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Solubility and mixing thermodynamic properties of (2,4,6-trimethylbenzoyl) diphenylphosphine oxide in pure and binary solvents

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ABSTRACT

The solubility of (2,4,6-trimethylbenzoyl) diphenylphosphine oxide (Lucirin TPO) in ten pure solvents and two binary solvent mixtures was measured from 273.15 K to 308.15 K by gravimetric method. The solubility of Lucirin TPO increased non-linearly with rising temperature in all the studied solvents. Furthermore, the solubility in mixed solvents presented a maximum-solubility effect. The modified Apelblat model, λh model, CNIBS/R-K model, NRTL model and Jouyban-Acree model were employed to correlate the experimental solubility data. The modified Apelblat model provided the best agreement in pure solvents, while the modified Apelblat model and CNIBS/R-K model gave better correlation results in binary solvent mixtures. Moreover, the thermodynamic properties of the mixing process, including the mixing Gibbs free energy, mixing enthalpy and mixing entropy were calculated from the solubility data using the NRTL model.

1. Introduction

UV-curable coatings have gained attention, which may due to its good environmental properties [1]. Moreover, their high-speed process involves numerous excellent merits, such as low-energy consumption and solvent-free formulations [2–4]. UV-curable systems commonly contain three fractions: oligomers, monomers, and photoinitiators [5,6]. As the crucial component, photoinitiators induce free-radical polymerization during the UV curing process [7,8].

Photoinitiator mixtures were developed by BASF in 1999. The photoinitiator mixtures contain monoacylphosphine oxide and diacylphosphine oxide [9]. (2,4,6-trimethylbenzoyl) diphenylphosphine oxide ($C_{22}H_{21}O_2P$, CAS Registry NO. 75980-60-8, Lucirin TPO, Fig. 1) is a typical monoacylphosphine oxide photoinitiator [10] developed to overcome the color instability of the frequently used photoinitiator, camphorquinone [11,12]. Furthermore, Lucirin TPO can be used in the absence of a co-initiator, with increased degrees of conversion and polymerization efficiency [13]. Hence, Lucirin TPO is a practical photoinitiator and is important in UV-curable industries.

Only high-quality photoinitiators can guarantee smooth progress of UV-curable systems. As essential operation units, crystallization and purification may determine the final purity and crystal habit to a large extent. In terms of solution crystallization, solubility remains a critical and essential physical property. Numerous synthetic routes of Lucirin TPO have been investigated, but the solubility data of Lucirin TPO is still unknown.

In this article, the solubility of Lucirin TPO was measured in ten pure solvents (methanol, ethanol, acetone, 1-propanol, 2-propanol, 1-butanol, 2-methyl-1-propanol, acetonitrile, methyl acetate, and ethyl acetate) and two binary solvent mixtures (methanol + ethyl acetate, ethanol + ethyl acetate) by gravimetric method. Then the mixing thermodynamic properties (mixing Gibbs free energy, mixing enthalpy, and mixing entropy) of Lucirin TPO were obtained from the solubility data.

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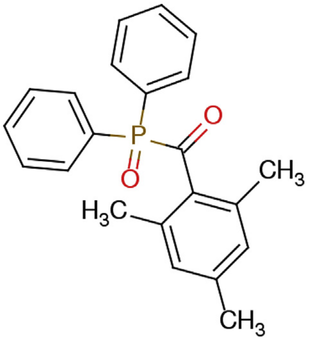

Fig. 1. Chemical structure of Lucirin TPO.

2. Experimental section

2.1. Materials

The pale yellow solid of Lucirin TPO was supplied by Hubei Gurun Technology Co., Ltd., China. In this study, for all organic solvents, including methanol, ethanol, acetone, 1-propanol, 2-propanol, 1-butanol, 2-methyl-1-propanol, acetonitrile, methyl acetate and ethyl acetate were purchased from Tianjin Yuxiang Technology Co., Ltd., China. The materials mentioned above were used without further treatment. More detailed information is presented in Table 1.

2.2. Thermal analysis

2.2.1. Thermogravimetric analysis

TGA (Thermogravimetric analysis) is a useful method of thermal analysis. In this study, the TGA instrument was Mettler-Toledo TGA 1/SF thermo-balance. About 7.87 mg Lucirin TPO was put into the crucible in the context of programmed temperature. The samples were heated at the heating rate of 5 K·min^{-1} from 298.15 K to 773.15 K. From the TGA curve, the decomposition temperature and the weight percentage of resulting mass change could be obtained.

2.2.2. Differential scanning calorimetry

The DSC (Differential scanning calorimetry) curve of Lucirin TPO was measured by Mettler-Toledo DSC 1/1500. With reference to an identical empty pan, approximate 6.56 mg sample in an aluminum pan was heated linearly from 298.15 K to 523.15 K, with a heating rate of 5 K·min^{-1}. In this measurement, nitrogen was used as shielding gas. The thermal behavior of Lucirin TPO was observed during the scanning, the melting temperature (T_m) and the enthalpy of fusion ($\Delta_{fus}H$) were obtained as well.

2.3. Characterization

PXRD (Powder X-ray diffraction) was used to ensure the raw material and all experimental samples are the same crystal form. The PXRD patterns were obtained from a powder X-ray diffraction equipment (Rigaku D/MAX 2500, Cu Kα radiation 0.15418 nm) over a range of diffraction angle from 2° to 40° with a scanning speed of 8° min^{-1} in the context of a voltage of 40 kV and a current of 100 mA.

2.4. Solubility measurements

The gravimetric method, which is favored by many researchers [14–16], was adopted in this work. The experimental equipment mainly consisted of jacked glass vessel, thermostat (Julabo CF41, Germany), and electromagnetic stirring. The circulating water pumped by a thermostat with temperature stability of ±0.02 K provided constant ambient temperature for the jacked glass vessel. Excess amounts of Lucirin TPO and appropriate amounts of organic solvents were added to the same jacked glass vessel. The solute and solvent were mixed for 12 h by electromagnetic stirring to completely achieve solid–liquid equilibrium. Afterward, agitation was ceased, and the solution was allowed to stand for 3 h. Approximately 3 ml supernatant fluid was withdrawn by a syringe and filtered rapidly through an organic membrane filter (0.22 μm) before the liquid was collected with a pre-weighed beaker. Then, the beaker containing solution obtained from the previous step was weighed using an analytical balance (Mettler Toledo ML204, Switzerland) with accuracy of ±0.0001 g. The entire saturated solution was obtained and placed in a vacuum drying oven at 313.15 K until constant sample weight. All the experiments were repeated three times, and the average value was used to calculate the solubility of Lucirin TPO.

The mole fraction solubility in pure solvents was calculated by Eq. (1), and the mole fraction solubility in binary solvent mixtures was calculated by Eq. (2).

$$x_1 = \frac{m_1/M_1}{m_1/M_1 + m_2/M_2} \tag{1}$$

$$x_1 = \frac{m_1/M_1}{m_1/M_1 + m_2/M_2 + m_3/M_3} \tag{2}$$

The initial mole fraction of methanol or ethanol in binary solvent mixtures could be obtained by Eq. (3):

Table 1
The sources and purity of all the chemicals used in the experiments.

Chemical name	Source	Mass fraction purity	Purification method	Analysis method
Lucirin TPO	Hubei Gurun Technology Co., Ltd., China	≥0.990	None	HPLC[a]
methanol	Tianjin Yuxiang Technology Co., Ltd., China	≥0.995	None	GC[b]
ethanol	Tianjin Yuxiang Technology Co., Ltd., China	≥0.995	None	GC[b]
acetone	Tianjin Yuxiang Technology Co., Ltd., China	≥0.995	None	GC[b]
1-propanol	Tianjin Yuxiang Technology Co., Ltd., China	≥0.995	None	GC[b]
2-propanol	Tianjin Yuxiang Technology Co., Ltd., China	≥0.995	None	GC[b]
1-butanol	Tianjin Yuxiang Technology Co., Ltd., China	≥0.995	None	GC[b]
2-methyl-1-propanol	Tianjin Yuxiang Technology Co., Ltd., China	≥0.995	None	GC[b]
acetonitrile	Tianjin Yuxiang Technology Co., Ltd., China	≥0.995	None	GC[b]
methyl acetate	Tianjin Yuxiang Technology Co., Ltd., China	≥0.995	None	GC[b]
ethyl acetate	Tianjin Yuxiang Technology Co., Ltd., China	≥0.995	None	GC[b]

[a] High-performance liquid chromatography.
[b] Gas chromatography.