Solubility of Potassium *p*-Chlorophenoxyacetate in Ethanol + Water from (295.61 to 358.16) K

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By use of a laser-monitoring observation technique, the solubilities of potassium *p*-chlorophenoxyacetate in ethanol + water were measured at temperatures ranging from (295.61 to 358.16) K using a synthetic method at atmospheric pressure. The experimental data were correlated with an empirical equation. Results indicated that the method was practical and the data measured were acceptable.

1. Introduction

Potassium *p*-chlorophenoxyacetate is a new plant growth regulator. Its pure product is a flashing scaled crystal that is suitable to dissolve in water, safe to mankind and animals, and harmless to fish. It is paid comprehensive attention because of its low concentration with an obvious physiological effect in use and little harm compared with a traditional reagent such as 2,4-D (2,4-dichlorophenoxyacetic acid). Potassium *p*-chlorophenoxyacetate could supplement the deficiency of plant auxin, which improves the rootability, germination, and maturing of the plant, protecting from dropped blossoms and fruit and the formation of seedless fruits. It can also inhibit germination, eliminate ill weeds, and so forth. In recent years, great attention has been paid to the research and development of potassium *p*-chlorophenoxyacetate.[1]

Crystal separation by dissolution in a solvent is an effective method of purification because the handling capacity is large. However, solubility data of potassium *p*-chlorophenoxyacetate in solvents are needed to enable the separation and reclamation of valuable compounds in the solid waste.

There are no reports of the solubility of potassium *p*-chlorophenoxyacetate in ethanol + water. In this paper, the solubility values of potassium *p*-chlorophenoxyacetate in ethanol + water at temperatures ranging from (295.61 K to 358.16 K) at atmospheric pressure were measured using a synthetic method.[2−7] The experimental values were correlated with the equation[8]

$$\ln x = A + \frac{B}{T/\mathrm{K}} + C \ln(T/\mathrm{K}) \qquad (1)$$

2. Experimental Section

Chemicals. Ethanol, which was purchased from Tianjing Kemio Chemical Reagent Develop Center, was of AR grade with a purity of 99.5%. Potassium *p*-chlorophenoxyacetate, which was purchased from Shanghai Chemical Reagent Research Institute, was of CR grade with a purity of 98%. Deionzied water was self-made. Potassium *p*-chlorophenoxyacetate was purified by dissolving in water and recrystallizing. Ethanol was purified by fine distillation. The final purities of the chemicals used were as follows: potassium *p*-chlorophenoxyacetate (≥99.5%) and ethanol (≥99.7%).

Apparatus and Procedure. The solubility of potassium *p*-chlorophenoxyacetate in ethanol and water was measured online by the synthetic method.[9] Figure 1 is the process flowchart of a laser-monitoring observation technique. The solubility apparatus consisted of a jacketed glass vessel (120 cm^3) maintained at the desired temperature by circulating water that was provided by a constant-temperature bath (type CS501, Shanghai Pudong Rongfeng Laboratory Instrument Works Co. Ltd). The water temperature was controlled by a workstation with a temperature accuracy of ±0.1 K. A magnetic stirrer (type 85-2, Shanghai Sile Co.) achieved continuous stirring, and a condenser was fitted to reduce the solvent's evaporation. A thermometer with an uncertainty of ±0.01 K was used to determine the temperature of the system. A laser beam was used as a tool to observe the system of the dissolving solid in liquid. The signal transmitted through the vessel was collected by a detector (type FGF-III) that decided the rate of temperature rise and estimated the equilibrium point of the given system on the basis of the signal change.

The solute and the solvent were prepared using an electronic balance (type AB204-N). The balance (Mettler-Toledo Group) had a range of measurement of up to 210 g with an uncertainty of ±0.0001 g. The estimated uncertainty in the mole fraction was less than 0.001. The solubility of potassium *p*-chlorophenoxyacetate in ethanol + water was measured as follows. A predetermined quantity of solute and solvents was placed into the jacketed vessel. The system was slowly heated with continuous stirring. When the solute particles disappeared thoroughly, the signal approached a maximum value. The workstation judged the signal difference at 10-min intervals; if the interval was less than 10, then the workstation gave an order to stop heating and record the temperature. The temperature recorded was the liquid temperature of a given composition upon the complete dissolution of potassium *p*-chlorophenoxyacetate.

3. Results and Discussion

The experimental solubility data of potassium *p*-chlorophenoxyacetate in ethanol + water are presented in Table 1, where T is the absolute temperature, x (mole fraction) is the experimental solubility, and x_c is a calculated value. All of these systems were correlated with eq

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10.1021/je049611n CCC: $30.25
Published on Web 03/09/2005

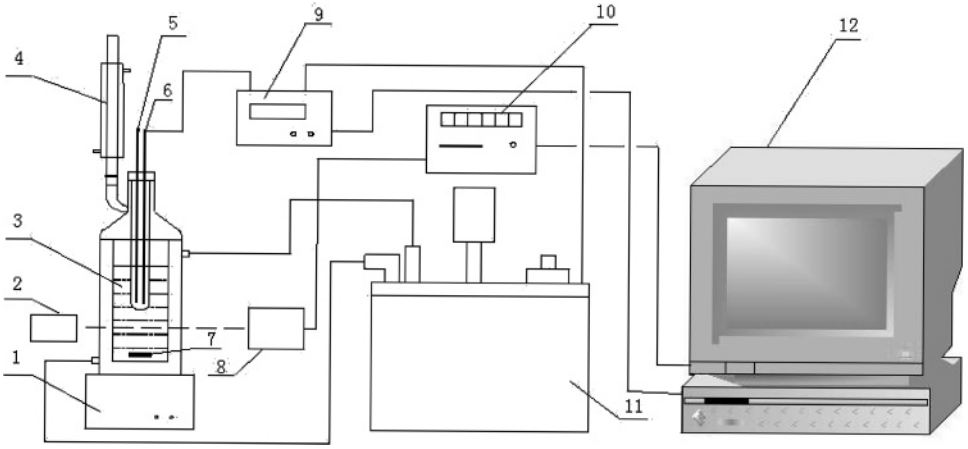

Figure 1. Process flowchart of a laser-monitoring observation technique: 1, magnetic stirrer; 2, laser generator; 3, jacketed glass vessel; 4, condenser pipe; 5, thermometer; 6, thermocouple; 7, rotor; 8, photolectric transducer; 9, controller; 10, laser strength display; 11, constant-temperature bath; 12, workstation.

Table 1. Mole Fraction Solubilities of Potassium *p*-Chlorophenoxyacetate in (*w*)Ethanol + (1 − *w*)Water with *w* = Mass Fraction

T/K	*x*	x_c[a]	*T*/K	*x*	x_c
		$w = 0.0000$			
306.68	0.01680	0.01642	336.96	0.03706	0.03738
312.46	0.01979	0.01957	339.56	0.04048	0.03971
318.70	0.02322	0.02341	344.60	0.04483	0.04446
324.64	0.02670	0.02750	349.07	0.04926	0.04895
327.94	0.03006	0.02996	354.70	0.05444	0.05495
332.74	0.03349	0.03378	358.16	0.05888	0.05883
		$w = 0.0990$			
300.84	0.01248	0.01366	329.22	0.03390	0.03315
306.40	0.01592	0.01672	334.15	0.03808	0.03739
311.46	0.01937	0.01985	339.12	0.04220	0.04184
316.61	0.02311	0.02335	344.34	0.04629	0.04667
321.13	0.02714	0.02668	350.17	0.05128	0.05218
324.94	0.03056	0.02965			
		$w = 0.4008$			
295.61	0.01258	0.01280	325.63	0.03191	0.03188
300.54	0.01497	0.01530	329.27	0.03524	0.03471
305.00	0.01831	0.01780	335.24	0.03948	0.03950
311.36	0.02179	0.02172	340.46	0.04369	0.04379
317.01	0.02522	0.02554	345.37	0.04784	0.04787
320.87	0.02855	0.02831	350.27	0.05206	0.05194
		$w = 0.6963$			
299.53	0.008220	0.008560	330.50	0.01881	0.01907
303.66	0.009713	0.009632	334.66	0.02103	0.02095
310.44	0.01179	0.01160	341.58	0.02390	0.02436
317.17	0.01423	0.01382	345.21	0.02668	0.02629
324.85	0.01661	0.01670	351.02	0.02959	0.02957
		$w = 1.000$			
307.22	0.0001823	0.0002017	333.68	0.0006081	0.0005965
312.26	0.0002528	0.0002583	338.29	0.0006892	0.0006860
317.01	0.0003249	0.0003200	341.82	0.0007845	0.0007570
322.27	0.0004129	0.0003978	346.40	0.0008577	0.0008511
327.84	0.0005003	0.0004901			

[a] x_c is the calculated value from eq 1, and x is the experimental value; both are mole fractions.

1, and parameters A, B, and C are listed in Table 2. σ is defined as

$$\sigma = \frac{[\sum_{i=1}^{N} |(x - x_c)/x|]}{N} \times 100 \qquad (2)$$

where N is number of experimental points. The mean absolute errors of every component are given in Table 2.

Table 2. Parameters of Equation 1 for the Water + Ethanol System at Various Contents of Potassium *p*-Chlorophenoxyacetate in the Mixed Solvent

w	*A*	*B*	*C*	σ
0.0000	63.577	-5.5836×10^3	−8.6415	1.14
0.0990	168.93	-1.0687×10^4	−24.130	2.73
0.4008	168.67	-1.0434×10^4	−24.210	0.946
0.6963	24.427	-3.5218×10^3	−3.0567	1.52
1.000	335.75	-1.9832×10^4	−48.835	2.96

The overall σ of 54 data points for the water + ethanol system at various contents of potassium *p*-chlorophenoxyacetate in the mixed solvent is 1.8%. It can be seen that eq 1 is satisfied to correlate the experimental data.

Figure 2 shows that the solubility of potassium *p*-chlorophenoxyacetate in different proportions of ethanol + water studied is somewhat large and that the solubility reaches a maximum at 0.4008 mass fraction of ethanol. This means that water, ethanol, and its mixture are good solvents for separating potassium *p*-chlorophenoxyacetate from the mixture solid waste. The phenomenon that the solubility reaches a maximum at 0.4008 mass fraction of ethanol is caused by the solution properties of the mixture solvent, which can be described with thermodynamic property functions such as partial molar properties (partial molar enthalpy, partial molar volume), excess molar en-

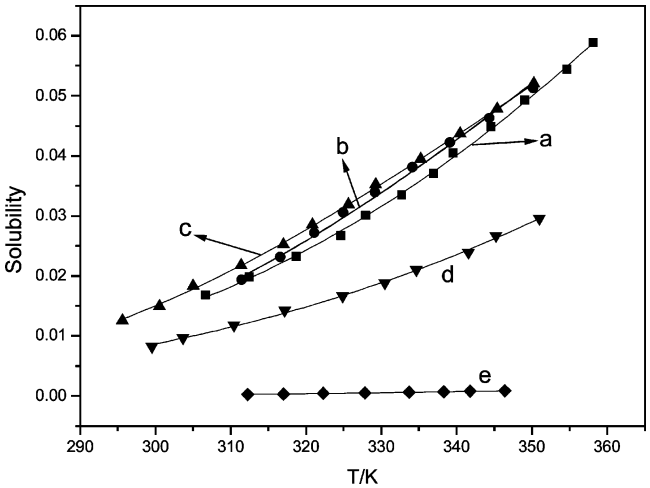

Figure 2. Mole fraction solubility of potassium *p*-chlorophenoxyacetate in (*w*)ethanol + (1 − *w*)water, where *w* = mass fraction: (a) $w = 0.0000$; (b) $w = 0.0990$; (c) $w = 0.4008$; (d) $w = 0.6963$; (e) $w = 1.000$.

thalpies, and excess molar volumes. A more detailed study is necessary.

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Received for review November 6, 2004. Accepted February 10, 2005.

JE049611N