

measured the intrinsic viscosities,  $[\eta]$ , of the PVA (fraction I) solution in various NaCl and sucrose concentrations. From pure water to 0.5 *M* NaCl or sucrose,  $[\eta]$  remained virtually constant at 1.3 dl./g. At higher salt or sucrose concentrations, it dropped to 0.97 at 1 *M*, clearly indicating a coiling up of PVA. Beyond 1 *M* NaCl or sucrose,  $[\eta]$  began to increase, probably because of aggregation; at 1.5 *M* it was 1.5 in sucrose and 1.15 in NaCl; at concentrations higher than 1.5 *M*, PVA began to precipitate. We also found that KCl, KF, and CsCl, but not LiBr (see section c), are all poor solvents for PVA, as is NaCl.

(c) *Divalent Cations*. In contrast to the monovalent salts (except LiBr), the divalent cations,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ , and  $\text{Cu}^{2+}$  swelled the PVA film. The film elongated about 1 and 5% in 2 *M*  $\text{CaCl}_2$  and  $\text{MgCl}_2$ , but dissolved in 4 *M*  $\text{CaCl}_2$  or 3 *M*  $\text{MgCl}_2$ . The film length increased about 3% in 1 *M*  $\text{CuCl}_2$ , about 50% after 20 hr. in 2 *M*  $\text{CuCl}_2$ , and about 400% in 3 *M*  $\text{CuCl}_2$ . Furthermore, with  $\text{Cu}^{2+}$  the elongation was irreversible. For comparison, we found that the intrinsic viscosity of the PVA (fraction II) solution increased from 0.89 dl./g. in water (pH 6.4) to 1.18 in 3 *M*  $\text{MgCl}_2$  (pH 5.7) and 1.08 in 4 *M* LiBr (pH 8.1). Thus, the chlorides of the three divalent cations and LiBr studied have a strong affinity for the PVA molecules. They penetrate into the film, probably break up the crystalline regions, and expand the polymer coils. This in turn prevents the "osmotic contraction" observed previously for some monovalent salts and small organic compounds. In this respect we note that LiBr,  $\text{CaCl}_2$ ,  $\text{MgCl}_2$ , and  $\text{CuCl}_2$  are all soluble in ethanol, whereas NaCl and KCl are only slightly soluble, and KF is insoluble in ethanol. Perhaps the different behavior of PVA with different salts is closely related to the affinity between the hydroxyl groups of PVA and these salts.

(d) *Urea and Guanidine Hydrochloride*. The PVA film elongated by about 7% in 8 *M* urea (Fig. 2). Guanidine hydrochloride is a more effective dispersing agent than urea; in 5 *M* salt the film dissolved after several hours of exposure. These two compounds are well known as denaturing agents for globular proteins, although the mechanism of denaturation is still unsettled. The effect of urea on a neutral polymer, polyvinylpyrrolidone, was studied by Klotz and Russell.<sup>6</sup> They found a slight decrease in the intrinsic viscosity when the polymer was dissolved in 8 *M* urea instead of pure water; this they attributed to a possible decrease in the degree of hydration of the macromolecule. We found, however, that the intrinsic viscosity of a PVA solution (fraction II) increased from 0.89 dl./g in water to 1.02 in 8 *M* urea. Thus,

the PVA molecules can be swamped with urea or guanidine hydrochloride molecules, although the mechanism of such interaction is still unknown.

*Acknowledgment*. We thank Professor M. F. Morales for his stimulating discussions. Technical assistance by Miss K. Graham is gratefully acknowledged.

(6) I. M. Klotz and J. W. Russell, *J. Phys. Chem.*, **65**, 1274 (1961).

### Common Ion Effects on the Solubility of Silver Chloride and Thallous Bromide in Fused Nitrate Solvents

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The authors<sup>2</sup> have recently calculated solubilities for salts of type AC in fused salt solvents BD from the thermodynamic properties of the two components and those of the reciprocal salt pair AD and BC. In the systems investigated, where the solubilities were small, reasonable agreement of calculated and experimental values was found. It was thought to be of interest to extend the measurements to include the changes in solubility produced by the addition of salts having an ion in common with the solute to see to what extent similar thermodynamic calculations would serve to predict the observed effects. For this purpose the solubilities in potassium nitrate of thallous bromide in the presence of added thallous nitrate and potassium bromide and the solubility of silver chloride in sodium nitrate in the presence of added silver nitrate and sodium chloride have been measured.

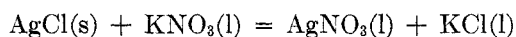
In an earlier note one of the authors<sup>3</sup> showed how the solubility of silver chloride at 300° expressed as mole fraction of AgCl increased from a value of  $7 \times 10^{-4}$  in pure potassium nitrate on addition of silver nitrate to a mole fraction of 0.55 in pure silver nitrate. This behavior is qualitatively reasonable. When silver chloride dissolves in silver nitrate the number and kind of nearest neighbor, anion-cation interactions must be essentially equal to those existing in the separate com-

(1) From the Ph.D. Thesis of Paul E. Field, Pennsylvania State University, August, 1963; supported by the U. S. Atomic Energy Commission under contract AT(30-)-1881.

(2) R. P. Seward and P. E. Field, *J. Phys. Chem.*, **68**, 210 (1964).

(3) R. P. Seward, *ibid.*, **63**, 760 (1959).

ponents. Hence, the energy increase accompanying solution is very near to the heat of fusion of silver chloride. In contrast, when silver chloride dissolves in potassium nitrate, both silver and chloride ions acquire new nearest neighbors, to a large extent at least. These new contacts introduce interaction energies which are different from those existing in the pure components. In consequence the energy change accompanying the solution process approaches that of the metathetic reaction

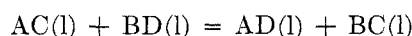


the magnitude of this energy change being approximately five times that of the heat of fusion of silver chloride.

In the first mentioned report<sup>2</sup> the relation

$$-RT \ln N_1^2 = \Delta G_F^\circ + (\Delta G_R^\circ + \Delta H_{\text{mix}})(1 - N_1)^2 \quad (1)$$

was derived for the solubility ( $N_1$ ) of a salt AC in the molten salt solvent BD,  $\Delta G_F^\circ$  and  $\Delta G_R^\circ$  being standard state changes in free energy for fusion of AC and for the liquid phase reaction



respectively.  $\Delta H_{\text{mix}}$  is the enthalpy increase accompanying solution of AD(l) and BC(l) in excess BD(l). When the same procedure is applied to a solution constructed from  $n_1$  moles of AC,  $n_2$  moles of BD, and  $n_3$  moles AD (or BC), the resulting equation is

$$-RT \ln N_1(N_1 + N_3) = \Delta G_F^\circ + (\Delta G_R^\circ + \Delta H_{\text{mix}})(N_2 + N_3)N_2 \quad (2)$$

$N_1$  as before is the desired solubility and  $N_2$  and  $N_3$  the mole fractions of the solvent salts. Equation 2 can be seen to become identical with (1) as  $N_3$  approaches zero. Equation 2 at the other extreme, where  $N_2$  approaches zero and  $N_1 + N_3$  approaches unity, becomes

$$-RT \ln N_1 = \Delta G_F^\circ = \Delta H_F(T_0 - T)/T_0$$

the simple ideal solubility equation when  $\Delta C_p$  is assumed to be zero.

The above relations in any case involve the assumption that the A cations are randomly dispersed among the B cations and that the C anions are randomly dispersed among the D anions. If there is preferential association or incomplete dissociation these relations will fail to describe the facts. It is shown below that although the calculated solubility of silver chlo-

ride in sodium nitrate is substantially correct, calculated solubilities where sodium chloride or silver nitrate have been added are far from the experimental values. In the case of thallous bromide, however, the calculations come much closer to accounting for the observed solubilities.

## Experimental

Except for preparation of the mixed solvents and some necessary modification of the analyses, the experimental technique is that which has been previously described.<sup>2</sup>

*Experimental and Calculated Solubilities.* Experimentally determined solubilities of silver chloride at 600°K. in sodium nitrate in the presence of added silver nitrate and sodium chloride are given in Table I together with solubilities calculated by means of eq. 2 for the same solvent mixtures.  $\Delta G_F^\circ$  and  $\Delta G_R^\circ$  were evaluated from the thermodynamic data employed in the earlier report.<sup>2</sup> Because of uncertainty in its application to the mixed solvents, the  $\Delta H_{\text{mix}}$  term was omitted in the calculations. Its inclusion would produce a small and essentially constant shift in the calculated solubilities.

**Table I:** Effect of Added  $\text{AgNO}_3$  and  $\text{NaCl}$  on the Solubility of  $\text{AgCl}$  in  $\text{NaNO}_3$  at 600°K.

| Added salt    | Mole %<br>added salt | 10 <sup>2</sup> × mole % $\text{AgCl}$ in solution |       |
|---------------|----------------------|--|-------|
|               |                      | Experi-<br>mental                                  | Eq. 2 |
| ...           | 0.00                 | 7.76   | 6.20  |
|               | 0.22                 | 3.19   | 1.63  |
|               | 0.50                 | 2.73   | 0.78  |
|               | 1.00                 | 2.81   | 0.43  |
|               | 2.00                 | 3.70   | 0.26  |
| $\text{NaCl}$ | 5.00                 | 8.93   | 0.15  |
|               | 0.25                 | 3.54   | 1.48  |
|               | 0.50                 | 2.84   | 0.78  |
|               | 1.00                 | 3.32   | 0.43  |
|               | 2.00                 | 4.68   | 0.26  |
|               | 4.00                 | 7.65   | 0.20  |

Examination of Table I reveals that eq. 2, although it predicts a solubility minimum, is far from adequate to account for the observed solubilities. The assumption of random distribution of the ions must be in error and the solubility changes may better be interpreted in terms of the formation of complexes such as  $\text{AgCl}$ ,  $\text{AgCl}_2^-$ , and  $\text{Ag}_2\text{Cl}^+$ . The empirical equations

$$N_1 = 1.30 \times 10^{-4} + 46 \times 10^{-8}/N_{\text{Cl}^-} + 1.57 \times 10^{-2} N_{\text{Cl}^-} \quad (3)$$

$$N_1 = 1.30 \times 10^{-4} + 46 \times 10^{-8}/N_{\text{Ag}^+} + 1.10 \times 10^{-2} N_{\text{Ag}^+} \quad (4)$$

account reasonably well for the observed solubilities of AgCl in NaNO<sub>3</sub> in the presence of added NaCl and AgNO<sub>3</sub> respectively,  $N_{\text{Cl}^-}$  being moles of Cl<sup>-</sup> divided by total moles of anion and  $N_{\text{Ag}^+}$  being moles of Ag<sup>+</sup> divided by total moles of cation. In eq. 3 and 4 the numerical value of  $1.30 \times 10^{-4}$  may be interpreted as a constant concentration of AgCl,  $46 \times 10^{-8}$  as a solubility product constant  $N_{\text{Ag}^+} \times N_{\text{Cl}^-}$ , and the third constant as the product of the first and an equilibrium constant for  $\text{AgCl} + \text{Cl}^- = \text{AgCl}_2^-$  in eq. 3 and for  $\text{AgCl} + \text{Ag}^+ = \text{Ag}_2\text{Cl}^+$  in eq. 4. In contrast to its behavior in aqueous solution AgCl appears to form cation complexes in excess Ag<sup>+</sup> to nearly the same extent that it forms anion complexes in excess Cl<sup>-</sup> ion solutions.

Table II shows experimental and calculated solubilities for thallos bromide in potassium nitrate in the presence of added thallos nitrate and of added potassium bromide.

**Table II:** Effect of TlNO<sub>3</sub> and KBr on the Solubility of TlBr in KNO<sub>3</sub> at 660°K.

| Added salt        | Mole % added salt in solvent | Mole % TlBr in solution Experimental | Eq. 3 |
|-------------------|------------------------------|--------------------------------------|-------|
| ...               | 0.0                          | 6.23                                 | 7.18  |
| TlNO <sub>3</sub> | 5.0                          | 5.11                                 | 5.45  |
| TlNO <sub>3</sub> | 10.0                         | 4.97                                 | 4.67  |
| TlNO <sub>3</sub> | 20.0                         | 6.54                                 | 4.74  |
| KBr               | 2.0                          | 5.59                                 | 6.35  |
| KBr               | 5.0                          | 4.88                                 | 5.45  |
| KBr               | 10.0                         | 4.62                                 | 4.67  |

The maximum deviation of the calculated from the experimental solubilities of TlBr in Table II is for the 20% thallos nitrate solvent where the calculated value is 73% of the experimental in contrast to the AgCl solubilities shown in Table I where the calculated values are as low as 2% of the experimental ones. Although the product of the ion fractions of Tl<sup>+</sup> and Br<sup>-</sup> increases by as much as a factor of four on the addition of a salt with a common ion and hence there is no constant solubility product, there seems to be no need to attribute the increase to the formation of complex ions since eq. 3 gives solubilities in reasonable agreement with the experimental figures.

## Diamagnetic Studies on Some Alkoxy Silanes and Silanols

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A survey of the literature reveals that very few papers have appeared on the magnetic studies of organosilicon compounds. Much controversy exists over the atomic susceptibility value of silicon; values ranging from 20.7 to -3.01 have been reported.<sup>1-3</sup> To justify the validity of Pascal's law in silicon chemistry, different values for  $\chi_{\text{Si}}$  in two different homologous series have been reported recently. Naturally we wish to determine how many different values are to be assigned to  $\chi_{\text{Si}}$  or to conclude that there is something more fundamental which is involved in such studies. Keeping this point in view, the present note deals with the diamagnetic susceptibilities of five silicon compounds having Si-O bonds, and the results are discussed from the structural point of view.

## Experimental

The substances used were of A.R. quality. Before the magnetic measurements were taken, the purity was checked by standard methods. The magnetic susceptibility of the compounds was measured with a very sensitive microbalance devised by Neogy and Lal.<sup>4</sup> This microbalance was capable of measuring the total susceptibility with an accuracy of the order of  $0.5 \times 10^{-12}$  c.g.s. e.m.u.

A capsule was filled with the compound whose susceptibility was to be measured. This capsule was then suspended from one end of the beam. When the field was switched on, the whole capsule experienced a force which was measured by sending a current through the copper coil and measuring the potential drop across the standard 1-ohm resistance with the help of a high-precision portable PYE potentiometer capable of measuring 0.05 mv. The push on the capsule filled with the sample was compared with that on the same capsule filled with pure benzene, mass susceptibility<sup>5</sup> =

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