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ALKALI METAL SOLUTIONS. EFFECT OF CRYPTANDS ON SOLUBILITY AND SPECTRA IN TETRAHYDROFURAN, DIOXANE AND TOLUENE

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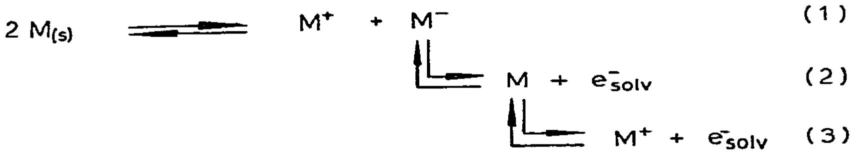
Summary

By use of alkali cation complexing agents of the cryptand type, alkalimetals solutions can be prepared which contain different species depending on the nature of the solvent. In THF, in the presence of cryptand, M^- and e^-_{solv} have been observed, and quantitative values of the molar extinction coefficients, the temperature coefficients ($d\nu/dt$, $d\epsilon/dt$) and the oscillator strength (f) have been determined. In dioxane alone, only cesium gives a blue solution (Cs^-); in the presence of cryptand, Na, K, Rb and Cs dissolve well, but only the M^- absorption is observed.

In toluene, the metals are normally insoluble and a cation complexing agent is required to dissolve them; in all the examined cases the addition of cryptand tended to give an aromatic radical anion. Blue solutions are obtained only for Na; in that case the solution exhibits ESR and optical behavior which indicates the presence of both anion radical and M^-.

Introduction

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



An increase in the solvating power and dielectric constant of the solvent

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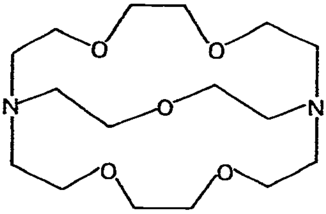
shifts all three equilibria to the right. The use of a cation-complexing agent (C) seems to provide enough stabilization energy to yield solvated electrons in solvents in which the metals would otherwise be insoluble [3], and this has been confirmed in the studies described below.

The effect of (C) may be represented by the following in addition to equilibria 1—3.

$$2\,M_{(s)} + C \rightleftharpoons M^+C + M^- \tag{4}$$

$$M^- + C \rightleftharpoons M^+C + 2e^-_{solv} \tag{5}$$

Many complexing agents have been used which belong to the classes of linear polyethers [4—6], crowns and cryptands [3,2]. This paper presents some new results obtained with cryptands I, II and III.



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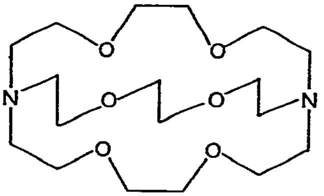

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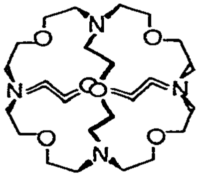

(III)

Experimental

The high reactivity of the species e^-_{solv} requires the use of high vacuum techniques and all glass apparatus. All glassware was cleaned [3] with an HF solution and thoroughly rinsed 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) and dioxane were first dried with potassium hydroxide and calcium chloride. They were then distilled on to potassium and finally stored under vacuum over Na/K (1/3) alloy, which yielded blue solutions. Toluene was treated with sulfuric acid, then distilled on to potassium, and finally stored under vacuum over n-butyllithium. The metals were vacuum-distilled into bulbs filled with break-seals. The cation-complexing agents were recrystallized from n-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 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, the solution was poured through the coarse frit (G_2) into the thermostated quartz cell B. An excess of complexing agent (b) could be added through a breakseal (c).

Optical spectra were obtained with a Beckman DK-2A spectrophotometer. The optical path length of the cells was determined with standard solutions of

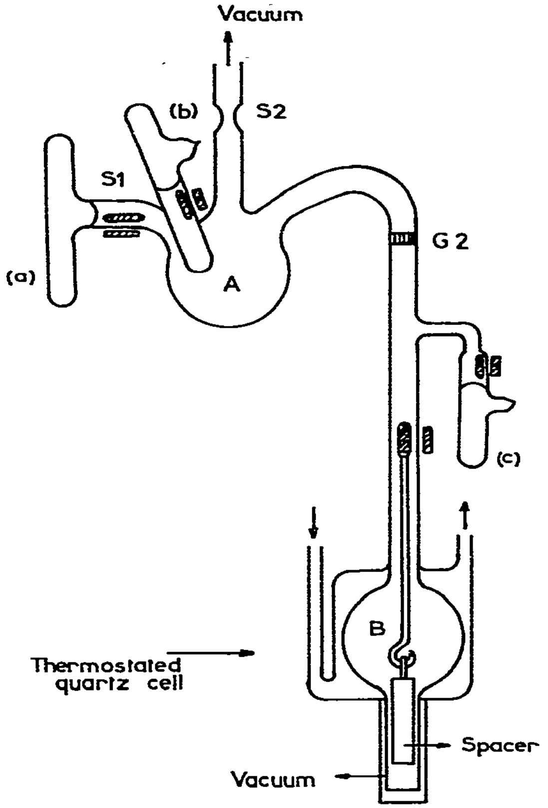

Fig. 1. Apparatus for the preparation and spectroscopic studies of alkali metal solutions.

potassium dichromate (l 0.51 ± 0.01 and l 0.057 ± 0.001 cm) without and with the spacer, respectively.

The total metal concentration in solution was estimated by flame photometry (Electrosynthèse PHF 62A). Temperature was controlled by means of an Ultrakryostat Haake KT 52.

Results and discussion

I. Alkali metal solution in tetrahydrofuran

A. λ_{max}, ϵ_{max}

In our experiments, solution of the metals in THF in the presence of cryptands were formed directly at —78°C (exothermic reaction). The optical absorption spectra were measured at —50°C. Solutions stored at —50°C for several days showed no visible signs of decomposition. The spectra of metal solutions have been studied extensively [8—20,31—34] but most of these studies have failed to provide quantitative values for the molar extinction coefficients, but Dye et al. [12,31] obtained ϵ for Na^- and e^- in ethylendiamine. Our results are given in Table 1.

TABLE 1

ABSORPTION MAXIMA AND MOLAR EXTINCTION COEFFICIENTS OF M^- AND e^-_{solv} IN THF AT −50°C

	e^-_{solv}	Na^-	K^-	Rb^-	Cs^-
λ_{max} (nm)	1870	680	845	880	970
$\epsilon_{max} \times 10^{-5}$ ($cm^{-1}\ l^{-1}\ mol^{-1}$)	0.27 ± 0.01	1.1 ± 0.1	1.2 ± 0.2	1.3 ± 0.2	1.4 ± 0.2

Two methods were used to determine the molar extinction coefficients.

Kinetic method. The addition of complexing agent I, II or III on to an alkali metal mirror covered by THF produces an immediate dissolution of the metal (equilibria 4 and 5). At a given time the concentration of the dissolved metal M is given by the relation:

$$(M) = 2[M^-] + [e^-_{solv}] \qquad (6)$$

The absorption bands of the metal—THF solutions after removal from the metal mirror allow the determination of the absorbances (A_{M^-} and $A_{e^-_{solv}}$). The total metal concentration (M) was estimated by flame photometry.

Application of the Lambert—Beer law gives:

$$(M) = \frac{A_{e^-_{solv}}}{\epsilon_{e^-_{solv}} \times l} + 2\frac{A_{M^-}}{\epsilon_{M^-} \times l} \qquad (7)$$

Several experiments at different times of contact (t_c) between the complexing agent in THF and the metal mirror allowed us to estimate: ϵ_{Na^-}, ϵ_{K^-}, $\epsilon_{e^-_{solv}}$.

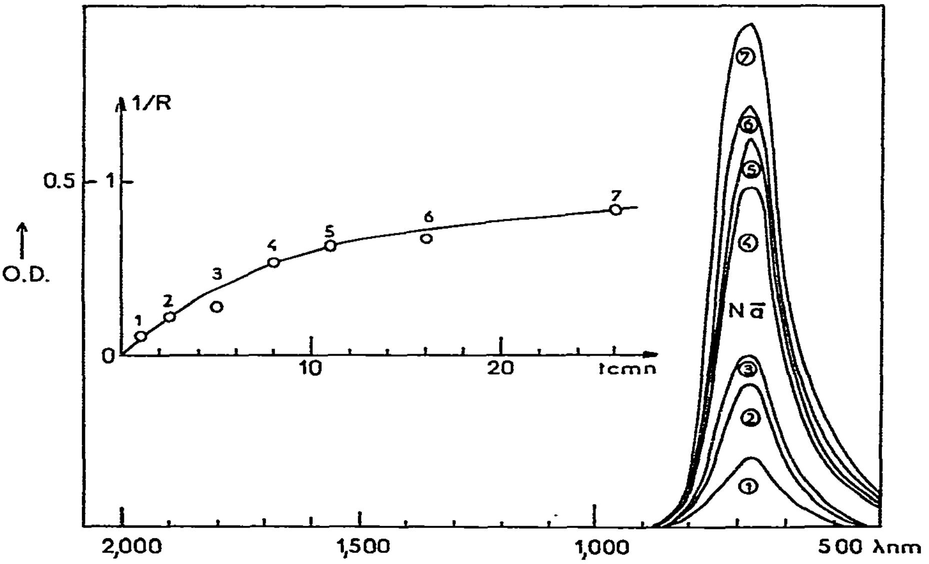

Fig. 2. Dissolution kinetics of sodium ([cryptand I] = 2.94 × 10^{-4} mol l^{-1} T −50°C). (R = [C]/[M], [C] and [M] representing the concentrations, respectively, of complexing agent and of metal in solution.)

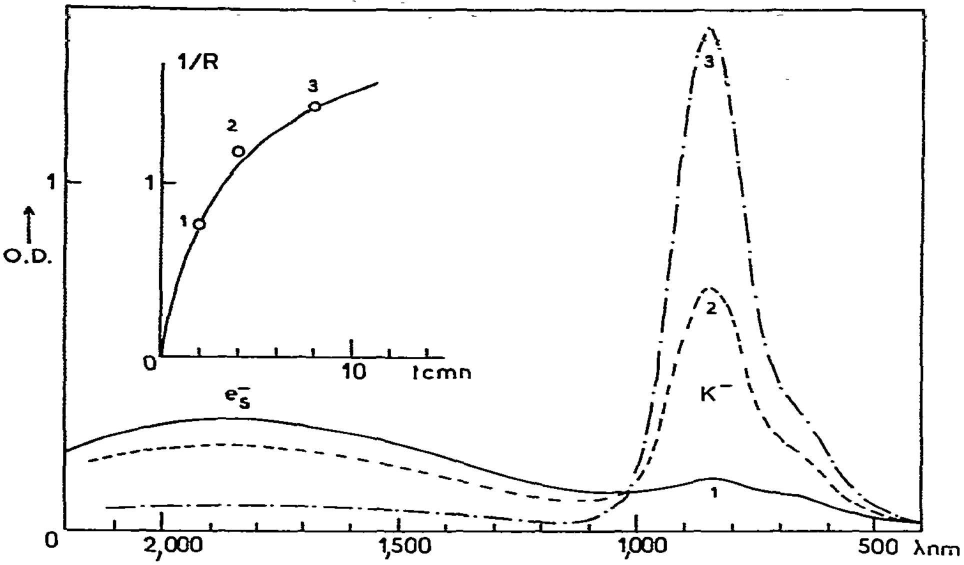

Fig. 3. Dissolution kinetics of potassium ([Cryptand I] = 3.29×10^{-4} mol l^{-1} T —50°C).

Static method. For a given contact time (t_l), equation 6 gives the concentration at equilibrium (M) = $2[M^-]_l + [e^-_{solv}]_l$. Figs. 2 to 5 show the dissolution of the alkali metals as a function of time. Rubidium and potassium metals dissolve most rapidly in the presence of complexing agent (I) in agreement with the good selectivity of compound (I) for the corresponding cations [7] (Table 2).

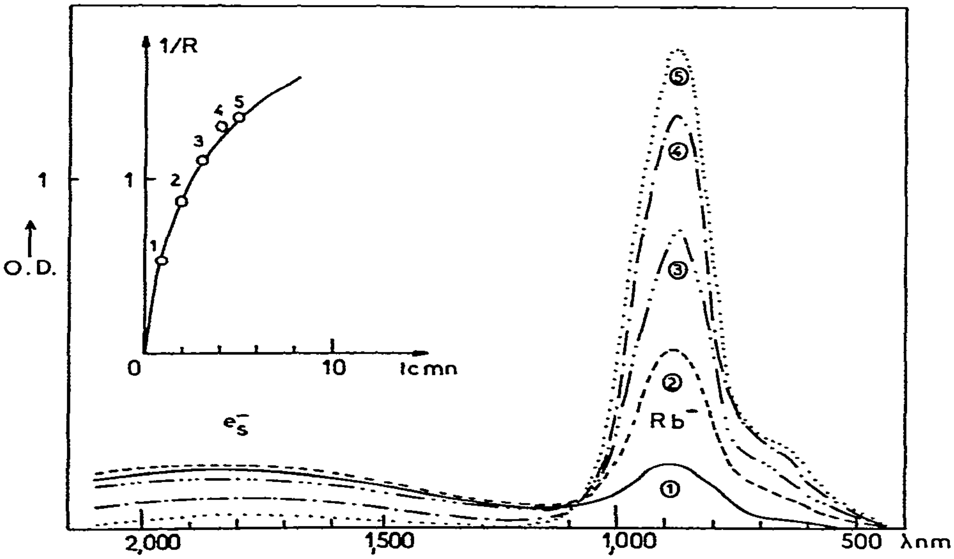

Fig. 4. Dissolution kinetics of rubidium ([cryptand I] = 2.91×10^{-4} mol l^{-1} T —50°C).

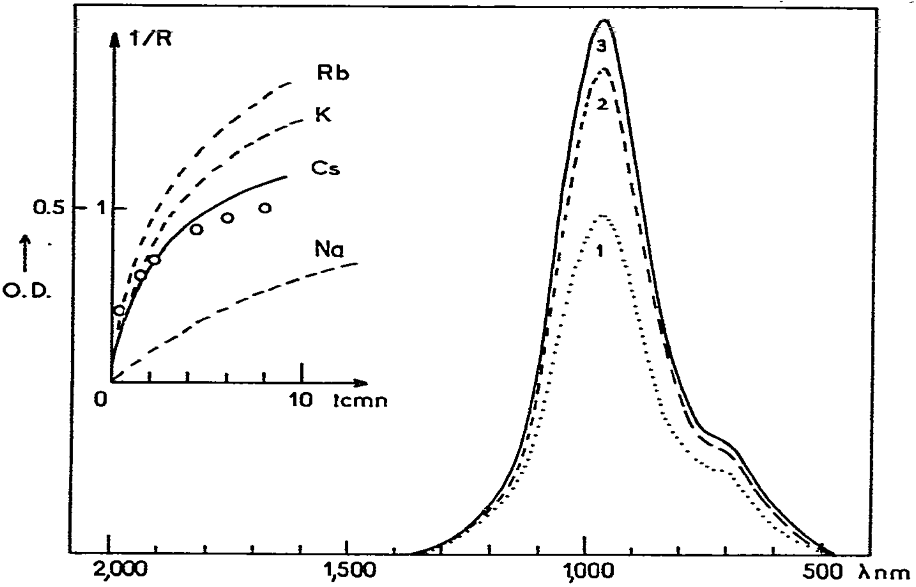

Fig. 5. Dissolution kinetics of cesium ([cryptand I] = 1.25 X 10^{-4} mol l^{-1} T —50° C).

TABLE 2

INTRAMOLECULAR CAVITY AND CATION RADII [8,9]

Cation	Cation radius (Å)	Intramolecular cavity radius (Å)	Complexing agent
Na^+	1.12	1.15	II
K^+	1.44	1.4	I
Rb^+	1.58		
Cs^+	1.84	1.8	III

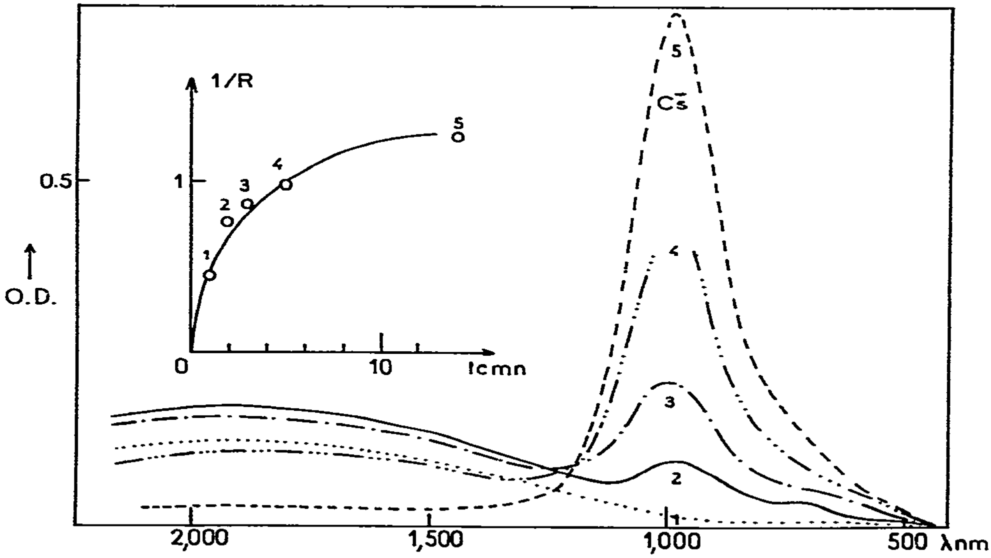

Fig. 6. Dissolution kinetics of cesium ([cryptand III] = 1.78 X 10^{-4} mol l^{-1} T —50°C).

The use of compound (III) Fig. 6, specific for cesium, increases the dissolution and a higher proportion of e^-_s is observed for a short time of contact. This last study shows the intramolecular cavity cation selectivity.

We also note that Rb and K present the highest proportion of e^-_{solv} at early stage of the reaction. Sodium is only slightly soluble; its rate of dissolution is slow and the limiting value $1/R = 2$ is not reached. The use of compound II, specific for this metal, increased the dissolution only slightly. Moreover, only small amounts of solvated electrons are obtained in short contact times. We must therefore conclude that the high ionization potential of Na^- in solution is responsible for this phenomenon. Cesium, although easily ionizable, dissolved more slowly than rubidium and potassium in the presence of compound I.

If an excess of complexing agents I, II or III is added to the metal solution after separation from the metal mirror, equilibrium 5 is shifted to the right, and part of the M^- is transformed into e^-_{solv}, the total metal concentration being constant.

$$(M) = 2[M^-]_1 + [e^-_{solv}]_1 = 2[M^-]_2 + [e^-_{solv}]_2$$

$$\frac{\epsilon_{M^-}}{\epsilon_{e^-_{solv}}} = 2\frac{A_{(M^-)_1} - A_{(M^-)_2}}{A_{(e^-_{solv})_2} - A_{(e^-_{solv})_1}} \tag{8}$$

We used the values of $\epsilon_{e^-_{solv}}$, ϵ_{K^-} and ϵ_{Na^-} obtained by the kinetic method to check the static method which was used to estimate ϵ_{Rb^-} and ϵ_{Cs^-}.

B. Temperature dependence of λ_{max} and ϵ_{max}

Several authors [3,10,21] have shown that M^- and e^- absorption bands are characteristic of a CTTS * band: a linear correlation of the position of its absorption maximum with temperature is expected. Our experimental results (Fig. 7) fit well with this correlation. The peak positions proved to be strongly temperature dependent. A linear blue shift with decreasing temperature was observed in all cases. The temperature coefficients for M^- and e^-_{solv} are listed in Table 3.

The molar extinction coefficients are temperature sensitive; we found a linear correlation, as observed by Stein and Sterling [22] for the iodide anion.

By application of Beer's law, if $d\epsilon/dT$ is estimated from the variation of optical density at the absorption maximum, and account taken of the variation of the solvent density (ρ).

$$d(A)/dt = d\epsilon/dt + d\rho/dT \tag{9}$$

$$(d\rho/dT)_{THF} = 10^{-3} \text{ [23]}$$

The results listed in Table 3 show a temperature independent molar extinction coefficient for e^-_{solv}. A similar result was found by pulse radiolysis [24,25].

C. Oscillator strength (f)

The oscillator strength of a species is represented by an integral over its absorption band.

$$f = 4.3 \times 10^{-9} \int_{E_1}^{E_2} \epsilon \, dE \tag{10}$$

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* CTTS = charge-transfer-to-solvent.

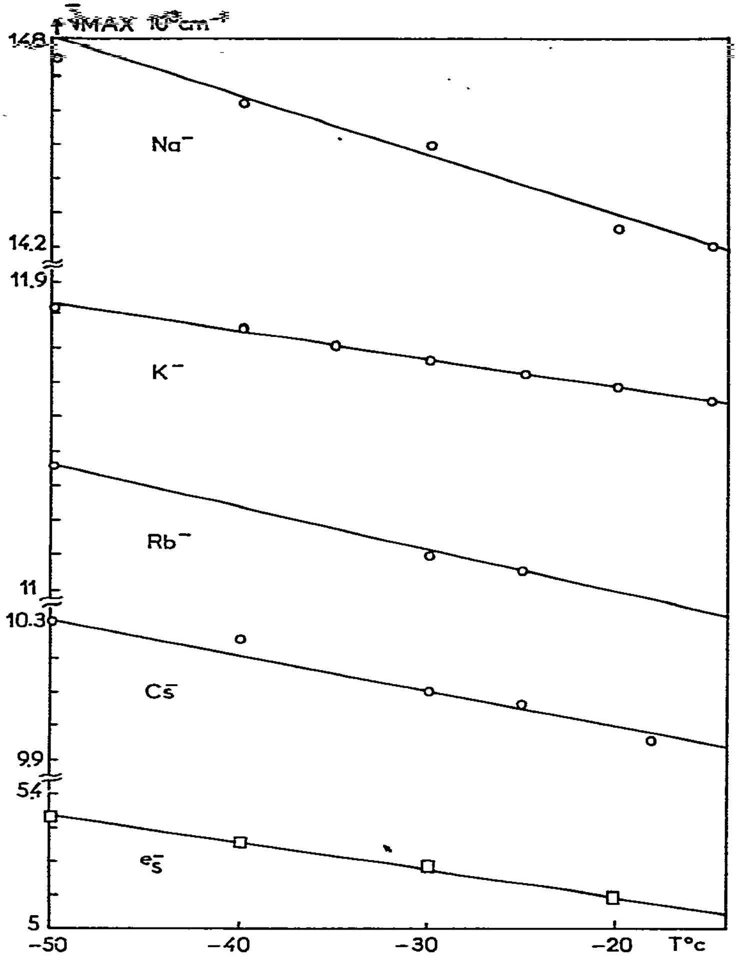


Fig. 7. Temperature dependence of the position of the band maximum for M$^-$ in THF. Note the displacement of the vertical scale.

For a weakly bound species, *f* represents the number of electrons involved in the electronic transition [12,26,32].

Because of the characteristic asymmetry of the absorption bands it seems inappropriate to attempt to fit the bands with symmetrical functions. As shown by Dye, Debacker and Dorfman [32], the absorption band shapes are conveniently and accurately described by a combination of a Gaussian function at low energy and a Lorentzian function at high energy as, shown in equation 11 in which

TABLE 3

TEMPERATURE COEFFICIENTS FOR Na$^-$, K$^-$, Rb$^-$, Cs$^-$, AND e_{solv}^- IN THF

	e_{solv}^-	Na$^-$	K$^-$	Rb$^-$	Cs$^-$
$-d\bar{\nu}/dT$ (cm^{-1} deg^{-1})	8 ± 2	17.5 ± 0.9	8.0 ± 0.5	12 ± 0.3	11 ± 1
$-d\epsilon/dT \times 10^3$ (l mol^{-1} deg^{-1})	0	4.2 ± 0.4	4.2 ± 0.4	3.4 ± 0.4	4.4 ± 0.4

TABLE 4

OSCILLATOR STRENGTHS OF Na^-, K^-, Rb^- AND Cs^-

	Na^-	K^-	Rb^-	Cs^-
f	2.1 ± 0.2	1.5 ± 0.3	1.8 ± 0.3	1.9 ± 0.3

$W_{1/2G}$ and $W_{1/2L}$ represent the half-widths respectively of the Gaussian and the Lorentzian portions. The results obtained are listed in Table 4.

$$f_{M^-} = 4.3 \times 10^{-9}\,(1.065\,W_{1/2G} + 1.571\,W_{1/2L})\,\epsilon_{M^-} \tag{11}$$

We found that the half-width increases with the temperature in such a way that it counter-balances the variation of ϵ.

$$\mathrm{d}f/\mathrm{d}T = \mathrm{d}w/\mathrm{d}T + \mathrm{d}\epsilon/\mathrm{d}T = 0 \tag{12}$$

Thus, the oscillator strength is temperature independent.

An oscillator strength of nearly 2 is obtained for the M^- band. We would expect that an oscillator strength of about two would require at least two equivalent electrons to be involved in the transition. The species M^- fulfills this requirement as has been previously shown for Na^- in ethylenediamine [32].

$$M^- \rightarrow M^+ + 2\,e^-_{\mathrm{solv}} \tag{13}$$

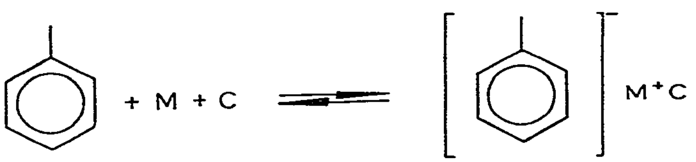
For e^-_{solv}, the oscillator strength was not determined because of the solvent absorption above 2200 nm; nevertheless the half-width of the absorption band at high energy ($W_{1/2L} \simeq 2700\ \mathrm{cm}^{-1}$) agrees well with the expected value of ~1 for f [12,13,18,31,32]. The half-width is temperature independent, and since $\mathrm{d}\,\epsilon_{e^-_{\mathrm{solv}}/\mathrm{d}T} = 0$ the oscillator strength of e^-_{solv} is also temperature independent.

II. Solutions of alkali metals in dioxane and toluene

In order to study the efficiency of e^-_{solv} and M^- as initiators in anionic polymerization, we tried to prepare them in two solvents of particular interest, dioxane and toluene [23].

In dioxane alone, only cesium gives a blue solution (Cs^-). In the presence of complexing agent I, Na, K, Rb and Cs dissolve well, but only the M^- absorption band is observed (Fig. 8). This result is consistent with a significant shift of equilibria 4 and 5 to the left.

In toluene, the metals are normally insoluble and a cation complexing agent (I) is required to dissolve them [7,27,30]. In all cases examined, the addition of cryptand I tended to give an aromatic radical anion, as demonstrated by ESR spectroscopy. This behavior may be represented by the following equilibrium.



(14)

We obtained blue solutions in toluene only for Na. In that case the solution

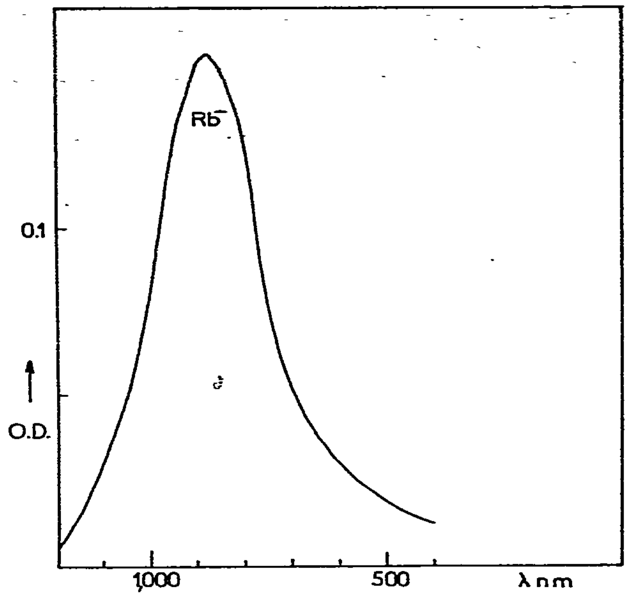
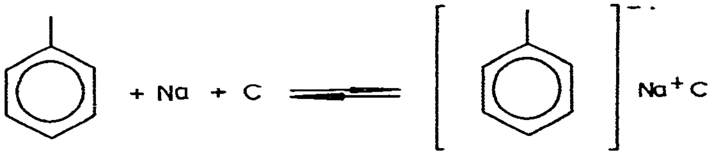


Fig. 8. Spectrum at 11°C of Rb^- in dioxane in the presence of I. (l 0.05 cm, t_c 20 min, [I] 1.2 × 10^{-3} mol l^{-1}).

exhibited ESR and optical behavior (Fig. 9) which indicated the presence of both the anion radical and Na^-. The properties of this absorption band and that in THF are given in Table 5. The peak position and temperature coefficients in toluene allow us to infer the presence of Na^-.

The overall equilibrium scheme given previously (equilibrium 14) must then be modified to include the presence of Na^-.



(14)

(15)

TABLE 5

PEAK POSITIONS AND TEMPERATURE COEFFICIENTS FOR Na^- IN TOLUENE AND THF

	THF	Toluene
λ_{max} (nm) at −50°C	680	690
$d(\bar{\nu}_{max})/dt$ (cm^{-1} deg^{-1})	17.5 ± 0.9	15 ± 1

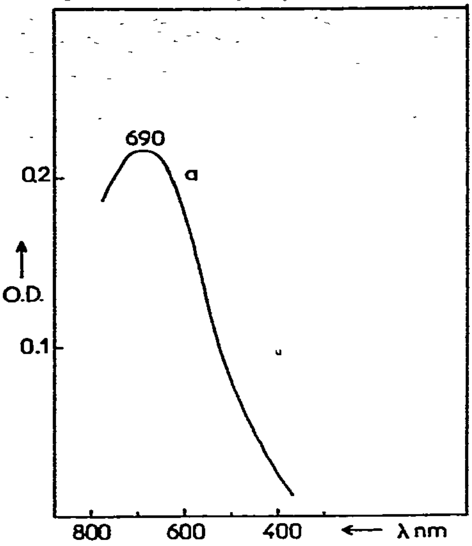


Fig. 9. Spectrum at −50°C of Na^- in toluene in the presence of I. (l 0.51 cm, t_c 1 h, [I] 1.9 × 10^{-2} mol l^{-1}, R = 100).

The concentration of total Na in toluene solution indicates the low efficiency of complexing agent (I) in this solvent.

([Total Na]/[I] $\simeq$ 0.01, [Na^-]/[Total Na] $\simeq$ 0.05).

Acknowledgements

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References

1 J.L. Dye, M.G. Debacker and V.A. Nicely, J. Amer. Chem. Soc., (1970) 5226.
2 J.L. Dye, M.T. Lok and F.J. Tehan, Ber. Bunsen, Gesellsch. Phys. Chem., 75 (1971) 659.
3 M.T. Lok, F.J. Tehan and J.L. Dye, J. Phys. Chem., 76 (1972) 2975.
4 J.L. Down, J. Lewis, B. Moore and G.W. Wilkinson, a Proc. Chem. Soc., (1957) 209. b J. Chem. Soc., (1959) 3767.
5 I.M. Panayotov, C.B. Tvetanov and I.V. Berlinova, Makromol., Chem., 134 (1970) 313.
6 I.M. Panayotov, I.V. Berlinova and N.P. Matev, a C.R. Acad. Bulg. Sci., 2410 (1971) 1231. b Mona. Fur. Chem.,103 (1972) 1119.
7 a J.M. Lehn, S. Boileau, B. Kaempf, F. Schué, J. Cau, J. Moinard and S. Raynal. Br. Fr. No. 7335061 (1973). b S. Boileau, B. Kaempf, S. Raynal, J. Lacoste and F. Schué, Polymer Letters Ed., 12 (1974)

211. c B. Kaempf, S. Raynal, A. Collet, F. Schué, S. Boileau and J.M. Lehn, Angew. Chem. Inter. Ed., 13 (1974) 611. d J. Lacoste, B. Kaempf, S. Bywater and F. Schué, Polymer Letters Ed., 14 (1976) 291.

8 M. Gold, W.L. Jolly, Inorg. Chem., 1 (1962) 818.

9 J.G. Kloosterboer, L.J. Giling, R.P.H. Rettschnick and J.D.W. van Voorst, Chem. Phys. Lett., 8 (1971) 462.

10 R.R. Dewald and J.L. Dye, J. Phys. Chem., 68 (1964) 121.

11 M. Ottolenghi, K. Bar Eli, H. Linschitz and T.R. Tuttle Jr., J. Chem. Phys., 49 (1964) 3729.

12 M.G. Debacker and J.L. Dye, J. Phys. Chem., 75 (1971) 3092.

13 J.W. Fletcher, W.A. Seddon and F.C. Sopchyshyn, Can. J. Chem., 51 (1973) 2975.

14 E.A. Shaede, L.M. Dorfman, G.J. Flynn and D.C. Walker, Can. J. Chem., 51 (1973) 3905.

15 G.A. Salmon, W.A. Seddon and J.W. Fletcher, Canad. J. Chem., 52 (1974) 3259.

16 W.A. Seddon, J.W. Fletcher, F.C. Sopchyshyn and J. Jevcak, Canad. J. Chem., 52 (1974) 3269.

17 V. Mazzacurati and G. Signorelli, Lett. Nuovo Cimento. 12 (1975) 347.

18 F.Y. Jou and L.M. Dorfman, J. Chem. Phys., 58 (1973) 4715.

19 S. Nehari and K. Bar Eli, Electrons in fluids, D.J. Jortner and N.R. Kestner 1973.

20 S. Nehari and K. Bar Eli, J. Phys. Chem., 80 (1976) 2117.

21 S. Matalon, S. Golden and M. Ottolenghi, J. Phys. Chem., 73 (1969) 3098.

22 G. Stein and A. Treinin, Trans. Faraday Soc., 55 (1959) 1086, 1091.

23 M. Szwarc, Carbanions living polymers and electron transfer process Interscience Interscience (1968).

24 Farhataziz, L.M. Perkey and R.R. Hentz, J. Chem. Phys., 60 (1974) 717, J. Phys. Chem., 79 (1975) 1651. Int. J. Rad. Phys. Chem., 7 (1975) 719.

25 R.K. Quinn and J.J. Lagowski, J. Phys. Chem., 73 (1969) 2326.

26 W. Kuhn, Z. Phys., 33 (1925) 408.

27 S. Raynal. Thèse de Doctorat d'Université, Montpellier, 1975.

28 M. Viguier, Thèse de Doctorat de 3ème Cycle, Montpellier, 1975.

29 S. Alev, Thèse de Doctorat de 3ème Cycle, Montpellier, 1976.

30 A. Collet, Thèse de Doctorat de 3ème Cycle, Montpellier, 1976.

31 J.L. Dye, M.G. Debacker, J.A. Eyre and L.M. Dorfman, J. Phys. Chem., 76 (1972) 839.

32 J.L. Dye, M.G. Debacker and L.M. Dorfman, J. Chem. Phys., 52 (1970) 6251.

33 M.G. Dague, J.S. Landers, A.L. Lewis, and J.L. Dye, Chem. Phys. Lett., 66 (1979) 169.

34 J.L. Dye, Angew. Chem. Int. Ed. Engl., 18 (1979) 587.