# 2 : 2 Cation–Crown Ether Complex Formation in Solvent Extraction

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12-Crown-4 (1,4,7,10-tetraoxacyclododecane) was shown to form 2 : 2 cation–ligand complexes with sodium, potassium, rubidium, and silver ions upon solvent extraction of aqueous metal picrates.

We have recently demonstrated that several crown ethers, not restricted to the large-ring examples, form dicationic 2 : 1 complexes with small- to medium-sized cations upon solvent extraction[1] as is the case with the crystalline complexes,[2] while such complex stoicheiometry has not been reported in the homogeneous-phase complexation.[3] The facile extraction of dicationic complexes upon solvent extraction is attributed to the effective charge-shielding co-ordination by the bulky, lipophilic picrate anions in the contact ion-pair complex extracted. The result prompted us to explore the complex stoicheiometry in the solvent extraction in further detail. Here we report the formation of novel 2 : 2 cation–ligand complexes in the solvent extraction of aqueous metal picrates with 12-crown-4 in dichloromethane.

Quantitative solvent extraction studies were carried out at 25 °C to determine the extraction equilibrium constant $K_{ex}$ and the complex stoicheiometry, by varying the concentration of 12-crown-4 (0.02—0.08 mol dm$^{-3}$) with a fixed concentration of alkali and heavy metal picrates (0.003 mol dm$^{-3}$). A set of data obtained for each cation/ligand combination first analysed assuming the conventional 1 : 1 stoicheiometry according to the theoretical treatment and subsequent analyses is reported.[1] As can be seen from Figure 1a, the plots for lithium, caesium, and thallium picrates give good straight lines of unit slope, indicating the formation of conventional 1 : 1 complexes; the intercepts afford the log $K_{ex}$ values of 2.62, 2.64, and 3.38 for $Li^+$, $Cs^+$, and $Tl^+$ picrates, respectively. Interestingly, those for the other picrates deviate substantially from the theoretical line for 1 : 1 complexation. With those cation/ligand combinations that show systematic deviation from the theoretical line, analyses assuming a sandwich-like 1 : 2 or dicationic 2 : 1 stoicheiometry[1] were attempted, but significant deviations were apparent. We then applied the rather uncommon 2 : 2 stoicheiometry to these cases. As shown in Figure 1b, the 2 : 2 stoicheiometry, which leads to a slope of 2,[1] explains well the extraction behaviour of the cation/ligand combinations which could not be interpreted as 1 : 1, 1 : 2, or 2 : 1 complexes. Thus, sodium, potassium, and rubidium picrates were found to form uncommon 2 : 2 cation–ligand complexes upon extraction with 12-crown-4; the log $K_{ex}$ values for $Na^+$, $K^+$, $Rb^+$, and $Ag^+$ are 10.0, 9.00, 8.82, and 9.88, respectively.

Unfortunately, the continuous variation method, which was useful in proving the stoicheiometry of dicationic complexation,[1] does not appear to be applicable to the present case, since the substantial distribution (26%) of 12-crown-4 into the aqueous phase from the organic phase makes strict analysis difficult.

The formation of crystalline 2 : 2 complexes has been reported for 18-crown-6 with rubidium and caesium thiocyanates, in which two cation-crown units are co-ordinated by two bridging anions.[4] Structurally-compelled 2 : 2 complexation has been exemplified with a silver nitrate complex of [3]-cryptate possessing two diaza-12-crown-4 units linked by oxyethylene chains.[5] However, 12-crown-4 itself has not been considered to afford such 2 : 2 complexes in solution or solid phases.[2,3] Instead sandwich complexes of 12-crown-4 with some sodium salts were isolated and analysed crystallographically.[6] The driving force for the facile extraction of the unusual 2 : 2 complex is inferred to be its high lipophilicity

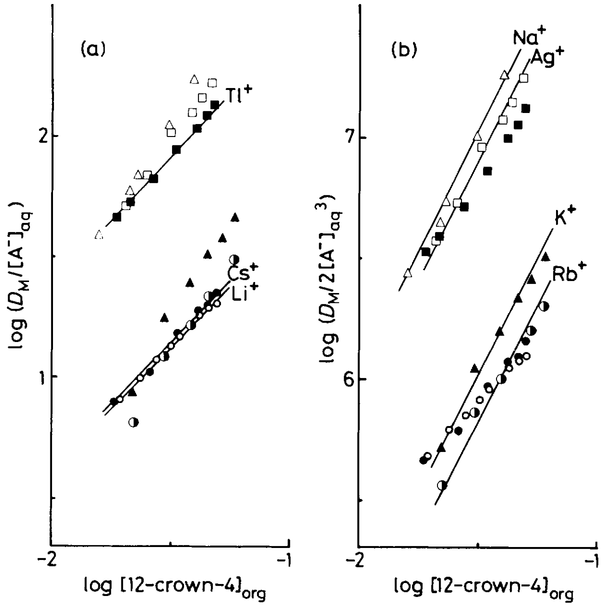

**Figure 1.** Plots for solvent extraction of aqueous lithium (○), sodium (△), potassium (▲), rubidium (◑), caesium (●), silver (□), and thallium picrate (■) with 12-crown-4 in dichloromethane: (a) 1 : 1 or (b) 2 : 2 stoicheiometry assumed; [12-crown-4]$_{org}$ and [A$^-$]$_{aq}$ refer to concentrations of 12-crown-4 in organic phase ($CH_2Cl_2$) and of picrate ion in aqueous phase at the equilibrium, and $D_M$ represents the distribution ratio of metal ion between organic/aqueous phases; for the derivation of equilibrium equations, see ref. 1.

enhanced by the bridging co-ordination of two picrate anions, since the lipophilicity of the complex, or the counter anion, to be extracted is one of the primary factors dominating extractability and cation selectivity in solvent extraction.[3,7,8] This does not mean however that there is no 1 : 1 or 1 : 2 complex formed in the aqueous phase, but rather indicates that only the highly lipophilic 2 : 2 complex, even though it may be a minor species in the aqueous phase, is extracted preferably into dichloromethane. Another point of interest is the cation selectivity. As a consequence of the different complex stoicheiometry applied, selectivity inversion is actually observed for several cation pairs, *e.g.* $Ag^+/Tl^+$, $Li^+/K^+$, $Rb^+/Cs^+$, as indicated by the crossing plots in Figure 1.

The present result indicates that the ion-pair complex extracted into the organic phase from aqueous solution, though it shares some resemblance with the crystalline complex,[1] possesses its own characteristic stoicheiometry which is distinctly different from those observed in the homogeneous or solid phase. Thus the complex stoicheiometry in solvent extraction is not a simple function of the size-fit concept but is influenced substantially by the lipophilicity of the ion-pair complex to be extracted. From the practical point of view, the different stoicheiometry for the specific cation pair may be used as a tool for controlling cation selectivity.

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