Solubility of Acephate in Different Solvents from (292.90 to 327.60) K

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The solubility of acephate in ethyl acetate, acetone, 2-propanol, and dichloromethane from (292.90 to 327.60) K were measured using a laser-monitoring observation under the atmospheric pressure. The experimental solubility data were correlated with a semiempirical equation. The results show that the solubilities of acephate in these four solvents all increase with the increase of temperature and that dichloromethane is the best solvent for the crystallization process of acephate.

Introduction

Acephate is the abbreviated form of *O*,*S*-dimethyl acetylphosphoramidothioate (CASRN 30560-19-1), which is an important organophosphorus insecticide for a wide range of aphids, leafminers, lepidopetrous larvae, and foliage pests. Its chemical structure is shown in Figure 1. It would probably be the most appropriate substitute of *O*,*S*-dimethylphoramidothioate for its higher medical effect, biological degradability, and lower toxicity.[6] Acephate is prepared by isomerization and acetylation of *O*,*O*-dimethylthiophosphorylamide.[5] In the industrial manufacture process of acephate, crystallization is the key operation unit to determine the quality of the final product. The selection and determination of solvent is the first task in the development and design of the crystallization process. One of the most important bases to determine the proper solvent is the solubility data of the material to be purified in different solvents.[2] However, it was found that no experimental solubility data for acephate were available in the literature. In this work, the solubility data of acephate in ethyl acetate, acetone, 2-propanol, and dichloromethane from (292.90 to 327.60) K under atmospheric pressure were experimentally determined using the iso-composition method[8] and a laser-monitoring observation technique.[3,4]

Experimental Section

Materials. The crude acephate with a purity of 0.91 in mass fraction supplied by Hubei Sanonda Chemical Co. (China) was purified three times by cooling recrystallization with dichloromethane as solvent. The crystalline acephate thus obtained with a purity of 0.995 in mass fraction was used as the feed material in the solubility measuring experiments. Ethyl acetate, acetone, 2-propanol, and dichloromethane (purchased from Tianjin Kewei Co. of China) used were of analytical reagent grade and were dehydrated with molecular sieves before use. Their purities were higher than 0.995 in mass fraction. Distilled deionized water was used throughout.

Apparatus and Procedure. The solubility of acephate in different solvents were measured with the iso-composition method.[8] The measuring principle and setup were similar to that described in the literature.[3] The solubility measuring experiments were performed in a glass, magnetically agitated, 100 mL, jacked vessel. The temperature in the vessel was controlled at the desired value by a continuous forced water circulation from a thermostat (temperature uncertainty of ± 0.05 K). A mercury-in-glass thermometer (uncertainty of ± 0.05 K) was used for the measurement of the temperature in the vessel. To prevent the evaporation of the solvent, a condenser was connected vertically on the vessel. The masses of the solid acephate and solvents were weighed using an analytical balance (Metler Toledo AB204-N, Switzerland) with an uncertainty of ± 0.0001 g.

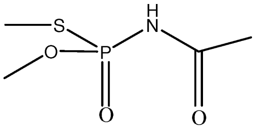

Figure 1. Chemical structure of acephate.

This method for solubility measurement was based on the fact that the laser intensity penetrated through the solution would increase with the dissolution of the solid acephate when the temperature was gradually increased. At the beginning of the experiment, the solid acephate and a certain solvent with predetermined quantity were simultaneity loaded into the jacketed vessel. The solid particles were completely suspended in the vessel by continuous stirring. Here the light intensity penetrated through the solution would reached its minimum value. Then the suspension system was heated with a rate of 2 $K \cdot h^{-1}$. With the temperature going up, the solid acephate gradually dissolved, and the intensity of penetrated light increased. When the light intensity increased to half the maximum value, which corresponds to the case that the light penetrates through the net solvent, the heating rate was slowed down to 0.05 $K \cdot h^{-1}$, and the light intensity was recorded every 10 min. When it nearly reached the maximum value and did not change between two readings, it was considered that the solid acephate had been completely dissolved and the dissolving equilibrium was believed to have been reached. Here the dissolving equilibrium temperature corresponding to the predetermined solution composition of acephate and the solvent used was determined. All the experiments were repeated three times, and the mean values were used to calculate the mole-

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Table 1. Mole Fraction Solubility x_1 of Acephate in Different Solvents

T/K	$10\,x_1^{exp}$	σ	$\frac{x_1^{exp}-x_1^{cal}}{x_1^{exp}}$	T/K	$10\,x_1^{exp}$	σ	$\frac{x_1^{exp}-x_1^{cal}}{x_1^{exp}}$	T/K	$10\,x_1^{exp}$	σ	$\frac{x_1^{exp}-x_1^{cal}}{x_1^{exp}}$
					Ethyl Acetate						
307.90	0.3496	0.0042	0.0555	318.40	0.6475	0.0024	−0.0090	327.60	1.1850	0.0055	0.0211
310.75	0.4082	0.0051	0.0235	321.55	0.7792	0.0056	−0.0230				
314.20	0.4901	0.0075	−0.0182	324.95	0.9648	0.0048	−0.0212				
					Acetone						
299.45	0.6796	0.0081	0.0128	306.40	0.9861	0.0059	−0.0085	313.75	1.4924	0.0084	0.0014
302.60	0.8109	0.0064	0.0097	309.80	1.1931	0.0091	−0.0065	315.80	1.6717	0.0071	0.0041
305.20	0.9226	0.0073	−0.0079	311.40	1.3105	0.0077	−0.0005				
					2-Propanol						
299.30	0.6062	0.0034	0.0119	310.75	1.1816	0.0052	0.0073	319.45	1.9257	0.0037	−0.0046
303.95	0.7730	0.0039	−0.0201	313.35	1.3717	0.0068	0.0060	322.00	2.2410	0.0055	0.0021
306.70	0.9255	0.0081	−0.0011	316.45	1.6263	0.0087	−0.0021				
					Dichloromethane						
292.90	1.7580	0.0044	−0.0044	298.45	2.1045	0.0061	0.0054	302.30	2.3333	0.0076	−0.0027
295.20	1.9002	0.0058	0.0015	299.60	2.1741	0.0052	0.0041	303.25	2.4053	0.0085	0.0011
297.30	2.0333	0.0083	0.0053	301.05	2.2608	0.0046	0.0013				

fraction solubility x_1 based on the following equation:

$$x_1 = \frac{m_1/M_1}{m_1/M_1 + m_2/M_2} \quad (1)$$

where m_1 and m_2 represent the masses of the solute and solvent; $M_1$and M_2 represent the molecular weights of the solute and the solvent, respectively. The uncertainty of the experiments in the solubility values is estimated to be less than 1.0 %.

Results and Discussion

The solubilities of acephate in ethyl acetate, 2-propanol, acetone, and dichloromethane at different temperatures are presented in Table 1 and more visually given in Figure 2. T is the absolute temperature, and x_1^{exp} and x_1^{cal} denote the experimental and calculation values of the solubilities, respectively. In Table 1, σ denotes uncertainty values of the solubilities, which is defined as the following:

$$\sigma = \left\{\frac{1}{3}\sum_{i=1}^{3}[(x_i^{exp} - x_i^{mean})/x_i^{mean}]^2\right\}^{1/2} \quad (2)$$

where x_i^{mean} are the mean values of the three repeated experimental data.

From Table 1 and Figure 2, it can be seen that the solubilities of acephate in different solvents are temperature dependent. For the sake of the practical employment, it is common to fit the experimental data with a theoretical semi-empirical expression. According to the solid−liquid phase equilibrium theory, the temperature dependence of the solubility of a material in the pure solvents can be correlated by the following semi-empirical equation:[7]

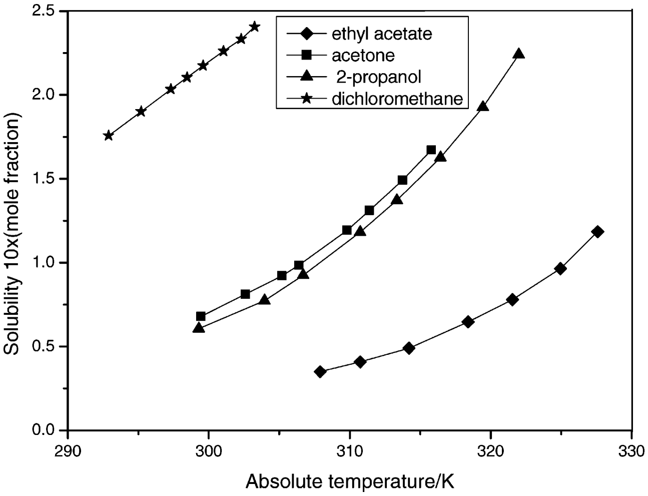

Figure 2. Solubility of acephate in different solvents.

$$\ln x_1 = -\frac{\Delta H_1^{fus}}{RT_{fus}}\left(\frac{T_{fus}}{T} - 1\right) - \frac{\Delta C_{p,1}^{fus}}{R}\left(\frac{T_{fus}}{T} - 1\right) + \frac{\Delta C_{p,1}^{fus}}{R}\ln\frac{T_{fus}}{T} - \ln\gamma_1 \quad (3)$$

where x_1, ΔH_1^{fus}, T_{fus}, R, and $\Delta C_{p,1}^{fus}$ stand for the experimental solubility of the solute in mole fraction, the fusion enthalpy, the melting temperature of the solute, the gas constant, and the difference of heat capacities of the solute between the solid and liquid phases at the melting temperature, respectively. γ_1 is the activity coefficient, and for regular solution it can be given by

$$\ln\gamma_1 = a + \frac{b}{T} \quad (4)$$

where a and b are empirical constants. By introducing eq 4 into eq 3, the following expression for the solubility in such systems can be obtained:

$$\ln x_1 = \left[\frac{\Delta H_1^{fus}}{RT_{fus}} + \frac{\Delta C_{p,1}^{fus}}{R}(1 + \ln T_{fus}) - a\right] - \left(b + \frac{\Delta H_1^{fus}}{R} + \frac{\Delta C_{p,1}^{fus}}{R}T_{fus}\right)\frac{1}{T} - \frac{\Delta C_{p,1}^{fus}}{R}\ln T \quad (5)$$

Equation 5 can also be written as the modified Apelblat equation:[9−11]

$$\ln x_1 = A + B/T + C\ln T \quad (6)$$

where A, B, and C are semi-empirical constants.

The experimental solubility values were fitted with eq 6 by the least-square method. The values of the three parameters A, B, and C are listed in Table 2 together with the root-mean-square deviation (rmsd), namely, the standard deviation, which is defined as following:

$$\mathrm{rmsd} = \left[\frac{1}{N}\sum_{i=1}^{n}(x_i^{exp} - x_i^{cal})^2\right]^{1/2} \quad (7)$$

where N is the number of experimental points.

Table 2. Parameters of Equation 6 for Acephate in Different Solvents

solvent	A	B	C	10^3 rmsd	R^2
ethyl acetate	−78.131	−1942.5	14.142	1.67	0.9966
acetone	−74.810	−1159.5	13.325	0.64	0.9996
2-propanol	−149.94	2044.1	24.607	0.83	0.9998
dichloromethane	109.71	−7201.0	−15.293	0.74	0.9987

From Table 2, it can be seen that the values of parameter C for the four solvents used are relative small, which represents the relatively small $\Delta C_{p,1}^{\text{fus}}$. This is true for many compounds under most conditions, so the last term of eq 6 is neglectable in many cases.[7] For a given solute, the values of A and B vary with the solvents. Both of them reflect the variations in the solution activity coefficient and provide an indication of the effect of solution nonidealities on the solubility of the solute.

From Tables 1 and 2, the following conclusions can be drawn. First, the solubilities of acephate in ethyl acetate, acetone, 2-propanol, and dichloromethane all increase with the increase of temperature. Second, the solubilities of acephate increase with the solvent in the following order: ethyl acetate < 2-propanol < acetone < dichloromethane. Third, from the parameters listed in Table 2, we can conclude that the absolute values of the activity coefficient of acephate in dichloromethane are much higher than that in the other three solvents. This indicates that the acephate solution in dichloromethane is much more of a departure from the ideal one than that in the other three solvents. This may be an explanation for the high solubility in dichloromethane. Fourth, from Table 2, it can be seen that the parameter C in eq 6 has a positive value except for dichloromethane. This represents that the heat capacities of the acephate solution in ethyl acetate, acetone, and 2-propanol decrease when acephate transits from liquid to solid phase, while the case for dichloromethane is contrary. Fifth, from the values of the standard deviations (rmsd) listed in Table 2, it is seen that the solubility of acephate in ethyl acetate, acetone, 2-propanol, and dichloromethane can be correlated with eq 6 very well. Last, according to the solubility characteristic of acephate in the four solvents under considered, dichloromethane is the best solvent for the crystallization process of acephate.

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Literature Cited

(1) Hefter, G. T.; Tomkins, R. P. T. *The Experimental Determination of Solubilities*; John Wiley & Sons: Chichester, 2003.
(2) Mullin, J. W. *Crystallization*, 3rd ed.; Butterworth Heinemann: Oxford, 2000.
(3) Li, X. N.; Yin, Q. X.; Chen, W.; Wang, J. K. Solubility of hydroquinone in different solvents from 276.65 K to 345.10 K. *J. Chem. Eng. Data* **2006**, *51*, 127−129.
(4) Nyvlt, C. *J. Solid-Liquid Equilib*. **1997**.
(5) Jiao, F. P.; Liu, P. L.; Wang, L. J.; Luo, H. A. New separation technology of *O*,*S*-dimethyl *N*-acetyl phoramidothioate with high purity. *Chin. J. Pestic.* **2003**, *42*, 14−18.
(6) Xiong, Y.; Ai, Q. H.; Luo, H. A. Studies on acephate extraction technique. *Chin. J. Pestic.* **2005**, *44*, 363−367.
(7) Nie, Q.; Wang, J. K.; Wang, Y. L.; Wang, S. Solubility of 11α-hydroxy-16α,17α-epoxyprogesterone in different solvents between 283 K and 323 K. *J. Chem. Eng. Data* **2005**, *50*, 989−992.
(8) Roberts, K. L.; Rousseau, R. W.; Teja, A. S. Solubility of long-chain *n*-alkanes in heptane between 280 and 350 K. *J. Chem. Eng. Data* **1994**, *39*, 793−795.
(9) Apelblat, A.; Manzurola, E. Solubilities of *o*-acetylsalicylic, 4-aminosalic, 3,5,-dinitr-osalicylic, and *p*-toluic acid, and magnesium-DL-aspartate in water from $T = (278 \text{ to } 348)$ K. *J. Chem. Thermodyn.* **1999**, *31*, 85−91.
(10) Hao, H. X.; Wang, J. K.; Wang, Y. L. Solubility of dexamethasone dodium phosphate in different solvents. *J. Chem. Eng. Data* **2004**, *49*, 1697−1698.
(11) Wang, L. C.; Wang, F. A. Solubility of niacin in 3-picoline + water (287.65 to 359.15) K. *J. Chem. Eng. Data* **2004**, *49*, 155−156.

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