Weak Complexes of Sulphur and Selenium. Part 6.[1] Stability Constants of the Weak 1 : 1 Complexes of Sulphur Dioxide, Thionyl Chloride, and Sulphonyl Chloride with Halide Ions in the Mixed Solvent Acetonitrile–Dimethyl Sulphoxide at 25 °C

By **S. B. Salama**, University of Khartoum, Sudan
Saad Wasif *,† and **M. M. Omer**, University of Tripoli, Libya

The stability constants of $SO_2{\cdot}X^-$, $SOCl_2{\cdot}X^-$, and $SO_2Cl_2{\cdot}X^-$ (X^- = Cl^-, Br^-, or I^-) have been determined spectroscopically in different mixtures of acetonitrile and dimethyl sulphoxide as solvent. The values (at 25 °C) are not constant for different solvent mixtures. To account for this it is assumed that a number of interactions exist in these solutions, and of these solvent–solvent interactions are believed to play an important role.

A NUMBER of reports deal with the effect of solvents on chemical phenomena such as reaction kinetics, electrical conductance, and complex stability. Fewer workers have reported on chemical processes in mixed solvents and also specified the role of the solvent. The present work in acetonitrile–dimethyl sulphoxide (dmso) attempts to probe the role of solvent in the stability of weak complexes previously studied in MeCN and dmso separately.[2-5]

EXPERIMENTAL

The stability constant (K_c in $dm^3\ mol^{-1}$) in pure MeCN and dmso are quoted from earlier work.[2-4] The evaluation of K_c in the mixed solvents was as follows.

---

† *Present address:* Department of Chemistry, Faculty of Science, University of Alexandria, Maharren Bay, Alexandria, Egypt.

[1] Part 5, preceding paper.

[2] A. Salama, S. B. Salama, M. Sobeir, and S. Wasif, *J. Chem. Soc.* (*A*), 1971, 1112.

[3] S. B. Salama and S. Wasif, *J.C.S. Dalton*, 1973, 2148.

[4] S. B. Salama and S. Wasif, *J.C.S. Dalton*, 1975, 151.

[5] S. B. Salama and S. Wasif, *J.C.S. Dalton*, 1975, 2239.

Three solvents were prepared in which the amounts of dmso were 25, 50, and 75% by volume. These were used to prepare stock solutions of the ligands (Cl^-, Br^-, and I^-) in the form of their tetra-alkylammonium salts at concentrations varying from 10^{-2} to 10^{-3} mol dm^{-3}. The sulphur acceptors had a concentration of 10^{-5} mol dm^{-3}.

TABLE 1

Evaluation of K_c for $SO_2{\cdot}I^-$ in MeCN–dmso (1 : 3) at 25 °C

Solutions	1	2	3	4	5
$10^3[I^-]$/mol dm^{-3}	2.37	3.55	4.73	5.92	7.10
$10^3[SO_2]$/mol dm^{-3}	2.75	2.75	2.75	2.75	2.75
$D_{obs.}$	0.155	0.230	0.300	0.370	0.440
10^5 $[SO_2.I^-]_e$/mol dm^{-3}	8.52	12.70	16.50	20.04	24.20
$10^3[I^-]_e$/mol dm^{-3}	2.28	3.42	4.56	5.73	6.85
$10^3[SO_2]_e$/mol dm^{-3}	2.66	2.62	2.58	2.55	2.50
K_c/dm^3 mol^{-1}	14.05	14.17	14.03	13.99	14.13

Graphical method: intercept = 0.55×10^{-3}, ε_c = 1 818 dm^3 mol^{-1} cm^{-1}, gradient = 0.0409×10^{-3}, K_c = 13.45 dm^3 mol^{-1}

For a typical run a set of mixtures was prepared in which the concentration of the sulphur acceptor was kept constant and that of the ligand increased progressively and was in excess of the sulphur compound. The absorbance of each mixture was recorded against a reference which contained the ligand only. The absorbance data were used to evaluate the K_c data of the different complex species with the help of the equations of Benesi and Hildebrand [6] and Ketelaar *et al.*[7] Table 1 includes the experimental data and shows the method of computing K_c values for different complex species.

TABLE 2

Stability constants (K_c/dm^3 mol^{-1}) of $SO_2{\cdot}X^-$, $SOCl_2{\cdot}X^-$, and $SO_2Cl_2{\cdot}X^-$ at 25 °C

	Solvent				
		MeCN			
Complex	dmso	1 : 3	1 : 1	3 : 1	MeCN
$SO_2{\cdot}I^-$	12 ± 0.1	14.1 ± 0.1	24.7 ± 0.6	36.7 ± 1	37.9
$SO_2{\cdot}Br^-$	21 ± 0.4	14.5 ± 0.2	24.1 ± 0.6	40.1 ± 0.2	160
$SO_2{\cdot}Cl^-$	26 ± 0.5	35.5 ± 1.3	50.0 ± 1.4	52.4 ± 2	372
$SOCl_2{\cdot}I^-$	35 ± 0.7	40.2 ± 1.2	58.9 ± 0.3	223.5 ± 1.8	150
$SOCl_2{\cdot}Br^-$	21 ± 0.4	22.9 ± 0.4	34.2 ± 0.6	71.7 ± 1	241
$SOCl_2{\cdot}Cl^-$	18 ± 0.5	66.7 ± 7	73.8 ± 0.8	113 ± 1.6	362
$SO_2Cl_2{\cdot}I^-$	6 ± 0.2	30.1 ± 1	50.1 ± 0.5	142.2 ± 2.3	76
$SO_2Cl_2{\cdot}Br^-$	14 ± 0.5	15.5 ± 0.3	24.6 ± 0.3	36.2 ± 0.5	41

The spectra were taken immediately after mixing the ligand with the sulphur compound using a Unicam SP 8000 spectrometer, in which the cell compartment was thermostatted at 25 °C, and 1-cm matched cells. All the chemicals were reagent grade and the solvents were suitable for spectroscopic work.

RESULTS AND DISCUSSION

Table 2 includes K_c data for $SO_2{\cdot}X^-$, $SOCl_2{\cdot}X^-$, and $SO_2Cl_2{\cdot}X^-$ at 25 °C in MeCN, dmso, and MeCN–dmso mixtures. The data in columns 1 and 5 were quoted from earlier work.[4] One feature appears throughout Table 2: the stability constants of all the complexes (at 25 °C) vary with solvent composition. In order to rationalise the K_c values we shall discuss the horizontal and vertical trends of Table 2.

Horizontal Trends of Table 2.—*The* $SO_2{\cdot}X^-$ *series.* The K_c values of $SO_2{\cdot}I^-$ change gradually between the limits set for MeCN and dmso as the solvent composition varies. In MeCN–dmso (3 : 1) the K_c value is reduced by 2.7% compared with that in 25% dmso solvent. For $SO_2{\cdot}Br^-$ and $SO_2{\cdot}Cl^-$ the K_c values are reduced in the same solvent by 76 and 85%. (The K_c values in MeCN are taken as a reference in each case.) Solvation of Br^- and Cl^- by dmso is clearly greater than for I^-. A similar conclusion was reached when K_c for the same species were determined in pure dmso and pure MeCN.[4]

To correlate the variations in K_c values with solvent composition it should be remembered that the molecules of different solvents can act as donors and acceptors. Even if both molecules have donor or acceptor character, a slight difference in the donor or acceptor properties between different solvent molecules will invite donor–acceptor interactions between them. The nature of such interactions in non-protic solvent mixtures such as MeCN–dmso has not been studied before.[8] Over a wide range of molecular ratios of MeCN and dmso one expects such interactions to exhibit different patterns which depend on the structural and geometrical characters of the molecules. We shall call this solvent–solvent interaction and may define it in terms of donor–acceptor interactions, or perhaps associations, which vary with solvent composition.

Such solvent–solvent interactions may occur at the expense of other interactions in solution. For example, in MeCN–dmso containing SO_2 molecules, Cl^- ligands, and $SO_2{\cdot}Cl^-$ complex species the following interactions are likely to occur: (*i*) Cl^-–dmso, (*ii*) Cl^-–MeCN, (*iii*) SO_2–dmso, (*iv*) SO_2–MeCN, and (*v*) MeCN–dmso. The stability constant of $SO_2{\cdot}Cl^-$ species is determined by the relative magnitudes of such interactions. A strong Cl^-–solvent interaction (solvation) would reduce the stability of $SO_2{\cdot}Cl^-$ species since this steric factor may prevent, to some extent, SO_2 and Cl^- from approaching each other for co-ordination. On the other hand, a strong MeCN–dmso interaction would allow more SO_2

---

[6] H. A. Benesi and J. Hildebrand, *J. Amer. Chem. Soc.*, 1949, **71**, 2703.

[7] J. A. A. Ketelaar, C. van de Stoppe, A. Goudsmit, and W. Dzcubas, *Rec. Trav. chim.*, 1952, **71**, 1104.

[8] 'Non-Aqueous Solvent Systems,' ed. T. C. Waddington, Academic Press, London, 1965.

to co-ordinate Cl^- ions and K_c becomes greater than the limits set by both solvents.

The data for $SO_2{\cdot}X^-$ show that the MeCN–dmso interaction accounts partly for the changing K_c with varying solvent composition. Ligand solvation is also important in determining K_c values. The K_c data show that while the I^-–solvent interaction is relatively weak and reduces K_c by 2.7% (in 25% dmso relative to its value in MeCN), those of Cl^-–solvent and Br^-–solvent are much stronger and reduce K_c by 85 and 76% for $SO_2{\cdot}Cl^-$ and $SO_2{\cdot}Br^-$ respectively.

The $SOCl_2{\cdot}X^-$ *and* $SO_2Cl_2{\cdot}X^-$ *series.* For $SOCl_2{\cdot}Cl^-$ and $SOCl_2{\cdot}Br^-$ the K_c values fall between the limits set for MeCN and dmso but that for $SOCl_2{\cdot}I^-$ exceeds the upper limit in MeCN by 30% (in 25% dmso solvent).

A change in solvent composition from 50 to 25% dmso is coupled with a sudden change in K_c for $SOCl_2{\cdot}I^-$. It appears that over this critical range of solvent composition the solvent–solvent interaction reaches its maximum. The nature of this interaction is not yet clear but is detectable from vapour-pressure measurements.[9] Such interactions have freed sufficient I^- ligands and $SOCl_2$ molecules for co-ordinating that K_c becomes 30% greater than its value in MeCN.

With $SOCl_2{\cdot}Cl^-$ and $SOCl_2{\cdot}Br^-$ (in 25% dmso) the K_c values are reduced by 69 and 71% from their values in MeCN. Thus, despite strong solvent–solvent interaction the Br^-–solvent and Cl^-–solvent interactions (solvation) have outweighed solvent–solvent interactions. Similar arguments apply to $SO_2Cl_2{\cdot}I^-$ and $SO_2Cl_2{\cdot}Br^-$ where K_c increases by 64% and decreases by 15% in 25% dmso respectively.

Vertical Correlations in Table 2.—The iodide complex series. Although the stability constants of $SOCl_2{\cdot}I^-$ and $SO_2Cl_2{\cdot}I^-$, in 25% dmso, are 30 and 64% greater than the value in MeCN, we find that for the complex $SO_2{\cdot}I^-$ K_c is 2.7% less than that in MeCN. These differences in behaviour are probably due to differences in the manner in which the I^- ligand is co-ordinated, to the three acceptors. The I^- ligand is polarisable with diffuse *d* orbitals suitable for ion–dipole interaction. The dipole moments of the three acceptors are in the order SO_2 (1.61), $SOCl_2$ (1.60), and SO_2Cl_2 (1.84 D).* In 25% dmso solvent, strong solvent–solvent interaction favours $SO_2Cl_2{\cdot}I^-$ co-ordination so that the K_c value exceeds that in MeCN by 64%. The acceptor character of $SOCl_2$ is enhanced by the replacement of one oxygen (in SO_2) by two electronegative chlorine atoms and co-ordination by ion–dipole interaction is relatively stronger with I^- compared to SO_2. Solvent–solvent interaction helps co-ordination of $SOCl_2$ to I^- and results in K_c exceeding that in MeCN by 30%. In $SO_2{\cdot}I^-$ the ion–dipole interaction is probably so weak that it is nearly balanced by solvent–solvent interaction and K_c is slightly reduced by 2.7%.

The bromide and chloride complex species. The reduction in the K_c values of $SO_2{\cdot}Br^-$, $SOCl_2{\cdot}Br^-$, and $SO_2Cl_2{\cdot}Br^-$ in 25% dmso by 76, 71, and 15% resulted from Br^-–solvent interaction. The differences arise from differences in the modes of co-ordination of Br^- to the three acceptors.

For SO_2 and $SOCl_2$ back bonding is the principal mechanism by which co-ordination takes place (S^{IV}). For $SO_2{\cdot}Br^-$ and $SOCl_2{\cdot}Br^-$ solvent–solvent is outweighed by Br^-–solvent interaction and K_c is reduced accordingly. For $SO_2Cl_2{\cdot}Br^-$ sulphur is sexivalent and co-ordination occurs by an ion–dipole mechanism. The Br^- ligand being a borderline Lewis base responds favourably to this mechanism but its solvation by dmso slightly outweighs solvent–solvent interactions and K_c is reduced by a smaller extent than the other bromides. For $SO_2{\cdot}Cl^-$ and $SOCl_2{\cdot}Cl^-$ back bonding is the principal mechanism for co-ordination. In both species, Cl^-–solvent outweighs solvent–solvent interaction and K_c is reduced by 85 and 69% respectively. The differing effects on K_c might be due to selective solvation in the presence of different acceptors (environmental factors).

Comment on the Thermodynamics in Mixed Solvents.—The above arguments on weak complexes show that a number of interactions exist in mixed solvents. Such interactions require different undefined heat quantities. To determine thermodynamic parameters it is customary to vary the temperature by several degrees. The heats involved in the individual interactions will probably also vary with temperature and it is difficult to determine the real meaning of compound functions such as $\Delta H^\ominus$, $\Delta S^\ominus$, and $\Delta G^\ominus$. Other kinetic and conductance measurements for which thermodynamics are reported in mixed solvents obviously need revision.

[7/635 *Received, 14th April,* 1977]

---

* Throughout this paper: $1\ D \approx 3.33 \times 10^{-30}$ C m.

[9] S. Wasif, unpublished work.