Solubility of Naphthalene in Isobutyl Acetate, *n*-Butyric Acid, Ethyl Acetate, *N*-Methyl Pyrrolidone, *N*,*N*-Dimethylformamide, and Tetrahydrofuran

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The solubility of naphthalene in isobutyl acetate, *n*-butyric acid (butanoic acid), ethyl acetate (ethyl ethanoate), *N*-methyl pyrrolidone (1-methyl-2-pyrrolidone), *N*,*N*-dimethylformamide (*N*,*N*-dimethylmethanamide), tetrahydrofuran (oxacyclopentane), and acetone (propanone) between 278 K and 328 K was measured using a laser monitoring observation technique. Results of these measurements were correlated with a semiempirical equation. For the seven solvents studied, the data are well fitted with a semiempirical equation.

Introduction

Naphthalene (CAS registry no. 91-20-3) is a white or almost white crystalline powder. Naphthalene's chemical formula was determined by Michael Faraday in 1826. The structure of two fused benzene rings was proposed by Emil Erlenmeyer in 1866[1] and was confirmed by Carl Graebe 3 years later.

Naphthalene is the most abundant single component of coal tar. Whereas the composition of coal tar varies with the coal from which it is produced, typical coal tar is about 10 % naphthalene by weight. In industrial practice, the distillation of coal tar yields oil containing about 50 % naphthalene, along with a variety of other aromatic compounds. This oil, after being washed with aqueous sodium hydroxide to remove acidic components (chiefly various phenols) and with sulfuric acid to remove basic components, is fractionally distilled to isolate naphthalene. The crude naphthalene resulting from this process is about 95 % naphthalene by weight, which is often referred to as 78 °C (melting point). The chief impurity is the sulfur-containing aromatic compound benzothiophene. Petroleum-derived naphthalene is usually purer than that derived from coal tar. Where required, crude naphthalene can be further purified by recrystallization from any of a variety of solvents, resulting in 99 % naphthalene by weight, which is referred to as 80 °C (melting point).[2,3]

To determine the proper solvent and to design an optimized crystallization process, one must know its solubility in different solvents. In this article, the solubility of naphthalene in isobutyl acetate, *n*-butyric acid, ethyl acetate, acetone, *N*-methyl pyrrolidone (NMP), *N*,*N*-dimethylformamide (DMF), and tetrahydrofuran (THF) between 278 K and 333 K was measured using a laser monitoring observation technique at atmospheric pressure. The method employed in this work was classified as a synthetic method, which was much faster and more reliable than the analytical method.[4]

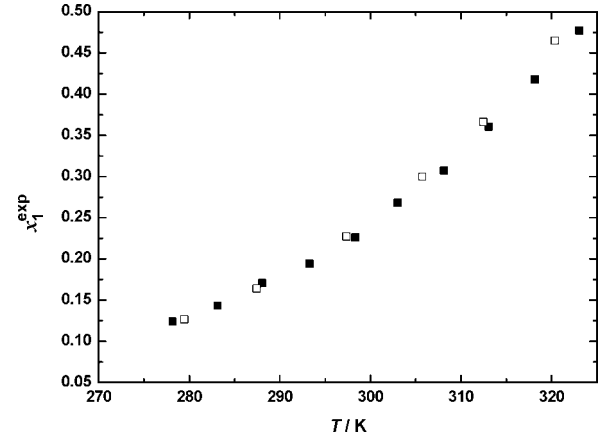

Figure 1. Mole fraction solubility of naphthalene x_1 in acetone: ■, this work; □, literature.[10]

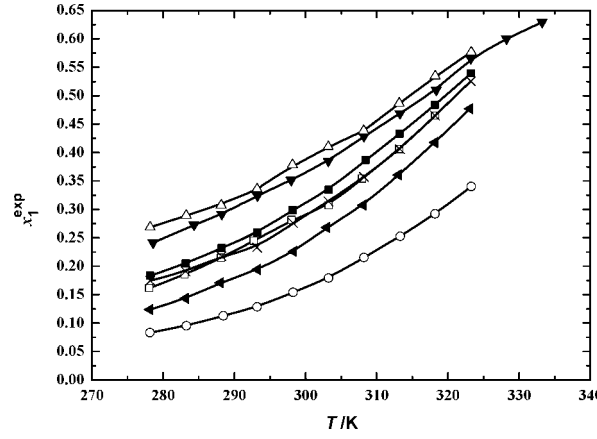

Figure 2. Mole fraction solubility of naphthalene x_1 in different solvents: Δ, NMP; ▼, THF; ■, isobutyl acetate; ×, ethyl acetate; □, DMF; tilted solid triangle, acetone; ○, *N*-butyric acid.

Experimental Section

Materials. Naphthalene (purity 99 %) was purchased from Tianjin Kermel Chemical Reagent and used as received. Its purity was checked by IR spectroscopy, and its melting point (356.90 K) was determined using a differential scanning calorimeter (Shimadzu, Japan). Other reagents were analytical research grade reagents from Shanghai Chemical Reagent. Distilled and deionized water of HPLC grade were used.

Apparatus and Procedure. The solubility was measured by a synthetic method. The laser monitoring observation technique was used to determine the disappearance of the last crystal particles in the solid + liquid mixture, which is similar to refs

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Table 1. Mole Fraction Solubility (x_1) of Naphthalene in Selected Solvents with the Temperature Range from (278.05 to 333.15) K

T/K	x_1^{exp}	x_1^{calc}	T/K	x_1^{exp}	x_1^{calc}
		DMF			
278.05	0.1615 ± 0.0003	0.1624	303.25	0.3071 ± 0.0003	0.3166
283.05	0.1852 ± 0.0003	0.1861	307.95	0.3539 ± 0.0003	0.3568
288.15	0.2150 ± 0.0003	0.2135	313.15	0.4059 ± 0.0003	0.4064
292.75	0.2444 ± 0.0003	0.2412	318.15	0.4649 ± 0.0003	0.4603
298.05	0.2814 ± 0.0003	0.2770			
		Acetone			
278.15	0.1237 ± 0.0002	0.1225	303.00	0.2681 ± 0.0002	0.2685
283.15	0.1433 ± 0.0002	0.1444	308.10	0.3073 ± 0.0002	0.3124
288.05	0.1707 ± 0.0002	0.1691	313.05	0.3606 ± 0.0002	0.3609
293.25	0.1941 ± 0.0002	0.1992	318.15	0.4175 ± 0.0002	0.4174
298.35	0.2260 ± 0.0002	0.2332	323.05	0.4771 ± 0.0002	0.4789
		NMP			
278.18	0.2685 ± 0.0004	0.2665	303.21	0.4101 ± 0.0004	0.4063
283.25	0.2893 ± 0.0004	0.2893	308.17	0.4383 ± 0.0003	0.4436
288.17	0.3073 ± 0.0004	0.3138	313.16	0.4864 ± 0.0003	0.4851
293.20	0.3358 ± 0.0004	0.3416	318.21	0.5346 ± 0.0003	0.5315
298.16	0.3785 ± 0.0004	0.3720	323.27	0.5767 ± 0.0003	0.5831
		Isobutyl Acetate			
278.18	0.1831 ± 0.0004	0.1816	303.23	0.3345 ± 0.0004	0.3372
283.20	0.2047 ± 0.0004	0.2058	308.45	0.3865 ± 0.0004	0.3828
288.22	0.2319 ± 0.0004	0.2331	313.20	0.4327 ± 0.0004	0.4294
293.23	0.2593 ± 0.0004	0.2639	318.17	0.4834 ± 0.0004	0.4839
298.19	0.2989 ± 0.0004	0.2981	323.21	0.5393 ± 0.0004	0.5459
		n-Butyric Acid			
278.17	0.08337 ± 0.00025	0.08218	303.22	0.1791 ± 0.0002	0.1800
283.27	0.09521 ± 0.00025	0.09607	308.20	0.2153 ± 0.0002	0.2112
288.45	0.1127 ± 0.0002	0.1128	313.30	0.2525 ± 0.0002	0.2490
293.20	0.1285 ± 0.0002	0.1309	318.19	0.2921 ± 0.0002	0.2918
298.26	0.1541 ± 0.0002	0.1536	323.28	0.3400 ± 0.0002	0.3445
		Ethyl Acetate			
278.20	0.1744 ± 0.0005	0.1722	303.20	0.3139 ± 0.0004	0.3099
283.17	0.1910 ± 0.0005	0.1917	308.21	0.3571 ± 0.0004	0.3529
288.21	0.2174 ± 0.0005	0.2149	313.23	0.4060 ± 0.0004	0.4034
293.19	0.2330 ± 0.0004	0.2417	318.17	0.4651 ± 0.0004	0.4616
298.25	0.2764 ± 0.0004	0.2735	323.21	0.5257 ± 0.0004	0.5310
		THF			
278.60	0.2412 ± 0.0003	0.2400	308.19	0.4284 ± 0.0003	0.4275
284.35	0.2726 ± 0.0003	0.2710	313.25	0.4685 ± 0.0003	0.4668
288.25	0.2918 ± 0.0003	0.2935	318.35	0.5102 ± 0.0003	0.5087
293.25	0.3242 ± 0.0003	0.3240	323.20	0.5657 ± 0.0003	0.5506
298.00	0.3516 ± 0.0003	0.3549	328.21	0.5999 ± 0.0003	0.5962
303.20	0.3849 ± 0.0003	0.3908	333.22	0.6292 ± 0.0003	0.6440

Table 2. Parameters of Equation *2* for Naphthalene in Different Solvents

solvent	A	B	C	10^3(rmsd)
ethyl acetate	−188.03	6434.2	28.986	4.43
N-butyric acid	−150.15	4199	23.552	2.25
NMP	−97.615	2991.6	15.198	4.91
isobutyl acetate	−76.770	1509.3	12.373	2.49
acetone	−40.240	−587.31	7.1518	7.43
DMF	−52.982	341.69	8.8730	4.41
THF	2.8997	−1600.7	0.25203	6.86

5 and 6. The laser set consists of a laser generator, a photoelectric transformer, and a digital display. The experiment was performed in a cylindrical double-jacketed glass vessel. The volume of this vessel was 150 mL. This vessel was maintained at a desired temperature by circulating water from a water bath with a thermoelectric controller. A condenser was connected to the vessel to prevent the solvents from evaporating. A mercury-in-glass thermometer was inserted into the inner chamber of the vessel (uncertainty of ± 0.05 K). An analytical balance (Sartorius CP124S, Germany) with an uncertainty of ± 0.1 mg was used. The mixtures of solute and solvent in the vessel were stirred with a magnetic stirrer.

Predetermined excess amounts of solvent and naphthalene of known mass were placed in the inner chamber of the vessel. The contents of the vessel were continuously stirred at the required temperature. In the early stage of the experiment, the laser beam was decreased by the undissolved particles of naphthalene in the solution. As the particles of the solute dissolved, the intensity of the laser beam gradually increased. When the solute dissolved completely, the solution was clear, and the laser intensity reached maximum. Then, additional solute of known mass (about 1 mg to 3 mg, which was determined by preliminary experiment) was introduced into the vessel. This procedure was repeated until the penetrated laser intensity could not return a maximum; in other words, the last addition no longer completely dissolved in the solvent. The interval of addition depended on the speed of dissolving at that temperature; it should last more than 30 min. The total amount of the solute consumed was recorded. The same solubility experiment was conducted three times, and each time showed good agreement. The mean values were used to calculate the mole fraction solubility x_1 based on

$$x_1 = \frac{m_1/M_1}{m_1/M_1 + m_2/M_2} \quad (1)$$

where m_1 and m_2 represent the mass of the solute and solvent, respectively, and M_1 and M_2 represent the molecular weight of

the solute and solvent, respectively. The estimated uncertainty of the solubility values based on error analysis and repeated observations was within 1.0 %.

Results and Discussion

The solubility data of naphthalene in isobutyl acetate, *n*-butyric acid, ethyl acetate, acetone, *N*-methyl pyrrolidone, *N*,*N*-dimethylformamide, and THF between 278 K and 328 K is presented in Table 1. The temperature dependence of naphthalene solubility in pure solvents is described by the modified Apelblat equation, which is a semiempirical equation[7−9]

$$\ln x_1 = A + \frac{B}{T/\mathrm{K}} + C \ln(T/\mathrm{K}) \tag{2}$$

where x_1 is the mole fraction solubility of naphthalene, T is the absolute temperature, and A, B, and C are the dimensionless parameters. The calculated solubility values of naphthalene are also given in Table 1. The values of parameters A, B, and C and the square deviations (rmsd) are listed in Table 2. The rmsd is defined as

$$\mathrm{rmsd} = \left[\frac{\sum_{j=1}^{N} (x_{1,j} - x_{1,j}^{\mathrm{calc}})^2}{N-1}\right]^{1/2} \tag{3}$$

where N is the number of experimental points, $x_{1,j}^{\mathrm{calc}}$ represents the solubility calculated from eq 2, and $x_{1,j}$ represents the experimental solubility values.

From data listed in Tables 1 and 2, we can draw the following conclusions: (i) The solubility of naphthalene increases with temperature in the seven solvents (see Figures 1 and 2). The solubility of naphthalene is the lowest in *n*-butyric acid and the largest in NMP. (ii) The experimental solubility and correlation equation in this work can be used as essential data and models in the purification process of naphthalene. The solubility calculated by eq 2 shows good agreement with experimental values.

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