bution.[18] The agreement shown in this figure does not imply that the interaction parameters are negligible, but indicates that the large β_{22} term and the terms containing β_{23} and β_{33} nearly cancel.

The filled circles in Figure 9 denote the B_2 values obtained osmometrically in this laboratory for the same NaPAA as used in the present work.[20] The agreement between the values is fairly good, but less satisfactory for a large m_3; m_3 giving $B_2 = 0$ is 2.5 by the vapor pressure measurements, whereas it is between 0.5 and 1 by our osmometry.[20] This discrepancy may be due in part to the invalidity of our assumption in the computation of B_2 from the vapor pressure measurements that the number of effective charges, α, is independent of m_3.

Acknowledgments. The authors gratefully acknowledge Professor Ichiro Sakurada's encouragement. They also express their thanks to the Toa Gosei Chemicals Company for having furnished the polyacrylate.

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(18) In previous studies, the large discrepancy between the observed B_2 and the value calculated from the Donnan term has often been noted; see, for example, ref 6a, 7a, and 19. In these studies, however, the Donnan term has been evaluated by using the stoichiometric valency z of a macroion, whereas the effective valency α is used in Figure 9.

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Solvation of Ions. XI.[1] Solubility Products and Instability Constants in Water, Methanol, Formamide, Dimethylformamide, Dimethylacetamide, Dimethyl Sulfoxide, Acetonitrile, and Hexamethylphosphorotriamide

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Abstract: Solubility products of silver, cesium, and potassium salts and instability constants of AgX_2^- and I_3^- in the protic solvents water, methanol, and formamide and in the dipolar aprotic solvents DMF, DMAC, DMSO, CH_3CN, and hexamethylphosphorotriamide at 25° are considered. Linear correlations are observed between equilibrium constants, expressed as concentration quotients, within each class of solvent, but there is absolutely no correlation of behavior between protic and dipolar aprotic solvents. The response of equilibria to transfer from protic to dipolar aprotic solvents is very dependent on the nature of any anions involved in the equilibria. The effects of solvation on the chemistry of anions in protic and dipolar aprotic solvents have been put on a quantitative basis by the tabulation of "*P* values." These measure the free energy of transfer of anions, relative to a standard anion, from a reference solvent to another solvent at 25°. *P* values range over 23 kcal mole^{-1} between acetate ion and the triiodide ion. Even bigger solvent effects than this can be anticipated.

Anion solvation strongly influences the relative solubilities of salts in protic and dipolar aprotic solvents.[3] To take a rather extreme example which is recorded in this paper, potassium chloride is very much less soluble ($\log K_S = -5.4$) than potassium perchlorate ($\log K_S = -0.1$) in DMF, whereas the situation is reversed in methanol, in that KCl ($\log K_S = -2.5$) is considerably more soluble than $KClO_4$ ($\log K_S = -4.5$) at 25°.

Instability constants of complexes are also strongly influenced by transfer from protic to dipolar aprotic solvents. The silver halides are slightly soluble in dimethylformamide and in water. Their solubility in the presence of excess chloride ion is very much greater in DMF than in water. This situation arises because AgX_2^- is much more stable in DMF than in water. The tribromide ion is likewise much more stable in DMF ($\log K_{\text{diss}} = -6.3$[4]) than in water ($\log K_{\text{diss}} = -1.2$[5]).

These observations are typical of the sometimes spectacular changes when systems are transferred from a protic solvent to a dipolar aprotic solvent.[3,6–8] We feel that these changes are often due to anion solvation, rather than to solvation of cations or of polar molecules. They arise because protic solvents have some structure and are hydrogen-bond donors and acceptors, whereas dipolar aprotic solvents have much weaker structures and are not hydrogen-bond donors. Small anions are strong H-bond acceptors, whereas large polarizable anions are not.[3]

Solubilities offer the most obvious way of studying solvation, but very few solubility products, for other

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(2) Author to whom inquiries should be addressed at the School of Chemistry, University of Western Australia, Nedlands, Western Australia.

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than aqueous solutions, have found their way into the literature.[5,9–11] Ionic association and other ionic strength effects must be considered when dealing with many saturated nonaqueous solutions of dielectric constant 30–45. However, provided that saturated solutions are dilute solutions, that they do not contain an appreciable fraction of ionic aggregates, and that the solid phase, in equilibrium with saturated solution, is the same in all solvents considered, then solubilities give a direct measure of the free energies of transfer of electrolytes from one solvent to another.[12]

Free energies of transfer are most conveniently expressed in terms of distribution coefficients or, as we prefer to call them, solvent activity coefficients, ${}^0\gamma_i^S$.[4,7,12,13] The change in the standard chemical potential of a solute, i, unimolar solution, hypothetically ideal with respect to Henry's law, on transfer from a reference solvent (superscript 0) to another solvent (superscript S) at temperature T is given by

$$\bar{\mu}_i^S - \bar{\mu}_i^0 = RT \ln {}^0\gamma_i^S \qquad (1)$$

The solubility product of a salt AB, expressed as an *activity quotient*, is the same in all solvents. The solubility product K_S^S, in solvent S, expressed as a *concentration quotient*, usually changes with solvent. Solubility products, on the molar concentration scale, are related to the solubility product in the reference solvent, K_S^0, through (2).

$$K_S^0 = K_S^S({}^0\gamma_{A^+}^S)({}^0\gamma_{B^-}^S) \qquad (2)$$

Expressions like (2) relate the constants[14] for a variety of equilibria, in a solvent S, to the equilibrium constants in an arbitrarily chosen reference solvent. In part IX[15] we dealt with acid–base equilibria, as well as with the equilibrium between reactants and transition states (*i.e.*, rates), in protic and dipolar aprotic solvents. In this paper, we deal with solubility products and instability constants, for silver and halogen complexes, in water, methanol, formamide, DMF, DMAC, DMSO, acetonitrile, and hexamethylphosphorotriamide (HMPT).

A few of our systems in nonaqueous solvents have been studied previously at various ionic strengths;[5,11] all of them have been studied in detail in water.[5] We have repeated most measurements, except those for water, so as to obtain a systematic set of results in single batches of solvent, under standard conditions of the highest practicable dilution. Minor discrepancies do exist in some cases where our work duplicates literature values, but these are not of sufficient magnitude to seriously influence our treatment of changes in equilibrium constants. Although our results lack some precision,[16] as is often the case with potentiometric measurements of solubilities,[5] the numbers which we derive are reproducible and allow us to demonstrate the major differences between protic and dipolar aprotic solvents. They fit our linear free-energy relationships most satisfactorily. It must be emphasized that a few of the values of log K may be only within ±0.5, but the majority are felt to be within ±0.2 log unit of the value at infinite dilution.

Experimental Section

Materials. Methanol[15] and CH_3CN[17] were purified by conventional methods. Formamide, HMPT, DMF, DMAC, and DMSO were dried with Type 4A molecular sieves and fractionated twice under a reduced pressure of dry nitrogen. DMSO was supplied by the Crown Zellerbach Corp. Dipolar aprotic solvents were stored over molecular sieves in dark bottles and were used within 7 days of purification.

The following salts were used as the source of the appropriate anion for potentiometric titrations: NEt_4Cl, NEt_4Br, NEt_4I, KI, KSCN, NEt_4SCN, and NBu_4OAc, $NaBPh_4$, NEt_4N_3, and NaN_3. Tetraalkylammonium salts were prepared from the recrystallized iodide or bromide. They were recrystallized from DMAC, acetone–ether, or ethyl acetate, washed with dry ether, and dried *in vacuo* at 20–80° just prior to use. Stock solutions were analyzed by titration with silver nitrate. These salts were of >97% purity. Other materials were Analar grade and were used as supplied. Silver salts and their stock solutions were stored in light-proof containers. Silver nitrate, 0.01 *M*, went brown, immediately when dissolved in HMPT and slowly when dissolved in formamide, but the concentration of silver ion, when estimated by titration with potassium bromide, was as required by the stoichiometric amount of $AgNO_3$. Solutions of potassium iodide in dipolar aprotic solvents acquired a yellow tinge after 24 hr. The amount of iodine formed must be negligible, however, because the iodide concentration was unchanged when tested by titration with silver nitrate.

Solubility Measurements.[12] Saturated solutions were prepared by shaking the solid with solvent in a stoppered flask at 35° for 24 hr. The flask was then shaken for a further 24 hr at 25°. The liquid phase was analyzed in a number of ways using routine procedures, *e.g.*, (a) potentiometric titration with potassium iodide in water (silver salts) or with silver nitrate (halides, azides, thiocyanates); (b) spectrophotometry on a Unicam SP500 spectrophotometer (picrates, *p*-nitrophenoxides, tetraphenylborides); (c) atomic absorption on a Techtron AAI atomic absorption spectrophotometer (silver salts) and by flame photometry (potassium perchlorate); (d) gravimetrically by pouring into water or methanol and weighing the precipitate (tetraphenylborides, perchlorates); (e) titration with potassium thiosulfate (iodine solutions).

The solid phase was washed with solvent and dried at 1 mm for 48 hr at room temperature. Silver chloride from DMF, silver thiocyanate from DMAC, silver bromide from DMSO, and silver tetraphenylboride from DMF were converted to their water-soluble cyanide complexes and analyzed by atomic absorption, using a silver lamp. No solvates were detected by this procedure, *i.e.*, the solid had the expected molecular weight.

Solubilities of silver salts in formamide, DMF, DMAC, or DMSO, when measured by analyzing saturated solutions, have little

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(16) We feel that better values than we report here could be obtained, but this would require knowledge of the Debye–Hückel behavior and the dissociation constants of all the electrolytes in all the solvents used in this work. We are reporting here a general survey of equilibria in dipolar aprotic solvents in electrolyte solutions at *ca.* 10^{-2} *M*. We have used experimental techniques which are well established and routine for aqueous solutions[12] and have made no special concessions to the fact that our solvents are nonaqueous.

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Table I. Solubility Products[a] of Silver Salts at 25°

	AgX	$-\mathrm{Log}\ K_S$, *i.e.*, $\mathrm{p}K_S = -\log\,[\mathrm{Ag^+}][\mathrm{X^-}]$ H₂O	CH₃OH	HCONH₂	DMF	DMAC	DMSO	CH₃CN	HMPT
1	AgCl	(9.8)[c]	13.1 (13.1)[c]	9.4[g]	14.5	14.3	10.4 (10.4)[i]	12.9 (12.4)[i]	11.9
2	AgBr	(12.3)[c]	15.2 (15.2)[c]	11.4	15.0	14.5	10.6 (10.6)[i]	12.9 (13.2)[i]	12.3
3	AgI	(16.0)[c]	18.3 (18.2)[c]	14.5	15.8 (16.4)[h]	14.7	11.4 (12.0)[i]	. . . (14.2)[i]	. . .
4	$\mathrm{AgN_3}$	(8.6)[c]	11.2	7.7[e]	11.0	10.8	6.5[e]	9.6	8.5[e]
5	AgSCN	(11.9)[c]	13.9 (13.7)[c]	9.9	11.5	10.5	7.1[e]	10.0	7.4[e]
6	AgOAc	(2.4)[c]	6.1[e]	. . .	10.2	9.7	4.4[e]	7.4[e]	. . .
7	AgOTs[b]	1.3[d]	3.2[d]	. . .	1.3[d]	. . .	. . .	. . .	. . .
8	$\mathrm{AgB(C_6H_5)_4}$	(13.4)[f] 11.1	13.2	10.3	6.7[e]	5.9[e]	4.6[d]	7.2[e]	4.7[d]

[a] Calculated as concentration quotients at ionic strength 0.01–0.005 *M* from potentiometric titrations unless stated otherwise. Literature values in parentheses. [b] OTs = *p*-toluenesulfonate. [c] Reference 5, at infinite dilution. [d] From analysis of saturated solutions at an ionic strength corresponding to the solubility. [e] At ionic strength 0.10–0.05 *M*. [f] Reference 12a. [g] Y. M. Pozarov, V. E. Karazinov, Y. M. Kessler, and A. I. Gorbanev, *Russ. J. Inorg. Chem.*, **9**, 550 (1964), report 8.3 in formamide and 10.4 in N-methylformamide. [h] Reference 19a. [i] Reference 11, at ionic strength 0.10 *M*, formal.

Table II. Solubility Products of Alkali Metal Salts at 25°

Salt	$-\mathrm{Log}\ K_S = \mathrm{p}K_S$ H₂O	CH₃OH	HCONH₂	DMF[e]	DMSO	CH₃CN	HMPT	CH₃CON-HCH₃[h]
KCl	−0.90[b]	2.5[e]	. . .	5.4	. . .	7.20[f]	. . .	−1.84
KBr	. . .	1.7[f]	. . .	2.4	0.60[g]	5.60[f]	4.0[e]	−0.74
KI	. . .	0.2[f]	. . .	−0.5	. . .	2.00[f]	. . .	+0.26
$\mathrm{KClO_4}$	1.66[c]	4.5[e]	. . .	0.1	−0.80[g]	. . .	. . .	−0.76
$\mathrm{KBPh_4}$	7.53[b]	5.0[b]	. . .	. . .	. . .	. . .	. . .	. . .
$\mathrm{KOC_6H_4NO_2}$-*p*	. . .	0.2[a]	. . .	0.4[a]	. . .	. . .	. . .	. . .
KPic	3.36[b]	4.2[e]	. . .	−0.2	. . .	4.55[d]	. . .	. . .
$\mathrm{NaOC_6H_4NO_2}$-*p*	0.91[d]	−0.2[e]	. . .	−0.58	. . .	5.42[d]	. . .	. . .
$\mathrm{NaN_3}$	. . .	0.9[a]	. . .	1.9	0.64[e]	. . .	. . .	. . .
NaCl	. . .	1.5[e]	. . .	. . .	. . .	9.0[f]	4.0[e]	−0.94
CsCl	. . .	1.7[f]	0.53[e]	4.9	. . .	6.8[f]	. . .	. . .
CsBr	. . .	2.2[f]	0.29[e]	3.3	. . .	4.4[f]	. . .	. . .
CsI	. . .	1.9[f]	0.23[e]	1.7	. . .	3.0[f]	. . .	. . .
CsPic	. . .	4.2[e]	. . .	0.5	. . .	. . .	. . .	. . .
$\mathrm{NEt_4Pic}$	. . .	2.0[e]	. . .	0.0	. . .	. . .	. . .	. . .

[a] At 0°. [b] Reference 12a. [c] Reference 9. [d] I. M. Kolthoff, M. K. Chantooni, and S. Bhowmik, personal communication. [e] This work. [f] T. Pavlopoulis and H. Strehlow, *Z. Physik. Chem.* (Leipzig), **202**, 474 (1954). [g] Reference 26. [h] At 40°: L. R. Dawson, J. E. Berger, J. W. Vaughn, and H. Eckstrom, *J. Phys. Chem.*, **67**, 281 (1963).

meaning if the solubility of the silver salt is less than $10^{-2}\ M$. This is because these solvents inevitably contain 10^{-3}–$10^{-5}\ M$ impurities (*e.g.*, ammonia, dimethyl sulfide, dimethylamine)[15] which complex with silver ion, so that nearly all slightly soluble silver salts, even silver iodide, appear to have solubility products of *ca.* 10^{-6}–10^{-8} in these solvents, when analyzed by other than potentiometric means.

Potentiometric Measurements.[11,12] These were made using as electrodes clean silver or platinum wires, which were cleaned after each titration. The cells were large test tubes wrapped in aluminum foil and equipped with stoppers. They were open to the atmosphere while measurements were being made. They were immersed in a 25° thermostat and were stirred magnetically, as titrant was added. The salt bridges were $\mathrm{NEt_4}$ picrate[4] solutions in inverted U-tubes, with ground-glass sleeves covering pin holes in ground-glass cones. A fresh bridge was used for each titration. The emf was measured on a Radiometer pH meter, Type PHM22r. It was established early in the work that effectively the same results were obtained no matter whether measurements were made in the dark on freshly prepared solutions, on solutions exposed to the atmosphere for 30 min, or on solutions kept under dry nitrogen during preparation and during titration. In later work no special effort was made to work in a dry inert atmosphere. Light was excluded as much as possible as a routine precaution. Titration curves were reproduced without difficulty in new batches of solvent.

The usual procedure was to titrate 0.01 *M* $\mathrm{AgNO_3}$ solution into a half-cell containing the silver wire immersed in 20 ml of 0.01 *M* salt, MX, in the appropriate solvent. The reference half-cell was a silver wire in 0.01 *M* $\mathrm{AgNO_3}$ in the same solvent. A plot of emf *vs.* milliliters of $\mathrm{AgNO_3}$ was then drawn.

Instability constants of $\mathrm{I_3^-}$ were determined in the cell B, which consisted of platinum wires immersed in solutions of iodine and potassium iodide.

Results

Solubility products[14] of silver salts and of alkali metal salts are in Tables I and II, respectively. Instability constants[14] are in Tables III and IV. The potentiometric measurements for silver salts were made on a thermostated cell, A, by titrating $\mathrm{AgNO_3}$ into the left-hand half-cell.[11,12] The Nernst equation was obeyed by solutions of silver nitrate in all solvents between 10^{-1} and $10^{-3}\ M$. Silver perchlorate gave effectively the same results, when substituted for silver nitrate.

$$\mathrm{Ag}\left|\begin{array}{c} 0.01\ M \\ \mathrm{MX}, \\ 20\ \mathrm{ml} \end{array}\right|\begin{array}{c} \text{bridge,} \\ \text{satd} \\ \mathrm{NEt_4Pic} \end{array}\left|\begin{array}{c} \mathrm{AgNO_3}, \\ 0.01\ M, \\ 20\ \mathrm{ml} \end{array}\right|\mathrm{Ag} \qquad \text{(A)}$$

The potentiometric measurements of the instability constants of triiodide were made in cell B.[4] Two sets of measurements were made. In the first, the left-hand half-cell contained 10 ml of 0.005 *M* KI and 10 ml of 0.01 *M* iodine, and the right-hand half-cell contained 20 ml of 0.01 *M* KI, to which was added successive 0.5-ml quantities of 0.01 *M* iodine. The cell emf was recorded after each addition. In the second series, the left-hand half-cell contained 10 ml of 0.01 *M* KI and 10

$$\mathrm{Pt}\left|\begin{array}{c} \\ \mathrm{KI},\quad \mathrm{I_2} \\ 0.005, 0.01M \end{array}\right|\begin{array}{c} \text{Satd} \\ \mathrm{NEt_4Pic} \\ \text{bridge} \end{array}\left|\begin{array}{c} \\ \mathrm{KI},\quad \mathrm{I_2} \\ 0.005, 0.01\ M \end{array}\right|\mathrm{Pt} \qquad \text{(B)}$$

Table III. Instability Constants for $AgX_2^- \rightleftharpoons Ag^+ + 2X^-$ at 25°

	Complex	$pK_{12} = -\log([Ag^+][X^-]^2/[AgX_2^-])$ H_2O^a	CH_3OH^b	DMF^c	$DMAC^c$	DMSO	CH_3CN	HMPT
1	$AgCl_2^-$	5.4	7.9	16.3	17.2	$11.7^c (12.0)^b$	$13.4^c (13.0)^b$	16.1^c
2	$AgBr_2^-$	7.6	10.6	16.6	16.9	$11.4^c (11.9)^b$	$13.7^c (13.7)^b$	16.5^c
3	AgI_2^-	11.2	14.8	$17.8 (18.1)^d$	17.3	$12.5^c (13.1)^b$	... $(15.1)^b$	...
4	$Ag(N_3)_2^-$	4.2	...	11.9	12.2	$7.0^{c,f}$	...	$11.4^{c,f}$
5	$Ag(SCN)_2^-$	8.2	...	11.9	11.4	$7.4^{c,f}$	...	$9.7^{c,f}$
6	$Ag(OAc)_2^-$	0.6^e	...	10.9	10.6	$5.8^{c,f}$	...	...

[a] Reference 5. [b] Reference 11 at 0.1 *M* ionic strength. [c] This work, at ionic strength 0.01–0.005 *M*. [d] Reference 19a. [e] F. H. McDougall and L. E. Topal, *J. Phys. Chem.*, **56**, 1090 (1952). [f] At 0.10–0.05 *M* ionic strength.

Table IV. Instability Constants of Trihalide Ions and Solvent Activity Coefficients of Iodine at 25°

	$pK = -\log([Hal_2][Hal^-]/[Hal_3^-])^a$ H_2O	MeOH	$HCONH_2$	CH_3CN	CH_3NO_2	$C_6H_5NO_2$	DMF	DMAC	DMSO
I_3^-	2.85^b	4.30^f	3.7^f	6.8^f $(6.6)^h$	6.7^h	6.6^b	7.0^f	7.4^f	6.9^f
Br_3^-	1.20^b	2.2^g	...	7^h	7.3^h	...	6.3^g	...	...
Cl_3^-	-0.7^b	...	...	10^h	$>13^h$	...	...	...	...
$\log {}^W\gamma_{I_2}{}^S$	0.0^c	-2.3^d	-1.8^d	-2.5^d	...	...	-4.1^e	-5.2^e	...

[a] Concentrations in moles per liter. [b] Reference 5. [c] The solubility of iodine in water at 25° is $\log S = -2.88$;[9] solubilities in other solvents are given by $-2.88 - \log {}^W\gamma_{I_2}{}^S$. [d] Estimated by direct measurement of the solubility of iodine. [e] Estimated potentiometrically (see text). [f] This work. [g] Reference 4. [h] Reference 22.

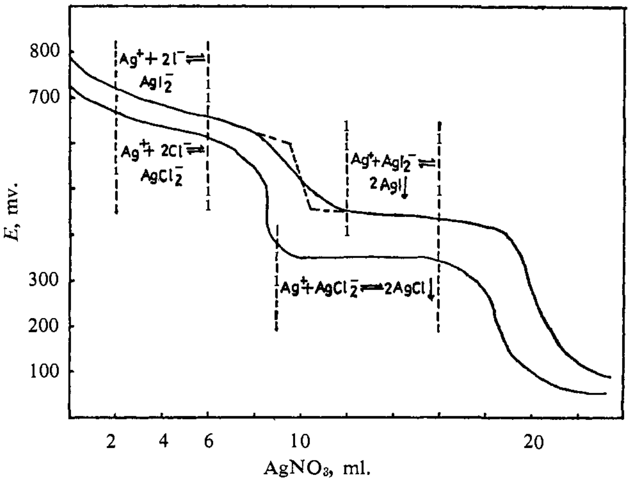

Figure 1. Lower curve: titration of 20 ml of 0.01 *M* NEt_4Cl *vs.* 0.01 *M* $AgNO_3$ in DMF at 25°. Upper curve: titration of 0.01 *M* KI *vs.* 0.01 *M* $AgNO_3$ in DMF at 25°.

ml of 0.005 *M* iodine. The right-hand half-cell contained 20 ml of 0.01 *M* iodine to which was added 0.5-ml amounts of 0.01 *M* KI.

Both methods gave smooth curves of emf *vs.* milliliters of titrant, with one inflection point corresponding to formation of I_3^-. The instability constants were calculated as described in part VI.[4]

Solubilities of Silver Salts in Methanol and Formamide. A solid was precipitated after a few drops of silver nitrate were added to solutions of MX in formamide or methanol. There was only one point of inflection in the titration curve of emf *vs.* milliliters of $AgNO_3$. This corresponded to the expected end point of the titration. The solubility product was calculated in the conventional way[12d] using the Nernst equation. The formal concentration of 0.01 *M* $AgNO_3$ in methanol in the right-hand half-cell of (A) was reduced to 0.0062 *M* for the calculations because silver nitrate is a weak electrolyte in methanol ($K_{diss} = 1.3 \times 10^{-2}$).[18] Silver nitrate, 0.01 *M* in formamide, was assumed to be a strong electrolyte.[18] Our solubility products agree closely with values in the literature (*cf.* Table I). The species AgX_2^- were not detected by our titration curves in methanol and formamide; their instability constants in methanol (Table III) are taken from Luehrs, Iwamoto, and Kleinberg.[11]

Solubility Products and Instability Constants in DMF, DMAC, CH_3CN, DMSO, and HMPT.[11,12] The titration curve shown in Figure 1 for titration of 0.01 *M* NEt_4Cl with 0.01 *M* $AgNO_3$ in DMF, using cell A, is typical of the curves obtained when silver nitrate is added to NEt_4Cl or NEt_4Br in DMF, DMAC, CH_3CN, DMSO, and HMPT. There are two well-defined "plateaus," the first corresponding to (3) the second to (4). Insoluble silver salt did not appear until half

$$Ag^+ + 2X^- \rightleftharpoons AgX_2^- \tag{3}$$

$$Ag^+ + AgX_2^- \rightleftharpoons 2AgX\downarrow \tag{4}$$

through the titration. Instability constants for AgX_2^- in (3) were calculated from the upper plateau (Figure 1) using the Nernst equation.[12d] The constants for (4) (Table V) were calculated from the emf along the lower "plateau" as shown in Figure 1. The two constants were combined giving the solubility product of AgX. Curves similar in shape to the "chloride curve" shown in Figure 1 were obtained for 0.01 *M* NaN_3 in DMF and

Table V

	$pK = -\log[Ag^+][AgX_2^-]$ at 25° H_2O^a	$MeOH^b$	DMF^c	$DMAC^c$	$DMSO^c$	CH_3CN^c	$HMPT^c$
$AgCl_2^-$	14.2	17.9	12.6	11.5	9.1	12.3	7.7
$AgBr_2^-$	17.0	19.6	13.3	12.0	9.8	12.1	8.1
AgI_2^-	20.8	21.6	13.8	12.1	10.3	...	...
$Ag(N_3)_2^-$	13.0	...	10.1	9.4	6.2^d	...	5.7^d
$Ag(SCN)_2^-$	15.6	...	11.0	9.5	6.6^d	...	5.1^d
$Ag(OAc)_2^-$	3.2	...	9.5	8.8	...	...	...

[a] Reference 5. [b] Reference 11. [c] This work. [d] At 0.10–0.05 *M* ionic strength.

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(18) R. S. Drago and K. F. Purcell in "Non-Aqueous Solvent Systems," T. C. Waddington, Ed., Academic Press Inc., London, 1965.

DMAC, for 0.05 *M* NEt_4N_3 in DMSO, and for 0.05 *M* NaN_3 in HMPT. It was necessary to use 0.05 *M* $AgNO_3$ in the latter two solvents because silver azide is quite soluble in DMSO and HMPT. The curves for titration of NBu_4OAc or of KSCN in DMF, DMAC, DMSO, and HMPT showed the usual two points of inflection, one half-way through the titration, the other at the expected end point. The curves were like the chloride curve, except that there was a sharp increase of up to 40 mv, immediately following the large decrease in emf at the first inflection point, upon the addition of a few more drops of silver nitrate. This corresponded to the first appearance of a precipitate. The usual plateau was then followed to the end point (*cf.* Figure 1). The equilibrium constant for (4) was calculated in the plateau region. It was necessary to use 0.10 *M* KSCN and $AgNO_3$ in HMPT, 0.10 *M* NBu_4OAc and $AgNO_3$ in DMSO, 0.05 *M* KSCN and $AgNO_3$ in DMSO, rather than 0.01 *M* reagents in the left-hand half-cell (A), because AgSCN and AgOAc are quite soluble. The constant for (3) was also estimated in these cases, using 0.01 *M* reagents and was only 0.2 log unit greater than the value using 0.1 *M* reagents.

The titration curves for 0.05 *M* NBu_4OAc, NEt_4N_3, and KSCN in acetonitrile were not as well defined as in other solvents. Precipitates appeared after 10–20% of the theoretical 0.05 *M* $AgNO_3$ was added. A well-defined point of inflection was obtained at the end point, but very small inflections were noticed only in the region of 10–25% titration. The curves were treated as though AgX_2^- was not present, and the solubility product was calculated as for methanol as solvent.

The titration curves for 0.01 *M* KI or NEt_4I presented some difficulties. The upper curve (Figure 1) for 0.01 *M* NEt_4I in DMF is typical of the curves which were acceptable to us. Precipitate appeared after 60–70% of the theoretical amount of silver nitrate had been added. It would appear that other complexes of silver, *e.g.*, $Ag_2I_3^-$ and $Ag_3I_4^-$, are present.[19] The major species is still AgI_2^-, however, and the curves were "rounded off" (dotted lines in Figure 1) to allow calculation of the equilibrium constants for (3) and (4). Titrations at 10^{-3} *M* reagents were better defined into two plateaus and gave values of the equilibrium constants which were comparable with those at 10^{-2} *M* reagents. The titration curve for NEt_4I in acetonitrile showed three sharp points of inflection between half and complete titration. A precipitate was formed at 33% titration. Although Luehrs, Iwamoto, and Kleinberg[11] obtained constants for this system, our curves were not well enough understood to be analyzed further. The curve for silver nitrate titration of KI in HMPT was complex also and was not analyzed.

The titration of sodium tetraphenylboride in dipolar aprotic solvents with silver nitrate showed no evidence for species corresponding to $Ag(BPh_4)_2^-$. A precipitate appeared as soon as the first drops of silver nitrate were added, and there was only one point of inflection, at the end point. It was necessary to use 0.10 *M* $NaBPh_4$ and 0.10 *M* $AgNO_3$, because $AgBPh_4$ is quite soluble in dipolar aprotic solvents.

Silver nitrate is not a strong electrolyte in DMF or acetonitrile, so the formal concentration of 0.01 *M* $AgNO_3$ in the right-hand reference cell of (A) was adjusted. The degree of dissociation of 0.01 *M* $AgNO_3$ is 0.42 in DMF[20] and 0.63 in acetonitrile.[21] We have assumed $\alpha = 0.5$ for 0.01 *M* $AgNO_3$ in DMAC because of its similarity to DMF as a solvent. In DMSO, which is of higher dielectric constant (45) and solvates silver cation very strongly,[11] we assume an α of 1.0. No data are available for HMPT and our calculations are for formal concentrations of 0.01 *M* $AgNO_3$ in the reference half-cell. If HMPT is a similar solvent to DMF, then the constants for infinite dilution would be 0.2–0.3 log unit more negative than recorded here. Constants for 10^{-3} *M* reagents in HMPT in the reference and titration half-cells were close to values for 10^{-2} *M* reagents, so that ion association may not be serious.

Instability Constants of I_3^-.[4,22] The titration curves for addition of iodine to potassium iodide in cell B showed one well-defined inflection point, corresponding to the expected end point for I_3^- formation in DMF, DMAC, CH_3CN, and DMSO. The titration curve for the reverse addition of potassium iodide to iodine in cell B gave the same instability constant from the Nernst equation. Iodine solutions were stable in all solvents and the emf of (B) was steady over several hours, as was the emf of an iodine–iodide half-cell *vs.* a silver–silver nitrate half-cell. The titration curves in HMPT showed a pronounced point of inflection at one-fourth titration, which may correspond to I_5^- formation. No other inflection points were detected in HMPT. The curve for addition of iodine to potassium iodide in HMPT had no point of inflection. This system was not examined further. There were no points of inflection, corresponding to I_5^- formation, in the other solvents, even when reagents were at 1 *M* concentration in cell B.

Distribution Coefficients of Iodine. Distribution coefficients were estimated from the ratio of solubilities of iodine in the reference solvent and in the other solvent. Potentiometric measurements were made in cell C, for those solvents (*e.g.*, DMF, DMA, DMSO) in which iodine is very soluble.

$$\text{Pt}\,|\text{I}_2,\ \text{KI}\,|\,|\text{AgNO}_3\,|\text{Ag bridge, NEt}_4\text{Pic} \qquad \text{(C)}$$

$[a^0], [b^0], [c^0]$: concentrations in reference solvent

$[a^S], [b^S], [c^S]$: concentrations in solvent S

If [a] > [b] in cell C, and if I_3^- is very stable, then $[b] = x$, where x is the equilibrium concentration of I_3^-. The difference between the emf of the cell C in the reference solvent and in solvent S is given by (5). In (5), K^0 and K^S are the instability constants of I_3^- in

$$\frac{\Delta E^S - \Delta E^0}{0.0296} = \log \frac{[b^S]^2([a^0] - [b^0])^3(K^0)^2[c^0]^2\{({}^0\gamma_{I^-}{}^S)({}^0\gamma_{Ag^+}{}^S)\}^2}{[b^0]^2([a^S] - [b^S])^3(K^S)^2[c^S]^2({}^0\gamma_{I_2}{}^S)} \qquad (5)$$

the reference solvent and in solvent S respectively. If $[a^0] = [a^S]$, $[b^0] = [b^S]$, and $[c^0] = [c^S]$, then (5) reduces

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[19] (a) H. Chateau and M. C. Moncet, *J. Chim. Phys.*, **60**, 1060 (1963); (b) D. J. Greenslade and M. C. R. Symons, *Trans. Faraday Soc.*, **62**, 307 (1966).

[20] H. Chateau and M. C. Moncet, *Compt. Rend.*, **256**, 1504 (1963).

[21] I. M. Kolthoff and F. G. Thomas, *J. Phys. Chem.*, **69**, 3049 (1965).

[22] R. T. Iwamoto and I. V. Nelson, *J. Electroanal. Chem.*, **7**, 218 (1964).

Table VI. Solvent Activity Coefficients of Silver Salts at 25° (Reference Solvent, Water)

	Log $K_S{}^W/K_S{}^S = \log ({}^W\gamma_{Ag^+}{}^S)({}^W\gamma_{X^-}{}^S)$							
	H_2O	CH_3OH	$HCONH_2$	DMF	DMAC	DMSO	CH_3CN	HMPT
AgCl	0.0	3.3	−0.4	+4.7	+4.5	+0.6	+3.1	+2.1
AgBr	0.0	2.9	−0.9	+2.7	+2.2	−1.7	+0.6	+0.0
AgI	0.0	2.3	−1.5	−0.2	−1.3	−4.6	...	...
AgN_3	0.0	2.6	−0.9	+2.4	+2.2	−2.1	+1.0	−0.1
AgSCN	0.0	2.0	−2.0	−0.4	−1.4	−4.8	−1.9	−4.5
AgOAc	0.0	3.7	...	+7.8	+7.3	+2.0	+5.0	...
AgOTs	0.0	1.9	...	0.0	...	...	...	...
$AgBPh_4$	0.0	2.1	−0.8	−4.4	−5.2	−6.5	−3.9	−6.4
$AgClO_4$	0.0	2[a]	...	−3.8	...	−6.3	...	...
AgPic	0.0	2[a]	...	−3.6	...	...	−3.2	...
$AgAgCl_2$	0.0	3.7	...	−1.6	−2.7	−5.1	−1.9	−6.5
$AgAgBr_2$	0.0	2.6	...	−3.7	−5.0	−7.2	−4.9	−8.9
$AgAgI_2$	0.0	0.8	...	−7.0	−8.7	−10.5	...	...
$AgAg(N_3)_2$	0.0	...	...	−2.9	−3.6	−6.8	...	−7.3
$AgAg(SCN)_2$	0.0	...	...	−4.6	−6.1	−9.0	...	−10.5
$AgAg(OAc)_2$	0.0	...	...	+6.3	+5.6	...	...	...
AgI_3[b]	0.0	−1.4	−4.1	−8.5	−11.0	...	−8.3	...

[a] This value chosen because of the pattern observed with other silver salts. The actual value is not known. [b] Calculated as described in the Discussion section: *P* values.

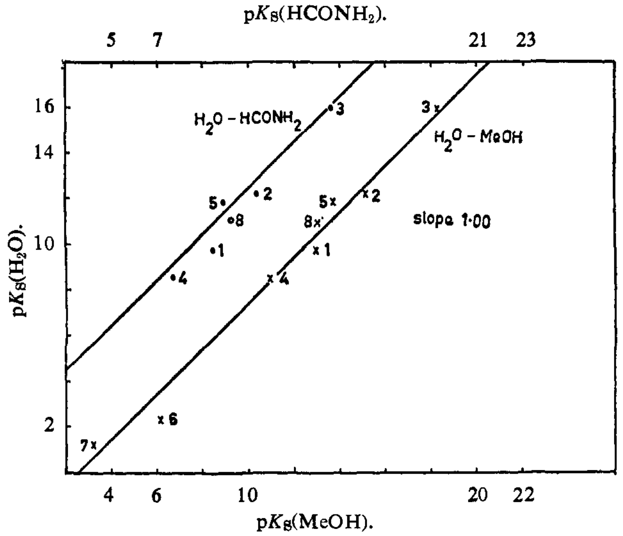

Figure 2. Solubility products of silver salts in protic solvents at 25°. Numbers refer to the silver salts in Table I. $pK_s = -\log [Ag^+][X^-]$.

to (6), in which the terms on the right-hand side are

$$\log {}^0\gamma_{I_2}{}^S = -\frac{\Delta E^S - \Delta E^0}{0.0296} + 2 \log \frac{K^0}{K^S} + 2 \log ({}^0\gamma_{Ag^+}{}^S)({}^0\gamma_{I^-}{}^S) \quad (6)$$

known (Tables IV and VI). Measurements were made at concentrations of 0.01 *M* or less, and the emf difference between cell C in the reference solvent and in solvent S was constant between 5 and 15 ml of potassium iodide added to the left-hand half-cell.

A procedure was also used in which [*b*] > [*a*] in cell C. The emf difference of cell C in the reference solvent and in solvent S is given by

$$\log {}^0\gamma_{I_2}{}^S = -\frac{\Delta E^S - \Delta E^0}{0.0296} + \log \frac{([b^S] - [a^S])^3}{([b^0] - [a^0])^3} \times \frac{[a^0]}{[a^S]} \frac{K^S}{K^0} \frac{[c^0]}{[c^S]} \{({}^0\gamma_{Ag^+}{}^S)({}^0\gamma_{I^-}{}^S)\}^2 \quad (7)$$

The reference solvent for these measurements was methanol, because iodine is only slightly soluble in water. Values of $\log {}^M\gamma_{I_2}{}^S$ obtained in this way were converted to $\log {}^W\gamma_{I_2}{}^S$ using the relationship $\log {}^W\gamma_{I_2}{}^M = -2.26$, which was established from solubilities of iodine in water and in methanol.

The solubility of iodine at 25° was 1.32×10^{-3} *M* in water,[9] 0.24 *M* in methanol, 0.46 *M* in acetonitrile, and 0.084 *M* in formamide. The value of $\log {}^M\gamma_{I_2}{}^{CH_3CN}$ from solubility was −0.3, and from cell C it was −0.5. Values of $\log {}^W\gamma_{I_2}{}^S$ are in Table IV.

Discussion

Solubility Products in Protic Solvents. There are tolerable linear relationships between the solubility products of silver salts in the protic solvents, water, methanol, and formamide (*cf.* Figure 2). These are described by eq 8 and 9.

$$\log K_S(H_2O) = \log K_S(CH_3OH) + 2.6 \pm 0.6 \quad (8)$$

$$\log K_S(H_2O) = \log K_S(HCONH_2) - 1.1 \pm 0.7 \quad (9)$$

The deviations from these equations are regular. Silver salts of large polarizable anions, *e.g.*, AgSCN, $AgBPh_4$, which are weak hydrogen-bond acceptors, tend to be more soluble in methanol and formamide than predicted by eq 8 or 9 from their solubility in water. Silver salts of small anions, which are strong H-bond acceptors, *e.g.*, AgCl and AgOAc, tend to be less soluble in methanol and formamide than predicted. The tendencies noted are not unlike those considered by Grunwald and Price[23] in their treatment of acid-base equilibria in water and alcohols. They attribute such trends to dispersion forces between polarizable anions and the alcohols, which are more polarizable than water. Perhaps one should also consider whether the ability to donate hydrogen bonds decreases in the series of solvents $H_2O > CH_3OH > HCONH_2$.[3]

Despite the deviations, eq 8 and 9 allow a helpful prediction, from the solubility products in water, of solubility products in these nonaqueous protic solvents.

The linear relationships of unit slope, which are in Figure 2, can be appreciated if solvent activity coefficients, related to water as reference solvent, are considered. Values of $\log ({}^W\gamma_{Ag^+}{}^S)({}^W\gamma_{X^-}{}^S)$ for silver

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(23) E. Grunwald and E. Price, *J. Am. Chem. Soc.*, **86**, 4517 (1964).

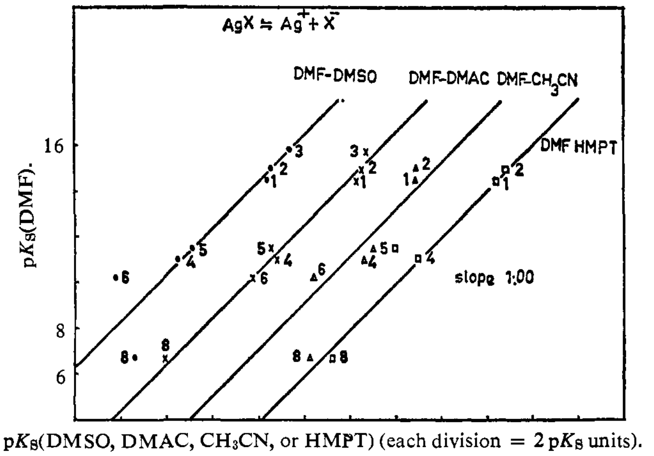

Figure 3. Solubility products of silver salts in dipolar aprotic solvents at 25°. Numbers refer to the silver salts in Table I. $pK_s = -\log [Ag^+][X^-]$.

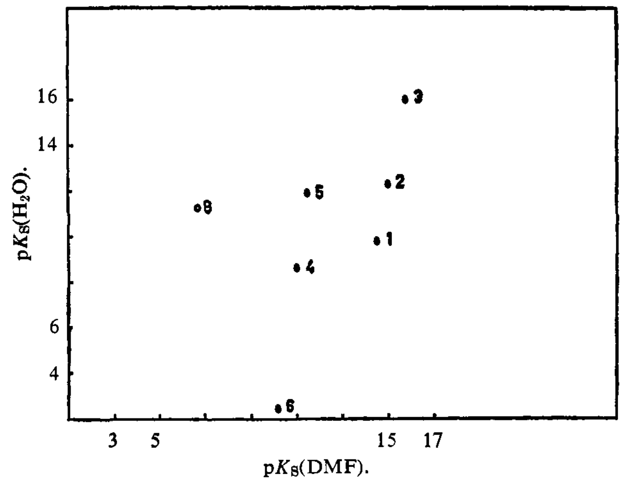

Figure 4. Solubility products of silver salts in water and in DMF at 25°. Numbers refer to the silver salts in Table I.

salts, AgX, in solvents, S, relative to water, are in Table VI. They are derived from solubility products through eq 2. For most anions, log $({}^{W}\gamma_{Ag^+}{}^{M})({}^{W}\gamma_{X^-}{}^{M})$ is close to 2.6 and log $({}^{W}\gamma_{Ag^+}{}^{F})({}^{W}\gamma_{X^-}{}^{F})$ is close to -1.1.[24] In effect, with the reservations noted above, the change in the standard chemical potential of an anion, on transfer from water to methanol, or to formamide, is virtually independent of the nature of the anion.

Solubility Products in Dipolar Aprotic Solvents. Satisfactory linear relationships (eq 10–13) exist between solubility products, K_S, expressed as concentration quotients, of silver salts in the dipolar aprotic solvents, DMF, DMSO, DMAC, CH_3CN, and HMPT (*cf.* Figure 3). With a few exceptions, solubility products of silver salts in any one dipolar aprotic solvent can be predicted from the solubility product in another dipolar aprotic solvent, through eq 10–13.

$$\log K_S(\text{DMF}) = \log K_S(\text{DMSO}) - 4.3 \pm 0.2 \quad (10)$$

$$\log K_S(\text{DMF}) = \log K_S(\text{DMAC}) - 0.6 \pm 0.4 \quad (11)$$

$$\log K_S(\text{DMF}) = \log K_S(\text{CH}_3\text{CN}) - 1.7 \pm 0.4 \quad (12)$$

$$\log K_S(\text{DMF}) = \log K_S(\text{HMPT}) - 2.6 \pm 0.1 \quad (13)$$

Acetates and tetraphenylborides sometimes show greater deviation than indicated by these equations. The deviations are such as to suggest that the "dipolar aprotic character" of these solvents increases slightly in the order of solvents, $CH_3CN < DMSO < DMF < DMAC < HMPT$.

The solvent activity coefficients, log $({}^{D}\gamma_{Ag^+}{}^{S})({}^{D}\gamma_{X^-}{}^{S})$, for silver salts in dipolar aprotic solvents, with DMF as reference solvent, are in Table VII. They are calculated from solubility products (Table I) and eq 2. As required by eq 10–13, the solvent activity coefficients show that the change in chemical potential of an anion, on transfer from one dipolar aprotic solvent to another, is little influenced by the nature of the anion. The small deviations are regular, in that acetate ion, a strong H-bond acceptor, deviates in the opposite sense to large polarizable anions like BPh_4^-.

Table VII. Solvent Activity Coefficients of Silver Salts at 25° (Reference Solvent, DMF)

	Log K_S^0/K_S^S = log$({}^{D}\gamma_{Ag^+}{}^{S})({}^{D}\gamma_{X^-}{}^{S})$				
	DMF	DMAC	DMSO	CH_3CN	HMPT
AgCl	0.0	−0.2	−4.1	−1.6	−2.6
AgBr	0.0	−0.5	−4.4	−2.1	−2.7
AgI	0.0	−1.1	−4.4	...	...
AgN_3	0.0	−0.2	−4.5	−1.4	−2.5
AgSCN	0.0	−1.0	−4.4	−1.5	−4.1
AgOAc	0.0	−0.5	−5.8	−2.8	...
$AgBPh_4$	0.0	−0.8	−2.1	+0.5	−2.0
$AgAgCl_2$	0.0	−1.1	−3.5	−0.3	−4.9
$AgAgBr_2$	0.0	−1.3	−3.5	−1.2	−5.2
$AgAgI_2$	0.0	−1.7	−3.5	...	...
$AgAg(N_3)_2$	0.0	−0.7	−3.9	...	−4.4
$AgAg(SCN)_2$	0.0	−1.5	−4.4	...	−5.9
$AgAg(OAc)_2$	0.0	−0.7	...	...	...
AgI_3	0.0	−2.5	...	+0.2	...

Solubility Products in Protic and in Dipolar Aprotic Solvents. Dipolar aprotic solvents tend to "level" and protic solvents tend to "differentiate" the solubility products of the silver halides. There is absolutely no correlation between solubility products of silver salts, expressed as concentration quotients, in a protic solvent and in a dipolar aprotic solvent. The attempted correlation between solubility products in DMF and water, shown in Figure 4, is a scatter diagram. It is on the same scale as are Figures 2 and 3. Clearly, each anion responds differently to transfer from a protic to a dipolar aprotic solvent, as is shown also in Table VI.

In a later paper we will consider the question of individual solvent activity coefficients for anions, divorced from ${}^{W}\gamma_{Ag^+}{}^{S}$. Although we cannot be sure, because individual activity coefficients of ions will never be known with certainty,[13,21] the data in Table VI are quite compatible with our qualitative ideas[3,7,25] on protic–dipolar aprotic solvent effects. In brief, small anions, which are strong H-bond acceptors (OAc^-, Cl^-), are much more solvated by protic than by dipolar aprotic solvents (*i.e.*, log ${}^{W}\gamma_i{}^{S}$ is positive), whereas large polarizable anions (I_3^-, ClO_4^-, AgX_2^-), which do not have strong H-bonding interactions with protic solvents, are more solvated by dipolar aprotic than by protic solvents (*i.e.*, log ${}^{W}\gamma_i{}^{S}$ is negative). The effects, whether they be associated with the structure of protic solvents, with H-bonding between anions and protic solvents, or with dispersion forces, are large and can account for

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[24] The superscripts denote water (W), methanol (M), and formamide (F).

[25] J. Miller and A. J. Parker, *J. Am. Chem. Soc.*, **83**, 117 (1961).

Table VIII. Solvent Activity Coefficients of Alkali Metal Salts at 25° (Reference Solvent, Methanol)

	$\log K_S{}^M - \log K_S{}^S = ({}^M\gamma_+{}^S)({}^M\gamma_-{}^S)^a$							
Salt	MeOH	H_2O	$HCONH_2$	$CH_3CONH(CH_3)^b$	DMF	DMSO	CH_3CN	HMPT
KCl	0.0	−3.4	...	−0.7	+2.9	...	+4.7	...
KBr	0.0	...	...	−1.0	+0.7	−1.1	+3.9	+2.3
KI	0.0	...	...	−0.5	−0.7	...	+1.8	...
$KClO_4$	0.0	−2.8	...	−3.7	−4.4	−5.3	...	...
$KBPh_4$	0.0	+2.5	...	...	...	...	...	...
$KOC_6H_4NO_2$-*p*	0.0[c]	...	...	...	+0.2[c]	...	...	...
KPic	0.0	−0.8	...	...	−4.4	...	+0.3	...
NaCl	0.0	...	...	−0.6	...	...	+7.5	+2.5
$NaOC_6H_4NO_2$-*p*	0.0	+1.1	...	...	−0.4	...	+5.6	...
CsCl	0.0	...	−2.2	...	+3.2	...	+5.1	...
CsBr	0.0	...	−2.5	...	+1.1	...	+2.2	...
CsI	0.0	...	−2.0	...	−0.2	...	+1.2	...
CsPic	0.0	...	...	...	−3.6	...	...	...

[a] A negative value means that the salt is more solvated by solvent S than by the reference solvent, methanol. Calculated from Table II and eq 2. [b] N-Methylacetamide at 40°. [c] At 0°.

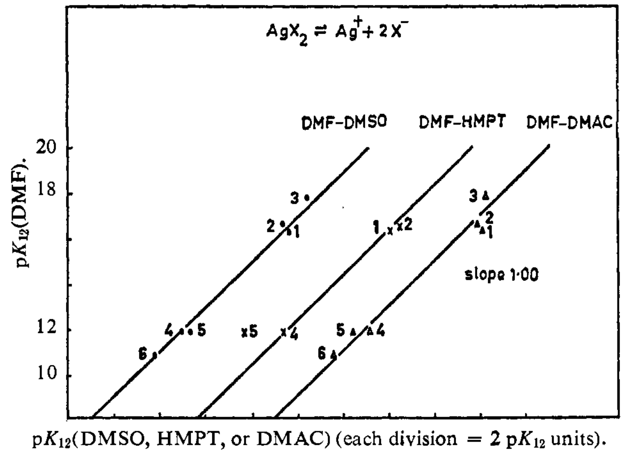

Figure 5. Instability constants in dipolar aprotic solvents at 25°. Numbers refer to complexes in Table III. $pK_{12} = -\log([Ag^+][X^-]^2/[AgX_2^-]$.

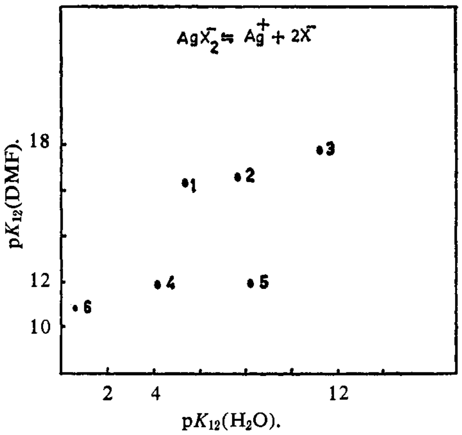

Figure 6. Instability constants in water and in DMF at 25°. Numbers refer to complexes in Table III. $pK_{12} = -\log([Ag^+][X^-]^2/[AgX_2^-])$.

differences of 10^{18} in some equilibrium constants. These are equivalent to a free energy difference of 23 kcal mole^{-1}.

Solubilities of Alkali Metal Salts. Solvent activity coefficients, calculated from the solubility products (Table II), in water, formamide, N-methylacetamide, DMF, DMSO, acetonitrile, and HMPT with methanol as reference solvent, are in Table VIII. These are subject to greater error than the values for silver salts, because the saturated solutions of alkali metal salts are more concentrated, and ion association may increase the apparent solubility. In addition, solvates have been detected in saturated solutions of alkali metal salts in DMSO.[26] Nevertheless the same trends, as have been commented on for silver salts, are observed. Within each class of solvent, the free energies of transfer of salts of the same cation are more or less independent of the anion. However, free energies of transfer from a protic solvent, *e.g.*, methanol, to a dipolar aprotic solvent, *e.g.*, DMF, are strongly dependent on the nature of the anion. Salts of small anions, *e.g.*, Cl^-, behave quite differently from picrates and perchlorates. The perchlorate anion is apparently a weak H-bond acceptor, so that those perchlorates which are only slightly soluble in protic solvents tend to be quite soluble in DMF and DMSO.

Instability Constants in Protic and Dipolar Aprotic Solvents. The silver complexes AgX_2^- are very much more stable in dipolar aprotic than in protic solvents (*cf.* Table III and ref 11) and the instability constants of $AgHal_2^-$ are leveled on transfer from protic to dipolar aprotic solvents. Instability constants, K_{12}, for equilibrium 3, expressed as concentration quotients, $[Ag^+][X^-]^2/[AgX_2^-]$, are linearly related in DMF, DMAC, DMSO, and HMPT (Figure 5). They can be predicted tolerably well in one dipolar aprotic solvent from eq 14–17 if the value in another dipolar aprotic solvent is known.

$$\log K_{12}(\text{DMF}) = \log K_{12}(\text{DMSO}) - 4.9 \pm 0.3 \qquad (14)$$

$$\log K_{12}(\text{DMF}) = \log K_{12}(\text{DMAC}) \pm 0.5 \qquad (15)$$

$$\log K_{12}(\text{DMF}) = \log K_{12}(\text{CH}_3\text{CN}) \pm 2.9 \qquad (16)$$

$$\log K_{12}(\text{DMF}) = \log K_{12}(\text{HMPT}) - 0.3 \pm 0.2 \qquad (17)$$

A plot of log K_{12} in water *vs.* log K_{12} in DMF is a scatter diagram (Figure 6). There is absolutely no simple relationship between instability constants of AgX_2^- in protic and in dipolar aprotic solvents. The

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(26) J. Kentämaa, *Suomen Kemistilehti*, **B33**, 179 (1960).

Table IX. *P* Values (Reference Solvent, Water, 25°)

	$\text{Log}\,\frac{K_S^W}{K_S^S}\,(\text{AgX}) - \log\frac{K_S^W}{K_S^S}\,(\text{AgSCN}) = \log {}^W\gamma_{X^-}{}^S - \log {}^W\gamma_{SCN^-}{}^S = {}^Wp^S$						
Anion	${}^Wp^M$ (MeOH)	${}^Wp^F$ ($HCONH_2$)	${}^Wp^D$ (DMF)	${}^Wp^{DMA}$ (DMAC)	${}^Wp^{DMSO}$ (DMSO)	${}^Wp^{CH_3CN}$ (CH_3CN)	${}^Wp^{HMPT}$ (HMPT)
OAc^-	1.7	...	8.2	8.7	6.8	6.9	...
Cl^-	1.3	1.6	5.1	5.9	5.4	5.0	6.6
Br^-	0.9	1.1	3.1	3.6	3.1	2.5	4.5
N_3^-	0.6	1.1	2.8	3.6	2.7	2.9	4.4
OTs^-	0.0	...	0.4	...	...	...	...
I^-	0.3	0.5	0.2	0.1	0.2	...	...
SCN^-	0.0	0.0	0.0	0.0	0.0	0.0	0.0
$AgCl_2^-$	1.7	...	−1.2	−1.3	−0.3	0.0	−2.0
$Ag(N_3)_2^-$	...	...	−2.5	−2.2	−2.0	...	−2.8
$AgBr_2^-$	0.6	...	−3.3	−3.6	−2.4	−3.0	−4.4
$Ag(SCN)_2^-$	...	...	−4.2	−4.7	−4.2	...	−6.0
Picrate	...	...	−3.2	...	...	−1.3	...
ClO_4^-	...	...	−3.4	...	−1.5	...	...
BPh_4^-	+0.1	+1.2	−4.0	−3.8	−1.7	−2.0	−1.9
AgI_2^-	−1.2	...	−6.6	−7.3	−5.7	...	...
I_3^-	−3.4	−2.1	−8.1	−9.6	...	−6.4	...

greater stability of AgX_2^- in dipolar aprotic solvents arises because $\log {}^W\gamma_{X^-}{}^S/{}^W\gamma_{AgX_2^-}{}^S$ is large and positive (Table VI); *i.e.*, X^- is often a small, strong hydrogen-bond acceptor, whereas AgX_2^- is a large more polarizable anion.[3]

The trihalide ions are likewise much more stable in dipolar aprotic than in protic solvents.[4,22,27] Iwamoto and Nelson[22] have commented on the reversal, shown in Table IV, of instability constants of the trihalide ions, on transfer from water to dipolar aprotic solvents. The Cl_3^- and Br_3^- ions are in fact more stable than I_3^- in dipolar aprotic solvents. Followers of the hard and soft acid and base principle[28] might get the impression, from instability constants in water, that "soft" basic halide ions (*e.g.*, I^-) form the most stable complexes with "soft" acidic halogens (*e.g.*, I_2) and that halogen basicity is $I^- > Br^- > Cl^-$, but this needs reexamination. Like carbon nucleophilicity[7,29,30] of the halide ions, the halogen basicity may be reversed by transfer from protic to dipolar aprotic solvents. The order $I^- > Br^- > Cl^-$ observed in water and sometimes attributed to polarizability is governed by the strong H-bonding solvation of chloride ion in water, relative to bromide and iodide ions.[31] It is not directly attributable to an intrinsic property, such as polarizability.

The instability constants of I_3^- (eq 18) in various solvents are related through (19), in which water is the reference solvent.

$$I_3^- \rightleftharpoons I_2 + I^- \qquad (18)$$

$$\log \frac{K^W}{K^S} = \frac{\log ({}^W\gamma_{I_2}{}^S)({}^W\gamma_{I^-}{}^S)}{({}^W\gamma_{I_3^-}{}^S)} \qquad (19)$$

The values of $\log {}^W\gamma_{I_2}{}^S$ in Table IV show that iodine is more solvated by dipolar aprotic than by protic solvents. On these grounds alone, one would expect I_3^- to be less stable in dipolar aprotic solvents. But the reverse is true, because $\log {}^W\gamma_{I^-}{}^S/{}^W\gamma_{I_3^-}{}^S$ (eq 19) is large and positive for dipolar aprotic solvents, S, relative to water (Table VI). This observation agrees with our expectation[3,4] that the very large, very polarizable triiodide ion is more solvated by dipolar aprotic than by protic solvents whereas the smaller, less polarizable iodide ion, which is a better H-bond acceptor than is I_3^-, is more solvated by protic solvents.

***P* Values.**[7] The solvent activity coefficients, $\log ({}^W\gamma_{Ag^+}{}^S)({}^W\gamma_{X^-}{}^S)$, in Table VI have been estimated in four ways: (i) from solubility products of silver salts, using eq 2; (ii) from the instability constants of I_3^-, the values of $\log {}^W\gamma_{I_2}{}^S$ in Table IV, and the values of $\log ({}^W\gamma_{Ag^+}{}^S)({}^W\gamma_{I^-}{}^S)$ in Table VI, using eq 19; this gives $\log ({}^W\gamma_{Ag^+}{}^S)({}^W\gamma_{I_3^-}{}^S)$; (iii) from the equilibrium constants in Table V, for (4) using an equation equivalent to (2); this gives $\log ({}^W\gamma_{Ag^+}{}^S)({}^W\gamma_{AgX_2^-}{}^S)$; (iv) from solubilities of cesium or potassium salts, *i.e.*

$$\log ({}^W\gamma_{Ag^+}{}^S)({}^W\gamma_{X^-}{}^S) = \log \frac{K_S^W}{K_S^S}\,(\text{AgY}) + \log \frac{K_S^W}{K_S^S}\,(\text{KX}) - \log \frac{K_S^W}{K_S^S}\,(\text{KY})$$

This was used for $\log ({}^W\gamma_{Ag^+}{}^S)({}^W\gamma_{ClO_4^-}{}^S)$ and $\log ({}^W\gamma_{Ag^+}{}^S)({}^W\gamma_{Pic^-}{}^S)$. Values calculated by this method could be subject to considerable error, because each of the six constants has some uncertainty.

As will be shown in subsequent papers, the numbers in Table VI are very useful for interpreting solvent effects on acid–base equilibria, on rates of S_N2 reactions, on instability constants of a variety of complexes, and on redox potentials. The numbers are conveniently recorded as "*P* values" for the anion X^-.

We arbitrarily chose thiocyanate ion as a standard anion and water as reference solvent. The thiocyanate ion is a moderately weak H-bond acceptor and is polarizable.[3] The *P* values for transfer of anions from water to other solvents are defined by (20). Of course it is not necessary to use only solubilities of silver salts, but these are most conveniently measured. *P* values are in Table IX. A positive number indicates that,

$${}^Wp_X{}^S = \log \frac{K_S^W}{K_S^S}\,(\text{AgX}) - \log \frac{K_S^W}{K_S^S}\,(\text{AgSCN}) = \log {}^W\gamma_{X^-}{}^S - \log {}^W\gamma_{SCN^-}{}^S \qquad (20)$$

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relative to SCN^-, the anion becomes less solvated on transfer from water to the new solvent; negative values show that the anion becomes more solvated, relative to the behavior of SCN^-, on transfer from water. The behavior shown in Table IX is in full agreement with our qualitative discussion of the effects of solvation on the chemistry of anions in protic and in dipolar aprotic solvents.[3,6–8] The numbers in Table IX put this discussion on a quantitative basis.

The range of *P* values is enormous; we show here values corresponding to a range of 23 kcal mole^{-1}, but even bigger differences are expected. The protic–dipolar aprotic solvent effects considered here could influence rates and equilibrium constants by 10^{18} upon solvent transfer. HMPT appears to exhibit the largest spread of *P* values, but salts are less soluble in this solvent so that DMF and DMAC are of greater practical value.

We are examining some extrathermodynamic methods[21,32,33] for the evaluation of log ${}^{W}\gamma_{Ag^+}^{S}$. It may be possible to estimate solvent activity coefficients for individual anions. This will give us numbers on which theories of protic–dipolar aprotic solvent effects can be based.

Acknowledgment. Helpful discussions with Professors R. T. Iwamoto and I. M. Kolthoff are gratefully acknowledged.

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The Structure of Iron(III) in Aqueous Solution

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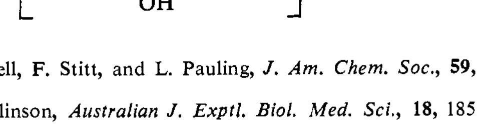
Received January 3, 1967

Abstract: [Fe^{III}HEDTA], the uncharged complex of ferric ion and the trianion of N-hydroxyethylethylenediaminetriacetic acid, reacts with equimolar amounts of NaOH to form a monomeric and dimeric species. The wine red dimer has two unpaired electrons. Magnetic and spectral data are used to describe the monomer–dimer equilibrium and possible structure of the dimer. Spin coupling *via* Fe–O–Fe bridging is proposed. The aquo dimer and polymer produced from the partial neutralization of ferric perchlorate solutions with bicarbonate were also investigated. Iron(III) in these materials is in an intermediate paramagnetic state, probably two unpaired spins per iron. Spin coupling *via* the bridging shown in structure B is proposed. Spin reduction in iron(III) pyrophosphate was also studied in a preliminary way. In a final section the possible role of dimeric structures in the spin reduction of iron(III) hemoproteins and porphyrin systems is discussed.

The structure of Fe(III) complexes in aqueous solution is a subject of considerable interest. One reason for the interest is the fact that many Fe(III) complexes with weak-field ligands exhibit solution magnetic moments significantly below the spin-only value of 5.92 BM expected for $S = {}^5/_2$ systems. For example, Pascal observed low moments for ammoniacal ferric pyrophosphate solutions;[2a] these moments increase on addition of HCl to the solutions. Later, Bose noted low magnetic moments for aqueous solutions of Fe(III) nitrate, chloride, and sulfate.[2b] Magnetic moments in the range expected for $S = {}^5/_2$ were obtained upon addition of the corresponding acids (nitric, hydrochloric, sulfuric). Bose suggested that the discrepancies were due to hydrolysis of the Fe(III) salts, but no specific analysis was given. A more comprehensive study yielded similar results.[3]

Coryell, Stitt, and Pauling found that the magnetic moment of ferrihemoglobin is pH dependent, decreasing to 4.47 BM on formation of ferrihemoglobin hydroxide.[4] This was interpreted as mononuclear Fe(III) with an intermediate spin of ${}^3/_2$, plus a large orbital contribution (the spin-only moment for $S = {}^3/_2$ is 3.88 BM). A similar study by Rawlinson showed that hematin in alkaline solution has $\mu_{\text{eff}} = 3.5$ BM.[5]

A relatively recent study is that of Mulay and Selwood, who observed that the magnetic susceptibilities of aqueous solutions of $Fe(ClO_4)_3 \cdot xH_2O$ decrease with increasing pH.[6] They attributed these results to the formation of a diamagnetic dimer of probable structure



$$\left[(H_2O)_4Fe\begin{matrix}\diagup OH \diagdown \\ \diagdown OH \diagup\end{matrix}Fe(H_2O)_4\right]^{4+}$$

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