

# Formation of complexes and ion-exchange equilibria on cation exchanger in mixed media

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The ion-exchange equilibria of Cu(II), Zn(II), and Fe(III) cations between the ion-exchanger phase of a strongly acidic cation exchanger and the solutions of perchloric or hydrochloric acid in methanol, ethanol, and acetic acid have been investigated. In the system containing perchloric acid the distribution coefficients increase with decreasing permittivity of solution which is related to the increased interactions between the cations and the fixed ions of ion exchanger. In the mixed medium of hydrochloric acid some negatively charged complexes containing Cu(II), Zn(II), and Fe(III) cations are formed and then this competitive equilibrium considerably decreases the sorption of the above ions on cation exchanger.

A great number of investigators have been already concerned with the problems of the exchange of inorganic ions in aqueous solutions [1]. Recently, an increased attention has been paid to the ion-exchanger systems containing mineral acids in the presence of organic solvent [2]. The exchange of ions in mixed and nonaqueous solutions has been hitherto much less studied than the exchange of ions in aqueous systems. By replacing the aqueous medium by the mixed medium some changes take place in the ion-exchanger phase [3] as well as in the outside solution [4]. These changes may essentially affect the ion-exchange process [5–7]. This study deals with the changes in the interactions among ions and the formation of complexes as well as the effect of these phenomena on the ion-exchange equilibria.

## Experimental

### *Ion exchanger*

All the experiments were carried out with a strongly acidic cation exchanger (Ostion KSX8; Research Institute of Synthetic Resins and Varnishes, Pardubice). Capacity: 5.20 mval/g of dry cation exchanger in the H<sup>+</sup> form, granulation in swollen state 0.3–0.8 mm. After purifying in the usual way [1], the cation exchanger in the H<sup>+</sup> form was air-dried at laboratory temperature (22 ± 1°C) to constant weight and kept in a well closed bottle. Simultaneously with the determination of capacity (Czechoslovak Standard 64 0920) the water content was established (Czechoslovak Standard 64 0902) in a sample of the stock ion exchanger dried at room temperature. The total content of water in the cation exchanger and the coefficient of moisture were determined by drying at 105–110°C to constant weight.

### Experiments

The cation exchanger ( $400 \pm 1$  mg) dried at laboratory temperature was weighed into a 50-ml polyethylene bottle. Then a solution of acid (25 ml) in aqueous or mixed media and 0.1 N- $M^{n+}$  (1.00 ml) in the same medium were added (the total volume of 26 ml was corrected with respect to the sorption of solvent [8]) and the solution was shaken for 24 hrs at  $22 \pm 1^\circ\text{C}$ . It was not necessary to adjust the temperature more accurately because the density of solution changed only by 0.1–0.2% per  $1^\circ\text{C}$  and the temperature coefficient of the cation exchanger swelling was very low [9]. After establishing the equilibrium between the ion exchanger and the solvent the content of metal ions in the external solution was determined.

The distribution coefficient is defined as the ratio of the total amount of substance in the ion-exchanger phase to the total amount of substance in the aqueous phase

$$D_E = M_{\text{HR}} V / M_{\text{H}_2\text{O}} G, \quad (1)$$

where  $M_{\text{HR}}$  and  $M_{\text{H}_2\text{O}}$  are the total amounts of  $M^{n+}$  in the ion-exchanger phase and aqueous phase respectively,  $V$  (in ml) is the volume of the aqueous phase, and  $G$  (in g) is the weight of dry cation exchanger.  $G$  is calculated by multiplying the weighed amount of the cation exchanger dried at room temperature by the coefficient of moisture.

For the determination of Cu(II), Zn(II), and Fe(III) in the aqueous phase the method of atomic absorption (Perkin–Elmer) was used. A correction for the content of impurities in the reagents used was also made.

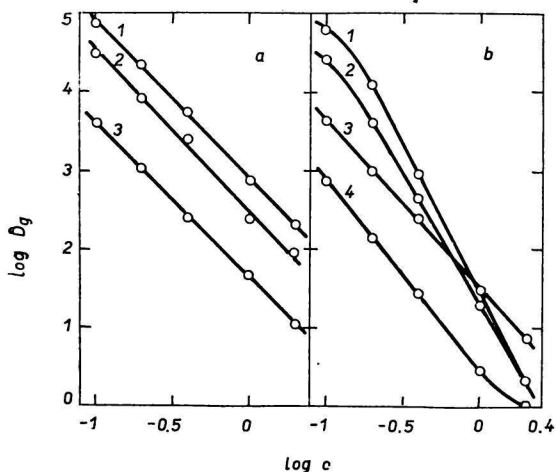
Solutions of perchloric and hydrochloric acid in mixed solvents were prepared from the stock solutions of 10 M- $\text{HClO}_4$  and 10 M- $\text{HCl}$  to which the calculated amounts of water and organic solvent (with the known water content) were added.

### Results and discussion

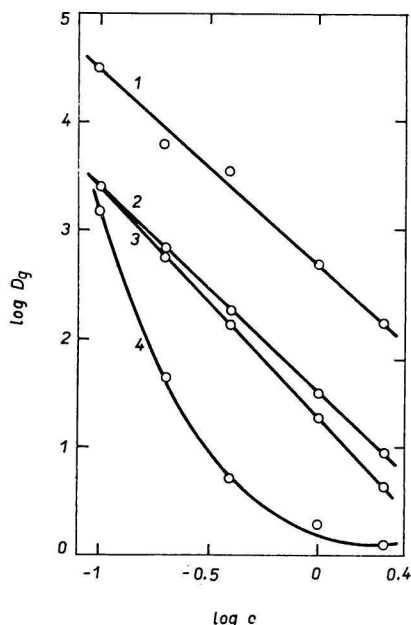
The slopes of the distribution curves (dependence of the logarithm of distribution coefficient on the logarithm of the concentration of acid) in the aqueous perchloric acid solution approximate to the value of  $-2$  for Cu(II) and Zn(II) ions and to  $-3$  for Fe(III) ions (Figs. 1–3). An analogous course of the distribution curves was found for Cu(II) and Zn(II) ions in the perchloric acid solutions in the presence of methanol, ethanol, and acetic acid and with smaller deviations also for Fe(III) ions. Thus it may be stated that the simple Cu(II), Zn(II), and Fe(III) ions take part in the exchange equilibria in the above media, the slopes of distribution curves being  $-2$  and  $-3$ .

The interactions cation–water play an important role in the exchange equilibria of cations in dilute solutions in the absence of complex-forming agents. The smaller the hydration radius of cation (in a given group of ions participating in the exchange), the higher is its sorption in cation exchanger and *vice versa*. When exchanging the aqueous medium for a mixed medium the change of hydration of cation into its solvation must be considered. As to solvation, it appears that the majority of ions prefers water to other solvents. Nevertheless a certain degree of solvation by active solvent must be taken into account in mixed media. The approximate order of solvents according to decreasing affinity is [10]:  $\text{H}_2\text{O}$ ,  $\text{HCONH}_2$ ,  $\text{CH}_3\text{OH}$ ,  $\text{C}_2\text{H}_5\text{OH}$ ,  $(\text{CH}_3)_2\text{O}$ ,  $\text{CH}_3\text{NO}_2$ , and dioxan. If the interactions between the cations and the molecules of organic solvent in mixed medium are prevalingly lower than the corresponding cation–water interactions in pure aqueous medium, it may be assumed that the fixed ions of ion exchanger may take part in the solvation of cations in the ion-exchanger phase in a higher degree. The interactions

between the solvated cations and the  $R-SO_3^-$  ions of ion exchanger become more intense which results in a remarkable increase of the distribution coefficients of cations in mixed medium (Figs. 1a, 2, 3a).



*Fig. 1.* Dependence of the distribution coefficient ( $\log D_g$ ) of Cu(II):  
 a) on the perchloric acid concentration:  
 1. 80% ethanol, 2. 80% methanol,  
 3. water;  
 b) on the hydrochloric acid concentration:  
 1. 80% ethanol, 2. 80% methanol,  
 3. water, 4. 80% acetic acid.



*Fig. 2.* Dependence of the distribution coefficient ( $\log D_g$ ) of Zn(II):  
 a) on the perchloric acid concentration:  
 1. 80% ethanol, 2. water;  
 b) on the hydrochloric acid concentration:  
 3. water, 4. 80% ethanol.

A comparison of the distribution curves of Cu(II), Zn(II), and Fe(III) cations shows that the magnitude of the charge of cation has also some influence on the course of sorption.

The results obtained evidence that the sorption of Cu(II), Zn(II), and Fe(III) cations increases with the content of organic solvent if passing from aqueous to mixed medium. A comparison of the distribution coefficients of the above cations in the perchloric acid solutions in water and in organic solvent indicates that the sorption of these cations increases in the order  $HAc < MeOH < EtOH$ . These results show that the sorption and the values of the distribution coefficients of cations in mixed medium depend on both the permittivity of solvent and the chemical character of the organic solvent.

Prediction of the extent of sorption of a given ion from a certain organic solvent of known permittivity is possible only if solvents of very similar chemical composition, *e.g.* aliphatic alcohols, are compared.

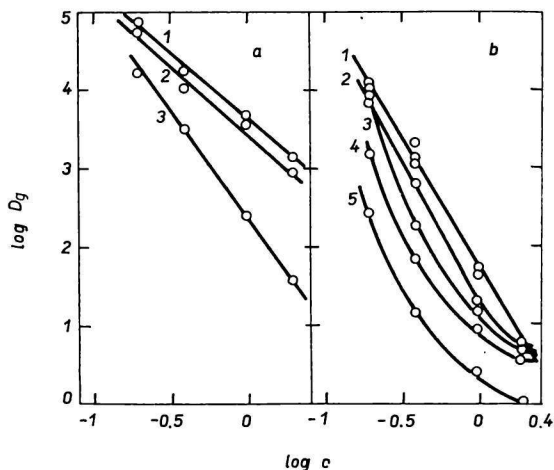


Fig. 3. Dependence of the distribution coefficient ( $\log D_g$ ) of Fe(III): a) on the perchloric acid concentration: 1. 80% ethanol, 2. 80% methanol, 3. water; b) on the hydrochloric acid concentration: 1. water, 40% methanol and 40% ethanol, 2. 80% methanol, 3. 80% ethanol, 4. 40% acetic acid, 5. 80% acetic acid.

In the systems containing hydrochloric acid in aqueous and organic solvent the logarithmic dependence of the distribution coefficient of Cu(II), Zn(II), and Fe(III) ions on the concentration of acid ceased to be linear and the value of the slope continued to deviate from the calculated values  $-2$  and  $-3$  with increasing content of organic solvent (Figs. 1b, 2, 3b). The obtained shape of distribution curves is related to a more complicated mechanism of the exchange process which is a result of several competitive equilibria (and involves the interactions of cations with bonded ions of the ion exchanger as well as the anions in the outer solution).

The formation of complexes plays a very important role in the ion-exchange equilibria in mixed solvents. A successive replacement of water by organic solvent results in a stepwise dehydration of ions, in a considerable increase of ionic interactions, and in an association in mixed solution. It is known that the stability of negatively charged complexes, e.g. chloro complexes of metal cations, may be evidently raised by an addition of organic solvent [2, 11]. By the effect of the formation of chloro or acetate complexes [12] the course of the sorption of Cu(II), Zn(II), and Fe(III) cations in a system containing hydrochloric acid differs from that in a system containing perchloric acid.

Table 1

Effect of methanol and ethanol on the distribution coefficients of the cations in perchloric and hydrochloric acid

$$(\Delta \log D_g = \log D_{g,\text{org}} - \log D_{g,\text{H}_2\text{O}})$$

Concentration [mol dm <sup>-3</sup> ]	Cu(II)				Zn(II)				Fe(III)	
	HClO <sub>4</sub>		HCl		HClO <sub>4</sub>		HCl		HCl	
	MeOH	EtOH	MeOH	EtOH	EtOH	EtOH	MeOH	EtOH	MeOH	EtOH
0.1	+0.88	+1.28	+0.76	+1.16	+1.10	-0.22				
0.2	+0.91	+1.31	+0.62	+1.10	+0.98	-1.12	+0.50	+0.62	-0.18	-0.06
0.4	+1.00	+1.36	+0.25	+0.57	+1.29	-1.42	+0.54	+0.74	-0.26	-0.80
1.0	+0.72	+1.21	-0.16	-0.01	+1.19	-0.98	+1.14	+1.28	-0.43	-0.55
2.0	+0.91	+1.28	-0.56	-0.56	+1.25	-0.52	+1.38	+1.58	-0.05	-0.10

org — 80% MeOH or 80% EtOH.

A comprehensive survey of the effect of organic solvent and the decrease in the permittivity of medium on the distribution coefficients of the Cu(II), Zn(II), and Fe(III) cations is presented in Table 1. In the system cation exchanger—HClO<sub>4</sub>, the presence of organic solvent manifests itself by a general increase in the distribution coefficients. In this case the interactions between the solvated cations and the R—SO<sub>3</sub><sup>-</sup> groups of ion exchanger play the main role. This increase in sorption within the investigated concentration range (0.1—2 M) is in the case of Cu(II) and Zn(II) practically independent of the perchloric acid concentration. The sorption of Fe(III) exhibits a slightly different character owing to the effect of other factors on the mechanism of the exchange equilibrium (anomalous sorption of Fe(III) in concentrated solutions of HClO<sub>4</sub> and association of Fe(III) with ClO<sub>4</sub><sup>-</sup>).

In the systems containing hydrochloric acid the presence of methanol and, in particular, ethanol supports not only the interactions between the solvated cations and the R—SO<sub>3</sub><sup>-</sup> groups of ion exchanger but also the formation of anionic complexes. Thus an interesting course of sorption ensues from these competitive equilibria. In the case of cations, the chloro complexes of which are more dissociated under the given conditions, e.g. Cu(II), the exchange equilibrium is shifted in the sense of sorption ( $D_{g,org} > D_{g,H_2O}$ ) at lower concentrations of hydrochloric acid (0.1—0.4 M) while the elution prevails only at higher concentrations of acid ( $D_{g,org} < D_{g,H_2O}$ ). In the case of other cations, e.g. Zn(II) or Fe(III), their sorption is decreased distinctly by the effect of the formation of chloro complexes in the whole concentration range (0.1—2 M-HCl).

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