AN IODINE-METHYL SULFOXIDE PRECIPITATE

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ABSTRACT.—The precipitate formed when I_2 and DMSO solutions are mixed is found to be preferentially solvated by DMSO. The solvation occurs in a manner which is predictable by a linear relation. The experimental evidence supports a 1:1 reaction.

In a solubility study of iodine in methyl sulfoxide (commonly called dimethylsulfoxide and designated DMSO) Jones and Musulin (1959) noted the formation of an unexpected precipitate at 45°C. The purpose of the present study was to investigate the nature of that precipitate at room temperature.

EXPERIMENTAL

Reagents. DMSO, supplied gratis by the Stepan Chemical Company, was purified by distillation with the recovery of a one degree boiling fraction which was stored in a dried glass flask stoppered with a foil covered cork. Resublimed iodine, Mallinckrodt A. R. grade, and carbon tetrachloride, Fisher A. C. S. grade, were used without further purification.

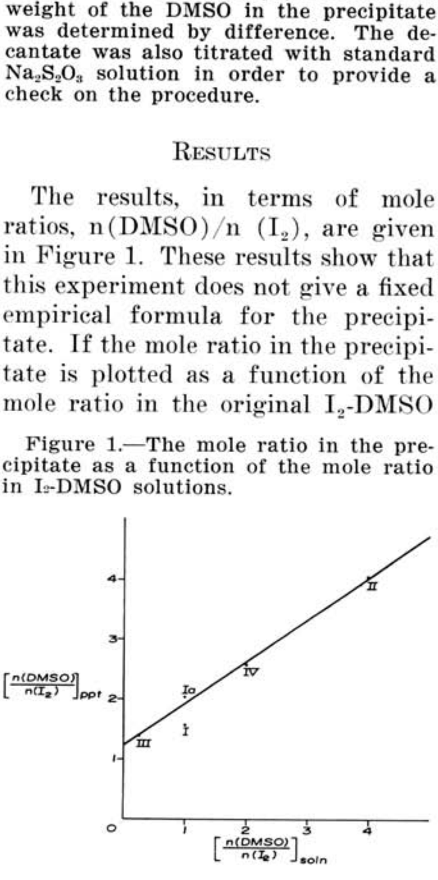
Procedure. Stock solutions of 0.1 M I_2 and 0.1 M DMSO (using carbon tetrachloride as a solvent) and a standard solution of 0.1 M $Na_2S_2O_3$ were prepared. Weighings were made on a Christian Becker, Model AB-2, Chainomatic balance while all volumetric measurements were made with 0.1, 1, and 10 ml uncalibrated pipets. Four different solutions and one check solution were prepared by mixing different ratios of the two stock solutions. The compositions of the new solutions (hereafter called I_2-DMSO solutions) are given in Table 1.

A black precipitate was formed upon the preparation of the I_2-DMSO solutions. Each precipitate was separated from its solution, dried and weighed. The weight of iodine in the precipitate was determined by a titration procedure using the standard $Na_2S_2O_3$ solution. The weight of the DMSO in the precipitate was determined by difference. The decantate was also titrated with standard $Na_2S_2O_3$ solution in order to provide a check on the procedure.

RESULTS

The results, in terms of mole ratios, n(DMSO)/n (I_2), are given in Figure 1. These results show that this experiment does not give a fixed empirical formula for the precipitate. If the mole ratio in the precipitate is plotted as a function of the mole ratio in the original I_2-DMSO

Figure 1.—The mole ratio in the precipitate as a function of the mole ratio in I_2-DMSO solutions.



solution, an excellent linear relation is obtained as can be seen from Figure 1. The equation of this line, found by a method of least squares (Scarborough, 1958), is

$$\left[\frac{n(\mathrm{DMSO})}{n(\mathrm{I_2})}\right]_{\mathrm{ppt}} = 0.69\left[\frac{n(\mathrm{DMSO})}{n(\mathrm{I_2})}\right]_{\mathrm{soln}} + 1.25 \quad (1)$$

The fitting procedure did not include the point for solution I. The standard deviation of the ordinate values given by Equation (1) is 0.05. Table 1 shows the individual deviations.

DISCUSSION

Equation (1) can be interpreted as indicating that molecules of DMSO are solvating the precipitate. That is,

$$a\mathrm{I_2} + (b + c)\,\mathrm{DMSO} \rightarrow [(\mathrm{I_2})_a : (\mathrm{DMSO})_b] \cdot [\mathrm{DMSO}]_c \quad (2)$$

where c represents the number of moles of solvating DMSO. In writing the reaction given by Equation (2) no claim is made as to whether a definite chemical reaction such as substitution, etc., has taken place or whether a molecular complex has been formed. The fact that Equation (1) is so definitely linear would indicate that as excess DMSO (in relation to the I_2) is added to an I_2-DMSO solution, a fixed amount would solvate any precipitate which has been formed. Obviously these same arguments would hold if one wished to interpret c as the amount of DMSO occluded in a precipitate crystal lattice. Finally, this interpretation would indicate a preferential solvation (or ability to be occluded) by the DMSO in relation to the solvent, CCl_4. Such behavior is not strange if one considers the differences in DMSO and CCl_4 as a Lewis base (Gould, 1962).

The intercept of Equation (1) establishes an upper limit for the ratio b/a of the subscripts appearing in Equation (2). However, one would expect a minimal amount of solvation in any precipitation reaction which would indicate that this upper limit is too high. Musulin, et. al. (1964) suggest (from spectrophotometric evidence) that the ratio b/a

TABLE 1.—I_2-DMSO Solution Data.

Solution Designation	Volume of 0.1 M I_2 Solution (ml)	Volume of 0.1 M DMSO Solution (ml)	Weight of Precipitate (mg)	Volume of 0.1 M $Na_2S_2O_3$ Solution (ml)	Weight of I_2 in Precipitate (mg)	Volume of 0.1 M $Na_2S_2O_3$ Decantate (ml)	$\left[\frac{n(\mathrm{DMSO})}{n(\mathrm{I_2})}\right]_{\mathrm{ppt}}$	
							(Calculated)	Deviation
I	10	10	138.3	7.4	93.60	12.25	1.94	.39
I_a	10	10	209.2	10.19	128.90	5.30	1.94	—.08
II	5	20	115.5	4.07	51.48	5.90	4.01	—.03
III	20	5	79.5	4.40	55.00	33.30	1.42	+.02
IV	10	20	226.7	9.97[1]	126.05[1]	9.85	2.63	+.05

[1] Back calculated.

should be 1. The current investigation supports a 1:1 reaction if one considers the product solvated.

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