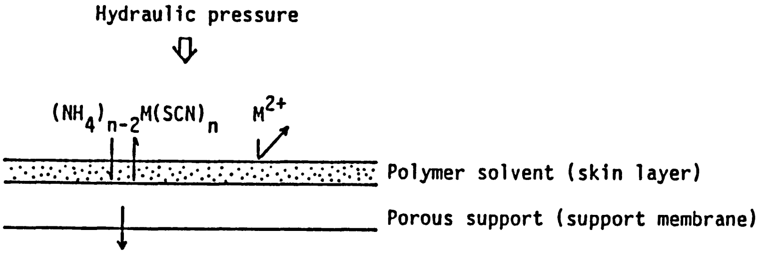
CHEMISTRY LETTERS, pp. 829-832, 1985.

SELECTIVE HYPERFILTRATION OF HEAVY METAL IONS. ION-ASSOCIATION SORPTION AND PERMEATION OF METAL COMPLEXES ON CELLULOSE ACETATE MEMBRANES

Takashi HAYASHITA, Motohiro HAMADA,† and Makoto TAKAGI
Department of Organic Synthesis, Faculty of Engineering, Kyushu
University, Hakozaki, Higashi-ku, Fukuoka 812
† Development Division, Toyo Soda Manufacturing Company,
Shin-nanyo, Yamaguchi 746

Various metal thiocyanate complexes in aqueous solution were found to be efficiently sorbed on cellulose acetate (CA) polymers. On the basis of this behavior, a new hyperfiltration process - a selective sorption to the membrane and a solvent flow-coupled permeation of metal complex species - was proposed for the separation of heavy metal ions in solution.



Scheme 1. Selective permeation of metal species under hydraulic pressure. Extraction (sorption) and solvent flow-coupled permeation of ion-association complexes.

Metal selective separation by membranes under hydraulic pressure is one of the future membrane technologies yet to be explored.[1,2] In modeling the mechanism of metal selective permeation, certain metal species have first to be preferentially sorbed or distribute to membrane phase over other metal species in solution. However, the metal-membrane interaction as well as their differences among metal ions is generally slight for hydrated (aquo) metal ions and conventional polymer membranes. This accounts for the difficulty in achieving metal selective hyperfiltration to ordinary metal salt solutions. On the other hand, it is known that metal halogeno or pseudo-halogeno complexes are effectively extracted in the form of ion-association complexes into oxygen-containing organic solvents,[3] and this has been widely used for the separation of metal ions.[4] In recent years, the extraction study has been extended to solid polymers,[5,6] and certain polymers such as polyurethane foam have been found to effectively substitutes organic solvents for sorption or "extraction" of some heavy metal complexes in aqueous solution.[7,8]

These have led the present authors to propose a new hyperfiltration process for the separation of heavy metal ions in aqueous solution. The principle is that an active membrane phase acts as a "polymer solvent" for the extraction of ion-association complexes and the extracted metal species are transported through the membrane by some coupling process with a solvent flow under hydraulic pressure. Metal species which lack an affinity to the active membrane phase do not permeate the membrane (Scheme 1). This paper presents experimental as well as theoretical considerations for the support of the proposed hyperfiltration.

Table 1. Sorption(%) of metal ions on polymers in the presence of thiocyanate ion[a)]

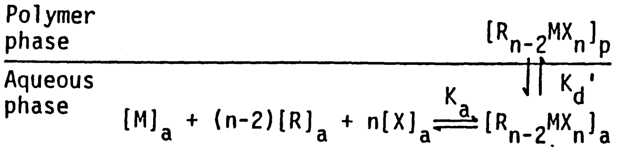
No.	Polymer	Fe^{3+}	Co^{2+}	Ni^{2+}	Cu^{2+}	Zn^{2+}	Pd^{2+}	Ag^{+}	Cd^{2+}	In^{3+}	Au^{3+}
1	CA	63.4	9.6	1.2	47.2	92.2	84.4	0.0	11.8	79.4	93.6
2	PAN	18.0	6.8	0.8	13.8	57.6	40.4	0.0	2.2	28.0	37.6
3	CE	0.0	0.0	0.0	5.6	0.4	3.4	0.0	0.0	0.6	0.0
4	PVC	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	3.6
5	PAG	1.2	0.0	0.0	0.0	1.6	0.0	0.0	0.8	0.6	0.0

a)Twenty milliliters of 0.5 mol dm^{-3} NH_4SCN solution containing 0.5x10^{-3} mol^{-3} dm^{-3} metal nitrate (pH 1.0, adjusted by HNO_3) was shaken with 2.0 g of polymer powder. CA: Cellulose acetate, PAN: Poly(acrylonitrile), CE: Cellulose, PVC: Poly(vinyl chlorive), PAG: Penta-acetyl-ß-D-glucose.

The sorption of metal complex species to polymer was first studied. An appropriate amount of polymers (in fine powders) was suspended in aqueous solution containing a metal nitrate salt of interest and an alkali and ammonium halide (or pseudo-halide). The mixture was mechanically shaken until the equilibrium was attained (90 min). The change in metal ion concentration in the bulk solutions was then measured by atomic absorption spectrophotometry (Japan Jarrel Ash Co. AA-1).

Sorption of metal thiocyanate complexes on some typical solid polymers are shown in Table 1. It is seen that a hydrophilic polymer such as cellulose (CE) and a hydrophobic polymer such as poly(vinyl chloride) (PVC) show no sorption capabilities. Metal thiocyanate complexes are sorbed only by polymers of intermediate polarity, such as cellulose acetate (CA, Acetyl content 39.8%, Eastman Kodak Co.) and poly(acrylonitrile) (PAN). As the metal thiocyanate complexes are not sorbed on the "monomeric" sorbent, penta-acetyl glucose (PAG), a polymer environment or some micro-structure of solid polymer matrix seems to be of vital importance for sorption to take place.

A mechanism of the sorption was studied by a simplified model depicted in Scheme 2. According to the model, the coordination number n of the "extracted" zinc thiocyanate complexes is determined from a log - log plot of modified distributon ratio (ßD') against thiocyanate concentration.[9)] As is shown in Fig. 1, the plots for zinc thiocyanate sorptions are linear with a slope is of n = 3.2 (NH_4SCN concentration was varied) and n = 3.5 (SCN^- concentration was varied, $NH_4(SCN + NO_3)$ = 0.75 mol dm^{-3}). Thus, $NH_4Zn(SCN)_3$ or $(NH_4)_2Zn(SCN)_4$ (or a



Scheme 2. Sorption equilibrium of metal halogeno complexes.

$$\log\beta D' = (n-2)\log[R]_a + n\log[X]_a + \log K_aK_d' \quad (1)$$

$$D' = \frac{[R_{n-2}MX_n]_p}{[M]_a + [MX]_a + \cdots + [MX_m]_a} \quad \text{and}$$

$$\beta = 1 + k_1[X] + k_1k_2[X]^2 + \cdots + k_1\cdot\cdot k_m[X]^m$$

($k_1, k_2 \cdots k_m$: complex formation constants).

mixture of the two) seems to be the main sorption species. This result verifies that the sorption of metal thiocyanate complexes occurs mainly by forming the ion-association complex in the polymer matrix.

Cellulose acetate coated membranes were prepared by repeatedly spraying and air-drying 0.5 wt% cellulose acetate solution (in acetone) onto a "Fluoropore" membrane (pore size 0.1 μm, Sumitomo Electric Industries Ltd.) until an apporopriate thickness of cellulose acetate (0.3 - 0.4 mg of CA per cm^2) was attained.[2,9] The permeation of metal thiocyanate complexes through CA-coated membrane was studied at 2.0x10^6 Pa and 25 °C by using a corrosion-resistant batch type hyperfiltration cell. Permeation behavior was evaluated by permeability (P) which is defined in Eq. 2.

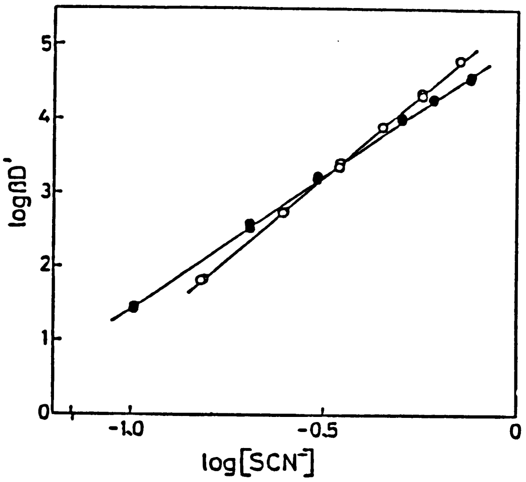


Fig. 1. Sorption of zinc thiocyanate complexes on cellulose acetate. Effect of thiocyanate concentration.
○ NH$_4$SCN concentration was varied. ● Only SCN$^-$ concentration was varied ([NH$_4$(SCN + NO$_3$)] = 0.75 mol dm^{-3}).

$$\text{Permeability (P)} = C_p/C_f \qquad (2)$$

C_p: Concentration of metal ion in the permeate. C_f: Concentration of metal ion in the feed.

Distribution ratio (D) of metal species between cellulose acetate and the aqueous solution was readily obtained for a specified composition of the feed solution by the method described before.[9] The metal distribution did not depend within experimental error on the

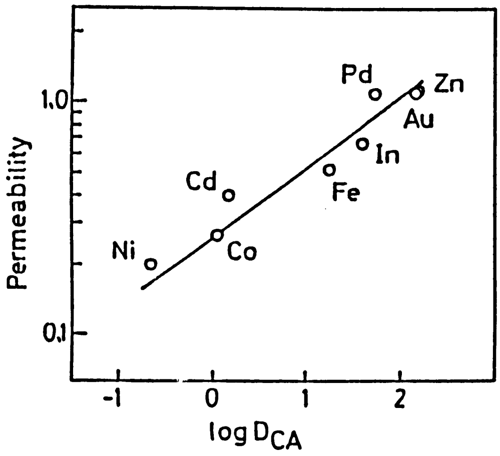


Fig. 2. Correlation of distribution ratio and permeability of metal thiocyanate complexes.
Feed: 0.5 mol dm^{-3} NH$_4$SCN - 0.1x10^{-3} mol dm^{-3} M(NO$_3$)n (except for Au(III); NaAuCl$_4$). Applied pressure 2.0x10^6 Pa at 25 °C.

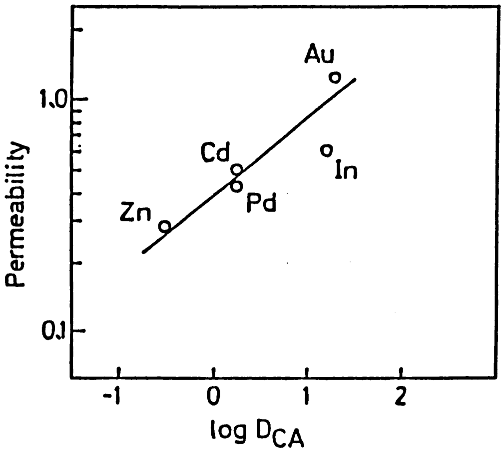


Fig. 3. Correlation of distribution ratio and permeability of metal iodide complexes.
Feed: 1.0 mol dm^{-3} NaI - 0.5x0.1 mol dm^{-3} M(NO$_3$)n (except for Au(III); NaAuCl$_4$). Applied pressure 2.0x10^6 Pa at 25 °C.

physical form (powder or dense membranes) of cellulose acetate used.

The relationship between the distribution ratio and the permeability of metal halogeno species is shown in Fig. 2 and Fig. 3 for thiocyanate and iodide complex systems, respectively. In both figures, a positive correlation is apparent between distribution ratio and permeability, i.e., the larger the distribution of metal species to the polymer (membrane) phase, the larger the permeability of the metal species through the membrane under pressure. In the absence of added thiocyanate or iodide ion, the permeability of metal species (aquo-complexes) is practically negligible. This is in harmony with the picture presented in Scheme 1.

It has been known for the hyperfiltration with cellulose acetate membranes that the rejection of phenolic compounds in aqueous solution is abnormally low; the rejection, depending on the conditions, adopts even negative values of -20 - -30% or the permeability reaches the value as high as 1.2 - 1.3 (enrichment of phenols in the permeate).[10] The increased permeability of phenols is ascribed to their ease of sorption to cellulose acetate membrane phase (preferred sorption of phenols over water molecules) and the subsequent solvent flow-coupled permeation of the sorbed species through the membrane. It seems reasonable to assume that the permeation of lipophilic ion-association complexes shows similar mechanistic features to those of the permeation of phenols. The permeability (P) of some metal species is in fact larger (though slightly) than unity as is seen in Figs. 2 and 3. A further study is needed, however, on the detailed mechanism of metal permeation.

In summary, the equilibrium study in Scheme 2 and Fig. 1 indicates that the sorption of metal species is essentially similar to the conventional solvent extraction of metal complexes. A polymer matrix (of cellulose acetate) may well be deemed as a "polymer solvent" to "extract" metal species. Figures 2 and 3 indicate that the metal permeation is governed essentially by the extraction selectivity of metals onto the polymer hyperfiltration membrane. Thus, the present hyperfiltration process is featured by a liquid-liquid extraction like selectivity of metal permeation. Somewhat similar attempt has been made by Igawa, Senō and coworkers for the permeation of copper(II) acetylacetonate complex by using "hydrophobic" membranes.[2] A proper combination of membrane materials and complex-forming systems according to the idea delineated in the present work should lead to a still further variety of metal permeation and separation, some of which may hopefully find application in practical metal processing.

This work was partially supported by the Grant in Aid for Scientific Reseach from the Ministry of Education, Science and Culture.

References

1) T. Hayashita, M. Takagi, and K. Ueno, Sepn. Sci. Techn., 18, 461 (1983); 19, 375 (1984). 2) M. Igawa, A. Saito, N. Sasamura, M. Tanaka, and M. Senō, J. Memb. Sci., 14, 59 (1983). 3) J. W. Rothe, Chem. News, 66, 182 (1892). 4) T. Sekine and Y. Hasegawa, "Solvent Extraction Chemistry," Dekker, New York (1977). 5) H. J. M. Bowen, J. Chem. Soc.,A, 1970, 1082. 6) R. F. Hamon, A. S. Khan, and A. Chow, Talanta, 29, 317 (1982). 7) T. Braun and A. B. Farag, Anal. Chim. Acta, 99, 1 (1978). 8) K. Watari, K. Imai, S. Shibata, and M. Miura, J. At. Energy Soc. Jpn., 26, 384 (1984). 9) T. Hayashita and M. Takagi, Talanta, in press. 10) H. K. Lonsdale, U. Merten, and R. L. Riley, J. Appl. Polymer Sci., 9, 1341 (1967); J. M. Dickson and D. R. Loyd, "Synthetic Membrane," ACS Symposium Series, II, (1981), p.293.

(Received March 26, 1985)