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Solubility and Activity Coefficients of Acidic and Basic Nonelectrolytes in Aqueous Salt Solutions. 2. Solubility and Activity Coefficients of Suberic, Azelaic, and Sebacic Acids in NaCl(aq), $(CH_3)_4NCl(aq)$, and $(C_2H_5)_4NI(aq)$ at Different Ionic Strengths and at $t = 25$ °C

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The solubility of three dicarboxylic acids, $(COOH)-(CH_2)_n-(COOH)$ ($n = 6, 7, 8$), was determined in NaCl(aq) (0.5 to 4.5) $mol\cdot L^{-1}$, $(CH_3)_4NCl(aq)$ (0.25 to 3) $mol\cdot L^{-1}$, $(C_2H_5)_4NI$ (0.25 to 1) $mol\cdot L^{-1}$, and in pure water at $t = 25$ °C. The solubility trend is $(C_2H_5)_4NI > (CH_3)_4NCl > NaCl$. The Setschenow constants and activity coefficients of neutral species were calculated from these data. To fully characterize the acid−base behavior of above dicarboxylic acids, the protonation constants were determined in the same conditions. From these data, together with solubility ones, Pitzer and SIT parameters were calculated.

Introduction

Several investigations from our research group have been dedicated to the study of acid−base properties of low and high molecular weight ligands. The most studied ligand class was that of polycarboxylic acids (see refs 1−8 and references therein). Protonation constants and protonation enthalpies were determined in different ionic media (alkali metal and tetralkylammonium halides) at different ionic strengths. The dependence on medium and on ionic strength was modeled by several approaches: (i) simple Debye−Hückel type equations, often coupled with the ion pair formation model;[9] (ii) SIT[10−12] (Specific ion Interaction Theory) and Pitzer equations.[13,14] Activity coefficients, together with the relative parameters for the dependence on medium and on ionic strength, can be easily derived from the dependence on ionic strength of protonation constants studied in different media by making some assumption, such as that of considering the activity coefficient of neutral species, γ_N, independent of medium, i.e., $\gamma_N = 1$. This simplification is often inappropriate since in many cases $\log \gamma_N > |0.1|$, and γ_N is quite different in different media.

To complete the picture of acid−base properties of different ligands (carboxylates, amines, amino acids, etc.), we thought it important to undertake a study on the activity coefficients of acidic and basic nonelectrolytes. In the first part of this series of studies, we reported quantitative data on phthalic acid and cystine activity coefficients.[1] Two interesting results were obtained in this work: very different Setschenow coefficients[15] were obtained for different supporting electrolytes, with the trend $(C_2H_5)_4NI > (CH_3)_4NCl > NaCl$ for phthalic acid and the opposite for cystine; and γ_N values, in many conditions, very different from unity (for example $\gamma_N > 2$ for phthalic acid at $c_{NaCl} > 2\ mol\cdot L^{-1}$).

In this work we report a study on the solubility of three dicarboxylic acids, $(COOH)-(CH_2)_n-(COOH)$ ($n = 6, 7, 8$), in NaCl(aq) (0.5 to 4.5) $mol\cdot L^{-1}$, $(CH_3)_4NCl(aq)$ (0.25 to 3) $mol\cdot L^{-1}$, $(C_2H_5)_4NI$ (0.25 to 1) $mol\cdot L^{-1}$ and in pure water at $t = 25$ °C. Few data can be found in the literature on activity coefficients of carboxylic acids, regarding mainly phthalic acid.[16−19] No report was found on γ_N of aliphatic dicarboxylic acids, except for succinic acid.[16]

Experimental Section

Chemicals. $(COOH)-(CH_2)_6-(COOH)$ (suberic, **6D**), $(COOH)-(CH_2)_7-(COOH)$ (azelaic, **7D**), and $(COOH)-(CH_2)_8-(COOH)$ (sebacic, **8D**) acids (Fluka products) were used without further purification. Their purity was checked alkalimetrically and was found to be > 99 %. Sodium chloride solutions were prepared by weighing pure salt (Fluka, p.a.) previously dried in an oven at 110 °C. Tetramethylammonium chloride, Me_4NCl (Fluka), and tetraethylammonium iodide, Et_4NI (Fluka), were recrystallized from methanol. Tetraethylammonium hydroxide solutions were prepared from concentrated Et_4NOH (Fluka puriss. electrochemical grade) and standardized against potassium biphthalate. Hydrochloric acid solutions were prepared from concentrated ampules (Fluka) and standardized against sodium carbonate. All solutions were preserved from atmospheric CO_2 by means of soda lime traps. Grade A glassware and twice-distilled water were employed in the preparation of all the solutions.

Apparatus. The free hydrogen ion concentration was measured with a Metrohm model 713 potentiometer (resolution ± 0.1 mV, reproducibility ± 0.15 mV) connected to a Metrohm 665 automatic buret and to a model 8101 Ross type Orion electrode, coupled with a standard calomel electrode. The potentiometer and the buret were connected to a personal computer which, using suitable software, allowed automatic data acquisition. The measurement cells were thermostated at (25 ± 0.1) °C. Purified N_2 was bubbled into the solutions in order to exclude the presence of CO_2 and O_2. To avoid systematic errors, some measurements were carried out using different apparatus (Metrohm model 809 titrando) and software (Metrohm TiAMO 1.0) for the automatic data acquisition.

Procedure. Saturated solutions of **6D**, **7D**, and **8D** acids were prepared by adding an excess of acid to a solution of Et_4NI or

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Table 1. Experimental Total Solubility of 6D, 7D, and 8D Acids at t = 25 °C

6D		7D		8D	
c_{MX}[a]	log S^T	c_{MX}[a]	log S^T	c_{MX}[a]	log S^T
		Et$_4$NI			
0	−1.8511 ± 0.0019[b]	0	−1.9430 ± 0.0033[b]	0	−2.9046 ± 0.0030[b]
0	−1.8424 ± 0.0019	0	−1.9423 ± 0.0033	0	−2.9203 ± 0.0030
0.250	−1.7611 ± 0.0014	0	−1.9715 ± 0.0033	0.249	−2.8379 ± 0.0021
0.250	−1.7612 ± 0.0014	0.255	−1.8918 ± 0.0031	0.499	−2.7791 ± 0.0024
0.502	−1.6709 ± 0.0016	0.531	−1.7926 ± 0.0049	0.796	−2.7030 ± 0.0038
0.502	−1.6682 ± 0.0016	0.753	−1.7015 ± 0.0069	0.996	−2.6509 ± 0.0050
0.748	−1.5936 ± 0.0022	0.904	−1.6553 ± 0.0084		
0.748	−1.5941 ± 0.0022				
0.892	−1.5292 ± 0.0027				
0.892	−1.5376 ± 0.0027				
		Me$_4$NCl			
0.250	−1.8477 ± 0.0018	0.491	−2.0090 ± 0.0029	0.250	−2.9563 ± 0.0027
0.496	−1.8255 ± 0.0019	0.590	−1.9662 ± 0.0028	0.590	−2.9394 ± 0.0023
1.761	−1.8322 ± 0.0044	0.998	−1.9701 ± 0.0028	0.998	−2.9551 ± 0.0024
2.268	−1.8286 ± 0.0056	1.498	−2.0358 ± 0.0032	1.498	−2.9832 ± 0.0031
3.004	−1.8459 ± 0.0075	2.456	−2.0126 ± 0.0046	2.268	−3.0093 ± 0.0047
		3.004	−2.0537 ± 0.0056		
		NaCl			
0.500	−1.9360 ± 0.0018	0.500	−2.1305 ± 0.0022	0.998	−2.9551 ± 0.0039
0.999	−2.0225 ± 0.0019	0.998	−2.2562 ± 0.0026	0.998	−2.9551 ± 0.0046
1.998	−2.1596 ± 0.0032	1.998	−2.4532 ± 0.0026	1.498	−2.9832 ± 0.0047
3.499	−2.4272 ± 0.0084	2.995	−2.6133 ± 0.0025	1.498	−2.9832 ± 0.0094
2.998	−2.3117 ± 0.0064	4.532	−2.8566 ± 0.0039	2.268	−3.0093 ± 0.0042
4.521	−2.4147 ± 0.0126				

[a] In mol·L^{-1}. [b] ± standard deviation.

Table 2. Log S_c^0 and Log S_m^0 Values of 6D, 7D, and 8D Acids in Different Ionic Media at t = 25 °C

6D				7D				8D			
c_{MX}[a]	log S_c^0	m_{MX}[b]	log S_m^0	c_{MX}[a]	log S_c^0	m_{MX}[b]	log S_m^0	c_{MX}[a]	log S_c^0	m_{MX}[b]	log S_m^0
					Et$_4$NI						
0.250	−1.7582	0.262	−1.7363	0.255	−1.8869	0.269	−1.8632	0.249	−2.8442	0.262	−2.8206
0.250	−1.7584	0.262	−1.7366	0.531	−1.7873	0.591	−1.7409	0.499	−2.7842	0.551	−2.7391
0.502	−1.6682	0.555	−1.6244	0.753	−1.7016	0.876	−1.6351	0.796	−2.7118	0.936	−2.6398
0.502	−1.6656	0.555	−1.6218	0.904	−1.6613	1.087	−1.5805	0.996	−2.6661	1.222	−2.5756
0.748	−1.5977	0.870	−1.5316								
0.748	−1.5982	0.870	−1.5322								
0.892	−1.5392	1.071	−1.4594								
0.892	−1.5478	1.071	−1.4681								
					Me$_4$NCl						
0.250	−1.8550	0.258	−1.8415	0.491	−2.0144	0.520	−1.9891	0.250	−2.9760	0.257	−2.9639
0.496	−1.8326	0.525	−1.8071	0.590	−1.9728	0.632	−1.9425	0.590	−2.9592	0.632	−2.9287
1.761	−1.8372	2.178	−1.7441	0.998	−1.9758	1.121	−1.9247	0.998	−2.9729	1.121	−2.9193
2.268	−1.8326	3.005	−1.7092	1.498	−2.0398	1.791	−1.9612	1.498	−2.9994	1.791	−2.9204
3.004	−1.8480	4.436	−1.6776	2.456	−2.0158	3.342	−1.8807	2.268	−3.0227	3.005	−2.8966
				3.004	−2.0579	4.436	−1.8874				
					NaCl						
0.500	−1.9441	0.506	−1.9388	0.500	−2.1433	0.506	−2.1380	0.499	−3.0835	0.505	−3.0781
0.999	−2.0287	1.021	−2.0190	0.998	−2.2651	1.019	−2.2556	0.997	−3.1730	1.018	−3.1636
1.998	−2.1598	2.083	−2.1414	2.995	−2.4597	3.192	−2.4318	1.998	−3.3466	2.083	−3.3277
3.499	−2.4254	3.775	−2.3920	4.532	−2.6150	5.018	−2.5708	2.998	−3.5022	3.196	−3.4732
2.998	−2.3118	3.196	−2.2834	1.998	−2.8727	2.083	−2.8537	4.521	−3.7635	5.004	−3.7177
4.521	−2.4359	5.004	−2.3909								

[a] In mol·L^{-1}. [b] In mol·kg^{-1}.

Table 3. Dependence on Medium Concentration of the Total Solubility (in mol·L^{-1}) of 6D, 7D, and 8D Acids in the Different Ionic Media at t = 25 °C

		Et$_4$NI	Me$_4$NCl	NaCl	
	log S_0^T	a[a]	a[a]	a_∞[b]	a_0[b]
6D	−1.845 ± 0.002[c]	0.346 ± 0.007[c]	0.007 ± 0.003[c]	−0.131 ± 0.005[c]	−0.222 ± 0.010[c]
7D	−1.955 ± 0.003	0.322 ± 0.010	−0.032 ± 0.002	−0.141 ± 0.002	−0.461 ± 0.010
8D	−2.917 ± 0.003	0.274 ± 0.007	−0.041 ± 0.003	−0.143 ± 0.005	−0.341 ± 0.015

[a] From the one-parameter equation (eq 2). [b] From the two-parameters equation (eq 2a). [c] ± standard deviation.

Me$_4$NCl or NaCl at pre-established ionic strength values [NaCl (0.5 to 4.5) mol·L^{-1}, Me$_4$NCl (0.25 to 3) mol·L^{-1}, Et$_4$NI (0.25 to 1) mol·L^{-1}]. Solutions were stirred at t = 25 °C for 24 h. Preliminary tests established that longer stirring times were unnecessary. A volume of 25 mL of the filtered solution was titrated with standard Et$_4$NOH. Separate titrations of HCl at the

Table 4. Empirical Parameters of Equations 4 and 4a for 6D, 7D, and 8D Acids in the Molal Concentration Scale ($mol \cdot kg^{-1}$)

	$\log S_0^0$	k_∞	k_0	$10^2 \cdot \sigma_{fit}{}^b$	k_m	$10^2 \cdot \sigma_{fit}{}^c$
			6D			
Et_4NI	-1.848 ± 0.002^a	-0.237 ± 0.023^a	-0.483 ± 0.023^a	0.4593	-0.367 ± 0.006^a	1.1003
Me_4NCl		-0.026 ± 0.004	-0.096 ± 0.012	0.7596	-0.043 ± 0.003	1.4502
NaCl		0.093 ± 0.008	0.253 ± 0.025	3.5920	0.132 ± 0.004	5.2292
			7D			
Et_4NI	-1.953 ± 0.002	-0.317 ± 0.043	-0.382 ± 0.037	1.0019	-0.365 ± 0.011	1.2186
Me_4NCl		-0.022 ± 0.008	0.011 ± 0.028	1.9802	-0.018 ± 0.003	2.0675
NaCl		0.041 ± 0.004	0.529 ± 0.016	1.4351	0.128 ± 0.005	5.4332
			8D			
Et_4NI	-2.914 ± 0.002	-0.175 ± 0.014	-0.401 ± 0.021	0.3721	-0.321 ± 0.012	2.8962
Me_4NCl		-0.027 ± 0.007	0.058 ± 0.017	1.5788	-0.015 ± 0.003	1.7646
NaCl		0.117 ± 0.003	0.374 ± 0.012	0.9003	0.164 ± 0.004	4.1655

[a] ± standard deviation. [b] Standard deviation in the fit of eq 4a. [c] Standard deviation in the fit of eq 4.

Table 5. Activity Coefficients of 6D, 7D, and 8D Acids at $t = 25$ °C

6D		7D		8D	
$m_{MX}{}^a$	γ_m	$m_{MX}{}^a$	γ_m	$m_{MX}{}^a$	γ_m
		Et_4NI			
0.10	0.899	0.10	0.917	0.10	0.916
0.25	0.779	0.25	0.809	0.25	0.815
0.50	0.630	0.50	0.660	0.50	0.687
0.75	0.521	0.75	0.542	0.75	0.591
1.00	0.436	1.00	0.447	1.00	0.515
1.25	0.369	1.25	0.370	1.25	0.453
		Me_4NCl			
0.10	0.980	0.10	1.002	0.10	1.012
0.25	0.954	0.25	1.004	0.25	1.024
0.50	0.920	0.50	1.002	0.50	1.035
0.75	0.892	0.75	0.998	0.75	1.038
1.00	0.869	1.00	0.991	1.00	1.036
2.00	0.797	2.00	0.955	2.00	1.006
3.00	0.741	3.00	0.914	3.00	0.961
3.50	0.715	3.50	0.893	3.50	0.937
4.00	0.692	4.00	0.873	4.00	0.912
4.50	0.670	4.50	0.852	4.50	0.887
		NaCl			
0.10	1.056	0.10	1.118	0.10	1.084
0.25	1.136	0.25	1.281	0.25	1.204
0.50	1.258	0.50	1.523	0.50	1.394
0.75	1.375	0.75	1.734	0.75	1.577
1.00	1.489	1.00	1.923	1.00	1.760
2.00	1.962	2.00	2.543	2.00	2.543
3.00	2.506	3.00	3.062	3.00	3.497
4.00	3.162	4.00	3.551	4.00	4.716
5.00	3.966	5.00	4.043	5.00	6.298
5.50	4.435	5.50	4.295	5.50	7.260

[a] In $mol \cdot kg^{-1}$.

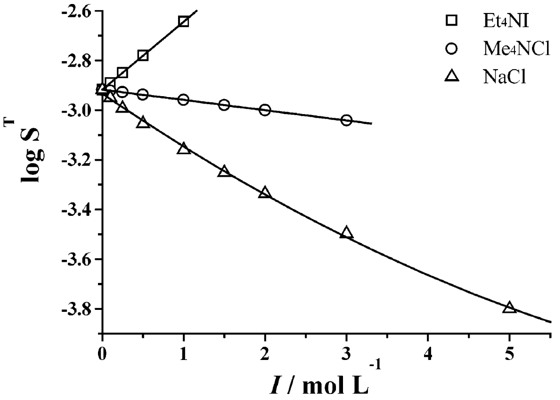

Figure 1. Log S^T values vs ionic strength (molar concentration scale) of **8D** acid in different ionic media at $t = 25$ °C.

same ionic strength as the sample under study were carried out to determine the standard electrode potential $E°$ and the junction potential coefficient j_a ($E_j = j_a[H^+]$). To avoid systematic errors, independent experiments were performed at least three times.

ISE-H^+ measurements for the determination of protonation constants were carried out by titrating 25 mL of a solution containing the acids at different concentrations depending on their solubility (0.5 to 10 $mmol \cdot L^{-1}$ for **D6** and **D7** acids, 0.1 to 1.0 $mmol \cdot L^{-1}$ for **D8**), Et_4NI, Me_4NCl, or NaCl at the same pre-established ionic strength values adopted for the solubility measurements with standard Et_4NOH, Me_4NOH, or NaOH. The standard electrode potential $E°$ and the junction potential coefficient j_a ($E_j = j_a[H^+]$) were determined as reported above.

Calculations. Calculations relative to the refinement of parameters for acid−base titrations were carried out by the computer program ESAB2M.[20] The general least squares computer program LIANA[21] was used for the refinement of solubility parameters. Other details on solubility measurements and on data analysis are reported in the first part of this series.[1]

Results and Discussion

Solubility. Total solubility of **6D**, **7D**, and **8D** is reported in Table 1. The solubility in different ionic media follows the trend: $Et_4NI > Me_4NCl > NaCl$. The behavior is the same found in the previous paper on *o*-phthalic acid.[1] For example, Figure 1 shows the dependence of total solubility on ionic strength for **8D**: dependence is linear for Me_4NCl(aq) and Et_4NI(aq) while it is fairly nonlinear for NaCl(aq). Owing to proton dissociation, the total solubility of dicarboxylic acids is due to the neutral and deprotonated species, according to

$$S^T = [H_2L^0] + [HL^-] + [L^{2-}] = S^0\left(1 + \frac{1}{K_2^H[H^+]} + \frac{1}{K_1^H K_2^H [H^+]^2}\right) \quad (1)$$

where L^{2-} is the anion of dicarboxylic acids, S^T is the total solubility, and S^0 is the solubility of neutral species. By using K_i^H values obtained in the same medium and at the same ionic strength (see hereafter), one can calculate S^0. The solubility of neutral species are reported in Table 2, in both molar ($mol \cdot L^{-1}$) and molal ($mol \cdot kg^{-1}$) concentration scales. Total solubility can be expressed as a function of concentration of supporting electrolyte using the following linear (eq 2) or non-linear (eq 2a) equations:

$$\log S^T = \log S_0^T + a c_{MX} \quad (2)$$

$$\log S^T = \log S_0^T + \left[a_\infty + \frac{a_0 - a_\infty}{c_{MX} + 1}\right] c_{MX} \quad (2a)$$

Table 6. Smoothed Protonation Constants of 6D, 7D, and 8D Acids in NaCl, Me_4NCl, and Et_4NI at t = 25 °C

	6D		7D		8D	
I[a]	$\log K_1^H$	$\log K_2^H$	$\log K_1^H$	$\log K_2^H$	$\log K_1^H$	$\log K_2^H$
			Et_4NI			
0.1	5.133 ± 0.001[b]	4.367 ± 0.001[b]	5.144 ± 0.007[b]	4.398 ± 0.004[b]	5.126 ± 0.003[b]	4.486 ± 0.002[b]
0.5	5.135 ± 0.002	4.449 ± 0.001	5.170 ± 0.012	4.493 ± 0.006	5.190 ± 0.005	4.471 ± 0.003
0.75	5.221 ± 0.004	4.536 ± 0.004	5.260 ± 0.013	4.580 ± 0.009	5.267 ± 0.003	4.592 ± 0.001
1	5.323 ± 0.008	4.627 ± 0.008	5.362 ± 0.025	4.669 ± 0.018	5.339 ± 0.005	4.759 ± 0.005
			Me_4NCl			
0.1	5.097 ± 0.002	4.332 ± 0.002	5.103 ± 0.003	4.351 ± 0.001	5.070 ± 0.006	4.489 ± 0.001
0.5	4.969 ± 0.004	4.303 ± 0.005	4.990 ± 0.008	4.309 ± 0.004	4.997 ± 0.017	4.372 ± 0.003
0.75	4.978 ± 0.004	4.333 ± 0.006	5.005 ± 0.009	4.337 ± 0.004	5.027 ± 0.018	4.375 ± 0.003
1	5.005 ± 0.003	4.374 ± 0.006	5.037 ± 0.008	4.377 ± 0.004	5.071 ± 0.017	4.401 ± 0.003
2	5.182 ± 0.006	4.579 ± 0.008	5.224 ± 0.009	4.592 ± 0.004	5.286 ± 0.015	4.607 ± 0.003
3	5.400 ± 0.016	4.809 ± 0.014	5.447 ± 0.018	4.840 ± 0.010	5.523 ± 0.041	4.882 ± 0.008
			NaCl			
0.1	5.090 ± 0.001	4.318 ± 0.001	5.100 ± 0.001	4.336 ± 0.001	5.061 ± 0.002	4.442 ± 0.002
0.5	4.938 ± 0.003	4.243 ± 0.002	4.970 ± 0.003	4.248 ± 0.002	4.958 ± 0.007	4.193 ± 0.006
0.75	4.934 ± 0.003	4.249 ± 0.002	4.972 ± 0.004	4.252 ± 0.002	4.973 ± 0.009	4.140 ± 0.006
1	4.949 ± 0.003	4.269 ± 0.003	4.991 ± 0.004	4.271 ± 0.002	5.002 ± 0.009	4.120 ± 0.006
2	5.081 ± 0.003	4.400 ± 0.003	5.121 ± 0.003	4.413 ± 0.002	5.166 ± 0.009	4.196 ± 0.005
3	5.257 ± 0.004	4.565 ± 0.003	5.285 ± 0.002	4.596 ± 0.003	5.356 ± 0.008	4.379 ± 0.008
4	5.450 ± 0.007	4.744 ± 0.003	5.462 ± 0.004	4.796 ± 0.006	5.557 ± 0.010	4.604 ± 0.016
5	5.651 ± 0.010	4.930 ± 0.004	5.645 ± 0.007	5.005 ± 0.009	5.763 ± 0.015	4.850 ± 0.024

[a] In mol·L^{-1}. [b] ± standard deviation.

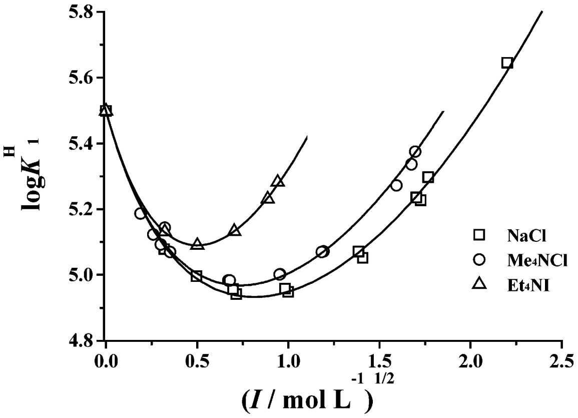

Figure 2. Log K_1^H of **6D** acid vs ionic strength, in different ionic media and at t = 25 °C.

where S_0^T is the total solubility in pure water; a, a_∞, and a_0 are empirical parameters; and c_{MX} is the molar concentration of supporting electrolyte (eqs 2 and 2a can be applied to the molal scale by substituting c_{MX} for m_{MX}). As observed above, data in Me_4NCl and in Et_4NI are linearly dependent on the concentration of supporting electrolyte and can be expressed by eq 2 while the dependence of data in NaCl is nonlinear and can be expressed by eq 2a. The relative parameters are reported in Table 3. In the same table, total solubility in pure water is reported. Values obtained for **6D**, **7D**, and **8D** acids are lower with respect to those obtained for *o*-phthalic acid[1] [$\log S_0^T = -1.443$ (S_0^T in mol·L^{-1})].

Setschenow Coefficients and Activity Coefficients of Neutral Species. According to Long and McDevit,[16] the solubility of a neutral species is related to the activity coefficient by

$$\log y = \log \frac{S_0^{\ 0}}{S^0} = k_c c_{MX} \tag{3}$$

$$\log \gamma = \log \frac{S_0^{\ 0}}{S^0} = k_m m_{MX} \tag{4}$$

Table 7. Protonation Constants at Infinite Dilution of 6D, 7D, and 8D Acids at t = 25 °C

	$\log K_1^{H\,a}$	$\log K_2^{H\,a}$	ref
6D	5.498	4.526	7
	5.497	4.524	
7D	5.498	4.550	7
	5.497	4.548	
8D	5.450 ± 0.001[b]	4.720 ± 0.002[c]	this work
	5.447	4.719	

[a] First row, molar concentration scale (mol·L^{-1}). Second row, molal concentration scale (mol·kg^{-1}). [b] ± standard deviation.

in the molar (y) and molal (γ) concentration scales, respectively. The parameters k_c and k_m are the Setschenow coefficients in the two concentration scales. Equations 3 and 4 are valid under the assumption that in pure water the activity coefficients are equal to unity (i.e., $y_0 = \gamma_0 = 1$: this assumption is valid when the solubility is low, $S < 0.05$ mol·L^{-1}). Since we observed that the function solubility versus ionic strength of the dicarboxylic acids here investigated depends on ionic medium (see also the preceeding section), we used two equations to calculate the Setschenow coefficients; the first one was the linear eq 4, while the second was an equation in which the Setschenow coefficient (k_m) was expressed as

$$k_m = \left(k_\infty + \frac{k_0 - k_\infty}{m_{MX} + 1}\right) \tag{4a}$$

where k_0 and k_∞ are the relative values at $m_{MX} \rightarrow 0$ and $m_{MX} \rightarrow \infty$, respectively. Table 4 reports the Setschenow coefficients k_m calculated by using the different equations; the k_m values here obtained are fairly different with respect to those observed in a previous paper[1] for the *o*-phthalic acid. For example, in Et_4NI we have −0.367, −0.365, and −0.321 for **D6**, **D7**, and **D8**, respectively, while in the same ionic medium we obtained for *o*-phthalic acid a value of −0.489. In NaCl aqueous solutions, the salting parameter values obtained for the **D6**, **D7**, and **D8** acids (0.132, 0.128, and 0.164, respectively) can be considered similar to the value of 0.163 obtained for the *o*-phthalic acid[1] in the same ionic medium. Comparison with literature data

Table 8. Empirical Parameters for the Dependence of Protonation Constants on Ionic Strength, for 6D, 7D, and 8D Acids in NaCl, Me_4NCl, and Et_4NI at $t = 25$ °C

	i	$c_\infty^{a,b}$	$c_0^{a,b}$	$c_\infty^{a,c}$	$c_0^{a,c}$	σ^d	P_1^e	P_2^e	P_3^e	σ^f
6D										
Et_4NI	1	0.543	0.738	0.311	0.699	0.017	0.285	3.007	0	0.005
	2	0.401	0.618	0.184	0.574		0.202	1.797	0	
Me_4NCl	1	0.267	0.379	0.113	0.436	0.005	0.260	0.734	−0.0163	0.017
	2	0.260	0.251	0.126	0.241		0.164	0.829	−0.00273	
NaCl	1	0.227	0.308	0.193	0.326	0.014	0.388	0.983	−0.0175	0.014
	2	0.203	0.098	0.167	0.119		0.293	0.214	−0.0145	
7D										
Et_4NI	1	0.489	0.872	0.224	0.852	0.012	0.227	3.339	0	0.011
	2	0.351	0.702	0.164	0.640		0.187	1.930	0	
Me_4NCl	1	0.266	0.443	0.121	0.477	0.008	0.278	1.774	−0.0183	0.008
	2	0.286	0.184	0.129	0.231		0.221	0.730	−0.0104	
NaCl	1	0.204	0.413	0.173	0.429	0.011	0.365	1.214	−0.0170	0.010
	2	0.229	0.029	0.198	0.0464		0.268	0.210	0.0029	
8D										
Et_4NI	1	0.183	1.228	0.0417	1.135	0.017	0.0572	4.102	0	
	2	1.183	−0.289	0.773	−0.248		0.731	−0.436	0	
Me_4NCl	1	0.266	0.606	0.109	0.663	0.020	0.283	2.086	−0.0232	0.016
	2	0.346	−0.168	0.162	−0.0739		0.364	−0.268	−0.0455	
NaCl	1	0.224	0.511	0.177	0.576	0.026	0.303	1.732	0.00158	0.026
	2	0.292	−0.677	0.252	−0.637		0.240	−0.920	0.0248	

[a] Equations 5 and 5a. [b] In mol·L^{-1}. [c] In mol·kg^{-1}. [d] Standard deviation in the fit of eqs 5 and 5a. [e] Equation 8. [f] Standard deviation in the fit of eq 8.

Table 9. SIT (eqs 6−6b) and Pitzer (eqs 7−7h) Interaction Parameters

c	a	ϵ_∞	ϵ_0	σ^a	$\beta^{(0)}_{c,a}$	$\beta^{(1)}_{c,a}$	$C^{(\phi)}_{c,a}$	σ^b
6D								
Et_4N^+	L^{2-}	−0.217 ± 0.007	0.498 ± 0.007	0.005	−0.477 ± 0.005	2.30 ± 0.01	0	0.005
	HL^-	−0.356 ± 0.005	0.003 ± 0.005		−0.493 ± 0.003	0.84 ± 0.01	0	
Me_4N^+	L^{2-}	−0.076 ± 0.004	0.464 ± 0.012	0.017	0.048 ± 0.003	1.90 ± 0.02	−0.050 ± 0.003	0.017
	HL^-	−0.053 ± 0.003	0.114 ± 0.008		−0.034 ± 0.002	0.51 ± 0.02	−0.011 ± 0.001	
Na^+	L^{2-}	0.220 ± 0.003	0.408 ± 0.009	0.014	0.477 ± 0.002	1.42 ± 0.02	−0.051 ± 0.002	0.014
	HL^-	0.163 ± 0.002	0.167 ± 0.006		0.267 ± 0.002	0.19 ± 0.01	−0.017 ± 0.001	
7D								
Et_4N^+	L^{2-}	−0.322 ± 0.026	0.718 ± 0.020	0.012	−0.549 ± 0.013	2.77 ± 0.04	0	0.012
	HL^-	−0.374 ± 0.023	0.071 ± 0.015		−0.495 ± 0.010	0.94 ± 0.03	0	
Me_4N^+	L^{2-}	−0.040 ± 0.002	0.521 ± 0.005	0.008	0.122 ± 0.001	1.83 ± 0.01	−0.065 ± 0.001	0.008
	HL^-	−0.025 ± 0.001	0.128 ± 0.004		0.026 ± 0.001	0.41 ± 0.01	−0.019 ± 0.001	
Na^+	L^{2-}	0.227 ± 0.002	0.434 ± 0.008	0.011	0.425 ± 0.002	1.64 ± 0.01	−0.025 ± 0.001	0.010
	HL^-	0.190 ± 0.002	0.090 ± 0.001		0.243 ± 0.001	0.19 ± 0.01	0.0009 ± 0.0007	
8D								
Et_4N^+	L^{2-}	0.147 ± 0.016	0.159 ± 0.016	0.017	−0.129 ± 0.008	1.18 ± 0.03	0	0.015
	HL^-	0.279 ± 0.011	−0.773 ± 0.011		0.088 ± 0.006	−1.40 ± 0.02	0	
Me_4N^+	L^{2-}	−0.016 ± 0.002	0.404 ± 0.011	0.020	0.274 ± 0.003	1.15 ± 0.02	−0.121 ± 0.002	0.016
	HL^-	0.011 ± 0.001	−0.174 ± 0.008		0.169 ± 0.002	−0.59 ± 0.01	−0.054 ± 0.001	
Na^+	L^{2-}	0.320 ± 0.007	−0.067 ± 0.023	0.026	0.377 ± 0.006	1.03 ± 0.06	0.032 ± 0.005	0.026
	HL^-	0.280 ± 0.005	−0.557 ± 0.016		0.252 ± 0.004	−0.95 ± 0.04	0.023 ± 0.002	

[a] Standard deviation in the fit of eqs 6−6b. [b] Standard deviation in the fit of eqs 7−7h.

cannot be made because of the absence of solubility data and of Setschenow coefficients for these aliphatic dicarboxylic acids. Nevertheless, in the paper of Long and McDevit[16] some k_c values for succinic acid are reported in the molar concentration scale at $t = 18$ °C; they report the Setschenow coefficient values in different ionic media, namely, $k_c(LiCl) = 0.154$, $k_c(NaCl) = 0.066$, $k_c(KCl) = 0.018$, and $k_c(RbCl) = 0.0005$. These values can be considered comparable with our data, taking into account the different temperature. In Table 5, the activity coefficients of **6D**, **7D**, and **8D** are reported in the molal concentration scale (data in molar concentration scale are reported as Supporting Information) in NaCl, Me_4NCl, and Et_4NI at $t = 25$ °C. Errors in activity coefficients can be deduced from errors in the solubility and range, on average from ± 0.01 γ_m to ± 0.03 γ_m. The different dependence of solubility and of Setschenow coefficients on ionic media can be explained considering that the salting (in/out) effect varies regularly varying the ionic size of the supporting electrolytes. Generally for large ions such as Et_4N^+, we observe a salting-in effect (negative values of the k_m parameter), while for small ions (Na^+) we have the opposite trend and positive k_m values.

Protonation Constants. The protonation constant values follow the trend: $\log K^H (Et_4NI) > \log K^H (Me_4NCl) > \log K^H (NaCl)$ as already observed for O-donor ligands.[7,8] Dependence on ionic strength in different supporting electrolytes is shown in Figure 2 for $\log K_1^H$ of **6D**. Some smoothed values of protonation constants of **6D**, **7D**, and **8D** are reported in Table 6, at different ionic strengths (tables of experimental values are reported as Supporting Information). The dependence on ionic media can be explained taking into account the interacting nature of Na^+ respect to Me_4N^+ and Et_4N^+, which can be considered non-interacting cations toward polycarboxylic anions. The lower

Table 10. Pitzer Parameter for the Neutral Species (eq 7b)

		λ^a	λ^b
6D	Et_4NI	−0.422	$-0.272 - \frac{0.284}{m_{MX} + 1}$
	Me_4NCl	−0.049	$-0.0299 - \frac{0.0806}{m_{MX} + 1}$
	NaCl	0.152	$0.107 + \frac{0.184}{m_{MX} + 1}$
7D	Et_4NI	−0.420	$-0.365 - \frac{0.0748}{m_{MX} + 1}$
	Me_4NCl	−0.021	$-0.0253 + \frac{0.0379}{m_{MX} + 1}$
	NaCl	0.147	$0.0472 + \frac{0.562}{m_{MX} + 1}$
8D	Et_4NI	−0.369	$-0.201 - \frac{0.260}{m_{MX} + 1}$
	Me_4NCl	−0.017	$-0.0311 + \frac{0.0979}{m_{MX} + 1}$
	NaCl	0.189	$0.135 + \frac{0.296}{m_{MX} + 1}$

[a] Calculated from eq 9 by using the Setschenow coefficient (k_m) calculated with eq 4. [b] Calculated from eq 9 by using the Setschenow coefficient (k_m) calculated with eq 4a.

values of protonation constants in NaCl are due to the formation of fairly stable ion pairs Na^+−dicarboxylate anion. The protonation constants reported in Table 6 for **D6** and **D7** in Et_4NI and NaCl aqueous solutions are comparable with those reported in a previous paper,[7] while no literature data are reported for **D8**. Table 7 reports the protonation constants at infinite dilution for the three aliphatic dicarboxylic acids studied here.

Dependence on Ionic Strength of Log K_i^H. Protonation constants of **6D**, **7D**, and **8D** acids are related to the equilibrium:

$$H^+ + H_{i-1}L^{i-3} = H_iL^{i-2} \quad (K_i^H)$$

and, in a generic salt MX, can be expressed by

$$\log_{10} K_i^H = \log_{10} {}^TK_i^H + \log_{10} \gamma_H + \log_{10} \gamma_{H_{i-1}L} - \log_{10} \gamma_{H_iL}$$

where ${}^TK^H$ is the protonation constant at infinite dilution and γ_i is the activity coefficient of the ith component. The dependence on ionic strength of protonation constants can be studied using different models: a Debye−Hückel type, SIT, and Pitzer equations.

The Debye−Hückel type equation used is[9]

$$\log K^H = \log {}^TK^H - z^* \frac{0.51 I^{1/2}}{1 + 1.5 I^{1/2}} + CI \qquad (5)$$

where

$$z^* = \sum {z_{\text{reactants}}}^2 - \sum {z_{\text{products}}}^2$$

K^H is the formation constant, ${}^TK^H$ is the formation constant at infinite dilution, z is the charge, and C is a function of ionic strength that can be expressed as

$$C = c_\infty + \frac{c_0 - c_\infty}{I + 1} \qquad (5a)$$

According to the SIT (Specific ion Interaction Theory) equation,[10−12] the activity coefficients of a cation or an anion can be expressed as

$$\log \gamma = -z^2 \frac{0.51 I^{1/2}}{1 + 1.5 I^{1/2}} + \sum \epsilon m_i \qquad (6)$$

and for a neutral species can be expressed as

$$\log \gamma = k_m I \qquad (6a)$$

where ϵ is the interaction coefficient expressed, such as eq 5a, by

$$\epsilon = \epsilon_\infty + \frac{\epsilon_0 - \epsilon_\infty}{I + 1} \qquad (6b)$$

According to the Pitzer equations,[13,14] in the presence of a 1:1 salt MX, the activity coefficients of a cation or an anion are given by

$$\ln \gamma_{H^+} = f^\gamma + 2I(B_{HX} + IC_{HX}) + I^2(B'_{MX} + C_{MX}) + I(2\theta_{HM} + I\psi_{HMX}) \qquad (7)$$

$$\ln \gamma_L = {z_L}^2 f^\gamma + 2I(B_{ML} + IC_{ML}) + I^2({z_L}^2 B'_{MX} + z_L C_{MX}) + I(2\theta_{LX} + I\psi_{LMX}) \qquad (7a)$$

($L = L^{2-}$ or HL^-), and for neutral species are given by

$$\ln \gamma_{H_2L} = 2\lambda I \qquad (7b)$$

where I is ionic strength in the molal scale, and

$$B_{c,a} = \beta^{(0)}_{c,a} + \frac{\beta^{(1)}_{c,a}}{2I} f_1 \qquad (7c)$$

$$B'_{c,a} = \frac{\beta^{(1)}_{c,a}}{2I^2} f_2 \qquad (7d)$$

$$C_{c,a} = \frac{C^{(\phi)}_{c,a}}{2|z_c z_a|^{1/2}} \qquad (7e)$$

$$f^\gamma = -0.391[I^{1/2}(1 + 1.2I^{1/2})^{-1} + 1.667 \ln (1 + 1.2I^{1/2})] \qquad (7f)$$

$$f_1 = 1 - (1 + 2I^{1/2}) \exp(-2I^{1/2}) \qquad (7g)$$

$$f_2 = -1 + (1 + 2I^{1/2} + 2I) \exp(-2I^{1/2}) \qquad (7h)$$

(c,a = generic cation and anion, respectively) $\beta^{(0)}$, $\beta^{(1)}$, and $C^{(\phi)}$ represent interaction parameters between two ions of opposite sign; θ represents an interaction parameter between two ions of the same sign (+ +, − − interactions); ψ is a triplet interaction parameter (+ − +, − + −); and λ is an interaction parameter of neutral species.

Owing to the complexity of the Pitzer equation, we also tested a simplified version depending on three empirical parameters only:

$$\ln K^H = \ln {}^TK^H + 2zf^\gamma + 2P_1 I + P_2 I^2 + P_3 f_1 + 2z\beta^{(1)}_{MX} f_2 \qquad (8)$$

with

$$f_1 = 1 - (1 + 2I^{1/2}) \exp(-2I^{1/2}) \qquad (8a)$$

$$f_2 = I \exp(-2I^{1/2}) \tag{8b}$$

where P_1, P_2, and P_3 are empirical parameters and f_1 and f_2 are functions defined in the Pitzer equation.[13,14] All models are described in previous papers.[7,22,23]

Tables 8 and 9 report the empirical parameters for the dependence of protonation constants on ionic strength, obtained by using different models (Debye−Hückel, SIT, and Pitzer equations); in particular in the SIT equations, we used as interaction parameter of the neutral species, the Setschenow coefficient calculated from solubility data and reported in Table 4, while for the interaction coefficients of HCl we used $\epsilon_\infty = 0.136$ and $\epsilon_0 = 0.0848$,[23] and for HI $\epsilon_\infty = 0.171$ and $\epsilon_0 = 0.205$ (unpublished data). In the calculation carried out with the Pitzer equations, we used for Et_4NI, Me_4NCl, NaCl, HCl, and HI, the literature interaction parameters [Et_4NI: $C^{(\phi)} = 0.0412$, $\beta^{(1)} = -0.571$; Me_4NCl: $C^{(\phi)} = 0.0078$, $\beta^{(1)} = -0.029$; NaCl: $C^{(\phi)} = 0.00127$, $\beta^{(1)} = 0.2664$; HI: $\beta^{(0)} = 0.2211$, $C^{(\phi)} = 0.00482$, $\beta^{(1)} = 0.4907$; HCl: $\beta^{(0)} = 0.1775$, $C^{(\phi)} = 0.00080$, $\beta^{(1)} = 0.2945$; $\Theta_{H,Na} = 0.036$; $\Psi_{H,Na,Cl} = -0.004$];[13] while the λ parameter was calculated from the linear and nonlinear Setschenow coefficients reported in Table 4 by using the following equation:

$$\lambda = \frac{\ln 10 k_m}{2} \tag{9}$$

In Table 10, we report the λ parameter for the neutral species of dicarboxylic acids.

Conclusions

By solubility and acidimetric measurements we obtained the complete picture of protonation constants of suberic, azelaic and sebacic anions at $t = 25$ °C. The protonation constants here reported are in quite good accordance with those given in ref 7 [NaCl, $(C_2H_5)_4NI$] and with those reported by Adell[24] at 18 °C (NaCl). Only this author reported the dependence on ionic strength and proposed the following values: $I = 0$ mol·L^{-1}, $\log K_1^H = 5.414$ and 5.413, $\log K_2^H = 4.516$ and 4.541; $I = 3$ mol·L^{-1}, $\log K_1^H = 5.219$ and 5.221, $\log K_2^H = 4.568$ and 4.595 for suberic and azelaic acids, respectively. Only two references[25,26] were found in the literature for sebacic acid: $I = 0.2$ mol·L^{-1} (KNO_3) and $t = 25$ °C, $\log K_1^H = 5.23$, $\log K_2^H = 3.83$; $I = 0.1$ mol·L^{-1} and $t = 20$ °C, $\log K_1^H = 5.22$, $\log K_2^H = 4.40$. Other information on protonation and metal complex formation constants can be found in the databases of May and Murray,[27] Martell et al.,[28] and Pettit and Powell.[29] No data are reported in the literature on protonation constants of suberic, azelaic, and sebacic acids in $(CH_3)_4NCl$. As regards the salting coefficients, it is interesting to note that the trend in different supporting electrolytes is the same for different dicarboxylic acids. Moreover, the linear HOOC−$(CH_2)_n$−COOH diacids show a trend as a function of the number of methylenic groups n. As an example, the parameter λ (see also Table 10) can be expressed as $(\lambda \pm 0.01) = -0.589 + 0.0265n$ (Et_4NI), $(\lambda \pm 0.005) = -0.141 + 0.016n$ (Me_4NCl), and $(\lambda \pm 0.01) = 0.033 + 0.019n$ (NaCl).

Supporting Information Available:

Four additional tables detailing activity coefficients and experimental protonation constants of **6D**, **7D**, and **8D** acids. This material is available free of charge via the Internet at http://pubs.acs.org.

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