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Studies of the Interaction between the Hexyl Anion and Alkali Metal Ions

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The Hexyl(2,4,6,2′,4′,6′-hexanitrodiphenylamine) anion forms ion-pairs with alkali metal cations to some extent in an aqueous solution. The association constants of these ion-pairs were determined both in nitrobenzene by conductivity measurements and in water by the solvent extraction method. The association constants in nitrobenzene (K_o^{MR}) decrease in the following order: $Li>Na>K>Rb>Cs$. The plot of log K_o^{MR} against the ionic potential of the alkali metal ions was found to be linear. In nitrobenzene saturated with water, however, the constants vary from 2 to 4. In water the asscoiation constants (K_a^{MR}) vary from about 10 to 400, and the value increases as follows: $Li<Na<K<Rb$ ($<Cs$). A plot of log K_a^{MR} against the reciprocal of the effective diameter of the hydrated alkali metal ions was found to be linear.

The extraction of alkali metal ions with the Hexyl anion into nitrobenzene has been reported by several authors.[1,2] The mechanism of the extraction is very attractive to us, because many alkali metal salts are well known to be very soluble in water but not in ordinary organic solvents immiscible with water. Generally alkali metal salts, such as chlorides and nitrates, are completely dissociated in an aqueous solution. However, potassium, rubidium, or cesium ions with larger radii than those of other cations, form a precipitate with such a large and symmetric anion as the perchlorate, tetraphenylborate, or Hexyl anion, and this precipitate is occasionally extracted into an organic solvent immiscible with water. This fact implies that the alkali metal ions associate to some extent with a large anion in an aqueous solution to form ion-pairs which can be extracted into nitrobenzene, and that such salts as alkali metal tetraphenylborate or Hexylate would be dissociated in nitrobenzene. In the present paper, the dissociation constants of the Hexyl salts in nitrobenzene were measured by electric conductance measurements. The constants in water were determined by the solvent extraction method.

Experimental

Reagents. Hexyl salt with an alkali metal ion was prepared by dissolving Hexyl into an aqueous solution of an equivalent amount of each alkali metal hydroxide or carbonate. The resulting precipitates were filtered and recrystallized two or three times from ethanol or acetone. The salts were dried at 50°C for 3—5 hr under a pressure of less than 10 mmHg.

The nitrobenzene for the conductivity measurements was prepared by distilling special-grade nitrobenzene which had been dried over anhydrous sodium sulfate. The fraction was collected at 75°C under a pressure of 5 mmHg and was stored in an ampoule to protect it from moisture. The nitrobenzene thus obtained had a specific conductance of $3—5\times10^{-9}$. This value is, however, satisfactory enough for the present purposes.

Potassium chloride for calibrating the conductance cell was purified by recrystallizing it from distilled water and was dried at 45°C in an electric furnace for three hours.

All the other chemicals used were of an analytical reagent grade and were used without further purification.

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1) M. Kyrs, *Collection Czechoslov. Chem. Commun.*, **27**, 2380 (1962).

2) T. Iwachido and K. Tôei, This Bulletin, **37**, 1276 (1964).

Electric Conductance Measurements. The electric conductivity of the nitrobenzene solution was determined by the use of a conductometer, CM-1DB, from Toa Electronics Ltd. Measurements were made in a jacketted vessel equipped with platinized platinum electrodes, a thermometer, and a microburet. The jacketted vessel was maintained at 25°C by circulating water from a constant-temperature bath. To a known amount of pure nitrobenzene in the vessel, small quantities of a concentrated nitrobenzene solution of these salts were introduced successively from the microburet.

Extraction Procedure. Twenty milliliters of an aqueous solution of the alkali metal ion (the pH being adjusted to about 11 with each alkali metal hydroxide or carbonate) was shaken moderately with 20 m*l* of a nitrobenzene solution containing each Hexyl salt for about thirty minutes. After this mixture had been allowed to stand for one or two hours, the organic and the aqueous layers were separated and the Hexyl salt in each phase was determined spectrophotometrically by using a Hitachi-Perkin Elmer Spectrophotometer, Model 139. The final pH of the aqueous phase was 10—11.

All the procedures were made in a constant-temperature room (25±1°C).

Calculations

Association Constants of Hexyl Salt in Nitrobenzene. In non-aqueous systems, where the dielectric constant of the solvent is about 40 or less, to evaluate the limiting conductance, Λ_∞, and the dissociation constant, K_S, from the conductance data, Shedlovsky[3] proposed this equation:

$$\frac{1}{\Lambda S}=\frac{1}{\Lambda_\infty}+\frac{C\Lambda Sf^2}{K_S\Lambda_\infty{}^2} \tag{1}$$

where C is the analytical concentration of 1-1 electrolytes, f is the activity coefficient, $S\equiv\left(\frac{z}{2}+\sqrt{1+\left(\frac{z}{2}\right)^2}\right)^2$, and z is defined as:

$$z=\alpha\sqrt{C\Lambda}/\Lambda_\infty{}^{3/2} \tag{2}$$

where α is the Onsager coefficient.

From Eq. (1), $1/\Lambda S$ is found to be linear against $C\Lambda Sf^2$ at low concentrations, and Λ_∞ and K_S are obtained from the intercept and the slope.

Hexyl salts are associated in nitrobenzene as follows:

$$M^+ + R^- \overset{K_o{}^{MR}}{\rightleftharpoons} MR$$

The association constant in nitrobenzene, $K_o{}^{MR}$, is written as:

$$K_o{}^{MR}=\frac{[MR]_o}{[M^+]_o[R^-]_of_o{}^2}\left(=\frac{1}{K_S}\right) \tag{3}$$

where the subscript O refers to the organic phase where $[M^+]$, $[R^-]$, and $[MR]$ are the concentrations of the alkali metal ions, the Hexyl anion, and the ion-pairs respectively.

Association Constants of Hexyl Salts in Water. The data of the solvent extraction of Hexyl salts were treated in the following way. Consider the association reaction:

$$M^+ + R^- \overset{K_a{}^{MR}}{\rightleftharpoons} MR$$

where M^+ represents an alkali metal ion, R^-, a Hexyl anion, and MR, an ion-pair. The association constant of the above equilibrium is:

$$K_a{}^{MR}=\frac{[MR]_a}{[M^+]_a[R^-]_af_a{}^2} \tag{4}$$

Where [ ] indicates the concentration of the substance indicated, where the subscript a refers to the aqueous phase, and where f_a is the activity coefficient.

Besides, at a distribution equilibrium of the two phases, the partition coefficient of the ion-pair MR, D_{MR}, is:

$$D_{MR}=\frac{[MR]_o}{[MR]_a} \tag{5}$$

The distribution ratio of the Hexyl salt, q_R, is written as:

$$q_R\equiv\frac{C_o{}^R}{C_a{}^R}=\frac{[MR]_o+[R^-]_o}{[MR]_a+[R^-]_a} \tag{6}$$

where $C_o{}^R$ and $C_a{}^R$ represent the total concentrations of the Hexyl salt in the organic and the aqueous phases respectively.

The combination of Eqs. (3), (4), (5) and (6) leads to Eq. (7):

$$\frac{Y}{q_R}=\frac{1}{D_{MR}}+\frac{1}{D_{MR}\cdot K_a{}^{MR}\cdot f_a{}^2[M^+]_a} \tag{7}$$

where:

$$Y\equiv\{0.5+(0.25+C_o{}^RK_o{}^{MR}f_o{}^2)^{1/2}\}/C_o{}^RK_o{}^{MR}f_o{}^2+1$$

From Eq. (7), a plot of Y/q_R against $(f_a{}^2[M^+]_a)^{-1}$ should give a straight line and from the intercept and the slope D_{MR} and $K_a{}^{MR}$ are obtained.

Results and Discussion

Association Constants of Hexyl Salts in Nitrobenzene. The association constants, $K_o{}^{MR}$, were calculated from Eq. (1). The starting value of Λ_∞ was determined by the extrapolation of a plot of Λ against $C^{1/2}$. The Λ_∞ was then inserted into Eq. (2), and S and f were calculated. From a plot of $1/\Lambda S$ *vs.* $C\Lambda Sf^2$, Λ_∞ and K_S were obtained. The above-mentioned process was repeated (usually three or four times) until a plot of $1/\Lambda S$ against $C\Lambda Sf^2$ showed linearity. In Figs. 1 and 2, the equivalent conductances are plotted against the square root of C. In these figures the Λ values at $C^{1/2}=0$ are the calculated Λ_∞ values. From the Λ-$C^{1/2}$ curves, it is obvious that in nitrobenzene, Hexyl salts except Hexyl-Li are very strong electrolytes and that in nitrobenzene almost saturated with water (0.14M) even Hexyl-Li behaves like a very strong electrolyte. Figures 3 and 4 show the

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

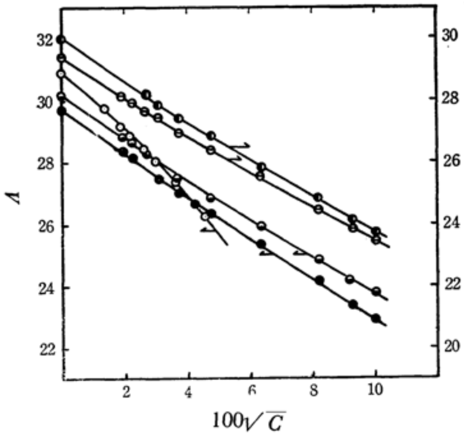

Fig. 1. The Λ-$\sqrt{C}$ curves of Hexyl salts in nitrobenzene.
○ Hexyl-Li, ◐ Hexyl-Rb, ● Hexyl-Na,
⊖ Hexyl-Cs, ◒ Hexyl-K

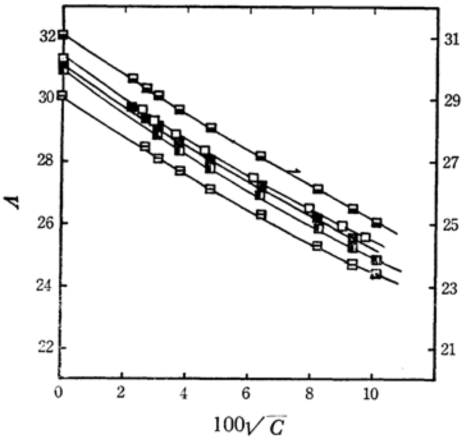

Fig. 2. The Λ-$\sqrt{C}$ curves of Hexyl salts in nitrobenzene saturated with water.
□ Hexyl-Li, ◧ Hexyl-Rb, ■ Hexyl-Na,
⊟ Hexyl-Cs, ⬓ Hexyl-K

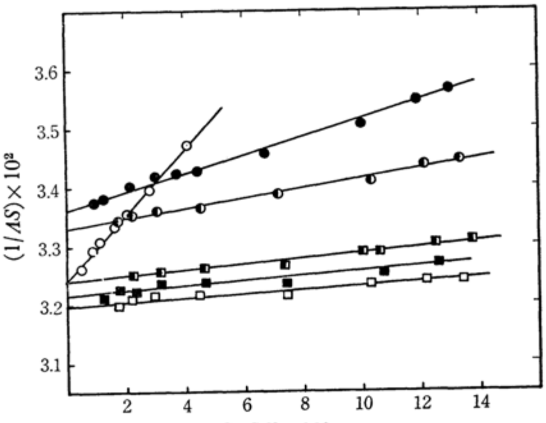

Fig. 3. Shedlovsky plot for Hexyl salts.
The symbols used are the same as those in Figs. 1 and 2.

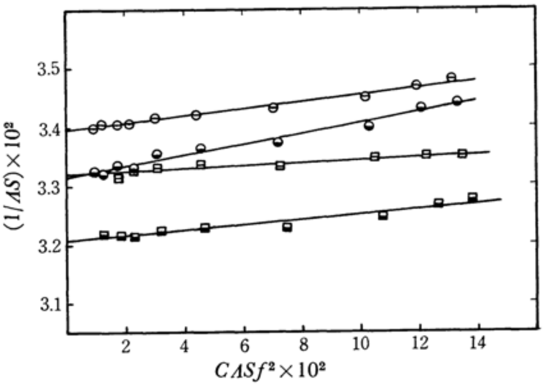

Fig. 4. Shedlovsky plot for Hexyl salts in nitrobenzene saturated with water.
The symbols used are the same as those in Figs. 1 and 2.

plots of $1/\Lambda S$ *vs.* $C\Lambda Sf^2$. The linearity of each plot is very good, and the constants, Λ_∞ and K_o^{MR}, were obtained algebraically by the method of least squares. $\Lambda_{\infty(\mathrm{H_2O})}$ and $K_{o(\mathrm{H_2O})}^{\mathrm{MR}}$ refer to Λ_∞ and K_o^{MR} in nitrobenzene almost saturated with water (0.14M) and have been calculated on the assumption that nitrobenzene containing water has the same values of the dielectric constants and viscosity as those of pure nitrobenzene. The constants thus obtained, Λ_∞, $\Lambda_{\infty(\mathrm{H_2O})}$, K_o^{MR} and $K_{o(\mathrm{H_2O})}^{\mathrm{MR}}$, are listed in Table 1. In Fig. 5 shows a plot of log K_o^{MR} against the ionic potential of alkali metal (the ratio of the charge to the radius[4] z/r).

In nitrobenzene, the ionic mobilities[5] of hydrogen, sodium, and potassium ions are 23, 17.2, and 19.2 ($\mathrm{cm^2\,sec^{-1}}\,V^{-1}$) respectively; that is, the difference between the limiting conductances of Hexyl-Na and Hexyl-K in Table 1 is smaller than expected ($\sim$0.5). This result may be ascribed to the residual water in nitrobenzene ($\sim 10^{-3}$M), because the water saturated in nitrobenzene shows a tendency to increase the limiting conductance and, furthermore, the effect of the water is striking in going from $\mathrm{Cs^+}$ to $\mathrm{Na^+}$, as is shown in Table 1.

It is clear that the larger the radius of the alkali metal ion, the smaller the association constant, K_o^{MR}. However, the association constants, $K_{o(\mathrm{H_2O})}^{\mathrm{MR}}$, are

TABLE 1. THE LIMITING CONDUCTANCE AND ASSOCIATION CONSTANT FOR HEXYL SALTS IN NITROBENZENE

MR	Λ_∞	K_o^{MR}	$\Lambda_{\infty(\mathrm{H_2O})}$	$K_{o(\mathrm{H_2O})}^{\mathrm{MR}}$	
Hexyl-Li	30.9	52.6	31.3	3.3	
Hexyl-Na	29.7	13.9	31.1	4.0	25[6]
Hexyl-K	30.2	9.5	31.2	4.6	
Hexyl-Rb	30.0	7.7	30.9	4.7	
Hexyl-Cs	29.4	5.2	30.1	2.3	13[6]

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[4] L. Pauling, "The Nature of the Chemical Bond," 3rd Ed., Cornell Univ. Press, New York (1960).

[5] "Kagaku Benran," Maruzen Co., Tokyo (1966).

nearly the same. It seems that these facts are attributable to the solvation of the alkali metal ions with water. In nitrobenzene containing little water, the ion-pairs are formed between non-solvated metal ions and the Hexyl anion. The association constants, K_o^{MR}, have, therefore, a very close relation with the crystal ionic radius of the cation, as is shown in Fig. 5. However, in nitrobenzene containing much water, as the free cation is strongly solvated with water, the ion-pairs will be formed between hydrated metal cations and the Hexyl anion. Therefore, the formation of the ion-pairs will be more difficult than in nitrobenzene containing little water.

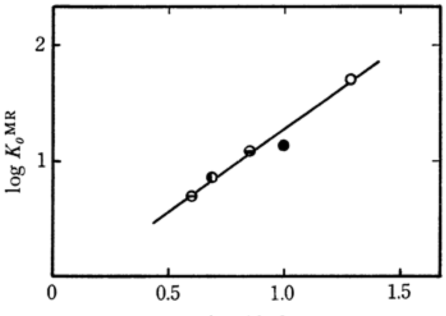

Fig. 5. The plot of $\log K_o^{\mathrm{MR}}$ *vs.* z/r.
The symbols used are the same as those in Fig. 1.

These concepts are supported by the following two facts. One is that water is coextracted in nitrobenzene with Hexyl salts, the amount of the coextracted water, as determined by the Karl-Fisher method, decreases in the folowing order: Hexyl-Li (5.5 H_2O mol/Hexyl salts mol) > -Na (3.5) > -K (1.3) > -Rb (0.7), -Cs (0.7), showing that lithium and sodium are solvated very strongly with water. The other fact is that a plot of $\log K_o^{\mathrm{MR}}$ *vs.* z/r shows a linearity; that is, the association affinities of Hexyl salts are found to be electrostatic and to be determined chiefly by the ionic radius of the alkali metal.

Kyrš[6] obtained the dissociation constants (K') of Hexyl salts by solvent extraction. His values ($1/K'$) are different from the values ($K_{o(\mathrm{H_2O})}^{\mathrm{MR}}$) obtained by the present authors and are closer to the constants, K_o^{MR}, rather than to $K_{o(\mathrm{H_2O})}^{\mathrm{MR}}$.

Distribution Ratio of Hexyl Salts. q_{R} was calculated from C_o^{R} and C_a^{R} which had been determined spectrophotometrically. In nitrobenzene, the calibration curves of Hexyl salts follow Beer's law under the conditions of $C_o^{\mathrm{R}}=1$—10×10^{-5}M at 470 mμ ($\varepsilon=19500$) and $C_o^{\mathrm{R}}=1$—10×10^{-4}M at 545 mμ ($\varepsilon=885$) and in water follow Beer's law under the conditions of $C_a^{\mathrm{R}}=1$—10×10^{-6}M at 430 mμ ($\varepsilon=26200$), $C_a^{\mathrm{R}}=1$—10×10^{-5}M at 505 mμ ($\varepsilon=8920$), and $C_a^{\mathrm{R}}=1$—10×10^{-4}M at 525 mμ ($\varepsilon=4580$).

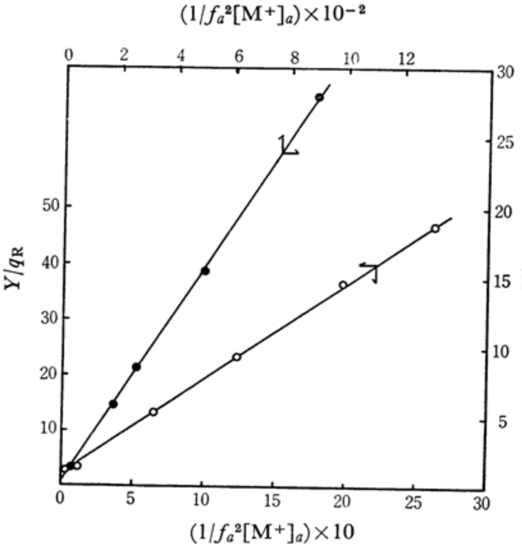

Fig. 6. The plot of Y/q_{R} *vs.* $1/f_a^2[\mathrm{M}^+]_a$.
The symbols used are the same as those in Fig. 1.

In a nitrobenzene solution, the molar extinction coefficients of Hexyl-alkali metal salts are identical; this is also true in water. Besides, no difference between the molar extinction coefficients of the ion-pair and the Hexyl anion was noticed.

Association Constants of Hexyl Salts in an Aqueous Solution. The values of K_a^{MR} can be estimated from Eq. (7). The extractions were carried out by shaking the nitrobenzene solution of Hexyl salts with an aqueous solution containing a known amount of the same kind of alkali metal.

Figures 6 and 7 show the plot of Y/q_{R} against $1/f_a^2[\mathrm{M}^+]_a$. All the straight lines were drawn by means of the method of least squares. In the case of Hexyl-Cs, the association constants could not be obtained, because the distribution ratio is very large, so q_{R} becomes very uncertain.

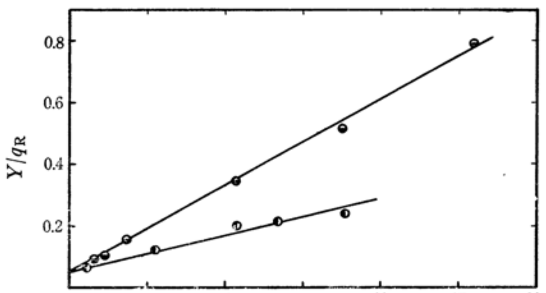

Fig. 7. The plot of Y/q_{R} *vs.* $1/f_a^2[\mathrm{M}^+]_a$.
The symbols used are the same as those in Fig. 1.

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[6] M. Kyrš and S. Podešva, *Collection Czech. Chem. Commun.*, **27**, 289 (1962).

In Table 2, the constants thus obtained, $K_a{}^{\mathrm{MR}}$ and D_{MR}, are shown; the extraction constants, E_{MR} $(=[\mathrm{MR}]_o/[\mathrm{M}^+]_a[\mathrm{R}^-]_a = D_{\mathrm{MR}}\cdot K_a{}^{\mathrm{MR}})$, are also shown in order to compare them with the results obtained by a different method.6) Though the extraction constant of Hexyl-Cs could not be obtained accurately, $\log E_{\mathrm{CsR}}$ was estimated to be more than 5. The values of the extraction constants in the present studies have the same tendency as the results obtained by a different method.

Figure 8 shows a plot of $\log K_a{}^{\mathrm{MR}}$ against z/r_{hyd}, where r_{hyd} is the effective diameter5) of the hydrated alkali metal ions in an aqueous solution. From this plot it is found that, in an aqueous solution, the association affinities depend chiefly upon the hydrated radius of the alkali metal ion, and that ion-pairs will be formed between the Hexyl anion and the hydrated alkali metal cation.

Table 2. The constants of $K_a{}^{\mathrm{MR}}$, D_{MR} and $\log E_{\mathrm{MR}}$ for hexyl salts

MR	$K_a{}^{\mathrm{MR}}$	D_{MR}	$\log E_{\mathrm{MR}}$	
Hexyl-Li	8.9	0.5	0.76	
Hexyl-Na	9.4	3.4	1.51	2.46)
Hexyl-K	174	20.4	3.55	
Hexyl-Rb	365	22.2	3.91	
Hexyl-Cs			(>5)	5.46)

From the association constants of Hexyl alkali metal salts in an aqueous solution, it is found that the larger the constant, $K_a{}^{\mathrm{MR}}$, the smaller the solubility of the Hexyl salts. When the extraction of the alkali metal is discussed, $K_a{}^{\mathrm{MR}}$, D_{MR} and $K_o{}^{\mathrm{MR}}$ are very important. The relation of the distribution ratio, q_{M}, to these values is shown by Eq. (8):

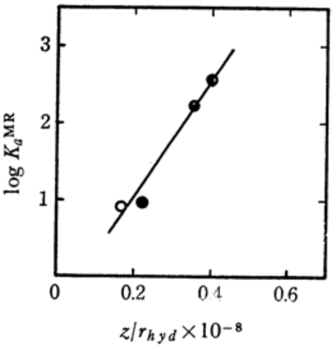

Fig. 8. The plot of $\log K_a{}^{\mathrm{MR}}$ vs. z/r_{hyd}.
The symbols used are the same as those in Fig. 1.

$$q_{\mathrm{M}} = \frac{C_o{}^{\mathrm{M}}}{C_a{}^{\mathrm{M}}} = D_{\mathrm{MR}}\left(1+\frac{1}{K_o{}^{\mathrm{MR}}[\mathrm{R}^-]_o f_o{}^2}\right) \times\left(1+\frac{1}{K_a{}^{\mathrm{MR}}[\mathrm{R}^-]_a f_a{}^2}\right)^{-1} \tag{8}$$

where $C_o{}^{\mathrm{M}}$ and $C_a{}^{\mathrm{M}}$ represent the total concentrations of alkali metal in the organic and aqueous phases respectively. From Eq. (8), it is clear that the extractability of the alkali metal increases with an increase in the values of $K_a{}^{\mathrm{MR}}$ and D_{MR} and with a decrease in the $K_o{}^{\mathrm{MR}}$ value.

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