J. Chem. Eng. Data **2008,** *53,* 363–367

Solubility and Acid–Base Properties of Ethylenediaminetetraacetic Acid in Aqueous NaCl Solution at $0 \leq I \leq 6$ mol·kg^{-1} and $T = 298.15$ K

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Solubility and protonation constants of ethylenediaminetetraacetic acid (EDTA) were determined in aqueous NaCl solutions at different ionic strengths ($0 \leq I \leq 6.0$ mol·kg^{-1}), at $T = 298.15$ K. Dependence on the ionic strength of protonation constants was modeled by the modified SIT approach on the molal concentration scale. From total solubility, we calculated the solubility of the neutral species S^0, and from these values, as a function of NaCl concentration, the Setschenow (k_m) coefficient was obtained, together with the values of K_{S0}.

Introduction

Some polyamino carboxylic compounds, such as ethylenediaminetetraacetic (EDTA), ethylenebis(dioxydiethylenediamine)tetraacetic (EGTA), diethylenetriaminepentaacetic (DTPA), triethylene tetraaminehexaacetic (TTHA), and nitrilotriacetic (NTA) acids, etc., generally called "complexons" are employed in many fields of application because of their strong sequestering ability toward almost all metal ions. In analytical chemistry, complexons (in particular EDTA) are used for quantitative determination of many metal cations.[1] The interaction of metals with different chelating agents is used in agriculture to avoid the effects of trace element deficiency: it is known[2] that when essential metals for plants are not available from the soil, owing to their low solubility, the addition of sequestering agents, such as polyamino carboxylic ligands, is a useful means of extracting metal ions from the soil and transporting them as chelates, via water, into the plants. EDTA exchange was used to investigate the stability of humic substance−metal complexes.[3] Recent applications of polyamino carboxylic ligands are: (i) in suppressing the unfavorable catalytic effects of some metal ions in chemicals production or as cleaning agents to maintain the efficiency of filters and avoid their occlusion by metallic salts, etc.; (ii) in the cosmetic and pharmaceutical industries, as well as in the production of foodstuffs and beverages, to prevent the formation of insoluble metal precipitates or the catalytic degradation enhanced by some metal ions such as copper and iron; (iii) as softening agents in the treatment of water supplies and in heat transfer equipment; (iv) in the leather industry, for the prevention and removal of stains caused by iron compounds; (v) in all chemical processes where the presence of free calcium and other metal ions must be avoided; (vi) in analytical chemistry procedures, for the sequestration or removal of interfering metal ions and for masking metals by chelation in quantitative complexometric titrations, etc.

Among chelating agents, ethylenediaminetetraacetic acid (EDTA) is the most known and used for both analytical and technical purposes. Since the 1940s, acid–base and complexing properties of complexons were well recognized.[4] In 1975, a critical survey of stability constants of EDTA complexes was published by Anderegg,[5] and more recently, the Nuclear Energy Agency (NEA) published a survey of protonation constants.[6] For a long time, technical applications of EDTA drew the attention of researchers, while the determination of thermodynamic parameters for the binding of proton and metal ions was fairly neglected. Few solubility data were reported,[6–9] and only two papers deal with the dependence on ionic strength of protonation constants.[10,11]

In this work we report a careful study on the protonation and solubility of EDTA in NaCl$_{aq}$, $I \leq 5.0$ mol·L^{-1}.

Experimental Section

Chemicals. Ethylenediaminetetraacetic acid (Sigma−Aldrich product) was used without further purification, and its purity, checked alkalimetrically, was found to be > 99.5 %. Sodium chloride solutions were prepared by weighing pure salt (Fluka, p.a.) previously dried at 383.15 K. Hydrochloric acid and sodium hydroxide solutions were prepared by diluting concentrated ampoules (Fluka), and then they were standardized against sodium carbonate and potassium hydrogen phthalate, respectively. 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 and Procedure. Saturated solutions of EDTA were prepared by addition of an excess of ligand to aqueous solutions of NaCl at different ionic strengths and pure water. Other checks were carried out in the same experimental conditions by addition of an excess of HCl (≤ 0.008 M) in the saturated solutions. Solutions were stirred at 298.15 K for 24 h. Preliminary tests established that longer stirring times were unnecessary. Saturated solutions were separated from precipitates by centrifugation and by filtration through cellulose membrane filters ($\varnothing = 0.45$ μm). A volume of 25 mL of the solution was titrated with standard NaOH. Separate titrations of HCl at the same ionic strength of the sample under study were carried out to determine the standard electrode potential E^0 and the junction potential coefficient j_a ($E_j = j_a \cdot [H^+]$).

To minimize systematic errors, two operators (A and B) carried out potentiometric titrations in a completely independent way, using different reagents and two separate systems: operator (A) used a model 809 Metrohm potentiometer (Titrando, Metrohm Corp.), equipped with a half-

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10.1021/je700391c CCC: \$40.75

Table 1. Protonation Constants of EDTA in $NaCl_{aq}$ at Different Ionic Strength and $T = 298.15$ K

I^a	$\log K_1{}^b$	I^a	$\log K_2{}^b$	I^a	$\log K_3{}^b$	I^a	$\log K_4{}^b$
0.020	9.949 ± 0.022^c	0.020	6.359 ± 0.018^c	0.020	2.854 ± 0.019^c	0.020	2.136 ± 0.023^c
0.054	9.396 ± 0.020	0.051	6.167 ± 0.017	0.053	2.805 ± 0.017	0.050	2.204 ± 0.022
0.055	9.349 ± 0.020	0.053	6.154 ± 0.017	0.052	2.776 ± 0.017	0.051	2.204 ± 0.022
0.098	9.239 ± 0.019	0.097	6.083 ± 0.015	0.100	2.672 ± 0.015	0.100	2.060 ± 0.020
0.100	9.436 ± 0.018	0.100	6.141 ± 0.015	0.101	2.721 ± 0.015	0.101	2.155 ± 0.020
0.110	9.137 ± 0.018	0.109	6.050 ± 0.015	0.113	2.704 ± 0.015	0.112	2.146 ± 0.019
0.231	9.015 ± 0.015	0.235	5.994 ± 0.012	0.249	2.651 ± 0.012	0.252	2.078 ± 0.014
0.233	8.995 ± 0.015	0.236	5.983 ± 0.012	0.250	2.635 ± 0.012	0.297	2.097 ± 0.013
0.297	9.092 ± 0.013	0.297	5.998 ± 0.011	0.297	2.552 ± 0.012	0.507	2.022 ± 0.009
0.453	8.793 ± 0.011	0.465	5.966 ± 0.009	0.500	2.497 ± 0.013	0.521	2.021 ± 0.009
0.463	8.740 ± 0.011	0.475	5.936 ± 0.009	0.506	2.466 ± 0.013	0.995	1.935 ± 0.006
0.500	8.877 ± 0.011	0.500	5.951 ± 0.009	0.514	2.500 ± 0.013	1.022	2.040 ± 0.006
0.887	8.656 ± 0.010	0.914	6.036 ± 0.007	0.995	2.434 ± 0.017	1.023	1.990 ± 0.006
0.879	8.672 ± 0.010	0.918	6.047 ± 0.007	1.000	2.499 ± 0.017	1.024	1.990 ± 0.006
0.995	8.727 ± 0.010	0.995	6.003 ± 0.007	1.015	2.396 ± 0.017	2.086	2.008 ± 0.007
1.022	8.689 ± 0.010	1.022	6.036 ± 0.007	1.022	2.373 ± 0.017	2.088	2.008 ± 0.007
1.022	8.649 ± 0.010	1.022	6.056 ± 0.007	2.064	2.385 ± 0.017	2.194	2.015 ± 0.007
1.773	8.562 ± 0.010	1.849	6.224 ± 0.006	2.159	2.412 ± 0.017	3.017	2.037 ± 0.006
1.775	8.547 ± 0.010	1.851	6.224 ± 0.006	2.972	2.503 ± 0.014	3.198	2.073 ± 0.006
1.875	8.536 ± 0.010	1.953	6.246 ± 0.006	2.994	2.443 ± 0.014	3.202	2.074 ± 0.006
2.722	8.606 ± 0.008	2.288	6.414 ± 0.005	3.133	2.473 ± 0.013	3.211	2.074 ± 0.006
2.724	8.606 ± 0.008	2.839	6.478 ± 0.005	3.135	2.488 ± 0.013	3.782	2.109 ± 0.005
2.744	8.582 ± 0.008	2.857	6.465 ± 0.005	3.683	2.546 ± 0.013	3.788	2.109 ± 0.005
2.994	8.676 ± 0.007	2.994	6.491 ± 0.005	3.704	2.481 ± 0.013	3.806	2.110 ± 0.005
3.006	8.637 ± 0.007	2.994	6.431 ± 0.005	4.253	2.576 ± 0.015	4.343	2.150 ± 0.005
3.223	8.626 ± 0.007	3.355	6.593 ± 0.005	4.282	2.617 ± 0.015	4.375	2.150 ± 0.005
3.244	8.666 ± 0.007	3.379	6.586 ± 0.005	4.978	2.609 ± 0.019	4.429	2.152 ± 0.005
3.245	8.612 ± 0.007	3.383	6.601 ± 0.005	5.287	2.718 ± 0.022	5.015	2.203 ± 0.005
3.711	8.699 ± 0.006	3.867	6.707 ± 0.006	5.404	2.767 ± 0.023	5.476	2.221 ± 0.006
3.758	8.696 ± 0.006	3.912	6.737 ± 0.006	5.445	2.669 ± 0.023	5.478	2.221 ± 0.006
3.799	8.713 ± 0.006	3.959	6.752 ± 0.006	5.593	2.669 ± 0.024	5.622	2.230 ± 0.007
4.723	8.809 ± 0.008	4.910	6.929 ± 0.010			5.626	2.230 ± 0.007
4.742	8.780 ± 0.008	4.924	6.940 ± 0.010			5.746	2.239 ± 0.007
4.767	8.782 ± 0.008	4.945	6.952 ± 0.010			5.749	2.239 ± 0.007
4.856	8.882 ± 0.009	5.003	6.969 ± 0.010				
4.883	8.828 ± 0.009	5.043	7.013 ± 0.010				
4.971	8.839 ± 0.009	5.074	7.007 ± 0.010				
5.003	8.881 ± 0.009	5.165	7.017 ± 0.011				
5.014	8.766 ± 0.009	5.206	6.971 ± 0.011				

[a] $mol \cdot kg^{-1}$. [b] Protonation constants, K_i, refer to the reaction: $H^+ + H_{i-1}L^{i-5} = H_iL^{i-4}$. [c] ± std. dev. (average values, 2–4 titrations).

Table 2. Parameters of Equation 3 for the Dependence of Protonation Constants on Ionic Strength, Calculated Using the SIT Equation

parameter	$i = 1^a$	$i = 2^a$	$i = 3^a$	$i = 4^a$
$\log K_i{}^b$	10.242 ± 0.015^c	6.663 ± 0.006^c	3.145 ± 0.005^c	2.364 ± 0.007^c
$\Delta\epsilon_\infty$	0.190 ± 0.004	0.262 ± 0.004	0.116 ± 0.004	0.087 ± 0.002
$\Delta\epsilon_0$	−0.114 ± 0.026	0.957 ± 0.018	0.072 ± 0.017	−0.017 ± 0.015
ϵ_∞	0.101 ± 0.006	0.046 ± 0.005	−0.080 ± 0.004	−0.060 ± 0.002
ϵ_0	0.351 ± 0.025	0.551 ± 0.021	−0.321 ± 0.018	−0.308 ± 0.012

[a] Indexes refer to the four protonation steps of EDTA. [b] Protonation constants of EDTA at infinite dilution in the molal concentration scale. [c] ± std. dev.

cell glass electrode (Ross type 8101, from Orion), coupled with a standard calomel electrode. Operator (B) used a model 713 Metrohm potentiometer connected to a model 665 Metrohm motorized burette and a combinated glass electrode (Ross type 8102SC, from Orion). The estimated reproducibility was ± 0.15 mV and ± 0.003 mL for emf and titrant volume readings, respectively, and was the same for both systems. The potentiometric systems were connected to a PC, and automatic titrations were performed using a suitable computer program to control titrant delivery and data acquisition and check for emf stability. All measurements were thermostatted at (298.15 ± 0.1) K, magnetically stirred, and N_2 bubbled through the solution to exclude the presence of CO_2 and O_2. Independent experiments were performed at least three times.

Calculations. All calculations relative to the refinement of parameters (protonation constants, analytical concentration of reagents, formal electrode potentials) of EDTA were carried out by the computer program ESAB2M;[12] this program was also used to check the ligand purity. The general least-squares computer program LIANA[13] was used for the refinement of the parameters for the dependence of protonation constants and of the solubility on ionic strength.

Protonation constants are related to the equilibrium

$$H^+ + H_{i-1}Y^{i-5} = H_iY^{i-4} \quad K_i$$

Other details on solubility measurements and on data analysis are reported in the previous papers on this topic.[14–17]

Results and Discussion

Protonation Constants. Saturated solutions of EDTA obtained from solubility measurements were used to perform potentiometric measurements to determine the protonation constants. The experimental protonation constants in molar concentration scale are reported as Supporting Information

Table 3. Smoothed Protonation Constants of EDTA, at T = 298.15 K, in $NaCl_{aq}$ at Different Ionic Strength[a]

I/mol·kg^{-1}	log $K_1{}^b$	log $K_2{}^b$	log $K_3{}^b$	log $K_4{}^b$
0.00	10.24 ± 0.02[c]	6.663 ± 0.006[c]	3.145 ± 0.005[c]	2.364 ± 0.007[c]
0.05	9.55 ± 0.01	6.197 ± 0.006	2.808 ± 0.005	2.193 ± 0.006
0.10	9.36 ± 0.01	6.096 ± 0.005	2.715 ± 0.004	2.145 ± 0.005
	9.50[d]	6.18[d]		
	10.26[e]	6.18[e]	2.78[e]	2.1[e]
0.25	9.06 ± 0.01	5.993 ± 0.004	2.583 ± 0.004	2.074 ± 0.004
0.30	9.18[f]	6.02[f]	2.56[f]	2.14[f]
	9.08[d]	6.08[d]		
0.50	8.84 ± 0.01	5.975 ± 0.004	2.489 ± 0.004	2.023 ± 0.003
0.61	8.82[d]	6.07[d]		
1.00	8.65 ± 0.01	6.048 ± 0.004	2.423 ± 0.004	1.992 ± 0.002
1.02	8.75[f]	6.03[f]	2.33[f]	2.09[f]
	8.67[f]	6.07[f]		
1.50	8.58 ± 0.01	6.152 ± 0.004	2.412 ± 0.004	1.993 ± 0.002
2.00	8.57 ± 0.01	6.263 ± 0.004	2.424 ± 0.003	2.008 ± 0.002
2.09	8.66[f]	6.27[f]	2.40[f]	1.88[f]
3.00	8.62 ± 0.01	6.497 ± 0.003	2.478 ± 0.001	2.057 ± 0.002
3.20	8.65[f]	6.48[f]	2.52[f]	2.01[f]
4.00	8.72 ± 0.01	6.736 ± 0.004	2.554 ± 0.003	2.120 ± 0.002
4.37	8.78[f]	6.72[f]	2.46[f]	2.06[f]
5.00	8.85 ± 0.01	6.979 ± 0.006	2.641 ± 0.006	2.190 ± 0.003
5.61	8.91[f]	6.96[f]	2.58[f]	2.21[f]
6.00	8.99 ± 0.02	7.226 ± 0.009	2.735 ± 0.010	2.264 ± 0.004

[a] Some relevant literature values are also reported. [b] Equilibrium refers to the reaction: $H^+ + H_{i-1}L^{i-5} = H_iL^{i-4}$. [c] ± std. dev. [d] Ref 10. [e] Recommended values from ref 7; molal conc. scale (I = 0.1006 mol·kg^{-1}), in KNO_3. [f] Ref 11.

Table 4. Total Molal Solubility of EDTA in NaCl Solutions, at Different Ionic Strengths and T = 298.15 K

I/mol·kg^{-1}	$-\log S^{Ta}$	pH[a]
0.050	2.854	2.770 ± 0.005[b]
0.101	2.824	2.745 ± 0.004
0.252	2.796	2.699 ± 0.002
0.507	2.745	2.658 ± 0.003
1.023	2.699	2.569 ± 0.003
2.088	2.699	2.553 ± 0.002
2.086	2.699	2.569 ± 0.002
3.202	2.721	2.585 ± 0.002
3.198	2.721	2.602 ± 0.002
3.782	2.745	2.620 ± 0.005
3.806	2.745	2.602 ± 0.003
4.343	2.745	2.620 ± 0.002
4.375	2.770	2.658 ± 0.003
5.478	2.796	2.678 ± 0.002
5.476	2.796	2.678 ± 0.002
5.626	2.796	2.721 ± 0.002
5.746	2.796	2.699 ± 0.002
0.051	2.854	2.796 ± 0.002
0.112	2.824	2.796 ± 0.008
0.252	2.770	2.721 ± 0.005
0.521	2.745	2.658 ± 0.004
1.024	2.699	2.602 ± 0.005
2.194	2.699	2.585 ± 0.004
3.211	2.721	2.620 ± 0.004
3.788	2.721	2.638 ± 0.004
4.429	2.745	2.678 ± 0.006
5.478	2.796	2.745 ± 0.007
5.622	2.796	2.745 ± 0.007
5.749	2.824	2.770 ± 0.008

[a] Concentrations calculated in molal concentration scale. [b] ± std. dev.

in Table 1S. The molar protonation constants and the ionic strength values were converted to the molal concentration scale (m/mol·kg^{-1} of water) following procedures already reported.[18] The molal protonation constants are reported in Table 1 (some values of the third and fourth protonation constant were discarded).

The dependence on ionic strength (I/mol·kg^{-1}) of molal protonation constants was modeled by using the SIT equation (assuming $I = m_{NaCl}$)[19–21]

$$\log K_i = \log K_i^0 - \frac{1.02 \cdot (5-i) \cdot \sqrt{I}}{(1 + 1.5 \cdot \sqrt{I})} + \Delta\epsilon \cdot I \qquad (1)$$

where $K_i{}^0$ is the constant at infinite dilution and $\Delta\epsilon$ is the difference in the specific interaction coefficients, given by the equation

$$\Delta\epsilon_i = \epsilon(H^+, C1^-) + \epsilon(H_{i-1}Y^{(i-5)}, Na^+) - \epsilon(H_i, Na^+) \quad (2)$$

In the SIT approach, specific interaction coefficients, ϵ, were considered dependent on ionic strength, according to the equation[14–16,22]

$$\epsilon = \epsilon_\infty + \frac{(\epsilon_0 - \epsilon_\infty)}{(I+1)} \qquad (3)$$

In some cases the equation $\epsilon = \epsilon_{(0)} + \epsilon_{(1)} \ln (I + 1)$ was also used,[20,21] but preliminary calculations showed a better fit when using eq 3.

The activity coefficients of the EDTA neutral species (H_4Y^0) can be calculated from solubility measurements by using the Setschenow equation[23,24] (see Solubility section) and following procedures reported in previous papers.[14–17] The specific interaction coefficient $\epsilon(H^+, Cl^-) = 0.136 - 0.0512/(I + 1)$ was taken from ref 22.

Molar protonation constants were fitted to eq 1, by substituting $\Delta\epsilon$ with B where

$$B = b_\infty + \frac{(b_0 - b_\infty)}{(I+1)} \qquad (4)$$

In this case, eq 1 becomes an extended Debye–Hückel type equation. The parameters for the SIT equation are reported in Table 2, while the extended Debye–Hückel type equation parameters are reported in Table 2S. Smoothed values of protonation constants are reported in Table 3, together with some literature data.

Solubility. Primary solubility data, S^T, together with pH values of saturated solutions, are reported in Table 3S in the Supporting Information, while the molal solubility data obtained from molar values (see ref 18) are reported in Table 4.

Total solubility data were fitted to the smoothing function tested in previous papers[14–17]

$$\log S^{\mathrm{T}} = \log S_0^{\mathrm{T}} + m_{\mathrm{NaCl}}\left(a_\infty + \frac{a_0 - a_\infty}{m_{\mathrm{NaCl}} + 1}\right) \tag{5}$$

where m_{NaCl} is the salt concentration expressed in the molal concentration scale [eq 5 can be applied to the molar concentration scale by substituting m_{NaCl} for c_{NaCl}], and S^{T} and S_0^{T} are the total solubility at different ionic strengths and the total solubility in pure water, respectively. a_∞ and a_0 are the parameters for the dependence of total solubility on ionic strength valid for $I \to \infty$ and $I \to 0$, respectively. In Table 5, we report the parameters of eq 5, while the corresponding values expressed in the molar scale are reported as Supporting Information in Table 4S.

The total solubility of a ligand is due to the sum of all its species in solution, namely, the neutral and deprotonated or partially protonated species. For a generic carboxylic acid (H_nL) we have

$$S^{\mathrm{T}} = [\mathrm{H}_n\mathrm{L}^0] + [\mathrm{H}_{n-1}\mathrm{L}^-] + \ldots + [\mathrm{L}^{n-}] \tag{6}$$

and with $[\mathrm{H}_n\mathrm{L}^0] = S^0$, where S^0 is the solubility of the neutral species, we have

$$S^{\mathrm{T}} = S^0\left[1 + \sum_{0}^{n-1}\left(\prod_{i}^{n} K_i[\mathrm{H}^+]^{n-i+1}\right)^{-1}\right] \tag{7}$$

In the case of EDTA, to obtain the solubility of the neutral species H_4Y^0, S^0, we must consider the dissociation of the acid, according to the equation[14–17]

$$S^0 = \frac{S^{\mathrm{T}}}{\left[1 + \dfrac{1}{(K_3K_4[\mathrm{H}^+]^2)} + \dfrac{1}{(K_4[\mathrm{H}^+])} + K_5[\mathrm{H}^+]\right]} \tag{8}$$

where K_3, K_4, and K_5 are the third, fourth, and fifth protonation constants of EDTA. In our experimental conditions, we observed by means of the program ES4ECI[13] that the formation percentages of the species Y^{4-} and HY^{3-} are very low and that their protonation constants are negligible in the calculations. The values of K_3 and K_4 were determined in this work, while K_5 was taken from the literature.[5,7] A rough estimate, $\log K_5 = (1.51 \pm 0.06)\cdot(I/\mathrm{mol\cdot L^{-1}} - 0.1)$ is sufficient in the calculations using eq 8, since the contribution to the solubility of H_5Y^+ is small (< 1 %), in our experimental conditions. The solubility of the neutral species is related to its activity coefficient, γ_{N}, by the Setschenow equation[23,24]

$$\log \gamma_{\mathrm{N}} = \log \frac{S_0^0}{S^0} = k_{\mathrm{m}}\cdot m_{\mathrm{NaCl}} \tag{9}$$

Table 5. Total Solubility (Molal Concentration Scale) of EDTA, at T = 298.15 K, and Parameters for the Dependence on NaCl Concentration

[a]	$\log -S_0^{\mathrm{T}b}$	$-a_\infty$	$(a_0 - a_\infty)$	σ^c	MD[d]
(A)	2.858 ± 0.004[e]	0.0476 ± 0.0077[e]	0.383 ± 0.015[e]	0.008	0.006
(B)	2.861 ± 0.003	0.0534 ± 0.0020	0.369 ± 0.013	0.010	0.008
(C)	2.858 ± 0.001	0.0492 ± 0.0012	0.343 ± 0.007	0.009	0.0075

[a] (A) Data of operator A; (B) data of operator B; (C) data of both operators A and B. [b] Total solubility of EDTA in pure water in molal concentration scale. [c] std. dev. in the fit of eq 5. [d] Mean deviation. [e] ± std. dev.

Table 6. Solubility of the Neutral Species (Molal Concentration Scale) H_4Y^0, at T = 298.15 K, for Different Salt Concentrations

I/mol·kg^{-1}	$-\log S^0$	$-\log K_{\mathrm{S0}}$
0.00	3.786 ± 0.005[a]	26.20 ± 0.02[a]
0.05	3.776 ± 0.004	24.53 ± 0.02
0.10	3.767 ± 0.004	24.08 ± 0.01
		24.60[b]
0.25	3.744 ± 0.003	23.46 ± 0.01
0.50	3.715 ± 0.003	23.04 ± 0.01
1.00	3.676 ± 0.003	22.79 ± 0.01
	3.43[c]	22.58[d]
1.50	3.651 ± 0.003	22.79 ± 0.01
2.00	3.633 ± 0.003	22.90 ± 0.01
3.00	3.605 ± 0.002	23.26 ± 0.01
4.00	3.584 ± 0.001	23.71 ± 0.01
5.00	3.567 ± 0.002	24.22 ± 0.01
6.00	3.551 ± 0.003	24.76 ± 0.02

[a] ± Std. dev. [b] $I \sim 0.1$ (K^+), ref 9. [c] $I = 1.05$ (H, Na) ClO_4, ref 8. [d] $I = 1.05$ (H, Na) ClO_4, ref 7.

where k_{m} is the Setschenow coefficient. Equation 9 is expressed in the molal scale, but it can be used also in the molar concentration scale by substituting m_{NaCl} for c_{NaCl}. S_0^0 represents the solubility of the neutral species in pure water. As shown for similar measurements for some carboxylic acids and for cystine,[14–17] often k_{m} is not a true constant and depends on the concentration of supporting electrolyte according to the equation

$$k_{\mathrm{m}} = k_{\mathrm{m},\infty} + \left(\frac{k_{\mathrm{m},0} - k_{\mathrm{m},\infty}}{m_{\mathrm{NaCl}} + 1}\right) \tag{10}$$

where $k_{\mathrm{m},0}$ and $k_{\mathrm{m},\infty}$ are the values at $m_{\mathrm{NaCl}} \to 0$ and $m_{\mathrm{NaCl}} \to \infty$, respectively. By fitting solubility data to eq 8, with k_{m} expressed by eq 10, we obtained

$$\log S_0^0 = -3.786 \pm 0.005 \quad (S_0^0 = 1.64\cdot 10^{-4}\ \mathrm{mol{\cdot}kg^{-1}})$$

$$k_{\mathrm{m},\infty} = -0.011 \pm 0.002, \quad k_{\mathrm{m},0} = -0.208 \pm 0.005$$

and therefore

$$\log \gamma_{\mathrm{N}} = -\left[0.011 + \frac{0.197}{(m_{\mathrm{NaCl}} + 1)}\right]\cdot m_{\mathrm{NaCl}} \tag{11}$$

The solubility product of EDTA

$$K_{\mathrm{S0}} = [\mathrm{Y}^{4-}]\cdot[\mathrm{H}^+]^4$$

can be obtained by the equation

$$k_{\mathrm{S0}} = \frac{[\mathrm{H}_4\mathrm{Y}^0]}{\beta_4} = \frac{S^0}{\beta_4} \tag{12}$$

using β_4 values determined in this work. Smoothed values of $\log S^0$ and $\log K_{\mathrm{S0}}$ are reported in Table 6, together with some literature values.

Literature Comparison. The literature reports several data (refs 6 to 11, and references therein) on the protonation of EDTA; however, most of these references contain data for dilute ionic media ($I \approx 0.1$ mol·L^{-1}), and few studies report data at ionic strengths greater than 1 mol·L^{-1}. Moreover, many data available in the literature cannot be considered reliable because they were obtained by experimental procedures that do not fulfill some of the following criteria: (1) the experimental conditions used for the measurements are not clearly defined; (2) the calibration method of the pH-electrode is not indicated, or the calibration is carried out by using standard pH buffers; this implies that the pH cannot be correctly expressed in the concentration scale; (3) the constant ionic strength method is used in conditions where the ligand contributes significantly to the total ionic strength; (4) the temperature, ionic strength, and ionic medium are not clearly reported in the paper. In ref 6, the authors proposed some selected protonation constants for EDTA and calculated corresponding values at infinite dilution taking into account also the formation of EDTA$-$Na$^+$ complex formation constants. Owing to the different interaction power of EDTA with Na$^+$ and K$^+$, protonation constants (in particular K_1 in K$^+$ media) are significantly higher than those obtained in Na$^+$ media. Our protonation constants obtained in NaCl aqueous solution over a wide range of ionic strength are in good agreement with those reported by Anderegg,[7] Daniele,[10] and Mizera[11] (some values are reported for comparison in Table 3). Extrapolated values of K_1 are very different according to the procedure adopted: (a) extrapolation of stoichiometric protonation constants without taking into account the interaction with Na$^+$;[10,11] (b) using formation constants for the ion pair Na(EDTA)$^{3-}$ (see refs 6 and 10). We think that, at present, only K_1 for $I \geq 0.05$ mol·kg^{-1} can be considered as reliable. Future work on this matter should include the accurate measurements of K_1 at very low ionic strength.

Similar considerations can be made for the solubility of EDTA. Few solubility data are reported in the literature,[6–9] and some of them cannot be considered reliable because they were not obtained at constant ionic strength. The solubility data reported in ref 6 as a function of [H$^+$] at constant ionic strength are obtained at different temperatures ($294 \leq T$/K ≤ 303), in different ionic media (e.g., (H,K)Cl; (H,Na)NO$_3$; (H,Na)ClO$_4$; (H,K)Cl; (H,K)NO$_3$), but no selected data are reported for NaCl aqueous solution. Our paper seems to be the first in which the dependence of total solubility and the solubility of neutral species was studied. The solubility of neutral species reported in some papers[6] is in fairly good agreement with our values.

Supporting Information Available:

Tables 1S to 4S. This material is available free of charge via the Internet at http://pubs.acs.org.

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Received for review July 10, 2007. Accepted December 15, 2007. We thank the University of Messina for financial support (PRA).

JE700391C