

Solvated Electrons and Electron–Cation Aggregates in *N,N*-Diethylacetamide, *N,N*-Dipropylacetamide, *N,N*-Dimethylpropanamide, Tetramethylurea, and Tetraethylurea

Sarah C. Guy,^a Peter P. Edwards,*^a and G. Arthur Salmon^b

^a *University Chemical Laboratory, Lensfield Road, Cambridge, CB2 1EW, U.K.*

^b *Cookridge Radiation Research Centre, University of Leeds, Leeds LS16 6QB, U.K.*

Pulse radiolytic studies on a variety of structurally related solvents are reported which establish the spectral characteristics of the solvated electron in these systems.

The solvents *N,N*-diethylacetamide (DEA), *N,N*-dipropylacetamide (DPA), *N,N*-dimethylpropanamide (DMP), tetramethylurea (TMU), and tetraethylurea (TEA) dissolve certain alkali metals to form metastable blue solutions of varying stability.¹ We report preliminary pulse radiolytic studies which establish the spectral characteristics of the isolated solvated electron in the above solvents, and also probe the structure

and reactivity of sodium cation–electron aggregate species in the metal–solvent system.²

We find that these structurally related solvents effectively span the range of possible competitive processes between electron attachment and electron solvation in non-aqueous solvents. In solutions of sodium tetraphenylborate (NaBPh₄) in DEA we observe transient absorption spectra which we

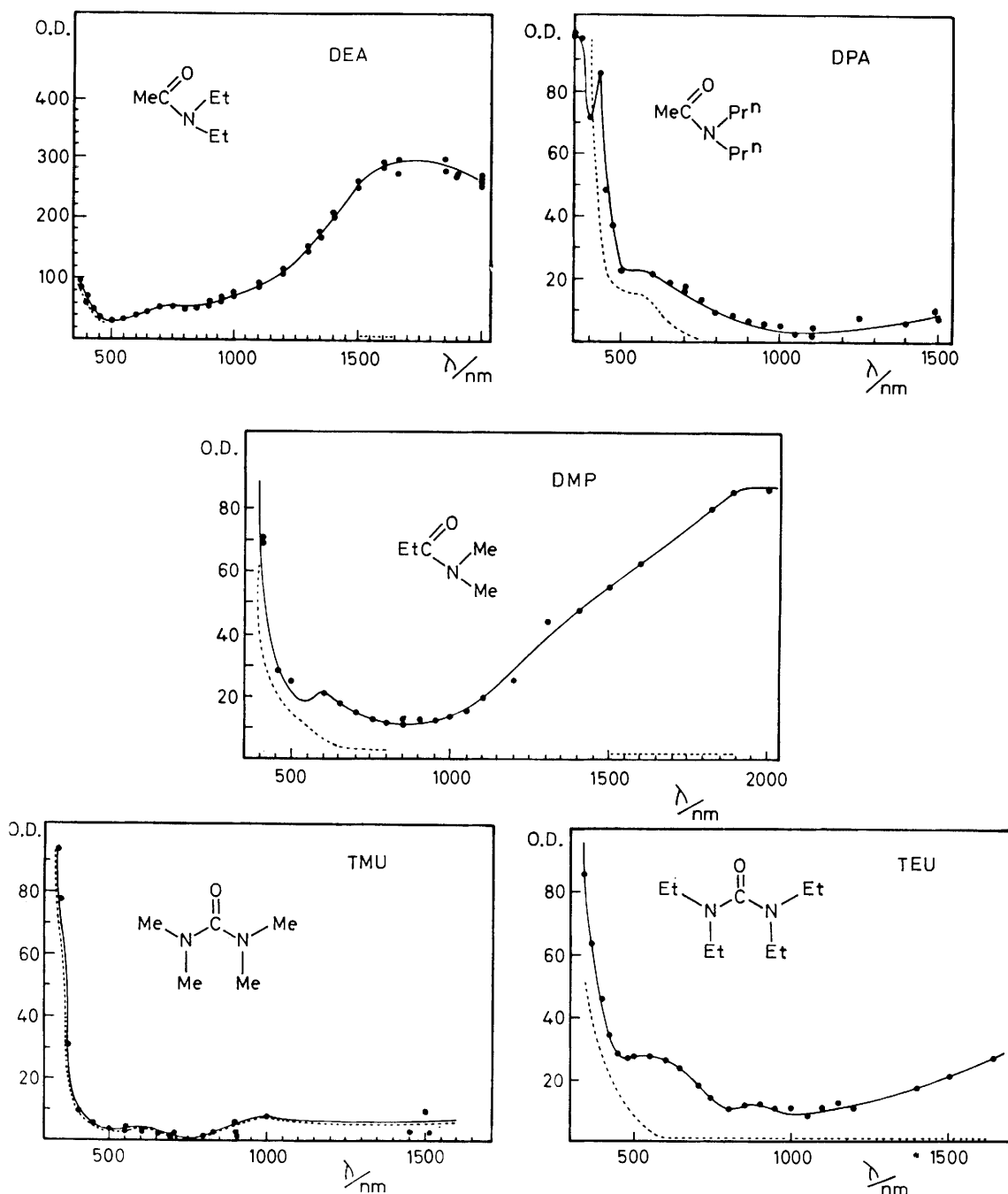


Figure 1. The end of pulse optical absorption spectra obtained from DEA, DPA, DMP, TMU, and TEU, with the corresponding absorption spectra for N_2O saturated solutions (dashed line). O.D. = optical density per unit dose (arbitrary units).

ascribe to Na^- and the sodium cation–electron pair, (Na^+, e_s^-). The relative stability of alkali metal solutions of these solvents may be related to the formation of these species which are known to have reduced reactivity with unsaturated organic molecules as compared with the solvated electron.²

Pulse radiolysis facilities and irradiation cells have been described previously.³ All solvents were obtained in the highest purity commercially available. DEA was purified by refluxing over calcium hydride for 12 h and then distilling under vacuum from freshly prepared Na–K alloy. The remaining solvents DPA, DMP, TMU, and TEU gave some decomposition products in the presence of Na–K alloy; these

solvents were therefore vacuum-refluxed and -distilled from calcium hydride.

The end of pulse spectra obtained using $0.6 \mu s$ electron pulses are shown in Figure 1; the dashed line in each case shows the corresponding absorption spectrum for N_2O saturated solutions. The optical absorption spectrum of DEA shows an intense, broad band at 1700 ± 50 nm, a shoulder at ca. 650 nm, and a steadily increasing absorption below 450 nm. The i.r. band is similar to the reported absorption of the solvated electron (e_s^-) in Na–DEA solutions.¹ The decay of the absorption at 1500 and 1600 nm was first-order with a half-life ($t_{1/2}$) of ca. $0.5 \mu s$. In addition, the i.r. absorption

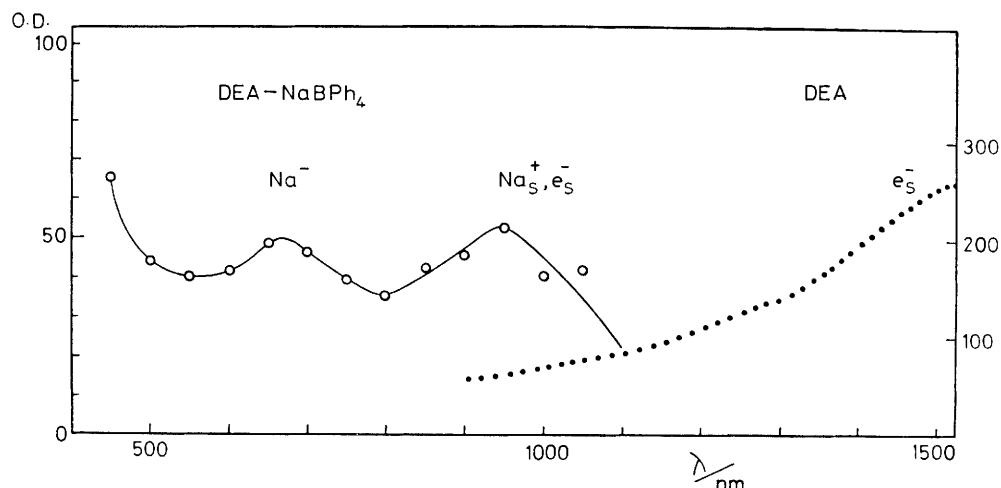


Figure 2. The absorption spectrum obtained from a solution of sodium tetraphenylborate (0.011 M) in DEA. The dotted line shows the absorption spectrum from the solvated electron (*i.e.* in pure DEA). O.D. = optical density per unit dose (arbitrary units).

was completely eliminated in the N_2O saturated solution and this is consistent with an assignment to solvated electrons.⁴

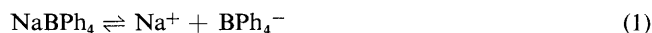
There is similar clear evidence for the solvated electron absorption in DMP. However, the absorption has already reached a steady state during the $0.6 \mu s$ pulse, and this indicates an upper limit of about $0.2 \mu s$ for the lifetime of e_s^- in this solvent. For DPA there is absorption in the i.r. region, some ten times weaker than in DMP, again implying a very short lifetime for e_s^- in this solvent. The absorption spectra for TEU and TMU illustrate the marked differences in solvated electron lifetimes for two similar solvents (Figure 1). In TEU the i.r. absorption is again apparent, and again eliminated in N_2O solution. The steady state absorption is approximately four times weaker than for DMP. In contrast, the absorption spectrum for TMU shows no evidence for a solvated electron indicating its lifetime is much less than $0.6 \mu s$.

The significant differences in the ability of these chemically similar solvents to stabilise and solvate electrons suggests that competitive processes such as reaction at the carbonyl group are subtly dependent on the electronic properties of the molecule. A previous study⁵ of *N*-methylacetamide suggested that the lack of stability of solvated electrons in this solvent was due to the occurrence of keto-enol tautomerism in the singly substituted amide. The present results indicate that solvated electrons are not necessarily stabilised in doubly substituted amides and that other factors may also influence their stability.

Additional absorptions in the visible and u.v. range were also observed. A general pattern emerges (Figure 1) of an absorption around 600 nm which is effectively eliminated in N_2O saturated solutions, and a strong, slowly decaying absorption below 450 nm which extends up to the solvent cut off (at *ca.* 250 nm) and which is unaffected by saturation with N_2O . The former is tentatively assigned to a radical ion species derived from e_s^- (for example the ketyl radical ion).

The addition of $NaBPh_4$ at a concentration of 0.011 M results in a considerable reduction in the decay of the i.r. absorption. Moreover the absorption spectrum changes quite dramatically and two new bands appear; one peak located at 650 ± 20 nm and another at 950 ± 20 nm (Figure 2). The former band is characteristic of the metal anion species Na^- observed in metastable Na -DEA solutions,¹ while the latter

is tentatively assigned to the encounter or ion-pair species (Na_s^+, e_s^-) formed *via* reactions (1) and (2). The large blue



shift of *ca.* 800 nm in the absorption maximum of the ion-pair relative to the isolated e_s^- band indicates a considerable 3s electron density at the sodium cation.⁶ Using previous optical-e.s.r. correlations⁶⁻⁸ in amine and ether solutions we estimate an atomic character of between 20 and 30% for the monomeric species in DEA solutions.

This association of e_s^- with the sodium cation leads to considerable changes in the optical and magnetic properties, and a concomitant reduction in the solvated electron mobility and reactivity towards solute species.

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