CCA - 54 546.571.2-86:541.8

Methorics of the Precipitation Processes. XV. Some Further Experiments on the Influence of the Solvent on the Complex Solubility of Silver Halides and Silver Thiocyanate*

J. Kratohvil and B. Težak

School of Public Health, Faculty of Medicine, and Laboratory of Physical Chemistry, Faculty of Science, University of Zagreb, Zagreb, Croatia, Yugoslavia

Received June 4, 1957

The complex solubility of silver chloride, silver bromide, silver iodide, and silver thiocyanate in halide or thiocyanate solutions in isodielectric mixtures of water with *n*-propanol, *iso*-propanol, ethylene glycol, glycerol or dioxane was determined. The increase of the complex solubility was nearly the same for the isodielectric mixtures of water with alcohols irrespective of the alcohol used. Dioxane showed some specific action. The results obtained are compared with previously reported data.

It was established in previous papers[1,2] that the complex solubility of silver halides and silver thiocyanate in halide or thiocyanate solutions increases, relative to that in water, with the increasing concentration of organic solvents in the solutions. This increase of the complex solubility had almost the same value for the isodielectric mixed solvents of water with alcohols, while the change of the complex solubility for solvents of different character was much greater.

In this note the results of the solubility determinations are given for silver halides and silver thiocyanate in the corresponding halide or thiocyanate solutions containing isodielectric quantities of various solvents, and are compared with previously reported data.

EXPERIMENTAL

The isodielectric mixtures of water with *n*-propanol, *iso*-propanol, ethylene glycol, glycerol or dioxane were used as solvents. The dielectric constants and the corresponding compositions of the mixtures used were interpolated from the data given by Akerlöf and Short[3]. The concentrations of the solvent mixtures were expressed in weight percent.

The experimental techniques used in this study were described previously[4]. All determinations were performed at 20° C in solutions with uncontrolled ionic strength for reasons given in previous papers.[1,2].

Chemicals of analytical purity grade were used. Solvents were distilled at least once over $AgNO_3$.

* Contribution No. 65 from the Laboratory of Physical Chemistry. The data of this study were partly presented at the International Conference on Coordination Compounds, Amsterdam, April 1955. See reference[2].

RESULTS AND DISCUSSION

The results obtained are shown in Tables I to IV. Each table gives the concentrations of halide or thiocyanate component at which, for a given concentration of silver nitrate, the solvent mixture is saturated with the corresponding silver compound.

TABLE I

The solubility of AgCl in solutions of HCl in isodielectric mixtures of water with n-propanol, iso-propanol, glycerol, and dioxane at 20°

C_{AgNO_3} (*M*)	C_{HCl} (*M*)					
	D = 62.6	D = 50.4		D = 29.0		
	Glycerol 57.0%	*n*-PrOH 42.0%	*iso*-PrOH 40.5%	*n*-PrOH 75.0%	*iso*-PrOH 71.0%	Dioxane 57.5%
0.001		2.25	2.3			0.95
0.0004		1.45	1.55	0.85	0.825	0.38
0.0002	1.25				0.44	
0.0001	0.77	0.575	0.61	0.225	0.21	0.085
0.00004	0.425	0.305	0.29	0.08	0.075	0.03
0.00002					0.0345	
0.00001	0.145	0.0875	0.085	0.0135	0.0135	0.0062
0.000004	0.065	0.0375	0.035	0.004	0.00375	0.0021
0.000002					0.0013	0.00085
0.000001	0.0155				0.00035	0.00033

These results confirm our previous conclusions about the influence of the solvent on complex solubility and complex formation. The changes of the complex solubility of silver halides and thiocyanate, relative to the water, were essentially the same for the isodielectric alcoholic mixtures, irrespective of the alcohols used (methanol, ethanol,[1] *n*-propanol, *iso*-propanol, ethylene

TABLE II

The solubility of AgBr in solutions of NaBr in isodielectric mixtures of water with n-propanol, iso-propanol, ethylene glycol, glycerol, and dioxane at 20°.

C_{AgNO_3} (*M*)	C_{NaBr} (*M*)							
	D = 62.6			D = 50.4		D = 29.0		
	iso-PrOH 24.0%	Ethylene glycol 55.0%	Glycerol 57.0%	*n*-PrOH 42.0%	*iso*-PrOH 40.5%	*n*-PrOH 75.0%	*iso*-PrOH 71.0%	Dioxane 57.5%
0.001	1.375		1.35		1.05			0.355
0.0004	0.90	0.93	0.875	0.65	0.675	0.375	0.385	0.155
0.0002							0.23	0.075
0.0001	0.425	0.425	0.42	0.275	0.29	0.011	0.125	0.039
0.00004	0.25	0.245	0.25	0.15	0.155	0.04	0.044	0.015
0.00002							0.01875	0.0076
0.00001	0.1025	0.105	0.105	0.045	0.0475	0.007	0.00675	0.0037
0.000004	0.06		0.0575					

glycol, and glycerol). It seems that the dielectric constant of the medium is a factor of primary importance for the complex formation in water-alcohols solutions.

But the results with water-dioxane and water-acetone[1] mixtures indicate that other factors seem also to be involved. These solvents showed some specific action often encountered in studies of the influence of solvents on various systems. This specific action manifested itself in our experiments in a much

TABLE III

The solubility of AgI in solutions of KI in isodielectric mixtures of water with n-propanol, iso-propanol, ethylene glycol, glycerol, and dioxane at 20°.

C_{AgNO_3} (*M*)	C_{KI} (*M*)							
	D = 62.6			D = 50.4		D = 29.0		
	iso-PrOH 24.0%	Ethylene glycol 55.0%	Glycerol 57.0%	*n*-PrOH 42.0%	*iso*-PrOH 40.5%	*n*-PrOH 75.0%	*iso*-PrOH 71.0%	Dioxane 57.5%
0.01				0.65				0.39
0.004				0.45	0.48			0.21
0.001	0.32	0.315	0.315	0.255	0.27	0.115	0.125	0.053
0.0004	0.215	0.225	0.21	0.16	0.167	0.055	0.0575	0.021
0.0002							0.03	
0.0001	0.0975	0.1025	0.105	0.065	0.0675	0.0115	0.0135	0.0055
0.00004	0.065	0.063	0.0625	0.031	0.029	0.00475	0.0054	0.0023
0.00002							0.0024	0.00115
0.00001	0.029	0.029	0.0285	0.008	0.0085	0.0009	0.00095	0.00056

greater change of the complex solubility with the change of the dielectric constant of the medium, as compared with the changes due to the alcohols.

The calculation of the stability constants of the complex species formed in mixed solvents which were used in this study may be superfluous for two

TABLE IV

The solubility of AgSCN in solutions of KSCN in isodielectric mixtures of water with n-propanol, iso-propanol, glycerol, and dioxane at 20°.

C_{AgNO_3} (*M*)	C_{KSCN} (*M*)					
	D = 62.6	D = 50.4		D = 29.0		
	Glycerol 57.0%	*n*-PrOH 42.0%	*iso*-PrOH 40.5%	*n*-PrOH 75.0%	*iso*-PrOH 71.0%	Dioxane 57.5%
0.01	0.425	0.35	0.365	0.265	0.285	0.185
0.004		0.24	0.235	0.150	0.175	0.1125
0.002					0.115	
0.001	0.155	0.115	0.115	0.0675	0.0725	0.037
0.0004		0.615	0.0625	0.0325	0.035	0.015
0.0002					0.019	
0.0001	0.0425	0.0215	0.02125	0.00875	0.0085	0.0031
0.00004	0.023	0.009	0.0095	0.00315	0.00285	0.00105
0.00002	0.013				0.00105	0.00045
0.00001	0.007	0.00145	0.00155	0.00055	0.0004	0.00022

reasons. First, the solubility curves of silver halides and thiocyanate are the same as was established previously[1,2]. This means that the graphical method for the analysis of the complex solutions[5] must give the same results, if the solubility products have equal values. Second, only few data can be found about the values of the solubility products of silver halides and thiocyanate in various solvents. Therefore the Ricci-Davis relation[6] has to be used to obtain the approximate values of the solubility products for the various dielectric constants of the medium, which was done in previous papers[1,2].

The results presented in this paper are in agreement with several experiments published recently by Golub[7] on the influence of solvents on the complex solubility of silver thiocyanate.

REFERENCES

1. J. Kratohvil and B. Težak, *Arhiv kem.* **26** (1954) 243.
2. J. Kratohvil and B. Težak, *Rec. trav. chim.* **75** (1956) 774.
3. G. Akerlöf, *J. Am. Chem. Soc.* **54** (1932) 4125; G. Akerlöf and O. A. Short, *J. Am. Chem. Soc.* **58** (1936) 1241.
4. K. Schulz and B. Težak, *Arhiv kem.* **23** (1951) 200; V. B. Vouk, J. Kratohvil and B. Težak, *Arhiv kem.* **25** (1953) 219.
5. J. Kratohvil, B. Težak and V. B. Vouk, *Arhiv kem.* **26** (1954) 191; B. Težak, *Proc. Symp. Coordination Chem.*, Copenhagen 1954, pp. 83—85.
6. T. W. Davis, J. E. Ricci and C. G. Souter, *J. Am. Chem. Soc.* **61** (1939) 3274; J. E. Ricci and T. W. Davis, *J. Am. Chem. Soc.* **62** (1940) 407; J. E. Ricci and A. R. Leo, *J. Phys. Chem.* **45** (1941) 1096; J. E. Ricci and G. J. Nesse, *J. Am. Chem. Soc.* **64** (1942) 2305.
7. A. M. Golub, *Zhur. Obshcheĭ Khim.* **26** (1956) 1837.

IZVOD

Metorika precipitacionih procesa. XV. Utjecaj otapala na kompleksnu topljivost srebrnih halogenida i srebrnog rodanida.

J. Kratohvil i B. Težak

Odredili smo kompleksnu topljivost AgCl, AgBr, AgJ i AgSCN u otopinama halogenidnih, odnosno rodanidnih iona u izodielektričkim smjesama voda — *n*-propanol, voda — *izo*-propanol, voda — etilen glikol, voda — glicerol i voda — dioksan. Povećanje kompleksne topljivosti podjednako je za smjese vode s alkoholima iste dielektričke konstante, a dioksan pokazuje neke specifične efekte. Rezultati su uspoređeni s podacima iz objavljenih radova.

ŠKOLA NARODNOG ZDRAVLJA
MEDICINSKI FAKULTET
I
FIZIČKO-KEMIJSKI INSTITUT
PRIRODOSLOVNO-MATEMATIČKI FAKULTET
SVEUČILIŠTA U ZAGREBU

Primljeno 4. lipnja 1957.