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The Kinetics of Selective Solvation of the Electron in a Binary Liquid System

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Summary Electrons formed by pulse-radiolysis at 107 K in 2-methyltetrahydrofuran (MTHF) containing 0·3 mole-fraction ethanol are first solvated by MTHF molecules which are then all displaced by ethanol molecules in a diffusion-controlled bimolecular process; the resultant e^-_{alc} species then either decompose unimolecularly or react bimolecularly with a positively charged entity.

THE absorption spectra of electrons in alcoholic media differ markedly from those of electrons in ether. Thus at 77 K λ_{max} for e^-_{alc} in ethanol is close to 600 nm whilst that for e^-_{eth} in MTHF is 1250 nm. At this temperature a mixture of these two substances is glassy over almost the whole composition range and Shields[1] showed that at mole-fractions of ethanol (x) $\geqslant 0·2$ the optical and e.s.r. spectra of the γ-irradiated glass are characteristic of e^-_{alc} whilst at $x \leqslant 0·1$ they are characteristic of e^-_{eth}. The question arises whether glasses of composition $x \geqslant 0·2$ are inhomogeneous on the molecular scale, *i.e.* comprise molecular aggregates of ethanol in a continuous MTHF medium, the newly formed electrons being trapped solely in these aggregates, or whether the glasses are molecularly random, the electrons being trapped in cavities lined with molecules in proportion dictated more by the bulk composition and the MTHF molecules are subsequently displaced by ethanol molecules. In principle this question should be answered by studying either the γ-irradiation at 4 K followed by warming the glass to 77 K (a technique applied by Higashimura[2] to equimolar glycol–water and other glasses) or by pulse radiolysis of the liquid mixture at temperatures where the molecular motions are slow enough to allow time-resolution.

We report here results obtained by the latter method. The apparatus was that described earlier[3,4] but improved in design and in the temperature control of the low temperature cell and the detector system. Generally 0·2 μs pulses of 2·9 MeV electrons delivering *ca.* 5 krad of energy to the cell contents were used and the results obtained for pure ethanol or MTHF agreed with earlier data, displaying in the case of ethanol the blue shift and narrowing of the spectrum observed by Baxendale *et al.*[5]

However for $x = 0·28$ the end-of-pulse spectrum is entirely characteristic of e^-_{eth} having $\lambda_{max} = 1200$ nm but then decays entirely and is replaced by a band with $\lambda_{max} = 575$ nm which is typical of e^-_{alc}. This is illustrated in the Figure for $T = 107$ K. The decay of e^-_{eth} and growth of e^-_{alc} are completely synchronous exponential processes, the time constant of which varies with temperature over the whole range investigated (92 to 134 K) according to equation (1), where $T_0 = 80$ K. The exponential term is

$$k_1 = 10^{9.4} \exp\,[-302/(T - T_0)]\ \mathrm{s}^{-1} \qquad (1)$$

not of the Arrhenius form but is typical of the temperature dependence of rate-processes involving translational displacements in glass-forming liquids, *e.g.* diffusion, ionic mobility, fluidity and diffusion controlled bimolecular reactions.[4,6] These results suggest that the electrons are first trapped mainly as e^-_{eth} in the MTHF which is the better glass-forming liquid and is therefore presumed to have more abundant cavities when not irradiated. These shallow traps are then converted to the deeper alcoholic traps by progressive replacement of MTHF molecules by ethanol molecules [in this multi-step process no isosbestic point is expected, nor is it seen]. If the impedance of the predominant MTHF molecules to the motion through them of ethanol molecules is the rate determining process then it is not surprising that T_0 is close to the value previously[6] proposed for diffusion-controlled processes in pure MTHF. However, we considered it necessary to make direct measurements of T_0 for a medium $x = 0{\cdot}3$ by measuring the temperature dependence of the diffusion-controlled dimerisation of benzyl radicals formed when 0·23 mol dm^{-3} solutions of benzyl chloride are pulse-irradiated. Assuming $\epsilon = 9000$ mol^{-1} cm^{-1}[7] at $\lambda_{max} = 318$ nm we obtained equation (2)

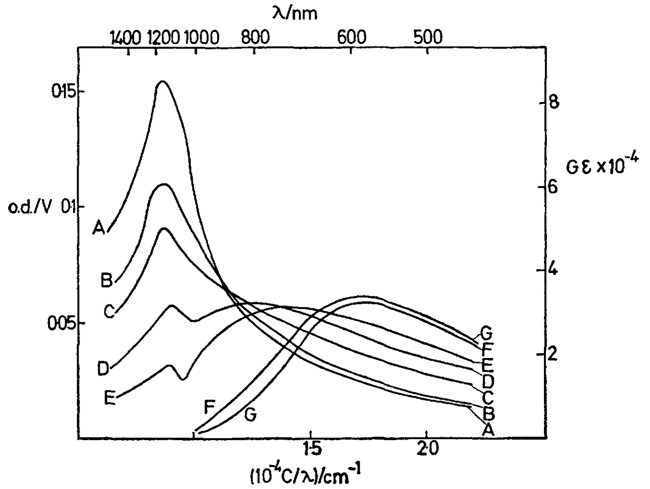

FIGURE. Spectrum of the solvated electron in 0·28 mole-fraction of ethanol in MTHF at 107K as a function of time in μs; A, $t = 0$; B, $t = 3$; C, $t = 10$, D, $t = 20$; E, $t = 30$; F, $t = 100$; G, $t = 180$.

$$k_{bl} = 10^{10.7} \exp\left[-424/(T - 80)\right] \text{M}^{-1}\,\text{s}^{-1} \qquad (2)$$

[The larger numerator in the exponent of equation (2) as compared with (1) is expected on the Cohen–Turnbull model[8] if a larger critical volume is required for translation of benzyl radicals as compared with ethanol molecules.] Finally, e^-_{alc} is not a permanent product but decays both spontaneously (perhaps to form EtO$^-$ + H) and by reaction with a positively charged centre. The rate constant for the former has the normal Arrhenius term, $\exp(-12kJ/RT)$, whilst that for the latter contains the term, $\exp[-293/(T - 80)]$.

The sequence of events in the ethanol–MTHF mixture may be depicted as in the Scheme.

$$\begin{tikzcd}
e^- \arrow[r] & e^-\text{ quasi-free} \arrow[r] & e^-_{eth} \arrow[r, "\text{(I)}"] & e^-_{alc} \arrow[r, "\text{(II)}"] \arrow[d, "\text{(III)}"', "+\text{H}^+_{alc}"] & \text{EtO}^- + \text{H}\cdot \\
& & & \text{H}\cdot &
\end{tikzcd}$$

SCHEME

Reactions (I) and (II) involve translation of molecules through the medium and (II) does not. It does not follow that all binary mixtures behave in this manner and recent evidence[9] indicates that for alcohol–alkane mixtures containing even very small amounts of alcohol any electron localisation in the alkane is undetectable at room temperature and the electron may be solvated only in pre-existing microscopic aggregates of alcohol molecules.

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