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Transition Energy Diagram for Solvated Electrons and Its Application to the Interpretation of Their Absorption Spectra

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The energy levels of solvated electrons have been calculated as a function of the static dielectric constant and of the cavity radius on the basis of a continuous dielectric model with an adiabatic approximation, and a contour diagram has been drawn up for the transition energy of solvated electrons. Using this diagram and the observed absorption spectra, the quantities on solvated electrons in alcohols have been estimated. The cavity radius, R, ranges from 0.9 to 1.6 Å, the charge distribution for the ground state, from 2.4 to 3.2 Å, and the variation in cavity radius, from 0.50 to 0.60 Å, at room temperature. From the calculations of the temperature dependence, $\mathrm{d}(h\nu)/\mathrm{d}t$, of the transition energy, it can be said that, for solvated electrons in alcohols, the contribution to $\mathrm{d}(h\nu)/\mathrm{d}t$ of the change in R with the temperature is rather more dominant than the change in the static dielectric constant with the temperature. It has also been found that there exists a correlation between the $\mathrm{d}R/\mathrm{d}t$ value and the ratio of the number of the OH bond to the total number of bonds involved in each alcohol.

The formation of the solvated electron by the action of ionizing radiations on some polar media has been well established in recent years. The electronic absorption spectra of solvated electrons in alcohols and the effect of the temperature on their absorption spectra have been observed by the pulse radiolysis technique.[1,2] The experimental results suggest a simple relationship between the optical transition energy of solvated electrons and the dielectric constant of the medium within a series of alcohols.

On the other hand, the theory of solvated electrons has been developed on the basis of the continuous dielectric model[3] and applied with considerable success to the interpretation of the optical properties of solvated electrons in metal-ammonia solutions,[4] hydrated electrons,[5] and trapped electrons in an organic glass.[6,7]

For the present paper, we have calculated the energy levels of solvated electrons as a function of the static dielectric constant of solvents and of the radius of a cavity in which an electron is located on the basis of a continuous dielectric model with an adiabatic approximation, we have then drawn up a contour diagram for the transition energy of solvated electrons.

Using this diagram and the observed absorption spectra, we have estimated the charge distribution, the cavity radius, and the range of the cavity radii of solvated electrons in alcohols. We have also examined the factors which may be responsible for the temperature dependence of their absorption spectra.

Method of Calculation

Transition Energy of a Solvated Electron. The solvated electron interacts with the polarization filed of the dielectric medium, and the interaction energy is determined by the long-range interaction. The potential function, $V(r)$, in which an electron is bound, is expressed as follows:

$$\left.\begin{aligned} V(r) &= -\beta e^2/r \quad \text{for } r > R, \\ V(r) &= -\beta e^2/R \quad \text{for } r < R, \end{aligned}\right\} \tag{1}$$

where $\beta = (1/D_{\mathrm{op}}) - (1/D_{\mathrm{s}})$, D_{s} and D_{op} are the static and optical dielectric constants, and where R is the cavity radius. The reference state is that of a non-polarizing electron located in the medium at an infinite distance from the cavity.

The calculations were carried out using the variation method. The one-parameter wave function used for the ground state was of this form:

$$\psi_{1s} = (\mu^3/\pi)^{1/2} \exp(-\mu r) \tag{2}$$

The energy of the ground state can be presented by:

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[1] M. C. Sauer, Jr., S. Arai and L. M. Dorfman, *J. Chem. Phys.*, **42**, 708 (1965).

[2] S. Arai and M. C. Sauer, Jr., *J. Chem. Phys.*, **44**, 2297 (1966).

[3] J. Jortner, *Mol. Phys.*, **5**, 257 (1962).

[4] J. Jortner, *J. Chem. Phys.*, **30**, 859 (1959).

[5] J. Jortner, *Radiation Res., Suppl.*, **4**, 24 (1964).

[6] K. Fueki, *J. Chem. Phys.*, **44**, 3140 (1966).

[7] M. J. Blandamer, L. Shields and M. C. R. Symons, *J. Chem. Soc.*, **1965**, 1127.

$$W_{1s} = \int_v \psi_{1s}[-h^2/8\pi^2 m \nabla^2 + V(r)]\psi_{1s} dv, \qquad (3)$$

where ∇^2 is the Laplacian operator.

For a given value of R and β, W_{1s} is obtained as a function of μ. The best value of μ is given by the condition $\partial W_{1s}/\partial\mu = 0$. The substitution of this value of μ into (2) and (3) yields the wave function and the energy for the 1s state respectively. The mean radius for the 1s state is given by $r_{1s} = 3/2\mu$. The 2p state can be treated in a manner similar to that used for the ground state.

According to the Franck-Condon principle, the value for R and the form of the potential selected for the 2p state are the same as those for the ground state. The energy of the 2p state was calculated using the one-parameter wave function:

$$\psi_{2p} = (\alpha^5/\pi)^{1/2} r \cos\theta \exp(-\alpha r) \qquad (4)$$

The mean radius for the 2p state can be presented by $r_{2p} = 5/2\alpha$. The electronic polarization energies for the 1s and 2p states are approximately given by:

$$\left.\begin{aligned} S_{1s} &= -(e^2\mu/3)(1-1/D_{op}), \\ S_{2p} &= -(e^2\alpha/5)(1-1/D_{op}). \end{aligned}\right\} \qquad (5)$$

Thus, the total energy is obtained as:

$$\left.\begin{aligned} E_{1s} &= W_{1s} + S_{1s}, \\ \text{and:} \quad E_{2p} &= W_{2p} + S_{2p}. \end{aligned}\right\} \qquad (6)$$

The energy for the 1s→2p transition is given by:

$$h\nu = E_{2p} - E_{1s}, \qquad (7)$$

which corresponds to the excitation energy at the absorption maximum.

Temperature Dependence of the Transition Energy. The energy shift presents the difference between the change in the energy of the ground and excited states:

$$d(h\nu)/dt = dE_{2p}/dt - dE_{1s}/dt, \qquad (8)$$

where t is the temperature.

The temperature coefficient of the 1s state is obtained in the form:

$$\frac{dE_{1s}}{dt} = \left[\frac{\partial E_{1s}}{\partial\beta} - \left(\frac{\partial S_{1s}}{\partial\mu}\right)\left(\frac{\partial^2 W_{1s}/\partial\beta\partial\mu}{\partial^2 W_{1s}/\partial\mu^2}\right)\right]\left(\frac{d\beta}{dt}\right) + \left[\frac{\partial E_{1s}}{\partial R} - \left(\frac{\partial S_{1s}}{\partial\mu}\right)\left(\frac{\partial^2 W_{1s}/\partial R\partial\mu}{\partial^2 W_{1s}/\partial\mu^2}\right)\right]\left(\frac{dR}{dt}\right) \qquad (9)$$

The temperature coefficient for the 2p state is given by Eq. (9) with E_{2p} substituted for E_{1s}, S_{2p} substituted for S_{1s}, and α substituted for μ. For a given value of R and β, dE_{1s}/dt and dE_{2p}/dt are presented by:

$$dE_{1s}/dt = a_1(d\beta/dt) + b_1(dR/dt), \qquad (10)$$

and:

$$dE_{2p}/dt = a_2(d\beta/dt) + b_2(dR/dt), \qquad (11)$$

where E is expressed in eV, where R is expressed in Å, and where a_1, b_1 and a_2, b_2 are defined by Eq. (9) and the corresponding equation for the 2p state respectively. From Eq. (8) we obtained:

$$d(h\nu)/dt = a(d\beta/dt) - b(dR/dt), \qquad (12)$$

where $a = a_2 - a_1$ and where $b = b_2 - b_1$.
The temperature dependence of the energy levels and of the transition energy may thus be attributed to the temperature dependence of the properties of the dielectric medium which are roughly expressed by the temperature dependence of D_s and D_{op}, and to the temperature dependence of the mean cavity radius.

Results and Discussion

Transition Energy Diagram. The transition energy, $h\nu$, of a solvated electron is dependent on β and R. Since the optical dielectric constant, D_{op}, of any substance is not different from 2, we use a constant value, 2, for D_{op} in the calculation of $h\nu$, so that we may deal with the problem in a systematic way. Thus, we can construct a transition energy diagram by calculating $h\nu$ as a function of D_s and R.

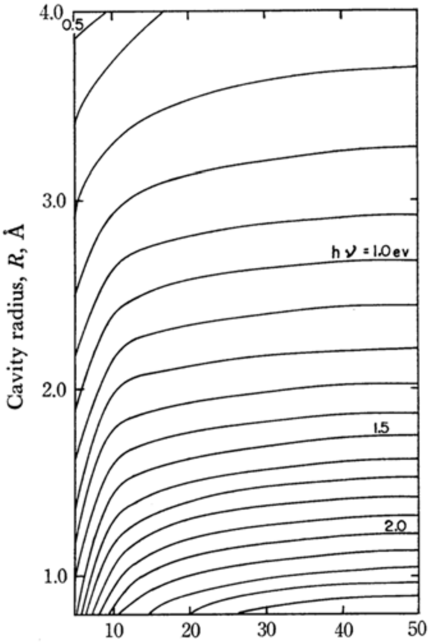

Fig. 1. Transition energy diagram for solvated electrons.

Figure 1 shows the calculated transition energy diagram, in which the contour lines for $h\nu$ are drawn every 0.1 eV, and where D_s the values range from 5 to 50 and the R values, from 0.8 to 4 Å. The results for high D_s values and the very small R values are not included in the diagram because the adiabatic approximation is less satisfactory for these cases. The adiabatic approximation is more satisfactory for low D_s values and large R values because the binding energy of a solvated electron is small in such cases.

Solvated Electrons in Alcohols. From the transition energy diagram and the observed absorption spectra, the quantities of solvated electrons in alcohols at room temperature are obtained; they are given in Table 1.

TABLE 1. CHARGE DISTRIBUTION, THE MEAN CAVITY RADIUS, AND THE RANGE OF CAVITY RADIUS OF SOLVATED ELECTRONS IN ALCOHOLS AT ROOM TEMPERATURE

Substance	$D_s^{25°C}$	$h\nu_{max}$ [1,2)] (eV)(obs.)	$\bar{r}_{1s}$ (Å)	$\bar{r}_{2p}$ (Å)	R (Å)	$\pm\Delta R$ (Å)
Methanol	32.6	1.97	2.65	5.75	1.15	0.53
Ethanol	24.4	1.77	2.88	5.95	1.32	0.60
n-Propanol	20.8*	1.67	3.00	6.02	1.40	0.54
Iso-propanol	17.7	1.51	3.19	6.25	1.60	0.50
n-Butanol	17.1	1.80	2.83	6.10	1.20	0.60
Ethylene glycol	38.7*	2.14	2.54	5.68	1.03	0.50
Glycerol	42.5	2.35	2.40	5.62	0.90	0.50

* 20°C

In Table 1, $\bar{r}_{1s}$ and $\bar{r}_{2p}$ are the mean radii for the 1s and 2p states respectively, R is the mean cavity radius, and ΔR is the range of the cavity radius, which will be discussed below.

Transition Energy and Cavity Radius. It can be seen from Table 1 that the mean cavity radius for solvated electrons in alcohols is 0.9—1.6 Å[*1] and that the mean radius of the solvated electron orbitals for the ground state is 2.4—3.2 Å.

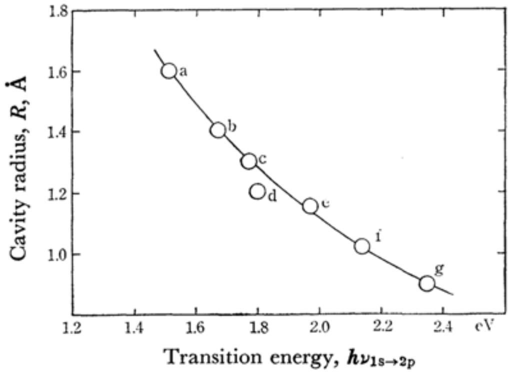

Fig. 2. Relation between the cavity radius and the transition energy for solvated electrons in alcohols.
a: isopropanol, b: *n*-propanol, c: ethanol, d: *n*-butanol, e: methanol, f: ethylene glycol, g: glycerol.

The mean cavity radius is plotted against the transition energy in Fig. 2. It may be seen that there is a correlation between the cavity radius and the transition energy. The transition energy increases with a decrease in the cavity radius. The cavity radius decreases with an increase in the static dielectric constant for all these alcohols except *n*-butanol (Fig. 3).

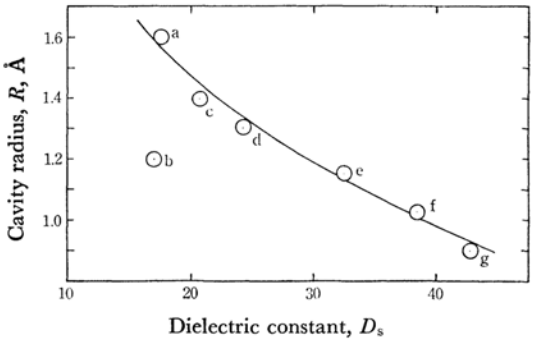

Fig. 3. Relation between the activity radius and the static dielectric constant for solvated electrons in alcohols.
a: isopropanol, b: *n*-butanol, c: *n*-propanol, d: ethanol, e: methanol, f: ethylene glycol, g: glycerol.

Absorption-band Width and the Range of the Cavity Radius. It is well known that the solvated electron exhibits a braod absorption spectrum. The high-energy side of the absorption band may be interpreted in terms of the transition of the solvated electron to higher excited states and an energy continuum as well as in terms of the broadening of the band due to variations in cavity size. On the other hand, the side with an energy lower than the band maximum is explicable only in terms of the broadening of the band due to various cavity sizes as long as the band maximum is interpreted as arising from the 1s→2p transition.

TABLE 2. ABSORPTION BAND WIDTH AND THE RANGE OF CAVITY RADIUS OF SOLVATED ELECTRONS AT DIFFERENT TEMPERATURES

Temp.	Substance	$h\nu_{max}$ [1,2,7)] (eV)(obs.)	$\Delta(h\nu)$ [1,2,7)] (eV)(obs.)	R (Å)	$\pm\Delta R$ (Å)
25°C	Methanol	1.97	0.45	1.15	0.53
	Ethanol	1.77	0.45	1.32	0.60
	n-Butanol	1.80	0.44	1.20	0.60
− 78°C	Methanol	2.17	0.41	1.07	0.38
	Ethanol	2.18	0.50	1.05	0.47
	n-Butanol	2.28	0.53	0.90	0.50
−196°C	Methanol	2.41	0.27	0.89	0.23
	Ethanol	2.41	0.35	0.88	0.35
	n-Butanol	2.47	0.48	0.83	0.48

[*1] It should be noted that, since the optical dielectric constants of methanol and ethanol are lower than 2 by about 10% the cavity radii for these alcohols will be found to be larger by about the same degree than those in Table 1 if the exact optical dielectric constants are used in these calculations.

TABLE 3. TEMPERATURE EFFECT ON THE TRANSITION ENERGY OF SOLVATED ELECTRONS IN ALCOHOLS

Substance	$\mathrm{d}(h\nu)/\mathrm{d}t$ (eV/deg) (obsd)[2]	$[\mathrm{d}(h\nu)/\mathrm{d}t]_\mathrm{I}$ (eV/deg) (calcd)	$[\mathrm{d}(h\nu)/\mathrm{d}t]_\mathrm{II}$* (eV/deg) (calcd)	$\mathrm{d}R/\mathrm{d}t$ (Å/deg)	$\frac{[\mathrm{d}(h\nu)/\mathrm{d}t]_\mathrm{I}}{\mathrm{d}(h\nu)/\mathrm{d}t}$
Methanol	-2.2×10^{-3}	-0.44×10^{-3}	-1.76×10^{-3}	1.5×10^{-3}	0.20
Ethanol	-3.4×10^{-3}	-0.41×10^{-3}	-2.99×10^{-3}	2.9×10^{-3}	0.12
Isopropanol	-3.5×10^{-3}	-0.60×10^{-3}	-2.90×10^{-3}	3.3×10^{-3}	0.18
n-Butanol	-4.5×10^{-3}	-0.77×10^{-3}	-3.73×10^{-3}	3.4×10^{-3}	0.17

* $[\mathrm{d}(h\nu)/\mathrm{d}t]_\mathrm{II} = \mathrm{d}(h\nu)/\mathrm{d}t - [\mathrm{d}(h\nu)/\mathrm{d}t]_\mathrm{I}$

Thus, the absorption-band width can be related to the cavity radius, which may be represented by the half-height width, ΔR, measured towards the low-energy side.

The values of ΔR for solvated electrons in alcohols at room temperature are given in Table 1. The effect of the temperature on ΔR is shown in Table 2. It can be seen from Table 2 that the range of the cavity radius decreases with a decrease in the temperature. It can also be seen that ΔR increases as the alkyl group in alcohols becomes bulky; this tendency is most clearly manifested at −196°C.*[2]

If the broadening of the absorption band towards the low-energy side is ascribed to the transition of solvated electrons in larger cavities, the photobleaching of these electrons by light with a selected energy limit will result in the blue shift of the absorption spectrum. Further experimental studies along this line are needed to substantiate such an interpretation.

Effect of Temperature on the Transition Energy. The calculated temperature dependence of the transition energies of solvated electrons in alcohols is given in Table 3, together with the observed one.

In these calculations the temperature dependence of β is presented approximately by $\mathrm{d}\beta/\mathrm{d}t=(1/D_\mathrm{s})\,\mathrm{d}(\ln D_\mathrm{s})/\mathrm{d}t$, since the temperature dependence of D_op is much smaller than that of D_s. The temperature coefficient of D_s is taken from the experimental data.

In Table 3, $[\mathrm{d}(h\nu)/\mathrm{d}t]_\mathrm{I}$ and $[\mathrm{d}(h\nu)/\mathrm{d}t]_\mathrm{II}$ represent the contribution to $\mathrm{d}(h\nu)/\mathrm{d}t$ of the changes in D_s and in the mean cavity radius with the temperature respectively. The contribution of the former to $\mathrm{d}(h\nu)/\mathrm{d}t$ is 20% at most, as is shown in the last column of the table. The calculated $\mathrm{d}R/\mathrm{d}t$ is also given in Table 3. In Fig. 4 the value of $\mathrm{d}R/\mathrm{d}t$ is plotted against the ratio of the number of the OH bond to the total number of bonds involved in each alcohol. There is a correlation between these quantities, probably indicating a relation between the expansion of a cavity and the strength of such intermolecular interactions as hydrogen bonding.

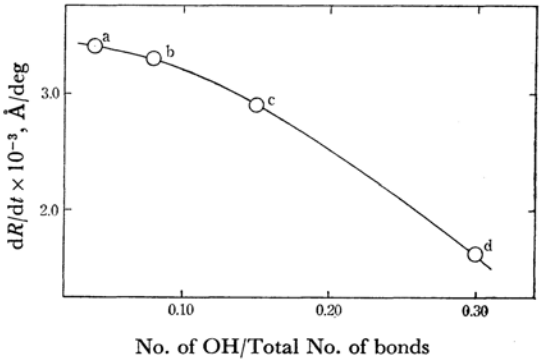

Fig. 4. Dependence of $\mathrm{d}R/\mathrm{d}t$ on the ratio of the number of the OH bond to the number of bonds involved in each alcohol.
a: *n*-butanol, b: isopropanol, c: ethanol, d: methanol.

It may be concluded that the temperature dependence of the transition energy of solvated electrons in alcohols is mainly attributable to the change in the cavity size with the temperature.

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*[2] Since there are no available data on D_s at −196°C, we have used the values of D_s at −78°C in the calculations at −196°C. This approximation is possible because the transition energy is relatively insensitive to the value of D_s for high D_s values (see Fig. 1) and because D_s is high enough to satisfy this requirement for alcohols at −78°C.