Alkali Metal Solutions in Liquid 15-Crown-5

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Potassium, rubidium, caesium, and mixed alkali metals dissolve in the liquid crown ether, 1,4,7,10,13-pentaoxacyclopentadecane (15-crown-5), to give intensely coloured solutions; spectroscopic studies (optical, e.s.r., and n.m.r.) revealed alkali metal anions, solvated electrons, and various cation–electron aggregates in these systems.

Although the chemistry of alkali metals in amine and ether solvents containing (external) complexing agents, *e.g.* crown ethers and cryptands, has been the subject of extensive research,[1] by comparison investigations of liquid complexing agents remains relatively unexploited.[2,3] Thus the crown ethers 12-crown-4 (12C4) and 15-crown-5 (15C5) are liquid under ambient conditions and they provide a medium which fulfils the dual functions of complexing agent and solvent. Here we describe the investigation of solutions of the alkali metals K, Rb, and Cs in 15-crown-5, as well as mixed metal samples.

The alkali metals potassium, rubidium, and caesium dissolve in 15C5 to give blue–black solutions, while mixed alkali metals dissolve more readily to give highly concentrated

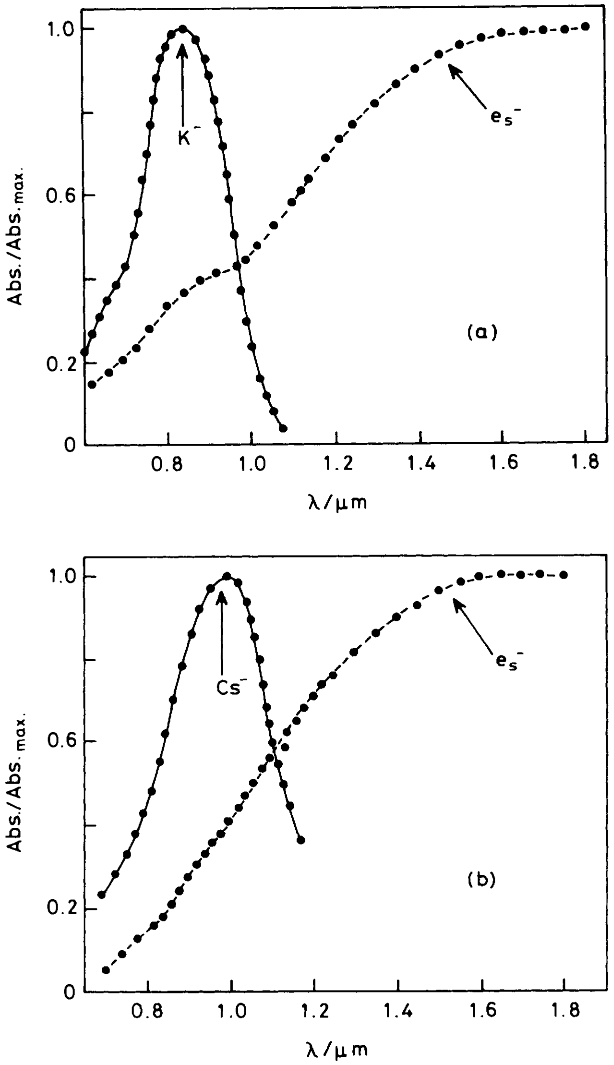

Figure 1. Room temperature optical absorption spectra of (a) potassium metal and (b) caesium metal in 12-crown-4 (——) and 15-crown-5 (----) solvents. The ordinate scale (unitless) shows the absorption, scaled to that at the peak maximum.

solutions which are bronze-red (NaK, NaRb, NaCs) or dark blue-black (KRb, RbCs). Interestingly, lithium and sodium appear to be insoluble in 15C5. This is surprising in view of the specificity[4] of the 15C5 cavity for Na^+ but we note that lithium, similarly, does not dissolve in 12-crown-4.[2] Sodium, however, dissolves in 15C5 in the presence of a heavier alkali metal or when an amine or ether cosolvent is added.

Three techniques have been used to identify the various species present in the metal solutions: optical, e.s.r., and n.m.r. spectroscopy. Figure 1 shows the room temperature optical absorption spectra in the near i.r. region for K and Cs solutions in 15C5 and 12C4. The spectra in 15C5 are dominated by a very broad absorption band extending from 0.8 to 1.8 μm which, by analogy with pulse radiolysis studies on neat 15C5,[5] is assigned to the solvated electron, e_s^-. For potassium solutions the shoulder observed at 0.85 μm is characteristic of the potassium anion, K^-.[1] In contrast, solutions of these metals in 12C4[6] do not noticeably exhibit a band due to the solvated electron (Figure 1); instead the spectra indicate the presence of very high concentrations of alkali metal anions, M^-. In the single metal–15C5 solutions our results suggest that formation of e_s^- and solvated cations, M_s^+, is favoured compared to the situation in 12C4 solutions; in simple terms, dissociation of the alkali anions appears to be facile in 15C5, *viz.* equation (1). Optical spectra of mixed metal–15C5 and -12C4 solutions should help to elucidate the thermodynamics associated with these processes; a study of the forty or so metal–solvent combinations is currently in progress.

$$M^- \rightleftharpoons M_s^+ + 2e_s^- \qquad (1)$$

E.s.r. spectra from frozen solutions of single and mixed metals in 15C5 exhibit a narrow resonance at $g = 2.0023 \pm 0.0004$ whose linewidth (ΔH_{pp}) varies between 3.0 and 5.0 G ($1\ G = 10^{-4}\ T$) and corresponds to a spin–spin relaxation time, T_{2e}, of the order of 10 to 20 ns. This e.s.r. signal saturates at very low microwave power levels, typically 0.01 mW, yielding spin–lattice relaxation times,[7] T_{1e}, in the range 0.2—0.3 ms. These features are entirely consistent with an assignment to the trapped or solvated electron in the vitreous solid.

The existence of metal (cation)-based aggregates in the frozen solutions is also clear from the e.s.r. spectra. At the present time it is, however, uncertain whether this is a loose 'ion-pair' species ($M_s^+e_s^-$) with unresolved hyperfine coupling to the metal nucleus or a contact ion-pair species showing a weakly resolved hyperfine interaction. In 12C4 solutions both these species have been identified.[6] On thawing both the single and mixed metal samples an extremely narrow e.s.r. line ($\Delta H_{pp} \simeq 0.08$ G) is obtained; this motionally-narrowed signal almost certainly represents a time-average of all paramagnetic species present in solution.

N.m.r. measurements were performed on the neat solvent, on single and mixed metal solutions and also on metal solutions containing added cosolvents. ^1H and ^{13}C spin–lattice relaxation times (T_{1n}) for neat 15C5 (250—310 K) yield an activation energy for the relaxation process of $\simeq 25$ kJ mol^{-1} which is comparable with the value obtained for neat 12C4.[8] Moreover ^1H and ^{13}C relaxation rates in metal–15C5 solutions are typically an order of magnitude faster than in the neat crown. The corresponding ^{39}K, ^{85}Rb, ^{87}Rb, and ^{133}Cs solutions show either very weak n.m.r. signals from the alkali anion (for $^{39}K^-$) or no anion resonance (^{85}Rb, ^{87}Rb, ^{133}Cs) at all. None of the samples exhibited cation resonances; this is indicative of a very large exchange width ($\sim\pi^{-1} < A_M^2 > \tau_M$) for the association complex $M_s^+e_s^-$ in solution. Here $<A_M^2>$ is the mean square coupling constant and τ_M is the electron–cation residence time. The lack of M^- signals is entirely consistent with our optical studies which indicate that e_s^- is the major negatively charged species in the single metal solutions (Figure 1).

^{23}Na N.m.r. spectra of mixed metal samples show a narrow signal ($\Delta\nu_{\frac{1}{2}} = 4.8$ Hz) diagnostic of Na^- ($\delta \simeq -61$ p.p.m.).[3,8] In the corresponding 12C4[8] solutions the width of this line was 1.9 Hz, reflecting the lower viscosity of the solvent [10 cP (12C4) *cf.* 29 cP (15C5)]. The spin–lattice relaxation time, T_{1n}, of Na^- in 15C5 is $\simeq 100$ ms at 300 K. The temperature dependence of T_{1n} suggests, once again,[8] that a relatively inefficient quadrupolar mechanism is responsible for relaxation in Na^-. Addition of a cosolvent to alkali metal–15C5 solutions increases the sample stability and allows routine detection of all the alkali metal anions Na^-, K^-, Rb^-, and Cs^- by n.m.r. spectroscopy.

It is of interest to note that metal–15C5 solutions are less stable than their 12C4 analogues. Addition of a $-CH_2-$ group to alcohols[9] or amines[10] has been observed to affect significantly the lifetime of radiation-induced e_s^-. Our pulse radiolysis studies[5] have indeed shown that the first order rate constant for electron decay in 15C5 ($\sim 5 \times 10^6$ s^{-1}) is considerably slower than in 12C4 ($\sim 2.5 \times 10^7$ s^{-1}).

Finally, in mixed metal–15C5 solutions at room temperature the formation of red–bronze (NaK, NaRb, NaCs samples), blue (KRb), and black (KCs, RbCs) crystalline materials has been routinely observed. It is likely that these are alkalide salts, $M^+(15C5)_2M^-$, or electrides, $M^+(15C5)_2e^-$, as isolated by Dye and coworkers[1,11] in ether and amine systems. Further studies of these solids are now in progress.

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