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(Paper for Symposium on 'Electrons in Liquids',
5th International Congress of Radiation Research,
Seattle, Wash., July 1974)

The Optical Absorption Spectrum of the
Solvated Electron in Polar Liquids and
in Binary Solutions *

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Running Head

Absorption Spectra of Solvated Electrons.

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Abstract

Optical absorption spectra are now known for a considerable variety of compounds ranging from strongly polar to weakly polar liquids in which the absorption maximum may fall in the region 500 nm to 2300 nm. Some new results for amides and amines are presented and considered along with the data for alcohols, ethers, water and other compounds with regard to the dependence of λ_{max} upon type of compound. Data for binary solutions are discussed. Correlations with one empirical relationship and with two theoretical models are mentioned. With regard to structure in the room temperature spectrum of e_{sol}^- , our recent measurements do not sustain reports that structure may be resolved in the spectrum in ethanol.

Introduction

In our investigations of the optical absorption spectrum of the solvated electron (1-6) in polar liquids we have, over the past four years, focussed much of our attention on the important question of whether, and to what extent, short-range interactions may be a dominant factor, along with the bulk solvent properties, in determining the optical properties of the solvated electron. We have approached this question with three different types of experiments: (a) a broad survey of the spectrum of e_{sol}^- in different classes of compounds (3-6) with a view to determining whether the spectral grouping (3,7) of these absorptions showed any marked dependence upon class of compound; (b) determination of the spectrum of e_{sol}^- in binary solutions (3,4), and notably of the dependence of λ_{max} upon composition (principally for solutions of polar liquids) in a search for evidence of selective short-range interaction; (c) determination of the effect upon the spectrum of coupling (8,9) of e_{sol}^- with alkali metals in certain liquids.

In the brief time available to us in this symposium I would like to discuss the results of the first two of these different types of experiments. Some new observations of the spectrum of e_{sol}^- in three liquid amides (6) and two amines have been added to this survey; the results for the amides, as will be seen, resolve a question we were faced with in attempting some classification of the spectral grouping. I would then like to indicate how these results for the amides fail to fit an empirical correlation which had been recently proposed (10) for λ_{max} of the spectra of e_{sol}^- . Finally I should like to touch briefly on the

question of whether structure is observable in the optical absorption spectrum of e_{sol}^- at room temperature, a question of considerable theoretical interest which has received some attention recently, and which I hope will be resolved by some recent measurements we have made.

I. Spectra of e_{sol}^- in Amides.

The optical absorption spectrum of the solvated electron has been determined, by the pulse radiolysis method, in each of three, pure liquid amides at room temperature: N,N-dimethylformamide (DMF), N,N-dimethylacetamide (DMAc) and N,N-diethylformamide (DEF). These absorption spectra, over the range 800 to 2100 nm, are shown in Fig. 1. The absorption maximum, in each case, occurs at the following wavelengths: DMF, 1680 ± 30 nm; DMAc, 1800 ± 50 nm; DEF, 1775 ± 150 nm. Reactivity of the transient species responsible for these absorptions toward N_2O and toward anthracene (with formation of anthracenide ion), together with the nature of the spectrum, is sufficient evidence to identify the species as the solvated electron.

These amides were of particular interest to us in examining the spectral grouping of the absorption of e_{sol}^- with class of compound, since Hayashi, et al (11) had recently reported absorption maxima of 650 nm for e_{sol}^- in DMF, and 625 nm in DMAc. Such values would have placed λ_{max} for these amide electrons directly in the spectral grouping of the hydroxy compounds, a result of significance for any concept of spectral grouping with type of compound. As is clear, however, our results for these amides are sharply at variance with the findings of Hayashi, et al as we find no peaks at 650 nm. As is shown in Fig. 2, in which the data for DMF from 580 nm to 2100 nm are presented, we fail to find any structure in the visible. We are at a loss to explain

such a drastic discrepancy in the results, although it may be that the fall-off, toward 900 nm, in the sensitivity of the detector used in the earlier work may have been a contributing factor. The peaks we do find for the three amides are in a region of the infra-red which seems consistent with the spectra of amines which have been reported.

II. Empirical Correlation of Freeman.

Our data for the absorption maxima in DMF, DMAd and DEF were also of interest to us as a further test of an empirical correlation recently proposed by Freeman (10) which directs attention to the role of short-range forces (particularly with functional groups of the molecule) in determining the nature of e_{sol}^- . Freeman has correlated the transition energy, E_{max} , for the optical absorption with a purely empirical term which involves the molecular polarizability and the Kirkwood correlation parameter (12,13) g_K , so that the importance of short range order in the liquid is taken into account. g_K is obtained from the equation: $[(D_s - 1)(2D_s + 1)/9D_s](M/d) = (4\pi N/3)[\alpha + (g_K^2 \mu^2/3kT)]$ where M is the molecular weight, d the density, N Avogadro's number, α the optical polarizability, μ the molecular dipole moment, k Boltzmann's constant and T the absolute temperature. A plot of E_{max} vs the purely empirical term $D_s d g_K^3 \alpha_p$, where the power of g_K , namely 3, was obtained by fitting the data for a variety of compounds, and α_p is the polarizability of the polar group rather than the molecular polarizability, is shown in Fig. 3. As Freeman contends, this correlation fits reasonably well for water, ammonia, some alcohols and ethers. It fails completely for the three amides for which we have determined λ_{max} , and for hexamethylphosphoric triamide (5) ($\lambda_{max} = 2200$ nm), as may be seen from Fig. 3.

The values of D_s for the amides, it will be noted, are considerably higher than for other liquids having similar values for $E_{\max}$.

III. Spectral Grouping of Absorption Maxima.

The variety of types of compound in which the spectrum of the solvated electron is now known has been greatly expanded with the development of fast infra-red detection (3,14) systems. In addition to the spectra in ammonia (15), water (16), and a number of alcohols (1), which have been known for quite some time, the optical absorption bands have been determined in a number of ethers (3,4) and amides and amines (3-6), systems in which $\lambda_{\max}$ may lie at wavelengths as long as 2300 nm. A number of these spectra are shown in Fig. 4.

Examination of such data indicates that there is indeed some spectral grouping (7) of $\lambda_{\max}$ with class of compound, even though there is, to be sure, substantial overlap among some of these different compounds. This may be seen somewhat more clearly in Fig. 5 in which the wavelength of $\lambda_{\max}$ is shown for a large number of compounds. The hydroxy compounds include water (16), several aliphatic alcohols from our earlier work (1), the recently determined spectrum in 2-methoxyethanol (17,6) and the interesting cases of 2-methyl-2-propanol and 2-methyl-2-butanol recently reported by Hentz and Kenney-Wallace (17). The data shown for the ethers, all far out in the infra-red, are from our reports of the past few years (3,4). The amides shown are the three described in the first section of this talk.

The liquids for which $\lambda_{\max}$ is shown in Fig. 5 have static dielectric constants ranging from 78.3 to 3.6 at room temperature. Although there is substantial overlap in the values of $\lambda_{\max}$ at room temperature, the

over-riding factor in the spectral grouping, as we have pointed out (7), seems to be the class of compound. The hydroxy compounds are mostly in the visible to the near infra-red, with 2-methyl-2-propanol and 2-methyl-2-butanol (17) slightly beyond 1200 nm (3-methyl-3-pentanol and 3-ethyl-3-pentanol (17), with $\lambda_{\max}$ as yet undetermined, appear to be beyond 1300 nm). It is noteworthy that no other compounds yet reported have $\lambda_{\max}$ in the visible to the near infra-red overlapping with the OH-compounds shown, and it seems reasonable to conclude therefore, that the optical properties of ϵ_{sol}^- in this class of compound are determined by properties of the hydroxyl group in the solvent structure. Hentz and Kenney-Wallace (17) have drawn attention to this and have suggested that the OH dipole configuration in a single solvation shell may be the dominating factor with the effect of branching structure of the alcohol superimposed. Such short range effects are reflected in different ways in molecular models (18), in which short range forces must be a dominant parameter, as well as in the cavity-continuum model (19) in which cavity radius is an important parameter. The amides and amines shown are in an intermediate region from about 1400 to 2050 nm. The ethers are farther into the infra-red with $\lambda_{\max}$ ranging from 1800 to 2300 nm. Our experimental data for THF were compared with calculations based on the cavity-continuum model of Copeland, et al (19,20). We find agreement between the experimental value for $E_{\max}$ and the calculated value, for an effective cavity radius of $4\text{\AA}$ (which is different from the radius of the stable configuration and from the void radius) and a coordination number of 6 or 8.

IV. e_{sol}^- in Binary Solutions.

The spectrum of the solvated electron in binary solutions (2,3) and the concentration dependence of λ_{max} in particular should provide evidence of selective solvation as well as furnishing further tests of the validity of theoretical models. Spectra of e_{sol}^- in a variety of binary systems have now been reported. In all such systems which we have investigated, only a single absorption band is seen, no matter how dissimilar the absorption maxima for the individual components (as, for example, water and THF (3), at 720 nm and 2120 nm respectively). A complete range of behaviour is seen in the dependence of λ_{max} upon composition. In some systems the dependence is very nearly linear, e.g. ethylenediamine-tetrahydrofuran (3), or slightly sigmoidal in shape as for ammonia-water or ethylenediamine-water (2). The optical properties are not dominated by one component in these systems. In other systems the composition dependence of λ_{max} is strongly dependent upon one component, as for water-tetrahydrofuran (3) in which water is the dominating component. In yet other systems, the wavelength of λ_{max} is so strongly dominated by one component as to be almost independent of the presence of the second. This is true for certain alcohol-alkane (21-22) solutions and for ethylenediamine-ethanol (21) in which the dominating component, ethylenediamine, has the lower static dielectric constant of the pair. A summary of some of the data illustrating these different types of dependence is presented in the accompanying table. In those systems in which λ_{max} is dominated by one component, that component is underlined.

Calculated data for the binary liquid system water-ammonia using the molecular model of Howat and Webster (18) have been compared (18)

Composition Dependence of $\lambda_{\max}$
of e^-_{sol} in Binary Solutions

Linear or Near Linear Dependence	$\lambda_{\max}$ Strongly Affected or Dominated by One Component ^a
EDA-THF	<u>H₂O-THF</u> ^c
H ₂ O-NH ₃ ^b	<u>EDA</u> ^d -C ₂ H ₅ OH
H ₂ O-EDA ^b	<u>C₂H₅OH</u> -Hexane
EDA-HMPA	<u>C₂H₅OH</u> -DiMeButane

- a. The compound underlined dominates the observed $\lambda_{\max}$.
- b. Sigmoidal dependence departing slightly from linearity.
- c. Dielectric constant dominated by THF.
- d. EDA has lower dielectric constant of the pair.

with experiment. For this tetramer model the calculated wavelength dependence is somewhat closer to linear than the experimental data, but the agreement is not unreasonable.

V. Structure in the Absorption Spectrum of e_{sol}^- .

The question of whether structure exists in the absorption spectrum of the solvated electron at room temperature, which has generally been reported as a broad, structureless band, is of theoretical interest. For a continuum model, one may speculate as to whether bands of the nature of a Rydberg series may exist. For a molecular model there may conceivably be structure related to molecular properties of the immediate molecular configuration around the electron.

Attention has recently been focussed on this interesting question in a series of papers (23,24) on ethanol and other alcohols in which it is reported that such structure is observable. This observation is in conflict with earlier data. We have, accordingly, repeated (25) the determination of the spectrum of e_{sol}^- in ethanol at room temperature. Our data, representing several determinations at each wavelength, are shown in Fig. 6 along with the data of Vannikov and Marevtsev (23). Our data fail to sustain the claim (23,24) of observable structure greater than a detection sensitivity of 1.3% of the total absorption. Moreover, comparison of the more recent report (24) on structure with the earlier paper (23) indicates also that random signal fluctuation may have been misinterpreted as structure.

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Figure Legends

- Fig. 1. Optical absorption spectra at room temperature of the solvated electron in liquid amides. DMF....., DMAd ---, DEF——.
- Fig. 2. Optical absorption spectrum at room temperature of the solvated electron in DMF showing individual data points. Each separate point represents individual experiments with separate samples; ∇ represents a superposition of such separate experiments.
- Fig. 3. Correlation of Freeman for transition energy for spectrum of e_s^- with liquid properties. $E_{\max}$ is plotted against $D_s dg_K^3 \alpha_p$; $\bigcirc$, various liquids at different temperatures; $\square$, amides; Δ HMPA.
- Fig. 4. Optical absorption spectra of the solvated electron in a variety of compounds. EG ethylene glycol, MeOH methanol, PDA propanediamine, DME dimethoxyethane, DEA diethylamine, DEE diethyl ether. The extinction coefficients are not known for the amides, DEF, DMF and DMAd, the spectra for which are arbitrarily positioned in this figure.
- Fig. 5. Optical absorption maxima for the solvated electron in various liquids at room temperature: — hydroxy compounds (— + are for water and 2-methoxyethanol); — — ammonia and amines; --- amides; ..... ethers.
- Fig. 6. Optical absorption spectrum of the solvated electron in ethanol at 296°K. The open circles represent our experimental data, each point being the average of two to seven individual data points. The dashed line represents the data of Vannikov and Marevtsev normalized to our data at 680 nm.

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FIG. 1.

FIG. 2.

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FIG. 3.

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FIG. 4.

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FIG. 5.

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FIG. 6.