac{\Lambda_{21}}{x_2+\Lambda_{21}x_1}\right] \tag{3}$$

$$\Lambda_{12} = \frac{V_2}{V_1}\exp\left(-\frac{\lambda_{12}-\lambda_{22}}{RT}\right) = \frac{V_2}{V_1}\exp\left(-\frac{\Delta\lambda_{12}}{RT}\right) \tag{4}$$

$$\Lambda_{21} = \frac{V_1}{V_2}\exp\left(-\frac{\lambda_{21}-\lambda_{11}}{RT}\right) = \frac{V_1}{V_2}\exp\left(-\frac{\Delta\lambda_{21}}{RT}\right) \tag{5}$$

and NRTL model:

$$\ln\gamma_1 = x_2^2\left[\frac{\tau_{21}G_{21}^2}{(x_1+G_{21}x_2)^2}+\frac{\tau_{12}G_{12}}{(x_2+G_{12}x_1)^2}\right] \tag{6}$$

$$G_{ji} = \exp(-\alpha_{ji}\tau_{ji}) \tag{7}$$

$$\alpha = \alpha_{ij} = \alpha_{ji} \tag{8}$$

$$\tau_{ij} = \frac{g_{ij}-g_{jj}}{RT} = \frac{\Delta g_{ij}}{RT} \tag{9}$$

The activity coefficient ($\ln\gamma_1$) in Eqs. (3) and (6) is calculated by Eq. (10).

$$\ln\gamma_1 = \frac{\Delta_{fus}H}{R}\left(\frac{1}{T_m}-\frac{1}{T}\right) - \ln x_1 \tag{10}$$

In these equations, $\Delta_{fus}H$ denotes the molar fusion enthalpy of 3,5-dimethylpyrazole at the fusion temperature $T_m$; $R$ is the gas constant (8.314 J K$^{-1}$ mol$^{-1}$). $\gamma_1$ is the activity coefficient of 3,5-dimethylpyrazolee in saturated solutions. $\Delta\lambda_{ij}$ and $\Delta g_{ij}$ are the interaction parameters (J mol$^{-1}$) in Wilson model and NRTL model, respectively. $\alpha$ is considered as a parameter revealing the non-randomness of the solution.

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It is true that the determined solubility data is very essential for the purification and further study of 3,5-dimethylpyrazole. However there are some errors in the NRTL equation coefficients of the solubility model. The purpose of this communication is not to suspect the accuracy of the experimental data, but to only point out the mathematical errors on the NRTL model coefficients. One can easily observe that the reported equation coefficients of this NRTL model presented in Table 4 by Yao and co-workers of their published paper [1] yield mole fraction solubility that are different significantly from the observed values. According to the parameters' values reported in Table 4 [1], we carry out back-calculations to show the mistake of equation coefficients for the NRTL model. The authors measured the fusion point and fusion enthalpy of 3,5-dimethylpyrazole via DSC analysis, which were 381.75 K and 16.49 kJ mol$^{-1}$, respectively [1]. The solubility value requires iteration because it depends on activity coefficient of the solute. Here the graphical method is used to obtain the mole fraction solubility at a certain temperature.

Taken the 3,5-dimethylpyrazole + acetonitrile system as an example. The activity coefficients (expressed as ln $\gamma_1$) calculated with Eq. (6) should be equal to the computed ones with Eq. (10). Substituting the numerical values of the melting properties of 3,5-dimethylpyrazole and NRTL model coefficients presented in Table 4 of their published work ($\Delta g_{12} = -52.54$, $\Delta g_{21} = 645.09$ and $\alpha = 0.47$ into Eqs. (6) and (10), the functions $f(x)$ and $g(x)$ are acquired as

$$f(x) = (1-x)^2\left[\frac{\frac{645.09}{RT}\left[\exp\left(-0.47\times\frac{645.09}{RT}\right)\right]^2}{\left[x+\exp\left(-0.47\times\frac{645.09}{RT}\right)(1-x)\right]^2}+\frac{\frac{-52.54}{RT}\left[\exp\left(-0.47\times\frac{-52.54}{RT}\right)\right]}{\left[1-x+\exp\left(-0.47\times\frac{-52.54}{RT}\right)x\right]^2}\right] \tag{11}$$

$$g(x) = \frac{16490}{R}\left(\frac{1}{381.75}-\frac{1}{T}\right) - \ln x \tag{12}$$

here $x$ is the mole fraction solubility of 3,5-dimethylpyrazole. It is obvious that the intersection of the two curves $f(x)$ and $g(x)$ yields the calculated solubility value at temperature $T$. The plots of $f(x)$ and $g(x)$ versus $x$ at 283.15 K are shown graphically in Fig. 1(a) of this communication. As can be seen that the two curves intersect at $x = 0.1368$. No other solution is found in the range from $x = 0.1368$ to $x = 1$. The observed solubility is $x = 0.02758$ at 283.15 K as presented in Table 2 of the authors' published work [1]. There is larger difference between our back-calculated data and that reported in the authors' published work. The back-calculated solubility value by us is about 5.3 times the reported one by Yao and co-workers [1].

In addition, in the same way, we back-calculate the solubility of 3,5-dimethylpyrazole in methanol by substituting the authors' calculated equation coefficients ($\Delta g_{12} = 1249.23$ J mol$^{-1}$, $\Delta g_{21} = -412.83$ J mol$^{-1}$ and $\alpha = 0.20$) from Table 4 into $f(x)$ above:

$$f(x) = (1-x)^2\left[\frac{\frac{-412.83}{RT}\left[\exp\left(0.20\times\frac{-412.83}{RT}\right)\right]^2}{\left[x+\exp\left(0.20\times\frac{-412.83}{RT}\right)(1-x)\right]^2}+\frac{\frac{1249.23}{RT}\left[\exp\left(0.20\times\frac{1249.23}{RT}\right)\right]}{\left[1-x+\exp\left(0.20\times\frac{1249.23}{RT}\right)x\right]^2}\right] \tag{13}$$

The plots of Eqs. (12) and (13) are shown graphically in Fig. 1 (b). The solubility that we back-calculate using the authors' tabulated curve-fit equation coefficients, $x_1 = 0.2739$ at 313.15 K, is also not close to the values of $x_1 = 0.1902$ at 313.15 K that the authors present in Table 2 of their published work for the solubility of 3,5-dimethylpyrazole in methanol [1].

In order to show the difference clearly, the solubility data in the studied neat solvents at several temperatures are all back-calculated according to the equation coefficients that the authors' report in Table 4 of their published article by using the NRTL model. The back-calculated results by us and the authors' determined ones are tabulated in Table 1 of this communication, together with the values of average relative deviation (*RAD*) expressed as Eq. (14).

$$RAD = \frac{100}{N}\sum_{i=1}^{N}\left|\frac{x_1^{\exp} - x_1^{\text{cal,this work}}}{x_1^{\exp}}\right| \tag{14}$$

In addition, the back-calculated solubility data and the authors' reported ones of 3,5-dimethylpyrazole in acetonitrile and methanol are shown graphically in Fig. 2 of this communication. As can be seen that at all the studied temperatures from 283.15 K to 313.15 K, the numerical values of the NRTL equation coefficients reported in Table 4 of the published paper [1] do not correctly describe the measured solubility data. The calculated equation coefficients that the authors report in Table 4 of their published paper yield mole fraction solubilities that differ by several times of magnitude from the observed values. The largest *RAD* values obtained is 259.8% for 3,5-dimethylpyrazole dissolved in acetonitrile. Therefore as a precautionary note, readers should exercise caution in using the authors' tabulated equation coefficients.

In order to give readers the correct information, we have re-analysed the authors' experimental solubility data of 3,5-dimethylpyrazole dissolved in all the studied solvents in accordance with the NRTL model (Eq. (6)) above. The obtained equation coefficients of the NRTL model are presented in Table 2 of this communication, along with the acquired values of *RAD*. As is shown in Table 2, the model coefficients are different significantly from the values that Yao and co-workers report in Table 4 of their work [1]. We back-calculate the mole fraction solubility of 3,5-dimethylpyrazole in acetonitrile is $x_1 = 0.02873$ at 283.15 K by using the NRTL model according to our re-regressed equation

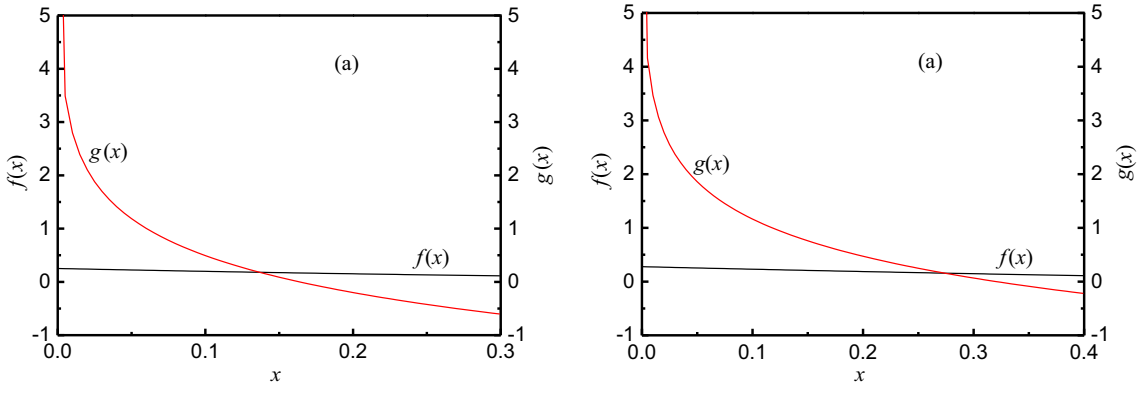


**Fig. 1.** The plots of $f(x)$ and $g(x)$ versus $x$ for (a) acetonitrile at 283.15 K and (b) methanol at 313.15 K.