Solubility of Decabromodiphenyl Ether in Different Solvents at (283.0 to 323.0) K

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The solubilities of decabromodiphenyl ether (DeBDE) in propanone, ethyl acetate, 1-methyl-4-(1-methylethenyl)cyclohexene, methylbenzene, and tetrahydrofuran were measured in the temperature range of (283.0 to 323.0) K by high-performance liquid chromatography (HPLC). The modified Apelblat equation was used to correlate the relationship between solubility and temperature. The correlated data showed a good agreement with the experimental results. These data of solubility can be used in the optimized separation of decabromodiphenyl ether.

Introduction

Decabromodiphenyl ether (DeBDE, CAS RN: 1163-19-5) is one of the most popular flame retardant additives of polymers in electrical and electronic equipment.[1,2] There are potential risks of bioaccumulation and photoreactivation in the lifetime of deBDE.[3−6] It would be crucial to separate the deBDE additives from the polymeric matrix in the polymer recycling of the waste electrical and electronic equipment plastics. Dissolution of polymer with an appropriate solvent is one of the cheapest and most effective recycling methods.[7] The concentration of deBDE in the recycled polymer will be determined by the solubility of deBDE in the solvent. The solubility of deBDE is also important to optimize the deBDE extraction in the contaminated soil and leachate.

DeBDE is in white powder form, and its chemical structure is shown in Figure 1. The toxicology and water solubility of deBDE were reported by de Wit[5] and Hardy,[8] respectively. An approximately solubility was found in the European Union Risk Assessment Report.[9] However, the solubility of deBDE at various temperatures in the solvents used in solid−liquid extractions and polymer recycling had not been published. In the present work, the solubilities of deBDE in five solvents were measured in the temperature range of (283.0 to 323.0) K. The solvents were chosen because propanone (CAS RN: 67-64-1), ethyl acetate (CAS RN: 141-78-6), methylbenzene (CAS RN: 108-88-3), and tetrahydrofuran (CAS RN: 109-99-9) were often used in the solid−liquid extractions in the literature,[10−13] and 1-methyl-4-(1-methylethenyl)cyclohexene (CAS RN: 138-86-3), which is also called limonene, was suggested as one of safe solvents used in the polystyrene recycling.[14]

Experimental Section

Materials. 1-Methyl-4-(1-methylethenyl)cyclohexene with a mass fraction of 0.951 was supplied by Sucocitrico Cutrale Ltd. (Santos, Brazil). Analytical grade reagents (propanone, ethyl acetate, methylbenzene, and tetrahydrofuran) were purchased from Sinopharm Chemical Reagent Corporation (Shanghai, China) and used without any treatment. High-performance liquid chromatography (HPLC) grade methanol was purchased from Lingfeng Chemical Reagent Corporation (Shanghai, China), and the water, used in the HPLC mobile phase, was purified by distillation twice.

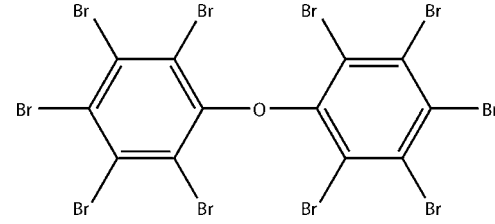

Figure 1. Structure of decabromodiphenyl ether.

The certified deBDE standard solutions, containing deBDE and other seven congeners, were purchased from AccuStand (New Haven, CT, USA). DeBDE solid powder was supplied by Sino-Brom Compounds Corporation (Langfang, China), and its mass fraction was found to be higher than 0.990. This was determined with the certified deBDE standard solutions by HPLC (Agilent 1100 with an autosampler and a varied wavelength detector, Santa Clara, CA, USA). The HPLC chromatograms of the deBDE samples and standards are shown in Figure 2.

Solubility Measurement

The solubilities were measured by the static analytical method.[15,16] Excess deBDE powder was added to 10 mL samples of each of the solvents used in this work, namely, propanone, ethyl acetate, 1-methyl-4-(1-methylethenyl)cyclohexene, methylbenzene, and tetrahydrofuran. The solutes and solvents were mixed well by shaking in the glass test tubes with caps, and then these tubes were placed in a constant-temperature thermostatic bath (Fufang 1250; Jinghua, China) over 24 h, which was sufficient to reach solid−liquid equilibrium, as longer hours would make no difference. The uncertainty of the temperature is 0.1 K. Aliquots of saturated deBDE solution were carefully withdrawn by preheated 1000 μL pipettors (Brand Transferpette, Wertheim, German), transferred into volumetric flasks, and then diluted quantitatively. The sampling procedure was as quick as possible to reduce the loss of the solvent at 323.0 K.

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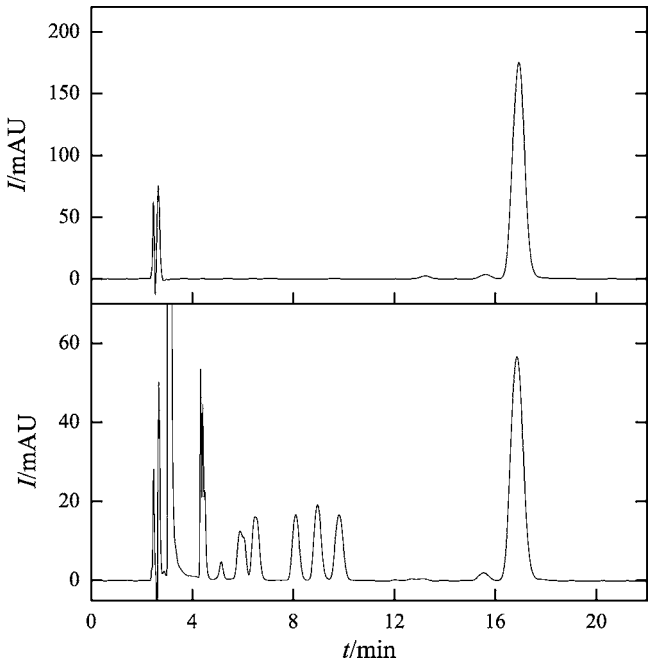

Figure 2. HPLC chromatograms of the certified deBDE standard mixture (bottom), where the retention time for deBDE is 16.9 min, and the deBDE solid powder (top).

The stock reference solution was prepared by diluting the weighed deBDE powder in the volumetric flask by tetrahydrofuran. The uncertainty in weighing was 0.1 mg. The calibration curve was obtained from the reference solutions, which contained (49 to 644) $\mu g \cdot mL^{-1}$ of deBDE and prepared by the consecutive dilutions of the stock reference solution. The solubility of deBDE was determined by HPLC, and each solubility of deBDE in different solvents at various temperatures was measured repeatedly three times. The chromatographic analysis was performed on an Agilent Hypersil ODS column (250 mm × 4.5 mm, 5 μm), and the mobile phase consisted of methanol and water in a volume ratio of 95:5. An isocratic elution scheme with flow rate of 1 $mL \cdot min^{-1}$ was adopted, and the detective wavelength was set to 230 nm. The average relative uncertainty of HPLC calibration was 1.5 %.

Table 1. Mole Fraction Solubilities of DeBDE in Different Solvents at T = (283.0 to 323.0) K

T/K	$10^4\,x$	$10^4\,x^{cal}$	$10^2(x - x^{cal})/x$
	Propanone		
283.0	0.44 ± 0.04	0.45	−1.49
293.0	0.60 ± 0.02	0.63	−5.12
303.0	0.91 ± 0.11	0.87	5.21
313.0	1.19 ± 0.02	1.14	3.72
323.0	1.45 ± 0.06	1.46	−0.34
	Ethyl Acetate		
283.0	1.33 ± 0.17	1.31	1.23
293.0	1.73 ± 0.07	1.81	−4.96
303.0	2.52 ± 0.17	2.49	1.34
313.0	3.46 ± 0.35	3.39	2.07
323.0	4.55 ± 0.24	4.59	−0.92
	1-Methyl-4-(1-methylethenyl)cyclohexene		
283.0	16.16 ± 1.54	17.15	−6.14
293.0	24.18 ± 2.84	22.69	6.18
303.0	28.24 ± 3.53	29.66	−5.04
313.0	39.71 ± 1.49	38.34	3.47
323.0	48.48 ± 2.37	49.04	−1.14
	Methylbenzene		
283.0	27.40 ± 1.94	27.51	−0.41
293.0	36.23 ± 1.38	37.56	−3.67
303.0	52.02 ± 4.16	49.38	5.08
313.0	65.06 ± 2.06	62.76	3.53
323.0	77.07 ± 2.21	77.41	−0.43
	Tetrahydrofuran		
283.0	44.87 ± 2.47	44.64	0.51
293.0	52.35 ± 3.25	52.21	0.27
303.0	60.74 ± 7.70	61.16	−0.69
313.0	69.49 ± 6.22	71.72	−3.21
323.0	85.04 ± 1.06	84.15	1.05

Table 2. Parameters of Modified Apelblat Model Equation 1 for DeBDE in Different Solvents

solvent	A	B/K	C	10^5 rmsd
propanone	95.31	−7021.12	−14.26	0.32
ethyl acetate	−81.53	861.29	12.32	0.56
1-methyl-4-(1-methylethenyl) cyclohexene	−35.11	−725.89	5.54	12.20
methylbenzene	105.98	−7023.07	−15.42	16.82
tetrahydrofuran	−71.04	1735.37	10.54	10.98

Results and Discussion

The solubilities of deBDE in propanone, ethyl acetate, 1-methyl-4-(1-methylethenyl)cyclohexene, methylbenzene, and tetrahydrofuran in the temperature range of (283.0 to 323.0) K are presented in Table 1, where x is the average mole fraction solubility of deBDE taken from three measurements at the same temperature, and expanded uncertainties (coverage factor, $k = 2$) are also shown. To describe the solid−liquid equilibrium behavior of deBDE in different solvents, the relationship between solubility and temperature was correlated by the modified Apelblat equation.[17,18]

$$\ln x = A + \frac{B}{T/\mathrm{K}} + C \ln(T/\mathrm{K}) \qquad (1)$$

The parameters A, B, and C in eq 1 were calculated by the least-squares method. The values of parameters are listed in Table 2 together with the root-mean square deviation (rmsd), which is defined as eq 2, where N is the number of experimental data points and x^{cal} is the mole fraction solubility calculated by the eq 1.

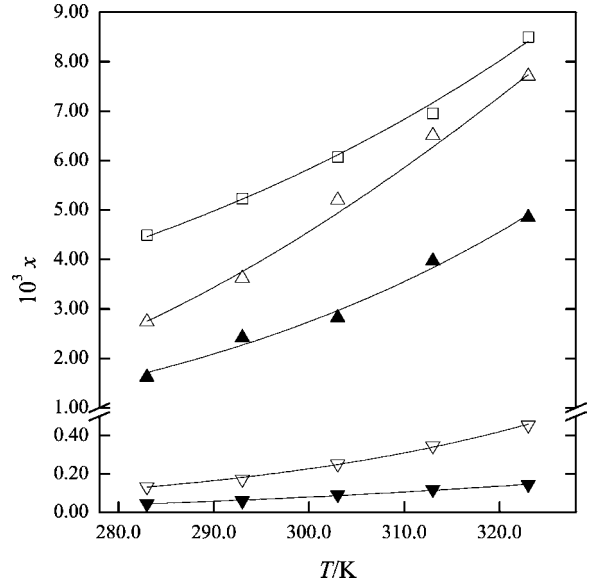

Figure 3. Mole fraction solubilities of deBDE: ▼, propanone; ▽, ethyl acetate; ▲, 1-methyl-4-(1-methylethenyl)cyclohexene; △, methylbenzene; □, tetrahydrofuran; and solid lines represent the correlated curves from eq 1 in the temperature range of (283.0 to 323.0) K.

$$\text{rmsd} = \left[\frac{1}{N}\sum_{i=1}^{N}(x_i - x_i^{\text{cal}})^2\right]^{1/2} \quad (2)$$

The correlated curves for the solubilities of deBDE in different solvents at various temperatures are illustrated in Figure 3. The calculated solubilities show good agreement with the experimental data. It indicates that the modified Apelblat equation describes the solubility of deBDE in the studied solvents as a function of temperature well.

In solid−liquid extraction, the high solubility of deBDE will increase the yield of the solute so that tetrahydrofuran may be a preferable solvent. In polymer recycling, however, the low solubility of deBDE will help to reduce the residual deBDE in the recycled polymer, so ethyl acetate may be more suitable than 1-methyl-4-(1-methylethenyl)cyclohexene in recycling polystyrene waste.

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