Solubility of Glyphosate in Ethanol + Water, 1-Propanol + Water, and 2-Propanol + Water from (293 to 333) K

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The solubility of glyphosate in water, ethanol + water, propan-1-ol + water, and propan-2-ol + water was measured by using a laser technique at temperatures from (293 to 333) K at a pressure of 0.1 MPa. The solubility of glyphosate in water and the binary mixtures increases with temperature and mole fraction of water. The solubility data were correlated with a semiempirical equation.

Introduction

N-(Phosphonomethyl)glycine (PMG, CAS No. 1071-83-6), also known as glyphosate, is a herbicide with a broad spectrum of activity.[1] It is very effective even on plant roots and has little harmful effect on the environment because of its biodegradability and absence of toxicity for animal life. Glyphosate forms a pH-dependent zwitterion in solution and possesses three donor groups (an amine group, a carboxylate group, and a phosphonate group) that are responsible for complexation reactions with metal ions and mineral surfaces.[2] Aqueous solubility is an important parameter for assessing environmental partitioning of different compounds. This paper is designed to study the solubility of glyphosate and the effect of organic solvents on the solubility of glyphosate.

Experimental Section

Chemicals. A white crystalline powder of glyphosate was supplied by QCC (Shandong) Co., Ltd. Its mass fraction purity, determined by high-performance liquid chromatography (HPLC), is > 0.98. Ethanol, propan-1-ol, and propan-2-ol, which were all purchased from Beijing Chemical Works, were of analytical grade and dehydrated with molecular sieves of (0.3 to 0.4) nm before use. The purities (mass fraction) of the solvents, determined by gas chromatography, were > 0.99. Deionized water was used throughout all experiments.

Apparatus and Procedure.[1] The solubilities were measured by a synthetic method, and the apparatus for the solubility measurement is the same as that described in the literature.[3–6] The experiments were carried out in a jacketed glass vessel with a working volume of 250 cm^3. Continuous stirring was achieved with a magnetic stir bar, and a thermometer was inserted into the solvent to determine the temperature of the system. The jacketed glass vessel was kept at the desired temperature by circulating water from a thermostat (temperature uncertainty of ± 0.05 K). The mass of the samples and solvents was determined by an electronic analytical balance (Sartorius CP124S, Germany) with a precision of 0.0001 g.

The concentrations of aqueous organic solutions x^o were based on the following equation:

$$x^o = \frac{m_O/M_O}{m_W/M_W + m_O/M_O} \quad (1)$$

where m_W and m_O represent the masses of water and organic solvent, respectively, and M_W and M_O are the molecular weights of water and organic solvent.

The solubility of glyphosate was determined by the laser system. During experiments, the fluid in the glass vessel was monitored by a laser beam. Predetermined solvents were placed in the inner cell of the vessel and were stirred continuously at a required temperature. Glyphosate was added to the vessel simultaneously. In the early stages of the experiment, the intensity of the laser beam increased gradually with the dissolving of the sample particles in the solution. When the solute dissolved completely, the solution was clear, and the laser intensity reached a maximum. Then, a little of the additional solute of known mass was introduced into the vessel. This procedure was repeated until the penetrated laser intensity could not return to the maximum. The same solubility experi-

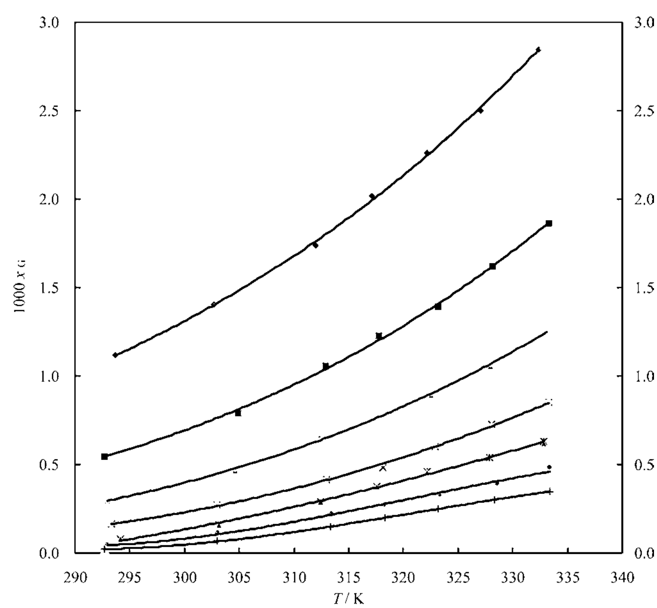

Figure 1. Experimental solubility of glyphosate in aqueous ethanol solution: ◆, $x^o = 0.0000$; ■, $x^o = 0.0417$; ▲, $x^o = 0.0906$; ×, $x^o = 0.1447$; ∗, $x^o = 0.2069$; ●, $x^o = 0.2808$; +, $x^o = 0.3692$.

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ment was carried out three times. The mean values were used to calculate the solubility in mole fraction solubility x_G based on the following equation:

$$x_G = \frac{m_G/M_G}{m_G/M_G + m_W/M_W + m_O/M_O} \quad (2)$$

where m_G, m_W, and m_O represent the mass of the glyphosate, water, and organic solvent, respectively, and M_G, M_W, and M_O are the molecular weights of the glyphosate, water, and organic solvent, respectively. The uncertainty of the experimental solubility values is about 2 %.

Results and Discussion

The solubilities of glyphosate in ethanol + water, propan-1-ol + water, and propan-2-ol + water are listed in Table 1. The relationship between temperature and solubility of glyphosate is correlated with a modified semiempirical equation:[7]

$$\ln x_G = A + \frac{B}{T/\mathrm{K}} + C \ln(T/\mathrm{K}) \quad (3)$$

where x_G is the mole fraction solubility of glyphosate in ethanol + water, propan-1-ol + water, and propan-2-ol + water, T is the absolute temperature, and A, B, and C are the empirical parameters.

The calculated (x_G^{cal}) solubilities of glyphosate in ethanol + water, propan-1-ol + water, and propan-2-ol + water are also presented in Table 1. Values of the empirical parameters A, B, and C are given in Table 2 together with the root-mean-square deviations (rmsd's) calculated according to the formula

$$\mathrm{rmsd} = \left[\sum_{i=1}^{n} \frac{(x_G - x_G^{cal})^2}{N}\right]^{1/2} \quad (4)$$

where N is the number of experimental points, and x_G^{cal} and x_G represent the solubilities calculated from eq 2 and the experimental values, respectively.

Table 1. Mole Fraction Solubility (x_G) of Glyphosate in Different Concentrations of Aqueous Ethanol, 1-Propanol, and 2-Propanol Solutions

T/K	$10^3\ x_G$	$10^3\ x_G^{cal}$	T/K	$10^3\ x_G$	$10^3\ x_G^{cal}$
		Ethanol + Water			
		$x^o = 0.0000$			
293.67	1.120	1.116	322.15	2.260	2.246
302.65	1.401	1.401	327.00	2.501	2.515
311.95	1.740	1.760	332.35	2.847	2.845
317.15	2.017	1.995			
		$x^o = 0.0417$			
292.65	0.5475	0.5432	323.15	1.391	1.407
304.93	0.7881	0.8124	328.15	1.618	1.621
312.87	1.059	1.039	333.30	1.866	1.868
317.80	1.225	1.204			
		$x^o = 0.0906$			
292.93	0.2971	0.2960	322.55	0.8919	0.9016
304.65	0.4686	0.4782	327.95	1.058	1.069
312.35	0.6516	0.6368	333.13	1.259	1.249
317.23	0.7607	0.7553			
		$x^o = 0.1447$			
293.27	0.1623	0.1644	322.88	0.6003	0.6012
302.97	0.2735	0.2664	328.07	0.7245	0.7183
312.95	0.4171	0.4118	333.25	0.8511	0.8471
318.15	0.4857	0.5053			
		$x^o = 0.2069$			
294.15	0.07670	0.07672	322.20	0.4588	0.4540
303.15	0.1601	0.1608	327.90	0.5394	0.5485
312.39	0.2926	0.2891	332.85	0.6323	0.6208
317.61	0.3775	0.3753			
		$x^o = 0.2808$			
292.95	0.04270	0.04371	323.35	0.3282	0.3423
303.05	0.1122	0.1078	328.60	0.3935	0.4077
313.40	0.2213	0.2150	333.35	0.4827	0.4594
318.35	0.2724	0.2772			
		$x^o = 0.3692$			
292.65	0.02210	0.02245	323.15	0.2473	0.2501
303.00	0.06780	0.06664	328.35	0.2986	0.3036
313.36	0.1488	0.1484	333.35	0.3524	0.3479
318.30	0.1946	0.1983			
		Propan-1-ol + Water			
		$x^o = 0.0000$			
293.67	1.120	1.116	317.15	2.017	1.995
298.05	1.245	1.248	322.15	2.260	2.246
302.65	1.401	1.401	327.00	2.501	2.515
307.40	1.580	1.575	332.35	2.847	2.845
311.95	1.740	1.760			
		$x^o = 0.0327$			
293.77	0.6661	0.6627	317.65	1.333	1.323
298.60	0.7593	0.7670	322.70	1.526	1.517
303.15	0.8827	0.8776	327.45	1.705	1.721
308.25	1.015	1.017	332.55	1.969	1.965
312.75	1.150	1.155			
		$x^o = 0.0694$			
293.45	0.4622	0.4602	317.55	0.9682	0.9717
298.55	0.5433	0.5434	322.60	1.123	1.124
303.25	0.6218	0.6308	327.53	1.290	1.290
308.35	0.7399	0.7386	332.68	1.484	1.486
312.85	0.8569	0.8460			
		$x^o = 0.1135$			
293.95	0.3416	0.3358	317.74	0.7435	0.7333
298.85	0.3912	0.3994	322.74	0.8595	0.8487
303.57	0.4655	0.4689	328.05	0.9701	0.9853
308.17	0.5426	0.5452	333.35	1.136	1.137
312.95	0.6351	0.6339			
		Propan-1-ol + Water			
		$x^o = 0.1655$			
293.60	0.2477	0.2473	318.15	0.5261	0.5217
298.60	0.2916	0.2899	322.60	0.5939	0.5921
303.55	0.3344	0.3382	328.10	0.6883	0.6899
308.25	0.3913	0.3901	333.25	0.7932	0.7935
313.45	0.4540	0.4552			
		$x^o = 0.2298$			
293.95	0.2013	0.2068	317.45	0.3723	0.3831
298.55	0.2391	0.2348	321.85	0.4291	0.4264
303.20	0.2767	0.2661	327.15	0.4940	0.4835
307.80	0.3021	0.3003	332.25	0.5419	0.5439
312.85	0.3315	0.3416			
		$x^o = 0.3092$			
293.65	0.1651	0.1687	317.95	0.2586	0.2615
298.35	0.1859	0.1836	322.35	0.2805	0.2832
303.45	0.2063	0.2013	327.55	0.3102	0.3112
308.25	0.2261	0.2195	332.75	0.3478	0.3418
313.25	0.2335	0.2402			
		Propan-2-ol + Water			
		$x^o = 0.0000$			
293.67	1.120	1.116	317.15	2.017	1.995
298.05	1.245	1.248	322.15	2.260	2.246
302.65	1.401	1.401	327.00	2.501	2.515
307.40	1.580	1.575	332.35	2.847	2.845
311.95	1.740	1.760			
		$x^o = 0.0330$			
293.75	0.6540	0.6509	317.70	1.235	1.238
298.47	0.7276	0.7360	322.15	1.405	1.402
303.33	0.8360	0.8370	327.65	1.636	1.637
307.85	0.9455	0.9451	332.70	1.882	1.890
312.85	1.081	1.083			
		$x^o = 0.0697$			
293.45	0.4287	0.4228	318.18	0.8427	0.8367
298.57	0.4729	0.4839	322.60	0.9535	0.9519
303.70	0.5494	0.5561	327.67	1.106	1.106
308.25	0.6354	0.6307	332.90	1.281	1.294
313.40	0.7240	0.7293			
		$x^o = 0.1143$			
293.47	0.2963	0.2985	317.94	0.5499	0.5583
298.37	0.3329	0.3366	322.53	0.6341	0.6318
303.30	0.3855	0.3809	328.25	0.7333	0.7388
308.00	0.4336	0.4297	333.60	0.8571	0.8569
313.03	0.4810	0.4900			
		$x^o = 0.1667$			
293.60	0.2341	0.2325	317.65	0.4164	0.4160
298.55	0.2552	0.2586	322.40	0.4782	0.4748
303.85	0.2954	0.2922	327.45	0.5553	0.5492
308.51	0.3316	0.3274	332.20	0.6284	0.6328
313.20	0.3622	0.3693			
		$x^o = 0.2313$			
293.85	0.1777	0.1770	317.65	0.3007	0.2933
298.45	0.1944	0.1928	322.48	0.3303	0.3306
303.64	0.2127	0.2139	327.75	0.3839	0.3787
308.25	0.2328	0.2360	332.65	0.4268	0.4318
313.05	0.2610	0.2630			
		$x^o = 0.3100$			
293.66	0.1319	0.1324	317.50	0.1867	0.1835
298.45	0.1403	0.1391	322.65	0.2053	0.2015
303.55	0.1471	0.1481	328.15	0.2241	0.2244
308.30	0.1578	0.1583	333.15	0.2457	0.2490
313.05	0.1640	0.1703			

Table 2. Parameters of Equation 3 for Glyphosate in Aqueous Ethanol, 1-Propanol, and 2-Propanol Solutions

binary system	x^o	A	B	C	10^5 rmsd
ethanol + water	0.0000	−53.7776	185.561	8.15643	1.36
	0.0417	−17.0493	−2054.60	2.91459	1.57
	0.0906	82.4149	−7133.55	−11.6529	0.97
	0.1447	199.422	−13013.3	−28.8258	0.86
	0.2069	986.147	−50599.0	−144.896	0.58
	0.2808	1068.82	−54729.0	−157.048	1.21
	0.3692	1305.17	−66416.1	−191.747	0.31
propan-1-ol + water	0.0000	−53.7776	185.561	8.15643	1.36
	0.0327	−32.1329	−1157.26	5.05967	0.80
	0.0694	−23.2293	−1737.03	3.77784	0.50
	0.1135	33.1339	−4461.43	−4.56693	0.80
	0.1655	−33.1715	−1271.31	5.13832	0.23
	0.2298	−16.8887	−1688.85	2.48976	0.75
	0.3092	−80.8128	1853.56	11.5822	0.45
propan-2-ol + water	0.0000	−53.7776	185.561	8.15643	1.36
	0.0330	−161.024	4864.14	24.1304	0.43
	0.0697	−187.330	5981.26	28.0156	0.71
	0.1143	−170.522	5359.4	25.3686	0.52
	0.1667	−271.069	10024.5	40.2237	0.42
	0.2313	−256.600	9591.44	37.8883	0.33
	0.3100	−268.524	10708.3	39.2661	0.29

Table 3. Parameters of Equation 5 for Glyphosate in Aqueous Ethanol, 1-Propanol and 2-Propanol Solutions

binary system		a	b	c
ethanol + water	A	−170.020	4104.55	176.562
	B	5612.43	−203189	0.00000
	C	25.3580	−603.295	−28.5072
propan-1-ol + water	A	−11.7067	−261.039	684.148
	B	−1818.84	3972.18	0.00000
	C	1.93854	41.4423	−116.807
propan-2-ol + water	A	−102.809	−713.627	478.700
	B	2391.07	28286.7	0.00000
	C	15.4472	106.409	−80.6969

Meanwhile, to each binary system, values of the empirical parameters A, B, and C change with the variation of the concentration of aqueous organic solutions x^o. The correlation is based on the following equation:

$$y = a + bx^o + c(x^o)^2 \quad (5)$$

where y represents the empirical parameter A (B or C), x^o is the concentration of aqueous organic solutions, and a, b, and c are parameters, the values of which are shown in Table 3.

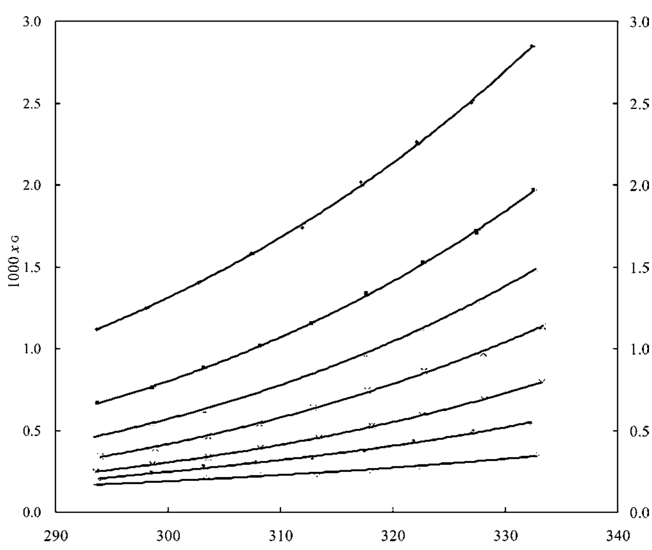

Figure 2. Experimental solubility of glyphosate in aqueous propan-1-ol solution: ◆, $x^o = 0.0000$; ■, $x^o = 0.03265$; ▲, $x^o = 0.06944$; ×, $x^o = 0.1135$; ∗, $x^o = 0.1655$; ●, $x^o = 0.2298$; +, $x^o = 0.3092$.

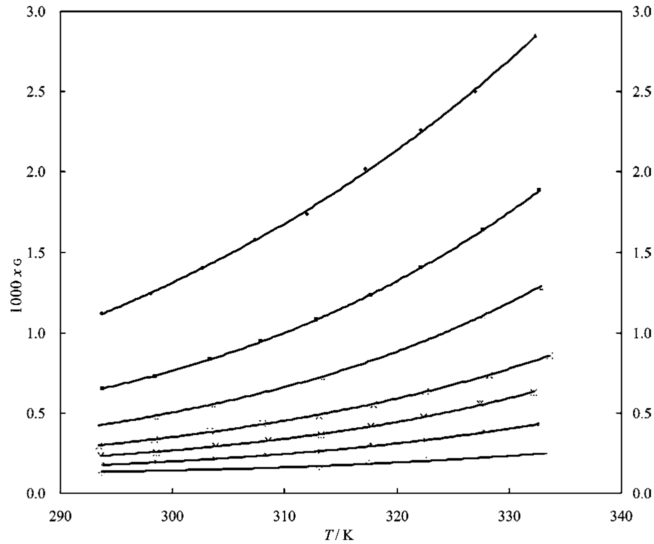

Figure 3. Experimental solubility of glyphosate in aqueous propan-2-ol solution: ◆, $x^o = 0.0000$; ■, $x^o = 0.03305$; ▲, $x^o = 0.06970$; ×, $x^o = 0.1143$; ∗, $x^o = 0.1667$; ●, $x^o = 0.2313$; +, $x^o = 0.3100$.

From Table 1 and Figures 1, 2, and 3, we can draw the following conclusions: (1) The solubility of glyphosate in pure water, ethanol + water, propan-1-ol + water, and propan-2-ol + water increases with temperature. (2) The solubility of glyphosate in ethanol + water, propan-1-ol + water, and propan-2-ol + water decreases with decreasing mole fraction of water. (3) The calculated solubilities of glyphosate in aqueous organic solutions show good agreement with the experimental values, and the experimental solubility and correlation equation in this work can be used as essential data and models in the practical purification process of glyphosate.

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