41. *Experimental Studies of Solution Processes. Part IV. Spectrophotometry of the System Iodine–Nitromethane–Carbon Tetrachloride.*

By P. A. D. de Maine and W. C. Ahlers.

Measurements of the absorption spectrum between 3500 and 6000 Å have been used to indicate an equilibrium reaction, $I_2 + MeNO_2 \rightleftharpoons$ Complex, whose constant equals 0·123 mole-fraction unit. Between 4900 and 6000 Å the spectrum remains unchanged with time, but below 4900 Å the absorption increases slowly. Increased concentrations of nitromethane increase the rate of this change. A quantitative interpretation of this is given.

Evidence for dimers of nitromethane in the pure liquid and in dilute solution is given in Part I [1] and in references therein. Azeotrope formation [2] and cryoscopic studies [3] suggest that nitromethane can form complexes with other molecules. Recent work [4] showed that in solution ferric chloride forms a 1 : 1 complex with nitromethane.

Mulliken [5] has explained variations in colour of solutions of iodine in different solvents by means of a "charge-transfer" hypothesis; and he suggested that in some cases the "outer complex" may slowly change to the energetically more stable ionic "inner complex."

Experimental

Carbon tetrachloride and nitromethane were purified as already described.[1] British Drug Houses' resublimed iodine was used. Part I [1] contains full details of the preparation of iodine–nitromethane–carbon tetrachloride solutions and nitromethane–carbon tetrachloride blanks, and a description of the Unicam absorption spectrophotometer. The absorption spectrum of each sample was measured from 6000 Å to the "cut-off" near 3500 Å for pure nitromethane. Optical densities between 0·050 and 0·900 unit were reproducible to better than 1%.

In all cases iodine–carbon tetrachloride and nitromethane–carbon tetrachloride solutions were mixed immediately before the initial spectral measurement was made. The concentration ranges studied were 0·547—4·137mm and 0·370—16·660m for iodine and nitromethane respectively.

Results and Discussion

(*A*) *Measurements made at the Time of Preparation of the Solution.*—The molar extinction curve for iodine in nitromethane–carbon tetrachloride changes markedly with the concentration of nitromethane (Fig. 1). At fixed nitromethane concentrations, iodine solutions obey Beer's law.

Graphical analysis of the spectroscopic data between 3500 and 6000 Å by both Ketelaar,

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[1] de Maine, de Maine, and Goble, *Trans. Faraday Soc.*, 1957, **53**, 427.

[2] "Azeotropic Data," Advances in Chemistry Series, published by American Chemical Society, 1952.

[3] Barton, Rothrock, and Kraus, *J. Amer. Chem. Soc.*, 1952, **74**, 786.

[4] de Maine and Koubek, *J. Inorg. Nuclear Chem.*, in the press.

[5] Mulliken, *J. Phys. Chem.*, 1952, **56**, 801.

van de Stolpe, Goudsmit, and Dzcubas's[6] and Scott's[7] methods showed that for the equilibrium $MeNO_2 + I_2 \rightleftharpoons$ Complex, $K = 0{\cdot}123 \pm 0{\cdot}030$ mole-fraction unit over all wavelengths in this region. The root-mean-square method was used to obtain a " best fit " for our data at 5300, 5400, and 5500 Å to the van de Stolpe equation. At these three wavelengths the best value for K was $0{\cdot}126 \pm 0{\cdot}040$ mole-fraction unit. A typical van de Stolpe-type plot is in Fig. 2. The minimum nitromethane concentration used in these calculations was 3·33M or 0·282 mole-fraction units.

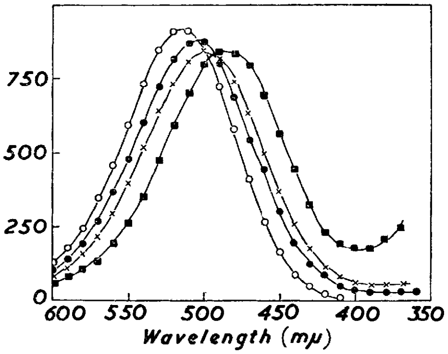
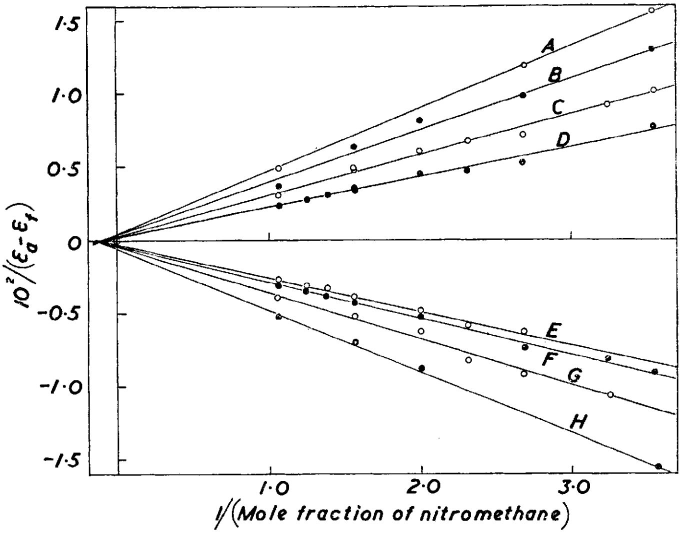


FIG. 1. *Molar extinction curves at* 18° *for iodine in pure carbon tetrachloride* (○) *and in carbon tetrachloride–nitromethane. Absorption by the solvent has been subtracted.*

Mole fraction of $MeNO_2$: ● 0·282, × 0·641, ■ 0·943.

The low value obtained for K and the value of 34·82 at 25° for the dielectric constant of nitromethane[8] suggest that the weak complex arises from charge-transfer interaction[5] between single iodine molecules, and single or dimer molecules of nitromethane.[1] The blue-shift of the visible band (Fig. 1) arises from a contribution of the molecular iodine transition (centre near 5160 Å in CCl_4) modified by the charge-transfer interaction.[5] With assumptions that $K = 0{\cdot}123$ mole-fraction unit and that the molar extinction coefficient

FIG. 2. *Plots of* $10^2/(\varepsilon_a - \varepsilon_f)$ *at* 18° *at various wavelengths.*



ε_a = measured optical density/total iodine concentration.
ε_f = molar extinction coefficient of iodine in pure CCl_4.
A, 4200; *B*, 4300; *C*, 4400; *D*, 4600; *E*, 5300; *F*, 5500; *G*, 5600; *H*, 5700 Å.

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[6] Ketelaar, van de Stolpe, Goudsmit, and Dzcubas, *Rec. Trav. chim.*, 1952, **71**, 1104.
[7] Scott, *Rec. Trav. chim.*, 1956, **75**, 787.
[8] Lange, " Handbook of Chemistry," 9th edn., Sandusky, Ohio, 1956, p. 1222.

for uncomplexed iodine is independent of the solution, the centre for the modified molecular iodine transition was calculated to be near 4700 Å at 18°. The absorption band for the " outer charge-transfer complex "[5] would be located towards the short-wavelength side of 3500 Å and would thus be within the nitromethane absorption region.

(*B*) *Measurements made Later.*—Between 3500 and 4900 Å the molar extinction curve for iodine in nitromethane–carbon tetrachloride increases slowly with increasing time after preparation of the solution. There was no measurable change with time at wavelengths between 4900 and 6000 Å. These effects are illustrated in Fig. 3 for a solution with 0·282 mole fraction of nitromethane. No change with time occurs in the ultraviolet and visible spectra for iodine–carbon tetrachloride and nitromethane–carbon tetrachloride solutions.

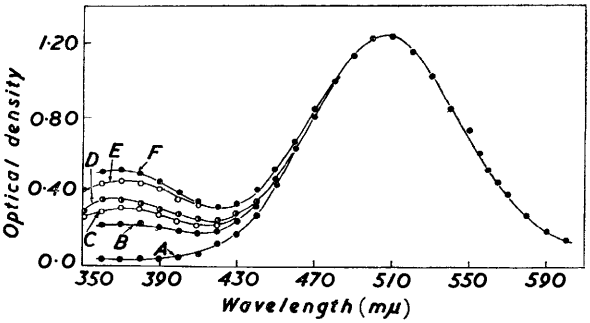


FIG. 3. *Optical densities at* 18° *at various times.*

Initial concns.: nitromethane, 0·282 mole-fraction unit; iodine, 1·436 mM.

A, 0·0; *B*, 14·0; *C*, 21·9; *D*, 36·4; *E*, 62·0; *F*, 56·0 hr.

Studies on a series of solutions containing a fixed iodine concentration and variable amounts of nitromethane showed that the rate of increase of absorption in the 3500—4900 Å region rises rapidly with increased nitromethane concentration (Fig. 4).

Our kinetic data can be explained quantitatively by one of the following mechanisms:

(i) $MeNO_2 + I_2 \xrightleftharpoons{K}$ Complex; Complex + Complex $\xrightarrow{k_1}$ Complex$_2$.

(ii) $MeNO_2 + I_2 \xrightleftharpoons{K}$ Complex $\xrightarrow{k_1}$ Complex$_2'$; Complex + Complex$_2'$ $\xrightleftharpoons{K_2}$ Complex$_3$.

For both mechanisms, $K = 0{\cdot}123$ mole-fraction unit; " complex " is the charge-transfer " outer " complex; complex$_2$, complex$_2'$, and complex$_3$ are other weak complexes. Complex$_2'$ could be the " inner " charge-transfer complex postulated by Mulliken.[5]

Scheme (i) can be described by the equation

$$1/\Delta D_t = 2/rC_A\varepsilon_{C_2} + 2/k_1r^2C_A{}^2t\varepsilon_{C_2}$$

where ΔD_t is the increase in absorption during " t " hours; ε_{C_2} is the molar extinction coefficient for complex$_2$; C_A is the initial concentration of iodine; and

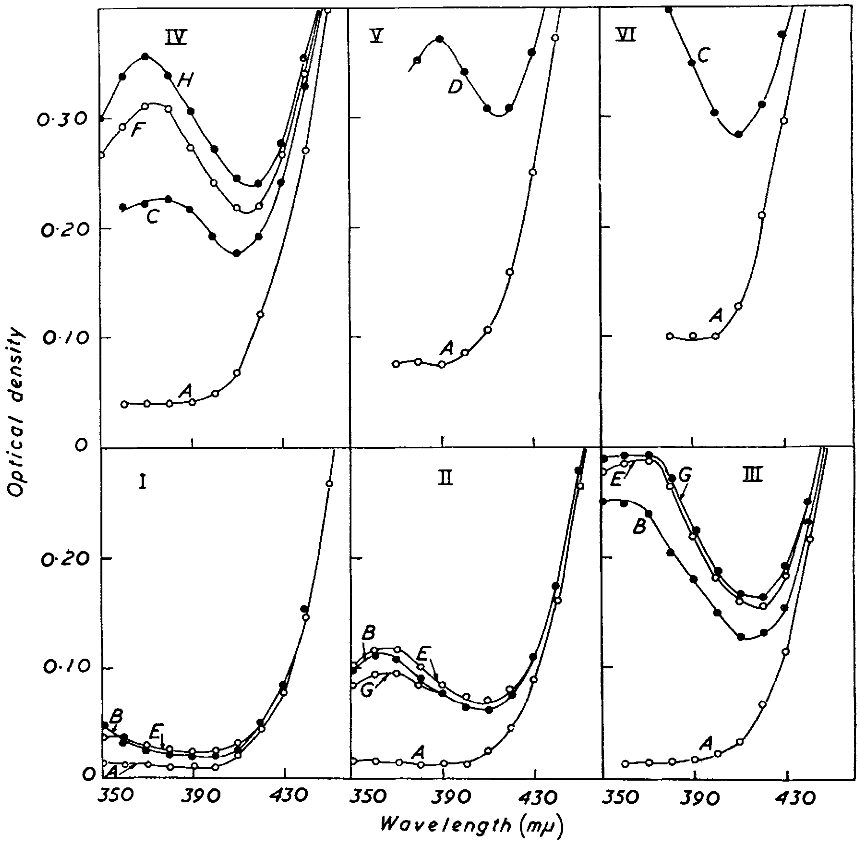
$$r = K[MeNO_2]/(1 + K[MeNO_2]);$$

$[MeNO_2]$ is the concentration of nitromethane as monomer. Scheme (ii) gives a similar equation. According to the equation, a plot of $1/\Delta D_t$ against " $1/t$ " will be linear with a positive intercept equal to $2/rC_A\varepsilon_{C_2}$. Fig. 5 shows these linear plots made with our experimental values. The positive intercepts multiplied by rC_A were approximately constant at each wavelength.

The experimental values also eliminated two possible mechanisms, (iii) and (iv). In mechanism (iii) it is assumed that the nitromethane contains a small, undetected amount of impurity and that one mole of impurity reacts with two moles of iodine to yield a product which absorbs between 3500 and 4900 Å. The equation would be

$$1/\Delta D_t = 2/C_A\varepsilon_{C_2} + 2/k_1[\text{Impurity}]C_A{}^2t\varepsilon_{C_2}$$

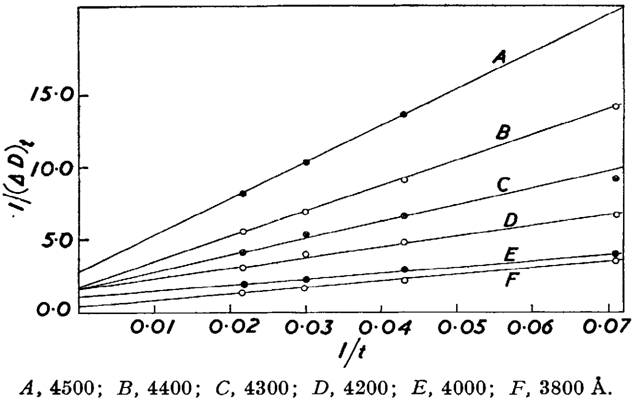
FIG. 4. *Optical densities at* 18° *at various times and concentrations of nitromethane.*



Iodine concn.: 1·436 mM throughout. Mole fraction of nitromethane: I, 0·0351; II, 0·0523; III, 0·1184; IV, 0·282; V, 0·500; VI, 0·641.

Times: *A*, 0·0; *B*, 12·0; *C*, 14·0; *D*, 14·1; *E*, 21·0; *F*, 21·9; *G*, 36·0; *H*, 36·4 hr.

FIG. 5. *Plots of* $1/\Delta D_t$ *against* $1/t$, *where* ΔD_t *is the increase in absorption at t hours, at* 18° *and concentrations as for Fig.* 3.



A, 4500; *B*, 4400; *C*, 4300; *D*, 4200; *E*, 4000; *F*, 3800 Å.

Again a linear relationship between $1/\Delta D_t$ and $1/t$ is predicted; however, the intercept should be independent of the impurity concentration, and thus independent of nitromethane concentration. That this prediction is not fulfilled is illustrated by solutions containing 0·282 and 0·500 mole-fraction units of nitromethane whose positive intercepts gave a ratio of 1·78 : 1·00 at most wavelengths. Mechanism (IV) is

$$\mathrm{MeNO_2} + \mathrm{I_2} \xrightleftharpoons{K} \text{Outer complex} \xrightarrow{K_1} \text{Inner complex followed by:}$$

$$\text{Inner complex} + \mathrm{I_2} \xrightleftharpoons{K_2} \mathrm{MeNO_2I^+ \ldots I_3^-}$$

Work by Awtrey and Connick [9] with KI_3^- in aqueous systems suggests that K_2 would be large and that the $MeNO_2\ I^+ \ldots I_3^-$ complex would absorb in the 3500—4900 Å region. As I_3^- has ε 26,000 near 3530 Å in water, very minute quantities would produce a large spectral increase below 4900 Å, yet leave the longer-wavelength spectrum of I_2 unchanged in intensity. However, this system does not predict a linear relation between $1/\Delta D_t$ and $1/t$, and our data do not fit equations which describe mechanism (iv).

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[9] Awtrey and Connick, *J. Amer. Chem. Soc.*, 1951, **73**, 1842.