# Electron Spin Resonance Spectra of Aquated Alkali Metal Atoms

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Electron spin resonance spectra are reported for $\gamma$-irradiated rubidium and caesium hydroxide aqueous glasses at 77 K, which differ markedly from those observed previously for lithium, sodium, and potassium hydroxide systems; one of the new features, more photosensitive than $e^-_{tr}$ in sodium and potassium systems and unaffected by deuteriation, is attributed to aquated rubidium atoms.

Extensive studies of $\gamma$-irradiated alkali metal hydroxide aqueous glasses using e.s.r. and optical absorption spectroscopy at 77 and 4 K have revealed the presence of species described as trapped (or solvated) electrons, $e^-_{tr}$.[1—8] These species are characterised by a single, easily saturated e.s.r. absorption with a width between points of maximum slope,

$\Delta H_{ms}$, of ca. 1.4 mT, and by a broad optical absorption with $\lambda_{max}$ of ca. 650 nm, which is responsible for the blue colour. Both features are readily removed on photobleaching with visible light.

All investigators have generally stressed that these spectral properties of $e^-_{tr}$ were independent of the nature of the alkali

metal cation, although, in some early work, Kevan[1] suggested a slight cation contribution to the linewidth of $e^-_{tr}$ in LiOH, NaOH, and KOH (2—5 M) aqueous ices, whilst Blandamer, Shields, and Symons[2] reported a slightly broader e.s.r. absorption in RbOH aqueous glasses.
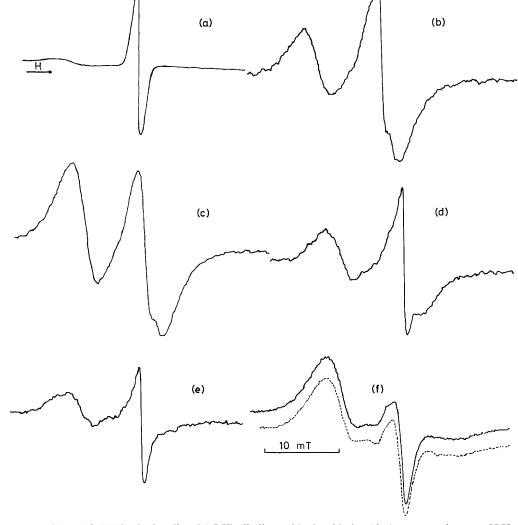
More recently, Kroh and collaborators[3—5] have reported minor perturbations in the optical and e.s.r. spectra of $e^-_{tr}$ at different concentrations (8 and 18 M) of NaOH in aqueous glasses, and on decreasing the temperature of irradiation from 77 to 4 K. These effects were explained in terms of electrons being associated with cations in shallow, relatively less stable traps, but the red shift at 4 K in the optical absorption of $e^-_{tr}$ for 8 M NaOH has also been attributed by van Leeuwen et al.[6] to electrons stabilised near positive holes. Furthermore, Lin and Kevan[7] have explained the decrease in $e^-_{tr}$ linewidth in irradiated 10 M NaOH with increasing temperature by an increase in vibrational and torsional motion in the local environment of the solvated electron complex.

We have examined the e.s.r. spectra of $\gamma$-irradiated RbOH aqueous glasses at 77 K and compared them with the equivalent KOH system. We find spectral characteristics quite different to those reported for NaOH and KOH systems. The new components are attributed to the presence of species best described

as aquated alkali metal atoms, $Rb_{aq}$. The parallel studies of KOH aqueous glasses are in full agreement with previous reports[5,8] and gave no evidence of $K_{aq}$.

Aqueous solutions of alkali metal hydroxides ($ca.$ 10 M), quenched in liquid nitrogen in spherical form and subjected to $\gamma$-irradiation at 77 K, were examined by e.s.r. spectroscopy using conventional techniques. Spectra were recorded on a JEOL FE—3X spectrometer (X-band, 9.1—9.2 GHz) and photobleaching with visible light ($\lambda >$ 340 nm) was performed in situ.

The e.s.r. spectrum of a RbOH aqueous glass immediately following $\gamma$-irradiation ($ca.$ 30 min at a dose rate of $2 \times 10^3$ Gy $h^{-1}$) is compared in Figure 1 with that obtained from a corresponding sample of KOH aqueous glass. Both spectra exhibit features attributable to $O^-$, but the sharp singlet resonance present in KOH glasses [Figure 1(a)] and assigned to $e^-_{tr}$, is clearly much less prominent in the spectrum of the heavier alkali metal system. In addition, a new broad feature is apparent in the spectrum of the Rb system [Figure 1(b)]. By subtraction, widths of $\Delta H_{ms} =$ 1.4 and 3.5 mT, respectively, were determined for these two features, with both $g$-factors close to the free spin value (2.0023). As the microwave power was increased both the narrow (1.4 mT) and the broad



**Figure 1.** E.s.r. spectra (9.1—9.2 GHz) of $\gamma$-irradiated (77 K) alkali metal hydroxide ($ca.$ 10M) aqueous glasses at 77 K. (a) KOH, microwave power $10^{-2}$ mW; (b) RbOH, microwave power $10^{-2}$ mW; (c) RbOH, microwave power 2 mW; (d) RbOH after a brief period of photobleaching ($\lambda >$340 nm; 15 s); (e) RbOH after a further period of photobleaching ($\lambda >$340 nm; 50 s); (f) CsOH, microwave power $10^{-2}$ mW, before (———) and after (– – –) prolonged photobleaching.

(3.5 mT) features in the RbOH system saturate much more rapidly than that of $O^-$ [Figure 1(c)].

The broad component in the e.s.r. spectrum of the RbOH aqueous glass was more photosensitive than the narrow line attributed to $e^-_{tr}$. For example, a brief period of photobleaching led to a decrease in the intensity of the broad component and a loss of a small fraction of the $O^-$ resonance [Figure 1(d)], before any significant bleaching of the narrow (1.4 mT) absorption had occurred (the e.s.r. spectrum of the KOH system was practically unchanged under similar conditions). Complete loss of the broad feature, accompanied by some loss of the narrow line (consistent with the loss of $e^-_{tr}$ in KOH), resulted from further photobleaching [Figure 1(e)]. Prolonged photo-irradiation led to the complete disappearance of the narrow component in both systems and significant loss of $O^-$ in RbOH aqueous glasses.

When similar experiments were conducted in $D_2O$ glasses the linewidth of $e^-_{tr}$ in the KOH system decreased to $\Delta H_{ms} = 0.45$ mT, as previously reported.[2,8] A similar narrowing of the 1.4 mT signal was observed for $RbOD-D_2O$, but the width of the 3.5 mT line remained unaffected by deuteriation, indicating that the width arises predominantly from hyperfine interactions with the cation.

In marked contrast to the RbOH systems, the e.s.r. spectra of irradiated CsOH aqueous glasses [Figure 1(f)] exhibited little or no trace of the 1.4 mT feature and showed remarkably little change on deuteriation or during photobleaching. The disappearance of the characteristic blue colour during photobleaching was, however, accompanied by some indication of the loss of a very broad feature in the e.s.r. spectra. However, because of restrictions imposed by the subtraction process to remove the $O^-$ contribution it is not possible to characterise signals of width $> ca.$ 10 mT with the same area as the 3.5 mT line observed in RbOH glasses. If the electron–cation hyperfine interaction in an aquated Cs atom were the same as in the Rb case, then we would predict a linewidth of $ca.$ 7 mT stemming from the larger nuclear moment of Cs, so that if either the electron–cation interaction had increased by a factor of $ca.$ 2, or the total yield had decreased by a similar factor, then we would not expect to observe the e.s.r. signals of $Cs_{aq}$ under our conditions.

Summarising, therefore, the saturation characteristics, linewidth, $g$-factor, lack of any anisotropy or resolved hyperfine interactions, and the photosensitivity of the 1.4 mT line in irradiated RbOH aqueous glasses are all very similar to those of the narrow line attributed to $e^-_{tr}$ in irradiated KOH aqueous glasses. These similarities together with the narrowing of this line in $D_2O$ lead us to assign this feature in RbOH aqueous glasses to $e^-_{tr}$.

The microwave power saturation characteristics of the 3.5 mT line clearly distinguish it from the $O^-$ radical ion, whilst the $g$-factor, lack of anisotropy, and photosensitivity are also indicative of a trapped extra electron centre. In support of this contention, the total yields of the centres responsible for

the narrow and broad e.s.r. lines in irradiated RbOH aqueous glasses are very similar to that of $e^-_{tr}$ alone in the KOH system.

Species described as solvated alkali metal atoms have previously been detected in frozen solutions of alkali metals in hexamethylphosphoramide (HMPA).[9] These species were clearly of two types, those exhibiting sharply resolved hyperfine coupling to the metal nucleus, and those in which the metal hyperfine interaction was unresolved but shown to be the predominant source of the linewidth. It appears that the species responsible for the broad component in irradiated RbOH aqueous glasses most resemble these latter centres. Accordingly, the 3.5 mT feature is assigned to *aquated Rb atoms*. We prefer this nomenclature to any ion-pairing description since there is no detectable anisotropy in the 3.5 mT e.s.r. line.

Although dissolution of alkali metals[10] in primary aliphatic amines and ethers, and pulse radiolysis[11] of alkali metal salts in the same solvents have yielded species described as solvated alkali metal atoms, this report is the first, to our knowledge, of the e.s.r. detection of solvated alkali metal atoms in high dielectric media, such as water and ammonia.

In view of the clear observation of two e.s.r. components in irradiated RbOH (10 M) aqueous glasses, and the dependencies of the absorption attributed to $Rb_{aq}$, this proposal is far less contentious than the arguments for the involvement of solvent shared ion-pairs in the e.s.r. spectra of irradiated NaOH aqueous glasses at higher concentrations.[5,12]

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