Methorics of the Precipitation Processes. XI.* The Complex Solubility of Silver Halides and Silver Thiocyanate in Mixed Solvents**

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The complex solubility of silver chloride, bromide, iodide, and thiocyanate in halide or thiocyanate solutions in isodielectric mixtures of water-methanol, water-ethanol and water-acetone was determined. Complex solubility of these precipitates increased, in regard to water, with increasing concentration of the organic component in solutions. The increase of complex solubility was nearly the same for water-methanol and water-ethanol mixtures of the same dielectric constant, but the change of complex solubility in corresponding water-acetone mixtures was much greater. The values of the ionic solubilities at different dielectric constants necessary for calculating the stability constants of the complex species present, were obtained from Ricci and Davis' relation. The lowering of the dielectric constant of the medium caused an increase of the stability constants of complexes. The differences observed in solutions of the same dielectric constant but of different composition (water-alcohols against water-acetone mixtures) are tentatively explained by the change in ion-dipole (solvent molecule) binding.

In the course of the investigation of precipitation and coagulation of silver halides in mixed solvents[1] it was of considerable interest to establish the change of complex solubility of these precipitates in various media. Such determinations may be of interest also from a more general point of view. It seems that very little has been done to investigate the influence of the composition and the properties of solvent on complex formation. One could expect that such data might give some insight into the character of forces operating in such systems. It is primarily refered to the contribution of the electrostatic forces in connexion with the change of the dielectric constant of the medium. From the point of view of electrostatics, a lower dielectric constant of the solvent should enhance the stability of the complex species.

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VII. B. Težak and S. Kratohvil-Babić, *Arhiv kem.* **24** (1952) 67.
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IX. V. B. Vouk, J. Kratohvil and B. Težak, *Arhiv kem.* **25** (1953) 219.
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Only few papers dealing with the complex solubility and complex formation of silver halides in mixed or non-aqueous solvents could be found in the relevant literature. Ishii[2] performed some determinations of the complex solubility of silver iodide in potassium iodide dissolved in water-ethanol and water-acetone media (from 0 to 100% of organic solvent). He established in both cases that the complex solubility increases with increasing concentration of ethanol or acetone, the increase in water-acetone mixtures being much greater than in the water-ethanol mixtures. Some data about the complex solubility of silver iodide in acetonic solutions of potassium iodide and sodium iodide may be found in a paper by Koch.[3] From the fact that the concentration ratio of silver and iodide ions at the solubility boundary is 3 : 4, Koch concluded that silver iodide was dissolved in the form of a complex $Ag_3I_4^-$. Enormous increase of complex solubility of silver chloride in solutions of beryllium chloride in pyridine was observed by Schmidt.[4]

Beside these papers we should note the papers by Mackor[5] and Sillén *et al.*[6] From potentiometric and conductometric measurements Mackor concluded that in complex solutions of silver iodide in water-acetone mixtures complex ion AgI^-_2 predominated if the concentration of potassium iodide was not more than 0.01 *N*. In less dilute iodide solutions the existence of polynuclear cmplexes, e. g. $Ag_4I_6^{2-}$, is most probable. Sillén *et al.* showed by means of potentiometric measurements that AgI^-_2 is found in diethylether-$LiClO_4$ (1.0 *N*) — LiI (< 0.05 *N*) solutions. With silver chloride and silver bromide in chloride and bromide solutions no complexes were found.

EXPERIMENTAL

We determined the complex solubility of AgCl, AgBr, AgI, and AgCNS in halide or thiocyanate solutions in isodielectric mixtures of water-methanol, water-ethanol, and water-acetone. The dielectric constants and the corresponding composition of the mixtures used were interpolated from the data given by Akerlöf.[7]

The experimental techniques used in this study were the same as described previously.[8] The concentration range in which the measurements were performed was limited because of decreased solubility of alkaly halides in solvents of smaller dielectric constant. At the same time the solubility of alkali nitrate formed in the precipitation reaction ($AgNO_3 + MX \rightarrow AgX + MNO_3$) was also decreased and the possibility of separation of solid MNO_3 arose. All measurements were performed at 20 ± 0.1° C.

Chemicals of analytical purity grade were used in all experiments. Methanol (Merck, puriss.), ethanol and acetone (commercial products) were distilled twice over $AgNO_3$. The concentrations of mixtures used were expressed in weight-percent.

RESULTS

The results obtained are given in Tables I to V. Each table gives the concentrations of halide or thiocyanate component at which, for a given concentration of silver nitrate and for a given composition of solvent, the solid phase (AgX) disappears. The values of the corresponding dielectric constants of the media are also indicated. The same results are shown in Figs. 1 to 4, where the logarithms of silver nitrate concentrations are plotted against

TABLE I

The solubility of AgCl in solutions of HCl in isodielectric mixtures of water-methanol, water-ethanol and water-acetone at 20⁰. The concentrations of organic solvents in the mixtures are given in weight percent. The dielectric constants (D) of the solvent mixtures are interpolated from the data of Akerlöf.[7] The solubility data for aqueous solutions (25⁰) are interpolated from the results of Forbes[14] and Pinkus and Timmermans.[15]

C_{AgNO_3} (*M*)	C_{HCl} (*M*)				
	Water *D* = 78.5	62% MeOH *D* = 50.4	50% EtOH *D* = 50.4	Me_2CO *D* = 50.4	82% Me_2CO *D* = 29.0
0.001	3.16	2.175		1.65	0.27
0.0004	2.24	1.35	1.425	0.85	0.088
0.0001	1.17	0.58	0.575	0.25	0.0155
0.00004	0.715	0.325	0.29	0.095	0.00525
0.00002	0.457				0.0023
0.00001	0.282	0.095	0.085	0.022	0.00095
0.000004	0.129	0.042		0.007	0.000325
0.000001	0.029	0.0085		0.00095	0.000055

TABLE II

The solubility of AgBr in solutions of KBr in water-ethanol mixtures at 20⁰ The data for aqueous solutions are from the paper of Vouk, Kratohvil and Težak.[8]

C_{AgNO_3} (*M*)	C_{KBr} (*M*)		
	Water *D* = 80.4	50% EtOH *D* = 50.4	90% EtOH *D* = 29.0
0.0015	1.6	0.9125	
0.001	1.38	0.7875	
0.0006	1.17	0.625	
0.0004	1.00	0.51	
0.00025	0.87	0.39	
0.00015	0.724	0.29	
0.0001	0.6	0.23	
0.00006	0.465	0.175	
0.00004	0.4	0.135	0.035
0.000025	0.324	0.097	0.022
0.000015	0.25	0.062	0.0123
0.00001	0.195	0.042	0.0074

the logarithms of halide or thiocyanate concentrations at the solubility boundaries.

Several conclusions can be drawn from these results:

(1) Complex solubility of silver halides and silver thiocyanate increases, in regard to water, with increasing concentration of organic solvents in solutions (increase of complex solubility means that for dissolving equal amount of solid phase less complexing halide ion is necessary; or that the same amount of complexing component in excess can dissolve more solid phase in complex form).

(2) Increase of complex solubility is nearly the same for water-methanol and water-ethanol mixtures of the same dielectric constant, but the change of complex solubility in corresponding water-acetone mixtures is much greater.

TABLE III

The solubility of AgBr in solutions of NaBr in isodielectric mixtures of water-methanol, water-ethanol and water-acetone at 20⁰.

C_{AgNO_3} (M)	C_{NaBr} (M)							
	Water $D = 80.4$	62⁰/₀ MeOH $D = 50.4$	30⁰/₀ EtOH $D = 62.6$	50⁰/₀ EtOH $D = 50.4$	70⁰/₀ EtOH $D = 39.1$	90⁰/₀ EtOH $D = 29.0$	48.5⁰/₀ Me_2CO $D = 50.4$	82⁰/₀ Me_2CO $D = 29.0$
0.01	3.335							
0.006	2.875							0.2125
0.004	2.575						0.95	0.15
0.002	2.07							0.0775
0.001	1.61	0.975	1.35	1.0125	0.775		0.48	0.03625
0.0006	1.38			0.78				0.021
0.0004	1.173	0.625	0.875	0.615	0.44		0.27	0.0135
0.0002	0.922			0.425		0.175		0.0063
0.0001	0.667	0.27	0.425	0.27	0.158	0.0925	0.095	0.002875
0.00006	0.52			0.195		0.0545		0.0018
0.00004	0.425		0.25	0.145	0.0675	0.036	0.044	0.00105
0.00002	0.29	0.0875		0.0875		0.01775		0.000525
0.00001	0.195		0.105	0.043	0.0163	0.00725	0.0115	0.00024
0.000006	0.15			0.0255		0.0045		
0.000004	0.115						0.004	

TABLE IV

The solubility of AgI in solutions of KI in isodielectric mixtures of water-methanol, water-ethanol and water-acetone at 20⁰. The solubility data for aqueous solutions are interpolated from the results of Schulz and Težak.[8]

C_{AgNO_3} (M)	C_{KI} (M)					
	Water $D = 80.4$	62⁰/₀ MeOH $D = 50.4$	50⁰/₀ EtOH $D = 50.4$	90⁰/₀ EtOH $D = 29.0$	48.5⁰/₀ Me_2CO $D = 50.4$	82⁰/₀ Me_2CO $D = 29.0$
0.04	1.23				0.2125	
0.02	1.08		0.825			
0.01	0.925		0.625		0.125	0.025
0.006	0,78		0.55			
0.004	0.7	0.44	0.48		0.085	0.0125
0.002	0.575		0.38	0.125		
0.001	0.45	0.25	0.28	0.0775	0.044	0.0042
0.0006	0.375		0.22	0.0525		
0.0004	0.325	0.155	0.17	0.038	0.025	0.0019
0.0002	0.235		0.105	0.02		
0.0001	0.17	0.0675	0.0625	0.00975	0.0105	0.000525
0.00006	0.135		0.04	000575		
0.00004	0.11	0.0325	0.029	0.00355	0.00475	0.00023
0.00002	0.081	0.0175	0.0155	0.001675		0.000115
0.00001	0.054		0.0085	0.000725	0.00125	0.0000575
0.000006	0.04		0.00525	0.000574		
0.000004	0.0325		0.00345	0.00022	0.0004	
0.000002	0.023					
0.000001	0.015					

TABLE V

The solubility of AgCNS in solutions of KCNS in isodielectric mixtures of water-methanol, water-ethanol and water-acetone at 20⁰.

C_{AgNO_3} (*M*)	C_{KCNS} (*M*)							
	Water *D* = 80.4	62⁰/₀ MeOH *D* = 50.4	30⁰/₀ EtOH *D* = 62.6	50⁰/₀ EtOH *D* = 50.4	70⁰/₀ EtOH *D* = 39.1	90⁰/₀ EtOH *D* = 29.0	48.5⁰/₀Me₂CO *D* = 50.4	*D* = 29.0 82⁰/₀ Me₂CO
0.1	1.205							
0.06	0.95			0.84				
0.04	0.84			0.68				
0.02	0.648			0.49				
0.01	0.485	0.36	0.43	0.35	0.285		0.205	0.102
0.006	0.42			0.285				0.075
0.004	0.36		0.29	0.23	0.19		0.125	0.0525
0.002	0.276			0.165				0.031
0.001	0.2025	0.115	0.145	0.11	0.0825	0.058	0.058	0.019
0.0006	0.179			0.082		0.04		0.0115
0.0004	0.1538	0.0625	0.0925	0.0615	0.0455	0.029	0.03125	0.0077
0.0002	0.108			0.037		0.0165		0.00365
0.0001	0.0795	0.023	0.0425	0.022	0.01375	0.0091	0.0095	0.001675
0.00006				0.0135		0.005		0.000875
0.00004		0.0095	0.021	0.00875	0.0048	0.00345	0.0040	0.000575
0.00002		0.0044	0.0115	0.00385	0.0021	0.00145	0.001625	0.00023
0.00001		0.00175	0.00575	0.001375	0.0009	0.00062	0.000725	0.0000875

(3) The difference between the complex solubility of silver bromide in solutions of potassium bromide and sodium bromide persists in the mixed solvents also.

(4) The order of complex solubility of various silver halides and silver thiocyanate in all solvents used is the same as in aqueous solutions (AgCNS > AgI > AgBr > AgCl), except for 82% acetone (AgI > AgCNS > AgBr > > AgCl).

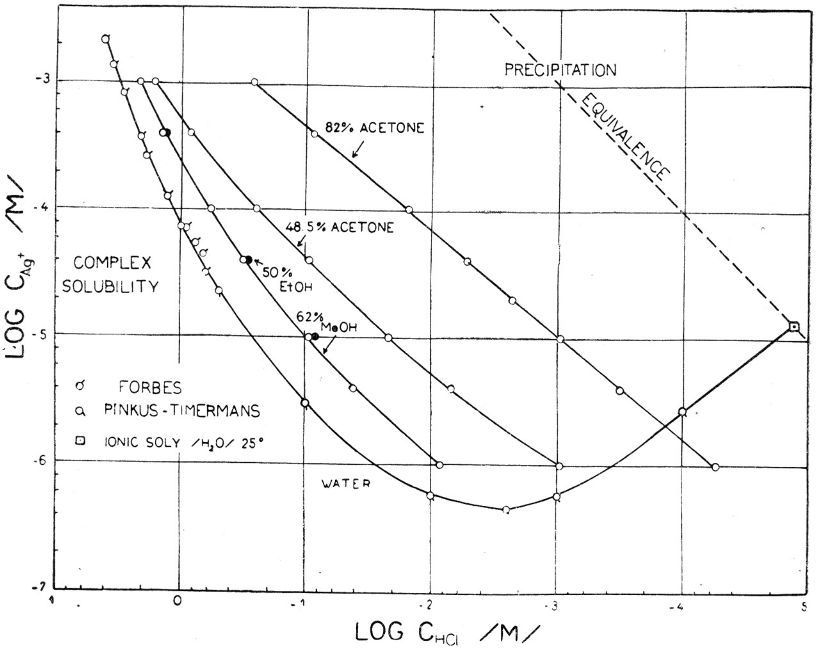

Fig. 1 The complex solubility curves of AgCl in water, 62% methanol, 50% ethanol, and in 48.5 and 82% acetone.

DISCUSSION

The most important measurable quantity concerned in any theory intended to explain and correlate the phenomena connected with complex formation is the stability constant of the complex. It seemed interesting to determine the stability constants of the complex species of silver halides present in various media and to see how they vary with the properties of the solvent.

At this point a difficulty arose: for calculating the stability constants it was necessary to know the values of the solubility products of silver halides for various media.[9] Very little has been done in this respect. In the literature we could find only the data of Koch[10] (AgCl, AgBr and AgI in methanol and ethanol), Buckley and Hartley[11] (AgCNS in methanol), Parton *et al.*[12] (AgCl in water-methanol mixtures), and of Mackor[5] (AgI in water-acetone mixtures). In order to obtain more systematic and complete set of ionic solubility data of silver halides and silver thiocyanate as a function of the dielectric constant of the medium, use was made of the Ricci-Davis relation.[13] The validity and usefullness of this relation was verified on the experimental material mentioned before (Table VI to VIII). It is apparent that Ricci-Davis relation gives the right order of magnitude for the ionic solubility values (except in two cases) and in most cases the differences between the experimental and the calculated values were small. This justified the use of this relation for our purposes.

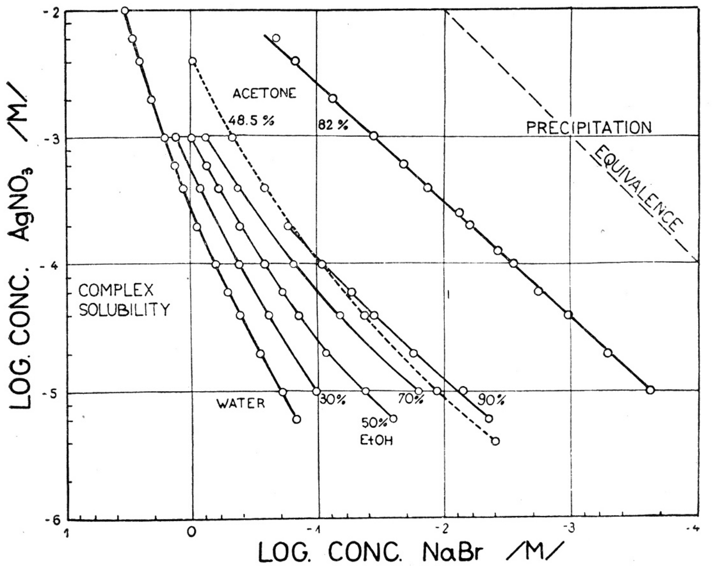

Fig. 2 The complex solubility curves of AgBr in water, 30, 50, 70 and 90% ethanol, and in 48.5 and 82% acetone. Values for 62% methanol are almost at the same place as the values for 50% ethanol (see Table III).

The evaluation of the composition of complex solutions and the calculation of the stability constants of complex species present was performed by a method described previously.[9] The existence of mononuclear complexes only was assumed. This assumption is justified by the fact that we dealt with rather dilute systems.

Tables IX to XII give the results of the interpretation of the solubility data. In each table the solvent composition and the corresponding dielectric constant, the solubility product of the solid AgX, the values of the slopes of the secants by which the solubility curve may be approximated,[9] the concentration range of the component in excess, the dominant complex ion present, its formation constant $k_{m,\,n-m}$, and finally the corresponding stability constant $\beta_{m,\,n}$ of the complex ion, are indicated. It must be kept in mind, however, that the values of stability constants, owing to the approximate values of the corresponding solubility products, are also approximate. From the recoprocal values of the formation constants of the complex AgI^-_2 in water-acetone mixtures and the solubility products of AgI given by Mackor,[5] we calculated the cor-

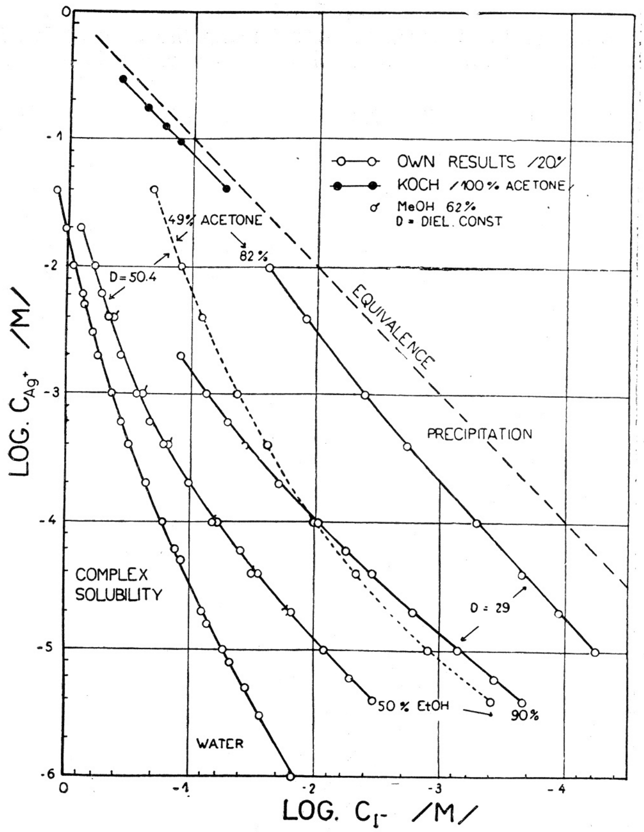

Fig. 3 The complex solubility curves of AgI in water, 62% methanol, 50 and 90% ethanol, and in 48.5 and 82% acetone. The data of Koch (100% acetone) are also included.

TABLE VI

The verification of the Ricci-Davis relation[13] *using the data of Parton et al*[12] *for the ionic solubility of silver chloride in water-methanol mixtures at 25°.*

MeOH wt. %	D	S_{exp} (M)	S_{calc} (M)	S_{calc}/S_{exp}
0	78.5	1.334×10^{-5}	—	—
10	74.1	9.23×10^{-6}	1.12×10^{-5}	1.2
20	69.2	7.67×10^{-6}	9.12×10^{-6}	1.2
50	54.9	3.02×10^{-6}	4.57×10^{-6}	1.5
75	42.5	1.12×10^{-6}	2.12×10^{-6}	1.9
100	31.5	3.9×10^{-7}	8.6×10^{-7}	2.2

responding stability constants. The results of this calculation are brought together in Table XIII with the corresponding data of Sillén *et al.*[6] for diethyl-ether — $LiClO_4$ medium.

TABLE VII

The verification of the Ricci-Davis relation[13] *using the data of Mackor*[5] *for the ionic solubility of silver iodide in water-acetone mixtures at 25⁰.*

Acetone wt. %	D	S_{exp} (M)	S_{calc} (M)	S_{calc}/S_{exp}
0	78.55	1.0×10^{-8}	—	—
44.2	53.19	6.54×10^{-9}	3.12×10^{-9}	0.48
73.5	34.52	2.6×10^{-9}	8.50×10^{-10}	0.33
94.7	23.80	1.4×10^{-10}	2.82×10^{-10}	2.0
100.0	20.94	1.0×10^{-11}	1.91×10^{-10}	19.1

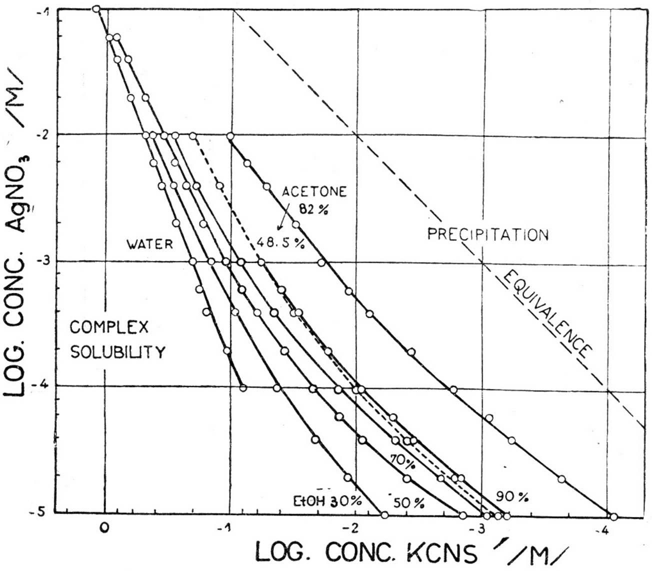

Fig. 4 The complex solubility curves of AgCNS in water, 30, 50, 70 and 90% ethanol, and in 48.5 and 82% acetone. Values for 62% methanol are at almost the same place as the values for 50% ethanol (see Table V).

TABLE VIII

The verification of the Ricci-Davis relation[13] *using the data of Koch*[10] *for the ionic solubility of AgCl, AgBr and AgI in methanol and ethanol, and the data of Buckley and Hartley*[11] *for the solubility of AgCNS in methanol at 25⁰.*

	MeOH ($D = 31.5$)			EtOH ($D = 24.3$)		
	S_{exp} (M)	S_{calc} (M)	$\frac{S_{calc}}{S_{exp}}$	S_{exp} (M)	S_{calc} (M)	$\frac{S_{calc}}{S_{exp}}$
AgCl	3.9×10^{-7}	8.6×10^{-7}	2.2	9.6×10^{-8}	3.9×10^{-7}	4.1
AgBr	3.0×10^{-8}	4.6×10^{-8}	1.5	8.7×10^{-9}	2.1×10^{-8}	2.4
AgI	6.2×10^{-9}	6.5×10^{-10}	0.1	2.1×10^{-10}	2.9×10^{-10}	1.4
AgCNS	1.2×10^{-7}	7.1×10^{-8}	0.6			

TABLE IX

The composition of complex solutions of silver chloride and the formation and stability constants, $k_{m,\,n-m}$ and $\beta_{m,\,n}$, of complex ions evaluated from the complex solubility data of Table I.

Solvent	D	L_{AgCl}	Slope, b	C_{Cl} (M)	Complex	$k_{m,\,n\text{-}m}$	$\beta_{m,\,n}$
Water (25°)	78.5	1.8×10^{-10}	0.0	0.001—0.01	AgCl (aq)	5.8×10^{-7}	3.3×10^{3}
			0.94	0.01—0.5	$AgCl_2^-$	4.5×10^{-5}	2.5×10^{5}
			1.95	0.6—2	$AgCl_3^{2-}$	7.6×10^{-5}	4.3×10^{5}
			2.98	3—6	$AgCl_4^{3-}$	3.0×10^{-5}	1.7×10^{5}
MeOH 62% and EtOH 50%	50.4	3.6×10^{-12}	1.02	0.01—0.3	$AgCl_2^-$	1.3×10^{-4}	3.6×10^{7}
			1.8	0.6—2	$AgCl_3^{2-}$	2.6×10^{-4}	7.2×10^{7}
Acetone 48.5%	50.4	3.6×10^{-12}	0.95	0.01—0.25	$AgCl_2^-$	3.7×10^{-4}	1.0×10^{8}
Acetone 82%	29.0	9.0×10^{-14}	0.85	0.0001—0.25	$AgCl_2^-$	2.9×10^{-3}	3.2×10^{10}

TABLE X

The composition of complex solutions of silver bromide and the formation and stability constants, $k_{m,\,n-m}$ and $\beta_{m,\,n}$, of complex ions, evaluated from the complex solubility data of Table III.

Solvent	D	L_{AgBr}	Slope, b	C_{Br} (M)	Complex	$k_{m,\,n\text{-}m}$	$\beta_{m,\,n}$
Water	80.4	2.9×10^{-13}	0.93	0.01—0.1	$AgBr_2^-$	2.5×10^{-5}	8.6×10^{7}
			2.06	0.3—1	$AgBr_3^{2-}$	2.3×10^{-4}	7.9×10^{8}
			3.18	1.2—3	$AgBr_4^{3-}$	2.0×10^{-4}	6.9×10^{8}
EtOH 30%	62.6	6.8×10^{-14}	1.98	0.4—1.3	$AgBr_3^{2-}$	5.5×10^{-4}	8.1×10^{9}
EtOH 50% and MeOH 62%	50.4	1.8×10^{-14}	1.1	0.025—0.14	$AgBr_2^-$	3.3×10^{-4}	1.8×10^{10}
			1.88	0.4—1	$AgBr_3^{2-}$	1.0×10^{-3}	5.6×10^{10}
EtOH 70%	39.1	4.0×10^{-15}	1.02	0.016—0.16	$AgBr_2^-$	6.6×10^{-4}	1.6×10^{11}
EtOH 90%	29.0	6.6×10^{-16}	0.92	0.004—0.1	$AgBr_2^-$	9.1×10^{-4}	1.4×10^{12}
Acetone 48.5%	50.4	1.8×10^{-14}	1.03	0.004—0.1	$AgBr_2^-$	1.1×10^{-3}	6.1×10^{10}
			1.83	0.25—1	$AgBr_3^{2-}$	4.2×10^{-3}	2.3×10^{11}
Acetone 82%	29.0	6.6×10^{-16}	0.92	0.00025—0.8	$AgBr_2^-$	2.1×10^{-2}	3.2×10^{13}

From Tables IX to XIII it is evident that the stability of the complex ions of silver halides and silver thiocyanate, expressed by the values of the stability constants, increases — in regard to water — with increasing concentrations of the organic solvent. This increase is greater for acetonic solutions than for methanolic or ethanolic solutions of the same dielectric constant.

TABLE XI

The composition of complex solutions of silver iodide and the formation and stability constants, $k_{m,\,n-m}$ and $\beta_{m,\,n}$, of complex ions, evaluated from the complex solubility data of Table IV.

Solvent	D	L_{AgI}	Slope, b	C_I (M)	Complex	$k_{m,\,n-m}$	$\beta_{m,\,n}$
Water	80.4	3.9×10^{-17}	2.0	0.03—0.3	AgI_3^{2-}	3.8×10^{-3}	1.0×10^{14}
			3.0	0.3—0.7	AgI_4^{3-}	1.2×10^{-2}	3.1×10^{14}
EtOH 50% and MeOH 62%	50.4	2.3×10^{-18}	1.1	0.003—0.06	AgI_2^-	2.1×10^{-3}	9.1×10^{14}
			1.85	0.16—0.3	AgI_3^{2-}	1.0×10^{-2}	4.3×10^{15}
			3.0	0.4—0.8	AgI_4^{3-}	4.0×10^{-2}	1.7×10^{16}
EtOH 90%	29.0	8.3×10^{-20}	0.96	0.0016—0.04	AgI_2^-	9.0×10^{-3}	1.1×10^{17}
Acetone 48.5%	50.4	9.0×10^{-18}	1.0	0.0004—0.01	AgI_2^-	8.3×10^{-3}	9.2×10^{14}
			2.0	0.025—0.12	AgI_3^{2-}	5.7×10^{-1}	6.3×10^{16}
Acetone 82%	29.0	3.0×10^{-19}	1.1	0.00006-0.004	AgI_2^-	3.6×10^{-1}	1.2×10^{18}
Acetone 100%(Koch)	21.0	1.0×10^{-22}	1.0	0.05—0.4	$Ag_3I_4^-$	2.5×10^{-1}	2.5×10^{65}
					(ratio $C_{Ag} : C_I = 3 : 4$)		

TABLE XII

The composition of complex solutions of silver thiocyanate and the formation and stability constants, $k_{m,\,n-m}$ and $\beta_{m,\,n}$, of complex ions, evaluated from the complex solubility data of Table V.

Solvent	D	L_{AgCNS}	Slope, b	C_{CNS} (M)	Complex	$k_{m,\,n-m}$	$\beta_{m,\,n}$
Water	80.4	1.0×10^{-12}	2.1	0.08—0.15	$AgCNS_3^{2-}$	2.0×10^{-2}	2.0×10^{10}
			2.8	0.15—1	$AgCNS_4^{3-}$	6.8×10^{-2}	6.8×10^{10}
EtOH 30%	62.6	2.3×10^{-13}	1.14	0.006—0.04	$AgCNS_2^-$	4.0×10^{-3}	1.7×10^{10}
			2.1	0.1—0.4	$AgCNS_3^{2-}$	6.0×10^{-2}	2.6×10^{11}
EtOH 50% and MeOH 62%	50.4	6.0×10^{-14}	1.03	0.004—0.04	$AgCNS_2^-$	6.0×10^{-3}	1.0×10^{11}
			2.1	0.16—0.8	$AgCNS_3^{2-}$	9.0×10^{-2}	1.5×10^{12}
EtOH 70%	39.1	1.3×10^{-14}	0.98	0.002—0.05	$AgCNS_2^-$	8.0×10^{-3}	6.1×10^{11}
			1.9	0.08—0.3	$AgCNS_3^{2-}$	1.1×10^{-1}	8.5×10^{12}
EtOH 90%	29.0	2.2×10^{-15}	1.03	0.003—0.016	$AgCNS_2^-$	1.4×10^{-2}	6.4×10^{12}
Acetone 48.5%	50.4	6.0×10^{-14}	0.91	0.0008—0.01	$AgCNS_2^-$	6.0×10^{-3}	1.0×10^{11}
			1.83	0.05—0.2	$AgCNS_3^{2-}$	1.8×10^{-1}	3.0×10^{12}
Acetone 82%	29.0	2.2×10^{-15}	0.92	0.0006—0.012	$AgCNS_2^-$	3.5×10^{-2}	1.6×10^{13}
			1.4	0.02—0.1	?		

TABLE XIII

The solubility products L of AgI, and the formation and stability constants $k_{1,1}$ *and* $\beta_{1,2}$, *of complex ion* AgI^-_2 *in water-acetone mixtures (Mackor*[5]*) and in diethylether —* $LiClO_4$ *(1.0 M) solutions (Sillén et al.*[6]*). Temp. 25*^{0}.

Acetone mol. %	L	$k_{1,1}$	$\beta_{1,2}$
0	1.0×10^{-16}	1.0×10^{-3}	1.0×10^{13}
61.35	1.25×10^{-18}	8.7×10^{-1}	7.0×10^{17}
72.62	2.0×10^{-19}	3.0	1.5×10^{19}
83.81	2.5×10^{-20}	7.1	2.8×10^{20}
100	1.0×10^{-22}	42.0	4.0×10^{23}
Diethylether —$LiClO_4$ (1.0 *M*)	3.55×10^{-24}	2.4×10^{-2}	6.8×10^{21}

On the basis of our results it may be said that the dielectric constant of the solvent is one of the important factors affecting the stability of complex ions. But since the complex formation may be regarded as the displacement of the solvent molecules around the metal ion by the ligands, the differences in ion-dipole (solvent molecule) binding become very important. This explains probably the enormous effect of acetone on complex solubility and complex formation of silver halides and silver thiocyanate.

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IZVOD

Metorika precipitacionih procesa. XI. Kompleksna topljivost argentum halogenida i argentum rodanida u miješanim otapalima

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Odredili smo kompleksnu topljivost AgCl, AgBr, AgJ i AgCNS u otopinama halogenid, odnosno rodanid iona u izodielektričkim smjesama voda-metanol, voda-etanol i voda-aceton kod 20^0. Kompleksna topljivost ovih precipitata raste s povećanjem koncentracije organskog otapala u otopini. Povećanje kompleksne topljivosti približno je jednako za smjese voda-metanol i voda-etanol iste dielektričke konstante, dok je promjena kompleksne topljivosti za smjese voda-aceton mnogo veća.

Pomoću relacije Ricci-a i Davis-a odredili smo približne vrijednosti ionske topljivosti argentum halogenida i rodanida u medijima s različitim dielektričkim konstantama, koje su bile potrebne pri izračunavanju konstanti stabiliteta prisutnih kompleksnih iona. Smanjenjem dielektričke konstante medija povećavaju se konstante stabiliteta.

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