

# Anion exchange in mixed solvent systems. IV. Determination of the mean ligand numbers of chloro complexes of Co, Ce, Ba, and Cs in mixed solvents and in anion exchanger

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The information on the prevailing complex form of radioactive micro-component in the liquid phase as well as inside the ion-exchange resin is very helpful for the appreciation of equilibrium states, mechanism and the rate of ion-exchange process in organic-aqueous solvent systems containing hydrochloric acid. In view of this fact the mean ligand numbers of some chloro complexes of Co, Ce, Ba, and Cs were determined for mixed solvent systems water—hydrochloric acid—organic solvent and for anion exchanger. The values of the mean ligand numbers of investigated chloro complexes in the liquid phase as well as inside the ion-exchange resin were correlated with the composition of mixed medium.

The method of ion exchange [1–3] is one of the methods suitable for the study of the complex forms of a microcomponent in aqueous solutions. This method may also be used for the determination of the complex forms of a microcomponent inside an exchanger. *Waki* [4] developed a method allowing to determine the complex forms of metallic elements inside the ion-exchange resin in aqueous solutions of complex-forming substances. The indirect method involving the combined procedure with cation as well as anion exchanger is used in order that some data concerning the state of a microcomponent in the inner solution of anion exchanger may be obtained.

*Greene* [5] modified the method of *Fritz* and *Waki* [6] for the determination of the mean ligand number in the phase of solution and ion exchanger. Provided the ionic strength is maintained constant, the mean ligand number  $\bar{m}$  in a solution containing cation exchanger may be calculated according to the following expression

$$\frac{d \log K_{dk}}{d \log (Cl^-)_t} = -\bar{m}, \quad (1)$$

where  $K_{dk}$  — equilibrium distribution coefficient of microcomponent in the system cation exchanger—mixed solvent,

$(Cl^-)_t$  — total analytical concentration of  $Cl^-$  ions (ligand) in solution,

$\bar{m}$  — mean ligand number in liquid phase.

The value of  $\bar{m}$  can be evaluated from the limiting slope of the curve  $\log K_{dk}$  vs.  $\log (Cl^-)_t$ .

The determination of the mean ligand number in the inner solution of anion exchanger  $\bar{n}$  may be calculated according to the expression

$$\frac{d(\log K_{da} + (\bar{m} - z) \log (Cl^-)_t)}{d \log [Cl^-]_t} = \bar{n} - z, \quad (2)$$

where  $K_{da}$  — equilibrium distribution coefficient of microcomponent in the system anion exchanger—mixed solvent,

$\bar{n}$  — mean ligand number in the inner solution of anion exchanger,

$z$  — charge of central atom,

$(Cl^-)_t$  — total analytical concentration of  $Cl^-$  ions (ligand) in the phase of solution.

$[Cl^-]_t$  — total analytical concentration of  $Cl^-$  ions (ligand) in the phase of exchanger obtained from the penetration of macrocomponent (ligand) into anion exchanger.

Provided  $(\log K_{da} + (\bar{m} - z) \log (Cl^-)_t)$  is expressed as a function of  $\log [Cl^-]_t$ , the value of  $\bar{n}$  may be obtained as the limiting slope at  $[ClO_4^-] = 0$  of this function.

The data about the state of a microcomponent in mixed solvents and anion exchanger thus obtained are of good use in understanding and stating the ion-exchange mechanism for different compositions of mixed solution. Moreover, they help to explain variances of the values of equilibrium distribution coefficients with the composition of liquid phase and give the basis for the study of the kinetics of anion exchange in mixed solvent systems.

## Experimental

The effect of the composition of mixed solvent system on the complex form of microcomponent was studied in mixed solutions water—hydrochloric acid—ethyl alcohol or acetone. The isotope  $^{60}Co$  was used as an indicator with respect to a suitable variability of the values of equilibrium distribution coefficients depending on the concentration of macrocomponents in mixed solution.

Cs, Ba, and Ce were chosen as indicator microcomponents of the groups of alkaline metals, alkaline earth and rare earth elements which are sorbed by anion exchanger only in the presence of a high content of organic solvents [7]. The study of the forms of these microcomponents was carried out only in mixed media with a high content of acetone.

The determination of the mean ligand numbers was carried out by batch equilibration method. The exchange system consisted of an anion exchanger Dowex 2X-8 (100–200 mesh) with the first portion of mixed solution and the cation exchanger Dowex 50 WX-8 (100–200 mesh) with the second portion of mixed solution. Before use the ion exchangers were so treated that the particles below the lower limit of exchanger grain-size were removed by countercurrent sedimentation. The suspension of exchanger was heated to 60°C and degased by a water pump. The anion and the cation exchangers were several times cyclically transformed into the forms  $Cl^- - OH^- - Cl^-$  and  $H^+ - Na^+ - H^+$  respectively, washed with distilled water, dried at 60°C, and kept in desiccator over silica gel.

The stock solutions of radionuclides with the activity of 10–20  $\mu Ci ml^{-1}$  and the following amounts of isotopic carriers were used:  $^{60}Co$  — 5  $\mu g ml^{-1}$ , carrier-free  $^{137}Cs$ , carrier-free  $^{141}Ba$ ,  $^{144}Ce$  — 0.7  $\mu g ml^{-1}$ . The concentration of metal in the stock solutions of isotopic carriers (cobalt(II) chloride, barium chloride, cerium(III) chloride, and caesium chloride) was 5  $mg ml^{-1}$ . All the chemicals used were of anal. grade.

The individual mixed solutions contained 20, 40, 55, 65, 75, 85, 90, and 95 volume %

of organic solvent, hydrochloric acid in the concentration range from 0.1 to 8 M, 1 ml of the stock solution containing the radioactive microcomponent with the isotopic carrier in the concentration  $20 \mu\text{g ml}^{-1}$  of final solution and concentrated perchloric acid in the amount necessary for maintaining a constant ionic strength of solution.

The liquid phase of the ion-exchange system was separated in two portions and 25 ml of each portion were given in 50-ml volumetric flasks. 1 g of the dry cation exchanger was added to the first portion while 1 g of the anion exchanger was added to the second portion. The samples were shaken in a laboratory shaker twice for two hours with an interruption of 16 hours.

Analyses were carried out radiometrically. Counting rates of aliquots of solutions containing gamma emitters were counted in a "well-type" scintillation counter in 5-ml thin-walled glass ampoules Str-5 by integral counting techniques.

In all cases the measurement of relative activities was performed in such a way that the relative error of measurement was smaller than 1%. The counting time was limited to 5 minutes.

The values of weight equilibrium distribution coefficients,  $K_d$ , were calculated from the values of relative activities of the solution phase before and after equilibration as follows

$$K_d = \frac{A_0 - A_e}{A_e} \cdot \frac{V}{w_i}, \quad (3)$$

where  $A_0$  — counting rate of liquid phase before equilibration [ $\text{des. min}^{-1} \text{ml}^{-1}$ ],

$A_e$  — counting rate of liquid phase after equilibration [ $\text{des. min}^{-1} \text{ml}^{-1}$ ],

$V$  — volume of liquid phase [ml],

$w_i$  — weight of dry exchanger in the system [g].

All the experiments were made twice at laboratory temperature.

## Results and discussion

The mean ligand number  $\bar{m}$  was determined according to relationship (1) for the phase of solution and according to equation (2) for the phase of anion exchanger  $\bar{n}$ . The calculation of these quantities was based on the values found for the penetration of macro-components into anion exchanger in mixed solvent systems which had been published in preceding paper [8].

For illustration, Table 1 presents the experimental data necessary to obtain the values of the mean ligand number of chloro complexes of cobalt in a mixed solvent containing 75 volume % of acetone and 1.5 M-HCl.

In Figs. 1—5 the mean ligand numbers in solution  $\bar{m}$  and in the phase of exchanger  $\bar{n}$  are expressed as a function of the content of the organic solvent in mixed solution.

From the above results it is obvious that cobalt exists predominantly in the form of free  $\text{Co}^{2+}$  ion provided the ionic strength of mixed solution is low ( $I \leq 0.5$ ). The form  $\text{CoCl}^+$  prevails in the outer solution if the content of ethyl alcohol exceeds 90%. The mean ligand number in the phase of exchanger is higher and attains the value of 2 what corresponds to a neutral complex (Fig. 1). Under equal conditions in a mixed solution containing acetone, cobalt forms a neutral complex in the liquid as well as in the resin phase (Fig. 2).

At higher concentrations of hydrochloric acid ( $I \geq 3$ ) cobalt forms chloro complexes even in aqueous solutions. Owing to the decrease in the dielectric constant of outer solution the value of ligand number increases. The mean ligand number reaches the

Table 1

Experimental data for the determination of the mean ligand numbers of cobalt chloro complexes in mixed solution

Solvent	Ionic strength $I$	$(c_{\text{HCl}})_t$ [mol l <sup>-1</sup> ]	$K_{\text{dk}}$ [ml g <sup>-1</sup> ]	$K_{\text{da}}$ [ml g <sup>-1</sup> ]	$[c_{\text{HCl}}]_t$ [mequiv. g <sup>-1</sup> ]	$\bar{m}$	$\bar{n}$
Acetone		1.50	10.32	137.4	1.07		
75 volume % 1.5 M-HCl	1.50	1.45	10.42	135.1	1.04		
		1.40	10.36	131.4	0.99	0.76	1.65
		1.35	10.97	127.3	0.95		
		1.30	10.93	128.0	0.90		
		1.25	11.12	121.0	0.87		

value of 1 at maximum content of ethyl alcohol (65%,  $I = 3$ ) (Fig. 1) while its value equals 2 at maximum content of acetone (65%,  $I = 3$ ) (Fig. 2). Provided the content of hydrochloric acid in outer solution is higher ( $I = 4$  or  $I \leq 3$  in inner solution of exchanger) cobalt exists predominantly in the form of  $\text{CoCl}_3^-$  ions and the existence of the forms  $\text{CoCl}_4^{2-}$  may be supposed (Figs. 1 and 2).

As evident from Figs. 3 and 4, caesium and barium do not form any chloro complexes in the phase of solution even at a high content of organic solvent in the mixture. But in solutions with 95% content of acetone their mean ligand number in the phase of exchanger attains the value of 2. This fact indicates an extraordinarily strong association of ions inside the exchanger, for which a rather low dielectric constant of inside medium under the conditions employed is responsible.

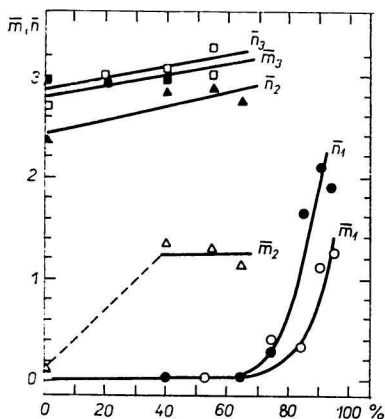


Fig. 1. Variation of the mean ligand numbers of cobalt with the content of ethyl alcohol in a mixed solution containing ethyl alcohol, water, and hydrochloric acid.

Indices: 1.  $I = 0.5$ ; 2.  $I = 3$ ; 3.  $I = 4$ .

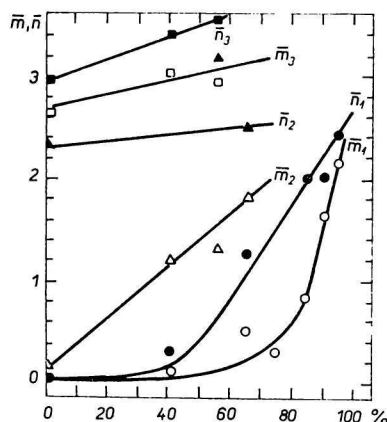


Fig. 2. Variation of the mean ligand numbers of cobalt with the content of acetone in a mixed solution containing acetone, water, and hydrochloric acid. Indices: 1.  $I = 0.5$ ; 2.  $I = 3$ ; 3.  $I = 4$ .

It is obvious from Fig. 5 that cerium exists as positive ions  $Ce^{3+}$  or  $CeCl_2^+$  in the liquid phase whereas the ions  $CeCl_2^+$  may also be assumed for 95% content of acetone. The formation of associates in the phase of exchanger is substantially higher so that cerium as well as barium form even a neutral complex at higher contents of acetone (Figs. 4 and 5).

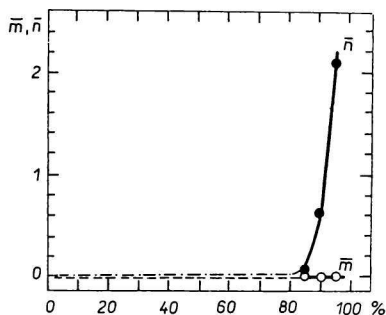


Fig. 3. Variation of the mean ligand numbers of caesium with the content of acetone in a mixed solution containing acetone, water, and hydrochloric acid.

$$I = 0.5.$$

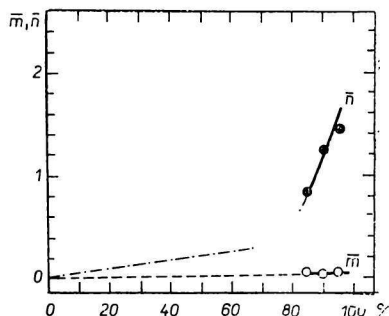


Fig. 4. Variation of the mean ligand numbers of barium with the content of acetone in a mixed solution containing acetone, water, and hydrochloric acid.

$$I = 0.5.$$

These relationships (Figs. 1–5) show that, in general, the tendency to ion association and to the formation of chloro complexes increases with decreasing dielectric constant of medium. This is also indicated by the results presented in preceding paper [8] in which the values of the association constant of hydrochloric acid are given for varying dielectric constant of medium.

It may also be stated that the remarkable changes in the values of mean ligand number in mixed solutions occur at high concentrations of organic solvent. With respect to a small amount of water in the system extensive changes in the hydrate sphere of ions take place in this case.

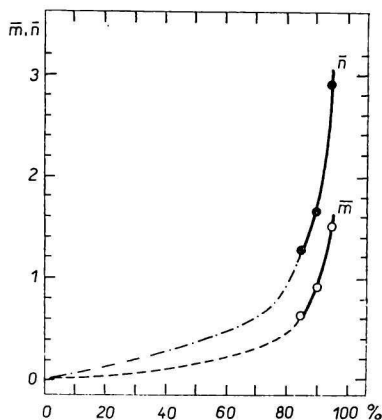


Fig. 5. Variation of the mean ligand numbers of cerium with the content of acetone in a mixed solution containing acetone, water, and hydrochloric acid.

$$I = 0.5.$$

For the determination of the mean ligand number of the ion inside the exchanger the value of its mean ligand number in the liquid phase is necessary. For this reason, a measurable sorption on the cation exchanger is assumed. The sorption of cobalt on the cation exchanger was not measurable or unreliably determinable in the medium containing either acetone or ethyl alcohol if the ionic strength was greater than 4. On the basis of measurements in these media it should be assumed that cobalt occurs predominantly in the form of negatively charged chloro complexes in this case.

It follows from the results obtained by the determination of the mean ligand numbers of barium and cerium that no chloro complexes are formed in the liquid phase at low concentrations of hydrochloric acid in mixed solution provided the content of organic solvent in mixed solution is high. Conversely, some neutral complex species are formed in the inner solution of exchanger (Figs. 3–5). These facts account for surprisingly high sorption of alkaline earth and rare earth elements on anion exchanger [7].

Moreover, the value of the mean ligand numbers of cobalt increases (Figs. 1 and 2) with the content of organic solvent, *i.e.* with decreasing dielectric constant of medium. This indicates a shift in the stepwise formation of the ion species to the advantage of complex formation.

Owing to the values of the ligand numbers of alkaline and alkaline earth metals in outer solution, the conditions favourable to the sorption of positively charged complex species on anion exchanger arise. Because of the value of dielectric constant in the phase of the inner solution of exchanger, the complexes are then formed through the counter-ion of exchanger. On the basis of this mechanism the value of equilibrium distribution coefficient in mixed solutions containing acetone may be explained [7]. In particular, this view accounts for the high values of the equilibrium distribution coefficients of alkaline earth and rare earth elements the sorption of which is negligible in aqueous and alcoholic media. The values of the mean ligand numbers of cobalt, cerium, barium, and caesium in mixed organic-aqueous solutions of hydrochloric acid as well as in the inner solution of anion exchanger are the basis for the appreciation of the phenomena involving the ion-exchange process in complicated systems.

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