

Weak Complexes of Sulfur and Selenium Oxo Species A Thermodynamic View on Solvent Effects in Mixed Solvents

S.B. Salama and S. Wasif

Khartoum University, Sudan and Zagazig University, Egypt

ABSTRACT. Free energies and enthalpies of formation of the weak complexes $\text{SO}_2 \cdot \text{X}^-$, $\text{SOCl}_2 \cdot \text{X}^-$, $\text{SOBr}_2 \cdot \text{X}^-$ and $\text{SO}_2\text{Cl}_2 \cdot \text{X}^-$ ($\text{X} = \text{Cl}, \text{Br} \ \& \ \text{I}$) in the mixed solvent acetonitrile-dimethylsulphoxide (MeCN-dmsO) can be described by the existence of solute-solvent and solvent-solvent interactions.

Stability constants of dmsO or MeCN with the sulphur compounds SO_2 , SOCl_2 , SOBr_2 and SO_2Cl_2 are evidence to solute-solvent interactions.

Solvent-solvent interactions are confirmed from ΔH_{vap} , ΔS_{vap} and ΔH_{ws} of the mixtures of MeCN and dmsO. They are supplemented by the excess functions from refractive index, dielectric constants and densities of solvent mixtures. Infrared and Raman shifts point to the formation of 1:1 MeCN-dmsO adducts.

The formation of any adduct (whether a stable compound or a weak complex) is the result of interaction of an electron donor with an electron acceptor. Two factors are of importance in deciding the stability of any adduct: (1) the specific properties of the donor and the acceptor, (2) the role which environment plays, *i.e.*, solvent effects.

Since thermodynamic stability is indeed a summation of various factors, it is logical to correlate solvent effects with stability.

The present study is concerned with weak, charge transfer, complexes of the type: $\text{SO}_2 \cdot \text{X}^-$, $\text{SOCl}_2 \cdot \text{X}^-$, $\text{SOBr}_2 \cdot \text{X}^-$ and $\text{SO}_2\text{Cl}_2 \cdot \text{X}^-$ ($\text{X} = \text{Cl}, \text{Br} \ \& \ \text{I}$) which were detected spectroscopically and their stability constants determined in acetonitrile (MeCN), dimethylsulphoxide (dmsO) and their mixtures (Salama and Wasif 1978).

Results and Discussion

A. The Significance of ΔG_f^0 of Complexes in Relation to Solute-Solvent Interactions

Table 1 includes the standard free energies of formation ΔG_f^0 of some complexes in various solvents.

The above data show that, for every complex species, there are several free energy minima, each corresponding to a different solvent composition. This situation is only possible if a change in the solvent composition affects continuously the coordinating ability of the halide ligand (X^-) with the sulphur acceptor, S (compound) and partially hinders them from adduct formation.

The change in the coordinating ability of donors with acceptors results from steric factors due to their interaction with the solvents by solute-solvents interaction (commonly known as solvation).

Preliminary studies (Wasif, unpublished work, 1983) show that halide ion solvation in MeCN and dmsO falls in the order $Cl^- > Br^- > I^-$ which agrees with their radii and charge densities.

Solvation of the sulphur acceptors was studied in the present work by UV spectroscopy. Figure 1 shows the absorbance of $SOBr_2$ in MeCN (a), dmsO (c) and 1:1 mixed solvent (b). It shows three distinct species which obey Beer's law. The intermediate absorbance of the 1:1 mixture shows that $SOBr_2$ forms an absorbing species of intermediate character between the species in dmsO and that in MeCN. There are two possibilities in which this could happen: (1) the formation of a constant ratio of the adduct species $SOBr_2 \cdot MeCN$ and $SOBr_2 \cdot dmsO$, (2) that $SOBr_2$ makes a species with a mixed solvent adduct, e.g. $SOBr_2 \cdot MeCN \cdot dmsO$. The present work favours possibility (1). Using CCl_4 as solvent, the species $SOBr_2 \cdot MeCN$ and

Table 1. $-\Delta G_f^0$ of complex species in different solvents.

	dmsO	dmsO: MeCN			MeCN
		3:1	1:1	1:3	
$SO_2 \cdot I^-$	1.48	1.57	1.92	2.15	2.17
$SO_2 \cdot Br^-$	1.82	1.61	1.89	2.20	2.03
$SO_2 \cdot Cl^-$	1.94	2.14	2.33	2.36	2.53
$SOCl_2 \cdot I^-$	2.12	2.20	2.43	3.22	2.99
$SOCl_2 \cdot Br^-$	1.82	1.87	2.10	2.55	3.27
$SOCl_2 \cdot Cl^-$	1.72	2.51	2.56	2.82	3.50

Salama and Wasif (1978), and ΔG_f^0 in units of $kcal \cdot mol^{-1}$

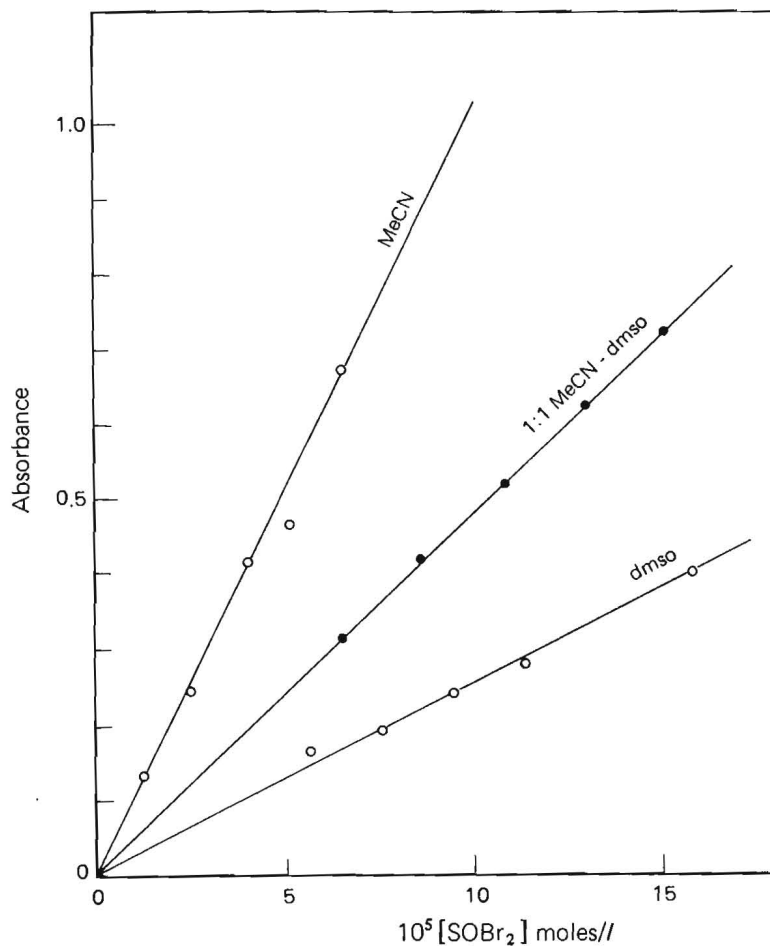


Fig. 1. Dependence of absorbance on solvent mole fraction.

$\text{SOBr}_2 \cdot \text{dms0}$ were detectable. Adducts of SO_2 , SOCl_2 and SO_2Cl_2 with MeCN and dms0 were also detectable. Stability constants of these new species were evaluated by Ketelaar's method (1952) and the data are given in Table 2.

The data of Table 2 show that the solvents MeCN and dms0 play a competing role against the halide ligands in their coordination with the sulphur acceptors. They also show dms0 to have a greater destabilising role, than MeCN, towards the complex species $\text{SO}_2 \cdot \text{X}^-$, $\text{SOCl}_2 \cdot \text{X}^-$, $\text{SOBr}_2 \cdot \text{X}^-$ and $\text{SO}_2\text{Cl}_2 \cdot \text{X}^-$ by its strong ability to solvate the halide ligands and the sulphur compounds.

Table 2. K_c data at 25°C for adducts of SO_2 , SOCl_2 , SOBr_2 and SO_2Cl_2 with MeCN and dmsO.

A =	SO_2	SOCl_2	SOBr_2	SO_2Cl_2
dmsO.A	2.82 ± 0.20	6.86 ± 0.04	3.73 ± 0.03	17.79 ± 0.05
MeCN.A	0.34 ± 0.02	0.07	0.11	0.68 ± 0.02

B. The Dependence of ΔH_f^0 and ΔS_f^0 of Complex Species on Solvent Composition

A second thermodynamic aspect would be to consider the significance of ΔH_f^0 and ΔS_f^0 for complex species in mixed solvents. Table 3 includes the standard thermodynamic constants for the formation of the complex species $\text{SOBr}_2 \cdot \text{Cl}^-$ and $\text{SOBr}_2 \cdot \text{Br}^-$. Since the significance of ΔG_f^0 was discussed in part (A) we turn our attention to ΔH_f^0 .

Table 3 shows that the standard enthalpy of formation varies widely as the solvent changes from MeCN to dmsO. For $\text{SOBr}_2 \cdot \text{Br}^-$, ΔH_f^0 is nearly 9 times the value in dmsO, but for $\text{SOBr}_2 \cdot \text{Cl}^-$ it is nearly 5 times greater in MeCN than in dmsO. These differences in ΔH_f^0 values suggest that the measured enthalpy of formation is a rather complex function. It does not, probably, represent the heat of formation of the complex species but other heat terms are possibly embodied in this term such as heats of solvation of the halide ligands and sulphur compounds in MeCN and dmsO.

Table 3. Thermodynamic constants of $\text{SOBr}_2 \cdot \text{Cl}^-$ and $\text{SOBr}_2 \cdot \text{Br}^-$ in different solvents at 25°C.

	dmsO	dmsO: MeCN			MeCN
		3:1	1:1	1:3	
$\text{SOBr}_2 \cdot \text{Br}^-$					
$K_c/L \cdot \text{mol}^{-1}$	12	19	25	32	203
$-\Delta G_f^0/\text{kcal} \cdot \text{mol}^{-1}$	1.40	1.76	1.92	2.07	3.17
$-\Delta H_f^0/\text{kcal} \cdot \text{mol}^{-1}$	0.45	1.10	1.10	4.80	4.60
$\Delta S_f^0/\text{cal} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$	3.2	2.2	2.7	-9.2	-4.8
$\text{SOBr}_2 \cdot \text{Cl}^-$					
$K_c/L \cdot \text{mol}^{-1}$	19	36	40	79	100
$-\Delta G_f^0/\text{kcal} \cdot \text{mol}^{-1}$	1.76	2.14	2.20	2.60	2.75
$-\Delta H_f^0/\text{kcal} \cdot \text{mol}^{-1}$	0.45	2.40	2.30	3.90	2.40
$\Delta S_f^0/\text{cal} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$	4.4	-0.7	-0.3	-4.3	1.2

If the standard enthalpy of formation be taken as a rough measure of the complex species thermal stability, then the data of Table 3 would show that the complex species $\text{SOBr}_2 \cdot \text{X}^-$ ($\text{X} = \text{Cl}, \text{Br}$) are more stable in MeCN than they are in dmsO.

A thorough discussion of the significance of ΔH_f^0 data requires a knowledge of the heats of solvation of the different species in both solvents which are not, at present, available. This situation permits a qualitative discussion of such data.

Since solute-solvent interaction is a dynamically changing process, we may expect that the magnitude of ΔH (solvation) values to change over the solvent concentration used which is confirmed indirectly from Table 3. With this situation, in a mixed polar solvent, a discussion of ΔS_f^0 values would be difficult to interpret.

C. (i) Solvent-Solvent Interaction and Complex Stability

The continuous change in the stability constants of different complex species with changing solvent composition is partly the result of a new type of interaction which we may call solvent-solvent interaction.

A polar solvent can act either as a donor or as an acceptor. Even if the two solvents behaved as donors or acceptors but differ slightly from each other in their donor or acceptor numbers, such differences invite solvent-solvent interaction by coordination.

The magnitude of solvent-solvent interaction decides, to an important extent, the complex stability constant in solution of the mixed solvents. A strong solvent-solvent interaction means that the complexing species, *i.e.* X^- ($\text{X} = \text{Cl}, \text{Br}$ and I) and sulphur compounds, have a greater chance to coordinate and this gives rise to K_c values greater than in either solvent, *e.g.* $K_c(\text{SOCl}_2 \cdot \text{I}^- \text{ in MeCN}) = 150 \text{ L.mol}^{-1}$, while its value in dmsO equals 35 L.mol^{-1} and in 1:1 MeCN-dmsO mixture K_c of $\text{SOCl}_2 \cdot \text{I}^- = 223 \text{ L.mol}^{-1}$ (Salama and Wasif 1978). On the other hand, a weak solvent-solvent interaction would mean a relatively stronger solute-solvent interaction which makes the complexing species in a less sterically favoured state to coordinate. This situation leads to the different K_c values for different solvent compositions.

C. (ii) Evidence for Solvent-Solvent Interactions

(a) Spectroscopic

To supplement this discussion on solvent-solvent interaction, mixtures of MeCN and dmsO were investigated by IR and Raman in CCl_4 as solvent.

Using IR technique, it is found that the $\text{S}=\text{O}$ vibration band of dmsO appears at 1080 cm^{-1} and on adding MeCN the band is shifted to 1070 cm^{-1} . The $\text{C}\equiv\text{N}$ vibration band of MeCN appears at 2250 cm^{-1} and adding dmsO, at $x_1 = 0.5$, the band is shifted to 2240 cm^{-1} .

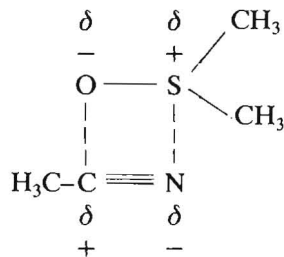


Fig. 2. MeCN-dmsO adduct.

With Raman spectra, it is found that for dmsO the S=O vibration band appears at 1044 cm^{-1} and on addition of MeCN a peak appears at 1062 cm^{-1} , while that at 1044 cm^{-1} disappears. For MeCN, the C≡N vibration band appears at 2255 cm^{-1} and on addition of dmsO the band disappears gradually.

The observed vibrational shifts may be taken as evidence for solvent-solvent interaction through adduct formation of the type represented by Fig. 2. A confirmation of such solvent-solvent adduct would be possible by a cryoscopic study of the MeCN-dmsO system. Such a study has not been done yet in the present work.

(b) Vapour Pressure, Viscosity and Excess Functions from Refractive Index, Dielectric Constant and Volume

Further confirmation to solvent-solvent interaction was obtained from measurements of vapour pressure and viscosity of MeCN-dmsO mixtures. Table 4 includes vapour pressures, viscosities and ΔH_{vap} , ΔS_{vap} and ΔH_{vis} of the mixtures over the whole composition range.

Figure 3 shows the plot of ΔH_{vap} and ΔH_{vis} against solvent composition. The plots, in Fig. 3, are not linear and deviate over the composition range 50-70% — maximum deviation — which may be taken to indicate solvent-solvent interaction. The ΔS_{vap} data show a minimum value at 75% dmsO suggesting maximum order for the system at this composition with probable formation of dmsO-MeCN adduct, Fig. 2.

The excess functions from refractive index, n^E , dielectric constant, ϵ^E , and density, V^E , of dmsO-MeCN mixtures were evaluated, and are given in Table 5 (Redlich and Kister 1948).

The data in Table 5 show that the magnitude of any excess function reaches a maximum at approximately 1:1 composition. This is, again, taken to indicate solvent-solvent interaction.

Table 4. Vapour pressures and viscosities of MeCN-dmsO mixtures
(a) Vapour Pressure Data

25% MeCN	t/°C	61.6	69.0	75.6	80.7	85.7	
	p/mmHg	58.0	72.0	84.0	99.0	115.5	
50% MeCN	t/°C	29.0	34.5	39.9	45.0	49.0	54.0
	p/mmHg	69.7	76.1	95.6	115.6	136.3	163.6
75% MeCN	t/°C	28.4	33.1	38.5	43.7	49.4	
	p/mmHg	78.9	95.4	119.4	147.9	186.9	
80% MeCN	t/°C	28.4	33.4	38.9	45.1	51.6	
	p/mmHg	84.7	106.5	134.0	160.0	213.0	

(b) Viscosity Data

t/°C	25.0	30.0	35.0
MeCN	3.55	3.38	3.30×10^{-4} Pas
75% MeCN	5.17	4.89	4.73
50% MeCN	7.44	7.04	6.68
25% MeCN	11.71	10.85	10.16
dmsO	19.57	17.88	16.40

(c) Thermodynamic Data for Vaporisation and Viscosity

Solvent	MeCN	80% MeCN	75% MeCN	50% MeCN	25% MeCN	dmsO
$\Delta H_{\text{vap}}/\text{kcal.mol}^{-1}$	7.94	7.59 ± 0.28	7.95 ± 0.10	6.95 ± 0.43	6.73 ± 0.25	12.64 ± 0.10
$\Delta S_{\text{vap}}/\text{cal.K}^{-1}\text{mol}^{-1}$	22.94	20.81 ± 0.92	21.84 ± 0.32	18.13 ± 0.14	14.98 ± 0.75	22.90
$\Delta H_{\text{vis}}/\text{kcal.mol}^{-1}$	1.31	1.57 ± 0.05	1.85 ± 0.01	1.97 ± 0.04	2.53 ± 0.07	3.19

Experimental

Dimethylsulphoxide, acetonitrile and carbontetrachloride were Merck products for spectroscopic use.

The refractive index was measured with a Carl Zeiss Jena immersion refractometer. The dielectric constant was measured with a dielectrometer which operates at 2 MHz with a cylindrical stainless steel cell of the MFL/3/S type, with a

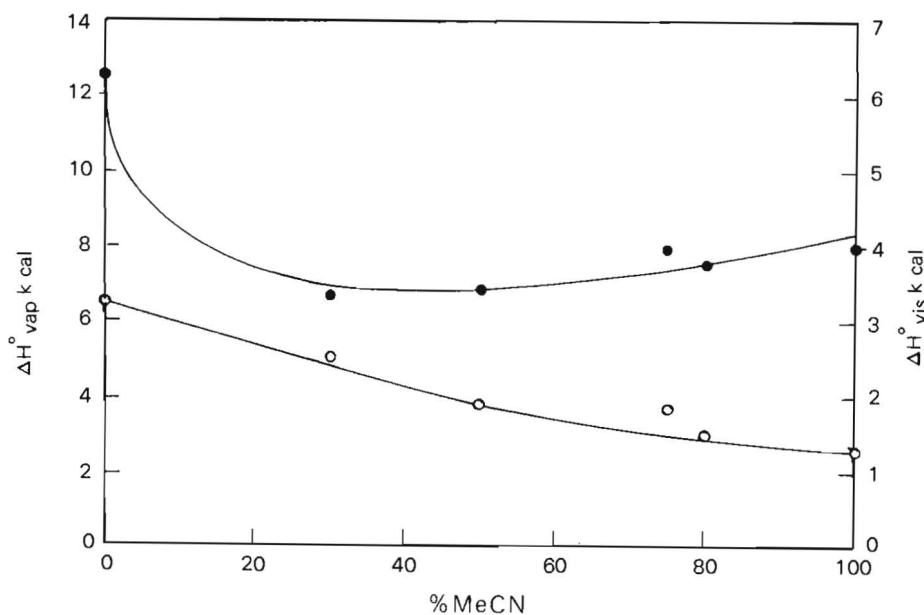


Fig. 3. Plot of $\Delta H_{\text{vap}}^{\circ}$ (●) and $\Delta H_{\text{vis}}^{\circ}$ (○) against % MeCN.

Table 5. Excess functions of dmsO-MeCN mixtures at 25°C
Refractive Index (n^E)

x_1	0.1319	0.2676	0.4258	0.6899	0.7836	0.8697
n^E	0.0030	0.0076	0.0087	0.0102	0.0065	0.0039

Dielectric Constant (ϵ^E)

x_1	0.1319	0.2676	0.4258	0.6009	0.6899	0.7836	0.8697
ϵ^E	0.5710	0.9540	1.3180	1.4910	1.3680	1.1960	0.8630

Volume (V^E)

x_1	0.1006	0.3066	0.6037	0.7061	0.8083	0.8999	0.9455
V^E	-0.1300	-0.2523	-0.2519	-0.1773	-0.1275	-0.0876	-0.0486

(x_1 = mole fraction of dmsO)

dielectric constant measuring range of 21 to 90. The density was measured by an Anton Paar model DMA 10 vibrating densitometer. The excess functions were fitted to a Redlich-Kister equation (1948);

$$n^E = x_1x_2(A_0 + A_1(x_1 - x_2) + A_2(x_1 - x_2)^2 \dots$$

where the coefficients $A_0 \dots$ were found by a computer program.

Vapour pressures were measured by the isotenoscope method suggested by Smith and Menzies (1910) and viscosity by Ostwald's method.

Infrared spectra were recorded by a Perkin-Elmer spectrophotometer model 457. The slit width was normal and the cells were equipped with KBr windows with path length 0.20 mm.

Raman spectra were recorded by a Coderg PHO spectrophotometer using an exciting radiation at 647.1 nm from a coherent radiation krypton laser.

Ultraviolet and visible spectra were recorded by a Perkin-Elmer SP800 spectrophotometer with matched silica cells, 1.0 cm, and the cell compartment was thermostated to $\pm 0.10^\circ\text{C}$. The use of spectral data to compute stability constants was reported earlier (Salama *et al.* 1971).

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رأى دينامى حرارى عن أثر المذيبات فى ثبات المعقدات الضعيفة لفصيلة من مركبات الكبريت والسيلينيوم الأوكسيجينية

سلامة بطرس سلامة و سعد واصف

قسم الكيمياء - كلية العلوم - جامعة الخرطوم - السودان؛ وقسم
الكيمياء - كلية العلوم - جامعة الزقازيق - مصر.

تشير قيم طاقات التكون الحرة للمعقدات الضعيفة التالية:
 $SO_2 \cdot X^-$, $SOCl_2 \cdot X^-$, $SOBr_2 \cdot X^-$, $SO_2Cl_2 \cdot X^-$ ($X = Cl, Br \& I$)
فى مزائج مكونة من أسيتونتريل MeCN وثنائى ميثيل
سلفوكسيد Dmsو إلى وجود قوى تأثير متبادلة بين المذيبات
والمواد المنحلة فيها وكذلك بين المذيبات بعضها البعض.

أمكن تعيين ثوابت التماسك بين المذيبات المستخدمة
فى هذه الدراسة وهى: Dmsو & MeCN وبين مركبات
الكبريت وهى $SOCl_2$ ، SO_2 ، $SOBr_2$ ، SO_2Cl_2 وتعد إثباتا
لوجود قوى التأثير المتبادلة بين المذيبات وبين مركبات
الكبريت. ولقد دلت قياسات كثافة محاليل مركبات
الهالوجين وكذلك قياسات الطين النووى المغنطيسى على
استحلال الشوارد Cl^- ، Br^- ، I^- ، بواسطة المذيبات المستخدمة
كما ظهر أيضا أن استحلال الشوارد بواسطة Dmsو أكبر أثرا
عنه بواسطة MeCN.

أوضحت نتائج دراسات الضغط البخارى واللزوجة لمزائج المذيبات عن وجود قوى التأثير المتبادلة بين جزيئات المزيغ . وتوافر المزيد من الأدلة عن هذه القوى من دراسة طيوفها (تحت الحمراء ورامان) وكذلك من قياسات قرائن الانكسار وثوابت العزل الكهربائى والكثافات للمزائج المختلفة والمستخدمة فى هذه الدراسة .