

Thermodynamic Functions for Transfer of Some Substituted Benzoic Acids, Pyridinecarboxylic Acids, and Naphthoic Acids from Water to Methanol + Water Mixtures at 35 °C

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The solubilities of benzoic, 3-methylbenzoic, 4-methylbenzoic, 2-aminobenzoic, 3-aminobenzoic, 4-aminobenzoic, 2-nitrobenzoic, 3-nitrobenzoic, 4-nitrobenzoic, pyridine-2-carboxylic, pyridine-4-carboxylic, 1-naphthoic, and 2-naphthoic acids have been determined in water and methanol (1) + water (2) mixtures ($x_1 = 0, 5.9, 19.6, \text{ and } 36.0 \text{ mol } \%$) at five temperatures, 35, 45, 55, 65, and 75 °C, respectively. From the solubility data, the values of the free energy of solution of these acids were found, and from these ΔG_s° values, the thermodynamic functions for the transfer of the acids from water to water + methanol were derived. The results are discussed on the basis of the sign of transfer functions and in terms of solute-solvent interactions.

Introduction

In this paper the solubilities of benzoic, 3-methylbenzoic, 4-methylbenzoic, 2-aminobenzoic, 3-aminobenzoic, 4-aminobenzoic, 2-nitrobenzoic, 3-nitrobenzoic, 4-nitrobenzoic, pyridine-2-carboxylic, pyridine-4-carboxylic, 1-naphthoic, and 2-naphthoic acids are reported in methanol (1) + water (2) mixtures ($x_1 = 0, 5.9, 19.6, \text{ and } 36 \text{ mol } \%$), at four different temperatures, 35, 45, 55, 65, and 75 °C, respectively. From the solubility data, the values of the free energy of solution have been computed, and from these ΔG_s° values, the values of thermodynamic functions for the transfer of the acids from water to methanol + water were derived. The results are discussed in terms of these parameters and solute-solvent interactions.

Experimental Section

The methanol was a reagent-grade chemical (Merck) and was used without purification. Water was distilled twice using an all-glass apparatus. The acids were also products of Merck and for synthesis were recrystallized from ethanol + water mixtures, dried at 105 °C, and stored in a desiccator over P_2O_5 . The solvents were prepared by mixing weighed quantities of water and cosolvent.

For the solubility measurements, an excess of acid was added to water or the mixed solvent in order to obtain saturated solutions, which were then agitated by a magnetic stirrer for 24 h at from 75 to 80 °C, transferred to a thermostated bath at five different temperatures (35-75 °C), and left for at least 3 days with continued stirring to attain equilibrium. Two aliquots of the same sample and four samples for each experiment were removed and analyzed by a titration method. The total solubility of each acid was quantified by titrating aliquots with standard NaOH solution and phenolphthalein indicator for water and mixed solvents. The values of solubilities were reproduced in these runs within $\pm 0.3-1 \%$. The samples were removed with a calibrated 5 cm^3 pipet which was washed carefully with the same solvent so that no acid could remain inside the pipet, and the solution was diluted to 50 cm^3 before titration.

Results and Discussion

The solubilities of the acids ($S, \text{ mol}\cdot\text{dm}^{-3}$) in different solvents and at various temperatures are recorded in Table I. No corrections were made for the ionization of the acids either in water or in the mixed solvents. The free energies

of solutions (ΔG_s°) of the acids at different temperatures were calculated using eq 1 and fitted by the method of least

$$\Delta G_s^\circ = -RT \ln S \quad (1)$$

squares to an equation of the form

$$\Delta G_s^\circ / (\text{kJ}\cdot\text{mol}^{-1}) = a + b(T/K) + c(T/K) \ln(T/K) \quad (2)$$

The values of the coefficients $a, b,$ and c are given in Table II. These are found to reproduce the experimental data to within $\pm 0.02 \text{ kJ}\cdot\text{mol}^{-1}$. The standard thermodynamic functions for transfer, i.e., standard Gibb's free energies (ΔG_{tr}°), entropies (ΔS_{tr}°), and enthalpy (ΔH_{tr}°), of acids from the reference solvent water to the methanol + water mixtures were calculated using eqs 3-5, where $T = 308.15 \text{ K}$ and

$$\Delta G_{tr}^\circ / (\text{kJ}\cdot\text{mol}^{-1}) = (a_s - a_w) + (b_s - b_w)T + (c_s - c_w) \ln T \quad (3)$$

$$\Delta S_{tr}^\circ / (\text{kJ}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}) = (b_w - b_s) + (c_w - c_s) + (c_w - c_s) \ln T \quad (4)$$

$$\Delta H_{tr}^\circ / (\text{kJ}\cdot\text{mol}^{-1}) = (a_s - a_w) - T(c_s - c_w) \quad (5)$$

subscripts s and w refer to the solvent mixtures and water, respectively. It was assumed that the ratio of the activity coefficients of the uncharged acid in the saturated solutions in water and in solvent mixtures is unity. This may not be correct in the case of acids and solvents where the solubility is high. The maximum uncertainties in the transfer function values were calculated from standard deviations associated with the coefficients $a, b,$ and c and were $\pm 5 \%$ in ΔG_{tr}° and ΔH_{tr}° and $\pm 10 \%$ in ΔS_{tr}° . The thermodynamic transfer functions are collected in Table II.

Table II shows that the ΔG_{tr}° values for all acids are negative and decrease with the addition of methanol in water. This decrease indicates preferential solvation of the acid molecules by alcohol. The values of ΔH_{tr}° for all acids in methanol + water mixtures have been found different. These values for 4-methylbenzoic, 4-aminobenzoic, 3-aminobenzoic, 4-nitrobenzoic, pyridine-2-carboxylic, and pyridine-4-carboxylic acids have been found to be negative, while those for all other acids are positive. As our solvent mixtures are mostly water-rich, the decrease in ΔH_{tr}° values for the above compounds is governed by the entropy term ΔS_{tr}° .

Table I. Solubilities, S , of Carboxylic Acids in Methanol (1) + Water (2) at Various Temperatures

$t/^\circ\text{C}$	$S/(\text{mol}\cdot\text{dm}^{-3})$								
	$x_1 = 0.0$	$x_1 = 0.059$	$x_1 = 0.196$	$x_1 = 0.36$	$t/^\circ\text{C}$	$x_1 = 0.0$	$x_1 = 0.059$	$x_1 = 0.196$	$x_1 = 0.36$
Benzoic Acid									
35	0.0402	0.0418	0.1983	1.026	65	0.1236	0.1400	0.5648	4.143
45	0.0531	0.0609	0.2789	1.719	75	0.1840	0.2180	0.8113	6.051
55	0.0817	0.0915	0.3952	2.725					
3-Methylbenzoic Acid									
35	0.0047	0.0104	0.0617	0.1420	65	0.0162	0.0232	0.2376	1.525
45	0.0071	0.0135	0.0987	0.3757	75	0.0247	0.0310	0.3602	2.435
55	0.0101	0.0176	0.1546	0.8216					
4-Methylbenzoic Acid									
35	0.0020	0.0055	0.0173	0.0786	65	0.0116	0.0138	0.0638	0.3000
45	0.0036	0.0065	0.0246	0.1266	75	0.0192	0.1827	0.1141	0.4389
55	0.0064	0.0075	0.0382	0.1972					
2-Aminobenzoic Acid									
35	0.0452	0.0610	0.0980	0.3140	65	0.1685	0.3257	0.4709	1.8373
45	0.0735	0.1179	0.1751	0.5819	75	0.2402	0.4759	0.7182	3.1471
55	0.1137	0.2052	0.3000	1.0472					
3-Aminobenzoic Acid									
35	0.0188	0.0412	0.0450	0.1915	65	0.2010	0.1920	0.3089	0.4362
45	0.0469	0.0741	0.0911	0.2488	75	0.3550	0.2859	0.5280	0.5672
55	0.1026	0.1266	0.1697	0.3318					
4-Aminobenzoic Acid									
35	0.0083	0.0550	0.1703	0.2163	65	0.0383	0.2126	0.8055	1.0031
45	0.0154	0.0919	0.2967	0.3536	75	0.0552	0.3108	1.2700	1.7262
55	0.0243	0.1417	0.4874	0.5868					
2-Nitrobenzoic Acid									
35	0.0460	0.0560	0.2100	0.806	65	0.2614	0.3695	2.7710	4.073
45	0.0795	0.0985	0.5238	1.454	75	0.4822	0.7504	5.5692	6.314
55	0.1447	0.1835	1.2760	2.500					
3-Nitrobenzoic Acid									
35	0.0142	0.0329	0.0850	1.2490	65	0.0800	0.2222	3.4841	5.2657
45	0.0375	0.0612	0.4120	2.2776	75	0.1383	0.4291	6.7816	6.8523
55	0.0457	0.1149	1.4098	3.6624					
4-Nitrobenzoic Acid									
35	0.0020	0.0030	0.0071	0.0171	65	0.0063	0.0091	0.0299	0.0737
45	0.0030	0.0045	0.0113	0.0286	75	0.0088	0.0124	0.0453	0.1155
55	0.0044	0.0065	0.0179	0.0460					
Pyridine-2-carboxylic Acid									
35	0.0347	0.4260	2.9410	3.274	65	0.2084	3.2704	5.8980	6.4977
45	0.0696	0.8502	3.8153	4.2840	75	0.3211	6.3050	7.2367	7.577
55	0.1256	1.6774	4.8180	5.4036					
Pyridine-4-carboxylic Acid									
35	0.0187	0.0232	0.0314	0.0469	65	0.0865	0.0891	0.0926	0.1153
45	0.0340	0.0375	0.0464	0.0623	75	0.1283	0.1314	0.1258	0.2585
55	0.0554	0.0585	0.0664	0.0843					
1-Naphthoic Acid									
35	0.0011	0.0015	0.0039	0.0416	65	0.0058	0.0058	0.0213	0.1071
45	0.00176	0.0022	0.0079	0.0616	75	0.0116	0.0112	0.2910	0.1303
55	0.0031	0.0036	0.0140	0.0830					
2-Naphthoic Acid									
35	0.0025	0.0049	0.0071	0.0119	65	0.0082	0.0155	0.0500	0.0968
45	0.0039	0.0077	0.0150	0.0247	75	0.1120	0.0205	0.0775	0.1780
55	0.0058	0.0121	0.0286	0.0490					

Table II. Coefficients of Equation 2 and Thermodynamic Transfer Functions of Carboxylic Acids from Water to Methanol (1) + Water (2) at 35 °C^a

$x_1/$ (mol %)	a	b	c	$-\Delta G_{tr}^\circ/$ (kJ·mol ⁻¹)	$\Delta H_{tr}^\circ/$ (kJ·mol ⁻¹)	$T\delta S_{tr}^\circ/$ (kJ·mol ⁻¹)	$x_1/$ (mol %)	a	b	c	$-\Delta G_{tr}^\circ/$ (kJ·mol ⁻¹)	$\Delta H_{tr}^\circ/$ (kJ·mol ⁻¹)	$T\delta S_{tr}^\circ/$ (kJ·mol ⁻¹)
Benzoic Acid													
0	15.208	0.412	-0.0755				19.6	77.307	-0.955	0.126	4.20	0.16	4.36
5.9	-103.573	2.819	-0.428	0.56	-10.00	-9.45	36.0	93.275	-1.222	0.161	8.70	5.34	14.05
3-Methylbenzoic Acid													
0	-57.297	1.897	-0.287				19.6	19.855	0.462	-0.084	6.59	8.00	14.59
5.9	-53.895	1.593	-0.237	1.98	-12.00	-10.02	36.0	424.917	-7.693	1.105	8.70	53.84	62.54
4-Methylbenzoic Acid													
0	3.188	0.868	-0.868				19.6	-268.553	6.345	-0.949	5.52	-23.68	-18.16
5.9	50.333	-0.514	0.069	2.58	-18.49	-15.9	36.0	48.597	-0.307	0.030	9.38	-8.21	1.17

Table II. (Continued)

x_1 / (mol %)	a	b	c	$-\Delta G_{tr}^\circ$ / (kJ·mol ⁻¹)	ΔH_{tr}° / (kJ·mol ⁻¹)	$T\Delta S_{tr}^\circ$ / (kJ·mol ⁻¹)	x_1 / (mol %)	a	b	c	$-\Delta G_{tr}^\circ$ / (kJ·mol ⁻¹)	ΔH_{tr}° / (kJ·mol ⁻¹)	$T\Delta S_{tr}^\circ$ / (kJ·mol ⁻¹)
2-Aminobenzoic Acid													
0	88.068	-1.174	0.159				19.6	106.800	-1.442	0.194	2.02	7.95	9.97
5.9	224.812	-3.861	0.550	0.81	16.26	17.07	36	22.698	0.403	-0.082	4.99	8.89	13.89
3-Aminobenzoic Acid													
0	262.967	-4.295	0.606				19.6	92.705	-0.959	0.119	2.34	-20.19	-17.95
5.9	162.659	-2.595	0.365	2.01	-26.04	-24.03	36.0	-20.253	0.834	-0.132	5.93	-55.81	-49.88
4-Aminobenzoic Acid													
0	170.565	-2.77	0.394				19.6	34.957	0.066	-0.029	7.73	-5.269	2.47
5.6	82.966	-1.026	0.136	4.85	-8.09	-3.25	36.0	-108.239	3.073	-0.473	8.37	-11.64	-3.27
2-Nitrobenzoic Acid													
0	-103.633	3.094	-0.477				19.6	173.688	-2.300	0.305	3.90	36.35	40.25
5.9	-212.710	5.452	-0.827	0.52	-1.238	-0.70	36.0	103.878	-1.351	0.177	7.34	5.983	13.32
3-Nitrobenzoic Acid													
0	-3.137	0.847	-0.142				19.6	801.732	-15.017	2.168	4.45	93.04	97.49
5.9	-105.712	3.139	-0.485	2.00	3.12	5.12	36.0	287.915	-5.372	0.772	11.31	9.40	20.71
4-Nitrobenzoic Acid													
0	53.908	-0.491	0.064				19.6	-34.609	1.476	-0.231	3.32	2.39	5.71
5.9	64.373	-0.735	0.100	1.13	-0.628	0.50	36.0	12.907	0.518	-0.092	5.57	7.07	12.64
Pyridine-2-carboxylic Acid													
0	202.868	-3.318	0.469				19.6	39.983	-0.491	0.061	11.36	-37.16	-25.79
5.9	-26.033	1.616	-0.266	6.158	-2.41	4.01	36.0	98.822	-1.723	0.243	11.64	-34.40	-22.77
Pyridine-4-carboxylic Acid													
0	143.887	-2.193	0.307				19.6	47.032	-0.416	0.051	1.33	-17.97	-16.64
5.9	45.408	-0.242	0.022	0.56	-10.66	-10.19	36.0	-59.666	1.755	-0.268	2.36	-26.37	-24.01
1-Naphthoic Acid													
0	-248.000	6.146	-0.922				19.6	347.476	-6.353	0.921	3.33	27.56	30.89
5.9	-207.476	5.135	-0.769	0.84	-6.62	-5.79	36	155.073	-2.734	0.394	9.40	-2.63	6.78
2-Naphthoic Acid													
0	95.910	-1.369	0.193				19.6	243.810	-4.104	0.585	2.68	26.71	29.39
5.9	123.187	-1.956	0.279	1.74	0.78	2.526	36.0	34.437	0.359	-0.076	4.00	21.42	25.42

^a Maximum uncertainties in ΔG_{tr}° and ΔH_{tr}° are ± 0.02 kJ·mol⁻¹, and those in $T\Delta S_{tr}^\circ$ are ± 0.1 kJ·mol⁻¹. The R^2 in regression was better than 0.98. The standard error of estimate was less than 0.02, and the estimated standard deviations of the coefficients b and c were less than 0.03%.

Most of the studies on the solubilities of different electrolytes and nonelectrolytes in mixed solvents have been explained on the basis of maxima or minima in the $T\Delta S_{tr}^\circ$ -composition profile based on the scaled particle theory and recent statistical theories of preferential solvation (1-10). All these calculations explain the solute-solvent interactions and the structure of the solvent systems. Due to the unavailability of various parameters used in the above referred to calculations (1-10), we have not attempted to divide our derived thermodynamic transfer functions into components nor explain the maxima or minima in these function-composition profiles.

Literature Cited

- (1) Das, K.; Das, A. K.; Bose, K.; Kundu, K. K. *J. Phys. Chem.* 1978, 82, 1442.

- (2) Datta, J.; Kundu, K. K. *J. Phys. Chem.* 1982, 86, 4055.
 (3) Talukdar, H.; Rudra, S. P.; Kundu, K. K. *Can. J. Chem.* 1988, 66, 461; 1989, 67, 315.
 (4) Chatterjee, J. P.; Basumallick, I. N. *J. Chem. Soc., Faraday Trans. 1* 1988, 84, 2697.
 (5) Marcus, Y.; Kamlet, M. J.; Taft, R. W. *J. Phys. Chem.* 1988, 92, 3613.
 (6) Marcus, Y. *J. Chem. Soc., Faraday Trans. 1* 1988, 84, 1465; 1989, 85, 3019; *Pure Appl. Chem.* 1990, 62, 2069.
 (7) Rudra, S. P.; Chakravorty, B. P.; Kundu, K. K.; Basumallick, I. N. *Z. Phys. Chem.* 1986, 150, 211.
 (8) Juillard, J. *J. Chem. Soc., Faraday Trans. 1* 1982, 78, 43.
 (9) Visser, C.; Perron, G.; Desnoyer, J. P. *J. Am. Chem. Soc.* 1977, 99, 5894.
 (10) Acree, W. E., Jr. *J. Phys. Chem. Liq.* 1990, 22, 107.

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