Short Articles

Solubility of Irganox 1010 in (Alcohol + Water) Mixtures from (293.15 to 333.15) K

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The solubility of Irganox 1010 in (methanol + water), (ethanol + water), and (2-propanol + water) mixed solvents was determined in the temperature range from (293.15 to 333.15) K by a static analytical method. The concentrations of the investigated Irganox 1010 in saturated solution were analyzed by UV spectrometry. A semiempirical equation was proposed to correlate the experimental data. The apparent molar enthalpies of Irganox 1010 in the three systems were determined from the temperature dependence of the solubilities.

Introduction

The chemical structure of Irganox 1010 {tetrakis[methylene-3-(3,5-di-*tert*-butyl-4-hydroxylphenylpropionate)]methane, $C_{73}H_{108}O_{12}$, FW 1177.65, CAS Registry No. 6683-19-8} involved in this study is shown in Figure 1.

Irganox 1010 is a high molecular weight hindered phenolic antioxidant and is widely used in plastic, rubber, and synthetic fiber.[1−3] Physical properties of Irganox 1010, such as granularity, stack density, and crystal morphology, are related to the solvents used in the crystallization process.[4−6] The solubility of Irganox 1010 in (alcohol + water) mixed solvents is quite significant for the optimization of the purification process. Unfortunately, no related solubility data are currently available in the literature. In this work, the solubilities of Irganox 1010 in three mixed solvents, i.e., (methanol + water), (ethanol + water), and (2-propanol + water), were determined in the temperature range from (293.15 to 333.15) K to provide important basic data for the development of the purification process.

Experimental Section

Chemicals. Methanol, ethanol, and 2-propanol were purchased from Tianjin Kewei Chemical Reagent Co., and all of them were analytical research grade with mass fraction purity higher than 99.5 % with no further purification. Irganox 1010, obtained from Tianjin Chenguang Chemical Factory Co., Ltd., was purified by recrystallizing from the solution of ethanol two times. The melting point and purity of Irganox 1010 determined by differential scanning calorimetry (Mettler DSC30) was 385.75 K and a mole fraction of 99.5 %. The literature value of the melting temperature is (385.15 to 387.15) K.[6] Deionized water was used.

Apparatus and Procedure. The solubility determination in this study was carried out by a static analytical method that was described in our previous work.[7,8] The apparatus consisted of a jacketed glass vessel, which was maintained at a desired temperature by water circulated from a constant-temperature water bath with a thermoelectric controller. The temperature could be maintained within ± 0.05 K of the required temperature. The experimental saturated solutions were prepared by excess solute, Irganox 1010, in the vessel containing the solvent. Solubilities were determined by equilibrating the solute with solvent in the water-jacketed vessel with magnetic stirring in a constant-temperature water bath for at least 3 days. Attainment of equilibrium was verified both by repetitive measurement after a minimum of three additional days and by approaching equilibrium from supersaturation by pre-equilibrating the solutions at a higher temperature. The actual temperature in the glass vessel was monitored by a mercury thermometer with an uncertainty of 0.05 K. The fluid between the internal and external glass tube can be exchanged by pressing or relaxing the gas bag at the top of glass tube. Portions of Irganox 1010 saturated solutions were transferred from the internal glass tube to the volumetric flasks to determine the amounts of samples diluted quantitatively with solvent mixtures at 254 nm using spectrophotometric analysis (Shimadzu UV-160A). The mole fractions of the dilute solutions were determined from a Beer−Lambert law absorbance versus composition calibration curves derived from the measured absorbance of solutions of known Irganox 1010 compositions.

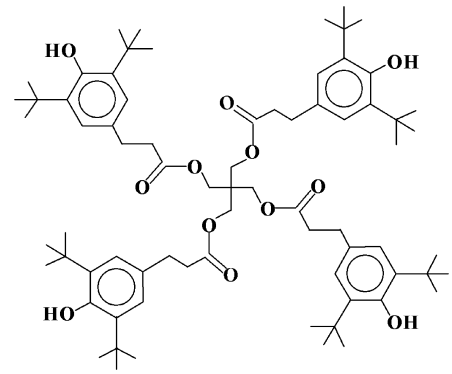

Figure 1. Structure of the Irganox 1010 molecule.

Results and Discussion

To check the reliability of the experimental method, known masses of Irganox 1010 were completely dissolved in ethanol,

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Table 1. Solubility of Irganox 1010 in Alcohol (1 − *w*) + Water (*w*) Solvents in the Temperature Range (293.15 to 333.15) K (*w* = Mass Fraction)

	$10^3\ x_1 \pm$ standard deviation		
T/K	$w = 0$	$w = 0.03$	$w = 0.05$
	methanol + water		
293.15	0.2208 ± 0.0028	0.1265 ± 0.0008	0.04156 ± 0.00038
298.15	0.3324 ± 0.0012	0.1924 ± 0.0018	0.06188 ± 0.00024
303.15	0.5440 ± 0.0019	0.2907 ± 0.0032	0.09271 ± 0.00020
308.15	0.8123 ± 0.0028	0.4327 ± 0.0031	0.1314 ± 0.0008
313.15	1.258 ± 0.033	0.6464 ± 0.0028	0.2058 ± 0.0014
318.15	2.031 ± 0.027	1.003 ± 0.014	0.3194 ± 0.0027
323.15	2.873 ± 0.008	1.539 ± 0.021	0.4504 ± 0.0012
328.15	4.290 ± 0.011	2.292 ± 0.020	0.6692 ± 0.0038
333.15	7.260 ± 0.035	3.299 ± 0.068	0.9166 ± 0.0058
	ethanol + water		
293.15	0.3022 ± 0.0020	0.1630 ± 0.0008	0.1389 ± 0.0022
298.15	0.4452 ± 0.0023	0.2787 ± 0.0029	0.2078 ± 0.0026
303.15	0.6846 ± 0.0018	0.4117 ± 0.0038	0.3024 ± 0.0032
308.15	1.051 ± 0.038	0.5517 ± 0.0041	0.4497 ± 0.0008
313.15	1.595 ± 0.028	0.8454 ± 0.0056	0.6601 ± 0.0056
318.15	2.378 ± 0.023	1.201 ± 0.018	0.9991 ± 0.0048
323.15	3.508 ± 0.032	1.748 ± 0.038	1.485 ± 0.028
328.15	5.100 ± 0.028	2.655 ± 0.043	2.213 ± 0.045
333.15	7.403 ± 0.008	4.025 ± 0.058	3.096 ± 0.072
	2-propanol + water		
293.15	0.1475 ± 0.0008	0.1287 ± 0.0011	0.09455 ± 0.00012
298.15	0.2388 ± 0.0016	0.2084 ± 0.0024	0.1346 ± 0.0028
303.15	0.4061 ± 0.0023	0.3385 ± 0.0028	0.2041 ± 0.0018
308.15	0.6314 ± 0.0057	0.5210 ± 0.0068	0.3166 ± 0.0031
313.15	0.9978 ± 0.0014	0.8069 ± 0.0058	0.5089 ± 0.0043
318.15	1.579 ± 0.028	1.223 ± 0.008	0.8014 ± 0.0029
323.15	2.524 ± 0.029	2.166 ± 0.012	1.244 ± 0.008
328.15	4.108 ± 0.058	3.221 ± 0.008	2.158 ± 0.057
333.15	6.378 ± 0.068	4.898 ± 0.048	2.928 ± 0.075

Table 2. Optimized Adjustable Parameters in Equation 1 for Irganox 1010 Solubility in Various Alcohol−Water Solvents

solvent	a_0	a_1	a_2	b_0	b_1	10^3rmsd
methanol + water	20.27	−34.08	−1010.12	−8440.65	14933.05	0.22
ethanol + water	18.74	−27.87	0	−7894.37	3471.38	0.18
2-propanol + water	22.74	−48.06	0	−9253.77	11073.34	0.28

and the concentrations of solution were measured by the spectrometer. The average relative uncertainty was 2.7 %.

The solubilities of Irganox 1010 in (methanol + water), (ethanol + water), and (2-propanol + water) with associated standard deviations are listed in Table 1. Six samples were taken and analyzed for each experimental point to minimize the errors. The solubility of Irganox 1010 in (alcohol + water) mixtures at different mole fractions is shown in Figures 2 to 4. From the results, we can see that the solubilities of Irganox 1010 in (alcohol + water) mixtures increase as the temperature and the concentration of alcohol in the mixture solvent increase.

A semiempirical equation as follows was proposed to correlate the experimental data

$$\ln x_1 = (a_0 + a_1 w + a_2 w^2) + (b_0 + b_1 w)/T/\mathrm{K} \qquad (1)$$

where x_1 and T are the mole fraction of the solute and absolute temperature, respectively; w is the mass fraction of water in the solvent mixture; and a_0, a_1, a_2 and b_0, b_1 are empirical constants. The parameter values of a_0, a_1, a_2 and b_0, b_1 are given in Table 2 with the root-mean-square deviation of solubility (rmsd). The rmsd is defined as the following

$$\mathrm{rmsd} = \left[\frac{1}{n}\sum_{j}^{n}(x_{1,j} - x_{1,j}^{\mathrm{calcd}})^2\right]^{1/2} \qquad (2)$$

where n is the number of experimental points; $x_{1,j}^{\mathrm{calcd}}$ is the solubility calculated from eq 1; and $x_{1,j}$ is the experimental value

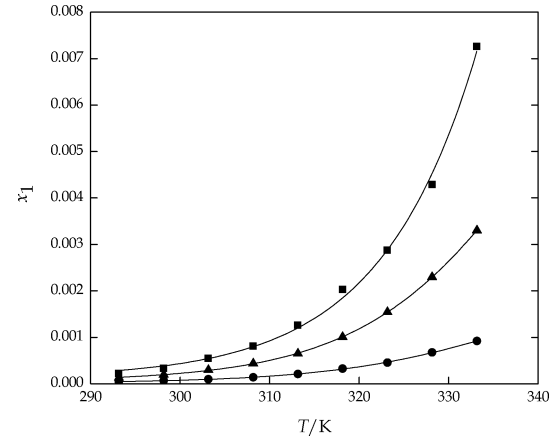

Figure 2. Solubility of Irganox 1010 in methanol (1 − *w*) + water (*w*) solvents from (293.15 to 333.15) K: ■, $w = 0$; ▲, $w = 0.03$; ●, $w = 0.05$. The line is the best fit of the experimental data calculated with the semiempirical eq 1.

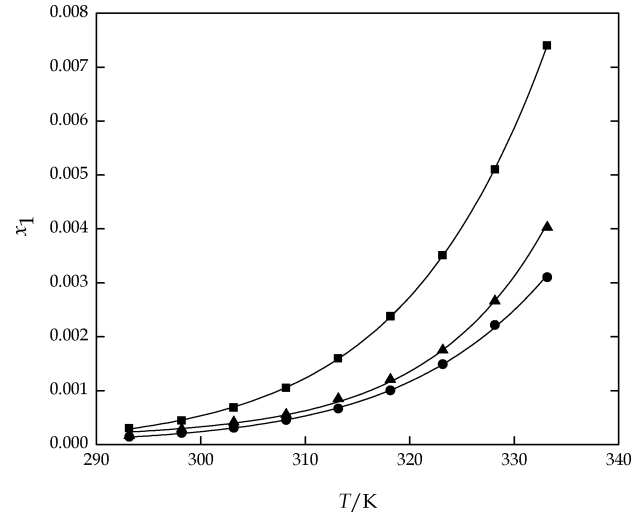

Figure 3. Solubility of Irganox 1010 in ethanol (1 − *w*) + water (*w*) solvents from (293.15 to 333.15) K: ■, $w = 0$; ▲, $w = 0.03$; ●, $w = 0.05$. The line is the best fit of the experimental data calculated with the semiempirical eq 1.

of solubility. Figures 2 to 4 show that the experimental data follow the semiempirical equation with good agreement.

At constant pressure, the solubility of a solid in a liquid as a function of temperature T is expressed by the relation[9]

$$\frac{\partial(\ln x_1)}{\partial\left(\frac{1}{T}\right)} = -\frac{\Delta_{\mathrm{sol}}H_{\mathrm{m}}}{R} \qquad (3)$$

where $\Delta_{\mathrm{sol}}H_{\mathrm{m}}$ is the apparent molar enthalpy of solution and R is the gas constant. From eq 1, eq 3 can be simplified to

$$\Delta_{\mathrm{sol}}H_{\mathrm{m}} = -(b_0 + b_1 w)R \qquad (4)$$

The apparent molar enthalpies of solution could be worked out by eq 4 with the parameters from Table 2 and are presented in Table 3. From the experimental results, it can be seen that the apparent molar enthalpies of Irganox 1010 in alcohol−water mixtures decrease as the concentration of water in the mixture solvent increases.

Conclusion

The solubilities of Irganox 1010 in (methanol + water), (ethanol + water), and (2-propanol + water) were measured in the temperature range from (293.15 to 333.15) K by a static

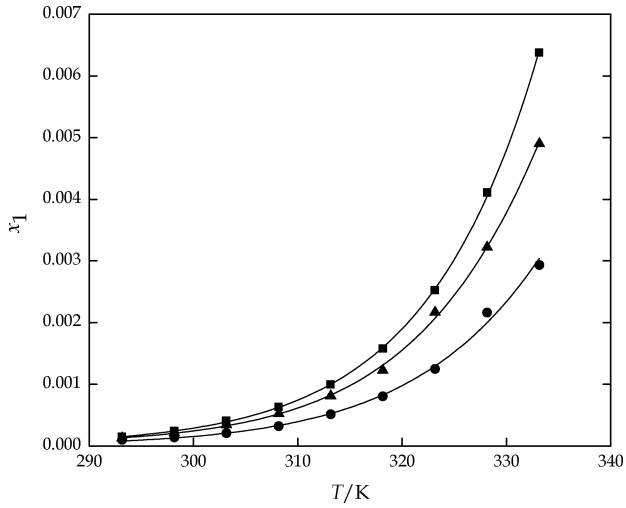

Figure 4. Solubility of Irganox 1010 in 2-propanol (1 − *w*) + water (*w*) solvents from (293.15 to 333.15) K: ■, $w = 0$; ▲, $w = 0.03$; ●, $w = 0.05$. The line is the best fit of the experimental data calculated with the semiempirical eq 1.

Table 3. Apparent Molar Enthalpies of Irganox 1010 in Alcohol (1 − *w*) + Water (*w*) Solvents

	$\Delta_{sol}H_m$		
solvent	$w = 0$	$w = 0.03$	$w = 0.05$
methanol + water	70.18	66.45	63.97
ethanol + water	65.63	64.77	64.19
2-propanol + water	76.94	74.17	72.33

analytical method. The solubility of Irganox 1010 in (alcohol + water) mixtures increases as the temperature and the concentration of alcohol in the mixture solvent increase. For three alcohols, the solubility of Irganox 1010 increases in the order ethanol > methanol > 2-propanol. A semiempirical equation was employed to correlate the experimental data with good agreement. The experimental solubility and correlation equation in this work can be used as essential models in the manufacturing and purifying processes of Irganox 1010 in industry. The apparent molar enthalpy of Irganox 1010 in the three systems has been determined, which provides a heat transmission basis for the design of a crystallizer.

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