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Studies of the Ion-pairing of Hexylate and Picrate Ions with Alkali Metal Ions by Capillary Analysis

Kazuaki SANO, Michio SAKUMA,[*1] Syoji MOTOMIZU,
Tadashi IWACHIDO* and Kyoji TÔEI

Department of Chemistry, Faculty of Science, Okayama University, Tsushima, Okayama
* *College of Liberal Arts, Okayama University, Tsushima, Okayama*

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The hexyl (Dipicrylamine) anion, hexylate, and picrate form weak ion-pairs with alkali metal cations in an aqueous solution. The composition and the association constants of the ion-pairs are determined by capillary analysis based on the difference in the adsorbability of the anions and of the ion-pairs on a filter paper. A new constant temperature-humidity apparatus is devised, and by means of it the analysis is successfully carried out. The compositions of the cation and the anion in the ion-pairs formed are 1 : 1, in either case; the association constants of the ion-pairs for Li, Na, K, Rb, and Cs cations are about 10^2, and they tend gradually to decrease with the ionic radii.

Interactions in electrolyte solutions can largely be explained by assuming that electrolytes completely dissociate into rigid, spherically-symmetrical ions and that the resulting ions exert long-range

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[*1] Present address: Kohkoku Chemical Industry Co., Ltd., Nishimiya-cho, Ashikaga-shi.

electrostatic forces on the other ions through the medium of the dielectric constant, ε. The interaction increases with the decrease in the distance of charge separation; that is, a small cation and a small anion may have enough attractive force compared with the thermal energy. Bjerrum[1] calculated the critical distance to be 3.57 Å for 1 : 1 electrolytes in water at 25°C and regarded ions which can approach within the distance as a virtually new entity, an ion-pair, of a sufficient stability. The association equilibrium between free ions and ion-pairs is expressed by means of K, and the ion-pair species is treated as neutral molecules of unit activity, if the electrolyte is symmetrical. So long as only the Coulomb force is assumed between the adjacent ions, ion-pairing would be at minimum in the salts of alkali metals with large, univalent anions. However, the reverse is true in the present case, so some other forces must be considered.

Several methods have been adopted to determine the association constant, K,——for example, conductivity[2] and solubility[3] measurements, polarography,[4] and spectrometric methods.[5] In any case, it is important to find a suitable way to detect a certain difference in physical properties between free ions and an ion-pair. In the present case, the method of capillary analysis was found to be successful in ascertaining the significant difference between them.

The so-called "capillary analysis" is a kind of paper chromatography. One end of a paper strip is dipped into the solution to be tested (which is in striking contrast to the usual paper chromatography). When the system is saturated as much as possible by water vapor in order to avoid undesirable vaporization during the development, the ratio of the movements of the solute and the solvent can be related to the association constant with the aid of the following assumptions: 1) the paper is regarded as being divided into successive layers of such a thickness that the solution issuing from each layer is in equilibrium with the mean concentration of the solute in the stationary phase throughout the layer; 2) the diffusion from one plate to another is negligible, and 3) the partition coefficient of the solute between two phases is independent of its concentration.

The purpose of the present paper is to show that, contrary to our expectations judging from the Bjerrum theory, there is a considerable amount of ion-pairing between alkali metal cations and large organic anions, such as picrate or hexylate, in an aqueous solution, that the largest cation, Cs$^+$, forms the most stable ion-pair with such anions, and that the method of capillary analysis is useful in determining the association constant of such ion-pairs.

Theoretical

The theory of capillary analysis was first proposed by Hayama[6] based on analogy with the plate theory of liquid-partition chromatography; Hayama applied it to the complex formation between dyes and non-ionic surfactants.

Hexylate and picrate anions form precipitates with heavy alkali metal cations in an aqueous solution; hence, it may be assumed that hexylate and picrate associate with alkali metal ions to form ion-pairs even in a dilute solution and that each species has different adsorbabilities on cellulose. In such a solution, the associated ion-pairs are in equilibrium with the free ions; also, each species is equilibrate with those in the stationary phase, as is shown in Fig. 1. and Eqs. (1) to (4).

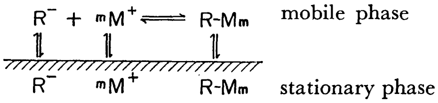

Fig. 1. Schematic representation of the behavior of hexylate and picrate, alkali metal ion and the ion-pair formed in an aqueous solution against a filter paper.

$$K = \frac{[\text{R-M}_m]_\text{a}}{[\text{R}^-]_\text{a}[\text{M}^+]_\text{a}{}^m} \tag{1}$$

(K: Association constant)

$$K_1 = \frac{[\text{R}^-]_\text{s}}{[\text{R}^-]_\text{a}} \tag{2}$$

(K_1: Distribution coefficient of the reagent anion)

$$K_2 = \frac{[\text{R-M}_m]_\text{s}}{[\text{R-M}_m]_\text{a}} \tag{3}$$

(K_2: Distribution coefficient of the ion-pair)

$$K_3 = \frac{[\text{R}^-]_\text{s} + [\text{R-M}_m]_\text{s}}{[\text{R}^-]_\text{a} + [\text{R-M}_m]_\text{a}} \tag{4}$$

(K_3: Distribution coefficient of the total reagent)

where R$^-$ denotes the reagent anions; M$^+$ and R-M$_m$, the alkali metal cations and ion-pairs; brackets, the concentration of each species, and the suffixes a and s, an aqueous and a stationary phase respectively.

From Eqs. (1), (2), (3), and (4), we obtain:

$$K_3 = \frac{K_1 + KK_2[\text{M}^+]_\text{a}{}^m}{1 + K[\text{M}^+]_\text{a}{}^m} \tag{5}$$

As the concentration of the reagent ions is much

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[1] N. Bjerrum, *K. Danske Vidensk. Selsk.* (*Math. fys. Medd.*) **7**, 1 (1926).

[2] T. Shedlovsky, *J. Franklin Inst.*, **225**, 739 (1938).

[3] H. E. Blayden and C. W. Davies, *J. Chem. Soc.*, **1930**, 949.

[4] E. Gelles and G. H. Nancollas, *ibid.*, **1956**, 4847.

[5] V. S. K. Nair, *Trans. Faraday Soc.*, **57**, 1988 (1961).

[6] N. Hayama, *Nippon Kagaku Zasshi*, **84**, 943 (1963).

lower than that of alkali metal ions, the equilibrium concentration of alkali metal cations, $[\mathrm{M}^+]_\mathrm{a}$, may be approximately replaced by the total concentration, neglecting the formation of the ion-pair.

On the other hand, according to the equation of capillary analysis, the distribution coefficient, K_3, is related to R_h by the following equation:

$$\alpha K_3 = \frac{1-\ln 2}{R_h - \ln(1+R_h)} - 1 \tag{6}$$

where α is the ratio of volumes of the stationary phase (cellulose) and the mobile phase (solution), and R_h, the ratio of the movement of the solute and the solvent.

By combining Eq. (5) with Eq. (6), we obtain Eq. (7), in which R_h is related to the concentration of free alkali metal ions.

$$\alpha K_3 = \frac{\alpha K_1 + \alpha K K_2[\mathrm{M}^+]_\mathrm{a}{}^m}{1+K[\mathrm{M}^+]_\mathrm{a}{}^m} = \frac{1-\ln 2}{R_h - \ln(1+R)} - 1 \tag{7}$$

When alkali metal cations are absent in the solution to be tested, $[\mathrm{M}^+]_\mathrm{a}=0$, we denote the values of R_h by $R_h{}^0$:

$$\alpha K_1 = \frac{1-\ln 2}{R_h{}^0 - \ln(1+R_h{}^0)} - 1 \tag{8}$$

On the contrary, when these cations are present in a large excess, and when most of the reagent anions associate completely to form ion-pairs, R_h is denoted by $R_h{}^\infty$. Then we obtain:

$$\alpha K_2 = \frac{1-\ln 2}{R_h{}^\infty - \ln(1+R_h{}^\infty)} - 1 \tag{9}$$

By substituting Eqs. (8) and (9) into Eq. (7), we obtain the following expression:

$$\frac{[\mathrm{R\text{-}M}_m]_\mathrm{a}}{[\mathrm{R}^-]_\mathrm{a}} = K[\mathrm{M}^+]_\mathrm{a}{}^m = \frac{\dfrac{1}{R_h{}^0 - \ln(1+R_h{}^0)} - \dfrac{1}{R_h - \ln(1+R_h)}}{\dfrac{1}{R_h - \ln(1+R_h)} - \dfrac{1}{R_h{}^\infty - \ln(1+R_h{}^\infty)}} \tag{10}$$

Equation (10) shows that the logarithmic plot of $[\mathrm{M}^+]_\mathrm{a}$ against the right-hand side of the equation allows us to estimate the K and m values. For the first approximation, $[\mathrm{M}^+]_\mathrm{a}$ was made equal to the initial concentration of the alkali metal cations; then K was determined, and the $[\mathrm{M}^+]_\mathrm{a}$ value calculated from the K value was used to determine a more accurate K value, after which the procedure was continued until a constant K value was obtained. Only for the values of picrate, activity correction was made simultaneously.

Experimental

Reagents. Hexyl (2,2′,4,4′,6,6′-hexanitrodiphenylamine) was prepared by treating an aqueous solution of a commercial Hexyl calcium (Mitsubishi Chemical Industries, Ltd.) with dil. hydrochloric acid, by filtering the hexyl thus formed, and by then purifying it by recrystallization from acetic acid.

The hexyl was dissolved by warming it in a lithium carbonate solution (0.006%); reagent-grade picric acid was then dissolved in water to give 2.62×10^{-4}M and 2.000×10^{-3}M solutions respectively.

Apparatus and Procedures. The ordinary procedure of capillary analysis is not siutable for the present purpose because of the unavoidable vaporization of the solvent during the development, as has previous been described. To avoid such trouble, a vessel of a constant humidity and temperature was devised (Fig. 2). A developing box was made of wood lined with a polyvinylchloride sheet and with a wet cloth on it. A gentle stream of water vapor introduced into the box from a saturation tower moistened the paper strips hung in it. The humidity was monitored by an Assmann aspiration psychrometer. A tower was filled with small pieces of polyvinylchloride pipes (2 cm in length and 1.5 cm in diameter). The water from a water bath was spreaded at the top of the tower, and the air in the box was blown upwards from the bottom through a column. Thus the humidity and the temperature in the box were kept at a constant values of 95 per cent and 25°C respectively. The room temperature was also controlled at 25°C.

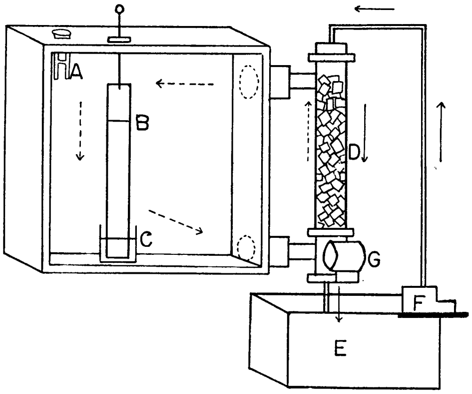

Fig. 2. Schematic representation of the apparatus. A: Assmann aspiration psychrometer, B: Filter paper (No. 50; 2×40 cm^2, Toyo Roshi Kaisha, Ltd.), C: Sample solution, D: Water vapor saturating tower, E: Water bath (25°C), F: Pump, G: Air blower

Some paper strips previously moistened in another vessel for 24 hr were hung upon the hooks of the supporting rods at the upper wall of the box. Under each strip, 50 m*l* of 1.31×10^{-4}M hexyl or 1.00×10^{-3}M picric acid solutions containing alkali salts in various amounts (10^{-4} to 10^{-1} g-ion/*l* for hexyl solutions or 10^{-3} to 10^{-1} g-ion/*l* for picric acid solutions) were placed.

On dipping the paper strips into the test solution, it was always necessary to adjust exactly the solution level to the mark on the paper by handling the supporting rods. When the solvent fronts came near the upper ends of the strips, the front panel of the box made of double-walled transparent acrylate resin plate was removed and the detached strips were laid on a large sheet of filter paper and dried quickly by using a hot blower. Then the fronts of the solvent and of the solute were marked. About two hours were requied for a single run.

Results and Discussion

The relationship between the R_h value and the free alkali metal ion concentration, $[\mathrm{M}^+]_a$, is shown in Figs. 3a and 3b. The R_h^0 values are obtained by extrapolating the curves to an infinite dilution, $[\mathrm{M}^+]_a=0$. To determine R_h^∞ values, R_h is plotted against the reciprocal of the alkali metal-ion concentration; the curves obtained are then extrapolated as in Figs. 4a and 4b.

The right-hand side of Eq. (10), evaluated in such a way, was plotted against the free alkali metal-ion concentration; these plots gave straight lines, as Figs. 5a and 5b show. The slopes of the five lines obtained are approximately unity; the $\log K$ values obtained by extrapolating these lines to $\log[\mathrm{M}^+]_a=0$ are about 2 for hexylates, are slightly larger for picrates, and slightly increase in the order of Li, Na, K, Rb, and Cs in either case, as is shown in Table 1. The agreement between the results of the capillary analysis and the solvent

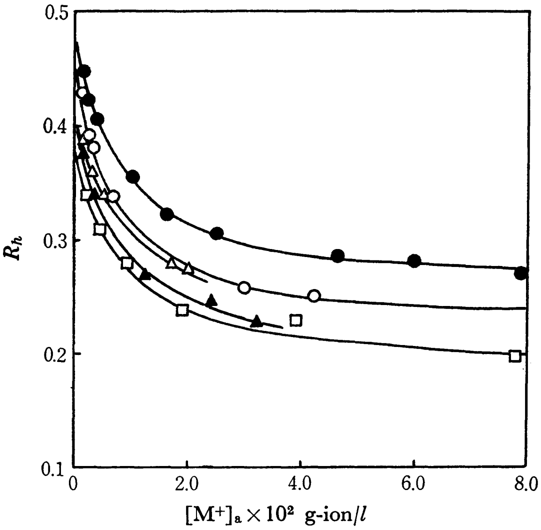

Fig. 3a. Relation between R_h and alkali metal ion concentration.
● Li, ○ Na, □ K, △ Rb, ▲ Cs-hexylate

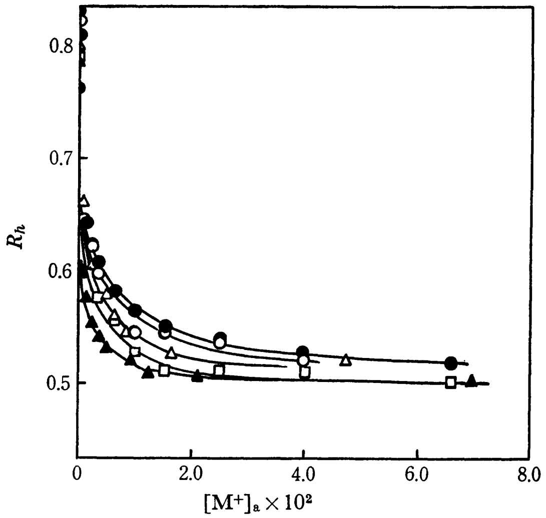

Fig. 3b. M-picrate.

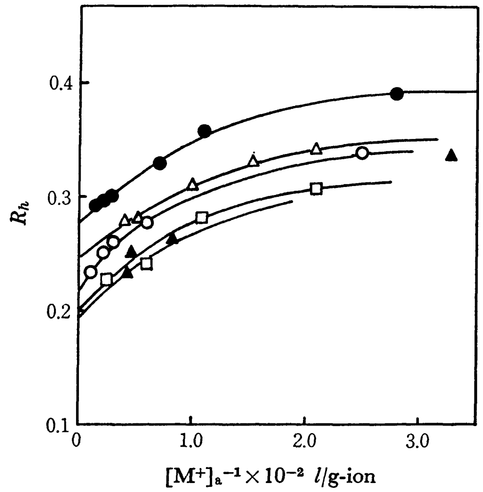

Fig. 4a. Relation between R_h and reciprocal of alkali metal ion concentration.
● Li, ○ Na, □ K, △ Rb, ▲ Cs-hexylate

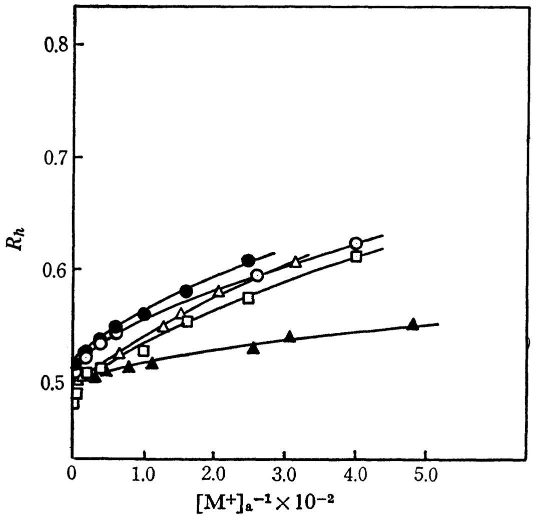

Fig. 4b. M-picrate.

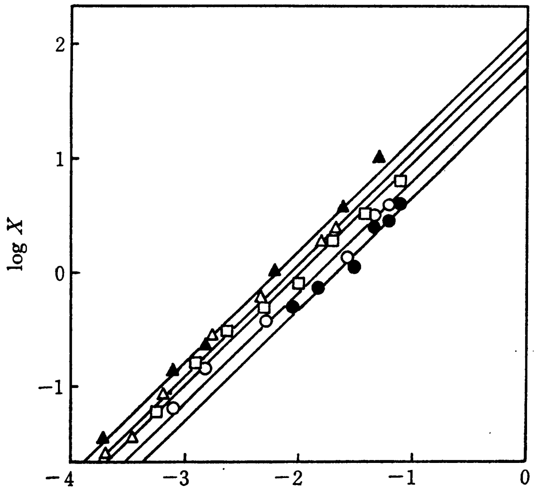

Fig. 5a. Interaction between Hexyl and alkali metals.

● Li, ○ Na, □ K, △ Rb, ▲ Cs-hexylate

$$X=\frac{1/[R_h^0-\ln(1+R_h^0)]-1/[R_h-\ln(1+R_h)]}{1/[R_h-\ln(1+R_h)]-1/[R_h^\infty-\ln(1+R_h^\infty)]}$$

extraction previously reported[7] is fairly good.

The log K value for sodium hexylate was also obtained by using a pNa-meter (Horiba Instruments, Inc., Type N-5 Sodium Ion Indicator). The concentration of free sodium ions was determined with a pair of electrodes, *i. e.*, a glass electrode especially sensitive to sodium ions and a reference electrode of the double-junction type, with a sodium chloride solution as the liquid junction to prevent the direct contact of the potassium ions in the inner solution of the electrode with the hexylate anions, and thus precipitating potassium hexylate at the junction.

The instrument was calibrated with 0.1 and 0.001 M standard sodium chloride solutions. Consequently, the pNa-meter directly measures the sodium-ion concentration in terms of moles per liter instead of activity.

Table 1. Combination ratio and association constant

	Alkali metal-ion	Li^+	Na^+	K^+	Rb^+	Cs^+
Hexylates	Combination ratio	0.95	0.95	0.98	1.0	1.0
	log$K$	1.7	1.9	1.9	2.0	2.1
Picrates*	Combination ratio	0.88	0.90	0.98	0.98	1.0
	log$K$	2.2	2.3	2.4	2.5	2.7

* Correcteed by activity coefficient.

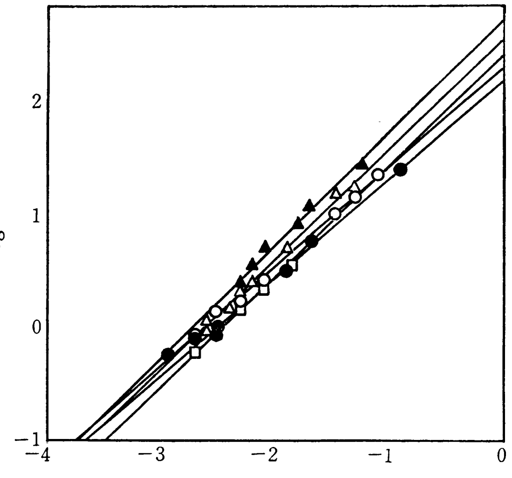

Fig. 5b. M-picrate.

Two sodium solutions, one with and one without hexyl, were prepared (Table 2); a certain amount of sodium hydroxide was added equally in order to avoid the hydrolysis of the hexylate anion. A few pairs of such solutions, differing only in total sodium concentration, were also prepared, the concentration of sodium hydroxide being kept unchanged.

The free sodium ion in each pair was measured, and the two were then compared with each other. The solution with hexyl is less alkaline than that without hexyl because of the neutralization of the hydroxide ion with hexyl. In order to estimate the effect of the hydroxide ion on the glass electrode, the solution without hexyl was neutralized with acetic acid just as with hexyl, and then the free sodium ion was measured. The pNa values thus obtained are in good agreement with those calculated on the assumption that the acetate ion does not form an ion-pair with the sodium ion.

From these findings, it can be concluded that, in the solutions without hexyl, the differences in pNa between the measured and the calculated values, Δ, are attributable to the large amount of hydroxide ions present, and that, in the solutions with hexyl, the sodium ion is determined correctly and the increases in pNa can be considered as a measure of the extent of ion-pairing.

The equilibrium in the solution with hexyl can be written as follows:

$$\text{Hexyl}^- + \text{Na}^+ \rightleftharpoons \text{Hexyl-Na}$$

$$K=\frac{[\text{Hexyl-Na}]}{[\text{Hexyl}^-][\text{Na}^+]} \tag{11}$$

If the total concentrations of hexyl and the sodium ion are denoted by C_R and C_{Na} respectively, we obtain:

$$C_R=[\text{Hexyl-Na}]+[\text{Hexyl}^-]$$
$$C_{Na}=[\text{Hexyl-Na}]+[\text{Na}^+] \tag{12}$$

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[7] S. Motomizu, K. Tôei and T. Iwachido, This Bulletin, **42**, 1006 (1969).

TABLE 2. DETERMININATION OF $\log K_2$ BY USING pNa-meter

Reagent concn., 10^2C_R (M)	Sodium concn. 10^2C_{Na} (M)		pNa			log *K*
	NaOH*	NaCl	measured	calcd.	Δ	
0	2.02	0	1.609	1.695	0.086	
2.0	2.02	0	1.908			1.72±0.02
0	2.02	0.10	1.584	1.674	0.090	
2.0	2.02	0.10	1.875			1.69±0.04
0	2.02	1.00	1.428	1.520	0.092	
2.0	2.02	1.00	1.686			1.66±0.05
0	2.02	10.00	0.896	0.920	0.034	
2.0	2.02	10.00	0.979			1.46±0.36
0	4.04	0	1.250	1.394	0.144	
4.0	4.04	0	1.699			1.72±0.01

* Sodium content was checked by flamephtometry.

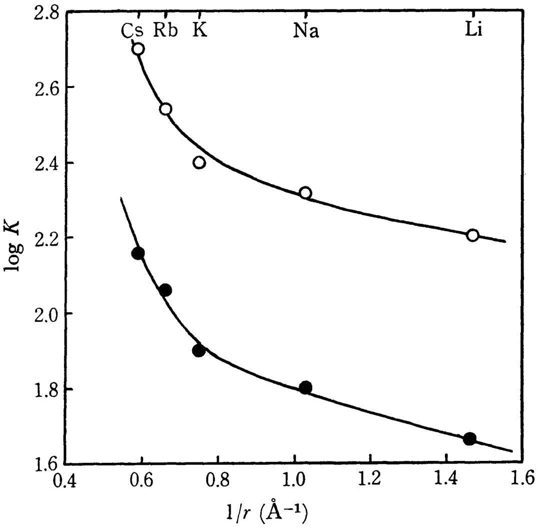

Fig. 6. log *K*'s of alkali metal salts.
○ Picrate, ● Hexylate

By substituting Eq. (12) into Eq. (11), we obtain:

$$K=\frac{C_{Na}-[Na^+]}{(C_R-C_{Na}+[Na^+])[Na^+]} \tag{13}$$

Thus, an association constant can be calculated from Eq. (13). The data necessary for the above calculation are given in Table 2, along with the log *K* values. The log *K* values thus obtained are very close to those obtained by capillary analysis.

Figure 6 shows the log *K* data for hexylates and picrates, plotted against the reciprocal of the radii of unhydrated cations. The curves thus obtained have negative slopes, unlike the common pattern of ion-pairing; that is, the cesium ion in the aqueous solution must be considered to be the smallest among the alkali metal cations as far as only the electrostatic force is concerned. In the ion-pairing of this type, it may be thought that the hydration of the cation is a predominant factor; *i. e.*, adjacent water dipoles rather than the hexylate or picrate ion are strongly affected by the field of the cation, and it is difficult for the hydration shell of the cation to be penetrated by such anions. The formation of the solvent-separated ion-pair is supported by the fact[7] that, with hexyl salts in dry nitrobenzene, lithium associates more firmly than cesium, while in nitrobenzene saturated with water the extent of ion-pairing decreases and by the fact that water is co-extracted with alkali metals into nitrobenzene.

The order among *K* values may be explained by the hydration, but it is difficult to explain these large values only in terms of the long-range, electrostatic force between adjacent ions; therefore, these large values lead us to suspect other forces, for example, the formation of a chemical bond, the contribution of the Van der Waals force, and the role of water-structure for the ion-pairing. It is of much interest to consider the last possibility, suggested by Diamond.[8] Considerations of these possibilities will, however, be described elsewhere; the present discussion will be confined to pointing out the similarity in ion-pairing between some oxy-acid anions and picrate or hexylate.

Some oxy-acid anions such as iodates[9] and thiosulfates[10] are known to associate with cations of the noble-gas configuration to form an ion-pair of this type; these anions have some common features with hexylate or picrate—for example, every ligand is large and has many ionic resonance forms, so that the negative charges on the ligands can be distributed over all the ligands.

The authors wish to thank Dr. Naomi Hayama for many helpful discussions and suggestions during this work.

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[8] R. M. Diamond, *J. Phys. Chem.*, **67**, 2513 (1963).

[9] W. C. Wise and C. W. Davies, *J. Chem. Soc.*, **1938**, 273.

[10] T. D. Denny and C. B. Monk, *Trans. Faraday Soc.*, **47**, 992 (1951).