Bull. Chem. Soc. Jpn., 56, 3491—3494 (1983)

Physicochemical Studies of Alkali Metal Solutions in Tetrahydrofuran

Jacques Lacoste and François Schué*

Laboratoire de Chimie Macromoléculaire, Université de Sciences et Techniques du Languedoc,
Place E. Bataillon, 34060 Montpellier Cedex, France

(Received December 21, 1982)

We have studied the rate of alkali metal dissolution in THF as a function of its nature and of the cryptand (C). The selectivity has been estimated through the equilibrium constant of the following equilibrium:

$$M^- + C \rightleftarrows M^+C + 2e^-_{solv}.$$

Both ΔH° and ΔS° for this reaction are negative. The entropy decrease reveals that the sum of the energies bonds between the cation and the ligand and the electrons and the solvent is higher than that necessary to desolvate and dissociate M^-.

Solutions of alkali metals in amines and ethers have been widely studied.[1–5, 12–14] The species which can exist in these solutions may be described by the following equilibria (1) to (3):[2]

$$\begin{array}{ll} 2M_s \rightleftarrows M^+ + M^- & (1) \\ \qquad\qquad\quad \upharpoonleft\downharpoonright & \\ \qquad\qquad\quad M + e^-_{solv} & (2) \\ \qquad\qquad\quad \upharpoonleft\downharpoonright & \\ \qquad\qquad\quad M^+ + e^-_{solv} & (3) \end{array}$$

An increase in the solvating power and dielectric constant of the solvent shifts all three equilibria to the right.

The use of a cation-complexing agent (C) seems to provide enough stabilization energy to yield solvated electrons in solvents in which the metals would otherwise be insoluble.[1] The effect of (C) may be represented by the following in addition to equilibria (1)—(3).

$$2M_{(s)} + C \rightleftarrows M^+C + M^- \qquad (4)$$

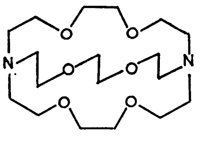
$$M^- + C \rightleftarrows M^+C + 2e^-_{solv} \qquad (5)$$

Many complexing agents have been used which belong to the classes of crowns and cryptands.

In a preliminary note,[6] we have studied equilibria (4) and (5) from a kinetic point of view.

At the early stage of the reaction (short time of contact between a solution of (C) and M solid), the complexing agent is in excess with respect to the dissolved metal and, under certain conditions, it is possible to obtain the solvated electron without the presence of M^-. With increasing time of contact, most of the free C is consumed by reaction (4); reaction (5) is reversed, and the M^- species predominates.

In this work, we have studied in more detail both the kinetics of metal dissolution as a function of the nature of the alkali metal and of the complexing agent **1**, **2**, and **3** and the thermodynamic parameters of equilibrium (5).



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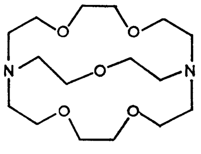

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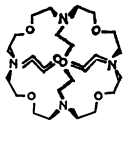

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Experimental

The high reactivity of the species e^-_{solv} and M^- requires the use of high vacuum techniques and all glass apparatus.

All glassware was cleaned[2] first with an HF solution followed by a thorough rinsing with distilled water. The cells were filled with boiling aqua regia which was allowed to remain in the cell for at least 10 h. After rinsing with distilled water, the cell was dried in an oven overnight.

Tetrahydrofuran (THF) was first dried with potassium hydroxide and calcium chloride. After initial drying, it was distilled onto potassium and finally stored under vacuum over Na:K (1:3) alloy which yielded blue solutions.

The metals were vacuum-distilled in bulbs supplied with break-seals. The cation-complexing agents were recrystallized in hexane, dried and sealed off under vacuum.

The experiments were carried out in the apparatus described in Fig. 1 according to the following procedure: after evacuation, the metal was distilled from the side arm (a) to form a mirror on the walls of vessel A. Then the solvent, stored on a vacuum line, was distilled under vacuum into A. When the complexing agent (b) had been added, after a given time of contact (t_c) at −78 °C (methanol–Dry Ice refrigerating mixture), the solution was poured through the coarse frit (G2) into the thermostated quartz call B. Excess complexing agent could be added through break-seal (c).

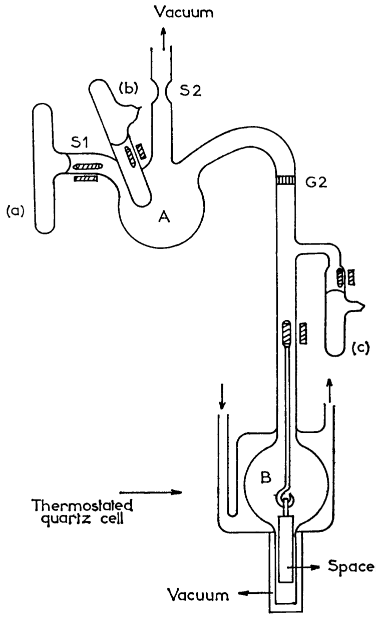

Fig. 1. Apparatus for the preparation and spectroscopic studies of alkali metal solutions.

Optical spectra were obtained with a Beckman DK-2A spectrophotometer. The spectroscopic parameters (λ_{max}, $d\varepsilon/dT$) were determined elsewhere.[7] The optical pathlength of the cells was determined with standard solutions of potassium dichromate ($l = 0.51 + 0.01$ and $l = 0.057 \pm 0.001$ cm). The total metal concentration in solution was estimated by flame photometry (Electrosynthese PHF 62 A). Temperature was controlled by means of an Ultrakryostat Haake KT52.

Results and Discussion

Kinetics of Dissolution. In order to carry out this study, we used less complexing agent than total metal. If we consider only reaction (4), the ratio R can reach a limiting value of 0.5.

$$R = \frac{[C_o]}{[M]} \tag{6}$$

$[C_0]$ and $[M]$ represent the concentrations respectively of complexing agent and of metal in solution. The simultaneous presence of reactions (4) and (5) will allow values of R higher than 0.5. High values of the ratio R can be due either to a low complexation efficiency or to a short contact time (Figs. 2 to 5).

The use of compound **3** (Fig. 6), specific for cesium, increases the dissolution and one can observe a higher proportion of e_s^- for a short time of contact. This last study shows the intramolecular cavity cation selectivity.

Complexation Effect. The kinetic studies have shown the influence of the metal and the complexing agent on the rate of dissolution of alkali metals in

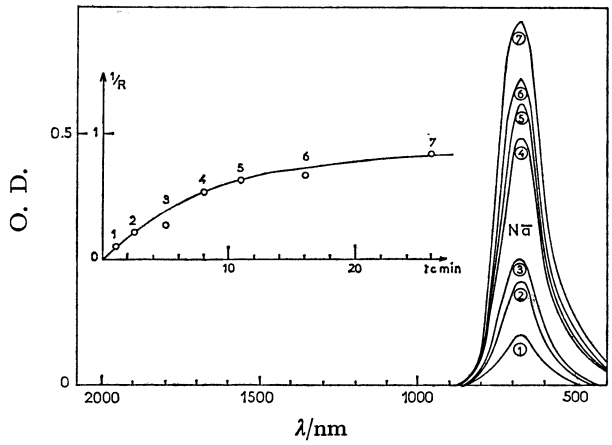

Fig. 2. Dissolution kinetics of sodium.
Cryptand I = 2.9×10^{-4} mol dm^{-3}, $t = -50$ °C.

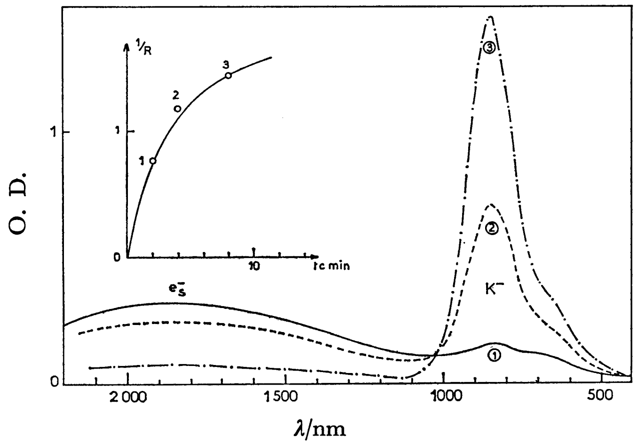

Fig. 3. Dissolution kinetics of potassium.
Cryptand I = 3.29×10^{-4} mol dm^{-3}, $t = -50$ °C.

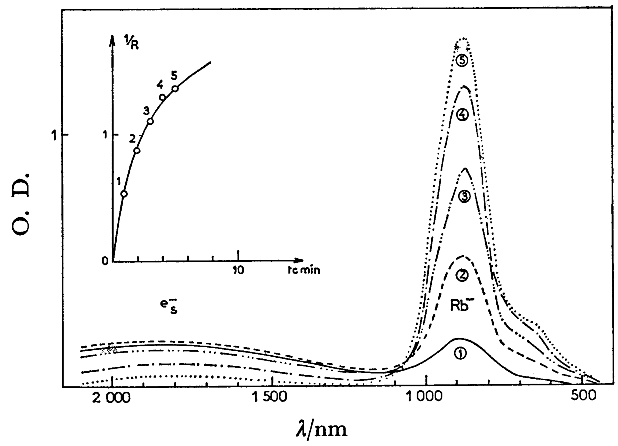

Fig. 4. Dissolution kinetics of rubidium.
Cryptand I = 2.91×10^{-4} mol dm^{-3}, $t = -50$ °C.

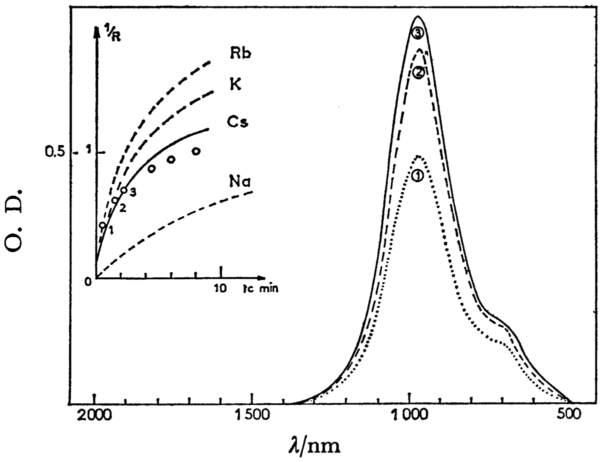

Fig. 5. Dissolution kinetics of cesium.
Cryptand I = 1.25×10^{-4} mol dm^{-3}, $t = -50$ °C.

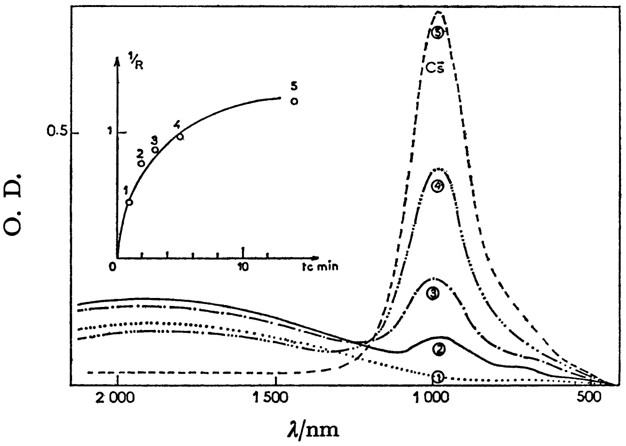

Fig. 6. Dissolution kinetics of cesium.
Cryptand III = 1.78×10^{-4} mol dm^{-3}.

THF. For a better understanding of these phenomena, we have studied the behavior of these solutions in the presence of an excess of complexing agent.

For a constant ratio *R*, we can expect the equilibrium (5) to be more or less shifted to the right according to the ionization potential of the metal anion and the selectivity of the complexing agent. Figure 7 shows the optical spectra after addition of an excess of compound **1**. A remarkable $K^+ > Rb^+ > Cs^+ > Na^+$ complexation selectivity displayed by ligand **1** is noted. Cesium and rubidium are less complexed than potassium. This shows that the intramolecular cavity-cation selectivity prevails over the ionization potential of the metal anion in these cases.

This selectivity can be illustrated by the equilibrium constant of reaction (5) at −50 °C.

$$K_5 = \frac{[M^+C][e^-_{solv}]^2}{[M^-][C]} \qquad (7)$$

now, $[M^+C] = [M^-] + [e^-_{solv}]$ and $[C] = [C_o] - [M^+C]$ leading to:

$$K_5 = \frac{\{[M^-] + [e^-_{solv}]\}[e^-_{solv}]^2}{[M^-]\{[C_o - ([M^-] + [e^-_{solv}])\}} \qquad (8)$$

The values obtained have been plotted as a function of the cationic radius (Fig. 8), and confirm the high selectivity for K^+.

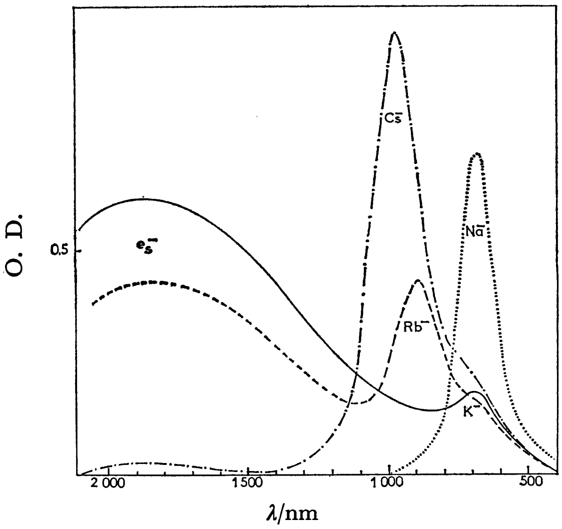

Fig. 7, Absorption spectra of sodium, potassium, rubidium and cesium in THF in the presence of cryptand I (*t* = −50 °C).
······: Na, *R*=9.2, ——: K, *R*=4.6, ----: Rb, *R*=4.4, —·—·—: Cs, *R*=6.5.

The use of compounds **2** and **3** have marked effects on equilibrium (5). The Cs^+–**3** and K^+–**1** complexes are comparable; but that is not the case for the Na^+–**2** complex for which the high ionization potential of Na^- prevails.

Thermodynamic Parameters. A deeper understanding of the thermodynamics of cryptate formation may be provided by analysis of the enthalpy, $\Delta H°$, and entropy $\Delta S°$, of complexation. Such data have

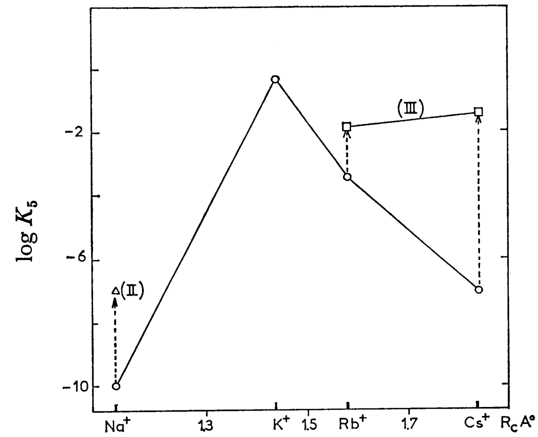

Fig. 8. Values of K_5 equilibrium constant in THF at −50 °C as a function of the cationic radius (see Table 1).
○: Cryptand I, △: cryptand II, □: cryptand III.

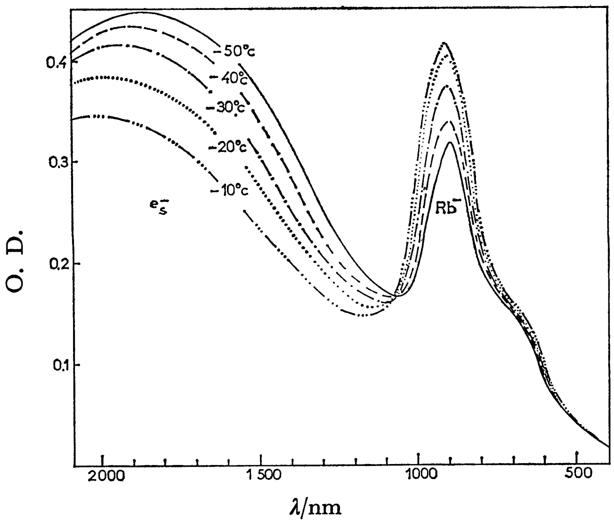

Fig. 9. Influence of temperature on a rubidium cryptand I THF solution.
Rb=3.97×10⁻⁴ mol dm⁻³, [cryptand I]=1.75×10⁻³ mol dm⁻³.

TABLE 1. THERMODYNAMIC DATA RELATIVE TO EQUILIBRIUM (5)

Metal	Complexing agent	K_5(−50 °C)	$-H°$/kJ mol^{-1}	$-S°$/J K^{-1} mol^{-1}
Na	**1**	10^{-10}	—	—
	2	10^{-7}	—	—
K	**1**	0.4	34±1	155±5
Rb	**1**	4×10^{-4}	8.8±0.5	105±2
	3	1.7×10^{-2}	16.7±0.6	109±3
Cs	**1**	10^{-7}	—	—
	3	3.6×10^{-2}	5.4±0.4	50±2

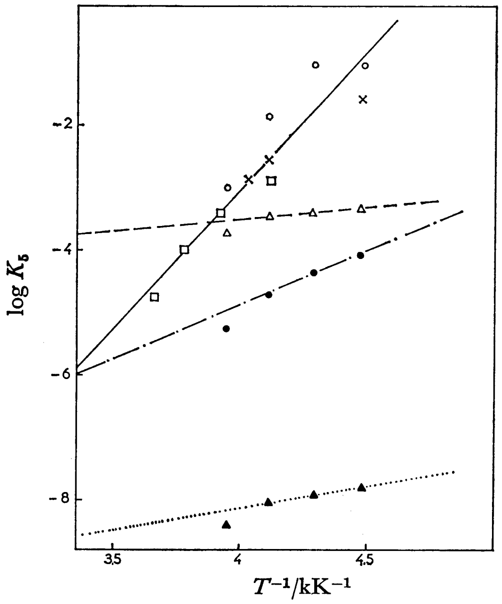

Fig. 10. Van't Hoff law applied to equilibrium (5). ×, ○, □: K/cryptand I, △: Cs/cryptand III, ●: Rb/cryptand III, ▲: Rb/cryptand I.

recently become available for a number of macrobicyclic ligands.[10)]

Figure 9 shows the influence of temperature on the absorption spectrum of a rubidium cryptand-I THF solution. Besides the shift of the equilibrium toward the formation of M$^-$ with increasing temperature, we note that the temperature dependence of the position of the absorption bands prevents the presence of an isosbestic point.

Figure 10 represents the Vant Hoff plots and the thermodynamic relation (9) allows the estimation of the enthalpy ΔH° and entropy ΔS° for reaction (5).

$$-\frac{\Delta G^\circ}{RT} = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} = \log K_5 \tag{9}$$

The data are given in Table 1.

Both enthalpies and entropies are negative. Negative enthalpies reveal that the sum of the energy of the bonds between the cation and the ligand and the electron and the solvent are higher than that necessary to desolvate and dissociate M$^-$.

The values observed are in agreement with the high values of the equilibrium constant K_5.

The entropy decrease can be explained by two kinds of complexation; the cation cryptand and the electron THF ones.

We wish to acknowledge support of this research by the Societé Nationale des Poudres et Exploisifs under Contracts N° 17.72 D, 13.73 D, 11.74 D, and 11.42 A.

Our special thanks go to Professor J. M. Lehn of the University of Strasbourg, for providing us with samples of the cryptand compounds and for useful discussions, to Professeur J. L. Dye of the Michigan State University of helpful exchanges of information and useful discussions, and to Dr. S. Bywater of the National Research Council of OTTAWA for useful discussions.

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