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Adsorption of *N'*-(2-Hydroxyethyl)-ethylenediamine-*N*,*N*,*N'*-triacetic Acid on the Hydrogen Form of Resin

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The adsorption of HEDTA (H_3Ch) on the hydrogen form of Dowex 50W, X-8, 100—200 mesh, has been studied as a function of the concentration of H_3Ch in the aqueous phase. The experiments were performed by means of either the column or a combination of the column and batch methods, with the latter being employed for the adsorption of HEDTA on the resin in equilibrium with dilute solutions. In solutions up to approximately 0.07 mol/*l*, such as H_3Ch, the experimental data are consistent with the Langmuir equation expressed by: $[H_3Ch]/(\overline{Ch}_T/E)=1/Bk+[H_3Ch]/B$. The adsorbed amount is represented in the term $\overline{Ch}_T/E$, where $\overline{Ch}_T$ is the total amount of cationic species of HEDTA on the resin, and E, the exchange capacity of resin. A good straight line is obtained with $B=0.571$ and $k=0.420$. The results show that, because of a high concentration of hydrogen ion inside the resin, the adsorbed HEDTA is present mainly in the H_5Ch^{2+} species and partly in the H_4Ch^+ species.

Due to the stable chelate formation of polyamino acids with metal ions, such buffered solutions as ethylenediaminetetraacetic acid (EDTA) and *N'*-(2-hydroxyethyl)ethlenediamine-*N*,*N*,*N'*-triacetic acid (hereafter abbreviated as HEDTA and H_3Ch)[1,2] were used as the eluants for the ion-exchange separation of the rare-earth series. For example, various compositions of HEDTA were employed for isolating the above series by ion exchange. When the rare earth is eluted with the HEDTA eluant with a closed composition to $(NH_4)_2HCh$ and with a hydrogen-retaining bed, a chelate band[3] corresponding to H_5Ch^{2+} in the resin phase is steadily formed between the rare earth and hydrogen bands; this band grows with the progress of the elution distance of the rare-earth band. The formation of the chelate band[4] during elution was investigated under several variables, such as the concentration and composition of the eluant, the crosslinkage of the cation exchanger and the temperature. The results show that the previously-proposed mechanism for the chelate band formation was only applicable within a narrow range of elution conditions and that it is difficult to explain all the phenomena observed in the resin in terms of this mechanism alone. Thus, the present authors have arrived at the opinion that the research into the adsorption of HEDTA on the hydrogen form of resin should be extended to high concentrations of H_3Ch.

Generally, polyamino acid molecules have some additional sites available for protonation. For example, the existence[5] of the protonated species, H_5Y^+ and H_6Y^{2+}, in strong acid solutions of EDTA (H_4Y) was confirmed by Olson and Margerum. The HEDTA molecule with a structure analogous to EDTA would also have the protonate forms, H_4Ch^+ and H_5Ch^{2+}, in strongly acidic solutions. The presence of the above protonated species can easily be predicted in the hydrogen form of resin, because of the extremely high concentration of hydrogen ions inside the resin matrix (approximately $[H^+]=6$—7 mol/*l* adsorbed solvent). Matorina[6—8] investigated the ion-exchange equilibrium of DTPA (diethylenetriaminepentaacetic acid; H_5A) in combination with a polystyrene type of resin (KU-2) and confirmed the presence of protonated species in the resin due to the reaction: $H_5A+\overline{2H^+} \rightleftarrows \overline{H_7A^{2+}}$. (Here the superscript barred quantities refer to the resin phase of the indicated species.)

The main object of this study is to investigate the adsorption of HEDTA species on the resin as a function of the concentration of H_3Ch in the aqueous phase, and to clarify the adsorption character.

Experimental

Using Dowex 50W, X-8, 100—200 mesh, as the cation exchanger and an analytical grade of HEDTA, the adsorption experiments of HEDTA on the resin were performed at 25°C by the following three methods.

Column Method-I. This procedure was applied for the experimental series corresponding to Exp. No. AE-1 to AE-9. With a flow of 0.26 cm/min, the HEDTA eluant buffered with ammonium hydroxide was passed through the top of a Pyrex column involving a hydrogen form of resin. The tail of the exchange column was connected in series with small appendages (exchange capacity=20—30 meq. per column) for the analysis of HEDTA species in the resin phase. With the progress in elution, the formation of a chelate band due to the adsorption of HEDTA on the hydrogen form of resin was seen between the eluant and hydrogen bands. After the elution system had arrived at a steady state, the HEDTA eluate from the chelate band was collected into small fractions and analyzed. The experimental conditions used are listed in detail in Table 1, in which the $\widetilde{Ch}_T$ and $\widetilde{NH}_{4T}$ symbols indicate the total concentrations of the anionic species of HEDTA and ammonium respectively in the eluant; the column dimensions are also given.

Column Method-II. This method was used for Exp. No. AE-1′ to AE-5′. Different concentrations of HEDTA solutions were passed through small exchange columns (exchange capacity=34 meq. per column) at a flow rate of 0.1 cm/min. After passing 4 to 5 *l* of a HEDTA solution for the attainment of equilibrium, the resin phase was separated from the aqueous phase and analyzed (Table 2).

Combination of Column and Batch Methods. This method was used for Exp. No. AE-10 to AE-15. When a dilute solution of HEDTA is used as the load solution for the column method, it takes a long time to reach equilibration. Therefore, the experiment was divided into two steps to save time. According to Column Method-II, a dilute solution of HEDTA corresponding to 15—20 *l* was passed through the hydrogen form of a resin column with a capacity of 10 meq. After that, the resin in the column was removed and mixed with one liter of the same load solution of HEDTA. The mixture was maintained at 25°C for 3 days in a constant-temperature-bath; then, after equilibration, the two phases were separated for analysis.

Analysis. The ammonium content in the HEDTA load solutions was determined by the usual Kjeldahl method; further, the total HEDTA was determined by chelometry with the standard $ZnCl_2$ and with E.B.T. (Eriochrome Black T) as the indicator. An ammonium chloride-ammonium hydroxide buffer solution with a pH of 10 was used in the titration.

The small appendages attached to the tail of the main exchange column for the analysis of the chelate band were analyzed as follows: after the aqueous solution had been removed by suction, the resin phase was eluted with 2 M NH_4Cl; the total of anionic species of HEDTA in the collected eluate was then determined by chelometry, using the zinc standard solution, according to the previously-described method.

Experimental Results and Discussion

The results obtained by the experimental methods described in the foregoing section are summarized in Table 2, in which the equilibrium compositions of the aqueous phase under different conditions are

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1) F. H. Spedding and A. H. Danne, "The Rare Earths," John Wiley, & Sons, New York (1961).

2) Z. Hagiwara, *J. Inorg. Nucl. Chem.*, **31**, 2933 (1969).

3) J. E. Powell and F. H. Spedding, *Trans. Met. Soc. AIME*, **215**, 457 (1959).

4) Z. Hagiwara, to be published.

5) D. C. Olson and D. W. Margerum, *J. Am. Chem. Soc.*, **82**, 5602 (1960).

6) N. N. Matorina, L. V. Shepetyuk and K. V. Chmutov, *Zhur. Fiz. Khim.*, **41**, 112 (1967).

7) N. N. Matorina, L. V. Shepetyuk and K. V. Chmutov, *ibid.*, **41**, 131 (1967).

8) N. N. Matorina, L. V. Shepetyuk and K. V. Chmutov, *ibid.*, **41**, 373 (1967).

TABLE 1. EXPERIMENTAL CONDITIONS USED FOR THE COLUMN EXPERIMENTS

Exp. No.	Composition of eluant				Column dimension cm	Total eluate volume l
	$\widetilde{Ch}_T$ mmol/l	$\widetilde{NH}_{4T}$ mmol/l	pH	$\widetilde{NH}_{4T}/\widetilde{Ch}_T$		
AE-1	44.64	105.8	8.64	2.37	2.2×80	5.0
AE-2	44.84	89.22	6.78	1.99	2.2×62	5.2
AE-3	45.04	59.63	5.10	1.32	2.2×41	5.0
AE-4	30.16	72.54	8.60	2.41	2.2×80	8.5
AE-5	30.04	60.42	6.99	2.01	2.2×62	7.6
AE-6	30.02	40.18	5.11	1.34	2.2×41	7.5
AE-7	15.09	36.34	8.70	2.41	2.2×80	16.5
AE-8	15.16	30.86	7.46	2.04	2.2×62	14.0
AE-9	15.11	22.18	5.31	1.47	2.2×41	12.0

Resin used: Dowex 50W, X-8, 100—200 mesh
Elution temperature: 25°C
Flow rate: 0.26 cm/min

TABLE 2. COMPOSITION OF THE RESIN AND AQUEOUS PHASES AT EQUILIBRIUM

Exp. No.	Aqueous phase				Resin phase
	Ch_T mmol/l	H_3Ch mmol/l	pH	$\overline{Y}$	$(\overline{Ch}_T/E)$ mmol/meq
AE-1	104.3	65.08	2.22	2.42×10^{11}	0.557
AE-2	95.54	61.73	2.18	3.08×10^{11}	0.555
AE-3	78.36	49.84	2.20	2.72×10^{11}	0.551
AE-4	69.69	42.66	2.24	2.14×10^{11}	0.536
AE-5	62.37	37.75	2.26	1.90×10^{11}	0.533
AE-6	51.28	30.65	2.27	1.79×10^{11}	0.520
AE-7	33.17	19.22	2.30	1.50×10^{11}	0.488
AE-8	30.20	17.17	2.32	1.33×10^{11}	0.481
AE-9	25.83	14.43	2.34	1.18×10^{11}	0.471
AE-10	15.18	7.52	2.45	6.20×10^{10}	0.409
AE-11	10.02	4.45	2.54	3.74×10^{10}	0.383
AE-12	6.04	2.23	2.67	1.82×10^{10}	0.343
AE-13	3.12	0.92	2.82	8.13×10^{9}	0.256
AE-14	2.09	0.51	2.93	4.58×10^{9}	0.219
AE-15	1.04	0.18	3.13	1.66×10^{9}	0.120
AE-1′	29.66	16.86	2.32	1.33×10^{11}	0.479
AE-2′	25.15	14.05	2.34	1.18×10^{11}	0.461
AE-3′	19.71	10.33	2.40	8.32×10^{10}	0.447
AE-4′	15.20	7.53	2.45	6.20×10^{10}	0.440
AE-5′	9.77	4.27	2.55	3.52×10^{10}	0.406

Resin used: Dowex 50W, X-8, 100—200 mesh
Temp: 25°C

also given. The mean values of Ch_T in the HEDTA fractions obtained in elution under the steady-state conditions are also listed in Table 2; the deviation of Ch_T is about ±2% from Exp. No. AE-1 to AE-9.

The concentration of H_3Ch in the aqueous phase can be calculated by the following relations:

$$[H_3Ch]=\frac{[H^+]^3}{k_1\cdot k_2\cdot k_3}\frac{Ch_T}{\overline{Y}}, \tag{1}$$

where:

$$\overline{Y}=\frac{[H^+]^3}{k_1\cdot k_2\cdot k_3}+\frac{[H^+]^2}{k_2\cdot k_3}+\frac{[H]^+}{k_3}+1.$$

The Ch_T symbol represents the concentration of the total anionic species of HDETA, while the $\overline{Y}$ represents the functions of the pH and of the three dissociation constants of HEDTA. Using Eq. (1) and the values of the dissociation constants of HEDTA ($pk_1=2.39$, $pk_2=5.37$, $pk_3=9.93$)[9] the values of H_3Ch are calculated as given in Table 2, in which the adsorbed HEDTA on the resin is expressed in the term $\overline{Ch_T}/E$, where $\overline{Ch_T}$ refers to the amount of the adsorbed HEDTA species in the resin, and E, the exchange capacity of the hydrogen form of resin employed for the equilibrium experiments (one gram of the dried hydrogen form of Dowex 50W, X-8, 100—200 mesh=4.84 meq).

The adsorption of HEDTA species is assumed to take place in the form:

$$H_3Ch + n\overline{H}^+ \rightleftarrows \overline{H_{3+n}Ch^{n+}},$$

where the superscript barred quantities refer to the resin phase of the indicated species. The apparent exchange constant can then be written:

$$K_n' = \frac{[\overline{H_{3+n}Ch^{n+}}]}{[H_3Ch][\overline{H}^+]^n} = \frac{A\dfrac{\overline{Ch_T}}{E}}{[H_3Ch]\left\{A\left(1-\dfrac{n\overline{Ch_T}}{E}\right)\right\}^n} \tag{2}$$

where the two symbols $\overline{H_{3+n}Ch^{n+}}$ and $\overline{H^+}$ related to the resin phase are expressed in the concentration unit of moles per unit gram of the hydrogen form of resin, and where the H_3Ch in the aqueous phase is expressed in m moles per liter. Further, the A is the exchange capacity of resin in meq per unit gram of resin on the basis of the hydrogen form.

Taking the logarithm of Eq. (2), one obtains:

$$\log\frac{A\dfrac{\overline{Ch_T}}{E}}{[H_3Ch]} = \log K_n' + n\log\left\{A\left(1-\frac{n\overline{Ch_T}}{E}\right)\right\}. \tag{3}$$

The plots of $\log(A\overline{Ch_T}/E)/[H_3Ch]$ with respect to $\log A\{1-(n\overline{Ch_T}/E)\}$ should give a straight line whose slope is n and whose intercept is $\log K_n'$. As is shown in Fig. 1, the former values are plotted against the latter on the assumption of $n=1$; a value of 6.8 is thus obtained as the slope of the straight line. This result indicates that the adsorption of HEDTA does not conform to the reaction expressed by $H_3Ch+\overline{H}^+ \rightleftarrows \overline{H_4Ch^+}$. Similar plots appear in Fig. 2, in which n is assumed to be equal to 2. However, the linearity is not maintained over the whole experimental range, and a linear relation with a slope of 1.9 is only obtained in a small range corresponding to Exp. No. AE-10 to AE-15. Therefore, it is obvious that the adsorbed form of H_5Ch^{2+} on the resin exists only in the region of 0.15 to 0.75 as the value of $-\log\{1-(2\overline{Ch_T}/E)\}$ in Fig. 2. Further, the linear relationship is not held at $n=3$. It may be concluded that the experimental data are not explained by Eq. (3).

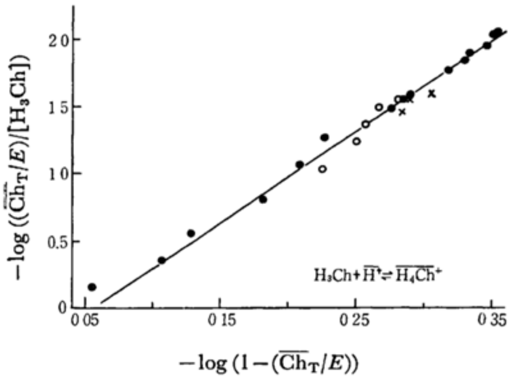

Fig. 1. $\log((\overline{Ch_T}/E)/[H_3Ch])$ *vs.* $\log(1-(\overline{Ch_T}/E))$.

- ● Exp. No. AE-1 to AE-15
- ○ Exp. No. AE-1′ to AE-5′
- × Experimental data concerning the chelate band obtained in the elution of erbium band

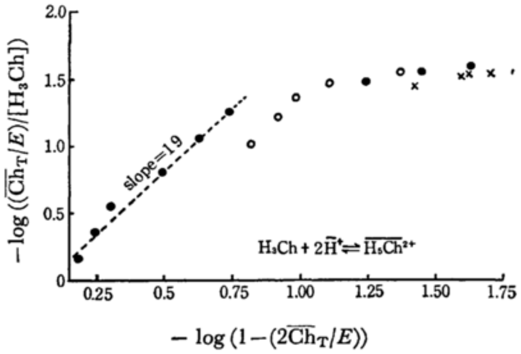

Fig. 2. $\log((\overline{Ch_T}/E)/[H_3Ch])$ *vs.* $\log(1-(2\overline{Ch_T}/E))$. Notations of experimental data are the same as those used in Fig. 1.

The adsorption of HEDTA on the resin is considered to take place according to an equation similar to that of Langmuir:

$$\frac{\overline{Ch_T}}{E} = \frac{Bk[H_3Ch]}{1+k[H_3Ch]}, \tag{4}$$

where B is the maximum amount of sorbed HEDTA per unit equivalent of resin at the maximum solubility of H_3Ch, and where k is a constant relating to the adsorption energy. It may be more convenient to utilize a plot which gives a straight line. Thus, Eq. (4) may be rearranged in the form:

$$\frac{[H_3Ch]}{\dfrac{\overline{Ch_T}}{E}} = \frac{1}{Bk} + \frac{1}{B}[H_3Ch]. \tag{5}$$

A plot of $[H_3Ch]/(\overline{Ch_T}/E)$ against H_3Ch is linear and yields the slope $1/B$ and the intercept $1/Bk$. Since H_3Ch, $\overline{Ch_T}$, and E are known experimentally, a plot of the term of the left side in Eq. (5) *versus* $[H_3Ch]$ leads to a straight line with the value of 1.75 as the slope and that of 4.17 as the intercept ($B=0.571$, $k=0.420$), as may be seen in Fig. 3.

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[9] T. Moeller and R. Ferrus, *J. Inorg. Nucl. Chem.*, **20**, 261 (1961).

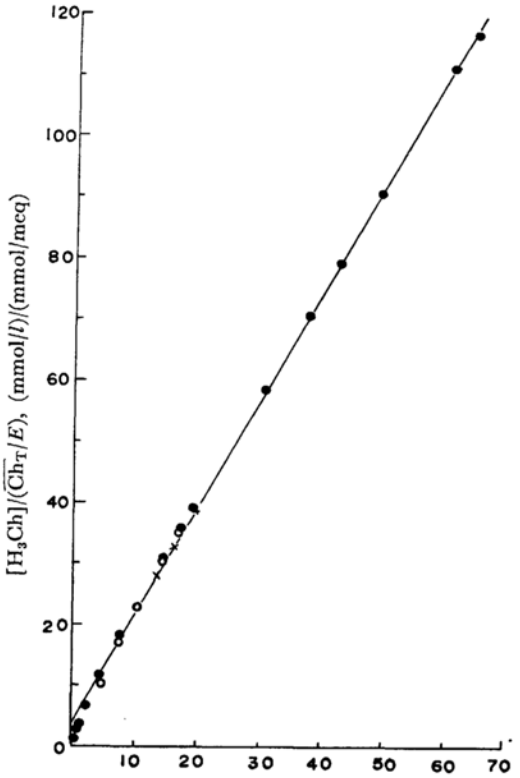

Fig. 3. Langmuir plots for the adsorption of HEDTA on the hydrogen form of resin at 25°C. Notations of experimental data are the same as those used in Fig. 1.

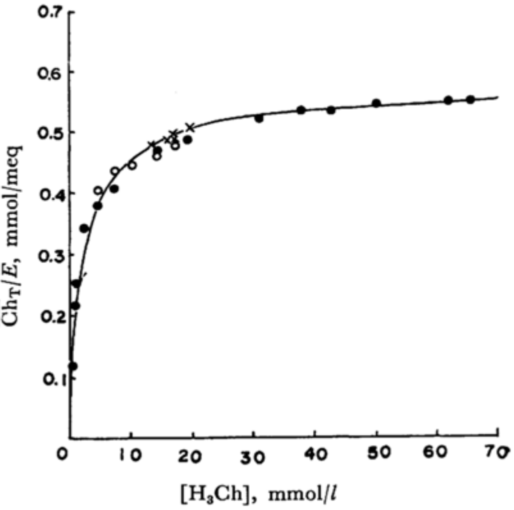

Fig. 4. Adsorption isotherm of HEDTA at 25°C. Notations of experimental data are the same as those used in Fig. 1.

In dilute concentrations less than 20 mmol/l, such as H_3Ch, a reciprocal number of B is equal to 2.0. It is obvious from the above fact that the adsorbed state of H_3Ch on the hydrogen form of resin may be attributed to the H_5Ch^{2+} species. In a higher concentration range, the decrease in $1/B$ is principally due to the formation of the H_4Ch^+ species as a minor constituent, in addition to H_5Ch^{2+}: $\overline{H_5Ch}^{2+} + H_3Ch \rightleftarrows 2\overline{H_4Ch}^+$.

Further, the adsorption isotherm of HEDTA on Dowex 50W, X-8, 100—200 mesh, is shown in Fig. 4, in which the calculated isotherm is represented by a solid line, using Eq. (4), where $B=0.571$ and $k=0.420$. For purposes of comparison, some experimental data concerning the chelate band formed in elutions of the erbium band with a 0.015 M HEDTA buffered solution are plotted in the same figure.

It may be concluded that the sorption of HEDTA on the hydrogen form of resin can be explained well by the Langmuir equation, and that the adsorbed HEDTA species is present mainly in H_5Ch^{2+} and partly in H_4Ch^+ due to a high concentration of hydrogen inside the resin.