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Solubility of cyclohexyl-phosphoramidic acid diphenyl ester in selected solvents

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ABSTRACT

Cyclohexyl-phosphoramidic acid diphenyl ester (CPADE) was synthesized and characterized by elemental analysis (EA), mass spectrum (MS), infrared spectroscopy (IR) and nuclear magnetic resonance (NMR). The thermostability of CPADE was measured by thermogravimetric analysis (TGA) and the melting temperature and the fusion enthalpy of CPADE were evaluated by using differential scanning calorimeter (DSC). The solubilities of CPADE in selected solvents were obtained by a gravimetric method. The experimental data were well correlated by the Wilson, nonrandom two liquid (NRTL), and universal quasichemical (UNIQUAC) equations. And the dissolution enthalpy, entropy, and the molar Gibbs energy of CPADE in the selected solvents are also calculated by the van't Hoff equation.

1. Introduction

Organic polymer materials that greatly improve the quality of modern life are used in many fields because of their good heat endurance, chemical corrosion resistance, desired mechanical properties and so on. Unfortunately, most of the polymers are flammable, which limited their applications [1]. So the polymer materials with high heat-resistant and flame-retardant properties are urgently required. The well-known method to enhance the flame retardancy is to blend the flame retardant additives into the polymer materials. The flame retardants mainly work as two modes of actions, condensed phase and/or gas phase activities [2]. The condensed phase effects of flame retardants are relevant to a char layer which can obstruct the polymer surface from heat and air [3–5], while the gas phase effects are related to the mechanism of hydrogen and hydroxyl radical scavengers [6,7].

In general, the halogenated compounds with the antimonous oxide are often applied to give the polymers flame retardancy because of their good flame-resistant characteristics. However, this material causes environmental problems as toxic combustion products are released during combustion [8]. Hence, non-halogenated based flame retardants become increasingly popular alternatives in replacing the halogenated flame retardants. Among the available non-halogenated based flame retardants, phosphorus containing compounds are often regarded as potential candidates, because these materials, working as the modes of condensed phase action and gas phase action during the flame retardancy process, typically do not generate any toxic gas [9]. In recent years, nitrogen–phosphorus flame-retardant synergism is recognized by the researchers [10]. The compounds containing phosphorus and nitrogen are usually named intumescent flame retardants owing to a foam char layer in the condensed phase [11]. The incombustible gases without toxic smoke and fog generated from these materials can dilute the concentration of the oxygen near the flame and foam superior protective barriers to the main materials against flame and heat while heating [12,13]. Now, most of the literatures on the halogen-free retardants are deeply relevant to the phosphorus–nitrogen-based products. Furthermore, they are believed to be the biggest growing share of the flame retardant market in the future [8].

Cyclohexyl-phosphoramidic acid diphenyl ester (CPADE) ($C_{18}H_{22}O_3PN$, CAS Registry No. 6372-21-0) is one of versatile intumescent flame retardants; its chemical structure is shown in Fig. 1.

This compound has a bright future, owing to its powerful flame retardancy to the polymers. It was widely used in Ethylene-Propylene-Diene Monomer (EPDM) [14], thermoplastic polyolefin [15], poly(styrene–ethylene/butene–styrene) (SEBS) [16], polyethylene [17,18], epoxy resins [19], polycarbonate (PC) [20] etc. However, some impurities have greatly affected its thermal property and applications. Thus, the purification process employed to obtain CPADE with high purity is very significant.

In the industry, the pure production of CPADE is always obtained by crystallization which is an important separation and purification process [21]. The (solid + liquid) equilibrium (SLE) measurements of CPADE in

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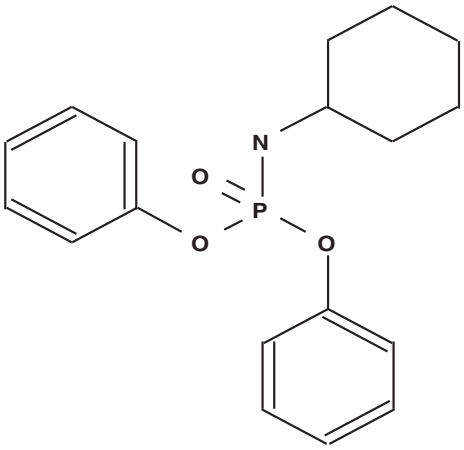

Fig. 1. Structures of the cyclohexyl-phosphoramidic acid diphenyl ester (CPADE).

organic solvents are helpful to determine and estimate some crystallization parameters and reaction kinetics or thermodynamics study. However, there has no report as to the solubilities of CPADE in selected solvents. In this work, CPADE was synthesized and characterized. To achieve more thermodynamic data on the crystallization of CPADE from some organic solvents, the solubilities of CPADE in the ten selected organic solvents were measured. The Wilson [22], nonrandom two-liquid (NRTL) [23], and UNIQUAC [24] models were employed to fit the solubility data based on the pure component thermophysical properties. Comparison and discussion of the solubility were also presented in this study. And the dissolution behaviors of CPADE in the selected solvents were also estimated by van't Hoff equation [25].

2. Experimental

2.1. Materials

Diphenyl chlorophosphate was purchased from Zhangjiagang Xinyi Chemical Co., Ltd. and purified by distillation before used. Triethylamine and cyclohexylamine were kindly supplied by Weisi Chemical Reagents Co., Ltd. All of the organic solvents used for the experiments were analytical grade reagents, which were purchased from Beijing Chemical Factory. Purities and sources of all the materials used in this study are shown in Table 1.

Table 1
The source, mass purity and purification method of the sample used in this paper.

Chemical name	Source	Mass purity	Purification method
Diphenyl chlorophosphate	Zhangjiagang Xinyi Chemical Co., Ltd	> 0.990	Distillation
Triethylamine	Weisi Chemical Reagents Co., Ltd	>0.990	None
Chloroform	Beijing Chemical Factory	>0.995	None
Cyclohexylamine	Weisi Chemical Reagents Co., Ltd	>0.990	None
Ethyl acetate	Beijing Chemical Reagents Co., Ltd	>0.995	None
Acetone	Beijing Chemical Factory	>0.995	None
Ethanol	Beijing Chemical Factory	>0.995	None
Methanol	Beijing Chemical Factory	>0.995	None
Tetrahydrofuran	Beijing Chemical Factory	>0.998	None
Dichloromethane	Beijing Chemical Factory	>0.995	None
Benzene	Beijing Chemical Factory	>0.995	None
Adipic acid	Sigma-Aldrich	>0.990	None
Toluene	Beijing Chemical Factory	>0.995	None
Acetonitrile	Beijing Chemical Factory	>0.995	None
CPADE	As prepared	>0.990	Recrystallization

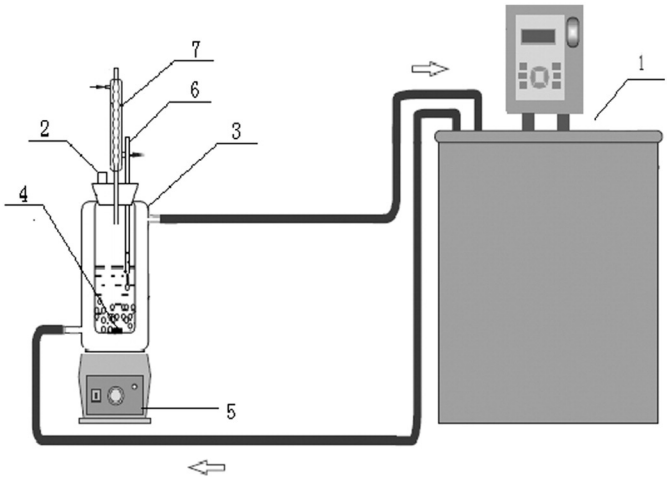

Fig. 2. Schematic diagram of the experimental apparatus: 1, thermostatic water-circulator bath; 2, sample gauge; 3, jacketed glass vessel; 4, magnetic stirrer; 5, magnetic agitator drive; 6, thermometer; 7, condenser.

2.2. Apparatus and procedure

The experimental apparatus for the solubility measurements was the same as it was described in our previous work [26]. The diagrammatic sketch of the experimental apparatus was shown in Fig. 2.

A jacketed equilibrium cell was applied for the solubility measurements with a working volume of 120 mL and a magnetic stirrer, and a circulating water bath was used with a thermostat (type 50 L, made from Shanghai Laboratory Instrument Works Co., Ltd.) with an uncertainty of ±0.01 K so that the system could reach and keep the required temperature. To prevent the evaporation of the solvent, a condenser was introduced. An analytical balance (type TG328B, Shanghai Balance Instrument Works Co., Ltd.) with an uncertainty of ±0.1 mg was used during the mass measurements.

Fourier transform infrared (FTIR) spectrum was performed on a Perkin Elmer 400 spectrometer (Connecticut, USA). The melting point and enthalpy of fusion were measured with a DSC Q100 (TA Instruments) differential scanning calorimeter (DSC) in flowing nitrogen at a heating rate of 10 $K \cdot min^{-1}$. The uncertainty of DSC measurement was the same as it was described in the literature [26]. The elemental

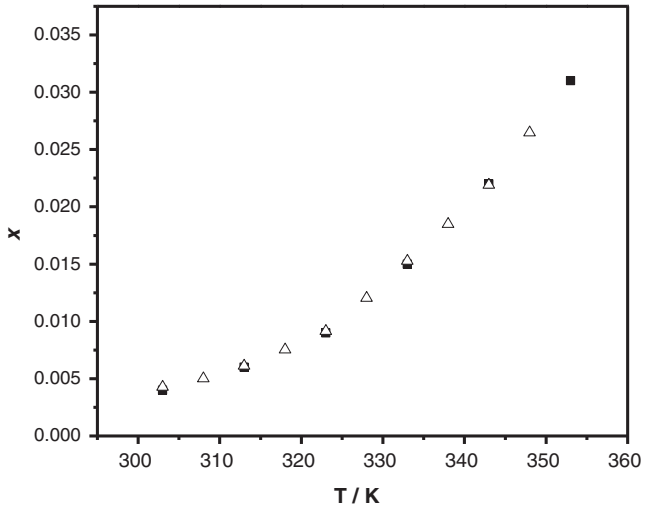

Fig. 3. Comparison of the literature and experimental mole fraction of adipic acid solubility (x) against temperature in water: ■, literature; △, this work.