838. *Unstable Intermediates. Part XXIV.* Solvated Electrons: A Confined Model.*

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Evidence that solvated electrons are quite strongly confined to cavities in the solvent is summarised, and a simple model is suggested which links the optical properties of solvated electrons to those of *F* centres in alkali-halide crystals and to those of solvated halide ions.

UNCERTAINTY still shrouds the identity of the paramagnetic species which results when metals are in dilute solution in ammonia and other solvents.[1] Trends away from the simple solvated anion model and towards one described as the " expanded metal atom " or " monomer," [2] having the unpaired electron centred in an " expanded " *s*-type orbital on the solvated cation have now been reversed to a considerable extent.[3,4] However, recent electron resonance results for various metal–amine solutions [5,6] seem to support the " expanded metal atom " theory for these solutions.

The discovery of a transient species in electron-irradiated water, having a strong absorption in the visible region with a maximum at about 14,300 cm.$^{-1}$, has been taken as evidence for " solvated " electrons in this medium.[7-9] Recently it has been found, using the pulsed-electron technique, that a species with a very similar absorption can be detected in alcohols.[10]

Our main purpose is to discuss these results in terms of current theories for " solvated " electrons and to propose a simple model which seems to accommodate them adequately.

* Part XXIII, preceding Paper.

[1] Symons, *Quart. Rev.*, 1959, **13**, 99.
[2] Becker, Lindquist, and Alder, *J. Chem. Phys.*, 1956, **25**, 971.
[3] Clark, Horsfield, and Symons, *J.*, 1959, 2478.
[4] Gold, Jolly, and Pitzer, *J. Amer. Chem. Soc.*, 1962, **84**, 2264.
[5] Vos and Dye, *J. Chem. Phys.*, 1963, **38**, 2033.
[6] Bar-Eli and Tuttle, *Bull. Amer. Phys. Soc.*, 1963, **8**, 352.
[7] Boag and Hart, *Nature*, 1963, **197**, 45; Keene, *ibid.*, 1963, **197**, 47.
[8] Hart and Boag, *J. Amer. Chem. Soc.*, 1962, **84**, 4090.
[9] Grossweiner, *Science*, 1963, **141**, 805.
[10] Taub, Sauer, and Dorfman, *Discuss. Faraday Soc.*, 1963, **36**, 206.

Symbols.—For convenience we list the following symbols and their definitions:

a	Lattice parameter.
R_0	Square-well radius.
R_e	Effective radius of solvated electron.
$(e^-)_{solv.}$	The solvated electron.
$E(e^-)$	The energy of the $1s \longrightarrow 2p$ transition of solvated electrons.
$E(I^-)$	The energy of the first ultraviolet absorption band for solvated iodide ions.
M^+	Any alkali metal ion.
M	Either the " expanded metal atom " [2] or an ion-pair, $M^+_{solv}(e^-)_{solv}$.
M_2	Diamagnetic species, thought to be either an " expanded metal molecule " or the species $[M^+_{solv}(e^-)_{solv}]_2$.

The Solvated Electron Model.—In order to understand the electrical properties of dilute ammonia solutions it seems necessary to invoke an equilibrium $M^+_{solv} + e^-_{solv} \rightleftharpoons M$, M being a non-conducting paramagnetic species. Since, under conditions in which the concentration of M must be quite high, there are no major changes in the magnetic or optical properties of these solutions, it seems probable that M is an ion-pair of some kind rather than the " monomer " postulated by Becker *et al.*[2] If this is correct then the ^{23}Na Knight shift [11] either arises through low concentrations of " expanded metal atoms " [4] having considerable free-atom character, or, more probably there is a small, but finite, interaction between the " solvated " electron and cations in the ion-pair unit.

The Polaron Model.—If the electron is not primarily influenced by the cation, then it must be bonded by solvent in some manner. Since there are no low-lying antibonding orbitals associated with the solvent molecules under consideration, the bonding must arise from a form of self-trapping *via* electronic and orientational polarisation of solvent molecules. If the resulting orbital is diffusely spread over many solvent molecules then the medium can be treated as a continuous dielectric. If, however, the electron is strongly confined to a small cavity in the solvent then it will resemble in some ways an anion such as iodide, and, provided its time of residence is not too short, it may be effectively bound by solvent molecules orientated around the cavity. This " anion " or " *F*-centre " model represents one extreme situation and our aim is to explore its utility and limitations. Before doing so, however, we summarise recent evidence in favour of a confined model. Earlier evidence has been discussed previously.[1]

Evidence for the Confined Nature of Solvated Electrons.—(i) Quantitative treatments of the problem using the continuous dielectric approximation give results which imply considerable localisation within cavities.[12]

(ii) The relatively high stability of electrons in irradiated water would be inexplicable if the electron was diffusely spread over a large volume, since back reactions would then be extremely easy.

(iii) The results for γ-irradiated alkali-hydroxide glasses, if correctly interpreted,[13] indicate a confinement at least as great as that for *F* centres. Thus the contribution to the width of the electron resonance spectra by the first shell of cations is small, and they have a negligible effect on the *g*-values, in marked contrast with results for *F* centres. On the other hand, protons of water molecules make an important contribution to the line-width.

(iv) Except for iodides, added salts have only a minor effect on the spin resonance and optical absorption spectra of metal–ammonia solutions.[14]

(v) There are marked similarities between the optical spectra of iodide ions solvated in

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[11] McConnell and Holm, *J. Chem. Phys.*, 1957, **26**, 1517.

[12] Jortner, Rice, and Wilson, " Metal Ammonia Solutions: Physico Chemical Properties," Mémoires et Travaux des Facultés Catholiques de Lille, France, W. A. Benjamin, Inc., New York, 1964.

[13] Blandamer, Shields, and Symons, *Nature*, 1963, **199**, 902; preceding Paper.

[14] Catterall and Symons, *J.*, 4342.

crystals and the spectra of electrons in comparable environments. These are indicated in Fig. 1, and support the concept that the environments are similar in each instance. This aspect is discussed in greater detail below.

(vi) There are also marked similarities between the absorption bands for *F* centres and solvated electrons, which are depicted in Fig. 2, and discussed below. Since electron-spin resonance results for *F* centres show clearly that the electron is strongly confined to the vacancy and the first shell of cations,[15] these similarities suggest that solvated electrons are also strongly confined.

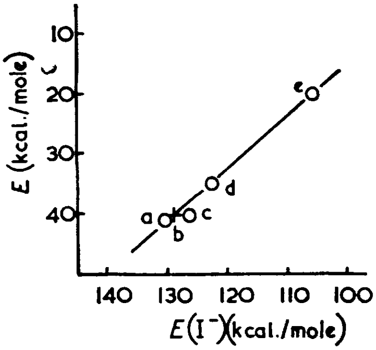

FIG. 1. Comparison of $E^{20}_{\max}$ for electrons and for iodide ions in various environments.

a, Ethanol. *b*, KI crystal. *c*, Water. *d*, 12M-Aqueous ammonia. *e*, Ammonia.

Square-well Model.—Since our concern is with the interpretation of spectra rather than with the far more difficult task of estimating total energies, and since we wish to probe in a simple way the concept that solvated electrons are rather strongly confined, we discuss these results in terms of a square-well model which has proved quite successful in accommodating the spectral properties of solvated halide ions.[16] This model is also the simplest which can accommodate the marked dependence of *F*-centre transitions upon the lattice parameter (*a*). This is shown in Fig. 2, where *a* is plotted against R_0, the square-well radius calculated from this equation.

TABLE 1.

Cavity radii and lattice parameters for the solvated electron.

System	$E^{20}_{\max}$ (kcal. mole^{-1})	R_0 (Å)	*a* (Å)	Cavity radius [a] (R_c) (Å)
e^-–NH_3	20·31 [b]	6·66	5·06	3·66
e^-–H_2O	40·53 [c]	4·72	3·50	2·10
e^-–EtOH	41·08 [d]	4·69	3·48	2·08
e^-–$MeNH_2$	21·71 [e]	6·45	4·91	3·51
e^-–$H_2N{\cdot}CH_2{\cdot}CH_2{\cdot}NH_2$	22·32 [f]	6·36	4·83	3·47
e^-–Alkali glass	48·59 [g]	4·31	3·17	1·77

[a] Calc. by *a* — 1·4, see text. [b] Ref. 4. [c] Refs. 7, 8, 9. [d] Ref. 10. [e] Blades and Hodgins, *Canad. J. Chem.*, 1955, **33**, 411. [f] Dewald and Dye, *J. Phys. Chem.*, 1964, **68**, 121. [g] Ref. 13.

$$E(e^-) = 1{\cdot}04\ h^2/8mR_0^{\,2} \qquad (1)$$

which is appropriate for the $1s \longrightarrow 2p$ square-well transition.[17] This shows that R_0 and *a* are nearly linearly related, and that R_0 is given approximately by the equation

$$R_0 = 1{\cdot}243a + 0{\cdot}353 \qquad (2)$$

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[15] Gourary and Adrian, *Solid State Physics*, 1960, **10**, 127.

[16] Smith and Symons, *Trans. Faraday Soc.*, 1958, **54**, 346; Griffiths and Symons, *ibid.*, 1960, **56**, 1125.

[17] Kauzmann, " Quantum Chemistry," Academic Press Inc., New York, 1957, p. 188.

More sophisticated treatments of the *F*-centre problem have been given,[15] but it does not seem reasonable to attempt such calculations for solvated electrons since very little is known about the structure of the solvent cavities.

One use of the correlation in Fig. 2 is that it provides a link between the experimental lattice parameters for alkali halides and the ill-defined square-well radius. Using Ivey's empircal rule connecting lattice parameter with the *F*-centre maxima,[18]

$$a^{1\cdot84} = \lambda_{\text{max.}}\,(\text{Å})/703 \qquad (3)$$

we have calculated an effective lattice parameter for electrons in various solvents, and include the results in Fig. 2.

It seems (Fig. 2) that electrons in water may be compared with electrons in iodide vacancies in crystals, whereas electrons in ammonia appear to be in somewhat larger cavities. Since the lattice parameter for crystals includes the cation radius, we can estimate a crude " ionic " radius (R_e) for the electron by subtracting about 1·4 Å from the value of a calculated from the spectrum.[16] The results are in Table 1, and seem to be in reasonable accord with expectations.[1]

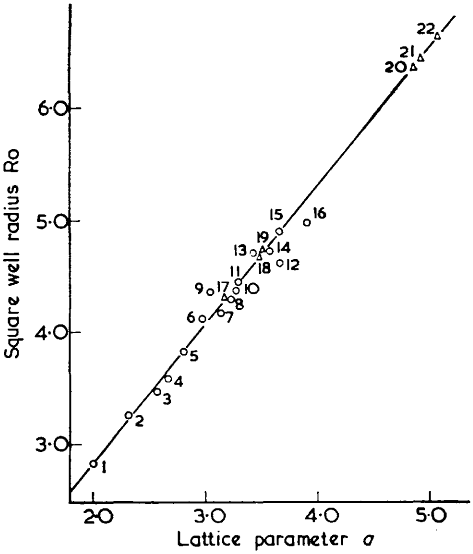

Fig. 2. Correlation of the calculated square-well radius R_0 with the experimental lattice parameter a (ref. 21) at room temperature. *F*-Centre absorption data for sodium chloride type crystals taken from ref. 15, for cæsium halides from Avakian and Smakula, *Phys. Rev.*, 1960, **120**, 2007. Lattice parameters for solutions of electrons calculated from Ivey's rule, $a^{1\cdot84} = \lambda_{\text{max.}}\,(\text{Å})/703$.

F Centres in 1, LiF; 2, NaF; 3, LiCl; 4, KF; 5, NaCl; 6, NaBr; 7, KCl; 8, NaI; 9, CsCl; 10, RbCl; 11, KBr; 12, CsBr; 13, RbBr; 14, KI; 15, RbI; 16, CsI.

Electrons in 17, alkali glasses (77°K); 18, alcohol; 19, water; 20, ethylenediamine; 21, methylamine; 22, ammonia.

Comparison with Iodide Ions and F *Centres.*—It is noteworthy that the shift, $\Delta E(\text{I}^-)$, in the band maximum of iodide on going from water to ammonia (20·6 kcal. mole^{-1}), is very similar to that for the absorption assigned to electrons in these solvents (20·2 kcal. mole^{-1}). This analogy is still more striking when it is realised that results for iodide ions in water are very close to those for iodide ions in crystals, just as is found for aquated electrons, and furthermore, for both systems, maxima for alcoholic solutions are slightly higher in energy than those for water. We stress that the environmental effects on halide ion spectra are unique to such systems, and clearly distinguish transitions which can be described as " charge transfer to solvent " from other electronic transitions.[19]

This parallel is predicted by the simple square-well model for the excited states of iodide ions,[16] which, despite criticisms,[20] has been found to be adequate in explaining many properties of the solutions. Thus we can write

$$\Delta E(\text{I}^-) = h^2/8m[1/R_0^{\,2}(\text{I}^-,\text{H}_2\text{O}) - 1/R_0^{\,2}(\text{I}^-,\text{NH}_3)] \qquad (4)$$

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[18] Ivey, *Phys. Rev.*, 1947, **72**, 341.

[19] Smith and Symons, *Trans. Faraday Soc.*, 1958, **54**, 338.

[20] Jortner and Treinin, *Trans. Faraday Soc.*, 1962, **58**, 1503.

whilst $\Delta E(e^-)$ for the $1s \longrightarrow 2p$ transition for solvated electrons is given by

$$\Delta E(e^-) = 1{\cdot}04h^2/8m[1/R_0^2(e^-,H_2O) - 1/R_0^2(e^-,NH_3)] \qquad (5)$$

These equations are consistent with the trends shown in Fig. 1.

One weakness of this comparison is that the calculated square-well radius for aquated iodide ions is close to the effective lattice parameter[16] whilst R_0 values for F centres and solvated electrons are larger, as given by eqn. (2) and indicated in Fig. 2. This discrepancy probably reflects a greater inadequacy of a square-well model for F centres, for which the $2p$ level cannot be far removed from the top of the well.

Other points of similarity between the spectrum of F electrons and halide ions are as follows: (1) The effect of increasing the temperature is in all cases to shift the band to lower energies in an approximately linear fashion. Some appropriate values are given in Table 2. (2) Similarly, the effect of added electrolytes is to shift the band for electrons in ammonia and for iodide ions in water to higher energies, the effect on solvated electrons being somewhat greater. (3) Both the shapes of the bands for F centres and for solvated electrons, and their oscillator strengths, are very similar (Table 2). Both bands show a greater broadening on the high energy side which appears to be characteristic of such systems.

TABLE 2.

Characteristics of absorption spectra of the electron and iodide ion in various media at room temperature.

	Electron			Iodide anion	
	Oscillator strength	ν_{max} (cm.$^{-1}$)	dE/dT (cal. mole^{-1} deg.$^{-1}$)	ν_{max} (cm.$^{-1}$)	dE/dT (cal. mole^{-1} deg.$^{-1}$)
NH_3	0·73 ± 0·05 [a] 0·65 ± 0·05 [b]	6837 6700	32 [k]	37,060 [n]	95
H_2O [c]		13,890 (i) 14,290 (ii)		44,270 [l]	32
EtOH	0·6 [d]	14,370 [e]		45,707 [l]	10
H_2O–NaOH [f] ...		17,000	not detectable		
NaCl	0·7 [g]	21,830 [i] 21,280 [j]	2·5 [m]		
KCl	0·83 [h] 0·66 [g]	17,990 [i]	5·5 [m]		
KBr	0·71 [g]	16,000	5·3 [m]		
KI	0·46 [g]	14,514 [i] 13,890 [j]	7·3 [m]		

[a] Douthit and Dye, *J. Amer. Chem. Soc.*, 1960, **82**, 4472. [b] Ref. 3. [c] (i) Boag and Hart, *Nature*, 1963, **197**, 45; (ii) ref. 8. [d] L. M. Dorfman, personal communication. [e] Ref. 10. [f] Ref. 13. [g] Rausch and Heer, *Phys. Rev.*, 1957, **105**, 914. [h] Pick, *Ann. Phys.*, 1938, **31**, 365. [i] Molner, Ph.D. Thesis, Massachusetts Institute of Technology, 1940, quoted in ref. 15. [j] Ottmer, *Z. Phys.*, 1928, **46**, 798. [k] Mean value calculated from Douthit and Dye, *J. Amer. Chem. Soc.*, 1960, **82**, 4472; Gold and Jolly, *Inorg. Chem.*, 1962, **1**, 818; Blades and Hodgins, *Canad. J. Chem.*, 1955, **33**, 411. [l] Ref. 19. [m] Mollwo, *Z. Physik.*, 1933, **85**, 56. [n] Ref. 16.

Electrons in Hydroxide-ion Vacancies.—Here we compare the value of the lattice parameter calculated by the use of Ivey's rule (3·17 Å) with that to be expected for an electron in a hydroxide-ion vacancy.[13] The radius for hydroxide ion, modified to accommodate experimental results for alkali halides,[21] is about 1·4 Å. This gives 2·8 Å for the lattice parameter, but neglects the free-space increment for solvated ions.[16,22] For iodide ions in water, at room temperature, this extra increment is thought to be about 0·45 Å,[22] but there should be a contraction on cooling. These alternative methods for estimating the effective lattice parameters give very similar results, and this adds further support for the F-centre model for the blue species in irradiated alkali hydroxide glasses.[13]

Structure of the Dimer.—If these concepts have any validity, then it seems that the

[21] Blandamer and Symons, *J. Phys. Chem.*, 1963, **67**, 1304.
[22] Hepler, *J. Phys. Chem.*, 1957, **61**, 1426.

postulate of an e_2^{2-} species in metal–ammonia solutions may still require consideration despite the strong arguments in favour of a diamagnetic unit having electrons paired, but associated with separate cavities.[4] Both species would presumably have one or two adjacent solvated cations.

The argument in favour of two neighbouring cavities is that the optical absorption of the diamagnetic and paramagnetic species are very similar, and hence that, from an optical viewpoint, each electron can undergo similar transitions whether paired or unpaired. This conclusion requires some modification in our view, since, in order for pairing to be effective the dimer unit must have a ground state so far removed from the next level that the splitting is both greater than the pairing energy and greater than the thermal energy. Otherwise the species should exist, at least in part, in a triplet spin state. The situation is indicated schematically in Fig. 3, and it seems that for the optical spectrum to consist of a single broad line in the 6000 cm.$^{-1}$ region, one or more coincidences are required. In that case, other models can be postulated which require comparable coincidences, one such being the e_2^{2-} model. As has been stressed,[1] by analogy with F' centres it might have been expected that the absorption band for this species would be found on the low-energy side of the band for solvated electrons. However, in contast with alkali halides, the solvent cavities can adjust to the new constraint, and if this consists of a general tightening of the cavities then the band would shift to higher energies and could well occur in a region comparable with that for the band for single electrons.

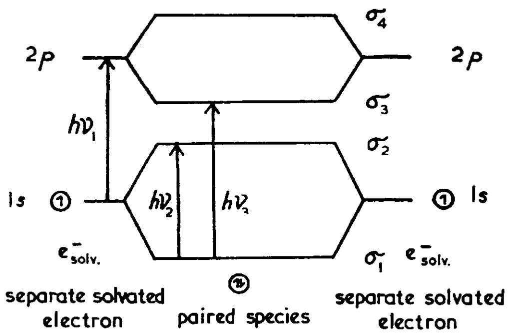

FIG. 3. Possible energy-level diagram for the diamagnetic species consisting of two adjacent cavities with one electron in each. Possible electronic transitions are indicated as $h\nu_i$.

Whilst we do not consider that there is strong support for this model, neverthless the following factors do seem to be significant: (i) Iodide ions interact very readily with " solvated " electrons. This has been explained in terms of a slight tendency for the electron to penetrate inside the solvent shell around iodide.[14] (ii) A similar interaction is found for iodide adjacent to trapped electrons in alkali hydroxide glasses.[13] In neither instance is it thought that the ion I^{2-} is a major component, but simply that it makes a real but slight contribution. Nevertheless, the situation is comparable with that for the e_2^{2-} species. Thus, when the electron is far removed from either I^- or $e^-_{solv.}$, it will experience a repulsion. When, however, it penetrates inside the solvent shell this repulsion is partly counterbalanced by the stabilising influence of the oriented solvent molecules. (iii) There is some evidence that a diamagnetic species of the sort under consideration can be formed in alkali hydroxide glasses.[13] In this case the absorption band is indeed on the low energy side of the e_1 band, but here, as with F' centres, there can be little or no adjustment of the cavity to suit the extra negative charge.

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