JOURNAL OF
CHEMICAL &
ENGINEERING
DATA

ARTICLE

pubs.acs.org/jced

Total and Specific Solubility and Activity Coefficients of Neutral Species of $(CH_2)_{2i-2}N_i(CH_2COOH)_{i+2}$ Complexons in Aqueous NaCl Solutions at Different Ionic Strengths, $(0 \le I \le 5)$ mol·L^{-1}, and 298.15 K

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S *Supporting Information*

ABSTRACT: The total solubility S^T of $(CH_2)_{2i-2}N_i(CH_2COOH)_{i+2}$ complexons (i = 1, nitrilotriacetic acid (NTA); i = 3, diethylenetriaminepentaacetic acid (DTPA); i = 4, triethylene tetraaminehexaacetic acid (TTHA)) in aqueous NaCl solutions at different ionic strengths, $(0 \le I \le 5)$ mol·L^{-1}, and at 298.15 K are determined and are reported in both molar (mol·L^{-1}) and molal (mol·kg^{-1}) concentration scales, together with the protonation constants. The total solubility in pure water S_0^T is (8.1, 8.9, and 4.5) mmol·L^{-1} for NTA, DTPA, and TTHA, respectively. Increasing the ionic strength from (0.1 to 5) mol·L^{-1} (NaCl), the total solubility decreases for NTA, while the opposite trend is observed for DTPA and TTHA. From total solubility and protonation constant data, the solubility of the neutral species S^0 and the solubility products K_{S0} are calculated. The dependence on ionic strength is analyzed, and the Setschenow (k_m) coefficients are obtained, together with the solubility of the neutral species in pure water S_0^0 [S_0^0 = (2.5, 5.2, and 1.1) mmol·kg^{-1}, for NTA, DTPA, and TTHA, respectively].

INTRODUCTION

Amino polycarboxylic acids, such as nitrilotriacetic (NTA), ethylenediaminetetraacetic (EDTA), diethylenetriaminepentaacetic (DTPA), and triethylene tetraaminehexaacetic (TTHA), generally called complexons, are versatile polyfunctional ligands with a strong metal complexing ability. The name complexon was introduced in 1945 by Schwarzenbach et al.[1] for a series of artificial amino acids, containing normally at least one iminodiacetic acid group, $-N(CH_2COOH)_2$, or two aminoacetic acid groups, $-NHCH_2COOH$. Further research demonstrated that, in solution, aminopolycarboxylate anions are able to form stable highly soluble complexes with almost all known metal ions. The high values for the stability constants of the complexes formed by these ligands are due to the cumulative effect of basic amino groups and the high negative charge of several carboxylate groups, as well as the formation of numerous stable five-membered chelate rings with the metal ions.

Owing to the capability to form strong chelate complexes with most metal ions, these ligands present widespread applications in analytical and applied chemistry, biology, medicine, agriculture, and industry.[2−6] The large-scale use of these strong chelating agents, however, involves some environmental risks since the classical complexons and their metal complexes are hardly biodegradable in aquatic ecosystems.

The broad and intensive applications of complexons require reliable stability constant data to allow equilibrium modeling and prediction of important technological, environmental, and pharmacokinetic equilibria. Following the pioneering work of Schwarzenbach, a great number of equilibrium constants can be found in the literature for the proton complexes and metal chelates of these agents.[7−9] Recently, a critical evaluation of the stability constants of metal complexes of complexons was published by Anderegg et al.[10] However, only a few references on solubility studies can be found.[11−18] Literature data on NTA and DTPA solubility are presented in Table 1, while there are no literature data on TTHA.

Table 1. Literature Solubility Data

L	T	I	log K_{s0}	log S^0	ref
NTA	298.15	0.1	−16.36	−2.78	16
	293.15	1	−15.55		14
	295.15	0.01 to 0.08	−16.89		14
	293.15	1 ($NaClO_4 + HClO_4$)	−15.68	−2.46	11
DTPA	298.15	0.1	−30.43	−2.47	16
		0.05 to 0.26	−30.54	−2.58	14
	294.15	1 ($NaClO_4 + HClO_4$)	−28.62	−1.69	15

In this work we report a careful study on the solubility of the $(CH_2)_{2i-2}N_i(CH_2COOH)_{i+2}$ complexons (i = 1, NTA; i = 3, DTPA; i = 4, TTHA) in aqueous NaCl solutions at different ionic strengths, $(0 \le I \le 5)$ mol·L^{-1}, and at 298.15 K.

EXPERIMENTAL SECTION

Chemicals. NTA, DTPA, and TTHA acids (Fluka or Sigma-Aldrich products) were used without further purification, and

Received: August 2, 2010
Accepted: January 3, 2011
Published: January 21, 2011

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Table 2. Solubility Data of NTA in NaCl Solutions at Different Ionic Strengths in the Molal Concentration Scale and T = 298.15 K

I mol·kg^{-1}	pH	log S^{T}	log S^{0}	log K_{s0}
0	1.910 ± 0.039[a]	−2.079 ± 0.005[a]	−2.443 ± 0.012[a]	−17.318 ± 0.011[a]
0.108	1.873 ± 0.001	−2.116 ± 0.004	−2.601 ± 0.012	−16.168 ± 0.010
0.529	1.867 ± 0.005	−2.109 ± 0.003	−2.660 ± 0.010	−15.610 ± 0.009
1.019	1.874 ± 0.009	−2.123 ± 0.004	−2.676 ± 0.009	−15.523 ± 0.008
3.182	1.920 ± 0.006	−2.264 ± 0.004	−2.716 ± 0.009	−16.112 ± 0.008
5.561	2.009 ± 0.029	−2.391 ± 0.009	−2.767 ± 0.017	−17.072 ± 0.015

[a] ± 95 % confidence interval.

Table 3. Solubility Data of DTPA in NaCl Solutions at Different Ionic Strengths in the Molal Concentration Scale and T = 298.15 K

I mol·kg^{-1}	pH	log S^{T}	log S^{0}	log K_{s0}
0	2.054 ± 0.001[a]	−2.142 ± 0.007[a]	−2.370 ± 0.004[a]	−33.149 ± 0.006[a]
0.165	2.012 ± 0.008	−2.005 ± 0.004	−2.328 ± 0.003	−29.565 ± 0.005
0.541	1.905 ± 0.008	−1.932 ± 0.002	−2.231 ± 0.001	−28.578 ± 0.005
1.029	1.977 ± 0.016	−1.878 ± 0.003	−2.205 ± 0.002	−28.413 ± 0.004
2.010	1.912 ± 0.007	−1.817 ± 0.003	−2.120 ± 0.002	−28.713 ± 0.007
3.021	2.028 ± 0.020	−1.766 ± 0.003	−2.095 ± 0.001	−29.343 ± 0.010
4.862	2.151 ± 0.013	−1.662 ± 0.005	−2.033 ± 0.002	−30.638 ± 0.016

[a] ± 95 % confidence interval.

Table 4. Solubility Data of TTHA in NaCl Solutions at Different Ionic Strengths in the Molal Concentration Scale and T = 298.15 K

I mol·kg^{-1}	pH	log S^{T}	log S^{0}	log K_{s0}
0	2.554 ± 0.004[a]	−2.336 ± 0.005[a]	−2.808 ± 0.022[a]	−42.118 ± 0.0012[a]
0.120	2.475 ± 0.007	−2.345 ± 0.004	−3.021 ± 0.022	−37.630 ± 0.012
0.480	2.345 ± 0.004	−2.272 ± 0.004	−2.931 ± 0.020	−35.718 ± 0.010
1.795	2.304 ± 0.015	−2.171 ± 0.005	−2.684 ± 0.013	−35.642 ± 0.006
2.665	2.345 ± 0.004	−2.111 ± 0.004	−2.539 ± 0.009	−36.530 ± 0.006
4.423	2.534 ± 0.004	−1.978 ± 0.004	−2.305 ± 0.008	−38.790 ± 0.012

[a] ± 95 % confidence interval.

Table 5. Total Solubility in Pure Water at 298.15 K and Parameters for the Dependence on NaCl Concentration in the Molar and Molal Concentration Scales

L	concn. scale	log S_0^{T}	a_∞	a_0	σ[a]
NTA	c/mol·L^{-1}	−2.093 ± 0.005[b]	−0.080 ± 0.004[b]	−0.019 ± 0.019[b]	0.022
EDTA[c]		−2.867	−0.0621	0.512	
DTPA		−2.049 ± 0.007	0.034 ± 0.004	0.267 ± 0.020	0.025
TTHA		−2.342 ± 0.005	0.069 ± 0.004	0.126 ± 0.018	0.013
NTA	m/mol·kg^{-1}	−2.092 ± 0.003	−0.060 ± 0.003	−0.022 ± 0.010	0.022
EDTA[c]		−2.858	−0.0492	0.392	
DTPA		−2.048 ± 0.006	0.038 ± 0.003	0.276 ± 0.019	0.025
TTHA		−2.341 ± 0.005	0.068 ± 0.003	0.141 ± 0.016	0.012

[a] ± std. dev. in the fit of eq 1. [b] ± 95 % confidence interval. [c] Ref 18.

their 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 ampules (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 solutions.

Apparatus and Procedure. Saturated solutions of NTA, DTPA, and TTHA were prepared by the addition of an excess of ligand to a solution of NaCl at pre-established ionic strength values $[(0 \leq I \leq 5)\ \mathrm{mol \cdot L^{-1}}]$. Solutions were stirred at 298.15 K for at least 24 h. Preliminary tests established that longer stirring times were unnecessary, and that the pH value of each solution, measured when the solubility equilibrium was reached, remains constant. Saturated solutions were centrifuged and filtered through a cellulose membrane filter (Ø = 0.45 μm). A volume of 25 mL of the filtered solution was titrated with standard NaOH. Separate titrations of HCl at the 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 ($E_j = j_a\,[\mathrm{H^+}]$). To avoid systematic errors, independent experiments were performed at least three times.

To minimize systematic errors, two operators carried out potentiometric titrations in a completely independent way, using different reagents and two separate systems: a model 809 Metrohm potentiometer (Titrando, Metrohm Corp.), equipped with a half cell glass electrode (Ross type 8101, from Orion), coupled with a standard calomel electrode; a model 713 Metrohm potentiometer connected to a model 665 Metrohm motorized buret, 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 personal computer, 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 for acid—base titrations were carried out by the computer program ESAB2M;[19] this program was also used to check the ligand purity. The general least-squares computer program LIANA[20] was used for the refinement of the parameters for the dependence of the solubility on ionic strength.

RESULTS AND DISCUSSION

Primary solubility data, that is, the total solubility S^T, together with pH values of saturated solutions, are reported in Tables 2 to 4, for NTA, DTPA, and TTHA, respectively, in the molal concentration scale (m/mol·kg^{-1} of water). Molal data were obtained from the molar ones following procedures already reported.[21] The molar solubilities are reported as Supporting Information in Tables 1S to 3S.

Total solubility data were fitted to the smoothing function tested in previous papers:[18,22]

$$\log S^{\mathrm{T}} = \log S_0^{\mathrm{T}} + \left(a_\infty + \frac{a_0 - a_\infty}{c_{\mathrm{NaCl}} + 1}\right) \cdot c_{\mathrm{NaCl}} \qquad (1)$$

Table 6. Calculated Total Solubility Values for NTA, DTPA, and TTHA in NaCl Aqueous Solutions at Different Ionic Strengths, in the Molar and Molal Concentration Scales, and T = 298.15 K

	$\log S^{\mathrm{T}a}$		
	NTA	DTPA	TTHA
c_{NaCl}/mol·L^{-1}			
0.1	−2.096 ± 0.004[b]	−2.025 ± 0.005[b]	−2.330 ± 0.004[b]
0.5	−2.113 ± 0.004	−1.955 ± 0.002	−2.289 ± 0.004
1	−2.143 ± 0.003	−1.899 ± 0.002	−2.245 ± 0.005
2	−2.213 ± 0.004	−1.826 ± 0.003	−2.167 ± 0.004
3	−2.289 ± 0.004	−1.773 ± 0.003	−2.094 ± 0.003
4	−2.366 ± 0.006	−1.727 ± 0.003	−2.022 ± 0.004
5	−2.444 ± 0.009	−1.686 ± 0.006	−1.952 ± 0.007
m_{NaCl}/mol·kg^{-1}			
0.1	−2.094 ± 0.003	−2.023 ± 0.005	−2.328 ± 0.004
0.5	−2.109 ± 0.002	−1.950 ± 0.002	−2.283 ± 0.004
1	−2.133 ± 0.002	−1.891 ± 0.002	−2.236 ± 0.004
2	−2.187 ± 0.003	−1.814 ± 0.003	−2.156 ± 0.005
3	−2.244 ± 0.004	−1.756 ± 0.003	−2.082 ± 0.004
4	−2.303 ± 0.006	−1.707 ± 0.003	−2.010 ± 0.003
5	−2.362 ± 0.008	−1.661 ± 0.005	−1.939 ± 0.005

[a] Calculated by eq 1 with values of Table 5. [b] ± 95 % confidence interval.

where S^{T} and S_0^{T} are the total solubility at different ionic strengths and the total solubility in pure water, respectively, c_{NaCl} is the molar concentration of NaCl, and a_∞ and a_0 are parameters for the dependence of total solubility on ionic strength valid for $c_{\mathrm{NaCl}} \rightarrow \infty$ and $c_{\mathrm{NaCl}} \rightarrow 0$, respectively. Equation 1 can be also applied to the molal scale by substituting c_{NaCl} for m_{NaCl}. Parameters of eq 1 are reported in Table 5, both in the molar and molal concentration scales. The calculated values of total solubility for NTA, DTPA, and TTHA in NaCl at different ionic strengths are reported in Table 6. As can be observed, increasing the ionic strength from (0.1 to 5) mol·L^{-1}, the total solubility S^{T} decreases for NTA [from (8.0 to 3.6) mmol·L^{-1}], while the opposite trend is observed for DTPA [from (9.4 to 20.6) mmol·L^{-1}] and TTHA [from (4.7 to 11.2) mmol·L^{-1}].

Owing to proton dissociation/association equilibria:

$$\mathrm{H^+} + \mathrm{H}_{i-1}\mathrm{L}^{(n-i+1)-} = \mathrm{H}_i\mathrm{L}^{(n-1)-} \qquad K_i$$

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 polycarboxylic acid ($\mathrm{H}_n\mathrm{L}$, with n = maximum protonation degree) we have:

$$S^{\mathrm{T}} = [\mathrm{H}_n\mathrm{L}^0] + [\mathrm{H}_{n-1}\mathrm{L}^-] + ... + [\mathrm{L}^{n-}] \qquad (2)$$

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

$$S^{\mathrm{T}} = S^0[1 + \sum_{0}^{n-1}(\prod_{i}^{n} \mathrm{K}_i[\mathrm{H}^+]^{n-i+1})^{-1}] \qquad (3)$$

The experimental protonation constants (K_i) of NTA, DTPA, and TTHA are reported in Tables 7 to 9 in the molal concentration scale, and in Tables 4S to 6S (Supporting Information) in

Table 7. Protonation Constant Values of NTA in NaCl Solutions at Different Ionic Strengths in the Molal Concentration Scale and T = 298.15 K

I/mol·kg^{-1}	log K_1	log K_2	log K_3	log K_4
0.115	9.312 ± 0.009[a]	2.482 ± 0.006[a]	1.694 ± 0.009[a]	1.314 ± 0.012[a]
0.120	9.276 ± 0.009	2.522 ± 0.006	1.684 ± 0.009	1.307 ± 0.012
0.128	9.260 ± 0.009	2.514 ± 0.006	1.679 ± 0.009	1.307 ± 0.012
0.129	9.258 ± 0.009	2.513 ± 0.006	1.679 ± 0.009	1.307 ± 0.012
0.130	9.256 ± 0.009	2.512 ± 0.006	1.678 ± 0.009	1.308 ± 0.012
0.130	9.267 ± 0.009	2.478 ± 0.006	1.708 ± 0.009	1.301 ± 0.012
0.515	8.907 ± 0.006	2.374 ± 0.005	1.605 ± 0.006	1.336 ± 0.012
0.525	9.007 ± 0.006	2.470 ± 0.005	1.700 ± 0.006	—
0.526	8.902 ± 0.006	2.373 ± 0.005	1.605 ± 0.006	1.337 ± 0.012
0.531	8.933 ± 0.006	2.369 ± 0.005	1.629 ± 0.006	1.399 ± 0.012
1.003	8.776 ± 0.007	2.358 ± 0.006	1.607 ± 0.007	1.371 ± 0.010
1.007	8.829 ± 0.007	2.382 ± 0.006	1.684 ± 0.007	1.458 ± 0.010
1.008	8.775 ± 0.007	2.358 ± 0.006	1.608 ± 0.007	1.372 ± 0.010
1.008	8.775 ± 0.007	2.358 ± 0.006	1.608 ± 0.007	1.372 ± 0.010
1.009	8.775 ± 0.007	2.359 ± 0.006	1.608 ± 0.007	1.372 ± 0.010
1.011	8.850 ± 0.007	2.407 ± 0.006	1.686 ± 0.007	—
1.013	8.774 ± 0.007	2.359 ± 0.006	1.608 ± 0.007	1.372 ± 0.010
2.034	8.741 ± 0.007	2.423 ± 0.006	1.678 ± 0.007	1.443 ± 0.008
2.035	8.741 ± 0.007	2.423 ± 0.006	1.679 ± 0.007	1.443 ± 0.008
3.034	8.805 ± 0.006	2.519 ± 0.005	1.772 ± 0.007	1.510 ± 0.008
3.046	8.806 ± 0.006	2.519 ± 0.005	1.773 ± 0.007	1.511 ± 0.008
3.052	8.806 ± 0.006	2.520 ± 0.005	1.773 ± 0.007	1.510 ± 0.008
3.103	8.805 ± 0.006	2.525 ± 0.005	1.779 ± 0.007	1.514 ± 0.008
3.104	8.811 ± 0.006	2.525 ± 0.005	1.779 ± 0.007	1.514 ± 0.010
3.106	8.923 ± 0.006	2.576 ± 0.005	1.901 ± 0.007	—
3.130	8.844 ± 0.006	2.503 ± 0.005	1.888 ± 0.007	—
3.134	8.813 ± 0.006	2.529 ± 0.005	1.782 ± 0.007	1.516 ± 0.010
4.835	8.987 ± 0.008	2.705 ± 0.005	1.949 ± 0.010	1.620 ± 0.014
4.835	8.987 ± 0.008	2.705 ± 0.005	1.949 ± 0.010	1.620 ± 0.014
5.236	9.032 ± 0.009	2.748 ± 0.006	1.989 ± 0.012	1.644 ± 0.016
5.457	9.057 ± 0.010	2.771 ± 0.007	2.010 ± 0.013	1.656 ± 0.018
5.466	9.116 ± 0.010	2.771 ± 0.007	2.124 ± 0.013	1.519 ± 0.018
5.474	9.096 ± 0.010	2.782 ± 0.007	2.154 ± 0.013	—

[a] ± 95 % confidence interval.

the molar concentration scale. Their dependence on ionic strength was modeled by using the SIT equation:

$$\log K_i = \log K_i^0 - 2(n-i)\frac{0.51 \cdot \sqrt{I}}{(1+1.5\sqrt{I})} + \Delta\varepsilon \cdot I \qquad (4)$$

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

$$\Delta\varepsilon = \varepsilon(\mathrm{H}^+, \mathrm{Cl}^-) + \varepsilon(\mathrm{H}_{(i-1)}\mathrm{L}^{(n-i+1)-}, \mathrm{Na}^+) - \varepsilon(\mathrm{H}_i\mathrm{L}^{(n-1)-}, \mathrm{Na}^+) \qquad (4a)$$

Specific interaction coefficients, ε, were considered dependent on ionic strength, according to the equation:[22]

$$\varepsilon = \varepsilon_\infty + \frac{\varepsilon_0 - \varepsilon_\infty}{(I+1)} \qquad (4b)$$

Values of K_i^0 and of $\Delta\varepsilon$ for NTA, DTPA, and TTHA are reported in Table 10. By these values, protonation constants were calculated at the same ionic strength of S^{T} and used to determine S^0 (eq 3). The solubility of the neutral species for NTA, DTPA and TTHA is reported in Tables 2 to 4, in the molal concentration scale, and in Tables 1S to 3S (SI) in the molar concentration scale.

In the same tables, the solubility products K_{s0} of the neutral species are reported, where K_{s0} is defined as:

$$K_{s0} = [\mathrm{L}^{n-}] \cdot [\mathrm{H}^+]^n \qquad (5)$$

and can be obtained by the equation:

$$K_{s0} = \frac{[\mathrm{H}_n\mathrm{L}^0]}{\beta_n} = \frac{S^0}{\beta_n} \qquad (6)$$

Table 8. Protonation Constant Values of DTPA in NaCl Solutions at Different Ionic Strengths in the Molal Concentration Scale and T = 298.15 K

I	log K_1	log K_2	log K_3	log K_4	log K_5	log K_6
0.111	10.158 ± 0.032[a]	8.668 ± 0.015[a]	4.196 ± 0.020[a]	2.705 ± 0.018[a]	2.141 ± 0.032[a]	—
0.165	9.876 ± 0.028	8.346 ± 0.013	4.063 ± 0.018	2.616 ± 0.015	1.991 ± 0.029	1.213 ± 0.028[a]
0.165	9.841 ± 0.028	8.236 ± 0.013	4.093 ± 0.018	2.621 ± 0.015	2.026 ± 0.029	1.303 ± 0.028
0.252	9.822 ± 0.023	8.294 ± 0.012	4.083 ± 0.015	2.619 ± 0.013	2.103 ± 0.025	—
0.496	9.550 ± 0.014	8.156 ± 0.010	4.037 ± 0.011	2.587 ± 0.010	2.12 ± 0.018	—
0.541	9.479 ± 0.013	8.094 ± 0.011	3.981 ± 0.010	2.555 ± 0.010	2.079 ± 0.017	1.053 ± 0.026
0.541	9.499 ± 0.013	8.129 ± 0.011	4.005 ± 0.010	2.539 ± 0.010	2.039 ± 0.017	1.183 ± 0.026
0.732	9.419 ± 0.010	8.118 ± 0.011	4.050 ± 0.011	2.579 ± 0.012	2.121 ± 0.015	—
0.970	9.334 ± 0.009	8.092 ± 0.012	4.064 ± 0.013	2.579 ± 0.014	2.125 ± 0.015	—
1.029	9.373 ± 0.009	8.091 ± 0.012	4.037 ± 0.013	2.565 ± 0.014	2.082 ± 0.015	1.290 ± 0.022
1.029	9.343 ± 0.009	8.081 ± 0.012	4.047 ± 0.013	2.535 ± 0.014	2.102 ± 0.015	1.410 ± 0.022
2.010	9.272 ± 0.013	8.110 ± 0.012	4.168 ± 0.017	2.577 ± 0.017	2.153 ± 0.016	1.102 ± 0.018
2.010	9.244 ± 0.013	8.122 ± 0.012	4.159 ± 0.017	2.589 ± 0.017	2.153 ± 0.016	1.302 ± 0.018
3.020	9.346 ± 0.014	8.259 ± 0.010	4.371 ± 0.015	2.711 ± 0.016	2.182 ± 0.015	1.724 ± 0.017
3.020	9.380 ± 0.014	8.249 ± 0.010	4.374 ± 0.015	2.687 ± 0.016	2.198 ± 0.015	1.669 ± 0.017
4.598	9.588 ± 0.019	8.515 ± 0.012	4.707 ± 0.011	2.875 ± 0.020	2.334 ± 0.016	1.968 ± 0.023
4.598	9.588 ± 0.019	8.517 ± 0.012	4.711 ± 0.011	2.875 ± 0.020	2.332 ± 0.016	1.966 ± 0.023
5.126	9.626 ± 0.024	8.577 ± 0.015	4.786 ± 0.012	2.879 ± 0.024	2.356 ± 0.019	1.936 ± 0.025
5.126	9.652 ± 0.024	8.557 ± 0.015	4.775 ± 0.012	2.890 ± 0.024	2.356 ± 0.019	1.961 ± 0.025

[a] ± 95 % confidence interval.

Table 9. Protonation Constant Values of TTHA in NaCl Solutions at Different Ionic Strengths in the Molal Concentration Scale and T = 298.15 K

I / mol·kg^{1-}	log K_1	log K_2	log K_3	log K_4	log K_5	log K_6	log K_7
0.040	10.942 ± 0.041[a]	9.887 ± 0.033[a]	6.306 ± 0.017[a]	4.006 ± 0.044[a]	2.610 ± 0.051	2.166 ± 0.043	1.575 ± 0.016
0.119	10.31 ± 0.033	9.334 ± 0.026	6.060 ± 0.014	3.952 ± 0.037	2.690 ± 0.044	2.196 ± 0.037	1.578 ± 0.015
0.480	9.763 ± 0.016	8.854 ± 0.009	5.839 ± 0.015	3.785 ± 0.027	2.563 ± 0.029	2.080 ± 0.026	1.589 ± 0.013
1.794	9.489 ± 0.023	8.643 ± 0.019	5.976 ± 0.017	3.889 ± 0.028	2.625 ± 0.028	2.137 ± 0.026	1.680 ± 0.020
2.664	9.556 ± 0.019	8.737 ± 0.016	6.201 ± 0.015	4.059 ± 0.023	2.738 ± 0.022	2.283 ± 0.022	1.784 ± 0.030
4.423	9.935 ± 0.007	9.133 ± 0.013	6.753 ± 0.026	4.474 ± 0.034	2.969 ± 0.032	2.720 ± 0.037	2.083 ± 0.051

[a] ± 95 % confidence interval.

According to Long and McDevit,[23] the solubility of a neutral species S^0 is related to activity coefficients by the equations:

$$\log y_N = \log \frac{S_0^0}{S^0} = k_c c_{NaCl} \qquad (7)$$

$$\log \gamma_N = \log \frac{S_0^0}{S^0} = k_m m_{NaCl} \qquad (7a)$$

where y_N and γ_N represent the activity coefficients of the neutral species in the molar (c_{NaCl}) and molal (m_{NaCl}) concentration scale, k_c and k_m are the Setschenow coefficients in the two concentration scales, and S_0^0 is the solubility of the neutral species in pure water. As shown for some carboxylic acids,[22,24] often k is not a true constant and depends on the concentration of supporting electrolyte according to the equation:

$$k_{(c,m)} = k_{(c,m),\infty} + \frac{k_{(c,m),0} - k_{(c,m),\infty}}{(c,m)_{NaCl} + 1} \qquad (8)$$

where k_0 and k_∞ are the values at $(c,m)_{NaCl} \rightarrow 0$ and $(c,m)_{NaCl} \rightarrow \infty$, respectively. By fitting solubility data to eq 3, with $k_{(c,m)}$

Table 10. Parameters of Equations 4 to 4b for the Dependence of Protonation Constants on Ionic Strength

L	i	$\log K_i^0$	$\Delta\varepsilon$	$\Delta\varepsilon_\infty$	$\Delta\varepsilon_0$	σ[a]
NTA	1	9.998 ± 0.012[b]	—	0.169 ± 0.005[b]	−0.132 ± 0.017[b]	0.03
	2	2.949 ± 0.008	—	0.129 ± 0.003	0.342 ± 0.012	0.02
	3	1.916 ± 0.012	—	0.127 ± 0.005	0.090 ± 0.018	0.04
	4	1.305 ± 0.007	0.065 ± 0.002	—	—	0.03
DTPA	1	11.21 ± 0.03	—	0.228 ± 0.003	0.112 ± 0.006	0.04
	2	9.34 ± 0.01	—	0.212 ± 0.004	0.525 ± 0.012	0.06
	3	4.79 ± 0.02	—	0.228 ± 0.005	0.719 ± 0.014	0.02
	4	3.10 ± 0.01	—	0.115 ± 0.005	0.421 ± 0.017	0.02
	5	2.33 ± 0.02	—	0.074 ± 0.002	0.286 ± 0.009	0.04
	6	1.09 ± 0.02	0.173 ± 0.003	—	—	0.13
TTHA	1	11.81 ± 0.05	—	0.357 ± 0.013	−0.150 ± 0.039	0.06
	2	10.61 ± 0.04	—	0.355 ± 0.014	−0.266 ± 0.045	0.05
	3	6.91 ± 0.02	—	0.370 ± 0.004	0.651 ± 0.007	0.01
	4	4.54 ± 0.05	—	0.268 ± 0.011	0.599 ± 0.039	0.04
	5	3.02 ± 0.06	—	0.146 ± 0.012	0.529 ± 0.040	0.06
	6	2.41 ± 0.05	—	0.275 ± 0.012	−0.226 ± 0.035	0.04
	7	1.54 ± 0.02	0.110 ± 0.007	—	—	0.04

[a] ± std. dev. in the fit of eqs 4 to 4b. [b] ± 95 % confidence interval.

Table 11. Solubility of the Neutral Species (Molal Concentration Scale) in Pure Water at 298.15 K and Parameters for the Dependence on NaCl Concentration (eqs 7a to 8)

L	$\log S_0^0$	k_m	$k_{m,\infty}$	$k_{m,0}$	σ[a]
NTA	−2.595 ± 0.012[b]	0.036 ± 0.004[b]	—	—	0.074
	−2.514 ± 0.019	—	−0.017 ± 0.008[b]	0.358 ± 0.051[b]	0.049
EDTA	−3.786[c]	−0.041[d]	—	—	
		—	−0.011[c]	−0.208[c]	
DTPA	−2.281 ± 0.006	−0.057 ± 0.002	—	—	0.043
	−2.369 ± 0.004	—	−0.014 ± 0.001	−0.335 ± 0.010	0.021
TTHA	−2.950 ± 0.022	−0.146 ± 0.006	—	—	0.079
	−2.938 ± 00044	—	−0.162 ± 0.023	−0.077 ± 0.12	0.079

[a] ± std. dev. in the fit of eqs 7a to 8. [b] ± 95 % confidence interval. [c] Ref 18. [d] Calculated from data of ref 18 in the range $(0 \le I \le 3)\ \mathrm{mol \cdot kg^{-1}}$.

expressed by eq 7 or 8, we obtained the values of S_0^0 reported in Table 11, in the molal concentration scale. The solubility in pure water and the k_m coefficients for EDTA are reported in the same table. By considering the simple one-parameter k_m (eq 7a), for the four complexons with i = 1, ..., 4, we found the linear correlation:

$$k_m = 0.088 - 0.056i \tag{9}$$

with correlation coefficient r = 0.97. A very good linear correlation with the stoichiometric coefficient i of $(CH_2)_{2i-2}N_i(CH_2COOH)_{i+2}$ complexons is also found for the solubility products K_{s0}. Using data at $I = 0\ \mathrm{mol \cdot kg^{-1}}$ ($-\log K_{s0}$ = 17.32, 26.20, 33.15, and 42.12 for NTA, EDTA,[18] DTPA, and TTHA, respectively, see Figure 1) we obtain:

$$-\log K_{S0} = 9.36 + 8.13i \tag{10}$$

with correlation coefficient r = 0.999.

Moreover, the Setschenow coefficients are linearly related to the water−octanol partition coefficient K_{ow}, as previously reported.[25,26] Using calculated K_{ow} values ($\log K_{ow}$ = −1.76, −0.43, 0.05, and 0.53 for NTA, EDTA, DTPA, and TTHA, respectively[27]), we obtain the following relationship:

$$-\log k_m = 0.081 + 0.072 \log K_{ow} \tag{11}$$

with correlation coefficient r = 0.95.

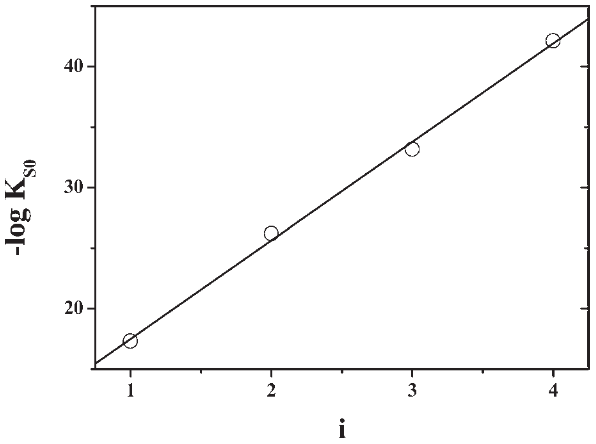

Figure 1. $\log K_{s0}$ values of $(CH_2)_{2i-2}N_i(CH_2COOH)_{i+2}$ complexons vs i at $I = 0\ \mathrm{mol \cdot kg^{-1}}$ and T = 298.15 K.

CONCLUSIONS

The main results can be summarized as follows.

1. The total solubility S^T of the $(CH_2)_{2i-2}N_i(CH_2COOH)_{i+2}$ complexons (i = 1, NTA; i = 3, DTPA; i = 4, TTHA) are determined in aqueous NaCl solutions at different ionic strengths, $(0 \leq I \leq 5)$ mol·L^{-1}, and at 298.15 K, together with the protonation constants. Data are reported in both the molar and the molal concentration scales.
2. The solubility of the neutral species S^0 and the solubility product K_{s0} are calculated and reported at different NaCl concentrations.
3. The dependence on ionic strength of both the total and the neutral species solubility is analyzed, and parameters for the dependence on ionic strength are reported.
4. For the $(CH_2)_{2i-2}N_i(CH_2COOH)_{i+2}$ complexons (i = 1, ..., 4), linear correlations with the stoichiometric coefficient i for the Setchenow coefficients k_m and the solubility products K_{s0} are proposed. For the Setschenow coefficients a linear correlation with the water−octanol partition coefficient K_{ow} is also reported.
5. The solubility products K_{s0} for NTA and DTPA are in quite good agreement with the literature values reported in Table 1.

ASSOCIATED CONTENT

S Supporting Information. Solubility and protonation constant data of NTA, DTPA, and TTHA in the molar concentration scale, in Tables 1S to 6S. This material is available free of charge via the Internet at http://pubs.acs.org.

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Funding Sources

We thank the University of Messina for financial support (PRA).

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