Charge-transfer Complexes of Imidazole-2-thiones and *N,N'*-Dialkylthioureas with Sulphur Dioxide

Andrzej Suszka
Institute of Chemistry, Technical University, 60-965 Poznan, Poland

The charge-transfer (CT) complexes of *N,N'*-dialkylthioureas and of alkyl substituted imidazole-2-thiones with sulphur dioxide in aprotic solvents of different polarity have been studied spectrophotometrically. In chlorinated hydrocarbons of increasing solvent polarity, a blue shift of the CT bands was observed. That indicates that the complexes are more polar in the ground state than in the excited state. For imidazolethiones containing an unsubstituted imine nitrogen, a bathochromic shift was found in *n*-donor solvents which is explained in terms of the *n*-donor ability of these solvents. The formation constants and thermodynamic functions, ΔH° and ΔS°, have been determined. Deviations in the estimation of formation constants observed in non-polar solvents for all donors except 1,3-dimethylimidazole-2-thione are ascribed to the self-association of donors as a result of hydrogen bonding. Two general numeric procedures for the calculation of self-association constants from spectrophotometric data are proposed and evaluated.

In 1927 Balaban and King described the formation of yellow adducts when sulphur dioxide was passed through the solutions of various imidazole-2-thiones.[1] Later, the observations were confirmed by Heath and co-workers.[2] Since then numerous complexes formed with sulphur dioxide have been studied, from weak complexes with benzene and its methyl homologues[3] to the strong ones with aliphatic tertiary amines. The latter are the most thoroughly investigated SO_2 complexes; the reported data include their thermodynamic parameters,[4] dipole moments,[5] and *X*-ray crystal structures.[6] This experimentally determined structure corresponds to that calculated by Kollman *et al.*[7] The infrared studies of SO_2-tertiary amine complexes in nobel gas matrices indicate that sulphur dioxide is serving as a π^* acceptor interacting with the lone pair of electrons on the nitrogen. At the same time, imidazolethiones and thioureas, like some other compounds containing thioamide groups, are good electron donors and form strong 1:1 charge-transfer complexes with, for instance, molecular iodine in aprotic solvents.[8–12] It would, therefore, be of interest to examine the spectral and thermodynamic parameters of the SO_2 complexes with imidazole-2-thiones and thioureas and to obtain information about the effects of solvation on the complex-formation equilibrium. However, because of the nature of donors, these complexes can only be studied to a limited extent. First, the non-volatility of imidazolethiones and thioureas excludes any gas-phase experiments, secondly, the complexes cannot be examined in aliphatic hydrocarbons as the donors are almost insoluble in these solvents. Even in carbon tetrachloride very few of the imidazolethiones are soluble enough to be studied, and those that are, are soluble only within a limited range of concentration.

In the present work, the following compounds were used as electron donors: 1,3-dimethylthiourea (Me_2TU), 1,3-diethylthiourea (Et_2TU), 1,3-dibutylthiourea (Bu_2TU), 1-methylimidazole-2-thione (1-MeIT), 1,3-dimethylimidazole-2-thione (1,3-Me_2IT), and 1,4,5-trimethylimidazole-2-thione (1,4,5-Me_3IT). The equilibrium measurements were made in aprotic solvents of varying polarity: carbon tetrachloride (CT), dichloromethane (DCM), and acetonitrile (AN). Our aim was to establish the effect of solvation on complex formation, and on the possible self-association of donor molecules. The solvent dependence of CT absorption-band shifts was studied in a wider range of solvents including, in addition to those mentioned above, chloroform (CLF), trichloroethylene (TRI), tetrahydrofuran (THF), ethyl acetate (EA), acetone (A), propionitrile (PN), and dimethyl sulphoxide (DMSO).

Experimental

Materials.—The dialkylthioureas and 1-MeIT were commercial products (Aldrich). Two of them, Et_2TU and Bu_2TU, were recrystallized twice from ethanol after their purity had been checked by t.l.c. 1,3-Me_2IT was prepared as previously described[13] and 1,4,5-Me_3IT was synthesized according to Sandstrom.[14] Solvents were purified by general procedures described by Perrin *et al.*[15] Stock solutions of the acceptor were obtained by saturating the solvents with dry gaseous sulphur dioxide.

Instruments.—U.v. spectra and absorbance measurements for equilibrium calculations were carried out on a Specord M-40 (C. Zeiss, Jena) spectrophotometer connected to a constant-temperature circulating bath. The temperature of cells was maintained to within 0.1 °C. Cumulative recordings of spectra of the same sample with a subsequent smoothing of the resulting curve, and subtraction of the spectra of different species, were performed with the help of a Data Handling I program cassette.

Equilibrium Measurements.—A working solution of sulphur dioxide (few mm^3), prepared before use, was placed in 50 cm^3 vials sealed with a silicon-rubber diaphragm through which 30 mm^3 aliquots were withdrawn with a Hamilton gas-tight syringe. These aliquots were transferred to a glass-stoppered silica spectrophotometric cell containing the donor solutions of varying concentration. Absorbance was measured at three wavenumbers: at ν_{max} and $\nu_{max} \pm 500$ cm^{-1}. A correction for donor absorbance was made using their absorption coefficients estimated in separate experiments. The concentration of the sulphur dioxide working solutions was determined at the beginning and at the end of a daily set of measurements. If the results of these determinations differed, the whole set of measurements was rejected.

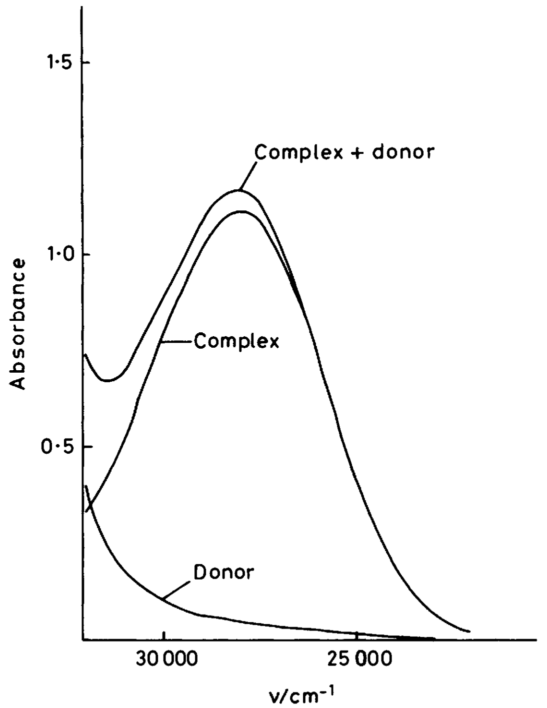


Figure 1. Absorption spectra of 1-methylimidazole-2-thione–sulphur dioxide complex in dichloromethane: $[D]_0 = 0.150$ mol dm^{-3}, $[A]_0 = 3.16 \times 10^{-4}$ mol dm^{-3}.

Determination of Sulphur Dioxide.—Sulphur dioxide in both stock and working solutions was determined coulometrically on a Radelkis OH-405 microcoulometer as follows: a 500 mm^3 sample of SO_2 solution was added to standard 0.02 mol dm^{-3} I_3^- solution in a phosphate buffer (pH 7) containing potassium iodide (0.1 mol dm^{-3}). The unchanged iodine was immediately reduced with 0.02 mol dm^{-3} sodium thiosulphate and the excess of the latter was coulometrically back-titrated with the generated iodine.

Results and Discussion

Electronic Spectra.—Absorption spectra of complexes were run for solutions in which the initial donor concentration was much greater than that of the acceptor, *i.e.* $[D]_0 \gg [A]_0$. This condition was chosen because of the low formation constants of the complexes: it ensures sufficiently high absorbance of the complex itself and also allows the absorbance of sulphur dioxide to be considered as negligible. Since in all cases the charge-transfer band more or less overlapped the donor band, the spectra of donors were recorded separately and subtracted from those of the equilibrium systems. As an example, the spectrum of a 1-methylimidazole-2-thione complex in dichloromethane is shown in Figure 1.

The spectroscopic data derived from the spectra are collected in Table 1. The complexes of thioureas show the charge-transfer (CT) band maxima at *ca.* 340 nm, whereas for the imidazolethione complexes, such maxima appear within the 358–374 nm region. The CT transition energy of dialkylthioureas decreases slightly with increased electron-donating ability of substituents in the order: butyl < ethyl < methyl. A similar effect is observed in the n–π^* transition of the thiocarbonyl group of these donors and in their complexes with iodine.[8]

An increasing number of methyl groups substituted to the imidazole ring also results in a decrease in the CT transition energy. As can be expected, the groups attached to the nitrogen positions 1 and 3 are more effective than those located at C-4 and/or C-5.

In order to correlate the CT band position with solvent polarity, the CT frequencies, ν_{CT}, were plotted against the solvent polarity parameter,[16] E_T.† In chlorinated hydrocarbons all the complexes studied show a hypsochromic shift with increased solvent polarity [Figure 2(*a*)]. The observed blue shift indicates that the polarity of complexes must be greater in the ground state than in the excited state. Thus, with increased solvent polarity the energy of the ground state is lowered more than that of the Franck–Condon excited state, and so results in hypsochromic shift.

Because of the scatter of points, no correlation between ν_{CT} and E_T was found for n-donor solvents. However, if the n-donor property, $\Delta\tilde{\nu}_D$,‡ used as a solvent parameter instead of E_T, a fairly good correlation can be obtained (Figure 3). n-Donor solvents, unlike halogenated hydrocarbons, cause a bathochromic shift of the CT band, proportional to the n-donor ability of the solvent. This effect was observed for complexes of all the donors studied, except for those of 1,3-Me_2IT. CT frequencies of the latter also correlate reasonably well with the E_T parameter in n-donor solvents, and similarly show the blue shift proportional to the solvent polarity [Figure 2(*b*)]. Since this compound has both its imine nitrogens substituted by methyl groups, it seems reasonable to suggest that the unsubstituted >NH hydrogen is involved in a specific interaction with n-donor solvent molecules; the interaction overcoming the general polarity solvent effect.

Equilibrium Parameters.—The 1:1 stoicheiometry of thiourea– and imidazolethione–SO_2 complexes was estimated by using Job's method of continuous variations.

The equilibrium measurements were carried out using a series of 8–12 solutions of varying donor concentration and a constant acceptor concentration. In all the experiments the donor concentration was kept much higher than that of the acceptor, except for the solutions in carbon tetrachloride (because of the low solubility of imidazolethiones and thioureas in this solvent). The formation constant, K_C, and the absorption molar coefficient of a complex, ε_{AD}, were calculated by the method proposed by Conrow.[17] Standard deviations of these parameters were obtained from the relationships described by Carta and Crisponi.[18] For comparison, calculations on the same experimental data were also carried out using the non-linear least-squares (NLLSQ) procedure.[19] In all the cases examined, essentially the same results were obtained for both K_C and ε_{AD}, as well as for their standard deviations. In our opinion, however, Conrow's method has the advantage over the NLLSQ method as it does not depend on the initial estimates of calculated parameters; the NLLSQ method, even with the Marquardt[20] procedure included, does not converge if initial

---

† E_T is a molar transition energy (in kcal mol^{-1}) for the intramolecular CT absorption band of pyridinium phenoxide betaine in a given solvent.

‡ $\Delta\nu_D$ is the variation of the O–D stretching frequency of deuteriated methanol in various solvents and can be taken as a measure of the electron-donating power of a given solvent.[28]

§ RSM is a ratio of error square sums, $\Sigma(\text{Abs} - \varepsilon_{AD}[AD])^2$, in a numerator of which the complex concentration [AD] is calculated for $K_C + 0.5K_C$ and the concentration in the denominator for (K_C, both originating from the equation $[AD] = ([A]_0 + [D]^0\ 1/K_C)/2 - ([A]_0 + [D]_0 + 1/K_C)^2 - [A]_0[D]_0)$. This ratio is equal to unity for completely non-significant data and increases to several hundreds as their reliability increases.

Table 1. Spectroscopic data on imidazole-2-thione and dialkylthiourea complexes with sulphur dioxide in aprotic solvents.

Donor	λ_{CT}/nm	$\nu_{1/2}$/cm^{-1}	$h\nu_{CT}$/eV	ε_{CT}/dm^3 mol^{-1} cm^{-1}	f
Carbon tetrachloride					
Me_2TU	343.4	3 850	3.61	10 550	0.18
Et_2TU	344.3	3 900	3.60	11 600	0.21
Bu_2TU	344.8	3 900	3.59	11 800	0.21
1-MeIT	360.2	4 700	3.44	10 270	0.22
1,3-Me_2IT	374.2	3 900	3.31	12 500	0.22
1,4,5-Me_3IT	373.1	4 800	3.32	—	—
Trichloroethylene					
Me_2TU	342.0	3 500	3.62	—	—
Et_2TU	344.3	3 600	3.60	—	—
Bu_2TU	344.3	3 600	3.60	—	—
1-MeIT	360.0	3 800	3.44	—	—
1,3-Me_2IT	373.7	4 100	3.32	—	—
1,4,5-Me_3IT	370.4	5 700	3.35	—	—
Chloroform					
Me_2TU	340.6	3 600	3.64	—	—
Et_2TU	341.1	3 700	3.63	—	—
Bu_2TU	341.1	3 700	3.63	—	—
1-MeIT	356.6	5 400	3.47	—	—
1,3-Me_2IT	371.5	4 300	3.34	—	—
1,4,5-Me_3IT	365.0	5 800	3.40	—	—
Dichloromethane					
Me_2TU	341.5	3 700	3.63	9 860	0.17
Et_2TU	342.0	3 700	3.62	10 100	0.17
Bu_2TU	342.5	3 750	3.62	11 910	0.20
1-MeIT	358.2	5 100	3.46	9 800	0.22
1,3-Me_2IT	372.0	4 450	3.33	12 270	0.25
1,4,5-Me_3IT	366.0	5 600	3.37	9 820	0.25
Acetonitrile					
Me_2TU	340.1	3 600	3.64	11 450	0.19
Et_2TU	340.6	3 700	3.64	11 200	0.19
Bu_2TU	342	3 780	3.62	11 700	0.20
1-MeIT	359.2	4 800	3.45	10 020	0.22
1,3-Me_2IT	369.2	4 500	3.35	12 030	0.26
1,4,5-Me_3IT	372.0	5 200	3.33	9 920	0.23
Propionitrile					
Me_2TU	341.1	3 700	3.63	—	—
Et_2TU	341.5	3 800	3.63	—	—
Bu_2TU	342.9	3 700	3.61	—	—
1-MeIT	364.4	4 400	3.40	—	—
1,3-Me_2IT	370.4	4 400	3.35	—	—
Ethyl acetate					
Me_2TU	342.5	3 500	3.62	—	—
Et_2TU	342.0	3 600	3.62	—	—
Bu_2TU	343.4	3 600	3.61	—	—
1-MeIT	362.2	4 500	3.42	—	—
1,3-Me_2IT	372.0	4 100	3.33	—	—
1,4,5-Me_3IT	371.5	4 900	3.34	—	—
Acetone					
Me_2TU	342.5	3 500	3.62	—	—
Et_2TU	342.0	3 600	3.62	—	—
Bu_2TU	343.4	3 800	3.61	—	—
1-Me_2IT	362.2	4 700	3.42	—	—
1,3-Me_2IT	371.5	4 400	3.34	—	—
1,4,5-Me_3IT	370.4	5 150	3.35	—	—
Tetrahydrofuran					
Me_2TU	346.7	3 700	3.57	—	—
Et_2TU	347.2	3 500	3.60	—	—
Bu_2TU	343.9	3 900	3.60	—	—
1,3-Me_2IT	372.6	4 400	3.33	—	—
Dimethyl sulphoxide					
1-MeIT	363.9	4 800	3.41	—	—
1,3-Me_2IT	369.3	4 600	3.36	—	—
1,4,5-Me_3IT	373.7	4 900	3.32	—	—

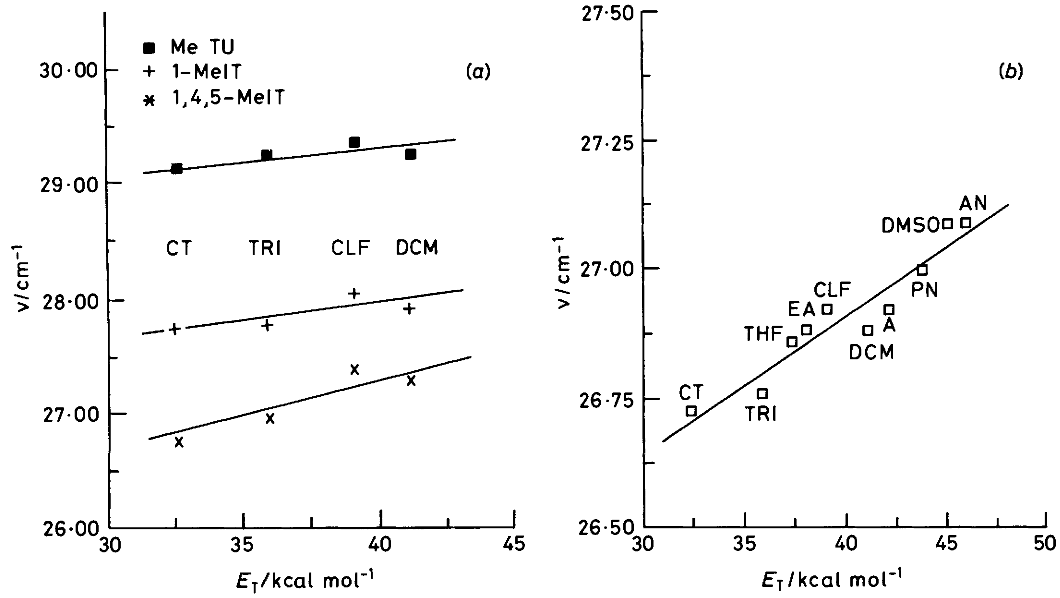


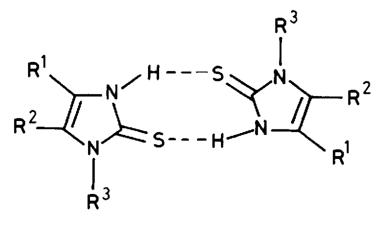
Figure 2. Plots of ν_{CT} *vs.* solvent E_T for : (*a*) *N,N'*-dimethylthiourea–, 1-methylimidazole-2-thione–, and 1,4,5-imidazole-2-thione–SO_2 complexes; (*b*) 1,3-dimethylimidazole-2-thione–SO_2 complex; solvents: carbon tetrachloride (CT), trichloroethylene (TRI), chloroform (CLF), dichloromethane (DCM), acetonitrile (AN), propionitrile (PN), tetrahydrofuran (THF), ethyl acetate (EA), acetone (A), and dimethyl sulphoxide (DMSO).

values are improperly chosen. In contrast, in the Conrow procedure identical results were obtained for the same set of experimental data no matter how much the input values of K_C differed.

For 1-MeIT in both chlorinated hydrocarbons, 1,4,5-Me_3IT in dichloromethane, and thioureas in carbon tetrachloride, the calculated values of ε_{AD} were much lower (1 700–3 900) than those obtained for 1,3-Me_2IT in the three solvents, and lower than those for all the donors in acetonitrile. The standard deviations of both K_C and ε_{AD} were as high as 25% of the mean values and the RSM§ factor[18] did not exceed 5. The experimental data were also plotted using the Scott[21] and Scatchard–Foster[22] equations to examine the linearity of the relationships: $[D]_0[A]_0/\mathrm{Abs}$ *vs.* $[D]_0$ and $\mathrm{Abs}/[D]_0$ *vs.* Abs, respectively, where Abs was the measured absorbance. These equations are much more sensitive to the deviations from linearity than the original Benesi–Hildebrand equation. For 1-MeIT and 1,4,5-Me_3IT in chlorinated hydrocarbons and for thioureas in carbon tetrachloride, curved plots were obtained (Figure 4).

Similar deviations from linearity have already been reported by Foster *et al.*[23] for the *p*-benzoquinone–hexamethylbenzene system and ascribed to the formation of termolecular complexes, AD_2. In order to verify such a hypothesis, a series of measurements was made under the conditon $[D]_0 \approx [A]_0$ in which the formation of the AD_2 complex was not favoured and its concentration was assumed to be insignificant. However, no appreciable improvement in the parameters was achieved in these experiments.

Alternatively, dimerization was considered to be a possible source of the deviations. Tanner and Bruice[24] have shown that large errors may be introduced into calculated association constants when the reactants undergo self-association. It has been found by i.r. spectroscopy that numerous azole-2-thiones undergo self-association as a result of hydrogen bonding and form dimers in non-polar solvents:[25]



If the self-association of a donor occurs along with complex formation, the two competing equilibria exist in the system:

$$2D = \text{with } K_D = [D_2]/[D]^2 \quad (1)$$

$$A + D = AD \text{ with } K_C = [AD]/\{([A]_0 - [AD])[D]\} \quad (2)$$

In order to determine the equilibrium constants, K_D and K_C, and the extinction coefficient of complex, ε_{AD}, a calculation procedure was designed based on the following logic. For simplicity, it was assumed that: (*i*) the self-associated donor is not reactive toward the acceptor, (*ii*) only donor and complex absorb at the wavelength of measurement, and (*iii*) the non-associated donor and the dimer have the same absorption coefficients at that wavelength. Thus, the measured absorbance will be the sum of donor and complex absorbances:

$$\mathrm{Abs} = \mathrm{Abs}_{AD} + \mathrm{Abs}_D \quad (3)$$

and

$$\mathrm{Abs}_D = \varepsilon_D([D]_0 - [AD]) \quad (4)$$

where $[D]_0$ and $[AD]$ are the initial concentration of the donor and the equilibrium concentration of complex, respectively, and ε_D is an absorption coefficient of the donor. The complex concentration can be taken as $[AD] = \mathrm{Abs}_{AD}/\varepsilon_{AD}$, which with equation (4) gives:

$$\mathrm{Abs}_{AD} = \mathrm{Abs}'/(1 - \varepsilon_D/\varepsilon_{AD}) \qquad (5)$$

where $\mathrm{Abs}' = \mathrm{Abs} - \varepsilon_D[D]_0$.

From the mass balance

$$[D]_0 = [D] + 2[D] + [AD] \qquad (6)$$

and equation (1), the equilibrium concentration [D] can be obtained

$$[D] = (\{1 + 8K_D([D]_0 - [AD])\}^{\frac{1}{2}} - 1)/4K_D \qquad (7)$$

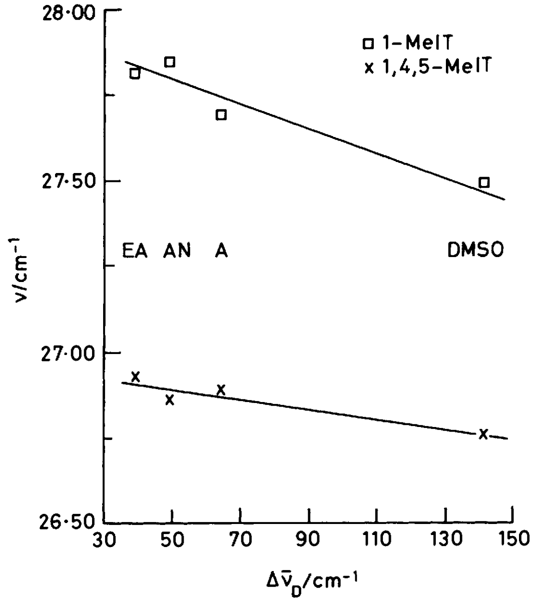


Figure 3. Plots of ν_{CT} *vs.* $\Delta\nu_D$ for 1-methylimidazole-2-thione- and 1,4,5-trimethylimidazole-2-thione–SO_2 complexes in *n*-donor solvents.

The calculated absorbance of the system can be derived by combination of equation (2), the relationship $[AD] = \mathrm{Abs}_{AD}/\varepsilon_{AD}$, and equation (5):

$$\mathrm{Abs}_{calc} = \frac{K_C[A]_0[D](\varepsilon_{AD} - \varepsilon_D)}{1 + K_C[D]} + \varepsilon_D[D]_0 \qquad (8)$$

The calculation algorithm consists of the following steps: (*a*) Using the initial estimate of K_D and taking $[AD] = 0$, the concentrations [D] are calculated from equation (7). (*b*) The estimated [D] values and the measured absorbances of solutions are used as input data in the Conrow procedure for the calculation of the first approximation of K_C and ε_{AD}. (*c*) From the approximate ε_{AD} the complex concentration can be obtained as $[AD] = \mathrm{Abs}'/(\varepsilon_{AD} - \varepsilon_D)$ and used for calculation of a new set of [D] from equation (7). (*d*) Steps (*b*) and (*c*) are repeated until a convergence of K_C and ε_{AD} is obtained. (*e*) The error-square sum $\mathrm{ESS} = \Sigma(\mathrm{Abs}_{exp} - \mathrm{Abs}_{calc})^2$ is calculated. (*f*) An appropriate optimum-seeking method[26] is used for finding such a K_D value that minimizes the ESS.

If $[D]_0 \gg [A]_0$, the complex concentration, [AD], in equation (7) can be neglected as being much lower than $[D]_0$; steps (*c*) and (*d*) are therefore omitted and the whole procedure becomes considerably simpler.

An alternative and simpler procedure to that derived above, but not including the error estimation, has also been used. Concentration of the non-associated donor is calculated from the expression for formation constant:

$$[D] = \frac{\mathrm{Abs}'}{K_C(\varepsilon_{AD}[A]_0 - \varepsilon_D[A]_0 - \mathrm{Abs}')} \qquad (9)$$

and substituted to the modified equation (6):

$$[D]_0 = 2k_D[D]^2 + [D] + \mathrm{Abs}'(\varepsilon_{AD} - \varepsilon_D)$$

The last two equations and the approximate values of K_D, K_C, and ε_{AD} together with their probable ranges were used in computer procedure described by Foster.[23]

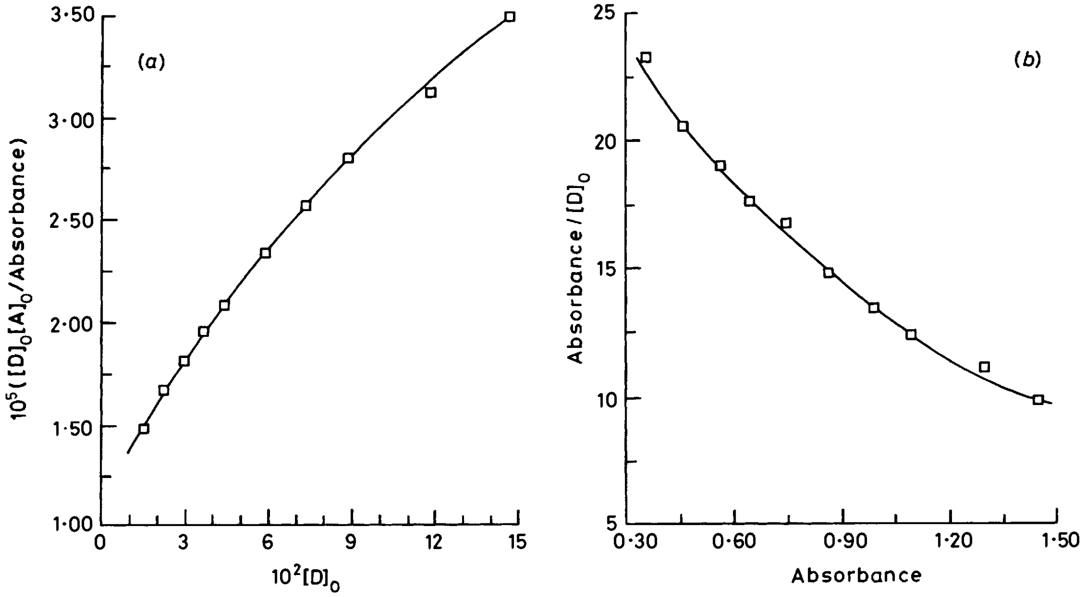


Figure 4. Plots of : (*a*) $[D]_0[A]_0$/absorbance *vs.* $[D]_0$, and (*b*) absorbance/$[D]_0$ *vs.* absorbance for 1-methylimidazole-2-thione–SO_2 complex in dichloromethane.

Table 2. Thermodynamic data on imidazole-2-thione and dialkylthiourea complexes with sulphur dioxide in aprotic solvents.

Donor	K_C^{298}/dm^3 mol^{-1}	K_D^{298}/dm^3 mol^{-1}	$-H^0$/kcal mol^{-1}	$-S^0$/cal mol^{-1} K^{-1}
		Carbon tetrachloride		
Me_2TU	10.8	1.5	—	—
Et_2TU	12.2	3.0	—	—
Bu_2	13.4	11.7	—	—
1-MeIT	13.4	213	—	—
1,3-Me_2	12.70 ± 1.30	—	—	—
		Dichloromethane		
Me_2TU	3.36 ± 0.08	—	3.84 ± 0.18	10.7 ± 0.6
Et_2TU	4.33 ± 0.12	—	3.98 ± 0.18	10.8 ± 0.6
Bu_2TU	6.60 ± 0.15	—	4.10 ± 0.25	10.9 ± 0.8
1-Me_2IT	7.09	6.1	4.60 ± 0.25	11.8 ± 0.9
1,3-Me_2IT	4.59 ± 0.10	—	4.30 ± 0.21	11.7 ± 0.7
1,4,5-Me_3IT	15.35	12.8	—	—
		Acetonitrile		
Me_2TU	2.11 ± 0.05	—	2.83 ± 0.13	8.2 ± 0.5
Et_2TU	2.39 ± 0.07	—	4.09 ± 0.37	12.1 ± 1.2
Bu_2TU	3.16 ± 0.16	—	4.55 ± 0.29	13.3± 0.9
1-MeIT	6.42 ± 0.14	—	3.67 ± 0.21	8.8 ± 0.7
1,3-Me_2IT	3.14 ± 0.08	—	3.94 ± 0.13	11.2 ± 0.4
1,4,5-Me_3IT	11.35 ± 0.25	—	4.83 ± 0.52	11.5 ± 0.7

In order to estimate the thermodynamic parameters, the equilibrium measurements were carried out at four different temperatures: 10, 15, 20, and 25 °C in dichloromethane, and 10, 20, 30, and 40 °C in acetonitrile and carbon tetrachloride. The calculated formation and dimerization constants and the thermodynamic parameters of *N*,*N*-dialkylthioureas and imidazole-2-thiones in those solvents are collected in Table 2. In CT solutions, in which the concentrations of donors were low and of limited range (because of their poor solubility), the insufficient reliability of the formation constants obtained (low RMS values) did not allow the calculation of reliable thermodynamic parameters in this solvent.

The formation constants increase with the decreasing solvent polarity. This trend is observed for most of the charge-transfer complexes except for the very strong complexes of iodine with *n*-donors,[8–12] and the sulphur dioxide–triethylamine[4,6] complex in which the stability increases as the polarity of the medium is increased.

In the series of thiourea complexes the stability increases with the increasing electron-donating ability of alkyl substituents in the order: Me < Et < Bu. A similar effect of substituents was observed for the thiourea–iodine complexes.[8] In the case of imidazolethiones, the presence of two alkyl groups in the 4 and 5 positions of the imidazole ring increases the stability of the complex owing to their inductive effect. In 1,3-Me_2IT, however, the second methyl group decreases the formation constant although in acetonitrile the enthalphy and entropy changes become more negative than those for 1-MeIT. According to the theory of Liptay,[27] ε_{CT} should increase with the increasing solvent polarity if the dipole moment increases on excitation, and should decrease for the reverse case. In fact, a decrease in ε_{CT} is observed in chlorinated hydrocarbons which supports the suggestion that the ground state is more polar than the excited state, but again in acetonitrile a deviation was observed for all complexes, except for 1,3-Me_2IT. As in the case of ν_{CT}, this deviation can be explained by a specific interaction of the complex with the *n*-donor solvent.

The dimerization of donors in acetonitrile was so low, if at all, that it had no observable effect on the determination of the complex association constant. In dichloromethane and carbon tetrachloride, however, self-association of imidazolethiones with unsubstituted >NH group was observed. In carbon tetrachloride, thioureas also dimerize to some extent.

References

1 I. E. Balaban and H. King, *J. Chem. Soc.*, 1927, 1858.
2 H. Heath, A. Lawson, and C. Rimington, *J. Chem. Soc.*, 1951, 2217.
3 D. Booth, F. S. Dainton, and J. K. Irvin, *Trans. Faraday Soc.*, 1959, **55**, 1293.
4 J. Grundness and S. D. Christian, *J. Am. Chem. Soc.*, 1968, **90**, 2239; *Acta Chem. Scand.*, 1969, **23**, 3585; J. Grundness, S. D. Christian, and V. Chean, *ibid.*, 1970, **24**, 1836.
5 J. A. Moode and C. Curran, *J. Am. Chem. Soc.*, 1949, **71**, 852.
6 D. Helm, J. D. Childs, and S. D. Christian, *J. Chem. Soc., Chem. Commun.*, 1969, 887.
7 J. E. Douglas and P. A. Kollman, *J. Am. Chem. Soc.*, 1978, **100**, 5226.
8 K. R. Bhaskar, R. K. Gosavi, and C. N. R. Rao, *Trans. Faraday Soc.*, 1966, **62**, 29.
9 A. Suszka, *J. Chem. Soc., Perkin Trans. 2*, 1985, 531.
10 F. Freeman, J. W. Ziller, H. N. Po, and M. C. Keindl, *J. Am. Chem. Soc.*, in press.
11 C. Raby, J. Claude, C. Moesch, and J. Buxeraud, *C.R. Acad. Sci., Ser. C*, 1979, **288**, 319.
12 J. Buxeraud, A. C. Absil, J. Claud, C. Raby, G. Catazano, C. Beck, and F. Claude, *Eur. J. Med. Chem., Chim. Ther.*, 1985, **20**, 43.
13 A. Suszka, *Pol. J. Chem.*, 1980, **54**, 2289.
14 G. Kjellin and J. Sandstrom, *Acta Chem. Scand.*, 1969, **23**, 2279.
15 D. D. Perrin, W. L. F. Armarego, and D. R. Perrin, 'Purification of Laboratory Chemicals,' Pergamon, Oxford, 1966.
16 K. Dimroth, C. Reichardt, T. Siepmann, and F. Bohlmann, *Justus Liebigs Ann. Chem.*, 1963, **661**, 1; C. Reichardt, *ibid.*, 1971, **752**, 64.
17 K. Conrow, G. D. Johnson, and R. E. Bowen, *J. Am. Chem. Soc.*, 1964, **86**, 1025.
18 G. Carta and G. Crisponi, *J. Chem. Soc., Perkin Trans. 2*, 1982, 53.
19 W. E. Wentworth, W. Hirsch, and E. Chen, *J. Phys. Chem.*, 1967, **71**, 218.
20 D. W. Marquardt, *J. Soc. Ind. Appl. Math.*, 1963, **11**, 431.
21 R. L. Scott, *Recl. Trav. Chim. Pay-Bas*, 1956, **75**, 787.
22 G. Scatchard, *Ann. N.Y. Acad. Sci.*, 1949, **51**, 660; R. Foster, D. L. Hammick, and A. A. Wardley, *J. Chem. Soc.*, 1953, 3817.

23 B. Dodson, R. Foster, A. A. S. Bright, M. I. Foreman, and J. Gordon, *J. Chem. Soc. B*, 1971, 1283.
24 D. W. Tanner and T. C. Bruice, *J. Phys. Chem.*, 1966, **70**, 3816.
25 E. Gentric, J. Lauransan, C. Roussel, and J. Metzger, *J. Chem. Soc., Perkin Trans. 2*, 1976, 565; 1977, 1015.
26 G. Beech, 'FORTRAN IV in Chemistry,' Wiley, New York, 1975.
27 W. Liptay, *Z. Naturforsch., Teil A*, 1966, **21**, 1605; *Angew. Chem., Int. Ed. Engl.*, 1969, **8**, 177.
28 T. Kagyia, Y. Sumida, and T. Inoue, *Bull. Chem. Soc. Jpn.*, 1968, **41**, 767.

Received 12*th February* 1988; *Paper* 8/00534F