Measurement and correlation of the solubilities of tetra(5,5-dimethyl-1,3-dioxaphosphorinanyl-2-oxy) neopentane in different pure solvents

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ABSTRACT

Using a static analytic method, experimental solubility data were obtained for tetra(5,5-dimethyl-1,3-dioxaphosphorinanyl-2-oxy) neopentane (DOPNP) in acetonitrile, acetone, methanol, ethanol, ethyl acetate, methyl acetate and methylethylketone at temperatures ranging from 293 to 333 K. Several commonly used thermodynamic models, including the ideal, modified Apelblat, Wilson, UNIQUAC and NRTL models, were applied to correlate the experimental solubility data. The binary interaction parameters of the above models were found to have a linear dependency on temperature and the coefficients were regressed. It can be seen that NRTL model is more suitable in describing the solubility data of DOPNP, compared with the other models. By using the van't Hoff equation, the dissolution enthalpy, dissolution entropy, and Gibbs free energy change of DOPNP are predicted in different pure solvents.

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1. Introduction

Polypropylene (PP) was the first synthetic stereo-regular polymer to achieve industrial importance and it has been extensively used in many applications, such as the furniture, electrical, building, and motor industries because of its characteristics of good mechanical properties, excellent water resistance, and low cost [1,2]. However, thermal resistance and flammability properties of PP are not enough satisfactory. Flame retardants (FRs) can improve fire performance of polymers to meet the requirement in the industry. Traditionally, halogen containing compound, alone or in combination with antimony trioxide, are one of the main flame retardants of PP [3,4]. But, halogenated flame retardants release large amounts of smoke and toxic gas upon burning, which is harmful to the environment and human health. As environmentally-friendly halogen-free products, intumescent flame retardants (IFRs) are expected to be used in PP in the place of the traditional halogen-containing ones. Generally, a typical intumescent system contains three active ingredients: an acid source as a catalyst, a charring agent, and a blowing agent [5,6]. Phosphorus-containing compounds are used as effective charring agents in IFRs because they form a surface layer of char rather than yielding CO or CO_2 during the process of decomposition [7].

Among these phosphorus-containing compounds, tetra(5,5-dimethyl-1,3-dioxaphosphorinanyl-2-oxy) neopentane (hereafter abbreviated as DOPNP; its formula is shown in Fig. 1, CAS RN 75607-57-7) has been useful as fireproofing agent in polymers [8]. DOPNP has high phosphorus content and shows high thermal stability and good char-forming ability due to the symmetrical structure. IFRs using DOPNP, as charring agent, showed better flame retardancy for PP. DOPNP could effectively raise limiting oxygen index (LOI) value of IFR-PP, increase the residual char amount, and promote the IFR systems to form a continuous, compact char layer. Synergistic effects of DOPNP and other active ingredients were crucial to fully exert the flame retardance of the IFR system [9].

In order to utilize effectively synergistic effects of DOPNP and other active ingredients in the IFR system, high purity for DOPNP is required. In the industrial process and design, the knowledge of solubilities of DOPNP in different solvents is very important for their preparation and purification. To the best of our knowledge, the solubilities of DOPNP in selected solvents have not been reported in the literature.

As our continuous efforts to search for high thermally stable fire retardant, DOPNP was synthesized and characterized. The solubilities of DOPNP in acetonitrile, acetone, methanol, ethanol, ethyl acetate, methyl acetate and methylethylketone were measured in the temperature range 293–333 K. The ideal, modified Apelblat,

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Fig. 1. Structures of the tetra(5,5-dimethyl-1,3-dioxaphosphorinanyl-2-oxy) neopentane (DOPNP).

a	empirical constant for the ideal model
b	empirical constant for the ideal model
A	empirical constant for the modified Apelblat equation
B	empirical constant for the modified Apelblat equation
C	empirical constant for the modified Apelblat equation
Δg_{12}	cross-interaction parameter for NRTL model
Δg_{21}	cross-interaction parameter for NRTL model
ΔG_d	Gibbs free energy change for the dissolution (J/mol)
ΔH_d	enthalpy of dissolution (J/mol)
$\Delta_{fus}H_1$	enthalpy of fusion at the melting point (J/mol)
m	mass
M	molar mass
N	number of experimental data
q	the surface parameter for UNIQUAC model
r	the volume parameter for UNIQUAC model
R	the gas constant (8.3145 J/mol K)
R^2	correlation coefficient
RSD	the root-mean-square deviation
ΔS_d	entropy of dissolution (J/mol K)
$\Delta_{fus}S_1$	entropy of fusion at the melting point (J/mol K)
T	the absolute temperature (K)
T_{m1}	melting temperature (K)
Δu_{12}	cross-interaction parameter for UNIQUAC model
Δu_{21}	cross-interaction parameter for UNIQUAC model
V	molar volume (cm^3/mol)
x	mole fraction
Z	coordination number

Greek letters

α_{12}, β_{12}, α_{21}, β_{21}	the optimized parameters for the Wilson model, UNIQUAC model and NRTL model
γ_1	activity coefficient
θ	the mean surface area fraction for UNIQUAC model
φ	the mean volume fraction for UNIQUAC model
$\Delta\lambda_{12}$	cross interaction energy parameter for Wilson model ($\lambda_{12} - \lambda_{11}$) (J/mol)
$\Delta\lambda_{21}$	cross interaction energy parameter for Wilson model ($\lambda_{21} - \lambda_{22}$) (J/mol)

Subscripts

1	solute (DOPNP)
2	solvent
d	dissolution
fus	fusion
m	melting

Superscripts

calc	calculated data
exp	experimental data
∞	infinite dilution

2. Experimental

2.1. Materials

Phosphorus oxychloride (analytical) was purchased from Tianjin Guangfu Fine Chemical Research Institute, neopentyl glycol from Sinopharm Chemical Reagent Co. Ltd., pentaerythritol from Kermel Tianjin Chemical Reagent Company, and triethylamine from Tianjin Bodi Chemical Reagent Company. All of the solvents were analytical grade reagents, which were purchased from Beijing Chemical Factory. Their mass fraction purities were all higher than 0.99. They were used without further purification. The water is double distilled before use. The sample properties and description are summarized in Table 1, including density and refractive index of organic solvents, purity and source. The literature values of these properties should be listed in Table 1, and calculated the average error from the experimental values.

2.2. Apparatus and procedure

The melting points and enthalpy of fusion were determined with a DSC Q100 (TA Instruments) differential scanning calorimeter (DSC) in flowing nitrogen at a heating rate of 10 K min^{-1}. Indium, tin, and zinc were utilized for multipoint temperature calibration in DSC. The calibration measurements were carried out with 3 heating and 2 cooling segments; the transition process was thus measured three times, but only the two last were used in the calibration. Heat capacity calibration was performed with sapphire (Al$_2$O$_3$) in DSC. Their melting behavior was analyzed, and data were saved as the calibration data for DSC. The uncertainty of DSC measurement is the same as that described in the literature [10]. The elemental analysis was performed on an Elementar Vario EL element analyzer. ^{1}H NMR and ^{31}P NMR spectra were obtained with a Bruker ARX-400 and JEOL ECA-600, respectively. Thermogravimetric analysis (TGA) was carried out with an SDT Q600 (TA Instruments) thermogravimetric analyzer at a heating rate of 10 K min^{-1} under nitrogen from 298.15 to 823.15 K.

The setup for the solubility measurement was the same as that described in the literature [11]. Fig. 2 shows the schematic diagram of the experimental apparatus. A jacketed equilibrium cell was used
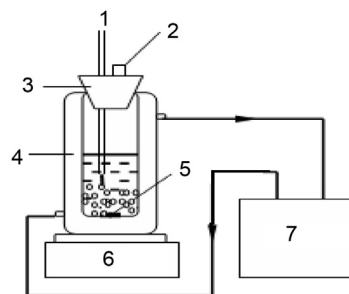
Fig. 2. Schematic diagram of the experimental apparatus: (1) thermocouple; (2) sample gauge; (3) rubber plug; (4) jacket; (5) equilibrium cell; (6) magnetic stirrer; (7) water cycling bath.

Wilson, UNIQUAC and NRTL models were applied to represent the experimental data. Comparison and discussion of the solubility and the capability of the models were then carried out. By using the van't Hoff equation, the dissolution enthalpy, dissolution entropy, and Gibbs free energy change of DOPNP a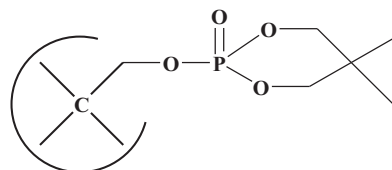re predicted in different pure solvents.