

The Permeation Behavior of Metal Complex Solutions through Cellulose Acetate Membranes

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Synopsis

Transport phenomena of several kinds of metal complexes were investigated with cellulose acetate membranes annealed at 65°–76°C. In reverse osmosis experiments, the rejections of metal complexes involving organic sequestering agents such as EDTA or citric acid were much higher than those of the corresponding metal ions. While, in the case of metal complexes involving small inorganic ligands such as NH_3 or SCN^- , their rejections did not necessarily increase with the increase in the coordination numbers of the metal ions. To more precisely understand such transport behaviors, the distribution and the diffusion coefficients of metal complexes were obtained by desorption-rate measurements with dense cellulose acetate membranes. The results revealed that the distribution of a metal ion to the membrane was largely depended on the coexisting ligands. Attempts were also made to explain the distribution coefficient from the microscopic point of view by using Glueckauf's equation.

INTRODUCTION

There have been numerous attempts to explain the salt and water transport mechanism through cellulose acetate membranes. This may be mainly attributed to the complex structure of the membrane. Basically, there seems to be three principal approaches to the problem: They are (1) the explanation of the transport phenomena in connection with the physical and/or chemical nature of the pore in the membrane^{1–4}; (2) the analysis of the experimental result in terms of the thermodynamical coefficients without much consideration of the membrane structure^{5,6}; and (3) the explanation based on the combination of two approaches mentioned above; that is, the explanation of the thermodynamical coefficients resulting from the data analysis from the microscopic point of view.^{7,8} For the details of these theories, one should be referred to other papers.⁹

In this paper, solutions involving metal complexes were chosen to gain an insight into the permeation behavior of a mixture system. Using the experimental data of reverse osmosis and desorption-rate measurements for metal complexes, the permeation behaviors of them were discussed in some detail. The values of the distribution coefficients obtained by the desorption-rate measurement were analyzed from the microscopic point of view by using the Glueckauf's equation.¹

EXPERIMENTAL

Reverse Osmosis

Twelve metal complexes listed in Table I were used in reverse osmosis experiments. The membrane used in the reverse osmosis experiments was prepared by the method reported by Loeb and Manjikian.¹⁰ The casting solution was composed of 25 wt% cellulose acetate (Eastman 398-3), 65 wt% acetone, and 10 wt% phosphoric acid. The annealing temperatures of the Loeb-type membranes were 65°, 70°, 73°, and 76°C. The evaporation temperature was 20° ± 1°C and the evaporation time was 40 sec for all Loeb-type membranes. The membranes thus prepared were rather opaque than transparent and had approximately 20% more fluxes, with the same rejection, as compared with standard (formamide-type) membranes.

The effective membrane area in the desalination cell was 12.6 cm². The pressurized (40 atm) solution was circulated along the surface of the membrane at 1.2 l/min to reduce concentration polarization. The membranes were pressurized at 60 atm for approximately 3 hr prior to use with 0.1 M NaCl solution.

When a solution was replaced by another one for the reverse osmosis test, the inside of the apparatus was washed thoroughly with the solution which was going to be tested. In all the experiments the permeated water was collected one hour after the beginning of the operation. The properties of the membrane were shown by water flux (m³/m² day) and desalination ratio. The desalination ratio is shown by¹² $Dr = C_f/C_p$, where C_p and C_f are the salt concentration of the product and feed solutions, respectively. The desalination ratio is a convenient expression to represent separation characteristics of the membrane especially in the range of high rejection more than 95%.

As it is known that the cellulose acetate membrane is deteriorated rapidly, with a loss of performance, by a strong acidic or basic solution,¹¹ experiments were carried out as rapidly as possible. The loss of performance of the membrane during the experiment was checked by the change in the water flux and the desalination ratio of NaCl between before and after experiment as shown in Table II.

Desorption-Rate Measurement

To understand the permeation behavior of metal complexes more precisely, the desorption-rate measurement was also carried out. In this method, a dense film was used as the substitute for the active layer of the Loeb-type membrane. It is probable that the membrane performance of the dense film is different from that of the active layer. However, judging from the fact that Lonsdale et al. explained the reverse osmosis results¹³ by using the data of the desorption-rate measurement with a good accuracy, the dense film could be considered to be analogous to the active layer. This method was described in detail by Lonsdale et al.¹³ and Yasuda et al.¹⁴ All membranes used in this study were cast from a solution composed of 25 wt% cellulose acetate and 75 wt% acetone. All membranes were cast at 20°C and permitted to dry until there was no residual smell of acetone. Disks of 5 cm diameter were punched and stored in a desiccator.

Thickness of each membrane was almost 30 μm , and normally a set of 10 disks were used in each run. The disks were annealed at 65° and 80°C prior to use. And then they were equilibrated with the solute of interest by allowing them to soak at 25°C for a time that was long compared to the characteristic diffusion time.

After the excess amount of the solution on the surface was rinsed and wiped out, the disks were introduced into 150 ml of distilled water.

The desorption rate was determined by the measurement of the concentration changes of the surrounding solution. The diffusion coefficient is determined from the desorption rate; the distribution coefficient is determined in the same experiment from the solute concentration in the membrane relative to that in the solution with which it was initially equilibrated.

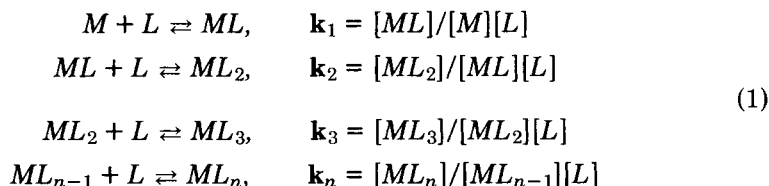
Analytical Procedure

Analytical procedures of metal ions were as follows. Analysis of each ligand was not carried out, although the pH of each solution was measured. Copper was determined by atomic absorption at 325 μm , or determined spectrophotometrically at 557 μm after reacting with 1-(2-pyridylazo)-2-naphthol (PAN). Iron was determined spectrophotometrically at 513 μm after reacting with *o*-phenanthroline at pH 4.2. Nickel was determined spectrophotometrically at 570 μm after reacting with PAN and extracting by chloroform thereafter. Cadmium was determined spectrophotometrically at 548 μm after reacting with PAN.

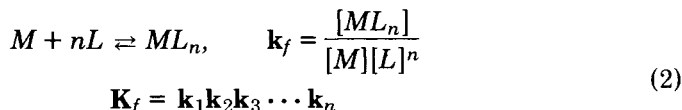
RESULT AND DISCUSSION

Effect of Complex Formation on Permeation of a Solute

The stepwise formation of a metal complex is generally expressed as follows¹⁵:



where M and L are a metal ion and the ligand, respectively, and k_1 to k_n is the stepwise stability constant. Therefore, the overall metal complex formation can be written



Now the fraction of the complex β_0 to β_n relative to the total metal ion concentration C_M is defined as follows:

$$\begin{aligned}
 \beta_0 &= [M]/C_M \\
 \beta_1 &= [ML]/C_M \\
 \beta_2 &= [ML_2]/C_M \\
 \beta_n &= [ML_n]/C_M
 \end{aligned}$$

TABLE I
List of Metal Complexes Used in Reverse Osmosis

Complex No.	Metal ion	Molecular concentration	Ligand	Molecular concentration	pH of solution	Stability constant
A-1	CuSO ₄	2.0 × 10 ⁻³	none	4.0 × 10 ⁻³	5.2	log k ₁ = 10.6
2			ethylene diamine	2.5 × 10 ⁻²	7.1	log k ₂ = 9.0
3			ethylene diamine		11.4	
B-1	Cu(NO ₃) ₂	1.0 × 10 ⁻²	none	5.0 × 10 ⁻³	4.40	log k ₁ = 5.40
2			citric acid	1.0 × 10 ⁻²	2.35	
3			citric acid	2.0 × 10 ⁻²	2.15	
4			citric acid		2.00	
C-1	Cu(NO ₃) ₂	1.0 × 10 ⁻²	none	5.0 × 10 ⁻²	4.40	log k ₁ = 3.99
2 ^a			ammonia		9.15	log k ₂ = 3.34
						log k ₃ = 2.73
						log k ₄ = 1.97
D-1	FeCl ₂	7.0 × 10 ⁻³	none		4.80	log k ₁ k ₂ k ₃ = 21.3
2			<i>o</i> -phenanthroline	1.25 × 10 ⁻³	4.80	
3			<i>o</i> -phenanthroline	3.0 × 10 ⁻³	4.80	
E-1	Cu(NO ₃) ₂	2.0 × 10 ⁻³	none	2 × 10 ⁻³	4.82	
2			EDTA		2.75	log k ₁ = 18.8
F-1	Ni(NO ₃) ₂	1.0 × 10 ⁻²	none	1.0 × 10 ⁻²	6.30	log k ₁ = 2.67
2 ^a			ammonia	2.0 × 10 ⁻²	8.35	log k ₂ = 2.12
3 ^a			ammonia	4.0 × 10 ⁻²	8.80	log k ₃ = 1.61
4 ^a			ammonia		9.20	log k ₄ = 1.07
						log k ₅ = 0.63
						log k ₆ = -0.09

G-1	Ni(NO ₃) ₂	2 × 10 ⁻³	none	5.80	
2			KSCN	5.70	log k ₁ = 1.18
3			KSCN	5.70	log k ₂ = 0.46
4			KSCN	5.70	log k ₃ = 0.17
5			KSCN	5.70	
H-1	Cu(NO ₃) ₂	2.0 × 10 ⁻³	none	4.80	log k ₁ k ₂ k ₃ = 5.19
2			KSCN	4.80	
3			KSCN	4.80	
I-1	Cu(NO ₃) ₂	2.0 × 10 ⁻³	none	4.85	log k ₁ k ₂ = 23.8
2			KCN	5.50	log k ₃ = 4.61
3			KCN	8.70	log k ₄ = 2.12
J-1	CD(NO ₃) ₂	2.0 × 10 ⁻³	none	5.30	log k ₁ = 5.18
2			KCN	7.65	log k ₂ = 4.42
3			KCN	10.50	log k ₃ = 4.32
					log k ₄ = 3.19

^a To prevent the formation of the hydroxide compound, ammonium nitrate (0.2 M/l) was added for each solution.

TABLE II
 Results of Reverse Osmosis Experiment

Solute complex no.	Membrane-65 ^a		Membrane-70 ^a		Membrane-76 ^a	
	Water flux	Dr	Water Flux	Dr	Water flux	Dr
A-1	1.32	20.0	0.94	62.5	0.85	100
2	1.22	435	0.94	1430	0.83	1670
3	1.39	13.0	1.01	40.0	0.90	20.0
NaCl 0.1 M { ^b	1.06	4.6	0.79	9.2	0.69	27.8
	1.39	3.8	0.93	7.8	0.82	9.5
B-1	1.76	19.6	1.07	24.0	0.43	333
2	1.62	143	1.06	250	0.43	2000
3	1.61	196	1.06	455	0.49	3300
4	1.50	200	0.99	600	0.47	4000
NaCl 0.1 M {	1.67	3.8	1.00	9.6	0.40	28.0
	1.58	4.5	0.96	10.9	0.40	34.0
C-1	1.72	31.0	1.28	60.7	0.73	167
2	1.75	90.0	1.34	64.0	0.74	323
NaCl 0.1 M {	1.60	4.6	1.08	13.5	0.61	35.7
	1.61	4.7	1.13	15.2	0.65	40.0
D-1	1.53	31.3	1.49	27.8	0.92	200
2	1.54	33.3	1.46	40.0	0.92	200
3	1.68	43.5	1.57	71.4	1.02	250
NaCl 0.1 M {	1.37	3.5	1.27	6.1	0.77	21.8
	1.46	3.7	1.36	6.8	0.82	22.7
E-1	1.60	13.2	1.53	13.3	0.79	62.5
2	1.64	34.6	1.48	34.1	0.90	77.0
NaCl 0.1 M {	1.43	3.5	1.31	5.9	0.79	21.3
	1.50	3.5	1.37	6.4	0.85	21.8
F-1	1.71	31.3	1.42	27.8	0.90	52.6
2	1.71	41.7	1.48	83.3	0.94	125
3	1.66	55.6	1.50	90.9	0.94	250
4	1.65	58.8	1.48	71.4	0.95	167
NaCl 0.1 M {	1.49	3.7	1.30	6.0	0.78	20.0
	1.48	4.0	1.31	7.0	0.80	22.4
G-1	1.48	3.2	1.28	39.1	0.76	50.0
2	1.53	4.0	1.31	44.4	0.77	61.4
3	1.50	3.7	1.27	36.2	0.74	55.9
4	1.48	4.9	1.25	43.5	0.74	43.5
5	1.59	4.5	1.30	22.0	0.74	23.8
NaCl 0.1 M {	1.35	3.2	1.07	14.9	0.63	31.3
	1.38	3.0	1.12	13.2	0.66	28.0
H-1	1.57	31.3	1.22	16.1	0.71	143
2	1.58	16.2	1.23	16.4	0.71	125
3	1.56	6.2	1.23	19.6	0.70	47.6
NaCl 0.1 M {	1.40	5.5	1.15	10.6	0.67	37.0
	1.42	5.7	1.08	9.3	0.64	40.0
I-1	1.53	28.2	1.22	10.5	0.68	167
2	1.58	9.5	1.23	21.7	0.69	55.6
3	1.54	28.4	1.21	13.0	0.69	90.9
NaCl 0.1 M {	1.35	5.6	1.01	8.9	0.58	38.5
	1.36	5.7	1.02	9.4	0.59	40.0
J-1	1.57	10.7	1.22	10.1	0.68	147
2	1.57	7.5	1.21	11.2		/67
200						
3	1.55	22.0	1.19	10.4	0.66	357
NaCl 0.1 M {	1.48	3.9	1.09	8.9	0.62	37.0
	1.44	3.7	1.00	8.3	0.60	35.7

^a Membrane-65: membrane annealed at 65°C.

^b NaCl 0.1 M { water flux and Dr of NaCl before the experiment;
 water flux and Dr of NaCl after the experiment;

unit of water flux: m³/m² day; operating pressure: 40 atm.

and

$$\beta_0 + \beta_1 + \beta_2 + \dots + \beta_n = 1 \quad (3)$$

From eqs. (1), (2), and (3), the existence ratios of various type complexes can be calculated as shown in Figure 1.

The values of k_1 to k_3 of Ni—SCN complex were cited from ref. 15. As many sequestering (chelating) agents are influenced by pH change on the formation of the complexes,¹⁵ the corrected values of the stability constants were employed when the effect was large. As for the structure of a metal complex in the aqueous solution, many problems are left to be unsolved. In this report, however, the data were analyzed mainly in connection with calculated values by using above-mentioned equations for simplicity. Results obtained in reverse osmosis experiments are summarized in Table II. Let us look at the effect of the complex formation on reverse osmosis results in typical mixture systems. The desalination ratio of copper ion vs citric acid concentration in the solution is shown in Figure 2. Before the concentration of citric acid reached a certain concentration, that is, the molar concentration of copper ion, the desalination ratio increased remarkably, but it remained almost constant in the higher concentration range

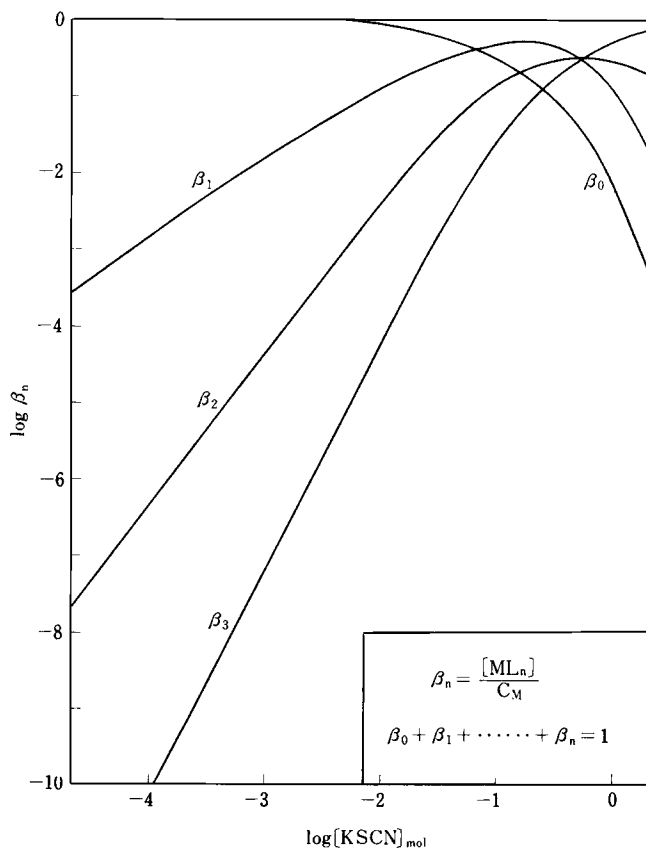


Fig. 1. Calculated values of β_0 – β_3 for Ni—SCN complex.

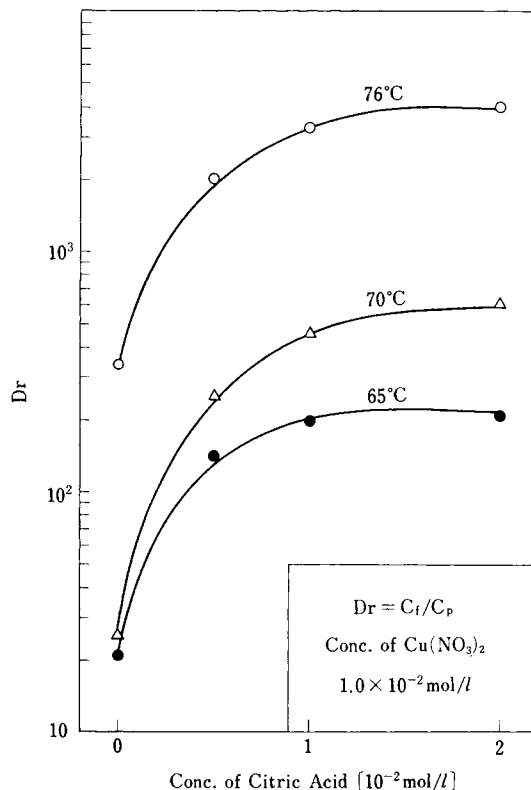


Fig. 2. Effect of ligand concentration on desalination ratio of Cu—citric-acid complex. The temperature on the line represents the annealing temperature of the membrane.

of citric acid. In this way, in the case of metal complexes which involve large organic ligands such as ethylene diamine tetra acetate (EDTA), the desalination ratios of them increased with the increase in the ligand concentration, before the ligand concentration reached the same concentration of the metal ion. The increase in the rejections may be due to the large sizes of the ligands. In these cases the coordination numbers of the metals are known to be one. This is also attributed to the steric effect of the ligands.

On the other hand, the desalination ratios of metal complexes which involve small inorganic ligands such as NH_3 , SCN^- and CN^- , did not necessarily increase with their coordination numbers. As shown in Figure 3, the desalination ratio of Ni— NH_3 complex increased before the ligand concentration reached a certain point at which the decrease of the desalination ratio occurred. In the case of Ni—ethylenediamine complex, the membrane was deteriorated because of its strongly basic solution as shown in Table II, but the trend of Dr vs the ligand concentration seems to be similar to that of Ni— NH_3 complex.

Interpretation of Transport Phenomena by Solution Diffusion Model

The solution diffusion model was employed to make clear the peculiar transport phenomena of Ni— NH_3 complex. According to the model, the solute flux was expressed as follows⁴:

$$J_2 = -D_2 K \Delta \rho_2 / \Delta x \quad (4)$$

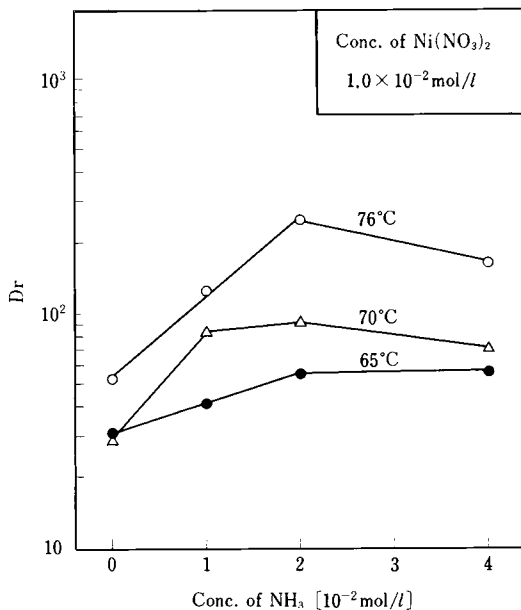


Fig. 3. Effect of ligand concentration on desalination ratio of Ni—NH₃ complex.

where J_2 is the solute flux and $\Delta\rho_2$ is the difference in solute concentration in the two solutions separated by the membrane. D_2 and K is the diffusion coefficient and the distribution coefficient of the solute, respectively.

Equation (4) is considered to be valid unless there is much coupled flow between water and the solute. D_2K is defined as the permeability of the solute and is often determined by the desorption-rate method.

The advantage of the desorption-rate method is that one can obtain these two coefficients simultaneously. On the other hand, the disadvantage of this method is that the concentration of the solution in which the membranes might be immersed should be high enough as 5 wt%, especially in the case of inorganic salts involving metal ions with high valencies. In these cases, the salt concentrations of the surrounding solutions in the desorption stage were extremely low. Therefore, one of the most important and troublesome jobs was to look for an analytical method having high sensitivity as described in the experimental section.

The distribution coefficient can be obtained by the following equation⁴:

$$K = \frac{\text{g salt/ml membrane}}{\text{g salt/ml solution}} \quad (5)$$

As mentioned above, there are various types of complexes in the solution and it is very difficult to interpret the distribution of the complex corresponding to each type of complex. Therefore the average coordination number was employed to discuss the distribution of the complex for convenience. The average coordination number is expressed as

$$\bar{n} = \sum_{\theta=0}^n \theta\beta_{\theta} \quad (6)$$

In this paper, the desorption-rate experiments were carried out for nickel

complexes, and SCN^- and NH_3 were chosen as the ionic and nonionic ligand, respectively.

In the case of Ni—SCN complex, as shown in Figure 4, the distribution coefficient increased remarkably with the increase in the average coordination number and went up to the value of 0.1 when the average coordination number was almost 2.

This value was surprisingly high compared with that of $\text{Ni}(\text{NO}_3)_2$, 0.0035. By the way, the distribution coefficient of NaCl was 0.030. This may be because the repulsive force between the ions and the membrane due to the charge of Ni^{2+} is reduced by the surrounding negative charge of SCN^- , although the binding force between these ions are covalent. On the other hand, in the case of Ni— NH_3 complex, plots of the distribution coefficient vs the average coordination number have maximum points as shown in Figure 5. Concerning this fact, it may be considered in the following way.

Nickel ions are surrounded by NH_3 molecules depending on the concentration in the solution, and the repulsive force to the membrane is gradually reduced with the concentration of NH_3 , although the effect is small as compared with SCN^- due to no charge of NH_3 .

Therefore, Ni— NH_3 complex tends to distribute in the membrane with the increase in the concentration of NH_3 , before the coordination number reached a certain value at which there occurs the steric effect, that is, the complex becomes too large to enter the membrane. Microscopic viewpoint on the distribution of Ni— NH_3 complex will be described later.

For diffusion into or out of semi-infinite slab, the relative concentration of the solute in the slab at time t is given by

$$\frac{S_f - S_t}{S_f} = \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp\left(-\frac{(2n+1)^2 \pi^2 D_2 t}{\Delta x^2}\right) \quad (7)$$

where S_f is the final concentration in the slab (i.e., the concentration at $t \rightarrow \infty$),

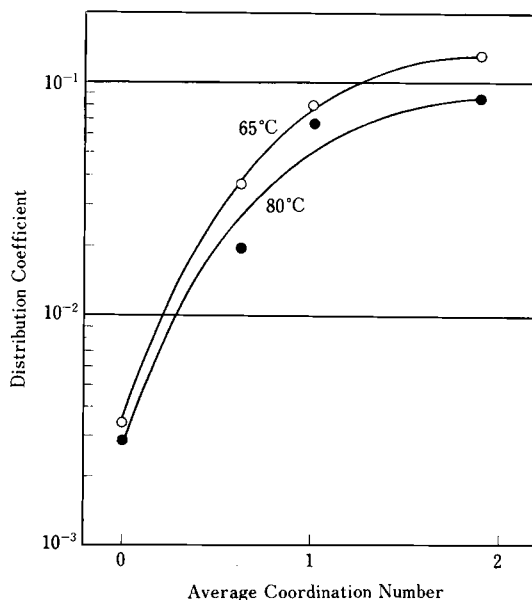


Fig. 4. Effect of ligand concentration on distribution coefficient of Ni—SCN complex.

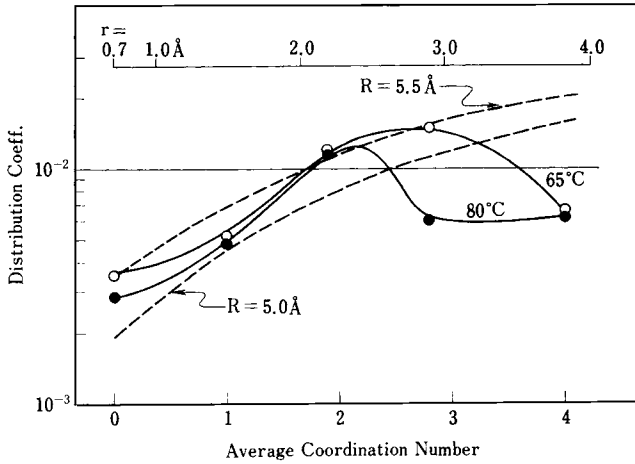


Fig. 5. Effect of ligand concentration on distribution coefficient of Ni—NH₃ complex.

and S_t is the concentration at time t . For times longer than $t = 0.1 x^2/\pi^2 D_2$, eq. (7) reduces to

$$(S_f - S_t)/S_f = (8/\pi^2) \exp(\pi^2 D_2 t / \Delta x^2) \tag{8}$$

Thus, a plot of $\log_{10} (S_f - S_t)/S_f$ vs time should be a straight line with a slope of $-\pi^2 D_2 / 2.3 \Delta x^2$ and an intercept of $\log_{10} 8/\pi^2$, i.e., 0.81.

The diffusion coefficient Ni—SCN complex is shown in Figure 6. The values of these data can not always be reliable. In the desorption-rate measurement water diffuses into the membrane in the opposite direction of the complex flow. The contact of pure water and the complex displaces the equilibrium in the

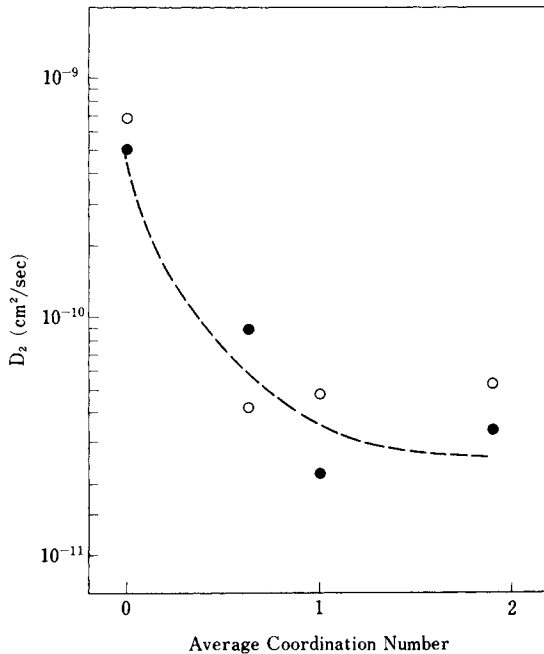


Fig. 6. Effect of ligand concentration on diffusion coefficient of Ni—SCN complex. O, membrane annealed at 65°C; ●, membrane annealed at 80°C.

membrane and the different type of the complex might be formed. In the case of complexes, thus, the determination of the diffusion coefficient is not appropriate.

There is a report describing that when alcohols diffuse in the film, the diffusion coefficient is inversely proportioned to carbon number of the alcohol.¹⁶ While, according to the data obtained by Lonsdale et al.,¹³ the diffusion coefficient of the solute seems to be affected by both its size and affinity to the membrane.

To my regret, in this report, the data of reverse osmosis experiments were not fully related to those of the desorption rate measurements. One of the main reasons was that the concentration at which the desorption-rate measurement was carried out is much higher than that at which the reverse osmosis experiment was carried out. The other reason was, as above mentioned, that diffusion coefficient obtained was not necessarily reliable.

However, it was considered to be meaningful to get the information that as both the distribution coefficient and the diffusion coefficient were greatly affected by the small change of the molecular size or the affinity to the membrane, the permeability, expressed by D_2K , also varied with the change of the state in the external solution and that the maximum value or minimum of D_2K might appear when the state of the feed solution (for example, the concentration or the carbon number of the solute, etc.) was continuously changed.

Microscopic Viewpoint on Distribution of Metal Complexes

Glueckauf extended Scatchard's theory¹⁷ and explained the salt rejection by a porous membrane based on the free energy difference of an ion between in a pore filled with water surrounded by a material of low dielectric constant and in bulk solution.

The Glueckauf's equation is

$$\log_{10} \bar{m}/m_x = e^2 Z^+ Z^- (1 - \alpha) Q / 4.6 \epsilon k T (R + \alpha r Q) \quad (9)$$

where \bar{m} is the concentration of the solution at the membrane surface, m_x is the concentration of the product solution, e is the electric charge, R is the radius of the membrane pore, r is the ionic radius, $Q = (\epsilon - \epsilon')/\epsilon'$, and $\alpha = 1 - (1 + \kappa^2 R^2)^{-1/2}$. ϵ is the dielectric constant of liquid and ϵ' is that of the membrane and $\kappa^2 = 4\pi e^2 / \epsilon k T \sum n_i Z_i^2$, k is the Boltzmann constant, T is temperature, and n_i is the number of particles in unit volume.

As Taniguchi et al. pointed out,¹⁸ m_x/\bar{m} corresponds to the distribution coefficient of the salt, and we can not predict the salt rejection from the value only.

I am of the opinion that eq. (9) is valid in high concentration of the feed solution, because the value of Debye length $1/\kappa$ becomes too large (more than 30 Å for 1-1 electrolytes) in lower concentration than 0.1 M and the value of m_x/\bar{m} has no physicochemical meanings.

In addition, it seems to be more appropriate to adopt $Z^+ Z^-$ instead of $(Z^+)^2$ in eq. (9) which is originally used in the literature, considering the effect of anions on the distribution coefficient. Taking into consideration of water content w , the relation between eqs. (5) and (9) is expressed as follows:

$$K = w \cdot m_x / \bar{m} \quad (10)$$

Using eqs. (9) and (10), one obtains the value of $R = 5.5$ Å from $K_{\text{NaCl}} = 0.030$ and $w = 0.12$ (g water/ml membrane) for the membrane annealed at 65°C.

The value of K increases with increasing ionic radius r , if R and the other parameters are kept constant. The dotted line in Figure 5 represents the calculated distribution coefficient vs. the ionic radius of 2-1 electrolytes. If one make the dotted line overlapped with the experimental data on the distribution of Ni—NH₃ complex, one could observe that the decrease in the distribution coefficient occurs when the size of Ni—NH₃ complex reached approximately 3 Å for the membrane annealed at 65°C.

From the result, one can estimate that when the radius of pore is 5.5 Å, the steric effect on the distribution of the solute might occur at the size of 3 Å or so. It is interesting to consider this experimental result in connection with the structure of Ni—NH₃ complex. Ni—NH₃ complex has a octahedral structure.¹⁹ The literature values of the interatomic distance between Ni and N, and the molecular volume is 2.6 ± 0.3 Å and 178 Å³, respectively. The accuracy of the estimation on the pore size of the membrane may be not good, because Glueckauf's equation can not always explain the experimental data with the good precision, and in addition the structure of the complex in the solution and in the membrane was not necessarily known sufficiently. However, it seems instructive that one can obtain some information regarding the structure of the various molecules or particles from the above-mentioned viewpoint.

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