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Experimental Measurement and Correlation of Solubility of Pentachloropyridine and Tetrachloropyridine in Methanol, Ethanol, and 2-Propanol

Jian-Hua Qin,* Zuo-Xiang Zeng, and Wei-Lan Xue

Institute of Chemical Engineering, East China University of Science and Technology, 200237 Shanghai, China

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The solubilities of pentachloropyridine (PCP) and tetrachloropyridine (TECP) in methanol, ethanol, and 2-propanol were measured respectively using an analytical method from (293.15 to 355.15) K. From the thermodynamics theory of solid−liquid equilibrium, the solubility model was derived, and the experimental data were regressed. The average deviation of the model was smaller than 5 %. The fusion enthalpies ($\Delta_{\text{fus}}H$) of PCP, TECP, and their infinite-dilution activity coefficientes (γ_2^{∞}) in methanol, ethanol, and 2-propanol were obtained by regressing the experimental data.

Introduction

2,3,5,6-Tetrachloropyridine is a type of white crystal. It is a component in insecticides and an important intermediate in the chemical industry.[1] It is useful in preparation of chlorpyrifos {*O*,*O*-dimethyl-*O*-(3,5,6-trichloro-2-pyridyl)phosphorothicate}, which is a highly efficient pesticide with low toxicity.[2,3] Furthermore, it is used as an intermediate for producing herbicidally effective α-[4-(3′,5′,6′-trichloropyridine-2′-yloxy)-phenoxy]-alkanecarboxylic acids and derivatives thereof.[1] TECP is mainly prepared from pentachloropyridine using organic solvent as the medium.[4−7] Because the reaction occurs in the solvent, the solubility of PCP and TECP has an important effect on the reaction rate and the yield of the product. There has been no report as to the solubility data of PCP and TECP in any solvents.

In this work, the solubilities of PCP and TECP in methanol, ethanol, and 2-propanol were measured using an analytical method. The solubility model including the enthalpy of fusion ($\Delta_{\text{fus}}H$) and the infinite-dilution activity coefficient (γ_2^{∞}) was derived.

Experimental Section

Materials. Pentachloropyridine prepared in the laboratory was recrystallized prior to use. Its mass fraction purity, determined by GC, was better than 99.0 %. Its melting point was 397.15 K. Tetrachloropyridine prepared in the laboratory was recrystallized prior to use. Its mass fraction purity, determined by GC, was better than 98.0 %. Its melting point was 363.15 K. The methanol, ethanol, and 2-propanol (purchased from Shanghai Chemistry Reagent Company, China) used for experiments were analytical reagent grade. Their mass fraction purities were better than 99.5 %.

Experimental Method. Methods of measuring the solubility of a solid in a liquid mixture can be classified as analytical and synthetic.[8,9] The advantage of the analytical method lies in the possibility of measuring a large number of samples simultaneously with a reliable method. The disadvantage is that it is tedious and time-consuming. The synthetic method involves weighing or measuring the individual components to obtain a system with a known composition; the state in which the solid-phase just disappears is then determined for this system. The disappearance of the solid phase can be achieved either by a change in the temperature or by the addition of a known amount of solvent.[10−12] In this work, an analytical method was used to determine the solubility data of PCP and TECP in different solvents.

Experimental Procedure. Solvent and excess solute were added to a vessel with a condenser, a stirrer, and a mercury thermometer calibrated to an uncertainty of ± 0.05 K. The vessel was put inside the thermostated water. At a fixed temperature the mixture was stirred vigorously for 1 h before stopping. After 15 min, (2 to 3) cm^3 clear liquid was dropped into the sampling vial by a heated pipet.The mass of the sample was determined using an analytical balance with an accuracy of ± 0.0001 g. To make the solute dissolute completely at normal temperature, more solvent was added into the sampling vial. By repeating the above procedure at different temperatures, a series of samples were obtained. All samples were analyzed by gas chromatography. The solubility of solute could be calculated at different temperatures.

All measurements were repeated at least twice, and the means were used to calculate the mole fraction solubility (x_2) based on the following equation:

$$x_2 = \frac{m_2/M_2}{m_2/M_2 + m_1/M_1} \tag{1}$$

where m_1 and m_2 represent the masses of the solvent and solute; M_1 and M_2 are the molecular weights of the solvent and the solute, respectively.

In the temperature range of 293.15 K to 355.15 K, the solubilities of PCP and TECP in methanol, ethanol, and 2-propanol were measured (shown in Table 1 and Table 2).

Solubility Model

When the solvent does not dissolve in the solid phase, the fugacity of the solid solute remains that of the pure solid, so the condition of equality of partial fugacities at equilibrium becomes

$$f_{2S} = \gamma_2 x_2 f_{2L} \tag{2}$$

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* Corresponding author. E-mail: wlxue@ecust.edu.cn.

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Table 1. Solubility Data of Pentachloropyridine in Methanol, Ethanol, and 2-Propanol

$\frac{T}{\mathrm{K}}$	$X_{2\mathrm{exp}}$	$\frac{x_{2\mathrm{exp}} - x_{2\mathrm{cal}}}{x_{2\mathrm{exp}}}$	$\frac{T}{\mathrm{K}}$	$X_{2\mathrm{exp}}$	$\frac{x_{2\mathrm{exp}} - x_{2\mathrm{cal}}}{x_{2\mathrm{exp}}}$
Methanol					
299.35	0.000488	0.0244	317.15	0.001029	−0.0338
302.05	0.000566	0.0439	320.35	0.001184	−0.0287
305.25	0.000661	0.0511	322.95	0.001300	−0.0442
308.05	0.000704	−0.0128	326.55	0.001602	0.0181
311.05	0.000760	−0.0726	329.55	0.001825	0.0280
314.15	0.000876	−0.0673	332.15	0.002040	0.0358
Ethanol					
297.15	0.000811	0.0390	328.05	0.003647	0.0353
302.95	0.001016	−0.0406	332.95	0.004153	−0.0515
308.35	0.001333	−0.0431	338.35	0.005175	−0.0646
313.35	0.001829	0.0284	343.35	0.006379	−0.0658
318.15	0.002232	−0.0012	346.15	0.008016	0.0475
323.05	0.002942	0.0463	351.45	0.009771	0.0300
2-Propanol					
298.15	0.001481	−0.0203	333.25	0.007832	−0.0650
303.25	0.001998	0.0096	338.15	0.009659	−0.0719
308.05	0.002721	0.0696	343.55	0.013120	0.0030
313.25	0.003347	0.0198	348.05	0.015679	−0.0109
318.15	0.004125	−0.0082	351.95	0.018662	−0.0017
328.35	0.006744	0.0079	355.55	0.023826	0.0872

Table 2. Solubility Data of Tetrachloropyridine in Methanol, Ethanol, and 2-Propanol

$\frac{T}{\mathrm{K}}$	$X_{2\mathrm{exp}}$	$\frac{x_{2\mathrm{exp}} - x_{2\mathrm{cal}}}{x_{2\mathrm{exp}}}$	$\frac{T}{\mathrm{K}}$	$X_{2\mathrm{exp}}$	$\frac{x_{2\mathrm{exp}} - x_{2\mathrm{cal}}}{x_{2\mathrm{exp}}}$
Methanol					
299.15	0.009184	0.0300	320.35	0.019849	0.0241
302.25	0.010514	0.0470	323.45	0.022040	0.0193
308.15	0.012103	−0.0310	326.35	0.023337	−0.0258
311.05	0.013669	−0.0150	329.15	0.027143	0.0268
314.05	0.014748	−0.0487	331.95	0.029543	0.0135
317.05	0.016988	−0.0139	335.15	0.032999	0.0116
Ethanol					
293.35	0.019677	0.0501	328.15	0.086855	−0.0109
297.95	0.021507	−0.0701	333.25	0.106511	−0.0506
303.05	0.029805	0.0309	336.15	0.124075	−0.0432
307.95	0.039124	0.0840	339.15	0.158834	0.0442
313.15	0.042024	−0.0707	342.15	0.190782	0.0540
318.05	0.054611	−0.0214	345.35	0.236942	0.0623
2-Propanol					
293.55	0.022515	0.0320	328.35	0.127244	0.0209
298.05	0.028447	0.0351	333.25	0.153882	−0.0500
303.25	0.034535	−0.0328	335.95	0.184603	−0.0168
307.95	0.043943	−0.0253	339.25	0.235927	0.0356
313.15	0.056007	−0.0397	342.15	0.293402	0.0713
318.15	0.078050	0.0453	345.15	0.344052	0.0318

where f_{2S} is the fugacity of solute in the pure solid phase, x_2 is the mole fraction solubility of solute in the solvent, γ_2 is the liquid-phase activity coefficient of solute, and f_{2L} is the fugacity of the pure solid solute in liquid phase.

Rearranging in simplified notation:

$$x_2 = \frac{f_{2S}}{\gamma_2 f_{2L}} \tag{3}$$

The ratio f_{2S}/f_{2L} of the fugacities of the solid and its liquid can be evaluated in terms of condition at the triple point. The fundamental equation of pure substance is

$$\mathrm{d}\ln f = -\frac{\Delta H}{RT^2}\,\mathrm{d}T + \frac{\Delta V}{RT}\,\mathrm{d}P \tag{4}$$

Equation 4 is applied to each phase, the results are subtracted, and the conclusion is

$$\mathrm{d}\ln\frac{f_{2S}}{f_{2L}} = \frac{H_L - H_S}{RT^2}\,\mathrm{d}T - \frac{V_L - V_S}{RT}\,\mathrm{d}P \tag{5}$$

$(H_L - H_S)$ is the enthalpy of fusion of solute at temperature T. It can be described by the enthalpy of fusion at the triple point $\Delta_{\mathrm{fus}}H_{\mathrm{tp}}$. Suppose the heat capacities of solid and liquid phases are taken independent of pressure, the expression can thus be written as:

$$H_L - H_S = \Delta_{\mathrm{fus}}H_{\mathrm{tp}} + \Delta C_p(T - T_{\mathrm{tp}}) \tag{6}$$

where ΔC_p is the heat capacity difference, and T_{tp} is the triple point temperature.

After eq 6 is substituted into eq 5, the result is integrated between $(T_{\mathrm{tp}}, P_{\mathrm{tp}})$ and the temperature and pressure of the system (T, P), the ratio of the fugacities becomes

$$\ln\frac{f_{2S}}{f_{2L}} = \frac{\Delta_{\mathrm{fus}}H_{\mathrm{tp}}}{R}\left(\frac{1}{T_{\mathrm{tp}}} - \frac{1}{T}\right) - \frac{\Delta C_p}{R}\left(\ln\frac{T_{\mathrm{tp}}}{T} - \frac{T_{\mathrm{tp}}}{T} + 1\right) - \frac{\Delta V}{RT}(P - P_{\mathrm{tp}}) \tag{7}$$

Substitution of eq 7 into eq 3 results in the general solubility equation:

$$x_2 = \frac{1}{\gamma_2}\exp\left[\frac{\Delta_{\mathrm{fus}}H_{\mathrm{tp}}}{R}\left(\frac{1}{T_{\mathrm{tp}}} - \frac{1}{T}\right) - \frac{\Delta C_p}{R}\left(\ln\frac{T_{\mathrm{tp}}}{T} - \frac{T_{\mathrm{tp}}}{T} + 1\right) - \frac{\Delta V}{RT}(P - P_{\mathrm{tp}})\right] \tag{8}$$

where the second and the third items are the correction of heat capacity difference and the pressure correction, respectively. Their contributions are often minor and negligible. Since triple point temperatures are usually about the same as atmospheric melting points and the latter are more often known, the solubility equation becomes

$$\ln\gamma_2 x_2 = \frac{\Delta_{\mathrm{fus}}H}{R}\left(\frac{1}{T_m} - \frac{1}{T}\right) \tag{9}$$

where T_m is the melting point temperature.

In eq 9, the activity coefficient (γ_2) is the function of molar concentration (x_2), which can be described by the symmetrical Margules equation:[13]

$$\ln\gamma_2 = (1 - x_2)^2 \ln\gamma_2^{\infty} \tag{10}$$

where γ_2^{∞} is the infinite-dilution activity coefficients of solute in solvent.

Substituting eq 10 into eq 9, we obtain

$$\ln x_2 + (1 - x_2)^2 \ln\gamma_2^{\infty} = \frac{\Delta_{\mathrm{fus}}H}{R}\left(\frac{1}{T_m} - \frac{1}{T}\right) \tag{11}$$

Equation 11 can be used to describe the variation with temperature of the solubility.

Results and Discussions

Model Regression Results. The melting point of PCP and TECP is 398.15 K and 363.15 K, respectively.[14] Relating the experimental data with the solubility model (eq 11), the model parameters were obtained by least-squares method. The comparison between calculated values and experimental ones is shown in Table 1 and Table 2.

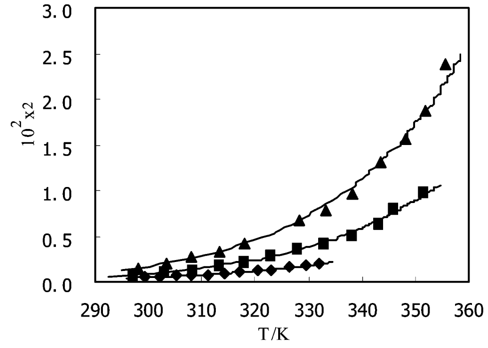

Figure 1. Comparation of solubility of PCP: ●, methanol; ■, ethanol; ▲, 2-propanol; —, calculated values.

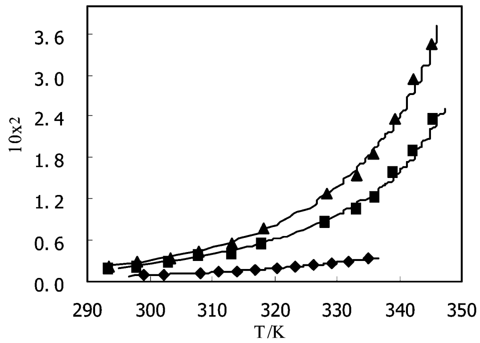

Figure 2. Comparation of solubility of TECP: ●, methanol; ■, ethanol; ▲, 2-propanol; —, calculated values.

Table 3. Model Parameters

parameter	$\Delta_{\mathrm{fus}}H$ / $\mathrm{J{\cdot}mol^{-1}}$	γ_2^{∞}	$10^3\sigma$
PCP-methanol	35445	61.60	0.04
PCP-ethanol	39067	23.34	0.23
PCP-2-propanol	39404	12.30	0.65
TECP-methanol	26976	17.46	0.47
TECP-ethanol	30703	5.05	6.17
TECP-2-propanol	35318	3.00	7.77

The values of parameters $\Delta_{\mathrm{fus}}H$, γ_2^{∞}, and the root-mean-square deviations (rmsd values) are listed in Table 3. The rmsd of the mole fraction was defined as follows:

$$\sigma = \sqrt{\frac{\sum_{i=1}^{N}(x_{2\mathrm{cal}i} - x_{2\mathrm{exp}i})^2}{N}} \qquad (12)$$

where N is the number of experimental points, $x_{2\mathrm{cal}i}$ represents the solubilities calculated from eq 11, and $x_{2\mathrm{exp}i}$ represents the experimental solubility values. It could be seen that the solubility model can be used to describe the variation with temperature of the solubility of solute.

Discussion. Figure 1 and Figure 2 are the solubility curves of PCP and TECP in methanol, ethanol, and 2-propanol at different temperatures. It can be seen that the solubilities of PCP and TECP in the alcohols increase with the increase of carbon number; the solubility of PCP in 2-propanol is obviously greater than in methanol and ethanol, and the solubilities of TECP in ethanol and 2-propanol are obviously greater than in methanol. At the same temperature and in the same solvent, the solubility of PCP is smaller than TECP's; for instance, at 313.35 K and in ethanol, the solubility of PCP is 0.001829, and the solubility of TECP is 0.042024.

The infinite-dilution activity coefficients of PCP and TECP in the alcohols decrease with the increase in the number of carbon atoms on the alcohol. The solubilities of PCP and TECP in methanol are low, but the infinite-dilution activity coefficient values are big; the solubilities of PCP and TECP in 2-propanol are high, but the infinite-dilution activity coefficiente values are small. It indicates that, for a solvent, the larger the solubility of a solute is, the smaller the infinite-dilution activity coefficient will be.

Table 3 shows that the enthalpies of fusion $\Delta_{\mathrm{fus}}H$ of PCP and TECP obtained by least-squares linear regression method from different solvents are consistent. The average value is 37972 $\mathrm{J{\cdot}mol^{-1}}$ and 30999 $\mathrm{J{\cdot}mol^{-1}}$, respectively; the average deviation is 4.4 % and 9.3 %, respectively.

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