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Determination and correlation of solubility of phenylphosphonic acid in selected solvents

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ABSTRACT

In this study, the solubility of phenylphosphonic acid in n-propanol, acetone, acetonitrile, ethyl acetate, and chloroform was determined by the static analytical method over the temperature range from 288.15 to 318.15 K. At a given temperature, the order of solubility is n-propanol > acetone > acetonitrile > ethyl acetate > chloroform. The modified Apelblat equation and λ*h* model were used to represent the experimental data with satisfactory correlation results. Moreover, the enthalpy, entropy, and Gibbs free energy of solution of phenylphosphonic acid in the selected organic solvents were calculated from the measured solubility data by the modified van't Hoff equation.

1. Introduction

Organic-inorganic hybrid compounds have received increasing attention owing to their novel and valuable properties [1]. Among those materials, organo-phosphonate derived compounds are very valuable, because of their easy preparation according to simple chemical routes [2]. Numerous metal phosphonates were prepared, exhibiting novel properties such as biocompatibility, chemical resistance, low solubility, acting as a host for intercalation, catalysis, ion exchange, and the ability to form thin films, with applications covering protective coatings or sealants, ionomer resins, materials for flame retardancy, and medicinal chemistry [3–6]. Phenylphosphonic acid $C_6H_5PO(OH)_2$ (PPA, CAS No. 1571-33-1) and its derivatives such as phenylphosphonyl chloride are well-known intermediates for the production of a number of organic phosphorus compounds including esters, free acids, and amides with applications as fungicides, insecticides, surface active agents, and petroleum additives [7].

In addition to use PPA for organophosphorus intermediate, fundamental solubility data of PPA are critical to understand final products' physicochemical properties, such as stability, density, crystal size distribution, crystal habits, purity, and yields. These data are also necessary for solubility modeling and understanding the interactions between PPA and various solvents. Our literature survey shows that the solubility of PPA in solvents has not been reported. In this study, the solubility of PPA in five solvents was measured over the temperature range from 288.15 to 318.15 K by the gravimetric method. The quantum chemical calculation was performed to understand the striking difference in the solubility of various solvents. The modified Apelblat equation and λ*h* model were used to correlate the experimental data. Finally, the enthalpy, entropy, and the change of Gibbs free energy of phenylphosphonic acid in the selected organic solvents were calculated from the measured solubility data by the modified van't Hoff equation.

2. Experimental

2.1. Materials

Phenylphosphonic acid was purchased from Alfa Aesar. The description of the solute and solvents used, including PPA, n-propanol, acetone, acetonitrile, ethyl acetate, and chloroform is listed in Table 1. All the organic solvents were used without further purification.

2.2. Thermal properties measurements

Thermogravimetric analysis (TGA) was carried out using a thermogravimetric analyzer (SDT Q600, TA Instruments) at a heating rate of 10 K·min^{-1} from 298 to 873 K at a flow rate of 100 mL·min^{-1} under nitrogen. The melting temperature (T_m) and enthalpy of fusion ($\Delta_{fus}H$) of PPA was determined by differential scanning calorimeter (DSC Q100, TA Instruments) in the temperature range 298 to 475 K at a constant heating rate of 10 K·min^{-1}, under a nitrogen flow rate of 25 mL·min^{-1}. The uncertainty and calibration of the DSC instrument are similar to the literature [8].

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0167-7322/

Table 1
Sources and mass fraction purity of the materials used in this paper.

Chemical name	Source	Mass fraction purity
Phenylphosphonic acid	Alfa Aesar	>0.98
n-Propanol	Shanghai Chemical Reagent Co.	0.995
Acetone	Shanghai Chemical Reagent Co.	0.995
Acetonitrile	Shanghai Chemical Reagent Co.	0.995
Ethyl acetate	Shanghai Chemical Reagent Co.	0.995
Chloroform	Shanghai Chemical Reagent Co.	0.995

2.3. Solubility measurements

The procedure of the measurement was followed as described in the literature [9]. A jacketed equilibrium cell was used for the solubility measurement with a working volume of 120 mL cylindrical double jacketed glass vessel under magnetic agitation, and a circulating water bath was used with a thermostat (type DCY-3006, Shanghai Laboratory Instrument Works Co., Ltd.), which is capable of maintaining the temperature within ±0.05 K. The temperature of the inner chamber of the vessel was measured using a calibrated mercury-in-glass thermometer (uncertainty of ±0.05 K). The mass of the sample was measured using an analytical balance with a precision of ±0.0001 g (type AB204, Mettler Toledo, Switzerland).

For each measurement, an excess mass of PPA was added to different solvents in a specially designed sealed dual-wall flask. Then, the equilibrium cell was maintained at a constant temperature under continuous stirring. After at least 4 h, the stirring was stopped, and the solution was placed still until it became clear. The upper clear solution was extracted by a preheated on-off injector with a 0.2 μm PTFE filter and evaporated in a vacuum drying oven at $T = 353.15$ K. Each experimental data point was repeated thrice, and their mean value was chosen as the solubility.

The mole fraction solubility of PPA in solvents was calculated as follows:

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

where m_1 and m_2 are the mass of the solute, solvent; and M_1, M_2 are the molar mass of the solute, solvent, respectively.

3. Results and discussion

3.1. Characterization of PPA

The results of the TGA and DSC measurement of PPA are shown in Figs. 1 and 2. The TGA results show that a two-step thermal degradation with remarkably charred residue 37% at $T = 873$ K. The melting point of PPA was characterized at $T = 440.75$ K; (Ref. [10], $T = 439.15$ K), and the uncertainty of the melting point measurement was 0.5 K. The enthalpy of fusion of PPA was 20.38 kJ·mol^{-1}, and the relative uncertainty of the enthalpy of fusion was 3%.

3.2. Solubility in the selected solvents

The mole fraction solubilities of PPA in n-propanol, acetone, acetonitrile, ethyl acetate, and chloroform against various temperatures are listed in Table 2 and shown in Fig. 3. The data show that the solubility of PPA increased with temperature in all the selected solvents. At a specific temperature, the solubility order in these solvents was determined as n-propanol > acetone > acetonitrile > ethyl acetate > chloroform.

The order of solvent polarities is acetonitrile > acetone > chloroform > ethyl acetate > n-propanol. The solubility of PPA, however, did not increase with increasing polarity of the solvents. It was evident that polarity was not the dominant factor for the solubility of PPA in these solvents, and the solubility was suspected to be dictated by the interactions between the solvent molecules and PPA. The results of the PPA's solubility can therefore be explained by considering the rule of "like dissolves like", which means a solute will dissolve best in a solvent that has a similar chemical structure or polarity to itself, and results from competing solute-solute, solvent-solvent and solvent-solute interactions. For n-propanol, it has a hydroxyl group, and acetone has a carbonyl group, they both have the similar chemical structure with PPA. The polarity of acetonitrile is higher than those of other solvents; therefore, the solubility in acetonitrile is moderate. The significantly lower solubility in ethyl acetate is because of its weak polarity and interaction between ethyl acetate and PPA. Finally, for chloroform, because of the saturated and stable molecular structure, it has weak interactions with PPA molecules, resulting in the lowest solubility.

3.3. Solubility correlation

In order to use the solubility data in the temperature range from 288.15 to 318.15 K, the solubility data of PPA in the selected

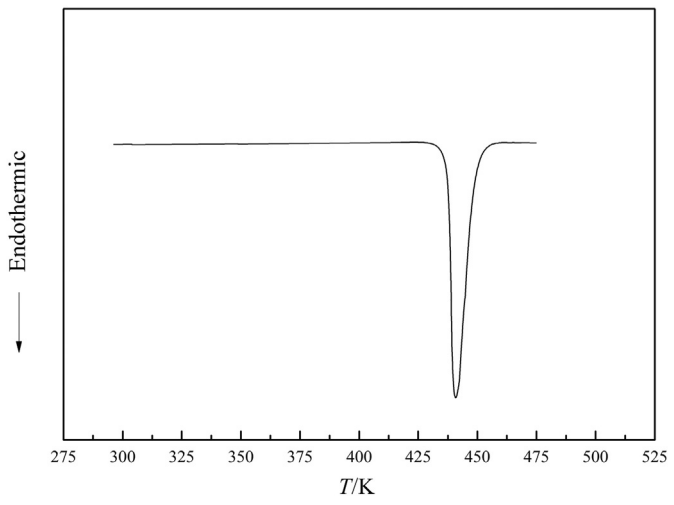

Fig. 1. Experimental heat Q flow from DSC measurement of PPA.

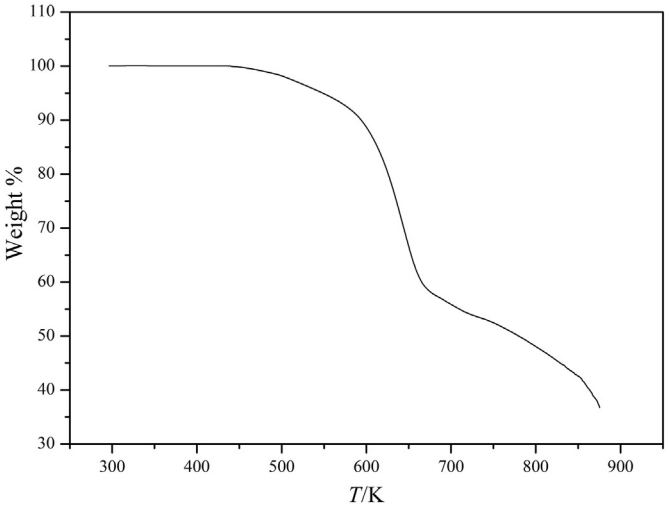

Fig. 2. TGA thermograms of PPA under N_2.