STUDY OF THE COMPLEX OF N-METHYL-2-PYRROLIDONE WITH IODINE

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Received March 20th, 1975

The charge transfer complex of N-methyl-2-pyrrolidone with iodine was studied by employing absorption spectrophotometry. The equilibrium constants of the complex were evaluated from the absorbance values of the charge transfer band in the UV region and of the shifted band of bound iodine in the visible region, using the Ketelaar equation. The equilibrium constant of the complex is 20·90 l mol^{-1} (20°C), $\Delta H = -23902$ J mol^{-1}, $\Delta S = -13{\cdot}40$ e.u.

Iodine forms electron donor complexes with many organic compounds[1-10]. With nonpolar aromatic or aliphatic hydrocarbons the iodine complexes are rather weak[11-16]; stable complexes are formed with some strongly polar compounds, such as thiourea, thioacetamide, or tertiary amide derivatives, where the bonding of iodine is localized at the nitrogen atom[17,18]. During the study of complexes of iodine with N-oxide derivatives, Kubota[19] found a higher stability of iodine complexes with N-oxides of aliphatic tertiary amides than with those of aromatic tertiary amides. In compounds containing a carbonyl group, iodine is bound preferably to the carbonyl oxygen, as proved by infrared spectroscopic studies of these compounds[20-23].

In this work we studied the complex of N-methyl-2-pyrrolidone with iodine.

EXPERIMENTAL

N-Methyl-2-pyrrolidone (MP) was a product of BDH Chemicals Ltd.; water content 0·05%, $n_D^{20} = 1{\cdot}469-1{\cdot}471$. Iodine was a chemical of Merck, heptane for spectrophotometry was a product of Fluka.

RESULTS AND DISCUSSION

The equilibrium constants of the complex N-methyl-2-pyrrolidone–iodine were calculated from the absorbances of the charge transfer complex as well as from those of the shifted band of iodine bound in the complex. The original and the shifted bands of iodine form an isosbestic point at 491 nm (Fig. 1). The occurrence of the isosbestic point confirms the formation of a single complex[1,24,25]. The maximum of the absorption band of the complex lies at ~252 nm (as determined by the band separation);

at this wavelength, however, the band overlaps partly with those of MP and of iodine. For the evaluation of the equilibrium constants we employed therefore the absorbances of the CT band at 270 nm, where the contributions of the free components are considerably lower (Fig. 2). Molar absorptivity of free iodine and free MP at that wavelength are $\varepsilon_{I_2}^{270} = 72$ l mol^{-1} cm^{-1} and $\varepsilon_{MP}^{270} = 0{\cdot}4$ l mol^{-1} cm^{-1}.

The maximum of the absorption band of iodine shifts on the formation of the complex with MP from 520 to 457 nm. As the absorbance of free iodine is still rather high at the latter wavelength, we calculated the equilibrium constants from the absorbances at 430 nm, where the molar absorptivity of free iodine is $\varepsilon_{I_2}^{430} = 24$ . . l mol^{-1} cm^{-1}.

For the calculation of the equilibrium constants we made use of the Ketelaar[26,27] equation, which is particularly suitable in the case of a partial overlap of the absorption band of the complex with those of the free components:

$$C_A/(A - A^0) = [K_c C_D(\varepsilon_c - \varepsilon_A - \varepsilon_D)]^{-1} + [\varepsilon_c - \varepsilon_A - \varepsilon_D]^{-1},$$

where C_A and C_D are the molar concentrations of the acceptor and the donor, respectively, ε_c, ε_A, ε_D are molar absorptivities of the complex, acceptor, and donor, respectively, A is the absorbance of the system, A^0 is the sum of absorbances of the components, and K_c is the equilibrium constant.

We chose the concentration of iodine, which acted as the acceptor, $2{\cdot}5 \cdot 10^{-4}$ mol l^{-1}; the concentrations of MP lay in the range of $2 \cdot 10^{-2}$ to $9 \cdot 10^{-2}$ mol l^{-1}.

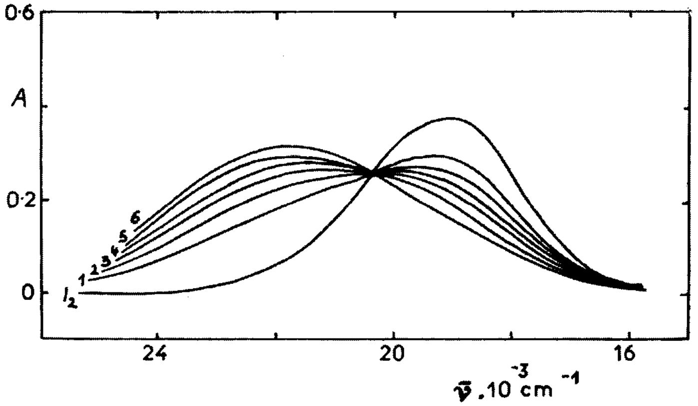

FIG. 1

Isosbestic Point between the Absorption Band of Free Iodine and the Shifted Band of Iodine Bound in the Complex

Concentration of iodine $2{\cdot}5 \cdot 10^{-4}$ mol l^{-1}, concentration of MP *1* $2 \cdot 10^{-2}$, *2* $3 \cdot 10^{-2}$, *3* $4 \cdot 10^{-2}$, *4* $5 \cdot 10^{-2}$, *5* $7 \cdot 10^{-2}$, *6* $9 \cdot 10^{-2}$ mol l^{-1}; cell thickness 2 cm.

The absorbances of the CT complex band (λ 270 nm) and those of the shifted band of bound iodine (λ 430 nm) were determined at five temperatures in the span of 20–40°C for the evaluation of the principal thermodynamic constants of the complex formation. For temperatures above 20°C the concentrations of iodine and MP were corrected with respect to the dilatation of heptane.

The linear dependences of $C_A/(A - A^0)$ on $1/C_D$ at various temperatures for the CT absorption band at 270 nm are plotted in Fig. 3, for the shifted band of bound iodine at 430 nm in Fig. 4. From these plots, the molar absorbance of the complex at the corresponding wavelength and the equilibrium constants at the temperatures applied were calculated by using the least squares method (Table I). The average values of absorbances at 270 and 430 nm in the temperature range used are $\varepsilon_{av}^{270} = 6370{\cdot}8 \pm 110{\cdot}4 \text{ l mol}^{-1} \text{ cm}^{-1}$ and $\varepsilon_{av}^{430} = 814{\cdot}3 \pm 19{\cdot}2 \text{ l mol}^{-1} \text{ cm}^{-1}$.

The average equlibrium constants $K_{c,av}$ calculated for the five temperatures were then used for the evaluation of the thermodynamic parameters of the complex formation, ΔH and ΔS. The dependence of $\ln K_{c,av}$ on $1/T$ is plotted in Fig. 5; from this dependence the following parameters of the formation of the MP – iodine complex were obtained by using the least squares method: $\Delta H = -23902 \text{ J mol}^{-1}$, $\Delta S = 13{\cdot}40$ e.u.

The suitability of the Ketelaar equation for the calculation of the equilibrium

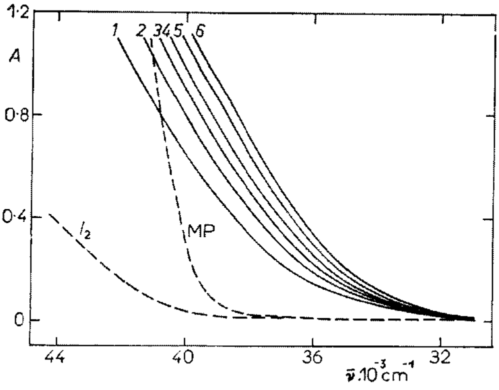

FIG. 2

Absorbances of the Complex MP-Iodine, Free Iodine, and Free MP in the Ultraviolet Region

Concentration of iodine and MP: curves *1*–*6* and curve I_2 as in Fig. 1; concentration of MP (curve MP) $9 . 10^{-2} \text{ mol l}^{-1}$; cell thickness 0·5 cm.

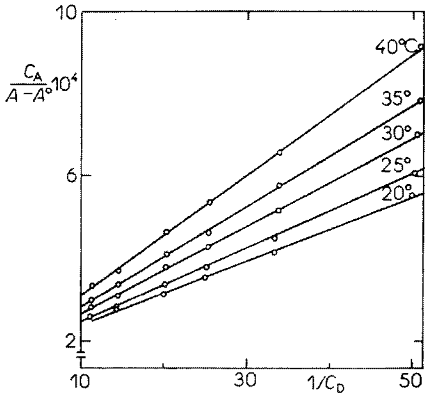

FIG. 3

Plots of $C_A/(A - A^0)$ *vs* $1/C_D$ for the Absorbances of the Charge Transfer Band of the Complex MP-Iodine at Different Temperatures

TABLE I

Molar Absorptivities of the Complex of N-Methyl-2-pyrrolidone with Iodine at the Wavelengths 270 and 430 nm and the Calculated Equilibrium Constants (with the standard deviations) at Different Temperatures

T °C	ε_c^{270} $\mathrm{l\,mol^{-1}\,cm^{-1}}$	$K_{c,1}$ $\mathrm{l\,mol^{-1}}$	ε_c^{430} $\mathrm{l\,mol^{-1}\,cm^{-1}}$	$K_{c,2}$ $\mathrm{l\,mol^{-1}}$
20	6 260	20·90 ± 0·36	—	—
25	6 568	17·39 ± 0·38	825	17·38 ± 0·21
30	6 363	14·88 ± 0·23	824	14·30 ± 0·25
35	6 389	13·02 ± 0·22	827	13·29 ± 0·38
40	6 274	11·01 ± 0·28	781	11·11 ± 0·13

constants of the complex of N-methyl-2-pyrrolidone with iodine is confirmed by the relatively good agreement of the values calculated from the absorbances of the CT band in the UV region and those of the shifted band of bound iodine in the visible spectral region. Molar absorptivities of the free components at the chosen wavelengths of 270 and 430 nm are rather low (0·4 $\mathrm{l\,mol^{-1}\,cm^{-1}}$ for MP and 72 and 24 $\mathrm{l\,mol^{-1}.\,.cm^{-1}}$, respectively, for iodine); despite the very low molar absorptivity of MP,

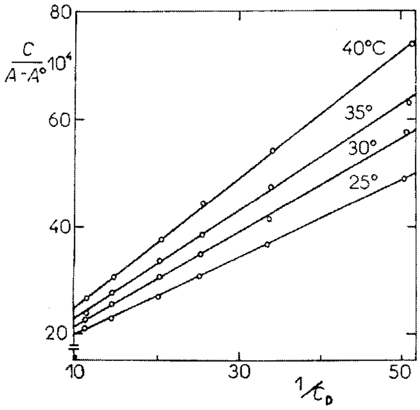

FIG. 4

Plots of $C_A/(A - A^0)$ *vs* $1/C_D$ for the Absorbances of the Shifted Band of Iodine in the Complex MP-Iodine at Different Temperatures

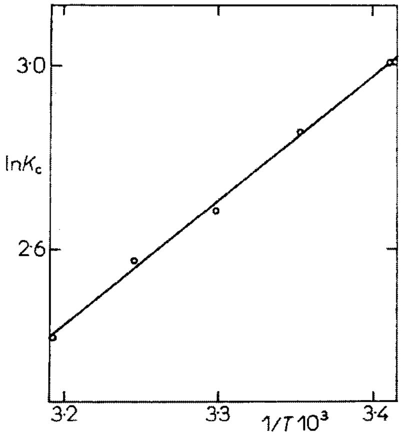

FIG. 5

Temperature Dependence of the Equilibrium Constant however, this substance yields measurable absorbances in the concentration range applied, which must be taken into account in the calculations of the equilibrium constants.

The bond of iodine in the complex N-methyl-2-pyrrolidone–iodine is localized at the oxygen atom, as evidenced by the infrared spectra of the complex[28].

Thanks are due to Mrs L. Cholujová for technical assistance.

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Translated by P. Adámek.