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A Relation between Ion-exchange Selectivity Coefficient and Degree of Distribution for Model Compounds in Solvent Extraction

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An analogy of solvent extraction to ion-exchange was taken to explain anion affinities to anion-exchangers. Distributions of the model compound whose cation was the ionogenic group of an anion-exchanger and whose anion the counter ion, between water and an organic solvent, were investigated. The degree of distribution of the model compound for a solvent layer was expected to increase with increasing anion affinities to the corresponding anion-exchanger. Cobalticinium, benziltrimetylammonium and benzildimethylamine salts were employed as model compounds for the polymeric olygomethylene cobalticinium anion-exchanger, the strong base anion-exchange resin and the weak base anion-exchange resin, respectively. The distribution sequences in solvent extraction were essentially identical with the ion affinity series in anion-exchange. From these correlations, the selectivity coefficient for an anion was explained as the affinity of an anion to an ionogenic group with the use of an ion-pair concept. Some differences between ion-exchanges and solvent extractions were discussed.

In recent years, many attempts have been made to predict selectivity coefficients for ion-exchange systems. It has been thought that the activity coefficient in an ion-exchanger phase and the strain energy of the molecular network in an ion-exchange copolymer most seriously influence selectivities. The former was found to be dominant for ion-exchange resins[1,2] and the latter cannot be attributed to osmotic pressure but to the diffusion of network molecules because ion-exchangers are not bound by semipermeable membranes from the external solution. The strain energy effect seems to be difficult to estimate. This paper pays attention to the activity coefficient only.

The relation between the selectivity coefficient and the activity coefficient, or the evaluation of the latter from the former, has been studied by many workers.[3-6] However, the difference in activity coefficients for different anions has not been explained as affinities of adsorbed ion to ionogenic groups. According to thermodynamic considerations, a lower activity coefficient, or a higher selectivity coefficient, is interpreted as the higher sorbability to ion-exchangers. If the affinity of an anion to the same monomeric cation as the ionogenic group is similar to that in the corresponding exchanger, the salt whose cation is the ionogenic group and whose anion the counter ion may be suitable as a model compound for the ion-exchanger. The affinity should increase in organic solvents of low dielectric constant. From this point of view, cobalticinium (π-dicyclopentadienyl cobalt(III)), benziltrimethylammonium and benzildimethylamine salts were selected as model compounds for the polymeric pentamethylene cobalticinium anion-exchanger, the strong base anion-exchange resin and the weak base anion-exchange resin, respectively. Some interrelations between them were found.

Experimental

Preparation of Cobalticinium, Benziltrimethylammonium and Benzildimethylamine Salt Solutions. Cobalticinium picrate ($(C_5H_5)_2CoOC_6H_2(NO_2)_3$) was obtained by the method mentioned in a previous paper.[7] The desired form of the cobalticinium

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[1] G. E. Myers and G. E. Boyd, *J. Phys. Chem.*, **60**, 521 (1956).
[2] G. E. Boyd, S. Lindenbaum and G. E. Myers, *ibid.*, **65**, 557 (1961).
[3] F. Helfferich, "Ion-exchange," McGraw-Hill Book Co., Inc., New York, N. Y. (1962).
[4] H. P. Gregor, *J. Am. Chem. Soc.*, **70**, 1293 (1948); **73**, 642 (1951).
[5] H. P. Gregor, J. Belle and R. A. Marcus, *ibid.*, **77**, 2713 (1955).
[6] J. A. Marinsky, *J. Phys. Chem.*, **71**, 1572 (1967).

salt was obtained by passing the picrate solution through Dowex 1 X-8 columns. The concentration of the resulting solution was 0.0444 M. The benziltrimethylammonium salt ($C_6H_5CH_2N^+(CH_3)_3X^-$) was obtained commercially. It was converted to the perchlorate by adding 2 M sodium perchlorate solution, and the perchlorate was purified by recrystallization. The perchlorate solution was converted to the desired salt forms by the same procedure as for the cobalticinium salt. The concentration of the resulting solution was 0.0500 M. Benzildimethylamine ($C_6H_5CH_2N^+H(CH_3)_2X^-$) was obtained commercially. The procedure for preparing the solution was similar to that used for the benziltrimethylammonium salt solution. The concentration of the solution was 0.0500 M.

The Solvent Extraction of Various Ions and Their Determination in the Organic Solvent Layer. *n*-Butanol, *n*-pentanol, *n*-hexanol, chloroform and benzene were used as organic solvents (obtained commercially). An aqueous solution of the salt (10 m*l*) and 10 m*l* of the solvent were shaken together for 10 min at room temperature. The solvent layer was separated and the concentration of salts determined colorimetrically using 1 cm quartz cells and a spectrophotometer (Hitachi EPU-2A). The wavelength employed was 340 mμ for cobalticinium and 262 mμ for both benziltrimethylammonium and benzildimethylamine. Calibrations were made by dissolving a known amount of perchlorate or picrate in a known amount of each solvent saturated with water.

Adsorption spectra in the UV region were measured on a Shimadzu multipurpose recording spectrophotometer.

Calculation of the Degree of Distribution. The degree of distribution of an anion A^- (K_A) was calculated according to the equation

$$K_A = \frac{[R^+]_w[A^-]_w}{[RA]_r},$$

where $[RA]_r$, $[R^+]_w$ and $[A^-]_w$ are the concentrations of RA in the solvent layer and cation R^+ and anion A^- in the aqueous layer, respectively. $[R^+]_w$ was always equal to $[A^-]_w$ in this experiment.

Results and Discussion

According to Bjerrum's theory,[8] the probability of an ion-pair formation increases with increasing concentration. Accordingly, ion-pair formation in ion-exchangers might be quite possible since the density of counterion arround an ionogenic group is very high. Further, many thermodynamic data for univalent cation exchanges[9-12] show that enthalpies decrease when entropies decrease in systems of decreasing free energy. This fact appears to support the assumption of ion-pair formation. One of the most typical theories of an ion-exchange equilibrium introducing the ion-pair concept has been proposed by Gregor.[5] He introduced a dissociation constant for ion-pair formation between an ionogenic group and a counter ion in an exchanger phase. For the processes of ion-pair formation,

$$RA \rightleftharpoons R^+ + A^- \quad \text{and} \quad RB \rightleftharpoons R^+ + B^-$$

dissociation constants D_A and D_B are given by

$$D_A = \frac{[R^+][A^-]}{[RA]}, \quad D_B = \frac{[R^+][B^-]}{[RB]},$$

where R's refer to ionogenic groups, A^- and B^- to exchange anions and brackets to the molality of each species. Neglecting strain energy effects, the molality of unpaired ions in the exchanger phase is related to that of these ions in the external solution according to the Donnan equilibrium condition and one obtains the equation

$$\frac{[A^-]_r}{[B^-]_r} = \frac{[A^-]_w}{[B^-]_w}$$

Then, selectivity coefficients K_A^B are given by

$$K_A^B = \frac{[B]_r}{[A]_r} \cdot \frac{[A^-]_w}{[B^-]_w} = \frac{[B^-]_r + [RB]}{[A^-]_r + [RA]} \cdot \frac{[A^-]_w}{[B^-]_w},$$

where A or B refers to the total amount of the species in the exchanger phase, subscript r and w to the exchanger and external solution phase, respectively. Additional conditions are

$$[R^+] = [A^-]_r + [B^-]_r$$
$$[RA] + [RB] + [R^+] = 1$$
$$[A^-]_w + [B^-]_w = 1$$

Then K_A^B is obtained as a function of $[A]_r$ or $[B]_r$ by a combination of the following equations:

$$K_A^B = \frac{D_A[A^-]_w + (D_B - D_A)x[A^-]_w}{D_B[A^-]_w - (D_B - D_A)x[B^-]_w}$$

and

$$\frac{[B]_r}{[A]_r} = \frac{D_A[B^-]_w + (D_B - D_A)x[B^-]_w}{D_B[A^-]_w - (D_B - D_A)x[B^-]_w},$$

where

$$x = \frac{-D_A + \sqrt{D_A^2 + 4D_A[A^-]_w + \dfrac{4D_A^2[B^-]_w}{D_B}}}{2\left(1 + \dfrac{D_A[B^-]_w}{D_B[A^-]_w}\right)}$$

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[7] T. Ito and T. Kenjo, This Bulletin, **41**, 614 (1968).

[8] N. Bjerrum, *Kgl. Danske Selskab*, **7**, No. 9 (1926).

[9] O. D. Bonnen and L. L. Smith, *J. Phys. Chem.*, **61**, 1614 (1957).

[10] K. A. Kraus, R. J. Raridon and D. L. Holcomb, *J. Chromatog.*, **3**, 178 (1960).

[11] F. Vaslow and G. E. Boyd, *J. Phys. Chem.*, **70**, 2507 (1966).

[12] K. A. Kraus and R. J. Raridon, *ibid.*, **63**, 1901 (1959).

Figure 1 shows the selectivity coefficient-molality curves calculated from the above equation for various D_A and D_B values. The figure indicates that a larger selectivity coefficient for anion A^- than for anion B^- means a smaller dissociation constant for A^- than that for B^-.

Ion-pair formation between an ionogenic group and the counter-ion can be analogized to the Langmuir adsorption process; that is, the dissociation constant in an ion-exchange corresponds to the eqilibrium constant of the process

$$\begin{array}{l} \text{adsorbed} \\ \text{molecules in a} \\ \text{solid phase} \end{array} \rightleftharpoons \begin{array}{l} \text{free mole-} \\ \text{cules in a} \\ \text{gas phase} \end{array} + \text{vacant sites.}$$

Therefore, the dissociation constant can be understood as an equilibrium constant for the process

$$\text{paired ions} \rightleftharpoons \text{unpaired ions} + \begin{array}{l} \text{unpaired} \\ \text{ionogenic} \\ \text{groups.} \end{array}$$

This process can be compared to the distribution of the model compound between a solvent layer and an aqueous layer,

$$\begin{array}{l} \text{paired ions in} \\ \text{solvent layer}^{*1} \end{array} \rightleftharpoons \begin{array}{l} \text{cations in an} \\ \text{aqueous layer} \end{array} + \begin{array}{l} \text{anions in} \\ \text{an aqueous} \\ \text{layer} \end{array}$$

From these analogies for ion-pair formation between an ion-exchanger and an organic solvent phase, it can be assumed that some correlation exists between selectivity coefficient sequences against a common anion and distribution sequences in solvent extraction for corresponding model compounds.

Tables 1, 2 and 3 give the degree of distribution for cobalticinium, benziltrimethylammonium and benzildimethylamine, respectively. From a comparison of selectivity coefficients in ion-exchange with the degree of distribution in solvent extraction, it is found that they are related to each other in sequences of values, except for the position of BrO_3^- and ClO_4^-.

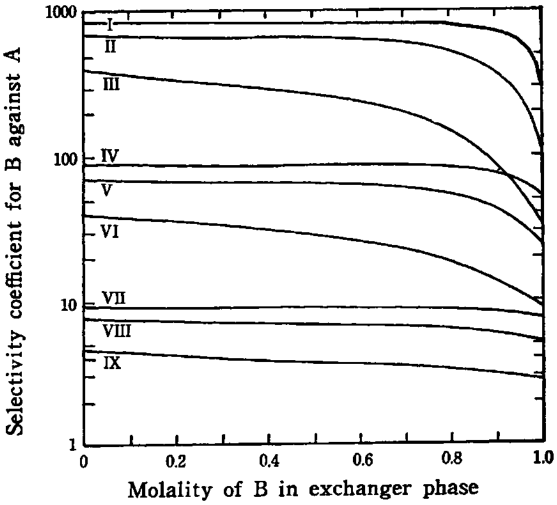

Fig. 1. Calculated curves for selectivity of anions A and B for the following sets of postulates;

I: $D_A=10^{-2}$ $D_B=10^{-5}$; II: $D_A=10^{-1}$ $D_B=10^{-4}$;
III: $D_A=1$ $D_B=10^{-3}$; IV: $D_A=10^{-2}$ $D_B=10^{-4}$;
V: $D_A=10^{-1}$ $D_B=10^{-3}$; VI: $D_A=1$ $D_B=10^{-2}$;
VII: $D_A=10^{-2}$ $D_B=10^{-3}$; VIII: $D_A=10^{-1}$ $D_B=10^{-2}$;
IX: $D_A=1$ $D_B=10^{-1}$

A possible difference between ion-exchange and solvent extraction is the effect of freedom of rotation. In the case that A is a monoatomic anion and B a polyatomic anion, the effect of freedom of rotation between A and B would be greater in ion-exchange than in solvent extraction; that is the effect promotes the dissociation of polyatomic anions from ionogenic groups in ion-exchange more readily than in solvent extractions, because ionogenic groups are fixed to one another while the corresponding cation is moving freely in solvents. However, the trend mentioned above was not found to be very remarkable in the experimental results; the affinity of the poly-

TABLE 1. DEGREE OF DISTRIBUTION FOR COBALTICINIUM SALTS IN VARIOUS SOLVENT SYSTEMS AND SELECTIVITY COEFFICIENTS (K_c) OF POLYMERIC PENTAMETHYLENE COBALTICINIUM ION-EXCHANGER (PPC)

	K_c of PPC[14]	Chloroform (M)	n-Butanol (M)	n-Pentanol (M)	n-Hexanol (M)	Benzene (M)
IO_3^-	0.202	4.53	0.651	7.90	28.3	5.35
Cl^-	1	3.36	0.363	5.20	20.0	42.3
BrO_3^-	1.25	3.27	0.419	6.04	20.2	9.79
Br^-	3.58	3.09	0.298	4.73	14.6	29.6
ClO_3^-	4.46	2.74	0.258	4.45	14.3	19.1
I^-	25.3	2.49	0.174	2.96	8.58	22.0
SCN^-	36.4	2.42	0.124	1.91	5.84	35.5
ClO_4^-	73.5	1.49	0.159	2.61	7.81	15.6

[*1] Almost all ions were found to form ion-pairs in a solvent witha very low dielectric constant.[13]

13) C. A. Kraus, *J. Phys. Chem.*, **60**, 129 (1956).

TABLE 2. DEGREE OF DISTRIBUTION FOR BENZILTRIMETHYLAMMONIUM SALTS IN VARIOUS SOLVENT SYSTEMS AND SELECTIVITY COEFFICIENTS (K_c) OF DOWEX 1X-8 (D1 X-8)

	K_c of D1 X-8[14]	Chloroform* (M)	*n*-Butanol (M)	*n*-Pentanol (M)	*n*-Hexanol* (M)
IO_3^-	0.198		0.648	7.34	
Cl^-	1		0.243	1.68	3.35
BrO_3^-	0.918		0.277	2.26	4.28
Br^-	3.14		0.137	0.856	1.71
ClO_3^-	3.35	96.0	0.0993	0.759	1.48
I^-	5.04	0.762	0.0439	0.243	0.137
SCN^-	6.89	8.35	0.0273	0.108	0.436
ClO_4^-	56.3	2.32	0.0311	0.166	0.606

* The salts of IO_3^-, Cl^-, BrO_3^-, and Br^- for chloroform and IO_3^- for *n*-butanol could not be detected in the solvent layer.

TABLE 3. DEGREE OF DISTRIBUTION FOR BENZILDIMETHYLAMMONIUM SALTS IN VARIOUS SOLVENT SYSTEMS AND SELECTIVITY COEFFICIENTS (K_c) OF AMBERLITE IR-45 (IR-45)

	K_c of IR-45[14]	Chloroform (M)	*n*-Butanol (M)	*n*-Pentanol (M)	*n*-Hexanol (M)
IO_3^-	0.528	21.6	0.446	3.88	2.89
Cl^-	1	19.0	0.175	1.01	1.75
BrO_3^-	1.21	10.6	0.190	1.35	2.19
Br^-	2.15	6.89	0.107	0.462	1.05
ClO_3^-	2.43	4.48	0.0850	0.397	0.942
I^-	2.38	0.622	0.0366	0.129	
SCN^-	3.61	0.868	0.0225	0.0579	0.257
ClO_4^-	5.46	4.07	0.0263	0.0998	0.433

atomic anion BrO_3^- was greater in the system of the cobalticinium type anion-exchanger and Amberlite IR-45 than in the corresponding solvent extraction systems. Accordingly, the effect of rotation of anions might be not very important.

Differences in interionic interactions between ion-exchange and solvent extraction can be mainly attributed to the difference in solvents. Possibly because of the effect of hydration, affinities of the counter ion to an ionogenic group in an aqueous layer are weaker than those of the same anion to the corresponding cation in solvents. The greater amount of water a solvent contains, the more similar to ion-exchange the solvent extraction system may be. In the system of benzene for cobalticinium halogenate (Table 1), the sequence is opposite to the affinity series for ion-exchange, and consistent with the order of solubilities.[14] This behaviour, perhaps, can be ascribed to the extremely low water content in the benzene layer. Because of the much lower dielectric constant of an organic solvent compared with that of water, an anion could approach a cation more closely in organic solvents than in water. Therefore, factors which are effective in a very short range *e.g.*, polarizability are more effective in an organic solvent than in water. Table 4 gives absorption peaks of UV spectra for benziltrimethylammonium in the *n*-butanol layer. It indicates that the absorption peak shifts to longer wavelength with increasing affinities. This result suggests some relation between the polarization of charge on ammonium cations and the interactive force between a cation and an anion.

TABLE 4. THE WAVELENGTH OF ABSORPTION PEAKS FOR BENZILTRIMETHYLAMMONIUM SALTS IN *n*-BUTANOL LAYER

	Wavelength (mμ)		Wavelength (mμ)
IO_3^-	215.3	ClO_3^-	219.8
Cl^-	218.4	SCN^-	226.0
BrO_3^-	218.6	ClO_4^-	220.2
Br^-	219.1		

Thus, these systems which consist of solvent extractions and model compounds have a possibility of being adequate models for ion-exchange although some differences can be pointed out.

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14) T. Ito and T. Kenjo, This Bulletin, **41**, 1600 (1968).