Monatshefte für Chemie 123, 891 – 897 (1992)

Monatshefte für Chemie
Chemical Monthly

Influence of the Medium upon the Rate of Complexing of In^{3+} and Ga^{3+}

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Summary. The rate and the rate constant of the process of complexing of In^{3+} and Ga^{3+} were evaluated in media containing hydrochloric acid, sulfuric acid or nitric acid and different organic solvents. It was established that the rate of the process is maximum in aqueous-acid environments (without presence of organic additions), in almost all investigated cases in the first minutes of the reaction.

Keywords. Reaction rate; Rate constant; Complexing; Gallium; Indium.

Einfluß des Reaktionsmediums auf die Komplexierungsgeschwindigkeit von In^{3+} und Ga^{3+}

Zusammenfassung. Es wurden die Komplexierungsgeschwindigkeiten von In^{3+} und Ga^{3+} in Lösungsmittelsystemen mit Salzsäure, Schwefelsäure oder Salpetersäure und verschiedenen organischen Lösungsmitteln gemessen. Dabei konnte gezeigt werden, daß die Geschwindigkeit in wäßrig-saurem Medium (ohne Zusätzen von organischen Verbindungen) und dann fast immer in den ersten Minuten der Reaktion am größten ist.

Introduction

The separation of Ga^{3+} and In^{3+} from solutions with small concentration is based mainly on the process of complexing of the ions [1 – 6]. Investigations on the influence of organic solvents on the state of Ga^{3+} and In^{3+} in solutions containing mineral acids are also made [4 – 6]. It is established that in acid solutions of $In(NO_3)_3$ hydroxo-complexes of In^{3+} are present [7]. Hydroxo-complexes of Ga^{3+} in acid environments are fixed at $pH = 1.5$ up to 2.5, mainly containing $Ga(OH)^{2+}$ [8]. The process of complexing of In^{3+} in acid solutions of chlorides and other halogens is also studied [9]. The coefficients of activity of Ga^{3+} are determined in concentrated aqueous solutions of chlorides, bromides, and thiocyanides. The values of these coefficients may be connected with the process of hydration of the ions [10].

The objective of the present work is to determine the influence of some organic compounds in acid solutions of Ga^{3+} and In^{3+} on the rate of complexing in these solutions.

Experimental Part

Solutions are prepared as follows:

1. $Ga(ClO_4)_3/H_2O$/mineral acid (HCl, H_2SO_4 or (HNO_3)/organic compound (CH_3OH, C_2H_5OH, C_3H_7OH or CH_3COCH_3).

2. $In(ClO_4)_3/H_2O$/mineral acid (HCl, H_2SO_4 or (HNO_3)/organic compound (CH_3OH, C_2H_5OH, C_3H_7OH or CH_3COCH_3).

The concentration of Ga^{3+} in the solutions was 57.3×10^{-5} mol/l (of In^{3+} 34.85×10^{-5} mol/l, respectively). The concentration of HNO_3 (HCl or H_2SO_4, respectively) was 0.3 mol/l. Experiments were carried out also with solutions containing a mineral acid with a concentration of 3 mol/l. The aqueous-organic media were obtained by addition of organic components mentioned above to the prepared solutions in quantity of 60% vol.

The change of the concentration of Ga^{3+} and In^{3+} in so prepared systems was determined periodically by using a spectro-photometrical method with employment of 1-(2-pyridil-azo)-resorcinol monosodium. The collected data were used for drawing of the kinetic curves i. e. the curves "concentration of the metal ion versus the time". The kinetic curves for In^{3+} in solutions of 3 mol/l HNO_3, HCl, and H_2SO_4 are shown in Figs. 1 – 3.

Results and Discussion

As it may be readily seen from the curves shown in Figs. 1 – 3 an intense development of the process of complexing occurs during the first 2 – 5 minutes only. It should be noted that a similar development of the process was found for all cases under consideration. The variation of the concentration of the metal ion was determined until it began to increase or to remain unchanged which may be explained by

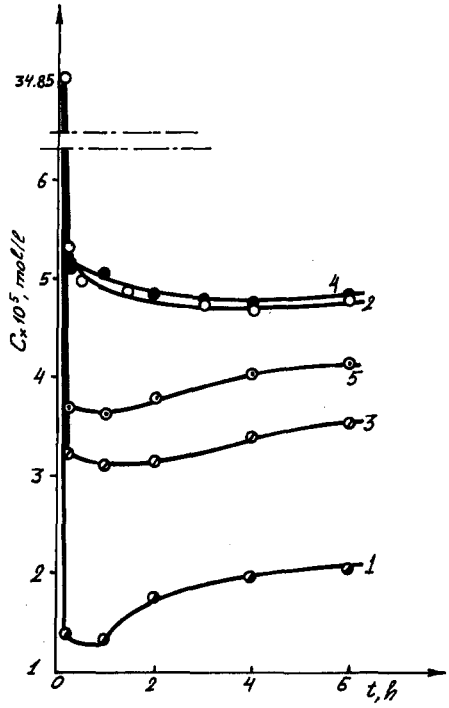

Fig. 1. Variation in the concentration of In^{3+} in solutions of 3 mol/l HNO_3: *1* without organic solvent; *2* with ethanol; *3* with methanol; *4* with n-propanol; *5* with acetone

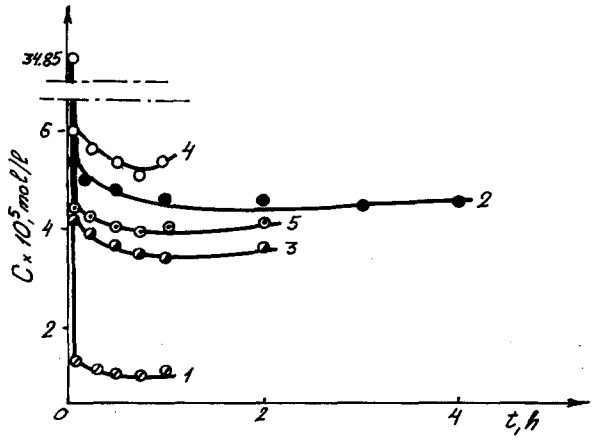

Fig. 2. Variation in the concentration of In^{3+} in solutions of 3 mol/l H_2SO_4: *1* without organic solvent; *2* with ethanol; *3* with methanol; *4* with n-propanol; *5* with acetone

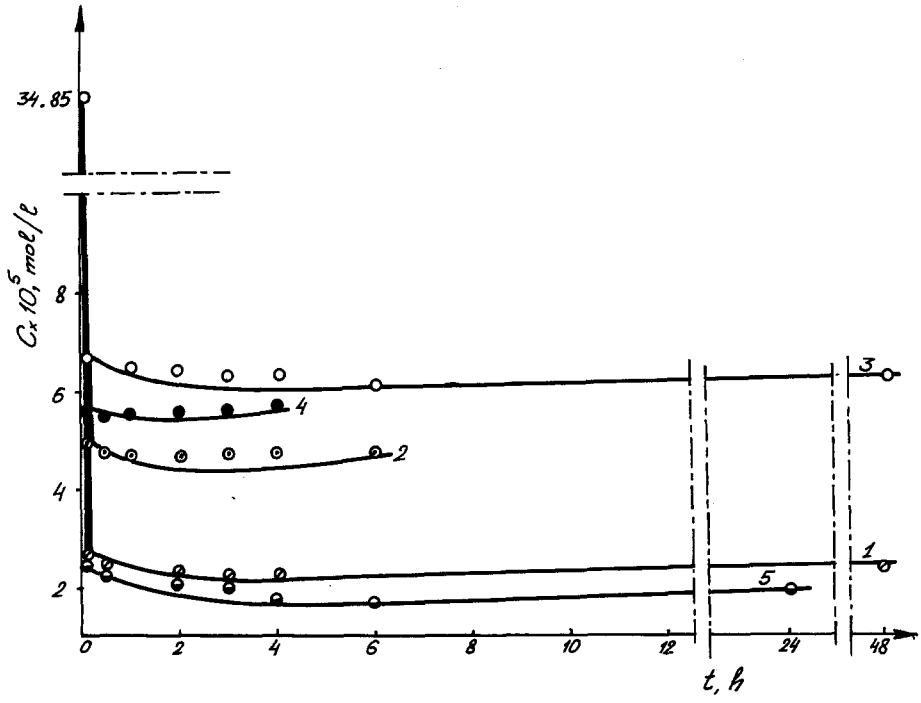

Fig. 3. Variation in the concentration of In^{3+} in solutions of 3 mol/l HCl: *1* without organic solvent; *2* with ethanol; *3* with methanol; *4* with n-propanol; *5* with acetone

development of a process of destruction of the complexes or by establishment of an equilibrium, respectively. Obviously, the kinetics of complexing of Ga^{3+} or In^{3+} may be divided into two periods. The first, in which the reaction takes place with a very high rate. The duration of this period is about 2 – 5 minutes. In the second one, the duration of which for distinct solutions is very different (from 20 minutes up to 198 hours) the rate of the process is much slower.

Table 1. Rate of the reaction of complexing of In^{3+} in different media

Addition of organic solvent	Rate of Complexing, W, mol/l·h × 10^5											
	In^{3+} in 0.3 mol/l H_2SO_4		In^{3+} in 3 mol/l H_2SO_4		In^{3+} in 0.3 mol/l HCl		In^{3+} in 3 mol/l HCl		In^{3+} in 0.3 mol/l HNO_3		In^{3+} in 3 mol/l HNO_3	
	1. period (0–2 min)	2. period	1. period (0–2 min)	2. period	1. period (0–2 min)	2. period	1. period (0–2 min)	2. period	1. period (0–2 min)	2. period	1. period (0–2 min)	2. period
–	1 006.2	0.6558 (2–45 min)	1 004.7	0.4326 (2–45 min)	947.4	0.1395 (2–45 min)	964.2	0.0821 (2 min–6 h)	988.8	0.1147 (2 min–5 h)	1 003.8	0.0621 (2–60 min)
Methanol	930.6	0.7966 (2–60 min)	917.1	0.9207 (2–60 min)	881.4	1.0448 (2–60 min)	846.9	0.0526 (2 min–12 h)	916.5	0.2999 (2–60 min)	946.2	0.2172 (2–60 min)
Ethyl alcohol	898.2	0.4465 (2–45 min)	883.8	0.3168 (2 min–3 h)	873.0	0.4474 (2 min–2 h)	897.3	0.2483 (2 min–1 h)	870.3	0.0821 (2 min–5 h)	885.6	0.1289 (2 min–5 h)
n-Propyl alcohol	876.3	1.2698 (2–45 min)	864.9	1.2558 (2–45 min)	846.9	0.1805 (2 min–12 h)	878.4	0.1928 (2–30 min)	881.0	0.2932 (2 min–90 h)	892.2	0.0605 (2 min–24 h)
Acetone	922.2	0.8791 (2–45 min)	914.1	0.6698 (2–45 min)	967.2	0.3857 (2–30 min)	972.61	0.1307 (2 min–6 h)	911.7	0.0517 (2–60 min)	934.8	0.0517 (2–60 min)

Table 2. Rate constants of the reaction of complexing of In^{3+} in different media

Addition of organic solvent	Average rate constants K, min^{-1}					
	for In^{3+} in H_2SO_4		for In^{3+} in HCl		for In^{3+} in HNO_3	
	1. period	2. period	1. period	2. period	1. period	2. period
–	95.7386	0.4549	73.8063	0.0374	92.1941	0.0600
Methanol	64.8799	0.2331	52.6915	0.0221	66.6988	0.0695
Ethyl alcohol	57.3948	0.0709	56.3336	0.0700	54.9609	0.0203
Propanol	53.6573	0.2552	52.4437	0.1125	56.5475	0.0324
Acetone	63.1751	0.2026	78.8237	0.1127	64.5205	0.0128

The average rate of complexing (W) was estimated by means of a graphical differentiation of the kinetic curves. The obtained values of W are shown in Table 1 for In^{3+} and in Table 3 for Ga^{3+}. The kinetic order of the process was determined by replacement of the experimental data in the kinetic equations of mono-molecular, bi-molecular and three-molecular reactions. It was established that the data satisfy the kinetic equations of mono-molecular reactions for both kinetic periods, for all investigated cases. The process of complexing of In^{3+} and Ga^{3+} in the used media should be considered as a reaction of first order. Further, the numerical values of the rate constants K of the process were evaluated by using the kinetic equation of mono-molecular reactions. The obtained values of K are shown in Tables 2 and 4 for In^{3+} and Ga^{3+}, respectively.

From the data shown in Tables 1 – 4 a few conclusions may be drawn:

1. The main amount of the complexes of In^{3+} and Ga^{3+} in the investigated media is obtained in the first minutes of the process of complexing. This observation may be useful for the manufacture of metallic gallium and indium and their compounds by means of complexing.

2. The process of complexing takes place with a higher rate in pure aqueous-acid environments without organic solvent additives.

Table 4. Rate constants of the reaction of complexing of Ga^{3+} in different media

Addition of organic solvent	Average rate constants K, min^{-1}					
	for Ga^{3+} in H_2SO_4		for Ga^{3+} in HCl		for Ga^{3+} in HNO_3	
	1. period	2. period	1. period	2. period	1. period	2. period
–	90.1253	0.2003	28.4483	0.5690	51.8952	0.0614
Methanol	5.1017	0.084	2.5594	–	13.7098	0.0359
Ethyl alcohol	8.9314	0.0985	4.1553	0.6671	9.2416	0.7053
Propanol	–	–	–	–	6.3215	–
Acetone	3.3905	0.1990	0.4076	–	3.3608	0.0412

Table 3. Rate of the reaction of complexing of Ga^{3+} in different media

Addition of organic solvent	Rate of Complexing, W, mol/l·h × 10^5											
	Ga^{3+} in 0.3 mol/l H_2SO_4		Ga^{3+} in 3 mol/l H_2SO_4		Ga^{3+} in 0.3 mol/l HCl		Ga^{3+} in 3 mol/l HCl		Ga^{3+} in 0.3 mol/l HNO_3		Ga^{3+} in 3 mol/l HNO_3	
	1. period (0–2 min)	2. period	1. period (0–2 min)	2. period	1. period (0–2 min)	2. period	1. period (0–2 min)	2. period	1. period (0–2 min)	2. period	1. period (0–2 min)	2. period
–	1 634.0	0.2930 (2–45 min)	1 638.0	0.5520 (2–30 min)	1 167.1	17.0512 (2–45 min)	1 041.3	2.1637 (2 min–6 h)	1 321.51	0.5198 (2 min–12 h)	1 484.7	2.6326 (2 min–2 h)
Methanol	281.1	3.6279 (2–45 min)	267.0	5.1628 (2–45 min)	129.3	6.7384 (2–15 min)	152.1	3.7241 (2–60 min)	557.4	0.1587 (2 min–168 h)	696.6	1.8654 (2 min–6 h)
Ethyl alcohol	455.0	3.4884 (2–45 min)	431.0	3.9130 (2–25 min)	230.1	4.6154 (2–15 min)	215.1	6.3333 (2–20 min)	–	–	454.2	3.9605 (2 min–4 h)
n-Propyl alcohol	–	–	–	–	–	–	–	–	–	–	324.9	–
Acetone	215.1	17.2800 (2–30 min)	152.1	6.0000 (2–25 min)	44.1	4.0800 (2–30 min)	5.040	4.7143 (2–30 min)	–	–	180.3	1.7430 (2 min–6h)

3. In general, the rate of the process of complexing is higher in solutions of H_2SO_4 in comparison with solutions of HNO_3 and HCl. This observation is valid especially for the complexing of gallium.

4. The rate of the process of complexing of Ga^{3+} in organic-aqueous environments is slower than for In^{3+}.

References

[1] Krans K. A., Nelson F., Smith J. (1954) J. Phys. Chem. **58**: 11
[2] Krans K. A., Michelson D., Nelson F. (1959) J. Am. Chem. Soc. **81**: 3204 and 3207
[3] Irving H. M., Rossotti F. I. (1952) Analist **77**: 801
[4] Alimarin I. P., Tzintzevitch E. P., Usova E. P. (1961) Newspaper of the University of Moscow (in Russ.) **2**: 31
[5] Shishkova L. G. (1982) Thesis (in Bulg.) Sofia
[6] Shishkova L. G. (1989) Annual of the Higher Institute of Mining and Geology (in Bulg.) **35** III: 267
[7] Caminiti R., Johanson G., Toth I. (1986) Acta Chem. Scand. **A40**: 435
[8] Davidov U. P., Kudriashov V. P., Mironov V. P. (1988) C. R. AN BSSR (chem. ser.) **5**: 25
[9] Strijov N. K. (1987) J. Gen. Chem. (Russ) **57**: 1142
[10] Kremer V. A. (1989) Proceedings of Conference "Chemistry and Using of Non-aqueous Solutions" (in Russ) Harkov **1**: 124

Received August 6, 1991. Revised October 14, 1991. Accepted October 22, 1991