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Remarks and further calculations on the thermodynamic properties of enantiotropic polymorphs of glycolide

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ABSTRACT

The dissolution thermodynamic properties of polymorphic glycolide in different organic solvents were researched by Huang and coworkers [J. Chem. Thermodynamics 111 (2017) 106–114]. The analysis of Differential Scanning Calorimetry (DSC) and Thermogravimetric Analysis (TG) indicated that glycolide form 1 has a phase transition between the experimental temperature and the melting point. It should be considered that the effect of phase transformation when calculating the activity coefficient of glycolide form 1 by NRTL model. Moreover, the dissolution properties, including Gibbs energy, enthalpy and entropy of form 1 and form 2 were not consistent with the formula ($\Delta H_{dis} = \Delta G_{dis} + T\Delta S_{dis}$) in published paper. In order to get a better understanding of solution behavior, we tried to further calculate and discuss the activity coefficient (γ_1^{∞}) and reduced excess enthalpy ($H_1^{E,\infty}$) at infinite dilution of glycolide form 1 and form 2 in this work.

1. Introduction

The solubility of polymorphic glycolide in five mono solvents at different temperatures under atmospheric pressure was experimentally measured by Huang and coworkers [1]. The solubility data and dissolution thermodynamic properties of two different polymorphic forms were researched by the thermodynamic models. According to the analysis of glycolide form 1 and form 2 by the DSC and TG, there is a phase transition between the experimental temperature and the melting point for glycolide form 1, while form 2 has only one melting peak in the published paper. As previously reported in the references [2,3], if a solid-solid phase transition occurs before fusion, the activity coefficient equations for temperatures below that of the phase transition must consider the effect of phase transformation when calculating the activity coefficient of glycolide form 1.

Based on the theory of solid-liquid phase equilibrium, the solubility of glycolide form 1 in organic solvents is given by Eq. (1) in terms of the mole fraction of solute:

$$-\ln x_i = \frac{\Delta_{\mathrm{fus}}H}{R}\left(\frac{1}{T/\mathrm{K}}-\frac{1}{T_{\mathrm{m}}/\mathrm{K}}\right)+\frac{\Delta H_{\mathrm{tr}}}{R}\left(\frac{1}{T/\mathrm{K}}-\frac{1}{T_{\mathrm{tr}}/\mathrm{K}}\right) - \frac{\Delta C_{\mathrm{P}}}{R}\left(\ln\frac{T/\mathrm{K}}{T_{\mathrm{m}}/\mathrm{K}}+\frac{T_{\mathrm{m}}/\mathrm{K}}{T/\mathrm{K}}-1\right)+\ln\gamma_i \qquad (1)$$

where R, x_i, γ_i, $\Delta_{\mathrm{fus}}H$, ΔH_{tr}, T_{tr}, T_{m}, T and ΔC_{p} stand for the universal gas constant, mole fraction of solubility, activity coefficient, enthalpy of fusion, enthalpy of the solid-solid phase transition, transition temperature, melting point of the solute, equilibrium temperature and difference in solute heat capacity between the solid and liquid at the melting point, respectively. Normally, the ΔC_{p} is less important than other terms on the right side [2,3]. Therefore, it can be neglected, and glycolide form 1, Eq. (1) could be further simplified to:

$$-\ln x_i = \frac{\Delta_{\mathrm{fus}}H}{R}\left(\frac{1}{T/\mathrm{K}}-\frac{1}{T_{\mathrm{m}}/\mathrm{K}}\right)+\frac{\Delta H_{\mathrm{tr}}}{R}\left(\frac{1}{T/\mathrm{K}}-\frac{1}{T_{\mathrm{tr}}/\mathrm{K}}\right)+\ln\gamma_i \qquad (2)$$

From the reference 1, the temperature of the solid-to-solid transition in glycolide form 1 is 316.55 K, the enthalpy of transition was calculated as 1.74 $\mathrm{kJ\cdot mol^{-1,}}$ the heat of fusion is 15.15 $\mathrm{kJ\cdot mol^{-1}}$ and the melting point is 356.15 K. Combining with those data, the solubility data of glycolide form 1 was recalculated and tabulated in Table 1. In addition, readers should note that the dissolution properties, including Gibbs energy, enthalpy and entropy of form 1 and form 2 were not consistent with the equation ($\Delta H_{dis} = \Delta G_{dis} + T\Delta S_{dis}$) in the published paper. For example, when substituted the numerical values of ΔS_{dis} = 2.91 $\mathrm{J\cdot k^{-1}\cdot mol^{-1}}$, ΔG_{dis} = −281 $\mathrm{J\cdot mol^{-1}}$ into the equation, the result of ΔH_{dis} should be 528.42 $\mathrm{J\cdot mol^{-1}}$ in the system of (glycolide form 1 + ethyl acetate) at T = 278.15 K. Moreover, there is a printing error when describing the NRTL model. For a binary system of solid-liquid equilibrium,

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Table 1
Parameters of the NRTL model for glycolide form 1 in five solvents.

Solvent	form 1		
	Δg_{12}	Δg_{21}	α_{12}
Ethyl acetate	8271.34	2264.01	0.47
1-Propanol	−901.61	13768.03	0.47
2-Propanol	683.39	10975.05	0.47
Ethanol	416.46	10313.77	0.47
1-Butanol	−6363.81	23864.39	0.22

the NRTL model [4] was put forward according to the local composition concept. The correct NRTL model can be expressed with Eqs. (3)–(6).

$$\ln \gamma_i = x_j^2 \left[\frac{\tau_{ji} G_{ji}^2}{(x_i + x_j G_{ji})^2} + \frac{\tau_{ij} G_{ij}}{(x_j + x_i G_{ij})^2} \right] \tag{3}$$

$$G_{ji} = \exp(-\alpha_{ji} \tau_{ji}) \tag{4}$$

$$\alpha_{ij} = \alpha_{ji} \tag{5}$$

$$\tau_{ij} = \frac{g_{ij} - g_{jj}}{RT} = \frac{\Delta g_{ij}}{RT} \tag{6}$$

After re-analyzing the model parameters and activity coefficients of form 2 in the published paper, we found the calculated values of activity coefficients were very close to the experimental data in different solvents. Thus, we just applied the model parameters of the published paper to recalculate the mixed properties except for ethyl acetate (The reason will be discussed in the next part of this work). According to the references [1,5], because the system maintains equilibrium during the phase transition, therefore, $\Delta G_{fus,1} = \Delta G_{fus,2} = 0$. The fusion entropies, the dissolution properties, including Gibbs energy, enthalpy and entropy of form 1 could be obtained by:

$$\Delta S_{fus} = \Delta H_{fus}/T_m \tag{7}$$

$$\Delta G_{dis} = \Delta G_{mix} \tag{8}$$

$$\Delta H_{dis} = \Delta G_{dis} + T\Delta S_{dis} \tag{9}$$

$$\Delta S_{dis} = \Delta S_{mix} + x\Delta S_{fus} \tag{10}$$

As described in the literature1, to recalculate the dissolution properties of form 1, the mixing properties of them in pure solvents should be calculated first. According to the Lewis-Randall rule in which the standard states are the actual states of the pure components, the mixing properties of solution could be calculated. For an ideal solution, the mixing Gibbs free energy, mixing enthalpy, and mixing entropy in pure solvent are expressed as [1,6,7]

$$\Delta_{mix} G^{id} = RT(x_1 \ln x_1 + x_2 \ln x_2) \tag{11}$$

$$\Delta_{mix} S^{id} = -R(x_1 \ln x_1 + x_2 \ln x_2) \tag{12}$$

$$\Delta_{mix} H^{id} = 0 \tag{13}$$

Where x_1 denotes the mole fraction of solute; and x_2, the corresponding solvent.

For non-ideal solution, the three thermodynamic mixing properties can be obtained with equations (13) and (14).

$$\Delta_{mix} M = M^E + \Delta_{mix} M^{id} \tag{14}$$

For

$$M = H, G \text{and} S \tag{15}$$

Here M^E denotes the excess property in real solutions. $\Delta_{mix}G$, $\Delta_{mix}H$, $\Delta_{mix}S$ are the mixing enthalpy, mixing Gibbs free energy, and mixing entropy, respectively. The superscript *id* denotes ideal state. In terms of the NRTL model, the excess mixing properties are described as Eqs. (16)–(18) [8].

$$G^E = RT(x_1 \ln \gamma_1 + x_2 \ln \gamma_2) \tag{16}$$

$$H^E = -T^2 \left[\frac{\partial (G^E/T)}{\partial T} \right] = -T^2 R \left(x_1 \frac{\partial \ln \gamma_1}{\partial T} + x_2 \frac{\partial \ln \gamma_2}{\partial T} \right) \tag{17}$$

$$S^E = \frac{H^E - G^E}{T} \tag{18}$$

The dissolution properties, including Gibbs energy, enthalpy and entropy of form 1 and form 2 were corrected and presented in Tables 2 and 3.

As we know, the activity coefficient (γ_1^∞) at infinite dilution describes not only solute-solvent interactions contribute to

Table 2
The dissolution properties of glycolide form 1 in five pure solvents (p = 0.1 MPa).[a]

T/K	ΔG_{dis}/J·mol^{-1}	ΔH_{dis}/J·mol^{-1}	ΔS_{dis}/J·k^{-1}·mol^{-1}
Ethyl acetate			
278.15	−285.67	669.22	3.433
283.15	−315.28	775.41	3.852
288.15	−346.94	897.29	4.318
293.15	−381.29	1041.37	4.853
298.15	−422.24	1233.39	5.553
303.15	−461.71	1437.83	6.266
306.15	−484.01	1561.68	6.682
308.15	−501.65	1668.34	7.042
1-Propanol			
278.15	−6.186	25.75	0.1148
283.15	−7.631	33.06	0.1437
288.15	−9.67	44.44	0.1878
293.15	−12.50	61.90	0.2538
298.15	−15.79	83.26	0.3322
303.15	−20.03	112.72	0.4379
306.15	−22.85	132.40	0.5071
308.15	−24.81	146.06	0.5545
2-Propanol			
278.15	−9.445	37.59	0.1691
283.15	−12.04	51.41	0.2241
288.15	−14.24	62.70	0.2670
293.15	−17.23	79.66	0.3305
298.15	−21.56	107.99	0.4345
303.15	−25.64	134.88	0.5295
306.15	−28.55	155.32	0.6006
308.15	−30.68	170.88	0.6541
Ethanol			
278.15	−14.51	56.59	0.2556
283.15	−17.48	70.86	0.3120
288.15	−21.28	90.64	0.3884
293.15	−26.35	119.79	0.4985
298.15	−31.89	153.20	0.6208
303.15	−38.95	199.84	0.7877
306.15	−44.35	238.72	0.9246
308.15	−47.83	263.86	1.0115
1-Butanol			
278.15	−7.648	21.64	0.1053
283.15	−9.198	28.21	0.1321
288.15	−11.17	37.30	0.1682
293.15	−13.56	49.50	0.2151
298.15	−15.86	61.99	0.2611
303.15	−18.49	77.28	0.3159
306.15	−20.46	89.39	0.3588
308.15	−21.65	96.80	0.3844

[a] The standard uncertainty are $u(T) = 0.05$ K, $u(p) = 5$ kPa. The combined expanded uncertainties u are $u_c(\Delta H_{dis}) = 0.02\Delta H_{dis}$, $u_c(\Delta G_{dis}) = 0.03\ \Delta G_{dis}$, $u_c(\Delta S_{dis}) = 0.02\ \Delta S_{dis}$.