Articles

Solubility of Imidacloprid in Different Solvents

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The solubilities of imidacloprid in water, methanol, ethanol, acetone, 2-butanone, dichloromethane, 1,2-dichloroethane, and trichloromethane were measured at temperatures from (293.15 to 353.15) K by a synthetic method at atmospheric pressure. The solubilities were correlated by the λh model, in which new parameters were introduced to express the activity coefficients of imidacloprid, determined from the experimental data. The experimental data were also correlated with the Apelblat equation.

Introduction

Imidacloprid (1-[(6-chloro-3-pyridinyl)methyl]-*N*-nitro-2-imidazolidinimine, CAS Registry No. 138261-41-3), which acts on the diverse acetylcholine receptor (nAChR) of insect origin, is a relatively new, selective, long-acting neonicotinoid insecticide which can be used with reasonable environmental safety.[1,2] The pure imidacloprid is obtained by crystallization, but the solubility data for imidacloprid have not been reported. We present solubilities of the imidacloprid in water, methanol, ethanol, acetone, 2-butanone, dichloromethane, and 1,2-dichloroethane and trichloromethane from about (293.15 to 353.15) K by a laser monitoring technique. The experimental data were correlated with the λh model and the Apelblat equation.

Experimental Section

Materials. Imidacloprid crystals (mass fraction purity ≥ 95 %) were recrystallized with acetone at least two times[3] to obtain the purity of 99.5 % by liquid chromatography, and the melting point was (416.95 to 417.35) K determined by a digital melting point apparatus (type RY-51,Shanghai Precision & Scientific Instrument Co. Ltd., China), which compares well with the literature value of (416.95 to 417.95) K.[4] The solvents used in the experiments are of AR grade with mass fraction purity of 99.5 % and were purchased from Laiyang Shuangshuang Co., Ltd. Distilled–deionized water was used.

Procedure. The solubility of a solid in a solvent was measured by a synthetic method.[5,6] The solubility apparatus was composed of a jacketed glass vessel (120 cm^3) kept at the desired temperature by circulating water that was provided by a constant-temperature bath (type CS501, Shanghai Pudong Rongfeng Laboratory Instrument Works Co. Ltd., China). An electric magnetic stirrer (type 85-2, Shanghai Yarong Co. Ltd., China) achieved continuous stirring for the mixing of the solution. A micro thermometer (uncertainty of ± 0.01 K) was used to determine the temperature of the system. A laser beam was used to observe the dissolution of the solid–liquid mixture. The light signal transmitted through the vessel was collected by a detector (type FGF-III), which decided the rate of temperature rise and estimated the equilibrium point of the given system on the basis of the signal change.

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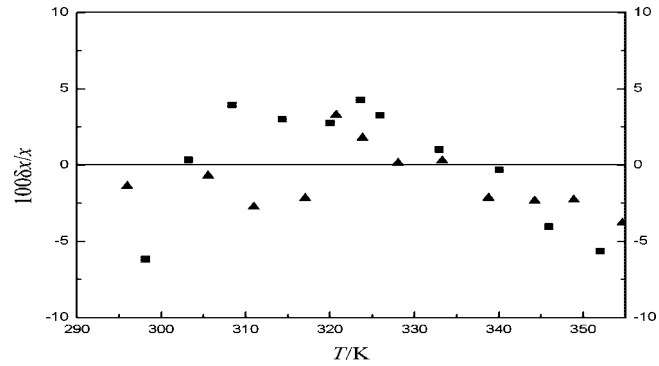

Figure 1. Relative errors of benzoic acid in water from T = (295.95 to 354.64) K. Comparison between the relative deviations of the solubility in this work and the literature[7] correlated with eq 3: ▲, this work; ■, literature.[7]

Table 1. Mole Fraction Solubility x of Benzoic Acid in Water

literature data				experimental data			
T/K	10^4x	10^4x(alp)	100 ADD	T/K	10^4x	10^4x(alp)	100 ADD
298.15	5.03	5.36	6.18	295.95	5.01	5.08	1.38
303.25	6.16	6.14	0.336	305.55	6.51	6.56	0.706
308.45	7.43	7.15	3.96	310.94	7.52	7.73	2.74
314.35	8.89	8.63	2.98	317.05	9.26	9.46	2.17
320.05	10.8	10.51	2.73	320.71	10.8	10.76	3.27
323.65	12.5	11.99	4.26	323.85	12.1	12.08	1.78
325.95	13.5	13.07	3.26	328.06	14.2	14.18	0.141
332.95	17.4	17.22	1.02	333.27	17.5	17.45	0.287
340.05	23.1	23.18	0.332	338.79	21.5	21.96	2.15
345.95	28.8	30.02	4.06	344.25	27.2	27.83	2.33
352.05	37.4	39.63	5.64	348.88	33.5	34.26	2.27
356.25	45.7	48.27	5.32	354.64	43.1	44.73	3.79
100AAD		3.34		100AAD		1.92	

The method for the solubility measurement was based on the fact that the light intensity penetrating through the solution would increase with the dissolution of the solid imidacloprid. When imidacloprid particles disappeared completely, the signal approached maximum value, and the temperature and the mass of the imidacloprid were recorded. At the beginning of the experiment, the mass of the solute and the solvent was given for an electronic analytical balance (type AB204-N, Mettler Toledo Group) with an uncertainty of ± 0.0001 g. The solvent

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Table 2. Mole Fraction Solubility x of Imidacloprid in Different Solvents

T/K	10^5x	$10^5x(\lambda h)$	100ADD	10^5x(alp)	100ADD	T/K	10^5x	$10^5x(\lambda h)$	100ADD	10^5x(alp)	100ADD
					Water						
302.76	2.678	2.316	13.525	2.387	10.842	334.52	16.88	16.42	2.734	16.39	2.892
308.62	3.938	3.417	13.228	3.476	11.736	340.44	23.10	22.85	1.054	22.84	1.114
314.75	4.870	5.059	3.877	5.096	4.640	344.57	28.74	28.65	0.295	28.66	0.277
324.15	8.348	8.991	7.705	8.988	7.667	346.87	32.28	32.45	0.536	32.47	0.585
329.34	11.87	12.20	2.823	12.18	2.649	348.94	36.26	36.28	0.053	36.30	0.112
330.75	13.20	13.24	0.249	13.21	0.069	100AAD			4.190		3.871
					Methanol						
293.79	102.1	93.26	8.652	103.4	1.318	315.38	282.8	287.8	1.794	282.7	0.030
295.38	111.2	101.9	8.390	111.1	0.040	320.59	360.9	370.4	2.636	363.3	0.685
299.81	136.1	129.6	4.809	136.0	0.092	323.37	413.1	422.6	2.290	415.9	0.662
302.15	155.7	146.8	5.721	151.5	2.687	328.11	529.6	527.1	0.481	524.3	1.000
305.86	179.3	178.2	0.584	180.1	0.446	330.75	598.4	595.0	0.580	597.1	0.225
309.32	210.7	212.8	0.979	211.9	0.553	333.34	676.0	669.2	1.009	678.6	0.381
312.62	246.7	251.1	1.817	247.8	0.448	100AAD			2.953		0.639
					Ethanol						
298.69	50.24	56.75	12.95	52.09	3.517	320.74	170.3	166.0	2.543	171.2	0.345
301.12	56.93	64.30	12.95	60.67	6.413	323.96	196.7	192.3	2.257	197.0	0.017
305.66	79.37	80.81	1.822	79.47	0.030	327.54	225.2	225.9	0.292	228.2	1.544
308.87	100.2	94.65	5.524	95.09	5.238	330.06	251.4	252.6	0.496	251.8	1.181
312.34	117.6	111.9	4.838	114.3	3.001	333.57	288.6	294.7	2.123	286.5	0.003
315.96	136.2	132.9	2.401	137.0	0.409	100AAD			4.270		1.756
318.07	151.3	146.7	3.041	151.5	0.056						
					Acetone						
294.64	1198	1156	3.563	1214	1.303	317.25	2323	2361	1.658	2324	0.052
300.05	1414	1380	2.386	1404	0.685	319.14	2478	2500	0.892	2465	0.527
301.76	1484	1458	1.782	1472	0.841	321.59	2645	2690	1.697	2662	0.630
305.05	1617	1619	0.164	1615	0.076	327.89	3253	3243	0.294	3260	0.232
307.77	1745	1764	1.082	1747	0.132	330.2	3526	3471	1.580	3517	0.275
310.17	1873	1901	1.503	1875	0.127	100AAD			1.509		0.444
					2-Butanone						
293.07	1588	1433	9.780	1619	1.914	323.87	4190	4284	2.269	4186	0.085
299.44	1920	1824	5.011	1939	0.970	326.73	4598	4706	2.363	4611	0.293
302.54	2128	2045	3.927	2124	0.210	329.81	5041	5202	3.184	5125	1.657
306.3	2378	2343	1.485	2379	0.029	332.97	5730	5757	0.480	5719	0.197
308.85	2603	2565	1.442	2573	1.146	335.21	6166	6183	0.279	6186	0.323
311.24	2807	2790	0.594	2773	1.216	337.54	6779	6656	1.813	6717	0.914
314.22	3076	3094	0.604	3049	0.893	340.65	7488	7338	2.000	7505	0.225
318.19	3458	3543	2.463	3467	0.240	343.2	8231	7945	3.482	8226	0.064
320.83	3794	3873	2.070	3782	0.328	100AAD			2.544		0.630
					Dichloromethane						
293.97	1318	1356	2.866	1346	2.063	307.80	2110	2106	0.174	2112	0.122
295.96	1458	1447	0.758	1441	1.168	309.60	2231	2226	0.202	2230	0.018
298.00	1567	1546	1.348	1545	1.457	311.66	2361	2371	0.427	2370	0.413
300.05	1664	1651	0.742	1653	0.626	313.14	2475	2479	0.188	2474	0.014
302.60	1768	1791	1.290	1796	1.589	313.93	2540	2539	0.006	2531	0.324
303.99	1890	1871	1.036	1877	0.697	100AAD			0.760		0.730
305.96	1991	1989	0.077	1996	0.274						
					1,2-Dichloroethane						
299.96	986.6	845.3	14.318	1006	2.002	331.34	3090	3204	3.696	3082	0.247
302.87	1076	966.0	10.223	1100	2.224	333.75	3452	3520	1.986	3401	1.463
304.97	1163	1062	8.692	1175	1.041	336.91	3924	3977	1.339	3879	1.169
310.08	1421	1332	6.300	1391	2.114	339.95	4415	4466	1.174	4411	0.076
314.14	1606	1586	1.188	1601	0.264	342.81	4896	4976	1.643	4989	1.903
317.43	1832	1823	0.481	1802	1.633	345.2	5463	5442	0.391	5537	1.341
321.31	2132	2142	0.445	2081	2.409	347.1	6121	5841	4.571	6020	1.640
325.67	2425	2557	5.474	2460	1.443	100AAD			4.291		1.465
328.74	2709	2891	6.729	2776	2.475						
					Trichloromethane						
292.04	848.5	806.2	4.990	882.6	4.021	316.75	1526	1615	5.797	1568	2.756
294.49	916.2	866.0	5.482	921.3	0.555	319.07	1674	1719	2.737	1679	0.341
298.22	1016	964.4	5.073	989.8	2.565	321.74	1834	1848	0.764	1822	0.658
303.84	1149	1131	1.527	1118	2.619	324.64	1984	1997	0.660	1996	0.597
307.04	1230	1237	0.532	1207	1.846	326.71	2147	2111	1.660	2135	0.559
310.05	1319	1344	1.921	1304	1.167	330.16	2403	2316	3.639	2396	0.275
314.03	1427	1499	5.097	1451	1.737	100AAD			3.068		1.515

was loaded into the jacketed vessel, and the corresponding light intensity penetrating through the solution was recorded and considered as the maximum value. Then a quantitative imidacloprid was loaded into the jacketed vessel, and the intensity of the penetrated light would reduce to its minimum value. The heating rate was controlled at 1 $K \cdot h^{-1}$ to approach the solid–liquid equilibrium point. Moreover, to testify the uncertainty of the measurement, a comparison with the literature

Table 3. Parameters of Equation 3 and Equation 4 for Imidacloprid in Different Solvents

	Apelblat equation			λh equation	
solvent	*A*	*B*	*C*	λ	h
water	−74.501	−2185.481	12.441	0.00636	971156.96
methanol	−266.772	8123.122	40.868	0.11523	41424.134
ethanol	344.140	−20532.865	−49.647	0.04368	104445.994
acetone	−244.776	8657.717	37.107	0.16715	16306.150
2-butanone	−247.864	8680.395	37.695	0.37932	8536.098
dichloromethane	71.451	−5898.118	−9.799	0.19326	13913.940
1,2-dichloroethane	−370.663	14085.705	55.948	0.39875	10309.078
trichloromethane	−399.612	16054.250	59.876	0.7763	29440.873

values[7] for the solubility of benzoic acid in water was made. The results were correlated with eq 3, and the relative deviation of solubility values between literature[7] and this work were listed in Table 1 and visually shown by Figure 1. From Figure 1, it can be seen that the relative deviation in the mole fraction solubility was less than 2 %.

Results and Discussion

The solubility data of imidacloprid in different solvents were listed in Table 1. The experimental points and calculated values were shown in Figures 2 and 3, where T is the absolute temperature and x and x(calcd) are the experimental and calculated mole fraction of the solubility, respectively. Moreover, x(λh) and x(alp) are the calculation value of the λh equation and the Apelblat equation, respectively. ADD is the relative error which is defined as follows

$$\mathrm{ADD} = \frac{|x(\mathrm{calcd}) - x|}{x} \tag{1}$$

The average absolute deviation (AAD) is given as follows

$$\mathrm{AAD} = \frac{\sum_{1}^{n} \mathrm{ADD}}{n} \tag{2}$$

where n is the number of experimental values.

The relationship between mole fraction of the solubility and temperature is generally modeled as follows[8]

$$\ln x = A + B/(T/\mathrm{K}) + C \ln(T/\mathrm{K}) \tag{3}$$

where A, B, and C are empirical constants. The values of A, B, and C obtained from the experimental solubility data in the systems are listed in Table 3, respectively.

The λh model developed by Buchowski et al. in 1981,[6,9] which is a semiempirical equation, is shown as follows

$$\ln\left[1 + \frac{\lambda(1-x)}{x}\right] = \lambda \mathrm{h}\left(\frac{1}{(T/\mathrm{K})} - \frac{1}{(T_m/\mathrm{K})}\right) \tag{4}$$

where λ and h are the model parameters determined by the experimental data and are listed in Table 3; x is the mole fraction of the solubility at the system temperature T; and T_m is the normal melting temperature.

From Table 2, Figure 2, and Figure 3: (1) The solubility of imidacloprid in different solvents is in the following order: ketone solvents > chloric alkyl > alcohol > water. It means that the solubility of imidacloprid decreases with the increase of the polarity of the solvents. (2) All the solubility curves are similar (Figure 2 and Figure 3). The solubility behavior of imidacloprid in dichloromethane is exceptive, and the mechanism needs to be further studied. (3) The solubilities of imidacloprid in dichloromethane, acetone, 2-butanone, dichloromethane, 1,2-dichloroethane, and trichloromethane are small at low temperatures but quickly increase at high temperatures. So they can be used for recrystallization of the imidacloprid. (4) According to AAD values in Table 3, it is found that the Apelblat equation was more accurate than the λh equation for this system, which could be used to correlate the solubility data of imidacloprid in industrial production.

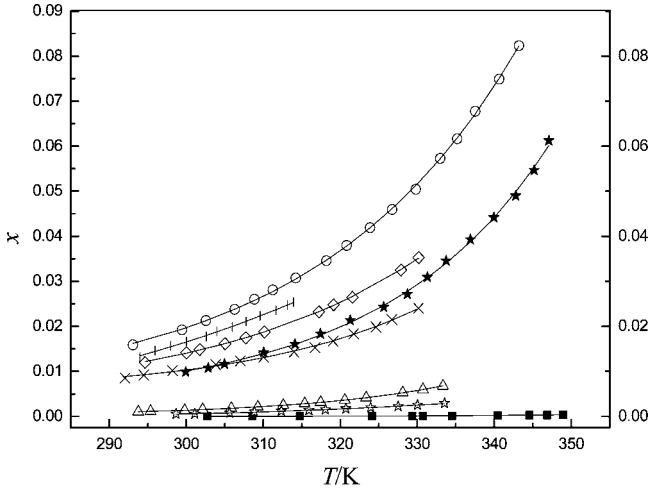

Figure 2. Mole fraction solubility x and calculated values from the λh model of imidacloprid in different solvents from T = (293.15 to 353.15) K: ■, water; △, methanol; ☆, ethanol; ◇, acetone; ○, 2-butanone; |, dichloromethane; ★, 1,2-dichloroethane; ×, trichloromethane; —, calculated values of tie-lines from the λh model at corresponding temperature.

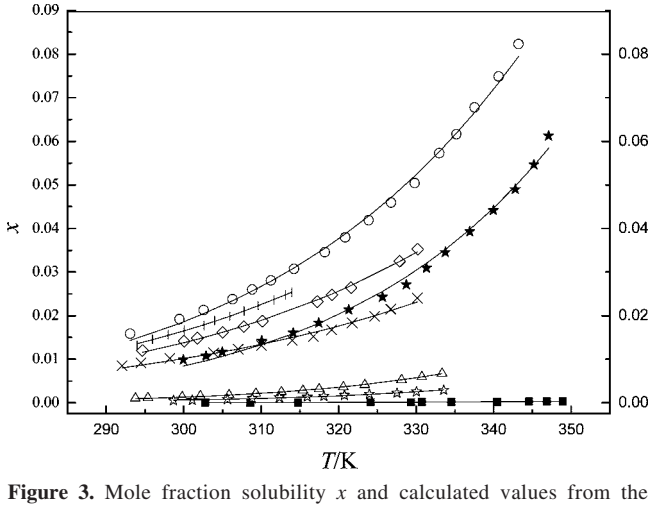

Figure 3. Mole fraction solubility x and calculated values from the Apelblat equation of imidacloprid in different solvents from T = (293.15 to 353.15) K: ■, water; △, methanol; ☆, ethanol; ◇, acetone; ○, 2-butanone; |, dichloromethane; ★, 1,2-dichloroethane; ×, trichloromethane; —, calculated values of tie-lines from the Apelblat equation at corresponding temperature.

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