Solubilities of Bis(2,2,6,6-tetramethyl-4-piperidinyl) Maleate in Hexane, Heptane, Octane, *m*-Xylene, and Tetrahydrofuran from (253.15 to 310.15) K

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Using the Glew−Hildebrand saturation technique, the solubilities of bis(2,2,6,6-tetramethyl-4-piperidinyl) maleate in hexane, heptane, octane, *m*-xylene, and tetrahydrofuran at temperatures from 253.15 K to 310.15 K were measured with the help of the classical equilibrium method. The experimental data were correlated with the modified Apelblat equation.

Introduction

Hindered amine light stabilizers (HASL) have been widely used in the synthesis of polypropylene, polyethylene, poly(vinyl chloride), polycarbonate, polystyrene, polyurethane, acrylic polymer, epoxy resin, and other kinds polymeric materials. Now they are noticeable and developing quickly worldwide.[1−3] Bis(2,2,6,6-tetramethyl-4-piperidinyl) maleate (BPMA, CAS RN 69096-19-1) is a key intermediate product for synthesizing HALS.[4−6] The authors[7] developed the new techniqe for synthesizing BPMA using dimethyl maleate and 2,2,6,6-tetramethyl-4-piperidinol as raw materials with zeolite-supported tetraisopropyltitanate as the catalyst and a xylene and ethylbenzene mixture as the solvent, which is characterized by short reaction time, high yield, good selectivity, recycled catalyst, and fewer wastes. But the solubility data of BAMA demanded for crystallization and purification process have not been reported in the literature. In this study, using the Glew−Hildebrand saturation technique,[8] the solubilities of BPMA in hexane, heptane, octane, *m*-xylene, and tetrahydrofuran (THF) were measured with the help of the classical equilibrium method[9] at temperatures from 253.15 K to 310.15 K. The experimental data were correlated with the modified Apelblat equation.[10]

Experimental Section

Materials. BPMA was synthesized and purified using the new technology of the authors.[7] The sample was analyzed with elemental analysis, mass spectrometry, infrared spectrometry, and NMR spectrometry; the results are consistent with theory values. There were no impurity peaks in the ion suppressor chromatographic (ISC) analysis. THF, hexane, heptane, octane, and *m*-xylene were obtained from Shanghai Chemical Corporation of China. They were all analytical reagent grade. THF (≥99.0%), hexane, heptane, octane, *m*-xylene (all ≥99.5%) were treated by appropriate procedures.[11] They were further purified by fractional distillation in a 1.5-m-long column and dehydrated by standing over 0.4-nm activated molecular sieves. There are no impurity peaks in the gas chromatographic analysis.

Densities, ρ, of pure solvents were measured to ±0.0001 $g \cdot cm^{-3}$ with an Anton Paar DMA-45 digital densimeter. Refractive indices, n_D, were measured using an Abbe refractometer. The measured values are reported in Table 1, and the results are consistent with the literature data.[12−15]

Table 1. Densities, ρ, and Refractive Indices, n_D, of the Pure Solvents at 298.15 K and Comparison with Literature Data

	ρ/g·cm^{-3}		n_D	
solvent	exptl	lit	exptl	lit
hexane	0.6551	0.6612[a] 0.65484[b] 0.65507[c]	1.3747	1.3755[a] 1.37226[b] 1.37228[d]
heptane	0.6794	0.6793[a] 0.67946[b]	1.3854	1.3857[a] 1.38511[b] 1.38518[d]
octane	0.6985	0.6984[a] 0.69862[b]	1.3954	1.3956[a] 1.39505[b] 1.39515[d]
m-xylene	0.8603	0.86070[e]	1.4947	1.4946[e]
tetrahydrofuran	0.8819	0.88195[d]	1.4047	1.40496[b] 1.40468[d]

[a] Reference 12. [b] Reference 11. [c] Reference 13. [d] Reference 14. [e] Reference 15.

Apparatus. An LC-10A HPLC, CR-3A automatic data processor, SPD-6AV ultraviolet detector, and L-200SM photoelectric analytical balance were provided by Shimadzu Co. Ltd. Bonded-phase column ZORBAX-ODS C_{18} was obtained from Dupont Co. Ltd. A TSQ700 mass spectrometer of electric spray ionization came from Finnigan MAT Co. Ltd.. A UNITY-400 NMR spectrometer, $CDCl_3$ that served as the solvent, and TMS that served as an internal standard were supplied by Varian Co. Ltd. PE-2400 elemental analysis was obtained from Perkin-Elmer Co. Ltd. The precise temperature controller was from Branun Co. Ltd. (type 850183, Germany).

Measurement of Solubility. The measure methods of solubility involve the equilibrium method and dynamic method.[16,17] The equilibrium method has often been used for systems where the rate of achievement of liquid−solid-phase equilibrium is slow.[18] This study uses the equilibrium method to measure the solubilities of BPMA. The solubilities were measured in a magnetically stirred saturator that was covered with a dark external sheath to protect the solutions from light. Temperatures of the solutions were kept constant by a precise temperature

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controller to within ±0.05 K. Using the Glew−Hildebrand saturation technique,[8] the saturated solutions of BPMA in the various solvents were prepared for all experiments by stirring under thermostated conditions for periods of 20 to 60 h. After saturating, the stirring was stopped. The solutions were kept for 24 h and then filtered through a thermostated funnel into a volumetric flask at constant temperature. In the volumetric flask, a quantitative mobile phase of ISC was placed in advance to keep the saturated solution from precipitating at normal temperature. At the same time, the concentration of BPMA was diluted to a limited range of the calibration curve. The initial builiding-up time of saturated solution is 50 h; then it was analyzed once every 5 h until the analyzing results were replicated three consecutive times. Each experimental data point was replicated at least three times.

Quantitative Analysis of Saturated Solutions. Because there are double bonds, amino groups, and other active groups in the BPMA molecule, if acetonitrile + water and methanol + water are used as mobile phases in common liquid chromatographic method, then there will be some problems such as asymmetric peaks, serious trailing, low resolution, and unstable retention values. Therefore, ion suppressor chromatographic technology[19,20] was adopted. Triethylamine served as the ionic inhibitor, and acetonitrile + citric acid + water served as the mobile phase. Quantitative results were achieved with an external standard method. Using refined BPMA as an external standard, the external standard samples for five systems were prepared and analyzed. Through the analysis procedure of automatically handling quantitative results, the standard curves were acquired. The standard curves used are all straight lines crossing the origin. In the actual analysis, the standard curves were often checked by an external standard sample to improve the analysis accuracy. The total relative deviation of the determination can be limited to the range of ±1%; this is also the accuracy of the determination of solubility.

Results and Discussion

Measured solubilities of BPMA in hexane, heptane, octane, *m*-xylene, and THF at different temperatures T are presented in Table 2, where x is the mole fraction experimental solubility of BMPA. From Table 2, we can find that the solubility of BPMA in THF is much higher than that in other solvents and that the solubility of BPMA in *m*-xylene is higher too, but the solubility of BPMA in paraffins is much lower. The probable reason is that the paraffins are nonpolar solvents; their dipole moments are zero. The dipole moment of *m*-xylene is 0.3 D; however, THF is a polar solvents with a dipole moment of 1.7 D. BPMA contains an amino group, double bonds, and other active groups. The phenomenon conforms to the principle of like dissolves like.

On the basis of the principles of solid−liquid equilibrium, Apelblat[21] used eq 1 to express the solubility of a solid in a liquid as a function of temperature T.

$$\frac{\partial \ln(m/\text{mol}\cdot\text{kg}^{-1})}{\partial(1/(T/\text{K}))}\left[1+\frac{\partial \ln \gamma}{\partial \ln(m/\text{mol}\cdot\text{kg}^{-1})}\right] = -(\Delta H_\text{m}/\text{kJ}\cdot\text{mol}^{-1})/(R/\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}) \quad (1)$$

where ΔH_m is the molar enthalpy of solution, R is the gas constant, T is the absolute temperature, and m and γ are the molality of the solute and its activity coefficient, respectively.

Table 2. Mole Fraction Solubilities x of Bis(2,2,6,6-tetramethyl-4-piperidinyl) Maleate in Different Solvents

T/K	10^3x	10^3x_c[a]	T/K	10^3x	10^3x_c
Hexane					
253.15	0.5275	0.4977	291.05	6.204	6.222
257.65	0.7276	0.6956	293.18	7.091	7.046
262.15	1.025	0.9622	295.25	7.914	7.940
265.05	1.205	1.180	297.65	9.064	9.102
268.85	1.555	1.532	300.05	10.36	10.41
273.65	2.126	2.110	302.05	11.75	11.63
278.25	2.804	2.841	305.86	14.30	14.32
282.65	3.753	3.747	308.25	16.27	16.27
285.66	4.504	4.507	310.15	18.01	17.98
288.86	5.454	5.465			
Heptane					
258.15	0.8902	0.8844	286.25	5.641	5.657
263.15	1.271	1.253	288.45	6.428	6.479
268.15	1.719	1.760	291.05	7.491	7.593
273.15	2.482	2.453	293.05	8.627	8.568
276.25	3.078	3.003	296.45	10.41	10.50
278.05	3.303	3.372	299.05	12.26	12.24
280.15	4.002	3.857	302.25	14.71	14.75
283.15	4.713	4.662	305.05	17.49	17.33
Octane					
257.15	0.9587	0.9751	286.05	6.562	6.536
262.26	1.371	1.384	288.26	7.511	7.505
268.86	2.113	2.154	291.05	8.789	8.924
273.15	2.871	2.859	293.16	9.971	10.16
275.95	3.422	3.431	296.26	11.99	12.28
278.25	4.069	3.981	299.15	14.71	14.63
280.88	4.751	4.717	302.25	17.49	17.62
283.68	5.692	5.629	305.75	21.66	21.69
m-Xylene					
255.15	3.886	3.930	284.05	22.68	22.90
259.05	5.191	5.273	285.45	24.41	24.41
263.13	7.222	7.025	288.07	27.61	27.37
267.85	9.673	9.552	291.65	31.23	30.96
273.16	13.01	13.10	293.18	33.96	33.66
276.35	15.23	15.62	295.95	37.27	37.32
278.26	16.68	17.27	298.07	39.93	40.22
279.37	18.01	18.27	298.85	41.01	41.31
281.95	20.49	20.75	300.85	43.73	44.15
282.66	21.88	21.46	302.10	45.92	45.95
Tetrahydrofuran					
253.15	2.779	2.779	285.65	142.5	141.8
258.15	6.597	6.469	288.15	165.3	167.9
263.15	13.65	13.67	290.05	186.9	188.9
268.15	27.01	26.42	291.65	205.1	207.2
273.15	47.51	46.93	293.18	223.1	225.0
275.15	61.88	60.73	296.03	257.2	258.5
278.25	80.08	77.82	298.18	285.3	283.4
280.15	94.94	92.11	299.65	303.3	300.1
282.65	110.8	113.2	302.05	332.9	326.0

[a] The solubility values calculated from eq 2.

On the basis of the assumption that the activity coefficient is constant and the temperature dependence of the molar enthalpy of solution exhibits straight-line behavior, eq 1 was integrated, and by substituting molar fraction x for m, the equation with three parameters for correlating solubilities was obtained:[10,22]

$$\ln x = A + \frac{B}{T/\text{K}} + C\ln(T/\text{K}) \quad (2)$$

where A, B, and C are parameters. The solubility data of BPMA in hexane, heptane, octane, *m*-xylene, and THF were correlated with eq 2. The values of parameters A, B, and C are presented in Table 3. The calculated solubilities x_c of BPMA using eq 2 are given in Table 2. The calculated

Table 3. Parameters of Correlation Equation for Various Systems

system	*A*	*B*	*C*	10^3rmsd
BPMA + hexane	−12.187	−3925.7	3.6301	0.0407
BPMA + heptane	−77.455	−1205.7	13.522	0.0747
BPMA + octane	−118.02	490.80	19.673	0.106
BPMA + *m*-xylene	319.51	−16973	−46.650	0.274
BPMA + tetrahydrofuran	1183.3	−55796	−175.06	2.40

results show satisfactory agreement with the experimental data. The root-mean-square deviations (rmsd's) are presented in Table 3. The rmsd is defined as

$$\text{rmsd} = \left[\sum_{i=1}^{N} \frac{(x_{ci} - x_i)^2}{N}\right]^{1/2} \qquad (3)$$

where N is the number of experimental points and x_{ci} and x_i refer to the solubility values calculated from eq 2 and to the experimental solubility, respectively.

As can be seen in Table 3, the values of parameters A, B, and C are dependent on solvent polarity. The stronger the solvent polarity, the larger the value of parameter A would be and the smaller the values of parameters B and C would be. For the three kinds of paraffins, the value of parameters A decreases, and the values of parameters B and C increase with the increase in the carbon number of paraffin molecules.

The experimental results show that the solubility of BPMA in THF is higher than the solubility of BPMA in hexane. The change in the solubility with temperature is more sensitive. Hexane should be a better solvent for crystallization and purification processes of BPMA.

It should be noted that the molecule of BPMA contains active groups that are chemically unstable. Although using ISC eliminated most of the interferences of chemical instability with quantitative analysis, sometimes it would lead to the result that the calibration curve is not linear in the wide concentration range or the line did not cross the origin in the quantitative analysis. To reduce the determination error caused by these factors, a series of external standard samples with different concentrations for five systems were prepared and analyzed respectively, and then standard curves that cross the origin for each system were selected. In actual analysis, the concentrations of samples were diluted to a limited range of the calibration curve. These procedures probably introduced the errors in determination.

The usual thermodynamic equation $\ln x = a + bT$ was used to correlate the experimental data. The correlation results for systems of BPMA + hexane, BPMA + heptane, and BPMA + octane are in agreement. But the BPMA + THF and BPMA + m-xylene systems have average relative deviations of 20.6% and 5.04% between experimental data and calculated values, respectively. The equation with three parameters yields an excellent fit, with average relative deviations of 1.28% and 1.11%, respectively, for the BPMA + m-xylene and BPMA + THF systems. But for the BPMA + octane, BPMA + m-xylene, and BPMA + THF systems, it leads to the solubility curve going through a maximum. This is probably concerned with the assumption that the activity coefficient is constant and the temperature dependence of the molar enthalpy of the solution exhibits straight-line behavior or has a limited range of measurement.

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