On the Temperature Dependence of Spectra of Solvated Anions

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Recently it has been noticed that the ultraviolet spectra of solvated halide ions depend upon the temperature. The bands in the ultraviolet region are considered to be due to the charge transfer from the ion to the solvent. However, with respect to the details of the mechanism, different models have been proposed by several authors. In particular, these models seem to lead to different conclusions on the effect of temperature.

In this paper, it is shown that the differences existing among the previous theories are only apparent in character, and some experimental data on the temperature dependence of the ultraviolet spectra of solvated iodide ions are given.

Experimental and Results

Measurements of absorption spectra were carried out with a Hitachi EPU-2 type spectrophotometer. The temperature was varied in the range 5～60°C and was kept constant within ±1°C, circulating the thermostatted water in the cell box by means of a small pump.

The absorption spectra for potassium iodide, ammonium iodide, codmium iodide, cobalt(II) iodide and bismuth(III) iodide in their aqueous solutions (10^{-5} mol./l.) have a common maximum wavelength irrespective of the cations (for example 225 mμ at 12°C) in agreement with the data of many authors[1,2]. As is well known, this maximum can be ascribed to the existence of the iodide ion in such dilute solutions. In Table I the values of the maximum wavelength ($\lambda_{\max}$) of potassium iodide, cadmium iodide and bismuth(III) iodide (10^{-5} mol./l. aqueous solution) are shown with the error of ± 0.2 mμ. In Fig. 1 the temperature dependence of the energy maximum ($h\nu_{\max}$) calculated from $\lambda_{\max}$ obtained is recorded. The slope in Fig. 1 gives $d(\boldsymbol{h}\nu_{\max})/dT = -32$ cal. deg^{-1} mol^{-1}, where $\boldsymbol{h}$ is Planck's constant. This is in agreement with the value of Smith and Symons[2]. Present results, that $d(\boldsymbol{h}\nu_{\max})/dT \approx -30$ cal. deg^{-1} mol^{-1} in these solutions, are in agreement with those obtained in many solvent systems[2-4]. Some theoretical considerations for this fact, i. e. the shift to longer wavelength with increasing temperature, will be given in the next section.

TABLE I. WAVELENGTHS OF MAXIMUM ABSORPTION (mμ) OF IODIDES (10^{-5} M IN WATER) AT SEVERAL TEMPERATURES

Temp., °C	KI	CdI_2	BiI_3
6.5	225.4	225.3	225.2
25.2	226.1	226.0	226.0
41.6	227.2	227.0	227.1
60.5	228.1	228.5	228.3

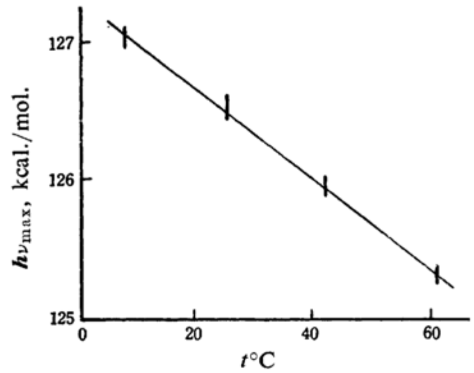

Fig. 1. $\boldsymbol{h}\nu_{\max}$ of I^- in aqueous solution (10^{-5} mol./l.).

Discussion

Many anions dissolved in polar liquids such as water exhibit absorption spectra in the ultraviolet region. These spectra are considered to be due to an electron transfer from the solvated anion to a quantum state, which is yielded by the resultant atom, the adjacent water molecules, and the external polarized dielectrics. The electron transfer is so fast that the positions of all atomic nuclei in all solvent molecules may be regarded as fixed throughout the transition process in accordance with the Franck-Condon principle. In other words the process may be regarded as a sort of non-equilibrium state associated with electron transition. From this point of view Platzman and Franck[5] calculated the positions of the absorption bands of the aqueous halide

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[2] M. Smith and M. C. R. Symons, *Trans. Faraday Soc.*, **54**, 338 (1958).

[3] E. Lederle, *Z. physik. Chem.*, **B10**, 121 (1930).

[4] E. M. Kosower, R. L. Martin and V. W. Meloch, *J. Chem. Phys.*, **26**, 1353 (1957).

[5] R. Platzman and J. Franck, *Z. Physik.*, **138**, 411 (1954).

ions. Their theoretical expression for the energy of the absorption $\boldsymbol{h}\nu$ is as follows.

$$\boldsymbol{h}\nu = E_{\mathrm{x}} + L_{\mathrm{x}^-} + \{\chi - L_{\mathrm{x}}\} - B \tag{1}$$

Here E_{x} is the electron affinity of the atom X, and L_{x} and L_{x^-} are the differences of energies associated with the solvation of the atom and of the ion, respectively. χ is the energy required to form the average solvation configuration of the solvent molecules (i. e. the correction term based on the Franck-Condon principle), and B is the energy of the excited electron resulting from the Coulombic force of the polarized solvent (i. e. hydrogen-like states) and from the electronic polarization induced by the electron in the excited state.

$$B = \frac{2\pi^2 m e^4}{\boldsymbol{h}^2 2^2} Z^2_{\mathrm{eff}} + \frac{1}{3}\,\frac{\pi^2 e^4 m}{\boldsymbol{h}^2}\, Z_{\mathrm{eff}}\left(1 - \frac{1}{D_{\mathrm{op}}}\right) \tag{2}$$

and

$$Z_{\mathrm{eff}} = \left(\frac{1}{D_{\mathrm{op}}} - \frac{1}{D_{\mathrm{s}}}\right) \tag{3}$$

where D_{op} and D_{s} are the optical and static dielectric constants, m is the mass of an electron. The values of $\boldsymbol{h}\nu$ calculated by using Eq. 1 were in good agreement with the experiment.

However, Smith and Symons[6,7], and Stein and Treinin[8] pointed out that the theory of Platzman and Franck fails to explain changes in the position of the absorption bands caused by changing temperature or solvent. Smith and Symons attempted to avoid the difficulties by adopting the "square well" model. According to this theory the electron after detachment from the ion still remains in the cavity previously occupied by the ion. Then the energy of the absorption $\boldsymbol{h}\nu$ is given by

$$\boldsymbol{h}\nu = E_{\mathrm{x}} + \frac{\boldsymbol{h}^2}{8 m r_{\mathrm{o}}^2} \tag{4}$$

where r_{o} is an empirical parameter which was introduced by Smith and Symons. This parameter may roughly be regarded as the radius of the spherical cavity. However, it is unlikely that the order of magnitude of r_{o} corresponds to any physically meaningful value, because it is greater (for example 4Å for I^-) than any value that may be reasonably expected. Stein and Treinin[8] modified the Platzman-Franck theory by introducting the concept of a variable radius parameter r^* as suggested by Smith and Symons. Their equation is given as

$$\boldsymbol{h}\nu = E_{\mathrm{x}} + (S_{\mathrm{ion}} + E_{\mathrm{p}}) - L_{\mathrm{x}} - B \tag{5}$$

where

$$S_{\mathrm{ion}} + E_{\mathrm{p}} = \frac{e^2}{r^*}\left(\frac{1}{2} + \frac{1}{2D_{\mathrm{op}}} - \frac{1}{D_{\mathrm{s}}}\right) \tag{6}$$

The difference between Platzman-Franck's Eq. (1) and Smith-Symon's (5) is that $(S_{\mathrm{ion}} + E_{\mathrm{p}})$ in Eq. 5 takes the place of $(I_{\mathrm{x}^-} + \chi)$ in Eq. 1. According to Stein and Treinin the valnes of the radius parameter r^* obtained from the spectroscopic data on the basis of Eq. 5 were in good agreement with the apparent ionic radii estimated from partial ionic volumes. The temperature dependence of $\boldsymbol{h}\nu$ was also explained in terms of the change of the radius of the cavity (or ionic radii), $\mathrm{d}r^*/\mathrm{d}T$. They emphasized that Franck and Platzman's procedure, taking into account L_{x^-} and χ, is inadequate for the treatment of the temperature dependence.

However, the concept of ionic radii in liquids corresponds to the rigid sphere model of liquids, and may be regarded as an appoximation for the behavior of liquids. The apparent ionic radii should be determined more rigorously from the relation between the total energy and ion-molecule distances. Thus Eq. 5 should in principle coincide with Eq. 1 apart from minor differences of mathematical expressions. Hence, the temperature dependence of $\boldsymbol{h}\nu$ will be considered here without using the concept of the radius parameter r_{o}.

In Platzman-Franck's equation the effect of temperature may be prominent in the terms L_{x^-}, χ and L_{x}, since these factors strongly depend on the positions of nuclei. The terms caused by the electronic polarization or the electronic motion can be unimportant, since $\mathrm{d}D_{\mathrm{op}}/\mathrm{d}T$ and $\mathrm{d}D_{\mathrm{s}}/\mathrm{d}T$ are so small that the calculated value for $\mathrm{d}(\boldsymbol{h}\nu_{\mathrm{max}})/\mathrm{d}T$ is at most about 1/10 of the observed values. Thus one can write

$$\frac{\mathrm{d}(\boldsymbol{h}\nu)}{\mathrm{d}T} = \frac{\mathrm{d}\{L_{\mathrm{x}^-} - (I_{\mathrm{x}} - \chi)\}}{\mathrm{d}T} \tag{7}$$

It seems to be impossible to define $\mathrm{d}(L_{\mathrm{x}} - \chi)/\mathrm{d}T$ in Eq. 7 by the usual thermodynamic method, though $\mathrm{d}(L_{\mathrm{x}^-})/\mathrm{d}T$ simply denotes the change of the thermodynamic specific heats ΔC_{x^-} as the following:

$$\frac{\mathrm{d}(L_{\mathrm{x}^-})}{\mathrm{d}T} = \Delta C_{\mathrm{x}^-} = C^{\mathrm{g}}{}_{\mathrm{x}^-} - C^{\mathrm{s}}{}_{\mathrm{x}^-} \tag{8}$$

where $C^{\mathrm{g}}{}_{\mathrm{x}^-}$ and $C^{\mathrm{s}}{}_{\mathrm{x}^-}$ show the specific heats of the ion in vacuo and in the solvent, repectively. As was noted by Stein and Treinin, ΔC_{x^-} of the process X^-(in solvent)→X^-(in

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6) M. Smith and M. C. R. Symons, *Discuss. Faraday Soc.*, **24**, 206 (1957).

7) M. Smith and M. C. R. Symos, *Trans. Faraday Soc.*, **54**, 346 (1958).

8) G. Stein and A. Treinin, ibid., **55**, 1086 (1959).

vac.) can be positive. On the other hand, for the neutral atom X one can write

$$\frac{\mathrm{d}(L_x-\chi)}{\mathrm{d}T}=\Delta C_{x^*}=C^g{}_{x^*}-C^s{}_{x^*} \tag{9}$$

corresponding to Eq. 8. However, $C^s{}_{x^*}$ does not denote the specific heat of the ion in the solvent to be defined in the equilibrium state, since $(L_x-\chi)$ does not correspond to the stable configuration for the atom. Substituting Eqs. 8 and 9 into Eq. 7, one obtains

$$\frac{\mathrm{d}(h\nu)}{\mathrm{d}T}=(C^g{}_{x^-}-C^g{}_{x^*})-(C^s{}_{x^-}-C^s{}_{x^*}) \tag{10}$$

Approximately $C^g{}_{x^-}$ is equal to $C^g{}_x$, because both ion and atom are monatomic particles in the gaseous phase and the contribution of electronic states may be disregarded in the range of room temperature. Thus

$$\frac{\mathrm{d}(h\nu)}{\mathrm{d}T}\approx-(C^s{}_{x^-}-C^s{}_{x^*}) \tag{11}$$

The configuration of the atomic nuclei, including the solvent molecules, will be similar in $C^s{}_{x^-}$ and $C^s{}_{x^*}$, though the ion-dipole interaction in $C^s{}_{x^-}$ may disappear in $C^s{}_{x^*}$ (i. e. only van der Waals interaction and the exchange repulsive energy). This means that the energy of interaction between the solute and the solvent will be much smaller in $C^s{}_{x^*}$ than in $C^s{}_{x^-}$. Then it is assumed that i) the ion-dipole interaction is so strong that the potential energy between the ion and the solvent molecule can be regarded as a classical vibration energy, and that ii) the interaction between the atom and the solvent molecule is negligibly weak compared with the ion-dipole interaction. Hence, it may be concluded that $(C^s{}_{x^-}-C^s{}_{x^*})$ is mainly due to the vibrational heat capacities (in the sense of classical mechanics) being proportional to the number of solvated molecules (or dipoles), n. Thus, from Eq. 11

$$\frac{\mathrm{d}(h\nu)}{\mathrm{d}T}\approx-kn \tag{12}$$

where k is the Boltzmann constant. As the order of magnitude of n is usually 10 (for example, 6 to 8 for the first layer of hydration in aqeous solution[9]), $\mathrm{d}(h\nu)/\mathrm{d}T$ calculated may be about -20 cal. deg^{-1} mol^{-1} in agreement with the observed values. The present consideration (12) will, essentially, not be different from the Smith-Symons and Stein-Treinin theories, since the increase of the radius of cavity r_0 should correspond to the change in the free energy of the solvated ion caused by the temperature rise. Examples of this sort are found in the models of the free volume for liquids i. e. the harmonic oscillator model and smoothed potential model[10].

Summary

The effect of temperature on the ultraviolet spectra of solvated anions is examined experimentally and theoretically. The shift of the spectrum to the longer wavelength with increasing temperature can be explained in terms of the oscillator model of the solvent molecules. This corresponds to the increase of the ionic radii (or the radius of the cavity) with the temperature rise.

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