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The Extraction of Alkali Metal Picrates into Benzene by Means of 18-Crown-6

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Synopsis. The distribution of alkali metal picrates between water and benzene was investigated in the presence of 18-crown-6. The overall equilibrium constants, K_{ex}, and some constituent equilibrium constants were determined. The K_{ex} value increases, passes through a maximum (at potassium), and falls off as the size of the alkali metal cation increases.

18-Crown-6 (CR) combines stoichiometrically with alkali metal cations to form complexes, in which the cation is accommodated into the hydrophilic molecular hole of the ligand (diameter: 0.26—0.32 nm).[1-3] The outer surface is then formed by the hydrophobic groups. From the 'metal in the hole' picture, the resulting complexes may be expected to be identical in size and in hydrophobicity. It is well known that there is a striking correlation between the stability of the complex and the size of the cation.[4] Among alkali metal cations, the potassium cation forms the most stable complex with the ligand; cations larger (Rb^+, Cs^+) or smaller (Li^+, Na^+) than the optimum size form destabilized complexes because, in the former, these cations are too large to fit into the ligand hole, while, in the latter, the hydration energy of these cations is predominant.[5]

In this paper, methods for obtaining the overall equilibrium constants will be reported. The extractability of alkali metal cations by CR will be discussed in terms of the stability constant of the complex.

Experimental

Materials. Commercial CR (Nisso Co., Ltd.) was used without further purification. The alkali metal picrates were prepared and purified as has previously been described.[6]

Extraction Procedure. The picrates were each dissolved in water containing lithium hydroxide at a concentration of 5×10^{-5} M (1 M=1 mol dm^{-3}). The concentrations were 10^{-2} M for sodium picrate, 10^{-3} M for potassium and rubidium picrates, and 5×10^{-3} M for caesium picrate. The CR was made up in benzene solutions, the concentration range being $(0.15-2)\times10^{-3}$ M. Equal volumes (20 cm^3) of the aqueous and benzene solutions were transferred into a 50-cm^3 centrifuge tube equipped with a stopper, shaken in a water bath thermostated at (25±0.01)°C for 20 min, and then allowed to stand for about 20 min. The picrate concentration in the benzene phase was determined spectrophotometrically at 425 nm. The molar absorption coefficients, ε, of the picrates in the benzene phase were determined to be $\varepsilon=8900$, 9400, 9100, and 9000 M^{-1} cm^{-1} at 425 nm for sodium, potassium, rubidium, and caesium picrates respectively. For this purpose, each of the benzene solutions was equilibrated with each of the aqueous picrate solutions as in the above procedure, after which the picrates extracted were completely back-extracted into water. The picrate concentrations were determined spectrophotometrically ($\varepsilon=14400$ M^{-1} cm^{-1} at 354 nm).

The Distribution Coefficient of CR. The CR was made up in benzene solutions ranging in concentration from 0.7×10^{-4} to 3.5×10^{-4} M. Each of the solutions was equilibrated with an aqueous 0.1 M potassium chloride solution containing lithium hydroxide (0.01 M) at 25 °C. The benzene phases separated from the aqueous phase were each shaken with the aqueous potassium chloride solution in the presence of an excess of the potassium salt of 2,2′,4,4′,6,6′-hexanitrodiphenylamine. The concentration of the resulting complex in the benzene phase was determined spectrophotometrically at 425 nm by means of the calibration method. The distribution constants thus obtained were averaged for use in subsequent calculations.

Results and Discussion

The equilibrium between an aqueous solution containing an alkali metal cation, M^+, and a picrate anion, A^-, and a benzene solution containing CR can be written as

$$M^+ + CR_o + A^- \rightleftharpoons MCRA_o,$$

$$K_{ex} = \frac{[MCRA]_o}{[M^+][CR]_o[A^-]}, \qquad (1)$$

where MCRA designates ion-pairs between alkali metal complexes, MCR^+, and picrate anions; the subscript o refers to the benzene phase, and the lack of a subscript, to the aqueous phase; the molar concentrations are given in brackets. The constituent equilibria are

$$CR \rightleftharpoons CR_o, \qquad D_c = \frac{[CR]_o}{[CR]}, \qquad (2)$$

$$M^+ + CR \rightleftharpoons MCR^+, \qquad K_s = \frac{[MCR^+]}{[M^+][CR]}, \qquad (3)$$

$$MCR^+ + A^- \rightleftharpoons MCRA, \quad K_{ass} = \frac{[MCRA]}{[MCR^+][A^-]}, \qquad (4)$$

$$MCRA \rightleftharpoons MCRA_o, \qquad D_{ip} = \frac{[MCRA]_o}{[MCRA]}. \qquad (5)$$

The mass balances are

$$T_M = [M^+] + [MCR^+] + [MCRA] + [MCRA]_o, \qquad (6)$$

$$T_{CR} = [CR] + [CR]_o + [MCR^+] + [MCRA] + [MCRA]_o, \qquad (7)$$

$$T_A = [A^-] + [MCRA] + [MCRA]_o, \qquad (8)$$

where T denotes the total concentration.

Table 1. Equilibrium constants for extraction of picrate with 18-crown-6 (CR) and dibenzo-18-crown-6 (DBC)

Ligand	Cation	Ionic diameter (nm)	D_c	$\log K_{ex}$	$\log K_s$	$\log (K_{ass}D_{ip})$	D_{ip}	K_{ass}
CR			0.0572					
	Na^+	0.194		3.31	<0.3[a]	>1.8	>0.4	
	K^+	0.266		6.00	2.06[a]	2.70	3.7	140
	Rb^+	0.294		5.43	1.5	2.7	>1[b]	
	Cs^+	0.334		4.28	0.8[a]	2.2	>1	
DBC			800					
	Na^+			2.21[c]	1.2[d]	3.9		
	K^+			4.65[c]	1.7[d]	5.9		
	Rb^+			3.75[c]	1.1[d]	5.6		
	Cs^+			3.07[c]	0.8[d]	5.2		

a) From Ref. 5. b) Estimated value. c) From Ref. 6. d) From Ref. 7.

Substituting Eqs. 2, 3, and 5 into Eq. 6, we obtain

$$[M^+] = \frac{T_M - [MCRA]_o(1+1/D_{ip})}{1+(K_s/D_c)[CR]_o}. \qquad (9)$$

Equations 2, 6, and 7 are combined to give

$$[CR]_o = \frac{[M^+] - T_M + T_{CR}}{1+1/D_c}. \qquad (10)$$

From Eq. 8, we obtain

$$[A^-] = T_A - [MCRA]_o(1+1/D_{ip}). \qquad (11)$$

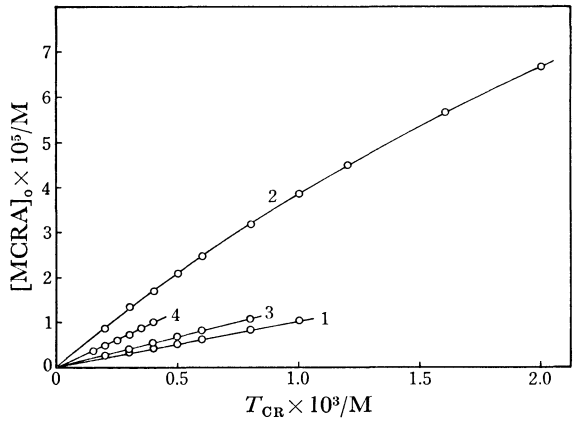

Fig. 1. Extraction of alkali metal picrate into benzene by 18-crwon-6. 1: Na, 2: K, 3: Rb, 4: Cs.

Combining Eqs. 1, 9, 10, and 11, we obtain a single relation with two unknowns, K_{ex} and D_{ip}. These were evaluated by a nonlinear regression fitting of 6—10 points per system, the deviation of the measured variable $[MCRA]_o$ being minimized in the process. In the case of rubidium, the relation thus obtained contains one more unknown, K_s. In view of the structural resemblance between $RbCR^+$ and $CsCR^+$, it is reasonable to estimate that $D_{ip}>1$ for rubidium. Thus, we can likewise estimate K_{ex} and K_s by regression analysis. As can be seen from Fig. 1, the calculated (solid line) and found (open circle) data agree within 2 percent. From Eqs. 9, 10, and 11, on the other hand, it is expected that a much simpler relation will hold between $[MCRA]_o$ and K_{ex} for MCRA of a low extractability:

$$[MCRA]_o = \frac{K_{ex}(T_M)^2}{1+1/D_c}T_{CR}. \qquad (12)$$

The K_{ex} values obtained from the slope of each straight line in Fig. 1 ($\log K_{ex}=3.30$ and 4.27 for Na^+ and Cs^+ respectively) are in good agreement with those listed in Table 1. The ion-association constant, K_{ass}, for potassium is calculated from the equation

$$K_{ex} = \frac{1}{D_c}(K_s K_{ass} D_{ip}). \qquad (13)$$

The data obtained, together with the values from the literature for dibenzo-18-crown-6 (DBC), are summarized in Table 1.

Table 1 shows that the $\log (K_{ass}D_{ip})$ values for CR are almost all equal in magnitude except for sodium. The same is true for its aromatic analogue, DBC. It follows from this finding that the observed sequence of K_{ex} for a given ligand is determined primarily by that of the stability constant, K_s.

Table 1 also shows that the distribution coefficient, D_c, of DBC is more than four decades greater than that of CR; this finding indicates that DBC is much more hydrophobic than CR. The hydrophobicity of the ligand shows virtually no effect on the stability of the complex, but it does have a slight effect on K_{ex}. It follows that the magnitude of K_{ex} for a given alkali metal is chiefly governed by that of $K_{ass}D_{ip}/D_c$ (*cf.* Eq. 13). It is noticeable that the less hydrophobic ligand is preferred as an extracting agent.

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