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A Spectrophotometric Study of the Hexamethylphosphotriamide–Iodine Complex

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The 1:1 molecular complex between iodine and hexamethylphosphotriamide (HMPT) has been studied in n-heptane and cyclohexane spectrophotometrically at 20, 25, 30, 40° C. The equilibrium constants $K = [HMPT \cdot I_2]/[HMPT][I_2]$ *were found to be 352, 284, 237 and 154. The corresponding changes in heat content, entropy and free energy of formation (at 20° C) were –7.3 kcal/mol, –13.2 cal/deg mol, and –3.4 kcal/mol respectively. The addition to a dilute* I_2 *solution of HMPT in appreciable amount gives rise to the appearence of two new bands at 3700 and 2950 Å. These peaks have been attributed to the absorbance of the* I_3^- *ionic species. The very intense absorbance of* $HMPT \cdot I_2$ *which appears at 2215 Å when iodine is dissolved in pure HMPT has been interpreted as a charge-transfer spectrum. A conductometric study on very dilute iodine solution in pure HMPT has been also made; the conclusions are that ionic species, namely* $HMPTI^+$ *and* I^- *ions, generated by dissociation of the* $HMPT \cdot I_2$ *complex, are present in large quantity*

Introduction

In the course of previous experiments[1] it was observed that potassium iodide, dissolved in hexamethylphosphotriamide (HMPT), gave weakly yellow colored solutions; the intensity of the colour was found to depend on the amount of the added salt and on the procedure employed in the purification of the solvent used. It was also observed that using very pure potassium iodide and freshly distilled HMPT the solution appeared colourless and became pale yellow after exposure to the air moisture for a long time. To explain these facts the presence in solution of some amount of a complex between the iodine and the HMPT molecule was assumed, free iodine in a potassium iodide in HMPT solution being generated by oxidative processes concerning the HMPT molecules.[2]

It is well known that iodine in the vapour state and in some solvents, like n-heptane, cyclohexane *etc.*, is characterized by an absorption in the visible region with a maximum at 5200 Å, while in other solvents it form yellow or brown colored solutions. This fact has been explained with the assumption that 1:1 molecular complexes between free iodine and the solvent molecules are formed in the yellow and brown solutions;[3] the extent to which the 5200 Å absorption peak is shifted toward shorter wavelengths, the equilibrium constant and the free energy of formation of the complex depend on the properties of the solvent used.

The aim of the present work is to study the thermodynamic properties of this complex; for this purpose a spectrophotometric investigation on dilute iodine solutions in two non-polar solvents, cyclohexane and n-heptane, in the presence of increasing amounts of HMPT has been made. The research has been extended up to iodine solution in pure HMPT where conductivity measurements were also made.

Experimental

The iodine was sublimed three times and the purity checked by titration with arsenious acid. The hexamethylphosphotriamide was purified following a method previously described.[1]

R.S. Carlo Erba n-heptane and cyclohexane (spectrophotometric grade) were used without further purification. The apparatus used for conductometric measurements as well as the cell employed have been described in a previous paper.[4]

Spectrophotometric determinations were performed with an Optica spectrophotometer using 1, 0.5 and 0.1 cm cell thicknesses. No precautions were taken to avoid moisture uptake during the experiments; the temperature was maintained at constant values by water circulation.

Results and Discussion

The Spectrum of Iodine plus HMPT in Cyclohexane and N-Heptane

The visible peak of iodine in n-heptane and in cyclohexane solution located at 5200 Å is shifted toward

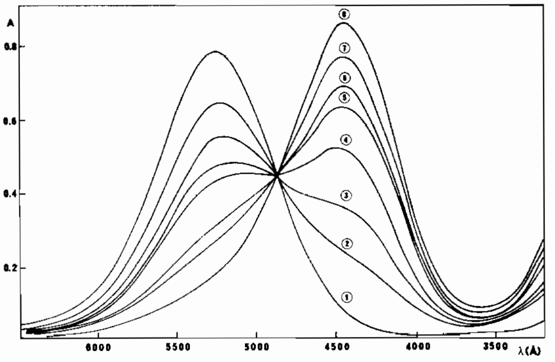

Figure 1. Plot of the absorbance against wavelength for iodine solutions in cyclohexane with increasing amounts of HMPT at 25° C. $C_{I_2} = 1.661 \times 10^{-3} M$. C_{HMPT} = 1) $0.00\,M$, 2) $1.05 \times 10^{-3} M$, 3) $2.09 \times 10^{-3} M$, 4) $4.19 \times 10^{-3} M$, 5) $6.28 \times 10^{-3} M$, 6) $8.37 \times 10^{-3} M$, $1.256 \times 10^{-2} M$, 8) $2.722 \times 10^{-2} M$.

shorter wavelengths at 4450 Å by addition of some amounts of HMPT to the solution.

The equilibrium

$$I_2 + HMPT \rightleftarrows HMPT \cdot I_2 \qquad (1)$$

was studied in the concentration range $10^{-3} \div 10^{-1} M$ for HMPT and $1 \times 10^{-3} \div 5 \times 10^{-3} M$ for I_2.

During the addition of small amounts of HMPT to a given dilute iodine solution a decrease of the absorbance at 5200 Å and a corresponding increase of the peak at 4450 Å is observed (Figure 1). Since the absorbance of HMPT at 4450 Å is almost zero, the equilibrium constant

$$K = [HMPT \cdot I_2]/[HMPT][I_2] \qquad (2)$$

has been determined as follows: at the wavelengths at which $\varepsilon_{HMPT} = O$ we have

$$A = l(\varepsilon_1[HMPT \cdot I_2] + \varepsilon_o[I_2]) \qquad (3)$$

where ε_1 is the molar absorption of the complex $HMPT \cdot I_2$ and ε_o the molar absorption of I_2.

Considering that $[I_2] + [HMPT \cdot I_2] = C_{I_2}$, where C_{I_2} is the analytical concentration of iodine, eq. (3) can be written:

$$A = l\,[\frac{\varepsilon_1 \cdot C_{I_2} \cdot K[HMPT]}{1 + K[HMPT]} + \varepsilon_o(C_{I_2} - \frac{C_{I_2} \cdot K[HMPT]}{1 + K[HMPT]})]$$

Writing A_o in place of $\varepsilon_o \cdot l \cdot C_{I_2}$ and rearranging we obtain

$$F = l\,\frac{C_{I_2}\,[HMPT]}{A - A_o} = \frac{1}{(\varepsilon_1 - \varepsilon_o)\,K} + \frac{[HMPT]}{\varepsilon_1 - \varepsilon_o} \qquad (4)$$

which is the equation of a straightline when the term F is plotted against [HMPT].

In equation (4) the concentration of free HMPT was firstly assumed as the analytical concentration; in this way a straightline equation of first approximation was calculated from which more correct values of the HMPT concentration are deduced. The final values of the coefficients of eq. (4), obtained by iteration, give the equilibrium constant K, these values calculated at three temperatures are reported in Table I.

The logarithms of the K values were reported in a plot against the reciprocal of the absolute temperature (Figure 2) and the heat of dissociation of $HMPT \cdot I_2$ complex was calculated to be 7.3 ± 0.2 kcal/mol. The free energy and the entropy changes for reaction (1) were also computed and the results are shown in the same Table I.

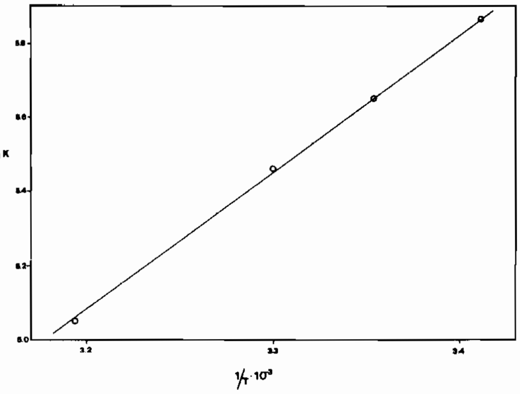

Figure 2. Plot of the lnK values against the reciprocal of the temperature for the equilibrium (1) between iodine and HMPT in cyclohexane.

TABLE I. Thermodynamic Quantities of $HMPT \cdot I_2$ Complex in Cyclohexane Solution.[a]

t (° C)	K (l/mol)	ΔG (Kcal/mol)	ΔH (Kcal/mol)	ΔS (cal mol^{-1} deg^{-1})
20	352 ± 7	−3.42 ± 0.01		−13.2
25	284 ± 6	−3.35 ± 0.01	−7.3 ± 0.2	−13.2
30	237 ± 5	−3.29 ± 0.01		−13.2
40	154 ± 3	−3.13 ± 0.01		−13.3

[a] Differences between the thermodynamic quantities in cyclohexane and in n-heptane solutions are within the experimental errors. Standard errors have been calculated according to W. J. Youden, "Statistical Methods for Chemistry", Wiley, 1951, ch. 5.

Many similarities exist between the complexes of I_2 in pyridine and in HMPT.[5] The complexes formed are in fact very stable in both solvents; the free energy and the entropy changes are very close in the temperature range 20 ÷ 40° C; the absorbance peak of I_2 in Py and in HMPT in the ultraviolet region and the shift of the peak of I_2 in the visible region are located at almost the same wavelength.

Further, the spectrum of I_2 in presence of HMPT, employing thin cells, shows a strong maximum (ε = 6.500) at 2216 Å. This peak is well known for complexes ArI_2 as a charge-transfer band. In pyridine it occurs at 2200 Å.

According to Mulliken[6] a quantum mechanical description of charge-transfer complexes may be given by writing the wave function of the ground state of a complex AB as

$$\Psi_N = a\,\Psi_0 + b\,\Psi_1$$

where Ψ_0 is a no-bond wave function $\Psi(A, B)$ and Ψ_1 is a wave function corresponding to the transfer of an electron from B to A, A and B being any pair of atoms or molecules in totally symmetrical singlet ground state. If A and B are molecules and their description is given in terms of molecular orbitals this means a closed shell structure.

The spectrophotometric charge-transfer band corresponds to the transition $\Psi_N \rightarrow \Psi_E$ where E is an excited state described by

$$\Psi_E = a^*\,\Psi_1 - b^*\,\Psi_0$$

A possible model for the complex $HMPT \cdot I_2$ can be envisaged as one with the iodine molecule partially bound to oxygen in the plane which contains the projection of the three lone pairs of the oxygen atom. This model is sufficiently compact to insure a good coulomb attraction energy in $W_1 = \int \Psi_1 H \Psi_1$. Further, this model let to obtain for Ψ_1 a totally symmetrical singlet state employing ground state of $HMPT^+$ and I_2^-.

The ionization of HMPT involves removal of an electron of one of the three lone pairs of oxygen orbitals. If we assume for the HMPT isolated molecule the C_{3v} symmetry, the complex $HMPT \cdot I_2$ has the C_{1h} symmetry. If we choose the *x* and *y* axes as in Figure 3 with the *z* axis up to this plane coinciding with the P–O bond, three MO's can be obtained with suitable linear combinations of the three lone pairs of the oxygen atom. The most easily ionizable should be l_{p2}–l_{p3}, which fall in the B representation of the C_{1h} group. Removal of an electron of this orbital give a ^2B state for the $HMPT^+$.

The six outer shell MO's for I_2 in the form they assume in this model can be approximated as

$$\begin{array}{llll} A\sigma_g & = X_1 + X_2 & B\sigma_u & = X_1 - X_2 \\ A'\pi_u & = Y_1 + Y_2 & B'\pi_g & = Y_1 - Y_2 \\ A''\pi_u & = Z_1 + Z_2 & B''\pi_g & = Z_1 - Z_2 \end{array}$$

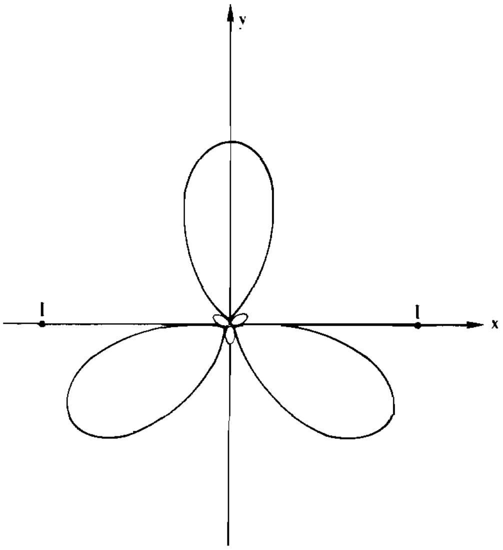

Figure 3. Schematic drawing of the bond between I_2 and the oxygen orbitals of HMPT.

where the first symbol gives the classification under C_{1h} and the second that for the isolated I_2 molecule of $D_{\infty h}$ symmetry. In the I_2^- ground state the added electron enters the strongly antibonding $B\sigma_u$ which is empty, giving a ^2B state. The required $^1A_1$ state for the complex can be obtained if $HMPT^+$ is also in a ^2B state. This model gives moreover the suitable symmetry for a favourable overlapping between the odd electrons.

As far as the dissociation of the complex molecules into ions is concerned, Kortum and Wilski[7] report that I_2 dissolved in freshly distilled Py at $10^{-4}M$ gives a conductivity larger than for most iodine complexes. They found an ionic dissociation constant of 4.6×10^{-8} for the equilibrium

$$Py \cdot I_2 \rightleftarrows PyI^+ + I^-$$

at variance with a previous paper of Audrieth and Birr[8] who found a high electrical conductivity for I_2 in pyridine.

The experiments in HMPT, performed using great precautions to exclude the air moisture in preparing the I_2 in HMPT solution give the following results: solutions as concentrated as $1.8 \times 10^{-4}M$ have a value of the specific conductance of 2.6×10^{-6} ohm^{-1} cm^{-1}. This value slowly changes during the experiments. Assuming for $HMPT^+$ and I^- λ_0 values of 5 and 16.5 respectively[9] by the equation Λ = 1000 k/C a dissociation degree of 0.66 can be calculated dividing the experimental concentration by the concentration obtained from the above equation if one puts in the above equation Λ_0 equal to Λ. To explain the high electrical conductivity of I_2 in pure HMPT the dipole moment of the solvent and the high electron density of its oxygen atom[10] must be considered; it is fair to guess that in pure HMPT the solvent molecules act as an electron donor toward I_2, thus promoting the formation of the HMPT·I_2 complex; at the same time the HMPT molecules acting as a polar medium should be able to dissociate into ions a large quantity of the complex formed. It should be emphasized at this point that the dissociation degree deduced by conductivity measurements do not mean necessarily an incomplete dissociation into ions of the complex; the presence of some amount of I_3^- contributes very probably to lower the value of the solution conductivity (see next section).

The Spectrum of Iodine in Concentrated HMPT Solution

Spectrophotometric determinations of I_2 in n-heptane and cyclohexane show a gradual increase of the peak at 4450 Å as HMPT in increasing amounts is added to the solution. However, when a concentration of HMPT equal to $10^{-1}M$ is reached, a new band at 3700 Å appears; correspondently the 4450 Å HMPT·I_2 band begins to be deformed and is completely masked by the 3700 Å peak at the higher HMPT concentrations.

The presence of a peak in the neighbourhood of 3700 Å has been found in the complexes of iodine in some other solvents and has been differently interpreted.

In the case of the iodine–pyridine complex[5] a possible explanation of the gradual shift of the 4220 Å Py·I_2 band in n-heptane to 3890 Å in pure pyridine has been given assuming a gradual clustering of polar pyridine molecules around the Py·I_2 molecules; alternatively, the 4220 and 3890 Å bands have been attributed to the completely unsolvated and fully solvated Py·I_2 molecules.

Some differences existing in the absorption spectra of I_2 complexes in Py and in HMPT suggest a different interpretation of our experimental results. In pyridine in fact the 4220 Å peak shifts toward shorter wavelengths as the pyridine concentration increases, reaching a maximum at 3890 Å in pure pyridine. On the contrary, in the case of the HMPT·I_2 complex on increasing the concentration of HMPT, no shift in the 4450 Å band was noted, but a simultaneous presence of two different peaks at 4450 and 3700 Å was observed. Figure 4 shows what happens when HMPT is added to a $9.7 \times 10^{-4}M$ iodine in n-heptane solution. As one can see, beginning from $0.1M$ of added HMPT an appreciable absorbance at 3700 Å is detectable (curve 3). From curves 4, 5 and 6 which refer to 0.2, 0.39 and $0.6M$ HMPT solutions respectively it is evident that the new absorbance at 3700 Å affects very little the 4450 Å peak. Lastly, in curve 7 which refers to pure HMPT solution the 3700 Å peak is high enough to mask the absorbance at 4450 Å.

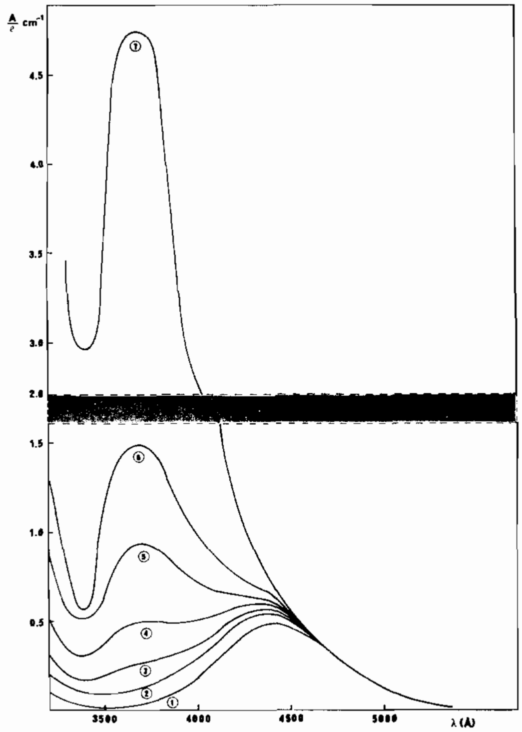

Figure 4. Plot of spectral changes with increasing HMPT concentration relative to $9.77 \times 10^{-4}M$ in iodine solutions. Solvent n-heptane. C_{HMPT} = 1) $2.5 \times 10^{-2}M$, 2) $5.0 \times 10^{-2}M$, 3) $0.1M$, 4) $0.2M$, 5) $0.39M$, 6) $0.6M$, 7) pure HMPT.

These results seem to indicate that two different entities absorbing at two different wavelengths are simultaneously present in the HMPT concentration range 0.1 ÷ pure HMPT. Therefore the hypothesis of a gradual clustering or a stronger interaction between the HMPT dipoles and the complex molecules formulated for the Py·I_2 complex does not seem acceptable in our case. A more suitable explanation is the following: at the higher HMPT concentration the equilibrium

$$\text{HMPT}\cdot I_2 \rightleftarrows \text{HMPTI}^+ + I^-$$

proceeding toward the right gives an appreciable quantity of ionic species as conductometric determinations have shown; the contemporaneous presence of I^- ions and the I_2 molecules generates the I_3^- ions which are responsible for the absorbance at 3700 Å. A further support of the above assumption is given by the simultaneous appearence of the peak at 3700 Å and a new band at 2950 Å of nearly double extinction coefficient.

The apparent extinction coefficient, based on I_2, in pure HMPT at 3700 Å was measured by increasing the I_2 concentration. The investigation was limited to the concentration range $1 \div 5 \times 10^{-4}M$ since our cell thickness could be changed only by a factor of ten.

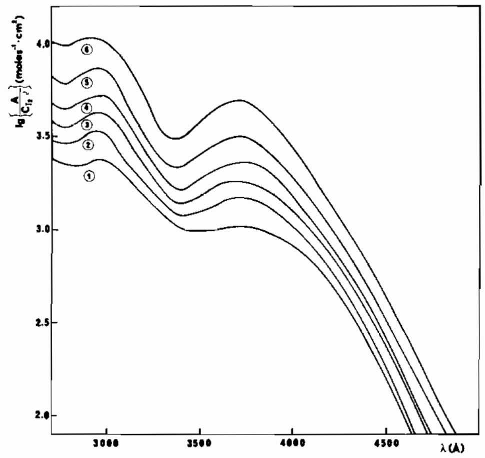

Figure 5. The spectrum in pure HMPT of iodine solutions at various concentrations. Wavelength range 2700–5000 Å. 1) $1.05 \times 10^{-4} M$, 2) $2.09 \times 10^{-4} M$, 3) $2.60 \times 10^{-4} M$, 4) $3.14 \times 10^{-4} M$, 5) $5.24 \times 10^{-4} M$, 6) $1.05 \times 10^{-3} M$.

The results are shown in Figure 4. As expected, the apparent extinction coefficient is higher in the more concentrated solution.

At the present time we are unable to calculate the constant of the equilibrium

$$I_2 + I^- \rightleftarrows I_3^-$$

which can be calculated if the extinction coefficient of I_3^- ion is a known function of the wavelength. As an alternative the same equilibrium constant could be obtained by conductometric measurements if the concentration dependence of the conductance of the different ionic species present in solution were known.

Acknowledgment

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References

1 P. Bruno and M. Della Monica, *J. Phys. Chem., 77,* 1258 (1973).
2 J. Gal and T. Yvernault, *Bull. Soc. Chim. France,* 839 (1972)
3 J.H. Hildebrand and B.L. Glascock, *J. Am. Chem. Soc., 31,* 26 (1909).
4 P. Bruno and M. Della Monica, *J. Phys. Chem., 76,* 1049 (1972).
5 C. Reid and R.S. Mulliken, *J. Am. Chem. Soc., 76,* 3869 (1954).
6 R.S. Mulliken, *J. Am. Chem. Soc., 72,* 600 (1950); R.S. Mulliken, *J. Phys. Chem., 56,* 801 (1952).
7 G. Kortum and H. Wilski, *Z. Physik. Chem., 202,* 35 (1953).
8 L.F. Audrieth and E.J. Birr, *J. Am. Chem. Soc., 55,* 668 (1933).
9 The λ_0 value of I^- ion has been deduced by the λ_0 of Bu_4NI and Pr_4NI salts; the λ_0 value of $HMPT^+$ ion has been roughly calculated by the Stokes law.
10 H. Normant, *Angew. Chem. Intern. Ed. Engl., 6,* 1046 (1967).