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Spectra of Anions in Pure Iodine Melt and Iodine Solution Containing Tellurium

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The absorption spectra in the ultraviolet and visible region were measured as a function of the temperature for pure molten I_2 and for I_2+Te solutions. The two peaks found at about 305 and 370 mμ can be attributed to the I_3^- ion. These peaks increase with the addition of Te indicating an increase in the concentration of the I_3^- ion. This result is consistent with the previous interpretation of the conductivity of molten I_2 containing Te. The ionization potential of I_3^- can be estimated to be about 3.1 eV on the basis of a cyclic analysis using the model of Stein and Treinin which was developed for anion spectra in aqueous solutions. The temperature shift of the absorption energy can also be interpreted in terms of the same model. The heat change for the $I_2(g)+I(g)=I_3(g)$ reaction is estimated as -48.0 kcal·mol^{-1}.

In a previous paper1) we have described our finding on the electrical conductivity of molten I_2+Te solutions, and pointed out that, in the I_2-rich region, the triiodide ion, I_3^-, probably resulting from some chemical reactions, may contribute largely to the electrical conduction.

This paper will report on the absorption spectra of the same solutions in the ultraviolet and visible regions. The experimental results confirm the presence of the I_3^- ion in these solutions and are discussed in terms of the theory given by Platzman and Franck2) and modified by Stein and Treinin3) for anion spectra in aqueous solutions.

Experimental

Materials. The tellurium used was 99.9999% pure. Guaranteed reagent-grade I_2 was dried at room temperature under a vacuum in order to remove the surface water and was purified by sublimation *in vacuo* at about 50°C.

Apparatus and Procedure. The absorption spectra in the ultraviolet and visible regions (230—700 mμ) were measured for the pure I_2 liquid and I_2+Te solutions. Measurements of diffuse reflectance spectra were carried out with a Beckman DK-2A ratio recording spectro-photometer. The quartz-drum-cell containing the sample, in which a fine powder phase was made of the guaranteed reagent-grade aluminum oxide, was sealed off under a vacuum. The observed temperature range was limited to below 200°C because of the limited temperature-supporting capacity of this spectrometer. The diffuse reflectance obtained for a given wavelengh was transformed to the optical density in arbitary units by means of the Kubelka-Munk equation.4)

Results

The absorption bands of the I_2+Te solutions at several concentrations and temperatures are plotted in Fig. 1. All the absorption spectra show two peaks with a charactristic spacing at about 305 and 370 mμ. Their optical densities increase with the addition of Te,

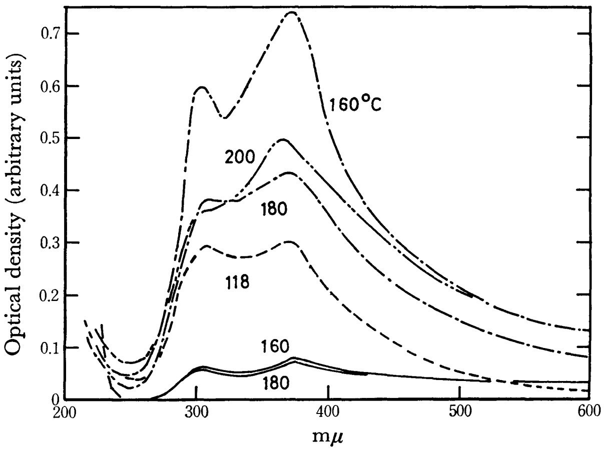

Fig. 1. Absorption spectra of I_2+Te solutions at various temperatures (——: pure, ----: I_2+2 at.% Te, —-—: I_2+4 at.% Te, and ——-—-: I_2+40 at.% Te).

TABLE 1. ABSORPTION BANDS OF TRIIODIDE ANION (10^4 cm^{-1})

150°C		Room temperature		
I_2	I_2+4 at.%Te	KI crystal $+I_2$7)	CsI_3 in water5)	KI+I_2 in water6)
3.260	3.295	3.454	3.478	3.478
2.699	2.722	2.821	2.846	2.846

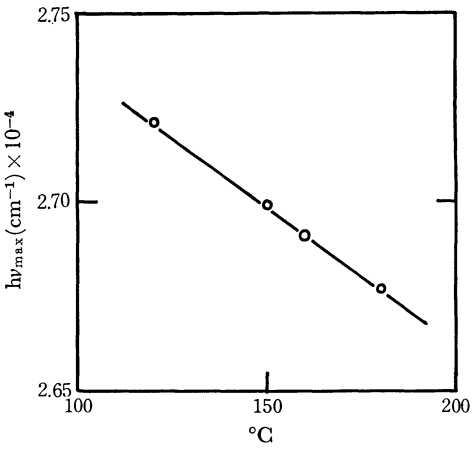

Fig. 2. $h\nu_{max}$ of molten iodine at various temperatures.

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1) K. Ichikawa, T. Ōkubo, and M. Shimoji, *Trans. Faraday Soc.*, **67**, 1426 (1971).

2) R. Platzman and J. Franck, *Z. Physik*, **138**, 411 (1954).

3) G. Stein and A. Treinin, *Trans. Faraday Soc.*, **55**, 1086 and 1091 (1959).

4) *E.g.*, R. J. H. Clark, *J. Chem. Educ.*, **41**, 488 (1964).

although the wavelengths of the peaks are almost unchanged. Above about 150°C the optical density decreases and the band width increases with the temperature. Table 1 shows the two absorption maxima in the molten I_2 and I_2+4 at.% Te systems at 150°C. The energy separation between these two band maxima is very small, with a range of only about 0.6×10^4 cm^{-1}. In Fig. 2 the temperature dependence of the $h\nu_{max}$ of the longer wavelength band in the pure I_2 liquid is recorded. The straight line gives $dh\nu_{max}/dT=-7.3$ cm^{-1} deg^{-1}.

Discussion

In our previous work,[1] the considerable increase in the conductivity of molten I_2, upon the addition of 0.1—4 at.% Te was interpreted in terms of a charge-transport mechanism, and the formation of the triiodide ion I_3^-, resulting from the $I_2+I^-\longrightarrow I_3^-$ reaction, was suggested. The existence of the I_3^- ion is now confirmed by the absorption maxima found at 305 and 370 mμ, as is shown in Fig. 1 and Table 1, in which the other data for the CsI_3,[5] $KI+I_2$[6] aqueous solutions and the $KI+I_2$[7] solid solutions are also cited. The two peaks of the absorption spectra suggest a doublet splitting of some kind in the electronic states of the I_3 molecule.

The magnitude of $h\nu_{max}$ and its temperature shift, $dh\nu_{max}/dT$, obtained here will be discussed using the theory of Stein and Treinin,[3] which accounts for the anion spectra in aqueous solutions in terms of the charge-transfer-to-solvent mechanism.[2,3,8–10] Since the solvent structure in their theory is approximated only by a dielectric continuum with a static dielectric constant, D_s, the formula proposed by them may be used for systems other than the aqueous solution. Thus, the absorption energy of the solvated I_3^- ion may be written, using Stein and Treinin's notation, by:

$$h\nu_{max}=E_X-L_X+\frac{e^2}{r_0}\left(\frac{1}{2}+\frac{1}{2D_{op}}-\frac{1}{D_s}\right)-\frac{e^2}{2\bar{R}_e}\left(1-\frac{1}{D_{op}}\right)-\left(\frac{\pi^2me^4}{2h^2}\right)\left(\frac{1}{D_{op}}-\frac{1}{D_s}\right)^2 \qquad (1)$$

The value of the apparent radius, r_o, of the cavity in the continuous medium can be determined from the relation $r_o\cong\alpha r_c$,[3] where r_c is the crystallographic radius and where α is a constant with a value of about 1.275. The value of r_c for I_3^- is taken as 3.51 Å from the crystallographic data of CsI_3,[11] by using the method of Gray and Waddington[12] for the calculation of the effective radius of N_3^-. The energy change associated with the non-thermodynamic dissolution of the I_3 molecule, $-L_X$, is roughly taken as $-3\Delta H_e/2$ by considering the dispersion forces. Here, ΔH_e[13] is the heat of evaporation of liquid I_2. The average distance of the excited electron from the center, $\bar{R}_e$, is calculated using the hydrogen-like wave function in the Coulomb force field due to the effective charge of the Landau type.

TABLE 2. IONIZATION POTENTIAL E_X OF I_3 EVALUATED BY MEANS OF EQ. (1) ENERGIES IN 10^4 cm^{-1}

	150°C molten I_2	Room temperature		
		aq. CsI_3	aq. $KI+I_2$	crystal $KI+I_2$
E_X	2.41	2.60	2.60	2.60
D_{op}	2.73	1.78	1.78	2.69
D_s	13.0	78.5	78.5	4.94
L_X	0.607	0.483	0.483	0.758

The values of the optical dielectric constant D_{op} and those of D_s for the liquids are referred to "Gmelins Handbuch der anorganischen Chemie" **8**, Jod, Verlag Chemie, Berlin (1933) p. 85, 649. and **5**, Sauerstoff, Verlag, Weinheim, (1963) p. 1550, 1591, and those for the crystal are taken from N. F. Mott and R. W. Gurney, "Electronic Processes in Ionic Crystals," Clarendon Press, Oxford (1940), p. 12.

No data have been obtained so far for the value of the ionization potential of the I_3^- ion, E_X. Therefore, the value shown in Table 2 is evaluated on the basis of Eq. (1) using the experimental $h\nu_{max}$ values. Similar calculations were also made for CsI_3 and $KI+I_2$ aqueous solutions and for the KI crystal containing I_2, where it is assumed that the values of $-L_X$ are 3/2 of the heats[13,14] of solution of I_2 into the respective solvents. The calculated E_X values in Table 2 are almost constant, ranging only (2.4—2.6) $\times10^4$cm^{-1}, despite the differences in the parameters of the respective solvents.

No quantitative calculations have been performed for the I_2+Te solutions, because no observed values of D_s in this system are available. The resemblance in the positions of the absorption maxima reported in Fig. 1 and Table 1, however, suggests the applicability of the same model for the extremely I_2-rich melts. In other words, the parameter values (for r_o, D_s, D_{op}, L_X, *etc.*) in the molten I_2 containing a small amount of Te below 4 at.% may not be very different from those in pure I_2. Further, the increase in the optical densities of the peaks (Fig. 1) upon the addition of Te and the decrease upon the raising of the temperature indicate an increase in the concentration of the I_3^- ion. These facts are consistent with the conclusion in the conductivity work[1] that the enthalpy change in the I_3^- formation must be negative, because the I_3^- concentration decreases with an increase in the temperature in these I_2-rich liquids.

Theoretically, the temperature shift can be written by a differentiation of Eq. (1) with respect to the temperature. The contribution from the temperature change in D_s and D_{op} is, at most, -1 cm^{-1}deg^{-1}, which is much smaller than the experimental value of -7.3

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13) *E.g.*, O. Kubaschewski and E. LL. Evans, "Metallurgical Thermochemistry", Pergamon Press, Oxford (1958).

14) "Selected Values of Chem. Thermody. Property," Technical Note 270—3, National Bur. Stand. (1968).

$cm^{-1}deg^{-1}$. The term of dL_X/dT can be calculated from the value of the heat capacity of the I_3^- ion in the excited state, $C_p(I_3(I_2)_n^-)$. The heat-capacity effect in the gaseous state practically vanishes[10] in these cyclic calculations, for its effect appears in the processes of both the ion removal and the radical solvation (*e.g.*, in the terms of E_1 and E_2 in Eq. (6) in the paper of Stein and Treinin,[3] from which Eq. (1) in this paper is obtained). $C_p(I_3(I_2)_n^-)$ is roughly taken as 3/2 of the heat capacity of the I_2 molecule in the liquid state. dr_0/dT is evaluated from the $\alpha dr_c/dT$ relation using the density data.[15] Thus, for pure I_2 the calculated $dh\nu_{max}/dT$ value of $-8.7\ cm^{-1}deg^{-1}$ is in fair agreement with the experimental value of $-7.3\ cm^{-1}deg^{-1}$ (Fig. 2). This temperature shift may also be interpreted alternatively in terms of the vibrational effect[10] of the solvated molecules.

In a simpler model, proposed by Smith and Symons,[8] the temperature effect is explained by considering only the change in the excited state, which is approximated as a state of a free particle in a spherical box. Adopting $E_X=2.41\ cm^{-1}deg^{-1}$ from Table 2 and $h\nu_{max}=26990\ cm^{-1}$, we get 10.2 Å for the radius, r_0^*, of the spherical box in their model. However, such a free-electron-like behaviour in the box may be difficult to correlate with any physical property of the ion, as was pointed out by Stein and Treinin.[3]

The heat of formation of triiodide molecules in the gaseous state has not previously been reported. However, the heat of reaction, $\Delta H_r(I_3^-(aq))$, for the equilibrium in aqueous solutions[16]:

$$I_2(aq) + I^-(aq) \rightleftharpoons I_3^-(aq) \qquad (2)$$

has been well investigated, and the heats[14] of hydration of the iodine molecule and ion, *i.e.*, $\Delta H_h(I_2)$ and $\Delta H_h(I^-)$, are konwn. Further, the ionization potential of the I^- ion, $E_X(I^-)$,[9] has been established, the heat of hydration of the I_3^- ion can be estimated theoretically by means of Born's equation,[17] and the semiempirical value of the ionization potential of the I_3^- ion, $E_X(I_3^-)$, is shown in Table 2 of this paper. Thus, if we use $\Delta H_r(I_3^-(aq))=-4.7\ kcal\cdot mol^{-1}$, $\Delta H_h(I_2)=-9.5$, $\Delta H_h(I)=-72.1$, $\Delta H_h(I_3^-)=-39.3$, $E_X(I^-)=72.5$, and $E_X(I_3^-)=71.5$, the heat of reaction, $\Delta H_r(I_3(g))$, for the reaction:

$$I_2(g) + I(g) = I_3(g) \qquad (3)$$

can be given by $-48.0\ kcal\cdot mol^{-1}$. This calculated result suggests that the I_3 molecule is stable in the gaseous phase, as is observed in the mass spectra.[17]

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[16] G. Jones and B. B. Kaplan, *J. Amer. Chem. Soc.*, **50**, 1845 (1928).

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