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The Ion-Association Sorption and Extraction of Metal Thiocyanate Complexes to Cellulose Acetate Polymer and Organic Solvents. Similarity in Distribution Mechanisms

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The sorption and extraction of heavy metal thiocyanate complexes from an aqueous solution were studied for a cellulose acetate polymer and conventional organic solvents. The ease of metal sorption to solid cellulose acetate correlated well with the ease of metal extraction to liquid glycerol triacetate. The distribution behavior of ammonium thiocyanatozincate complexes was studied in detail and compared among cellulose acetate, isobutyl methyl ketone, and glycerol triacetate. The chemical processes involved in the metal distribution to the organic phase were found to be essentially the same for these three media. Thus, cellulose acetate was conveniently considered a polymer solvent. The results were discussed in relation to metal-selective hyperfiltration through cellulose acetate membranes.

In the course of our study of metal-selective separation by means of polymer membranes,[1—4] we outlined an idea of metal-selective hyperfiltration. The principle of metal separation is based on a metal-selective sorption of ion-association complexes to the membrane phase and a subsequent transport of the sorbed metal species through the membrane by some coupling processes with a solvent flow under hydraulic pressure.[3,4] The sorption of heavy metal thiocyanate complexes to polymers took place predominantly on polymers of medium polyarity, such as cellulose acetate (CA) and polyacrylonitrile. An equilibrium study indicated that the sorption obeys the Langmuir adsorption isotherm and the Nernstian distribution law at high and low metal loadings respectively. An analysis of the Nernstian-type distribution suggested that the nature of the sorption to the polymer (CA) is essentially similar to that of the conventional liquid–liquid extraction of the metal-complex species. The permeability under hydraulic pressure of metal thiocyanate and iodide complexes through CA membranes correlated well with the sorptivity of metal species, suggesting a solvent flow-coupled permeation by the sorbed metal species. The present paper includes an extended study of metal sorption on a polymer (CA) and its comparison with liquid–liquid extraction, since their understanding is essential for the development of metal-selective hyperfiltration membranes.

Experimental

Reagents. The cellulose acetate (acetyl content 39.8%; ASTM viscosity, 3s) was obtained from Eastman Chemicals. The other reagents were reagent-grade commercial products and were used without further purification. Cellulose acetate powders finer than 50 mesh were used in the sorption experiments.

Sorption and Extraction. Sorption experiments were done by the procedure previously described.[3] Liquid-liquid extraction was carried out in a conventional manner. Ten to fifteen min mechanical shaking was enough to attain equilibrium. The volumes of the organic and aqueous solutions after equilibration were measured. The concentrations of the metal complexes were determined by means of atomic absorption spectrophotometry with a Japan Jarrel Ash Co. AA-1 instrument.

The sorption and extraction of metal complexes were estimated by means of the degree of sorption (or extraction) (E) and the distribution ratio (D):

$$E=\frac{[\mathrm{M}]_\mathrm{i}-[\mathrm{M}]_\mathrm{f}}{[\mathrm{M}]_\mathrm{i}}\times 100 \tag{1}$$

$$D=\frac{[\mathrm{M}]_\mathrm{i}-[\mathrm{M}]_\mathrm{f}}{[\mathrm{M}]_\mathrm{f}}\times\frac{V_\mathrm{w}}{W_\mathrm{m}}, \tag{2}$$

where $[\mathrm{M}]_\mathrm{i}$ and $[\mathrm{M}]_\mathrm{f}$ are the initial and final metal concentrations respectively, in an aqueous solution; V_w is the volume of the aqueous solution (ml) after equilibrium, and W_m is either the weight of CA (g) or the volume of the organic solution (ml) after equilibrium. In this definition, the dimensions of the metal-distribution ratio are not the same for sorption (to CA) and extraction (to organic solvent). Therefore, where a clear distinction between the two distribution constants should be made, D' is used for the volume-based liquid-liquid distribution ratio. The weight-based D value may be converted to the volume-based D' value by dividing it by the density of the dry polymer (1.25 g/cm^3 for CA) at the first approximation. The D and D' values are thus not very different numerically, and one can use either value for a direct comparison of the effectiveness of metal sorption and extraction.

Results and Discussion

Previous studies indicated that the sorption of metal thiocyanate complexes took place readily for

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Table 1. Extraction[a] and Sorption (%)[b] of Metal Thiocyanate Complexes

No.	Solvent	Fe^{3+}	Co^{2+}	Ni^{2+}	Cu^{2+}	Zn^{2+}	Pd^{2+}	Ag^{+}	Cd^{2+}	In^{3+}	Au^{3+}
1	TA	90	27	7.4	65	96	7.2	0.0	22	97	90
2	MIBK	100	96	0.0	87	100	33	0.0	23	100	100
3	DCE	0.0	0.8	2.6	0.0	0.0	0.0	0.0	0.0	0.0	0.0
4	CA	63	9.6	1.2	47	92	84	0.0	12	79	94

a) Ten ml of a 0.5 M (1 M=1 mol dm^{-3}) NH_4SCN solution containing 0.5 mM metal nitrate (pH 1.0, adjusted by HNO_3) were shaken with 10 ml of triacetin (TA), methyl isobutyl ketone (MIBK), and 1,2-dichloroethane (DCE). b) Twenty ml of a 0.5 M NH_4SCN solution containing 0.5 mM metal nitrate (pH 1.0, adjusted by HNO_3) were shaken with 2.0 g of CA powder. Data taken from Reference 4.

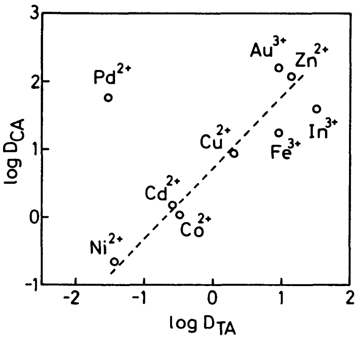


Fig. 1. Correlation between distribution ratios for the sorption and extraction of metal thiocyanate complexes. D_{CA}, distribution ratio in water-CA; D_{TA}, distribution ratio in water–TA. Conditions are similar to those in Table 1.

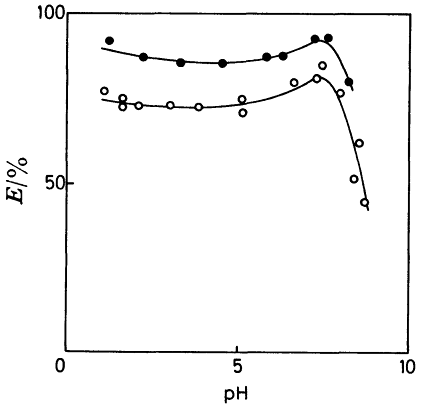


Fig. 2. Effect of pH on the sorption and extraction of zinc thiocyanate complexes. Sorption to CA (○): Twenty ml of 0.25 M NH_4SCN solution containing 0.5 mM $Zn(NO_3)_2$ were used. The pH was adjusted by adding HCl or KOH. The amount of CA was 2.0 g. Extraction to TA (●): 10 ml of 0.25 M NH_4SCN solution containing 0.5 mM $Zn(NO_3)_2$ were used. The volume of TA was 10 ml.

CA and polyacrylonitrile, but not for cellulose and poly(vinyl chloride).[3,4] In order to compare such sorption behavior with solvent-extraction systems, the extraction of metal thiocyanate complexes was investigated by using organic solvents of a related chemical structure. The results are shown in Table 1, along with the sorption data for CA. Oxygen-containing organic solvents, such as isobutyl methyl ketone (MIBK) and triacetin (TA, glycerol triacetate), have a high extraction ability. On the other hand, 1,2-dichloroethane shows little extraction ability. Such behavior is general in ion-association extraction systems.[5]

It is noteworthy that the sorption behavior of metal thiocyanate complexes on solid polymers correlates well with the liquid–liquid metal extraction. That is, CA effectively exhibits an "extraction" ability similar to those of oxygen-containing organic solvents, while poly(vinyl chloride) has little sorption ability, just like dichloroethane liquid–liquid extraction systems, Figure 1 shows the correlation of the distribution ratios between the sorption by cellulose acetate and the extraction by triacetin. The correlation is approximately linear except for palladium. This strongly suggests the similarity of metal-partition mechanisms between the solid polymer matrix and the structurally related organic solvent. The cause of the departure from the linearity for palladium is not apparent at present. It is possible, though, that a local micro-structure of the polymer matrix helps enhance the sorptivity of some particular metal complexes. A "cation chelation mechanism" has recently been described for the sorption of metal complexes by polyether-type polyurethane foam.[6,7]

The effect of the pH on the sorption and extraction of zinc thiocyanate complexes is shown in Fig. 2. The pH-E(%) profiles are quite similar for TA and CA. The E(%) values stay almost constant at pH 1—6 but drop sharply at pH>7.5. The latter effect is due to the hydrolysis of metal ions in the bulk solution.[3] As has been reported previously,[3,4] the zinc ion becomes sorbed on CA as ammonium thiocyanate complexes with an average composition of $(NH_4)Zn(SCN)_3$–$(NH_4)_2Zn(SCN)_4$ under weakly acidic conditions. The sorption and extraction were not studied under low pH conditions (pH<1) to avoid possible ester hydrolysis. However, the proton is known to act as a counter cation in such ion-association complexes as the trihydrated hydronium ion, and the increase in proton concentration is considered to enhance the sorption and extraction,[8,9] which may, in fact, be reflected in the increased metal extractions in the lower pH region.

The relationship of the distribution ratio and the zinc concentration (total concentration) in an aqueous solution at equilibrium is shown in Fig. 3. The figure shows that the sorption and extraction ability for zinc thiocyanate complexes increases in this order; MIBK>CA>TA. The metal distribution ratio for cellulose acetate is about five times higher than that for the triacetin extraction system at an ammonium thiocyanate concentration of 0.5 M. The similar is the case at 0.25 M ammonium thiocyanate. Thus, CA is substantially a better sorbent or extraction solvent than is TA for collecting zinc(II) thiocyanate complexes from aqueous solutions. This is quite interesting because it means that a "solid" polymer can be a better "extraction solvent" than its liquid analogue.

Figure 3 also shows that the distribution ratio decreases as the aqueous zinc concentration increases. For conventional solvent-extraction systems, such behavior is usually considered to indicate the dissociation of extracted ion-association complexes in an organic solution, and it is particularly common for liquid–liquid extraction using solvents with a moderate dielectric constant.[10] It is conceivable that a similar dissociation reaction is taking place in the CA polymer matrix. In fact, Oren et al. studied the sorption behavior of metal halogeno complexes by using open-cell polyurethane foam and confirmed the dissociation of the extracted ion-association species in the foam.[11] However, in our sorption system, as we showed in a previous paper,[3] the polymer (CA) has a maximum sorption capacity (the maximum load of metal according to the Langmuir adsorption isotherm) for each ion-association-complex sorption system.[3] Therefore, the saturation effect, which should lead to a decrease in D similar to that observed in Fig. 3, may not be negligible under the relevant conditions. Calculations according to the Langmuir adsorption equilibria indicated, however, that the saturation effect is quite negligible under the conditions shown in Fig. 3. Thus, the behavior of CA, being in line with that of MIBK and TA (Fig. 3), further strengthens the idea that CA serves as a "polymer solvent" for the extraction of ion-association complexes.

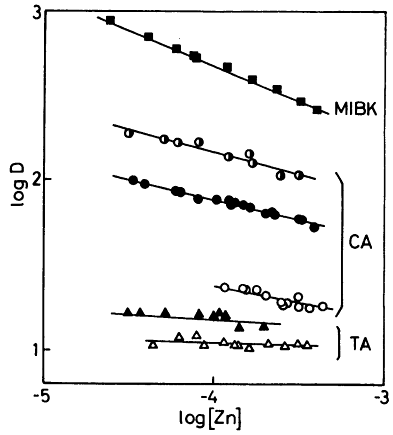


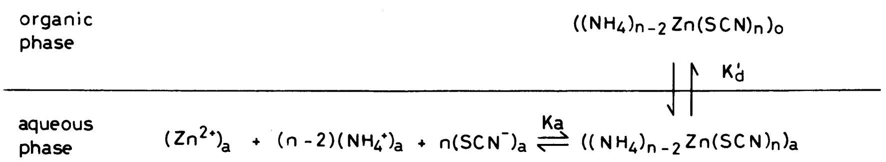
Fig. 3. Variation of zinc distribution ratio as a function of (total) zinc concentration in aqueous solution. Sorption to TA: Twenty ml of aqueous solution containing $Zn(NO_3)_2$ in various concentrations were shaken with 0.5—2.0 g CA. The aqueous solution contained NH_4SCN in concentrations 0.25 M (○), 0.50 M (●), and 0.75 M (◑). Extraction to TA and MIBK: Ten ml of aqueous solution containing $Zn(NO_3)_2$ in various concentrations were shaken with 5 ml TA or 2 ml MIBK. The aqueous solution contained NH_4SCN in concentrations 0.25 M (TA, △), 0.50 M (TA, ▲), and 0.50 M (MIBK, ■).

The mechanism of the sorption of metal species to CA was compared with that of extraction to the organic solvent with a related structure (TA). Scheme 1 shows a simplified model of metal distribution. The sorption and extraction of ammonium thiocyanatozincate complexes were studied at a relatively low metal loading in the organic phase. Under such conditions, both sorption and extraction can be treated according to the Nernstian distribution law, which gives these expressions, 3—5:[3,4]

$$\log \beta D' = (n-2)\log[NH_4^+]_a + n\log[SCN^-]_a + \log K_a K_d' \tag{3}$$

$$D' = [(NH_4)_{n-2}Zn(SCN)_n]_o / ([Zn^{2+}]_a + [Zn(SCN)^+]_a + \cdots\cdots + [Zn(SCN)_m{}^{2-m}]_a) \tag{4}$$

$$\beta = 1 + K_1[SCN^-]_a + K_1K_2[SCN^-]_a^2 + \cdots\cdots + K_1K_2\cdots\cdots K_m[SCN^-]^m \tag{5}$$



Scheme 1. Model for zinc thiocyanate complex distribution among organic and aqueous solutions.

where K_m stands for the mth successive complex formation constant in an aqueous solution.

Equation 3 indicates that the coordination number n of the extracted metal species can be determined from the plots of log $\beta D'$ vs. log $[SCN^-]_a$.

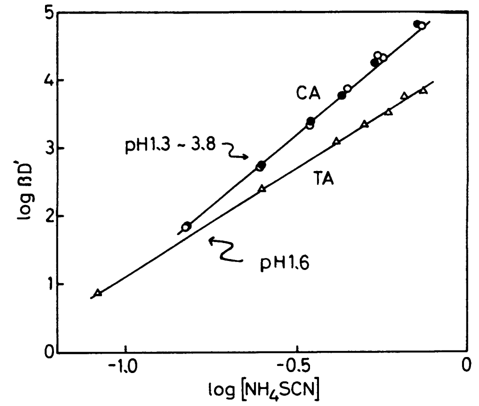


Fig. 4. Sorption and extraction of zinc thiocyanate complexes as a function of aqueous NH_4SCN concentration. Plots according to Equation 3. Sorption to CA (○,●): Twenty ml of aqueous NH_4SCN solution (○, pH 1.3; ●, pH 3.8. adjusted by HNO_3) containing 0.5 mM $Zn(NO_3)_2$ were used. The amount of CA was 2.0 g. Extraction to TA(△): Ten ml of aqueous NH_4SCN solution containing 0.5 mM $Zn(NO_3)_2$ (pH 1.6, adjusted by HNO_3) were used. The volume of TA was 10 ml.

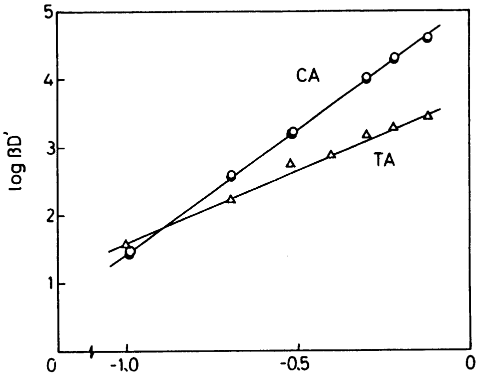


Fig. 5. Sorption and extraction zinc thiocyanate complexes as a function of aqueous SCN^- concentration. Plots according to Equation 3. Sorption to CA (○,●): Twenty ml of aqueous NH_4SCN solution (pH 1.6, adjusted by HNO_3) containing 0.5 mM $Zn(NO_3)_2$ were used. Total concentration of ammonium ion was adjusted to 0.75 M by NH_4NO_3. The amount of CA was 1.0 g (●) and 2.0 g (○). Extraction to TA (△): Twenty ml of aqueous NH_4SCN solution containing 0.5 mM $Zn(NO_3)_2$ (pH 1.6, adjusted by HNO_3) were used. Total concentration of ammonium ion was adjusted to 0.75 M by NH_4NO_3. The volume of TA was 5 ml.

Figure 4 shows one such plot, where the concentration of ammonium thiocyanate is varied (in this case, $[NH_4^+]_a=[SCN^-]_a=[NH_4SCN]_a$ in Equation 3). For the sorption on CA, the D' in Equation 3 was replaced by D. Figure 5 shows a similar plot, where $[NH_4^+]_a$ is maintained constant at 0.75 M and $[SCN^-]_a$ is varied. Figure 4 gives n values of 3.2 and 2.6 for the metal distributions to CA and TA respectively. Figure 5 similarly gives n values of 3.5 (CA) and 2.5 (TA). The sorbed or extracted metal species, therefore, seem to have average compositions of $(NH_4)_{1.2-1.5}Zn(SCN)_{3.2-3.5}$ in CA and $(NH_4)_{0.5-0.6}Zn(SCN)_{2.5-2.6}$ in TA.

As regards the similarity (as extraction solvents) between CA and carbonyl group-containing solvents (MIBK and TA), it seemed that it would be interesting to obtain some insight into the solvation of the extracted metal complex in the solid polymer. A solvation number (m) or a number of solvent (S) molecules associated with the extracted complex species may be defined by Equation 6:

$$((NH_4)_{n-2}Zn(SCN)_n)_a + m(S)_o$$
$$((NH_4)_{n-2}Zn(SCN)_n \cdot mS)_o \qquad (6)$$

where the suffixes "a" and "o" denote the aqueous and organic phases respectively. To obtain a rough measure of the m number, zinc thiocyanate complexes were extracted by an "inert" solvent, 1,2-dichloroethane, to which a variable concentration of MIBK or TA was added. Pure 1,2-dichloroethane does not extract the metal species at all, as shown in Table 1. A conventional manipulation then gives Expression 7 for the metal-distribution ratio (D) between the aqueous and the "active" solvent (S)-doped 1,2-dichloroethane phases:

$$\log D = m \log [S]_o + \text{constant} \qquad (7)$$

where $[S]_o$ stands for the molar concentration of the active solvent (MIBK or TA) in 1,2-dichloroethane.[12]

Equation 7 indicates that m is obtained as a slope of a linear plot, log D vs. $[S]_o$. Figure 6 shows such plots, from which the m value is determined to be 5.0 for both MIBK and TA. Although a TA molecule contains three carbonyl (or CH_3CO–) functional groups, it is most likely acting as a monofunctional carbonyl compound, as is MIBK. Since the nature of CA as an extraction solvent is between MIBK and TA (Fig. 3), it is quite probable that zinc thiocyanate complexes are stabilized by at least five carbonyl functional groups from CA in the polymer matrix.

In conclusion, there is now ample evidence that CA behaves just like ordinary carbonyl group-containing solvents, such as MIBK and TA, in "extracting" metal-complex species. Halogeno and pseudohalogeno complexes are especially easy to extract. Interestingly, CA membranes (including the

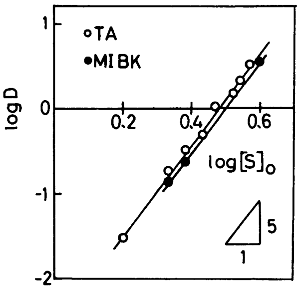


Fig. 6. Determination of solvation number according to Equation 7. Ten ml of 0.5 M NH_4SCN containing 0.5 mM $Zn(NO_3)_2$ were shaken with 10 ml of 1,2-dichloroethane containing TA or MIBK in variable concentration. The pH was adjusted to 1.0 by HNO_3.

hyperfiltration membrane) are quite similar to CA powders in such sorption properties.[13] In the light of these findings, it is no accident that CA membranes exhibit peculiar permeation characteristics to such metal complexes under hyperfiltration conditions.[1–4] At present, CA is the only polymer material which is a good sorbent for metal complexes and which can at the same time, be fabricated into hyperfiltration membranes. It is hoped that an understanding of the mechanism of metal sorption will give impetus to the development of a variety of polymer materials for the fabrication of metal-selective hyperfiltration membranes.

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12) The expression can be derived in a manner similar to that of Expression 3. The constant includes the extraction equilibrium constant for Reaction 6 as well as those equilibrium constants in an aqueous solution concerning the formation of zinc thiocyanate complexes and ion-association complexes. The constant is also a function of the concentration of ammonium and thiocyanate ions in an aqueous solution. Therefore, if the concentrations of ammonium thiocyanate and an active solvent are in a large excess of the zinc ion, and if the ammonium thiocyanate concentration is kept constant, the metal distribution ratio D becomes a function of only $[S]_o$.

13) T. Hayashita and M. Takagi, unpublished results.