

CORRELATION OF THE CTTS SOLVENT SCALE WITH ν_{\max} OF THE SOLVATED ELECTRON. PREDICTION OF BAND MAXIMA
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A good linear correlation has been presented for the absorption maxima of solvated electrons in 17 different solvents and 13 solvent mixtures versus the absorption maxima of the iodide ion in the same medium. It is concluded that the electronic transitions of the solvated electron parallel those of the charge-transfer-to-solvent (CTTS) transitions of iodide ion. The absence of a direct correlation between ν_{\max} of solvated electrons and the static dielectric constant of the medium is emphasized. Based on the CTTS scale of iodide, the optical transitions of e_{solv}^- in other solvents (e.g., alkyl nitriles, phosphates and carbonates) can be predicted.

The phenomenon of electron solvation in organic and inorganic liquids, and the stabilization of these excess electrons have been studied and considered at both the experimental and the theoretical levels (see refs. [1, 2] for recent reviews and references). Attempts have been made to interpret the nature of the optical transitions of solvated electrons in terms of certain properties of the solvent. Correlation with the static dielectric constant (ϵ_S) of the solvent was found [3] for e_{solv}^- in alcohols. Such a linear correlation could not accommodate other solvents such as water, liquid ammonia, amines and esters (a plot is given in ref. [4]). Correlation of the energy levels of e_{solv}^- with the reciprocals of the optical and static dielectric constants [5] was shown to be applicable for a limited range of solvents. Very recently empirical correlations were sought [4] to rationalise the optical properties of e_{solv}^- in a wide range of solvents.

Some years ago a correlation between ν_{\max} of solvated electrons and ν_{\max} of iodide ions was presented

by Anbar and Hart [6], and a linear relationship observed for water, methyl alcohol, ethyl alcohol, ethylenediamine and liquid ammonia. Such an analogy between the charge-transfer-to-solvent (CTTS) spectra of halide ions [7, 8] and that of an electron in the same medium had previously been suggested by Platzman and Franck [9]. However, few attempts have been made to extend this correlation and prove its validity.

Table 1 presents some literature data [10–18] on the absorption maxima (in wavenumbers) of solvated electrons at ambient temperatures in 17 different solvents, ranging from hexamethyl phosphoramide, tetrahydrofuran, ammonia, amine, and water to alcohols. In addition, data of e_{solv}^- in 13 aqueous-organic mixtures and 2 aqueous-electrolyte solutions are included. Some of the data on the absorption maxima of iodide ions in the same medium have recently [11, 19] been determined. The first absorption bands of iodide have been found [11, 19] to be the overall envelope of other underlying (CTTS) bands, and the ν_{\max} presented in table 1 is the resolved A_1 band of iodide. The contribution of other underlying bands to the A_1 band of iodide is particularly significant in red-shifting solvents such as hexamethylphosphoramide and dimethoxyethane.

Fig. 1 shows a plot of $\nu_{\max}(e_{\text{solv}}^-)$ versus $\nu_{\max}(I^-)$ taken from table 1. A reasonably good linear correla-

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Table I
Absorption maxima of iodide ions and solvated electrons in various solvents

No.	Solvent	$\epsilon_S^{\text{a)}$	e_{solv}^-		I^- ^{b)}	
			$T(^{\circ}\text{K})$	$\nu_{\text{max}}(\text{cm}^{-1})$	$T(^{\circ}\text{K})$	$\nu_{\text{max}}(\text{cm}^{-1})$
1.	hexamethyl phosphoramidate	30	298 [10]	4300 4440	298 [11]	37861
2.	methyl tetrahydrofuran	4.6	298 ^{b, c)}	4650	293 [13]	41040 ^{d)}
3.	tetrahydrofuran	8.2	298 ^{b, c)}	4765 ± 115	298 [13]	40675 ^{d)}
4.	dimethoxyethane	7.2	298 ^{b, c)}	5263 ± 223	298 [11]	40837
5.	<i>i</i> -butylamine		298 [6]	6550 ^{e)}	298 [11]	41494
6.	ammonia	17	[6]	6648 ^{f)}	298 [13]	38523 ^{d, f)}
7.	ethylenediamine	14.2	298 [13]	7600	293 [13]	41110 ^{d)}
8.	88% ammonia + 12% water		293 [14] ^{c)}	10300 ± 500	293 [14]	42200 ^{d)}
9.	91% dioxane + 9% water		298 [15]	10500	293 [14]	42600 ^{d)}
10.	79% dioxane + 21% water		298 [15]	12050	293 [14]	43050 ^{d)}
11.	<i>i</i> -propyl alcohol	18.3	300 [16]	12175	293 [13]	45454 ^{d)}
12.	66% dioxane + 34% water		298 [15] ^{c)}	12600	293 [14]	43150
13.	cesium iodide crystal		293 [13]	12600	293 [13]	43950 ^{d)}
14.	79% <i>i</i> -propyl alcohol + 21% water		293 [17]	12750	293 [14]	44300 ^{d)}
15.	rubidium iodide crystal		293 [14]	12800	293 [13]	43400 ^{d)}
16.	<i>n</i> -propyl alcohol	20.1	300 [16]	13465	293 [14]	45350 ^{d)}
17.	70% <i>i</i> -propyl alcohol + 30% water		298 [17] ^{c)}	13600	293 [14]	44200 ^{d)}
18.	80% ethyl alcohol + 20% water		298 [14] ^{c)}	13600	293 [14]	44550 ^{d)}
19.	90% ethyl alcohol + 10% water		298 [14]	13600	293 [14]	44750 ^{d)}
20.	26% dioxane + 74% water		298 [15] ^{c)}	13890	298 [14]	43350 ^{d)}
21.	47% dioxane + 53% water		298 [15] ^{c)}	13890	298 [14]	43550 ^{d)}
22.	H ₂ O	78	298 [6]	13890	298 [11]	43836
23.	47% ethyl alcohol + 53% water		298 [17] ^{c)}	13900	293 [14]	44250 ^{d)}
24.	64% ethyl alcohol + 36% water		298 [17] ^{c)}	14100	293 [14]	44550 ^{d)}
25.	<i>t</i> -butyl alcohol	11	300 [16]	14190	293 [13]	44745 ^{d)}
26.	D ₂ O	78.25	298 [18] ^{c)}	14270	298 [11]	44715
27.	ethyl alcohol	24.5	300 [16]	14271	293 [13]	45661 ^{d)}
28.	70% methyl alcohol + 30% water		298 [17] ^{c)}	14650	293 [14]	44500 ^{d)}
29.	<i>n</i> -butyl alcohol	≈ 1.6	300 [16]	14675	293 [13]	44920 ^{d)}
30.	6.4 M aqueous MgCl ₂		293 [6]	15350	293 [6]	44400 ^{d)}
31.	methyl alcohol	32.6	300 [16]	15803	298 [11]	45529
32.	12 M aqueous KF		293 [6]	16400	293 [6]	46280 ^{d)}
33.	12 M aqueous LiCl		293 [6]	16950	293 [6]	46350 ^{d)}
34.	ethylene glycol	≈ 39	300 [16]	17255	293 [13]	46450 ^{d)}
35.	glycerol	≈ 43	300 [16]	18950	293 [2]	46870 ^{d)}

a) Static dielectric constant; b) ν_{max} of the first resolved band A₁ of iodide, from ref. [11]; c) room temperature, assumed to be 298°K; d) for first absorption band, not for resolved band A₁; e) calculated from $\nu_{\text{max}}(e_{\text{solv}}^-)$ for diethylamine by adding the shift of ν_{max} for secondary → primary amines observed in glassy amines, ref. [20]; f) values extrapolated to 298°K from the liquid (atm. pressure) range of ammonia, as the pressure effects on ν_{max} at 298°K for both species are difficult to assess.

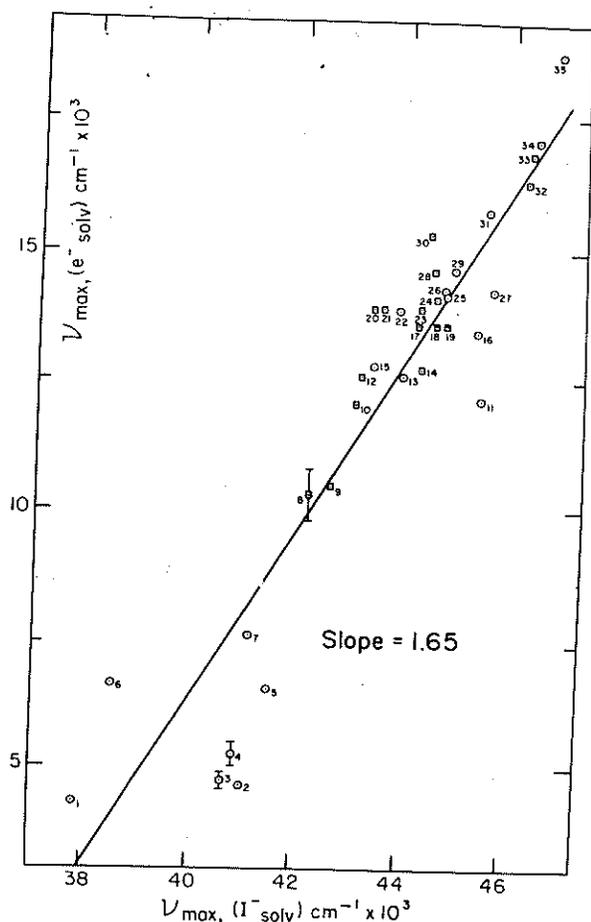


Fig. 1. Plot of ν_{\max} of the solvated electron in various solvents against the ν_{\max} of the first band of iodide ions in the same solvents at 293–298°K. See table 1 for the solvents listed.

tion can be noted. The correlation is not as good for the red-shifting solvents due, presumably, to experimental difficulties in determining $\nu_{\max}(e_{\text{solv}}^-)$ and in the envelopes of the non-resolved (from the A_2 and B_1 band [11, 19]) first absorption bands of iodide. Furthermore the e_{solv}^- bands are considerably asymmetric and the ν_{\max} values used are of non-resolved bands. It is interesting to note that from the least-squares curve a solvent sensitivity (slope) of ≈ 1.65 against iodide is obtained. Such solvent sensitivities (slopes) vary for each halide ion [11].

The following conclusions can be drawn: (a) the nature of the electronic transitions of the solvated electrons is close to that of the CTTS transition of ions,

and would appear to respond to similar environmental effects as observed for halide ions and other inorganic ions [7, 8, 11, 19]; (b) the radius parameter of the potential well for the solvated electron is thus probably of equal importance as the bulk solvent properties; (c) the plot in fig. 1 clearly excludes any direct correlation with the static dielectric constant of the solvent, see table 1 for ϵ_S values.

Based on the correlation presented in fig. 1, the $\nu_{\max}(e_{\text{solv}}^-)$ can be predicted provided $\nu_{\max}(I^-)$ is known. The latter values are known for a number of solvents [11, 13, 19], and therefore the following maxima of e_{solv}^- can be predicted (values in parentheses are in wavenumber, cm^{-1} , and wavelength, nm, respectively): cyanoethyl alcohol (15650, 640), alkoxy ethyl alcohols (14950, 670), dimethyl sulphone (11400, 880), alkyl carbonates (10900, 920), 1,4-dioxane (10500, 953), dichloroalkanes (8200, 1220), alkyl phosphates (7600, 1320), alkyl nitriles (6900, 1450) and acetone (5400, 1850). Small differences in ν_{\max} within each class of solvents can be expected. It is clear that the absorption maxima of the non-solvated electrons cannot be predicted based on a correlation with the CTTS scale of inorganic ions.

References

- [1] B.C. Webster and G. Howat, *Radiation Res. Rev.* 4 (1972) 259.
- [2] J. Jortner, *Ber. Bunsenges. Physik. Chem.* 75 (1971) 696.
- [3] M.S. Matheson and L.M. Dorfman, *Pulse radiolysis* (M.I.T. Press, Cambridge, 1969).
- [4] G.R. Freeman, *J. Phys. Chem.* 77 (1973) 7.
- [5] R. Lugo and P. Delahay, *J. Chem. Phys.* 57 (1972) 2122.
- [6] M. Anbar and E.J. Hart, *J. Phys. Chem.* 69 (1965) 1244; A.K. Pikaev, *The solvated electron in radiation chemistry* (Moscow, 1969).
- [7] M. Smith and M.C.R. Symons, *Trans. Faraday Soc.* 54 (1958) 346.
- [8] G. Stein and A. Treinin, *Trans. Faraday Soc.* 55 (1959) 1086; 56 (1960) 1393; I. Burak and A. Treinin, *Trans. Faraday Soc.* 59 (1963) 1490.
- [9] R.L. Platzman and J. Franck, *Z. Physik* 138 (1954) 411.
- [10] R. Catterall, L.P. Stodulski and M.C.R. Symons, *J. Chem. Soc. A* (1968) 437; J.M. Brooks and R.R. Dewald, *J. Phys. Chem.* 72 (1968) 2655; E.A. Shaede, L.M. Dorfman, G.J. Flynn and D.C. Walker, *Can. J. Chem.*, to be published.
- [11] M.F. Fox and E. Hayon, *J. Am. Chem. Soc.*, submitted for publication.

- [12] L.M. Dorfman, E.Y. Jou and R. Wageman, Ber. Bunsenges. Physik. Chem. 75 (1971) 681.
- [13] M.J. Blandamer and M.F. Fox, Chem. Rev. 70 (1970) 59.
- [14] L.P. Stodulski, Ph.D. Thesis, University of Leicester, Leicester, UK.
- [15] J.H. Baxendale and M.A.J. Rodgers, J. Phys. Chem. 72 (1968) 3849.
- [16] A. Ekstrom and J.E. Willard, J. Phys. Chem. 72 (1968) 4599.
- [17] S. Arai and M.C. Sauer, J. Chem. Phys. 44 (1966) 2297.
- [18] E.J. Hart and M. Aubar, The hydrated electron (Wiley-Interscience, New York, 1970).
- [19] M.F. Fox and E. Hayon, Chem. Phys. Letters 14 (1971) 442.
- [20] S. Noda, K. Fueki and Z. Kuri, Chem. Phys. Letters 8 (1971) 467.