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An Ion Exchange and Extinctiometric Investigation of the Nickel Thiocyanate System

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The aim of the present investigation is a quantitative study of the complex equilibria between nickel and thiocyanate ions. The investigations of this system reported in the literature, give information only of the composition of the saturated complex, existing at high thiocyanate ion concentrations, but not of the successive complex formation at lower thiocyanate ion concentrations, or of the strengths of the complexes formed. Thus, Brintzinger and Ratanarat [1] consider that dialysis measurements prove that at the concentration 2 C of thiocyanate ions and small nickel concentrations all of the nickel is present as the complex $Ni(SCN)_4^{2-}$. From extinction curves of solutions containing varying amounts of nickel and thiocyanate ions Csokán [2] concludes that, with nickel in excess, $NiSCN^+$ is formed, while at a large excess of thiocyanate the complex $Ni(SCN)_4^{2-}$ predominates. According to Major [3] an uncharged complex exists in saturated solutions of nickel thiocyanate.

THE INVESTIGATION METHODS

The cation exchange method, described in two preceding papers (Fronæus [4,5], referred to below as I and II), was used in the present investigation for the determination of the complexity constants of the mononuclear complexes. In order to check the results an independent extinctiometric method was also applied.

As in previous investigations on other systems, the measurements were carried out at the constant ionic strength $I = 1$ C with sodium perchlorate as a supplementary neutral salt in the solutions. The temperature was kept at 20.0° C.

CHEMICALS USED

Sodium thiocyanate, p.a. The concentration of a stock solution, prepared from a calculated amount of the dried preparation, was checked by Volhard titration.

The *other chemicals* used were prepared as described in II. All stock solutions had the ionic strength 1 C. The cation exchanger (Amberlite IR-105), transformed to the sodium form, and air-dried, had the exchange capacity 2.31 meq. per gram. This was determined by transforming a sample of the exchanger to the hydrogen form, treating it with sodium acetate until equilibrium was established, filtering off and washing the exchanger and titrating with sodium hydroxide the acetic acid set free.

THE ION EXCHANGE INVESTIGATION

Before the treatment with the cation exchanger the complex solutions had the composition:

C'_M mC $Ni(ClO_4)_2 + C'_A$ mC $NaSCN + (1\,000-3C'_M-C'_A)$mC $NaClO_4$ with a constant value of C'_M and varying values of C'_A within each measurement series. The ratio m/v between the mass of the dried resin and the initial volume of the solution was kept constant ($50.0 \text{ g} \cdot l^{-1}$) at all measurements. After shaking the solution with the resin for twenty-four hours an exchange equilibrium was attained, and the solution was separated from the resin.

The equilibrium nickel concentration C_M was determined extinctiometrically at the wave length 500 mμ by means of potassium dithio-oxalate. The apparatus and the method of measurement were the same as those described in II. As nickel thiocyanate complexes are weak compared with nickel dithio-oxalate complexes, the molar extinction with respect to nickel is independent of the thiocyanate ion concentration, when the dithio-oxalate is added in excess.

The determination of the equilibrium thiocyanate concentration C_A was carried out by Volhard titration after addition of an excess of silver nitrate to a portion of the solution.

For the reasons given in II it is impossible to determine the nickel load C_{MR} on the ion exchanger by direct analysis of the resin phase, whenever one of the complexes formed can be absorbed by the exchanger. Thus C_{MR} must be indirectly calculated from eq. (6) of II. As m/v was kept constant, the quantity δ in this equation, depending upon the swelling of the resin, was the same for all measurements. The concentration of free anions in the resin phase being negligible, the factor δ was obtained as the quotient C'_A/C_A from solutions with $C_M = 0$. At these measurements the value of δ was 0.985.

The transformation of the ion exchanger from the hydrogen to the sodium form had been finished at a rather low $p[H^+]$. For that reason, after equilibrium with the exchanger was attained, the value of $p[H^+]$ in the complex solutions

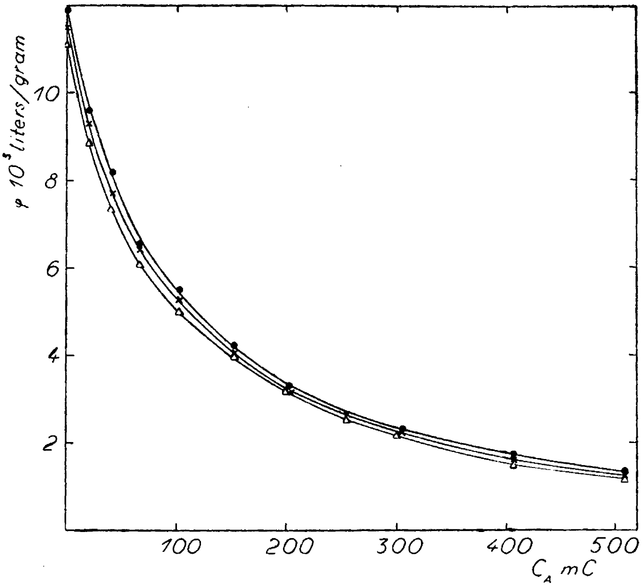

Fig. 1. *The function* $\varphi(C_A)$ *at given values of* C'_M.
●: $C'_M = 1.010$ *mC*; ×: $C'_M = 2.52$ *mC*; Δ: $C'_M = 5.05$ *mC*.

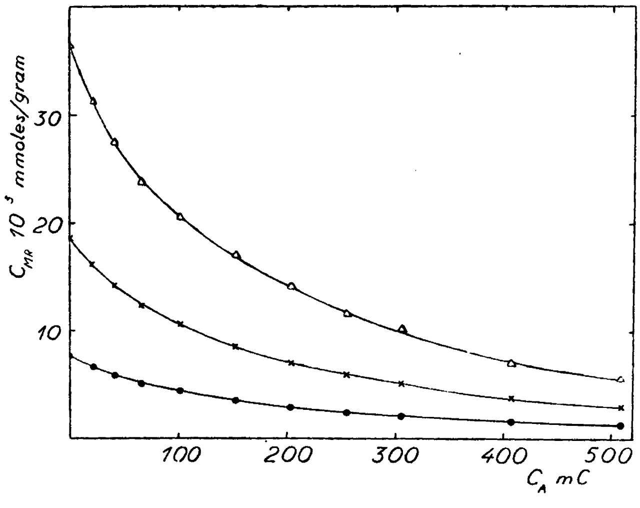

Fig. 2. *The function* $C_{MR}(C_A)$ *at given values of* C'_M.
●: $C'_M = 1.010$ *mC*; ×: $C'_M = 2.52$ *mC*; Δ: $C'_M = 5.05$ *mC*.

determined by emf measurements with a glass electrode, was constant and equal to 3.0. As the sorption affinity of Ni^{2+} for the exchanger used is dependent on the $p[H^+]$, it is necessary to work at a constant $p[H^+]$. Thiocyanic acid being a strong acid (*cf.* Gorman and Connell ⁶), it is possible to choose a low $p[H^+]$-value, and this is expedient, as will be shown below.

The values obtained from the measurements are collected in Figs. 1 and 2, the same notations being used as in II. The quantities φ and C_{MR} can be considered as functions of the initial nickel concentration C'_M and the equilibrium thiocyanate concentration C_A. Thus, in these figures the functions $\varphi(C_A)$ and $C_{MR}(C_A)$ are represented at three given values of the parameter C'_M. From these curves, pairs of values (C_{MR}, φ), corresponding to some given concentrations C_A, are obtained. They are to be found in Table 1.

Table 1. Determination of corresponding values of C_A, C_M, and φ at $C_{MR} = 6.00 \cdot 10^{-3}$ mmoles $\cdot g^{-1}$.

C_A mC	$C'_M = 1.010$ mC		$C'_M = 2.52$ mC		$C'_M = 5.05$ mC		$C_{MR} \cdot 10^3 = 6$ mmole $\cdot g^{-1}$
	$C_{MR} \cdot 10^3$ mmole $\cdot g^{-1}$	$\varphi \cdot 10^3$ l $\cdot g^{-1}$	$C_{MR} \cdot 10^3$ mmole $\cdot g^{-1}$	$\varphi \cdot 10^3$ l $\cdot g^{-1}$	$C_{MR} \cdot 10^3$ mmole $\cdot g^{-1}$	$\varphi \cdot 10^3$ l $\cdot g^{-1}$	$\varphi \cdot 10^3$ l $\cdot g^{-1}$
0	7.60	11.90	18.6	11.50	36.4	11.10	12.00
20.0	6.70	9.70	16.2	9.30	31.3	8.85	9.75
40.0	6.00	8.20	14.3	7.75	27.5	7.35	8.20
70.0	5.10	6.55	12.3	6.25	23.5	5.95	6.55
100.0	4.45	5.50	10.6	5.25	20.6	5.05	5.45
150.0	3.60	4.25	8.6	4.10	17.0	3.95	4.20
200	2.90	3.35	7.1	3.25	14.2	3.15	3.30
250	2.45	2.75	6.1	2.70	11.9	2.60	2.70
300	2.10	2.35	5.3	2.25	10.1	2.15	2.25
400	1.70	1.75	3.8	1.65	7.3	1.55	1.60
500	1.35	1.35	3.1	1.30	5.7	1.20	1.20

φ is then considered as a function of C_{MR} and C_A. From Table 1 it is evident that the dependence of φ upon C_{MR} at $p[H^+] = 3$ is very slight, so, by graphical interpolation, it is easy to determine the function φ (C_A) at a constant value of C_{MR} with great accuracy. In this case it was possible to choose the value of C_{MR} as low as $6.00 \cdot 10^{-3}$ mmoles $\cdot g^{-1}$. The corresponding equilibrium nickel concentrations C_M, that can be obtained from the relation $C_M = C_{MR} \cdot \varphi^{-1}$, are so small that the approximation $[A^-] = C_A$ is quite satisfactory at every C_A.

The basic principle of the calculations is that at small C_{MR} the distribution coefficients l_0 and l_1 of Ni^{2+} and $NiSCN^+$ are functions almost solely of C_{MR} and not of the ligand concentration $[A^-]$. This principle has been tested experimentally for the exchanger used on other complex systems in I and II and will be explained theoretically in a future paper.

In the present paper the calculation procedure of II is applied. The φ-value at $[A^-] = 0$ and at the constant C_{MR}-value selected gives the distribution coefficient $l_0 = 12.00 \cdot 10^{-3}$ l · g^{-1} (Table 1, last column). Then in Table 2

Table 2. Determination of corresponding values of φ_1, f and the polynomial X_2 at different values of $[A^-]$ and at $C_{MR} = 6.00 \cdot 10^{-3}$ mmoles · g^{-1}.

$[A^-]$ mC	φ_1 C^{-1}	f C^{-2}	$\frac{\Delta\varphi_1}{[A^-]}$ C^{-2}	$\frac{\Delta f}{[A^-]}$ C^{-3}	X_2 C^{-2}
0	*11.4*	*127*			
20.0	11.5				
40.0	11.6	128			46
70.0	11.9	129			50
100.0	12.0	131			49
150.0	12.4	134			52
200	13.2	141	9.0	70	57
250	13.8	147	9.6	80	60
300	14.4	154	10.0	90	62
400	16.2	173	12.0	115	70
500	18.0	192	13.2	130	78

the function φ_1 has been computed according to eq. (2) of II and from a graphic extrapolation of this function to $[A^-] = 0$, $\beta_1 - l = 11.4$ C^{-1} is obtained. In the next column of Table 2 the function f has been computed from eq. (3) of II and extrapolated to $[A^-] = 0$. The differences $\Delta\varphi_1$ and Δf in eq. (5) of II have the following signification in the present paper:

$$\Delta\varphi_1 = \varphi_1 - 11.4\ C^{-1}, \quad \Delta f = f - 127\ C^{-2}$$

They can be calculated accurately enough only at ligand concentrations ≥ 200 mC. If $\Delta f/[A^-]$ is plotted against $\Delta\varphi_1/[A^-]$ the relation can be represented by a straight line, the slope of which gives the complexity constant of the first mononuclear complex:

$$\beta_1 = 15.0 \pm 0.5\ C^{-1}$$

Table 3. The ligand numbers $\bar{n}$ and $\bar{n}_R$ and the distribution of C_M between the nickel ion and the different complexes at given values of $[A^-]$.

$[A^-]$ mC	$\bar{n}$	$\bar{n}_R$	$100\alpha_0$	$100\alpha_1$	$100\alpha_2$	$100\alpha_3$
10	0.136	0.035	86.7	13.0	0.3	0
50	0.532	0.155	53.6	40.1	5.9	0.4
100	0.857	0.265	33.3	49.9	14.6	2.2
200	1.29	0.42	15.9	47.8	28.0	8.3
300	1.58	0.52	8.9	40.1	35.3	15.7
400	1.79	0.59	5.5	33.0	38.7	22.8
500	1.95	0.64	3.6	27.2	39.8	29.4

Combining this value with that obtained for $\beta_1 - l$ the value $l = 3.6 \pm 0.5$ C^{-1} is found. In the last column of Table 2 the polynomial X_2 has been calculated from eq. (4) of II. The connection between X_2 and $[A^-]$ can be graphically represented by a straight line. The intercept on the X_2-axis gives: $\beta_2 = 44 \pm 4$ C^{-2} and from the slope: $\beta_3 = 65 \pm 10$ C^{-3} is obtained. The linear relation shows that no higher complexes than $Ni(SCN)_3^-$ are formed in measurable amounts within the concentration range of A^- used.

With the constants β_1, β_2, β_3, and l, the ligand numbers $\bar{n}$ and $\bar{n}_R$ (*cf.* I p. 860) and the composition (*cf.* II p. 1207) of the complex system have been calculated in Table 3.

The mass law products k_0 and k_1

As stated above $(\partial\varphi/\partial \overline{C}_{MR})_{[A^-]}$ has a very small value at all concentrations of A^- and low concentrations C_{MR}. Thus, under the conditions mentioned the distribution coefficients l_0 and l_1 are but little dependent upon C_{MR}. The same must hold for the mass law products k_0 and k_1 calculated from eq. (2) of I, as the sodium ion concentrations are nearly constant in both phases. Corresponding values of C_{MR} and l_0 at $C_A = 0$ are to be found in the first line of Table 1 and for $[Na^+]$ and $[Na^+]_R$ the approximate values 1 000 mC and 2.31 mmoles · g^{-1} can be used with sufficient accuracy. The corrections caused by diffusible non-exchange electrolyte absorbed have been neglected. The values of k_0 are collected in Table 4. Thus, at $p[H^+] = 3$ the dependence of k_0 upon C_{MR} is as slight as we should expect, if the nickel ions are either free within the resin phase or partly coordinated to groups that are fixed at the exchanger, and in *great excess*, for instance sulphonate groups.

Table 4. The mass law product k_0 as a function of C_{MR} at $p\,[H^+] = 3.0$ and $C_A = 0$.

$C_{MR} \cdot 10^3$ mmole $\cdot$ g^{-1}	$k_0 \cdot 10^{-3}$ $l^{-1} \cdot g$
7.6	2.23
18.6	2.15
36.4	2.08

The value of k_1 at $C_{MR} = 6 \cdot 10^{-3}$ mmoles $\cdot$ g^{-1} can be calculated from eq. (2) of II, using the relation $l_1 = l_0 \cdot l \cdot \beta_1^{-1}$; the value $k_1 = 1.3$ is obtained. Thus at the $p[H^+]$ used the affinity of the complex $NiSCN^+$ for the exchanger is of about the same magnitude as that of the sodium ion, indicating that the complex is a free ion within the resin phase.

The almost constant value found for k_0 shows that a small exchange of sodium ions for nickel ions does not appreciably influence the activity coefficients in the resin phase. We should expect that for the exchange Na^+—$NiSCN^+$, where both ions have equal valency, the influence is even less marked. Then the condition that l_0 and l_1 are independent of $[A^-]$ and can be treated as constants in the calculation of the complexity constants, must be very well fulfilled in the present case.

THE EXTINCTIOMETRIC INVESTIGATION

As shown previously (I p. 862) the cation exchange method can be used for the determination of the complexity constants of the mononuclear complexes at an arbitrary composition of the complex system. However, such measurements cannot give any information whether polynuclear complexes are also formed or not. The extinctiometric determination of the ligand number $\bar{n}$ has, therefore, been chosen as a check, as this method presupposes that mononuclear complexes are formed exclusively. The strength of the nickel thiocyanate system has moreover an appropriate magnitude for an accurate extinctiometric determination. The notations, the method of calculation, and the apparatus used are the same as described in a previous paper [7].

The measurements

The extinction curves of the nickel and thiocyanate ions and of a solution with $C_M = 25.0$ mC and $C_A = 925$ mC were determined in order to select the

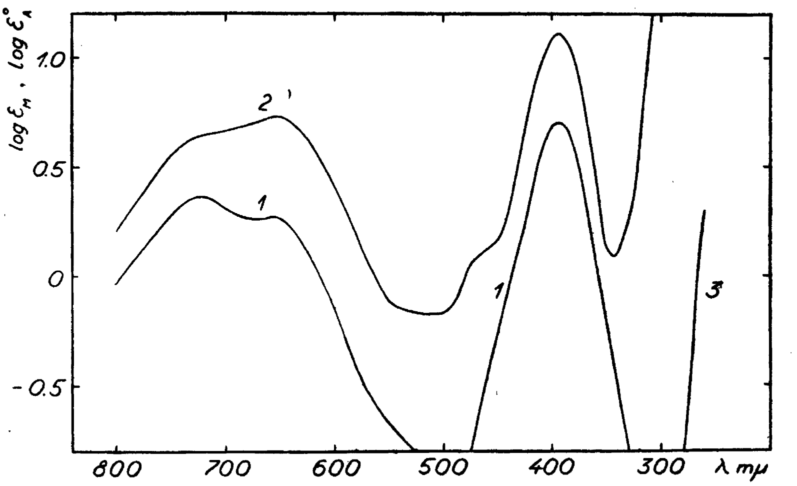

Fig. 3. Extinction curves of: 1. the nickel ion; 2. a complex solution with C_M = 25.0 mC and C_A = 925 mC; 3. the thiocyanate ion.

most suitable wave-length λ for the measurements, and are represented in Fig. 3. The two first-mentioned curves are in agreement in the main with those obtained by v. Kiss and Csokán [8].

On selecting a suitable wave-length the following two conditions should be considered. With the cells available the values of the total extinction must lie within an appropriate variation range. The C_M-values must not be so great that the ionic medium may be changed appreciably, and not so small that the difference $C_A - [A^-]$ cannot be determined with sufficient accuracy in any measurement series. In view of these conditions it can be seen that the low ε_M-values at $\lambda > 310$ mμ and the high ε_M-values at $\lambda < 290$ mμ make measurements impossible at such wave-lengths. Thus a narrow range remains, and 295 mμ was chosen as a suitable value of λ. At 295 mμ $\varepsilon_M^0 \approx 0$ and ε_A^0 is very small.

In one and the same measurement series, C_M and the layer thickness d were kept constant, and in the different series the product $d \cdot C_M$ was constant and equal to 25.0 cm · mC. Thus solutions with the same value of ε_M are measured at the same total extinction E, which is necessary to avoid certain systematic errors in the determination of $\bar{n}$ [7, p. 151].

The values measured are collected in Fig. 4.

The function $\varepsilon_M(C_A)$ is represented at three given values of the parameter C_M. From these curves pairs of values (C_M, C_A), corresponding to nine selected ε_M, are obtained (Table 5).

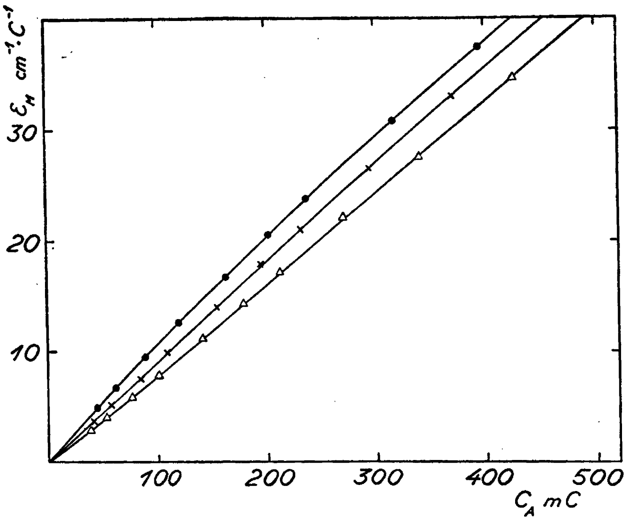

Fig. 4. The function $\varepsilon_M(C_A)$ at different values of C_M.
●: $C_M = 8.33$ mC; ×: $C_M = 25.0$ mC; △: $C_M = 50.0$ mC.

If C_A is plotted against C_M at a constant value of ε_M, practically a straight line is obtained, indicating that only mononuclear complexes are formed[7, p. 150]. Then the slope gives $\bar{n}$, and from the intercept on the C_A-axis we get the corresponding $[A^-]$. Owing to the almost rectilinear course of the curves in Fig. 4 all the values of $\bar{n}$ in Table 5 are obtained with about the same accuracy.

Table 5. Determination of the complex formation function from the extinction measurements.

ε_M cm^{-1} · C^{-1}	$C_M = 50$ mC	$C_M = 25$ mC	$C_M = 8.33$ mC	$C_M = 0$	$\bar{n}$	$\frac{\bar{n}}{[A^-]}$ C^{-1}
	C_A mC	C_A mC	C_A mC	$[A^-]$ mC		
5.00	67.5	56.5	46.0	42.0	0.53	12.6
7.00	92.0	79.0	65.0	61.0	0.65	10.7
10.00	129.0	111.0	93.5	87.5	0.86	9.85
15.0	189.0	165.5	144.5	137	1.06	7.75
20.0	250	221	197.0	187	1.28	6.85
25.0	310	278	251	240	1.42	5.90
30.0	371	335	308	297	1.48	5.00
35.0	431	394	367	355	1.54	4.35
40.0	492	454	426	414	1.56	3.75

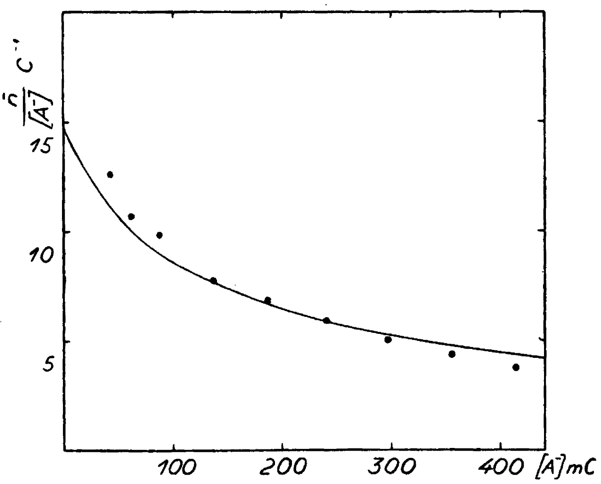

Fig. 5. *$\bar{n}/[A^-]$ as a function of $[A^-]$. Full circles relate to the extinction measurements, and the fulldrawn curve has been calculated from the ion exchange measurements.*

In Fig. 5, representing the function $\bar{n}/[A^-]$, the results from the two investigations can be compared. It will be seen that within the limits of experimental random errors the values determined extinctiometrically fall very well along the fulldrawn curve calculated from the values of $\bar{n}$ and $[A^-]$ in Table 3. This means that the extinction measurements give the same set of complexity constants as the ion exchange investigation.

Thus we are justified in concluding that the two methods have functioned well and that the constants obtained are real equilibrium constants. Furthermore it has been proved that mononuclear complexes are formed exclusively.

SUMMARY

The equilibria between nickel and thiocyanate ions are investigated at 20° C and at a constant ionic strength $I = 1$ C. Sodium perchlorate is used as a supplementary salt in the solution.

The investigation is performed in two ways, by an ion exchange method [4,5] and extinctiometrically [7]. The results obtained by the different measurements are consistent, proving the applicability of the methods to the present system. At thiocyanate ion concentrations ≤ 0.5 C the following three mononuclear complexes are formed: $NiSCN^+$, $Ni(SCN)_2$, and $Ni(SCN)_3^-$. In the conditions stated the values found for the complexity constants are:

$$\beta_1 = 15.0 \pm 0.5 \ C^{-1}, \ \beta_2 = 44 \pm 4 \ C^{-2}, \ \beta_3 = 65 \pm 10 \ C^{-3}$$

From the extinction investigation we arrive at the conclusion that practically no polynuclear complexes are formed.

The absorption of the complex $NiSCN^+$ in the ion exchanger is studied quantitatively. The measurements indicate that at $p[H^+] = 3$ this complex is free within the resin phase and not coordinated to structurally bound groups of the ion exchanger.

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