Solvated Electrons and Electron–Cation Aggregates in Solutions of the Alkali Metals in 12-Crown-4†

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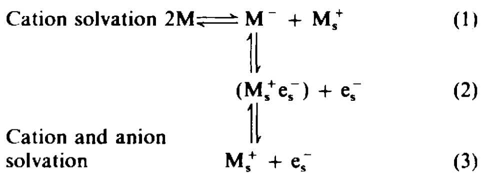
The alkali metals sodium, potassium, rubidium, and caesium dissolve in the cyclic ether 12-crown-4 (1,4,7,10-tetraoxacyclododecane) to give blue solutions containing metal cations, metal anions, electrons, and cation–electron pairs. The metal anions give rise to a characteristic optical absorption band; Na^- and Rb^- have also been detected by n.m.r. as singlet resonances at high field. E.s.r. signals due to solvated electrons and electron–cation pairs are detected in frozen solutions; on melting the two resonances combine to give a single, time-averaged signal.

The alkali metals, alkaline earth metals, and certain lanthanide elements dissolve spontaneously in anhydrous liquid ammonia and related solvents to form metastable blue solutions known as 'metal solutions'.[1] These solutions contain both solvated electrons (e_s^-) and solvated metal cations (M_s^+) in the dilute regime.[2,3] Increasing the metal concentration gives rise to a number of aggregate species, *e.g.* the ion pair, $M_s^+e_s^-$, and alkali metal anions, M^- (Scheme).[3]



$$\begin{array}{lcr} \text{Cation solvation } 2M \rightleftharpoons & M^- + M_s^+ & (1) \\ & \Updownarrow & \\ & (M_s^+e_s^-) + e_s^- & (2) \\ \text{Cation and anion} & \Updownarrow & \\ \text{solvation} & M_s^+ + e_s^- & (3) \end{array}$$

Scheme.

The relative proportions of M^-, $M_s^+e_s^-$, and e_s^- present are governed both by the nature of the non-aqueous solvent and the metal concentration.[4] A continuing problem in metal solution chemistry has been the limited solubility of metals in all but a few solvents. With the discovery of macrocyclic, polydentate ligands such as crown ethers and cryptands, this problem was largely overcome.[5] By adding these cation-complexing agents to metal solutions the range of solvents for dissolving metals has been greatly expanded; metal solubilities in excess of 0.2 mol dm^{-3} have been reported.[6] The crown ether or cryptand fulfils another function besides enhancing metal solubility. In most cases relatively strong complexes are formed between the added ligand and the metal cation. The cation is therefore stabilised by insertion into the complex, M^+L (L = crown or cryptand), equation (4), and spontaneous recombination of the metal

$$M^+ + L \rightleftharpoons M^+L \qquad (4)$$

cation and anion [as given in equation (1)] is thereby prevented. Thus the overall reaction in metal–crown ether or cryptand–solvent systems may be expressed in equation (5) and large

$$2M + L \rightleftharpoons M^+L + M^- \qquad (5)$$

concentrations of alkali metal anions may be generated. This led to the first observation of alkali metal anions in the condensed phase by n.m.r. spectroscopy[7] and has also permitted the synthesis of two new classes of ionic solid, namely 'alkalides' and 'electrides', in which the anions are alkalide ions, M^-, or trapped electrons respectively.[3]

Despite the fact that several crown ethers, such as 12-crown-4 and 15-crown-5 (1,4,7,10,13-pentaoxacyclopentadecane) are liquid at room temperature,[8] their use as potential solvents for the alkali metals has remained relatively unexploited.[9] Metal–crown ether solutions are therefore complementary to the corresponding three-component systems in which the crown ether is added as an external complexing agent to the metal solution. In the present systems, the crown ether is used to fulfil the dual functions of complexing agent and solvent. In this paper we describe the use of 12-crown-4 as a solvent for sodium, potassium, rubidium, and caesium metals. The paramagnetic and diamagnetic species present in metal–12-crown-4 solutions are characterised by a combination of e.s.r., n.m.r., steady-state optical absorption spectroscopy, and preliminary pulse-radiolysis measurements.

Results and Discussion

Metal–Crown Ether Solutions.—Sodium, potassium, rubidium, and caesium metals dissolve in anhydrous 12-crown-4 [m.p. 16 °C, b.p. 67—70 °C (0.5 mmHg)] to produce blue solutions.[9] These solutions are stable at ambient temperatures under high-vacuum conditions for prolonged periods; when in contact with excess metal they remain blue for several days at room temperature. The solubility of sodium in 12-crown-4 has been estimated[9] to be in excess of 1.6×10^{-2} mol dm^{-3}, but we have been able to dissolve sodium–potassium alloy (Na–K) in concentrations of *ca.* 0.3 mol dm^{-3} as gauged by n.m.r. The samples prepared for optical, e.s.r., and n.m.r. studies reported here were saturated metal solutions. The concentration of metal was found (by atomic absorption) to be *ca.* 0.1 (Na, K, Rb samples) or 0.4 mol dm^{-3} (Cs samples). Lithium metal does not dissolve in 12-crown-4.

Optical Absorption Spectra.—The room temperature optical absorption spectra obtained from solutions of sodium, potassium, rubidium, and caesium are shown in Figure 1(*a*). A single, intense band is observed in each case. The bands are broad, structureless and the wavelength of maximum absorbance is metal-dependent (Na, 670 ± 10; K, 840 ± 20; Rb, 890 ± 20; Cs, 990 ± 20 nm). Also, the bands are strongly asymmetric on the high-energy side. These features are consistent with an assignment to a species of stoicheiometry M^-, and by analogy with optical measurments in other solvents[5] the band is attributed to alkali metal anions. The wavelengths reported

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† 1,4,7,10-Tetraoxacyclododecane.

Non-S.I. units employed: mmHg ≈ 133 Pa, eV ≈ 1.60×10^{-19} J, G = 10^{-4} T.

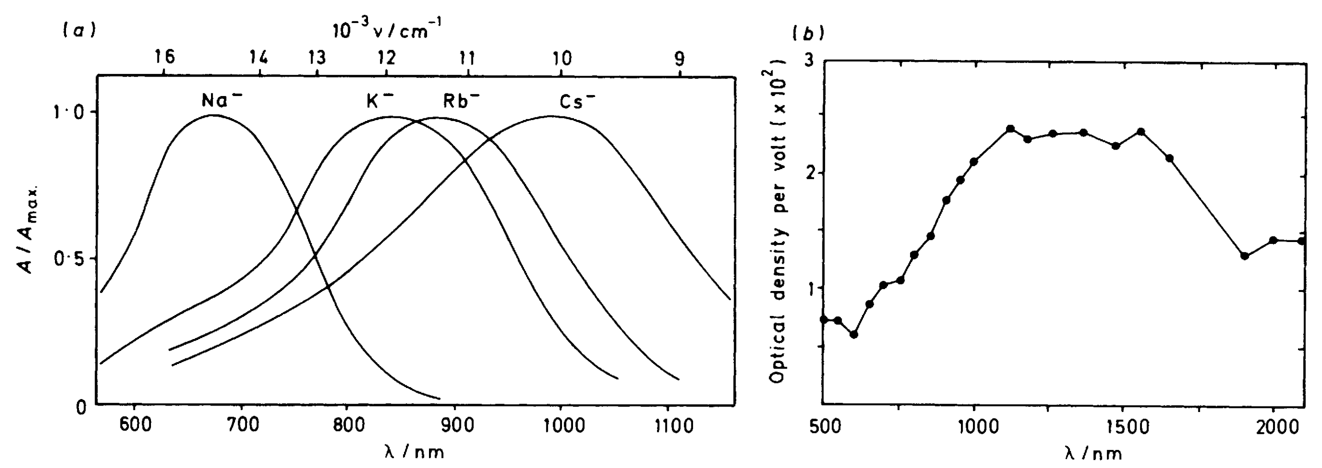

Figure 1. (*a*) Room temperature optical absorption spectra of metal–12-crown-4 solutions; (*b*) room temperature pulse radiolysis spectrum (arbitrary units) of neat 12-crown-4

here are in fair agreement with earlier reports of Na$^-$ ($\lambda_{max.}$ = 660 ± 20 nm) and K$^-$ ($\lambda_{max.}$ = 890 ± 20 nm) in 12-crown-4.[9] Note also the presence of Na$^-$ in K, Rb, and Cs solutions, almost certainly originating from sodium extracted from the Pyrex preparation cell.

No i.r. absorptions which could be attributed to solvated electrons were detected in the metal solutions, despite an earlier report of a band due to e_s^- in K–12-crown-4 at 1 800 nm.[9] The optical spectrum of e_s^- in 12-crown-4, obtained by pulse radiolysis of the pure solvent, is shown in Figure 1(*b*). The end of pulse spectrum (0.2-μs pulses) shows a peak between wavelengths of 1 100 and 1 500 nm; assignment to e_s^- was based on the complete disappearance of this peak when the solution was saturated with the electron scavenger N_2O.* The difference in absorption wavelength between the K–12-crown-4[9] and pulse radiolysis results may be an effect of metal concentration; a similar phenomenon is reported in metal–ammonia solutions, where $\lambda_{max.}$ shifts to longer wavelength with increasing concentration.[10] Alternatively, the band at 1 800 nm[9] may be a feature of the crown ether molecule itself; we have observed similar weak absorptions at 1 720 nm in the spectrum of pure 12-crown-4.

The wavelength of the solvated electron absorption maximum in 12-crown-4 is similar to that in ammonia (1 504 nm).[11] While $\lambda_{max.}$ strictly indicates the $1s \rightarrow 2p$ energy separation between the ground and excited states of e_s^-, a red shift is generally attributed to a decrease in electron solvation energy. Thus the chemical potential of e_s^- in 12-crown-4 is about the same as that in NH_3.

In summary, the optical spectra reveal high concentrations of M$^-$ in alkali metal–12-crown-4 solutions. Conversely, they provide no evidence for high concentration of e_s^- in these metal solutions. This is in accord with earlier work showing that in less polar solvents such as polyethers the ratio of metal anions to solvated electrons is generally larger than in liquid ammonia.[4]

N.M.R. Spectra.—The steady-state optical spectra do not allow distinctions to be made between the various possible structures for M$^-$ in solution.[3] The most logical description of this species is a 'genuine' alkali metal anion with two electrons in the outer *s* orbital. However, the optical spectra could also be assigned to species such as a triple ion, $e_s^-M_s^+e_s^-$, formed by aggregation of two solvated electrons and the solvated cation, or by an ion pair between M_s^+ and the electron pair e_2^{2-}, or by an 'expanded' anion in which two electrons are in an expanded orbital around a solvated metal cation.[12] The important feature of all these structures except the alkali metal anion is the presence of a *solvated* cation.

The observation of the ^{23}Na n.m.r. spectrum of Na$^-$ in Na–12-crown-4 solutions provided conclusive evidence that Na$^-$ is a genuine anion with two electrons in the 3*s* orbital.[13] The n.m.r. spectrum of Na$^-$ in 12-crown-4 is shifted little (δ = −61.8 ± 0.1 p.p.m. at 300 K relative to a Na$^+$–D_2O reference sample) from the value calculated for gaseous Na$^-$ (δ = −63.1 p.p.m.).[14] The absence of any large paramagnetic shift and the extreme narrowness of the line (width at half-height, $\Delta\nu_{\frac{1}{2}}$ = 10 Hz) show that the solvent is effectively excluded from interaction with the 2*p* electrons. This indicates that Na$^-$ is an alkali metal anion with the 3*s* orbital screening the 2*p* electrons from interaction with the solvent and providing a highly symmetric environment. All other models for the species of stoicheiometry M$^-$ involve cation solvation and would introduce a solvent-dependent paramagnetic shift.

The ^{87}Rb n.m.r. spectrum of Rb$^-$ in Rb–12-crown-4 solutions has been reported previously.[13] For this anion a moderate paramagnetic shift from the value for Rb$^-$ in the gas phase is observed: δ = −191 ± 2 p.p.m. for Rb$^-$ in 12-crown-4 at 300 K, compared with the calculated value of −213.6 p.p.m. for gaseous Rb$^-$.[13] In addition, the n.m.r. linewidth of Rb$^-$ in 12-crown-4 is broad ($\Delta\nu_{\frac{1}{2}}$ = 1 000 Hz at 300 K) and the nuclear relaxation rate is much higher ($T_1^{-1} \geqslant 1.25 \times 10^3$ s^{-1} at 297 K) than for Na$^-$ in the same solvent (T_1^{-1} = 5.35 s^{-1} for a Na–K–12-crown-4 solution at 300 K). However, the assignment of the ^{87}Rb n.m.r. resonance to the rubidide ion is unambiguous due to the extremely large diamagnetic shift from the Rb$^+$–D_2O reference. The other experimental parameters suggest that the nuclear shielding of Rb$^-$ in the liquid state is significantly decreased and that a considerable degree of interaction with the solvent exists for Rb$^-$. Incomplete shielding of the outer *p* electrons of Rb$^-$ and Cs$^-$ in metal–cryptand–solvent systems has been noted previously.[14] Evidence for a measureable degree of solvent participation in the ground-state wavefunction of K$^-$ and Rb$^-$ has also come from a study of the photodetachment of electrons from solvated alkali metal anions by e.s.r.[15]

Although the optical spectra indicate the presence of high concentrations of potassium and caesium anions in 12-crown-4

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* Extensive measurements will be reported elsewhere (A. Ellaboudy, D. M. Holton, J. Langan, G. A. Salmon, and P. P. Edwards, in preparation).

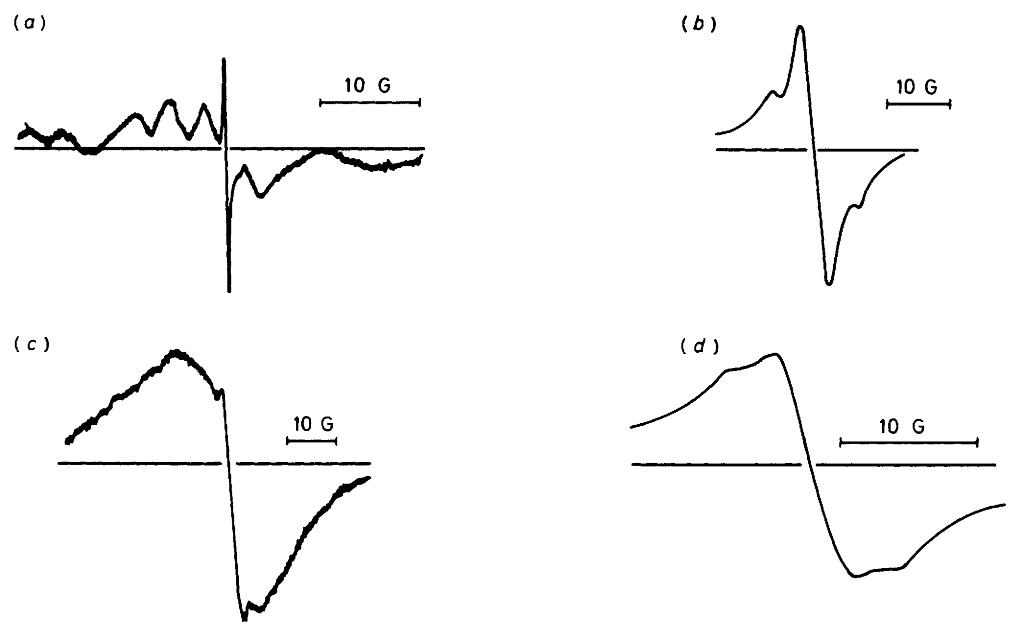

Figure 2. E.s.r. spectra of frozen M–12-crown-4 solutions: (*a*) M = Na, at 40 K, 1 mW microwave power; (*b*) M = K, at 120 K, 10 mW; (*c*) M = Rb at 125 K, 1 mW; (*d*) M = Cs at 25 K, 20 mW

solutions, we have been unable to detect these species by n.m.r. We stress that this is not a problem of sample instability. Exchange processes such as (6) and (7) which effectively limit

$$\mathrm{M_s^+e_s^-} + \mathrm{M^-} \rightleftharpoons \mathrm{M^-} + \mathrm{M_s^+e_s^-} \qquad (6)$$

$$\mathrm{M_s^+} + \mathrm{M^-} \rightleftharpoons \mathrm{M^-} + \mathrm{M_s^+} \qquad (7)$$

the lifetime of $\mathrm{M^-}$ in solution may be fast on the n.m.r. timescale for $\mathrm{K^-}$ and $\mathrm{Cs^-}$, causing the signals to be paramagnetically shifted and broadened beyond the limits of detection.

E.S.R. Spectra.—Metal–crown ether solutions are sufficiently stable in the liquid state for comparative e.s.r. measurments on liquid and solid phases to be made. Figure 2 shows the e.s.r. spectra obtained from frozen solutions of sodium, potassium, rubidium, and caesium in 12-crown-4. In each case, two paramagnetic species were detected which can be identified as the solvated electron, $\mathrm{e_s^-}$, and the corresponding ion pair species, $\mathrm{M_s^+e_s^-}$. The solid phase spectra were not generally reproducible after thawing and refreezing. Fluid solutions exhibited only a single, time-averaged e.s.r. signal. It is interesting to compare the relative intensities of this signal for the various metals. Sodium and rubidium samples, in which $\mathrm{Na^-}$ and $\mathrm{Rb^-}$ have been detected by n.m.r., give e.s.r. signals approximately 100 and 10 times weaker respectively than the corresponding K and Cs spectra. Potassium samples provided the most comprehensive set of results and these are discussed in most detail.

(*i*) *Potassium.* Frozen K–12-crown-4 solutions (Figure 2) showed two superimposed e.s.r. signals at $g = 2.0020$ with peak-to-peak derivative linewidths $\Delta H_{pp} = 2.5 \pm 0.5$ and 12 ± 1 G at 120 K. The narrow and broad resonances are assigned respectively to the electron ($\mathrm{e_s^-}$) and the ion pair ($\mathrm{K_s^+e_s^-}$). The broad linewidth of the ion-pair signal and its inhomogeneous 'power saturation behaviour' (discussed below) indicate unresolved hyperfine coupling to the metal nucleus. The ion-pair linewidth remained constant up to the melting point of the solution (*ca.* 290 K) while that of the electron decreased slightly to $\Delta H_{pp} = 2$ G near the melting temperature. The intensity of both signals diminished with heating.

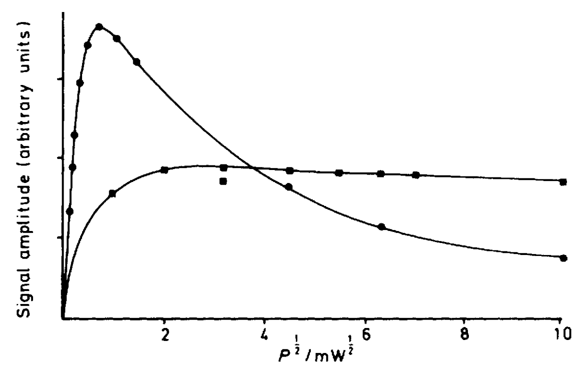

Figure 3. Power saturation of solvated electron (●) and ion-pair (■) resonances in frozen potassium–12-crown-4 solution at 120 K

The microwave power saturation behaviour of the two resonances is illustrated by Figure 3. The $\mathrm{e_s^-}$ resonance is a homogeneous signal; analysis of its saturation behaviour[16] yields relaxation times $T_1 = (5 \pm 2) \times 10^{-5}$ s and $T_2 = (2.6 \pm 0.5) \times 10^{-8}$ s at 120 K; T_1 decreases with heating. The ion pair resonance has a Gaussian lineshape, and its power saturation (Figure 3) is typical of an inhomogeneous signal.[16]

On melting, the two resonances of frozen K–12-crown-4 solutions were replaced by a single, Lorentzian line at $g = 2.0020 \pm 0.0003$ with $\Delta H_{pp} = 0.06$ G. This resonance arises from rapid exchange between $\mathrm{e_s^-}$ and $\mathrm{M_s^+e_s^-}$; similar narrow Lorentzian signals are seen in liquid metal–ammonia[17] and liquid metal–hexamethylphosphoramide (hmpa)[18] solutions. The resonance is approximately ten times stronger than that from $\mathrm{e_s^-}$ in solid 12-crown-4 glasses just below the melting point. A power saturation study gave $T_1 = (5 \pm 1) \times 10^{-6}$ s, $T_2 = (1.1 \pm 0.2) \times 10^{-6}$ s at 297 K.

The characteristics of the resonances in metal–12-crown-4 solutions are summarised in the Table.

(*ii*) *Rubidium.* As indicated in Figure 2 and the Table, the e.s.r. characteristics of Rb–12-crown-4 solutions are analogous to

Table. E.s.r. signals in M–12-crown-4 solutions

Phase (T/K)	M	g^a	ΔH_{pp}/G	T_1/s	T_2/s
Frozen solution e_s^- (120)	Na[b]	2.0027(5)	0.3 ± 0.1	$(5 \pm 2) \times 10^{-6}$	$(2.2 \pm 0.7) \times 10^{-7}$
	K	2.0020(3)	2.5 ± 0.5	$(5 \pm 2) \times 10^{-5}$	$(2.6 \pm 0.5) \times 10^{-8}$
	Rb	2.0016(5)	4 ± 1	$(1.0 \pm 0.5) \times 10^{-4}$	$(1.7 \pm 0.5) \times 10^{-8}$
	Cs	2.0020(5)	3.4 ± 0.5	$(1.5 \pm 0.5) \times 10^{-5}$	$(1.5 \pm 0.5) \times 10^{-8}$
Frozen solution $M_s^+e_s^-$ (120)	Na[b]	2.0050(10)	—	—	—
	K	2.0020(3)	12 ± 1	—	—
	Rb	2.0028(10)	17 ± 1	—	—
	Cs	2.0028(10)	11 ± 1	—	—
Fluid solution (297)	Na	2.0023(3)	0.075 ± 0.01	$(2.5 \pm 1.0) \times 10^{-6}$	$(8.7 \pm 1.0) \times 10^{-7}$
	K	2.0020(3)	0.06 ± 0.01	$(5 \pm 1) \times 10^{-6}$	$(1.1 \pm 0.2) \times 10^{-6}$
	Rb	2.0023(3)	0.53 ± 0.05	$(4.5 \pm 0.5) \times 10^{-7}$	$(1.3 \pm 0.1) \times 10^{-7}$
	Cs	2.0019(3)	0.25 ± 0.05	$(3.7 \pm 1.2) \times 10^{-7}$	$(2.4 \pm 0.4) \times 10^{-7}$

[a] Values in parentheses denote error in last digit. [b] Measured at 4 K.

those for K–12-crown-4. In the frozen solutions, resonances due to the electron and the ion pair $Rb_s^+e_s^-$ are observed. The linewidths of both species are independent of temperature over the range 4—200 K. The electron resonance has a Lorentzian lineshape while the shape of the ion-pair signal is between Lorentzian and Gaussian. Relaxation times for the electron resonance at 120 K are given in the Table; T_1 decreases with heating. The ion-pair signal is inhomogeneously broadened and saturates at a higher power than the solvated electron. Both signals diminish in intensity with heating.

On melting, the e.s.r. spectrum of Figure 2 collapsed to a single, homogeneous resonance as shown by the data in the Table.

(*iii*) *Caesium*. A frozen caesium sample displayed e.s.r. signals attributed to the electron and to an ion pair (Figure 2 and Table). A broad signal at higher g value, not shown in Figure 2, is assigned to a second ion-pair species. Relaxation times for the solvated electron were independent of temperature (Table).

The thawed sample gave e.s.r. spectra at room temperature consisting of a single Lorentzian line (Table).

(*iv*) *Sodium*. The e.s.r. spectra from frozen Na–12-crown-4 solutions, as shown in Figure 2, are rather different from those of the other metal–crown ether samples at low temperature. At 4 K, two distinct resonances are observed; a narrow singlet at g = 2.0027 and a quartet of lines centred at g = 2.0050 typical of hyperfine coupling to the ^{23}Na nucleus ($I = \frac{3}{2}$) in the ion pair $Na_s^+e_s^-$. The hyperfine coupling constant, A = 3.75 G, indicates 1.2% atomic character relative to gaseous atomic sodium (A_{iso} = 316 G).[19] Both paramagnetic species are present in low concentration, producing rather weak e.s.r. signals. The narrow linewidth and saturation behaviour of the singlet suggest that this resonance is due to the solvated electron (Table). In the liquid phase at 297 K the e.s.r. spectrum consists of a weak Lorentzian peak (Table).

Electron Relaxation in Metal–12-*Crown*-4 *Solutions*.—(*i*) *Frozen solutions*. The solvated electron and ion-pair signals both have g values close to free spin as expected. The ion-pair signal is inhomogeneously broadened; this arises from hyperfine coupling to the metal nucleus at the ion-pair site.[19] For the electron signal, $T_1 \neq T_2$ (Table), implying that $\omega\tau > 1$ where ω is the microwave frequency and τ the correlation time for magnetic interactions.[20] In contrast, we find that the electron signal in frozen potassium–hmpa solutions has $T_1 = T_2$ at 50 K.[19] The correlation time may be interpreted as the inverse of the 'hopping' frequency with which the electron moves between trapping sites in the matrix; the above results indicate a lower hopping frequency in 12-crown-4. Our pulse radiolysis results in the liquid phase suggest that the electron is better solvated by 12-crown-4 than by hmpa;[21] this is consistent with a greater trapping energy in the frozen glass and consequently a slower hopping frequency.

(*ii*) *Fluid solutions*. In the fluid solutions the correlation time is determined by the electron hopping rate $1/\tau_e$ and the correlation time due to diffusion in the liquid, τ_D: equation (8). The

$$1/\tau = 1/\tau_e + 1/\tau_D \qquad (8)$$

hopping rate now refers to motion of the electron among both the 'free electron' and 'ion-pair' sites. In metal–ammonia solutions both hopping and diffusion processes are significant.[17] The correlation time in a liquid of viscosity η should vary with temperature as η/T.[17] Viscosity data are not available for 12-crown-4 but the metal solutions were undoubtedly highly viscous at the temperature of this study which was just above their melting point. The long correlation time which this implies is consistent with the measured relaxation times T_1 and T_2 which differ by a factor of about five (Table). In metal–ammonia solutions the two relaxation times are almost equal[17] indicating a considerably shorter correlation time.

Conclusions

This paper describes the use of a combination of spectroscopic techniques to demonstrate the presence of solvated electrons, metal anions, and electron–cation pairs in solutions of the alkali metals in 12-crown-4. The anions Na^- and Rb^- are spherically symmetrical with two electrons in the outer s orbital. Solvated electrons and electron–cation pairs in frozen solutions exchange slowly enough to give distinct e.s.r. signals. On melting, a single time-averaged signal is seen; electron relaxation appears to be inhibited by the high viscosity of the solutions at room temperature.

Experimental

Sample Preparation.—Solutions of alkali metals in anhydrous 12-crown-4 were prepared in Pyrex apparatus using stringent high-vacuum techniques ($\leqslant 10^{-4}$ mmHg). The metals were melted under vacuum and forced into capillary tubes using dried argon gas. Final metal purification was achieved by multiple distillation in the sample preparation cell. 12-Crown-4 (Aldrich) was refluxed over sodium–potassium alloy for 1 h and distilled into break-seal ampoules, then distilled again from sodium–potassium alloy in the sample preparation cell. Finally, purified solvent and metal were mixed and the resulting blue solution transferred to an optical cell, n.m.r., or e.s.r. tube as required.

Optical Absorption Spectra.—These were recorded using a Cary 17 spectrophotometer with quartz optical cells. Due to the intense absorption of the solution, a film of liquid covering the inside walls of the cell was sufficient to give a strong spectrum.

Pulse Radiolysis.—The pulse radiolysis spectrum of pure 12-crown-4 was recorded using 0.2-μs pulses of 3-MeV electrons from a Van de Graaff generator at the Cookridge Radiation Research Centre, University of Leeds. The crown ether, purified as described above, was further distilled into a 1-cm path-length quartz radiolysis cell and degassed by three freeze–pump–thaw operations before sealing off under vacuum.

N.M.R. Spectra.—The n.m.r. spectra of ^{23}Na, ^{85,87}Rb, and ^{133}Cs were measured using a JEOL FX-90Q pulsed Fourier-transform spectrometer; the ^{39}K nucleus was studied using a Bruker WH 400 spectrometer. Chemical shifts were measured relative to a solution of the appropriate metal chloride in D_2O.

E.S.R. Spectra.—The spectra were recorded on a Varian E-109E *X*-band spectrometer; *g* values were measured by reference to the standard 1,1-diphenyl-2-picrylhydrazyl (dpph) radical at $g = 2.0036$. Low temperatures were maintained with either an Oxford Instruments ESR-900 helium cryostat or a home-built apparatus using nitrogen gas as refrigerant.

Acknowledgements

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