Monatshefte für Chemie 134, 655–667 (2003)
DOI 10.1007/s00706-002-0579-3

Monatshefte für Chemie
Chemical Monthly
Printed in Austria

Invited Review

Solubilities of the Silver Halides in Aqueous Mixtures of Methanol, Acetonitrile, and Dimethylsulfoxide

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Received September 30, 2002; accepted October 29, 2002

Summary. The solubilities of the silver halides in three non-aqueous solvents: methanol, acetonitrile, and dimethylsulfoxide, and in their aqueous mixtures, are reviewed. Values for the solubility product, K_{SO}, the enthalpies of solution, $\Delta_{sol}H^o$, and the equilibrium products for $AgX_i^{(i-1)-}$ silver halide complexes, β_i, are listed and, where possible, compared. The solvent systems provide examples for three types of mixed aqueous solvent system: aqueous alcohol mixtures and aqueous mixtures with dipolar aprotic solvents that are weakly or strongly basic. The experimental data are discussed in terms of the solvation of the silver and halide ions in the mixed solvents.

Keywords. Calorimetry; Solubility; Solvent effect; Thermodynamics.

Introduction

The variations in the solubilities of the silver halides, particularly chloride, bromide, and iodide, in non-aqueous and mixed solvent systems were central to the development of our understanding of solvation in these media. Thus, for example, the pioneering work of *Parker* [1, 2] into the solvation of anions in dipolar aprotic solvents made considerable use of the solubility products of the silver halides. Among the reasons for this were the relative ease of measuring silver halide solubilities of reasonable precision, particularly by potentiometric techniques, the purity of the solid phases and the absence of solid solvates, and their generally low solubility, which made corrections for ion–ion interactions relatively straight forward.

Silver halide solubilities have been measured in a wide range of non-aqueous and mixed aqueous solvent systems and a comprehensive review of these data is

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Dedicated to Prof. *Heinz Gamsjäger* on the occasion of his seventieth birthday beyond the scope of the present one. Thus, three mixed aqueous solvent systems will be considered: aqueous methanol, acetonitrile (*AN*), and dimethylsulfoxide (*DMSO*). These are representative of three broad classes of aqueous mixed solvents, aqueous-alcohols and mixtures of water with weakly basic (*AN*) or strongly basic (*DMSO*) aprotic solvents. They are also among the most extensively studied, so that it is possible to make some assessment of the experimental data and both solubility and enthalpy of solution data are available.

There are several hundred papers that report solubility data for the silver halides in water and no attempt has been made to review these. Thus, the values for the silver halides in water are based solely on those reported along with the data in the mixed solvent systems.

The original data have been measured at different solvent compositions, often using different composition scales. Where necessary, the solvent composition scales have been converted to the mole fraction scale and interpolated to systematic mole fraction intervals. In all cases the solubility and equilibrium products are reported on the molar concentration scale.

Thermodynamics

The principal thermodynamic variable is the solubility product, K_{SO}, which is simply the equilibrium constant for the reaction:

$$\mathrm{AgX_{(s)}} \rightleftharpoons \mathrm{Ag^+} + \mathrm{X^-} \qquad K_{SO} = [\mathrm{Ag^+}][\mathrm{X^-}] \tag{1}$$

where [Y] represents the activity of species Y and the solid phase activity is unity.

In the presence of excess of one ion, the solubility may be affected by formation of one or more complex species. At low concentrations, the silver halides predominantly form mononuclear complexes as:

$$\mathrm{Ag^+} + \mathrm{nX^-} \rightleftharpoons \mathrm{AgX_n}^{\mathrm{(n-1)-}}$$

for which the equilibrium product, β_n, is given by Eq. (2):

$$\beta_n = \frac{[\mathrm{AgX_n^{(n-1)-}}]}{[\mathrm{Ag^+}][\mathrm{X^-}]^n} \tag{2}$$

Enthalpies of solution, $\Delta_{sol}H^o$, provide the temperature coefficient of the solubility product; thus:

$$\Delta_{sol}G^o = -RT\ln K_{SO} = \Delta_{sol}H^o - T\Delta_{sol}S^o \tag{3}$$

and

$$\frac{d\ln K_{SO}}{dT} = \frac{\Delta_{sol}H^o}{RT^2} \tag{4}$$

Experimental Methods

Solubility and Equilibrium Products

The most direct method of measuring solubilities is, naturally, to equilibrate the solid phase with the solution and determine the concentration of the resulting saturated solution. Analysis of saturated solution can be made, for example, using electrochemical detection of the silver ion (as Ag/Ag$^+$) or halide ion (as X^-/AgX/Ag). The photo-sensitivity of the silver halides necessitates special precautions to ensure purity of the solid phase and it is preferable to determine the concentrations of both ions in the solution. In all solutions the formation of AgX_2^- and higher complex species $AgX_n^{(n-1)-}$ may raise the solubility in the presence of excess halide. This becomes more significant in organic or aqueous/organic solvents where the β_i can be quite large.

In general, analysis of the concentration of the saturated solution only provides a route to K_{SO}, although it is possible to determine B_i values from analyses of saturated solutions containing excess

Table 1. Solubility products[a] for silver halides in water, methanol, *AN* and *DMSO*

Water		Methanol		*AN*		*DMSO*	
Ref.	$\log_{10} K_{SO}$	Ref.	$\log_{10} K_{SO}$	Ref.	$\log_{10} K_{SO}$	Ref.	$\log_{10} K_{SO}$
Silver chloride							
[4]	– 9.75	[25]	– 12.7	[32]	– 12.4	[31]	– 10.4
[26]	– 9.75	[27, 28]	– 13.1	[29]	– 13.1	[26]	– 9.66
[30]	– 9.75	[11]	– 12.8	[31]	– 13.0		(– 10.4)
[14]	– 9.76	[32]	– 13.0			[33]	– 10.28
[34]	– 9.81	[35]	– 12.5			[36]	– 10.4
[15, 37]	– 9.94					[29]	– 10.4
[38]	– 9.80					[24]	– 10.81
[21]	– 9.7					[35]	– 10.8
[16]	– 9.75						
[17]	– 9.79						
[22]	– 9.77						
[24]	– 9.70						
[23]	– 9.74						
Average	– 9.77		12.82		12.8		10.39
Silver bromide							
[34]	– 12.37	[25]	– 14.95	[32]	– 13.2	[32]	– 10.6
[39]	– 12.46	[27, 28]	– 15.2	[31]	– 13.9	[36]	– 10.9
[15, 37]	– 12.32	[11]	– 15.0	[29]	– 13.7	[24]	– 11.03
[38]	– 12.13	[32]	– 15.2	[20]	– 13.90		
[20]	– 12.21	[34]	– 14.91				
[24]	– 12.19	[40]	– 15.37				
Average	– 12.28		– 15.10		– 13.7		– 10.8
Silver iodide							
[34]	– 15.96	[25]	– 17.8	[32]	– 14.2	[32]	– 12.0
[41]	– 15.8	[27, 28]	– 18.22	[42]	– 14.2	[42]	– 11.4
[15, 37]	– 15.91	[11]	– 16.4	[31]	– 15.0	[36]	– 12.1
[10]	– 16.14	[32]	– 18.2	[29]	– 14.7	[41]	– 11.9
[20]	– 15.88	[42]	– 18.3	[20]	– 14.49	[35]	– 12.1
[24]	– 16.07	[34]	– 17.84			[24]	– 12.5
		[35]	– 17.5				
Average	– 15.96		– 17.7		– 14.5		– 12.0

[a] Concentrations are mol dm^{-3}

halide. Where K_{SO} are measured from analysis of solutions with no added electrolyte, the concentrations are generally sufficiently low that ion–ion interactions are practically negligible.

The availability of electrodes reversible to both Ag^+ and X^- permits the determination of K_{SO} from the standard cell potential of, for example, the *Owen* [3, 4] cell:

$$\begin{aligned}&Ag/AgCl/KCl(xm) + KNO_3((1-x)m)//KNO_3(m)//AgNO_3(xm)\\&\quad + KNO_3((1-x)m)/Ag\end{aligned}$$

where variation of x allows elimination of the liquid junction potential, by extrapolation $x = 0$, and calculation of the activity coefficients using *Debye-Hückel* theory and extrapolation to zero molal concentration, m, gives the standard cell potential, ΔE^o, from which K_{SO} is calculated as:

$$\ln K_{SO} = -\frac{F\Delta E^o}{RT} \tag{5}$$

The additivity of cell potentials means that ΔE^o for the relevant cell can be determined from the standard potentials of the Ag/Ag^+ and $X^-/AgX/Ag$ electrodes. Evaluating the ΔE^o data is well beyond the scope of this review and K_{SO} data recovered from the standard potentials of the Ag/Ag^+ and $X^-/AgX/Ag$ electrodes are only included if they are reported by the original authors.

EMF data can be measured with good precision, certainly to 0.1 mV and so should provide $\log K_{SO}$ to round 0.02 log units. The use of the *Owen* cell is limited by the formation of AgX_2^-, which, in many non-aqueous solvent systems, will dissolve the AgX deposit from the Ag/AgX electrode.

The most common method for determining the solubility data for AgX in mixed and non-aqueous solvents has been from the results of potentiometric titrations, [5] using, for example, the cell:

$$Ag/AgClO_4(0.01\,M)//TEAPic(0.1\,M)//TEAX(0.01\,M) + AgClO_4/Ag$$

where TEA and Pic represent tetraethyl ammonium and picrate.

Table 2. Enthalpies of solution, $\Delta_{sol}H^o$/kJ mol^{-1}, of silver halides in water, methanol, *AN*, and *DMSO*

Water		Methanol		*AN*		*DMSO*	
Ref.	$\Delta_{sol}H^o$	Ref.	$\Delta_{sol}H^o$	Ref.	$\Delta_{sol}H^o$	Ref.	$\Delta_{sol}H^o$
Silver chloride							
[16]	66.2	[43]	51.0	[20]	32.6	[43]	28.9
[17]	67.1					[24]	33.1
[20]	65.7						
[24]	66.0						
Average	66.3		51.0		32.6		31.0
Silver bromide							
[20]	85.4			[20]	39.7	[31]	38.9
				[44]	38.9		
Average	85.4				39.3		38.9
Silver iodide							
[20]	112.5			[20]	51.5	[20]	52.3
				[44]	51.4	[31]	51.0
Average	112.5				51.4		51.6

The EMF of the cell is given by:

$$\Delta E = F \ln\left(\frac{[\mathrm{Ag}^+]}{[\mathrm{Ag}^+]_{ref}}\right) + \Delta E_{lj} \tag{6}$$

where ΔE_{lj} is the sum of the liquid junction potentials between the two half cells and the salt bridge solution. The salt bridge solution is chosen to minimise the liquid junction potentials; generally, this is taken to mean that the cation and anion mobilities are matched since the ΔE_{lj} takes the form [6]:

$$\Delta E_{lj} = \frac{1}{F}\sum z_i t_i \int d\mu_i \tag{7}$$

where z_i, t_i, and μ_i are the charge, transport number, and chemical potential of species i. In these experiments, the halide solution is titrated with the silver solution. The method has the advantage that it returns values for β_n as well as for K_{SO}. The resulting β_n and K_{SO} are generally corrected to infinite dilution by calculating the activity coefficients using an extended *Debye-Hückel* [7] equation or, more usually, an empirical equation, such as that due to *Davies* [8].

Enthalpies of Solution

Clearly, $\Delta_{sol}H^o$ can be calculated from the temperature variation of $\ln K_{SO}$ provided the data are of sufficient precision.

Table 3. Stability products[a] for AgX_2^- species in methanol, *AN*, and *DMSO*

Methanol		*AN*		*DMSO*	
Ref.	$\log_{10}\beta_2$	Ref.	$\log_{10}\beta_2$	Ref.	$\log_{10}\beta_2$
Silver chloride					
[32]	7.90	[31]	13.7	[32][a]	11.9
		[29]	13.7		(12.1)
		[32][b]	13.6	[33]	11.73
			(12.6)	[36]	11.7
				[29]	12.1
				[35]	11.7
Average	7.9		13.7		11.9
Silver bromide					
[32]	10.6	[31]	14.1	[36]	12.0
		[29]	13.8	[32][a]	11.7
		[32][b]	13.4		(12.3)
			(14.1)	[35]	13.0
Average	10.6		13.9		12.2
Silver iodide					
[32]	14.8	[31]	15.6	[36]	13.0
		[29]	16.7		
		[32][b]	14.6		
			(15.7)		
Average	14.8		15.7		13.0

[a] Concentrations are $\mathrm{mol\,dm^{-3}}$

[b] Values from potentiometric measurements, those in parentheses are from voltammetric measurements

Table 4. Solubility parameters[a] of silver halides in aqueous methanol mixtures

X_{MeOH}	.05	.1	.2	.3	.4	.5	.6	.7	.8
Ref.					Silver chloride				
$\log_{10} K_{SO}$									
[12, 13]	– 9.99	– 10.17	– 10.43	– 10.75	– 11.33				
[4]	– 9.93	– 10.11	– 10.46	– 10.78					
[30]	– 9.95	– 10.15	– 10.50	– 10.83					
[14]	– 9.99	– 10.17	– 10.47	– 10.82	– 11.40				
[34]	– 10.10	– 10.19	– 10.36	– 10.54	– 10.73				
[15, 37]	– 10.00	– 10.08	– 10.31	– 10.60	– 10.91				– 11.57
[16]	– 9.87	– 9.98	– 10.22	– 10.46	– 10.73	– 11.03	– 11.37	– 11.73	
[17]	– 9.92	– 10.07	– 10.42	– 10.82					
Average	– 9.97	– 10.11	– 10.40	– 10.70	– 11.02	– 11.0	– 11.4	– 11.7	– 11.6
$\Delta_{sol}H^o/\mathrm{kJ\,mol^{-1}}$									
[12, 13]	66.7	67.6	68.4	67.7	65.5				
[16]	68.8	70.7	72.9	71.5	67.2	62.2	55.9	44.4	
[17]	53.7			50.3					
Average	63.1	69.2	70.6	63.2	66.4	62.2	55.9	44.4	
					Silver bromide				
$\log_{10} K_{SO}$									
[34]	– 12.50	– 12.63	– 12.89	– 13.14	– 13.40				– 14.41
[39]	– 12.62	– 12.74	– 12.98	– 13.23	– 13.49				
[15, 37]	– 12.48	– 12.62	– 12.89	– 13.16	– 13.43				– 14.46
Average	– 12.53	– 12.66	– 12.92	– 13.18	– 13.44				– 14.44
[34]	– 16.10	– 16.19	– 16.37	– 16.56	– 16.74				– 17.42
[15, 37]	– 16.18	– 16.29	– 16.48	– 16.67	– 16.85				– 17.43
[10]	– 16.85	– 17.20	– 17.25	– 17.14	– 17.69				
Average	– 16.38	– 16.56	– 16.70	– 16.79	– 17.09				– 17.43

[a] Concentrations are mol dm^{-3}

Table 5. Solubility parameters[a] of silver halides in aqueous *AN* mixtures

X_{AN}	.05	.1	.2	.3	.4	.5	.6	.7	.8	.9
Ref.					Silver chloride					
$\log_{10} K_{SO}$										
[21]	– 8.1	– 7.4	– 7.4	– 7.6	– 7.7	– 7.9	– 8.2	– 8.8	– 9.7	– 11.0
[22]	– 9.17	– 8.65	– 8.22	– 8.12	– 8.29	– 8.74	– 9.43	– 10.24	– 11.11	– 11.91
[23]	– 8.67	– 8.14	– 7.76	– 7.91	– 8.27	– 8.66	– 9.00	– 9.35	– 9.92	– 11.03
Average	– 8.92	– 8.40	– 7.99	– 8.01	– 8.28	– 8.70	– 9.21	– 9.80	– 10.52	– 11.47
$\Delta_{sol}H^o/\mathrm{kJ\,mol^{-1}}$										
[20]	39.7	33.7	30.9	27.8	24.8	22.0	19.8	18.3	17.7	

(*continued*)

Table 5 (*continued*)

X_{AN}	.05	.1	.2	.3	.4	.5	.6	.7	.8	.9
Ref.					Silver bromide					
$\log_{10} K_{SO}$										
[19]	-12.20	-11.98	-11.64	-11.42	-11.28	-11.21	-11.18	-11.19	-11.24	-11.32
[20]	-11.21	-10.67	-10.16	-10.16	-10.38	-10.67	-10.94	-11.23	-11.66	
Average	-11.71	-11.32	-10.90	-10.79	-10.83	-10.94	-11.06	-11.21	-11.45	-11.32
$\Delta_{sol}H^o/\mathrm{kJ\,mol^{-1}}$										
[20]	57.3	51.6	45.7	43.7	42.4	40.4	37.5	35.4		
					Silver iodide					
$\log_{10} K_{SO}$										
[19]	-14.59	-14.09	-13.47	-13.22	-13.19	-13.25	-13.36	-13.48	-13.61	-13.80
[20]	-14.78	-14.08	-13.49	-13.46	-13.56	-13.58	-13.54	-13.85	-14.09	-14.32
Average	-14.68	-14.08	-13.48	-13.34	-13.37	-13.42	-13.45	-13.66	-13.85	-14.06
$\Delta_{sol}H^o/\mathrm{kJ\,mol^{-1}}$										
[20]	79.6	75.7	72.1	68.8	65.5	62.3	59.4	56.7	54.5	52.7

[a] Concentrations are $\mathrm{mol\,dm^{-3}}$

Table 6. Solubility parameters[a] of silver halides in aqueous *DMSO* mixtures

X_{DMSO}	.05	.1	.2	.3	.4	.5	.6	.7	.8	.9
Ref.					Silver chloride					
$\log_{10} K_{SO}$										
[26]	-9.81	-9.85	-9.84	-9.80	-9.78	-9.84				
[33]	-9.54	-9.53	-9.53	-9.53	-9.55	-9.58	-9.64	-9.73		
[38]	-9.70	-9.63	-9.55	-9.51	-9.50	-9.47				
[24]	-9.70	-9.90	-9.94	-9.88	-9.85	-9.84				
Average	-9.69	-9.73	-9.71	-9.68	-9.67	-9.68	-9.6	-9.7		
$\log_{10} \beta_2$										
[33]			7.50	7.67	8.03	8.53	9.14	9.81	10.49	11.14
$\Delta_{sol}H^o/\mathrm{kJ\,mol^{-1}}$										
[24]	63.4	60.5	54.6	49.9						
					Silver bromide					
$\log_{10} K_{SO}$										
[38]	-11.99	-11.85	-11.61	-11.41	-11.30	-11.28				
[24]	-12.15	-12.08	-11.89	-11.67	-11.43	-11.20				
Average	-12.07	-11.96	-11.75	-11.54	-11.37	-11.24				

(*continued*)

Table 6 (*continued*)

x_{DMSO}	.05	.1	.2	.3	.4	.5	.6	.7	.8	.9
Ref.					Silver bromide					
$\Delta_{sol}H^o$/kJ mol^{-1}										
[24]	80.3	75.7	68.0	62.0						
					Silver iodide					
$\log_{10}K_{SO}$										
[43]	-15.6	-15.3	-14.5	-13.8	-13.2	-12.7	-12.2	-11.9	-11.8	-11.8
[24]	-15.79	-15.52	-14.99	-14.48	-14.01	-13.59				
Average	-15.7	-15.4	-14.7	-14.1	-13.6	-13.1	-12.2	-11.9	-11.8	-11.8
$\Delta_{sol}H^o$/kJ mol^{-1}										
[24]	106.3	100.6	90.3	81.4	74.0	67.7	62.6	58.4	55.2	52.8

[a] Concentrations are mol dm^{-3}

In practice, direct calorimetric measurements generally provide a more precise route to $\Delta_{sol}H^o$, in the case of the silver halides it is the enthalpy of precipitation ($= -\Delta_{sol}H^o$) that is measurable. If the measured values are of sufficient precision, they are corrected to infinite dilution using the appropriate form of the *Debye-Hückel* expression or by simple extrapolation to infinite dilution [9].

The solubilities and related parameters in the neat solvents are listed in Tables 1 to 3 and those in the mixed solvents in Tables 4 to 6.

Results and Discussion

Methanol + Water

The solubility data for the aqueous methanol system are listed in Table 4 and the K_{SO} values are shown (as $\log_{10}K_{SO}$) in Fig. 1.

It is clear that the log K_{SO} values decrease practically linearly from water to methanol. There is excellent agreement among the values for silver bromide and generally good agreement for the other salts. The silver iodide data of *Anderson et al.* [10] are clearly out of line, as is the value of *Koch* [11] in pure methanol. Comparison with the other silver halides suggests that the apparent upward curvature in the silver chloride values of *Parton et al.* [12, 13] and *Anderson et al.* [14] and the downward curve in that of *Kazarjan* and *Pungor* [15] seem unlikely although there are insufficient data to draw a firm conclusion.

The $\Delta_{sol}H^o$ values for silver chloride were calculated from the temperature variation of K_{SO}. There is reasonable agreement between the data of *Parton et al.* [12] [13] and *Panichajukal* [16] and those of *Broadbank et al.* [17] are clearly out of line.

In contrast to the relatively small ($\sim$11.5 kJ mol^{-1}) and featureless variation in log K_{SO} the $\Delta_{sol}H^o$ values pass through a maximum at a methanol mole fraction of 0.2 and vary by 20 to 30 kJ mol^{-1}. This is typical, in that the enthalpy shows much

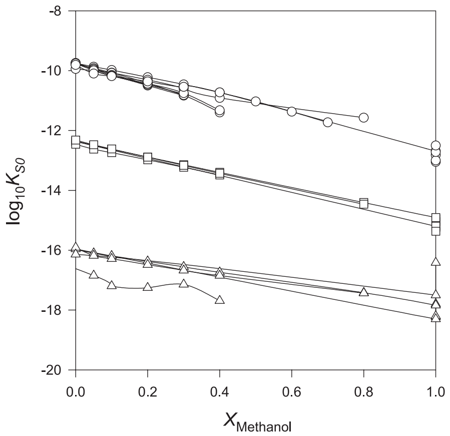

Fig. 1. Solubility products, as $\log K_{SO}$, of silver chloride (○), silver bromide (□), and silver iodide (△) in aqueous methanol mixtures

greater sensitivity to solvent change than does the free energy (and $\log K_{SO}$, *vide infra*) and reflects the compensation between the enthalpy and entropy.

The maximum in $\Delta_{sol}H^o$ is simply related to the excess enthalpy of mixing of the solvent. This has been discussed in detail elsewhere [18]; simply, as the solvent–solvent interactions become stronger it becomes enthalpically more expensive to accommodate the solute in the solvent structure. Where the solute is randomly solvated, as is commonly found in aqueous alcohols, this leads to:

$$\Delta_{sol}H^o = \Delta_{sol}H^o_W + x\Gamma - \Omega\Delta H^E \tag{8}$$

where Γ and Ω are constants reflecting (1) the relative strengths of interactions of the solute with the two components of the mixed solvent and (2) the extent of solvent disruption resulting from accommodation of the solute, respectively, and $\Delta_{sol}H^o_W$ is the enthalpy of solution in water. This is shown in Fig. 2 where the line

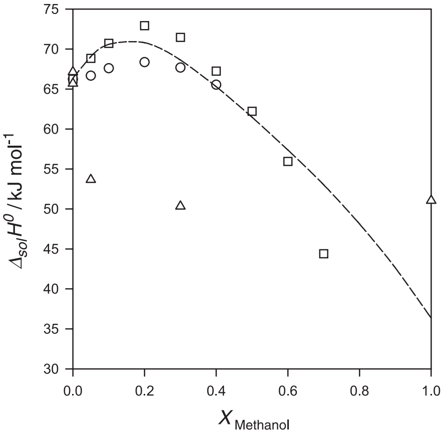

Fig. 2. Enthalpies of solution, $\Delta_{sol}H^o$, of silver chloride in aqueous methanol mixtures; data are from Ref. [12, 13] (○), Ref. [16] (□), and Ref. [17] (△)

through the experimental data points is calculated using Eq. (8) with Γ and Ω values of $-30\,\mathrm{kJ\,mol^{-1}}$ and 13.

Acetonitrile + Water

The solubility data are listed in Table 5 and the $\log K_{SO}$ data are shown in Fig. 3. There is reasonable agreement between the silver iodide values of *Butler* [19] and *Cox et al.* [20] but poorer agreement among the silver chloride data [21–23]. Without further data, it isn't possible to decide among these. *Kim* and *Duscher* [22] also report β_1, β_2, and β_3 values for silver chloride in these systems. It isn't possible to assess these without comparative data but it is striking that their value for $\log \beta_2$ (11.78) in pure *AN* is in poor agreement and their $\log \beta_3$ value (13.70) in excellent agreement with other literature values for $\log \beta_2$ (Table 3).

It is clear that the solubilities in the aqueous *AN* system are markedly different from those in the aqueous methanol system, increasing rapidly at low *AN* concentrations and passing through maxima. Moreover, the decrease in solubility at high *AN* concentrations is dependant on the anion, being greatest for the chloride and practically zero for the iodide. These trends are mirrored in the $\Delta_{sol}H^o$ values, shown in Fig. 4, which pass through minima that are similarly anion dependant.

The solvation of the silver halides in the aqueous *AN* system is dominated by preferential solvation of the ions [20]. Thus, the silver ion is preferentially solvated by *AN*, leading to enthalpic stabilisation of the silver ions by *AN*. This results in both the sharp decrease in $\Delta_{sol}H^o$ and the increase in $\log K_{SO}$ at low *AN* concentrations. In contrast the anions are preferentially solvated by water, with the extent of preferential solvation decreasing in the order $\mathrm{Cl^-} > \mathrm{Br^-} > \mathrm{I^-}$. This leads to increases in $\log K_{SO}$ and decreases in $\Delta_{sol}H^o$ as the water concentration is increased from zero (pure *AN*). These variations decrease in the same order as the extent of preferential solvation and become close to zero for silver iodide.

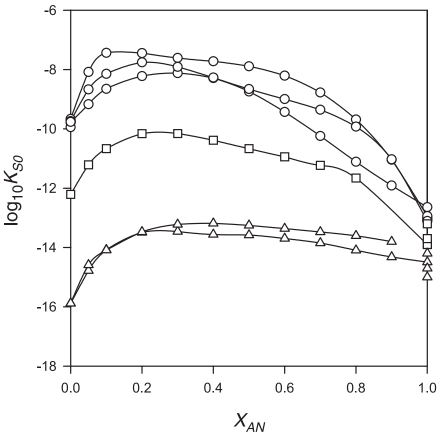

Fig. 3. Solubility products, as $\log K_{SO}$, of silver chloride (○), silver bromide (□), and silver iodide (△) in aqueous *AN* mixtures

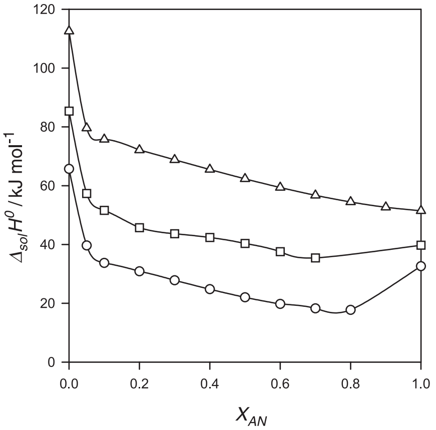

Fig. 4. Enthalpies of solution, $\Delta_{sol}H^o$, of silver chloride (○), silver bromide (□), and silver iodide (Δ) in aqueous *AN* mixtures

Dimethylsulfoxide + Water

The solubility data are listed in Table 6 and $\log K_{SO}$ and $\Delta_{sol}H^o$ are shown in Figs. 5 and 6. The $\log K_{SO}$ values for silver chloride fall into two pairs, each in excellent agreement, but with moderate discrepancies between them and there is good agreement between the two sets of silver bromide solubilities available. The agreement between the two data sets for silver iodide is much poorer, with K_{SO} values differing by almost a factor of ten. As is the case for the *AN* system there is only one available set of $\Delta_{sol}H^o$ for each salt [24] and assessment of these is difficult.

The aqueous *DMSO* system is similar to the *AN* system in that Ag^+ should interact more strongly with *DMSO*, which is more basic than water, while the smaller halide ions at least will interact more strongly with the protic water molecules. Thus, it could be expected that the variations in $\log K_{SO}$ and $\Delta_{sol}H^o$

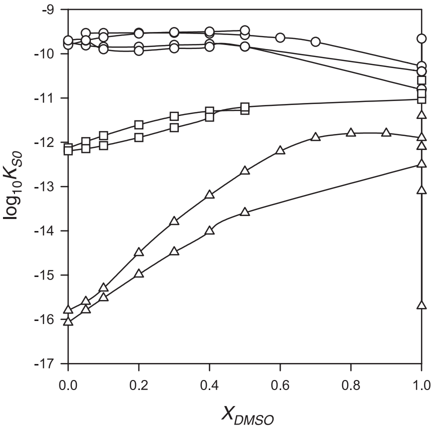

Fig. 5. Solubility products, as $\log K_{SO}$, of silver chloride (○), silver bromide (□), and silver iodide (Δ) in aqueous *DMSO* mixtures

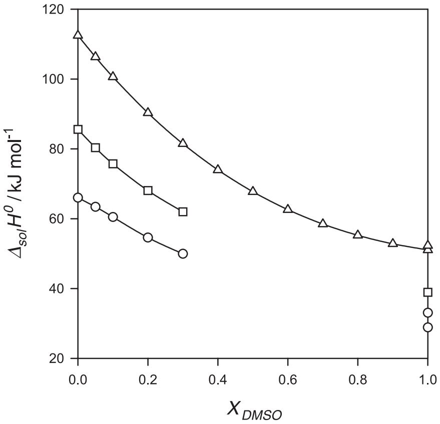

Fig. 6. Enthalpies of solution, $\Delta_{sol}H^o$, of silver chloride (○), silver bromide (□), and silver iodide (△) in aqueous *DMSO* mixtures

would be similar in these two systems. The systems differ in one important way, that is, there are strong hydrogen bonds between water and the very basic *DMSO*, while hydrogen bonding between water and *AN*, which is much less basic, is much weaker. This is reflected in the excess free energies of the mixtures, which are strongly positive in the *AN* mixtures but negative in the *DMSO* system. The effect of the strong hydrogen bonds is to bind the *DMSO* and water strongly to each other, reducing the extent of preferential solvation of the ions. In effect, the ions must compete with the co-solvent for the preferred solvent molecule. This reduces the marked variations in $\log K_{SO}$ and $\Delta_{sol}H^o$ observed in the aqueous *AN* system, with $\log K_{SO}$ passing through very small maxima or simply reaching plateaux and $\Delta_{sol}H^o$ decreasing monotonically rather than passing through minima.

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