Solubility of Iodine in Dimethyl Sulfoxide

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Figures for the solubility of iodine in dimethyl sulfoxide (DMSO) between 27 and 38° were pub-

lished by Jones and Musulin[1] in 1962. We have re-studied this system carefully over a larger range of temperature because of its interest from the standpoint of theory of solubility. The solubility parameter of DMSO is 13.0, close to that of iodine, 14.1,[2] and this liquid is moreover a strong electron donor.

Our supply of the liquid was from Matheson Coleman and Bell. We recrystallized it three times to a melting point of 18.32°. The solubility of iodine was determined with the apparatus described by Glew and Hildebrand.[3] Results are shown in Table I.

Table I: Mole Fractions of Iodine in Dimethyl Sulfoxide

|	19.56°	25.00°	30.72°	35.05°	40.20°
x_2 (obsd)	0.5626	0.5711	0.5789	0.5850	0.5925
x_2 (calcd)	0.5631	0.5707	0.5789	0.5851	0.5924

The figures in the third row were calculated by the equation $\log x_2 = 0.7450 \log T - 2.0879$. The relation of the solubility of iodine in DMSO to its solubility in other good solvents is shown in Figure 1. The points designated by black dots represent the determinations by Jones and Musulin. Their values are from 2 to 4% lower than ours. The line for this system lies well above the line for the activity of solid iodine. At 25°, 57.1 mole % or nearly 88 wt % of the solution is iodine. It is unlikely that any other solvent will be found which combines the high solubility parameter and complexing power possessed by DMSO.

We calculate the solubility parameter of DMSO from its heat of vaporization at 25° 12,640 cal mole^{-1}, according to Douglas,[4] and our own determination of its density at 25°, 1.0964. The energy of vaporization is then 12,050 cal mole^{-1}, the molal volume is 71.26 cc, and $\delta_1 = 13.0$. If there were no complexing, the line for $\log x_2$ would be expected to fall only a little below the line for $\log a_2{}^s$; the activity of solid iodine referred to liquid. The further increase in solubility results from strong complexing. The deviation from the line of $\log a_2{}^s$ decreases as the temperature increases, as expected in accord with decreasing stability of the complex.

One cannot calculate the entropy of solution from these data by the exact equation[2]

$$s_2 - s_2{}^s = R(\partial \ln x_2/\partial \ln T)_{sat} \times (\partial \ln a_2/\partial \ln x_2)_T$$

because the Henry's law partial differential cannot be set at unity in a solution so concentrated and nonideal. One can assert only that the system behaves essentially as expected.
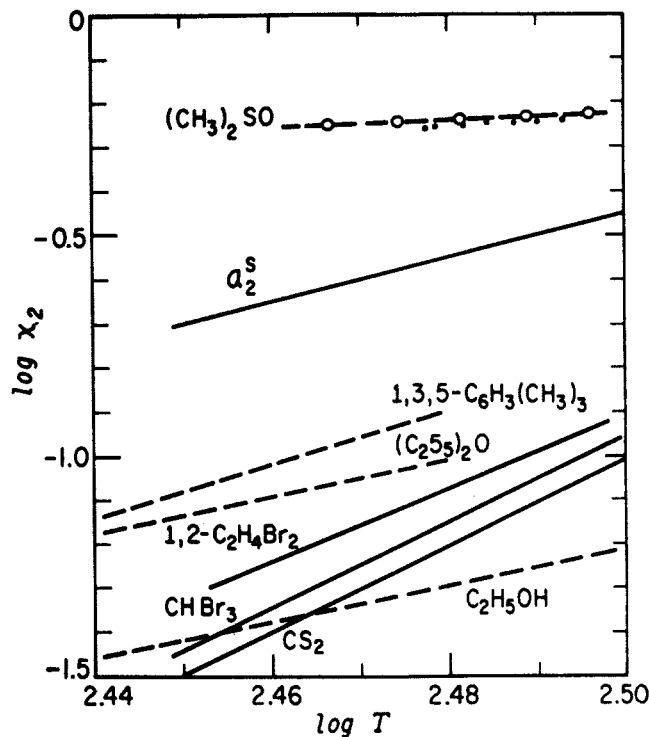
SOLUBILITY OF IODINE

Figure 1.

The partial molal volume of iodine in DMSO was determined by the method described by Shinoda and Hildebrand[5] to be 64.5 ± 0.4 cc at mole fractions less than 0.004.

We made a comprehensive spectroscopic study of these solutions while unaware of the masterly investigations of Klaeboe.[6] Our results agreed with his in all respects. For example, our value for the equilibrium constant of the 1:1 complex in CCl_4 at 25° is $K = 11.6$; the mean of their seven values is 11.4.

We made two observations, however, that they did not. In a freshly prepared solution of iodine in pure DMSO, two absorption bands were found, λ_{max} 367 mμ, ϵ_{max} 21,800 and λ_{max} 298 mμ, ϵ_{max} 40,400. A new sharp absorption band at 248 mμ slowly appeared and grew to a maximum in about 5 days. This band is evidently that of iodide ion in DMSO, because potas-

(1) W. J. Jones and B. Musulin, *J. Chem. Eng. Data*, **7**, 294 (1962).

(2) J. H. Hildebrand and R. L. Scott, "Regular Solutions," Prentice-Hall, Englewood Cliffs, N. J., 1962, p 117.

(3) D. N. Glew and J. H. Hildebrand, *J. Phys. Chem.*, **60**, 616 (1956).

(4) T. B. Douglas, *J. Am. Chem. Soc.*, **70**, 2001 (1948).

(5) K. Shinoda and J. H. Hildebrand, *J. Phys. Chem.*, **62**, 272 (1958).

(6) P. Klaeboe, *Acta Chem. Scand.*, **18**, 27 (1964).

sium iodide in DMSO gives the same sharp band at 248 mμ. Furthermore, the molar conductivity of a fresh solution of 0.008 M iodine in DMSO is very small, 2.6 mhos cm^{-2}, despite the high dielectric constant of DMSO, 46.6 at 25°, but the conductivity increases over a period of days parallel with the growth of the iodide absorption band to a level of approximately 11.6 mhos cm^{-2}. Our colleague, Professor A. Streitwieser, suggested that iodine catalyzes a slow disproportionation of DMSO into dimethyl sulfide and dimethyl sulfone, which may be written

$$2(CH_3)_2SO \cdot I_2 = (CH_3)_2SO_2 + (CH_3)_2S \cdot I_2$$

Tideswell and McCullough[7] had found that dimethyl sulfide, a strong electron donor, forms a 1:1 complex with iodine with a dissociation constant in CCl$_4$ solution of 1.40 × 10^{-2} at 25° and λ_{max} of approximately 430 mμ. This complex, when dissolved in a solvent with the high dielectric constant of DMSO, would be expected to ionize into $(CH_3)_2SI^+$ and I^-. The slow step in this sequence is evidently the initial disproportionation of DMSO. Each item in the evidence we have obtained seems to be in harmony with the above explanation.

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(7) N. W. Tideswell and J. D. McCullough, *J. Am. Chem. Soc.*, **79** 1031 (1957).

Intrinsic Viscosity of Polyvinyl Alcohol in Aqueous Salt Solutions[1]

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The role of salts on the intrinsic viscosity of an isoelectric protein[2a] (gelatin) and of two polypeptides,[2b] one cationic (poly-L-lysine), the other anionic (poly-L-glutamic acid), has recently been reported. We have considered it interesting also to explore the effect of the same salts on the viscosity of an uncharged polymer. This study is of interest *per se* since the behavior of uncharged polymers (*e.g.*, polyvinyl alcohol, poly-

acrylonitrile, etc.) in salt solutions has not been extensively investigated. In addition, the study is of interest in order to assess the contribution of the uncharged, hydrophilic portions of complex macromolecules, such as proteins, to their solution properties in the presence of salts.

Polyvinyl alcohol (PVA) was chosen for this investigation because of its water solubility and because its typical random-coil character simplifies the interpretation of the results. Limited data are also presented for dextran, a typical polysaccharide.

The PVA sample (Gelvatol 1-90) was produced by the Monsanto Co. This material was obtained by hydrolysis of polyvinyl acetate and the residual content of the latter was about 1% by weight. The weight-average molecular weight was about 120,000. The dextran sample was obtained from the U. S. Department of Agriculture (Northern Utilization Research and Development Division) through the courtesy of Dr. S. R. Erlander. It was produced by Leuconostoc mesenteroides (NRRL B-512F) and had a weight-average molecular weight of 68,000. Viscosity measurements were performed as previously reported.[2]

A stock solution of PVA ($c \simeq 1\%$) was obtained by dissolving the polymer in boiling water, leaving the solution for about 10 days at room temperature, and filtering through fritted glass. A similar procedure was followed for dextran.

Intrinsic viscosities are plotted as a function of salt concentration, C_s, in Figure 1 for PVA and for dextran. In KCl, insolubilization of PVA and dextran occurred, respectively, at $C_s > 0.27\ M$ and $C_s < 1\ M$. The instrinsic viscosity is increased (relative to the value in pure water) by some salts and is decreased by others. The results are compatible with the following ranking of the anions and cations for increasing intrinsic viscosity

$$Cl^- < I^- < SCN^- \tag{1}$$

$$K^+ < Li^+ < Ca^{2+} \tag{2}$$
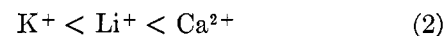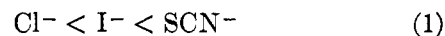
As expected, the variation of $[\eta]$ with C_s is more similar to that observed for isoelectric gelatin[2a] than for the cationic and anionic polypeptides.[2b] (In the latter case, $[\eta]$ decreased with C_s for all salts.) Series 1 and 2 are similar to those deduced from the viscosity of isoelectric gelatin[2a] and to those describing the increase of enrichment of salt within collagen networks.[3] Thus,

(1) Supported in part by the Centro Nazionale Chimica delle Macromolecole, Sezione V, Genova, Italy.

(2) (a) L. Rajagh, D. Puett, and A. Ciferri, *Biopolymers*, **3**, 421 (1965); D. Puett and L. Rajagh, *J. Macromol. Sci.*, in press; (b) E. Bianchi, A. Bicchi, G. Conio, and A. Ciferri, *ibid.*, **A5**, 909 (1967).

(3) A. Ciferri, R. Garmon, and D. Puett, *Biopolymers*, **5**, 439 (1967).