

The influence of organic solvents on the selectivity of a cation exchanger in acidic media

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The influence of organic solvents and inorganic acids on the selectivity of a strongly acidic cation exchanger towards bivalent cations was studied. The increase of the distribution coefficients of Mg^{2+} , Co^{2+} , and Mn^{2+} due to the addition of an organic solvent (methanol, ethanol, acetic acid) is nearly constant in 0.1–1 M acid solutions and the dependence of $\log D_x$ upon $1/\epsilon$ approximately linear. The course of sorption of Mg^{2+} in 0.1–2 M perchloric, hydrochloric, and sulfuric acids is in a good relation with the course of the mean activity coefficients of these acids.

Problems of the ion exchange in the systems containing inorganic and organic acids in organic solvents [1] have been studied only by a few investigators in comparison with an extensive research into the exchange of inorganic ions in aqueous solutions [2]. The theory of the ion exchange in mixed and nonaqueous media is also far less developed than in the purely aqueous systems. Theoretical investigations are difficult because of the lack of the necessary data. The partial replacement of the aqueous phase by an organic solvent usually increases sorption of inorganic ions [3]. The selectivity coefficient of a given pair of ions is usually higher when ions are dissolved in mixed or nonaqueous media, compared with the ion exchange from purely aqueous solutions [4, 5]. The replacement of water by an organic solvent in the ion-exchange system influences hydration, solvation, formation of ionic pairs and complexes in both the aqueous and the ion-exchanger phases. This work studies the influence of composition of the basic electrolyte and permittivity of the medium upon the sorption of bivalent ions by the cation exchanger.

Experimental

Ion exchanger

All the experiments were carried out with a strongly acidic cation-exchange resin (Ostion KSX8; Research Institute of Synthetic Resins and Varnishes, Pardubice). Its capacity was 5.10 mval/g of dry resin in the H^+ form, granulation of the swollen exchanger being 0.3–0.8 mm. After purification by the usual method, the cation exchanger in the H^+ form was air-dried to constant weight at room temperature and stored in a well-stoppered bottle. Parallel determinations of the water content and the capacity (Czechoslovak Standard 64 0920) of the sample of the exchanger dried at room temperature

were carried out. The total water content and the moisture coefficient (Czechoslovak Standard 64 0902) of the cation exchanger were determined by drying at 105–110°C to constant weight. The moisture coefficient is a ratio of the sample weights of the dried and swollen ion exchanger.

Experiments

The prepared ion exchanger in the H^+ form (with the known water content) was weighed (400 ± 1 mg) into a polythene bottle, a solution of acid (25.00 ml) in the aqueous or mixed medium and a 0.05 M solution of cation (1.00 ml) in the same medium were added. The mixture was shaken for 24 hrs at room temperature ($22 \pm 1^\circ C$) [6]. More precise thermostating was not necessary since the temperature gradients of the solution densities were only 0.1–0.2% per $1^\circ C$ and the temperature coefficient of swelling of the cation exchanger was also very low [7]. After establishing the equilibrium, an aliquot part of the solution was taken off, acid and organic solvent were evaporated and the cations were determined.

The distribution coefficient was calculated from the formula $D_g = M_{HR} V / (M_{H_2O} G)$, where M_{HR} and M_{H_2O} are amounts of cation M^{2+} in the ion exchanger and aqueous phase respectively. V (in ml) is the volume of the aqueous phase, G (in g) the weight of the dry cation exchanger. G is obtained by multiplying the weight of the cation exchanger dried in air at room temperature by the moisture coefficient.

An atomic absorption method (Perkin–Elmer) was used to determine the content of Mg^{2+} , Co^{2+} , and Mn^{2+} in the aqueous phase and the correction for impurities in the used reagents was made.

Solutions of perchloric, hydrochloric, nitric, and sulfuric acids were prepared from the stock solutions of 10 M- $HClO_4$, HCl , HNO_3 , and H_2SO_4 by mixing with a calculated amount of water and an organic solvent (with the known water content).

Results and discussion

The distribution coefficient D_g was chosen as a criterion of the selectivity of the ion exchanger. D_g is the ratio between the total amount of a trace component M in 1 g of the dry ion exchanger and the total amount of the same component in 1 cm^3 of the external solution

$$D_g = \frac{|M|_{HR}}{|M|}, \quad (1)$$

where $|M|_{HR}$ stands for the ion-exchanger phase and $|M|$ for the aqueous phase.

If the component H is in excess (HB is the basic electrolyte) and M only in trace concentrations, the concentration of H and the activity coefficients in the ion-exchanger phase remain constant ($|H|_{HR} = \text{const}$) even when $|M|$ varies within certain limits. The selectivity coefficient does not depend on the amount of the trace component ($K_{H/M} = \text{const}$) if the ratio of the activity coefficients in the aqueous phase is constant.

Eqn (1) together with a relationship for the selectivity coefficient gives

$$K_{H/M} = \frac{|M| |H|_{HR}^m}{|H|^m |M|_{HR}} \quad (2)$$

and after rearranging

$$D_g = \text{const} |H|^{-m}. \quad (3)$$

Thus the distribution coefficient of the component M is inversely dependent on the concentration of the basic electrolyte HB . If the charge of the basic electrolyte (H^+) is known, the charge of the cation M^{n+} can be determined from the angular coefficient of the dependence of $\log D_g$ upon $\log [H^+]$

$$\frac{d \log D_g}{d \log [H^+]} = -|m|. \tag{4}$$

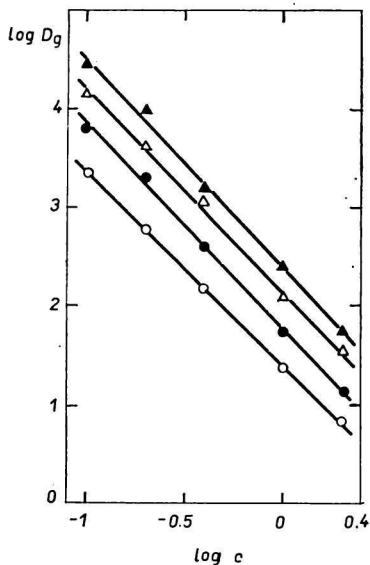


Fig. 1. Dependence of the distribution coefficient of Mg^{2+} ($\log D_g$) on the concentration of hydrochloric acid.
 ○ 0% methanol; △ 80% methanol; ▲ 80% ethanol; ● 80% acetic acid.

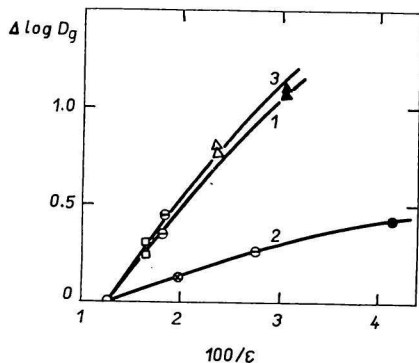


Fig. 2. Dependence of the distribution coefficients of Mg^{2+} and Mn^{2+} on the permittivity of mixed media with hydrochloric acid.

($\Delta \log D_g = \log D_{g,org} - \log D_{g,H_2O}$)
 ○ 0% methanol; □ 40% methanol;
 △ 80% methanol; ⊕ 40% ethanol; ▲ 80% ethanol;
 ⊗ 40% acetic acid; ⊙ 60% acetic acid; ● 80% acetic acid.
 Curves 1 and 2, Mg^{2+} ; curve 3 Mn^{2+} .

The angular coefficients of the distribution curves of Mg^{2+} , Co^{2+} , and Mn^{2+} ions in aqueous solutions of perchloric, hydrochloric, or nitric acids, are in good agreement with the calculated value -2 , corresponding to the exchange reaction between M^{2+} and H^+ (Fig. 1, Tables 1–3). Analogous values of the angular coefficients of the distribution curves were found also in mixed media, $H_2O-MeOH$, $H_2O-EtOH$, and H_2O-HAc at 40 and 80% concentrations of the organic solvent. Thus only the simple hydrated or solvated cations Mg^{2+} , Co^{2+} , and Mn^{2+} take part in the exchange equilibrium.

The course of the sorption of Mg^{2+} cations is apparently in relation with the course

of the mean activity coefficients of strong acids in the range of 0.1–2 M. At a given concentration, the mean activity coefficients [8] decrease in the order $\text{HClO}_4 > \text{HCl} > \text{HNO}_3 > \text{H}_2\text{SO}_4$ which is in accordance with the decrease of values of the distribution coefficients (Table 1).

A general comparison of the distribution coefficients of Mg^{2+} , Co^{2+} , and Mn^{2+} ions in solutions of perchloric, hydrochloric, nitric, and sulfuric acids reveals that the transition from the aqueous to mixed media brings about an increase of the distribution of these bivalent ions in the order $\text{HAc} < \text{MeOH} < \text{EtOH}$. Relatively lower distribution coefficients in the mixed media of acetic acid with low permittivity ($\epsilon_{\text{H}_2\text{O}-\text{Ac}} < \epsilon_{\text{H}_2\text{O}-\text{MeOH}}, \epsilon_{\text{EtOH}}$) indicate a substantial role of other factors. For example, competitive equilibria due to

Table 1

Dependence of the distribution coefficient of Mg^{2+} ($\log D_g$) on the concentrations of acid and organic solvent

Concentration of HClO_4 [mol dm ⁻³]	0%	80% MeOH	80% EtOH
0.1	3.45	4.25	4.50
0.2	2.88	3.65	4.18
0.4	2.25	3.12	3.20
1.0	1.56	2.09	2.63
2.0	0.96	1.60	1.90
Concentration of HCl [mol dm ⁻³]	0%	80% MeOH	80% EtOH
0.1	3.36	4.15	4.45
0.2	2.79	3.53	4.00
0.4	2.18	3.06	3.20
1.0	1.38	2.08	2.41
2.0	0.82	1.55	1.75
Concentration of HNO_3 [mol dm ⁻³]	0%	80% MeOH	80% EtOH
0.1	3.28	4.13	4.40
0.2	2.70	3.64	3.92
0.4	2.20	3.12	3.27
1.0	1.46	2.24	2.57
2.0	0.90	1.66	1.96
Concentration of H_2SO_4 [mol dm ⁻³]	0%	80% MeOH	80% EtOH
0.1	3.00	4.11	4.24
0.2	2.56	3.58	3.65
0.4	1.98	2.90	3.10
1.0	1.29	1.92	2.08
2.0	0.74	1.34	1.52

Table 2

Dependence of the distribution coefficient of Co^{2+} ($\log D_g$) on the concentrations of acid and organic solvent

Concentration of HCl [mol dm ⁻³]	0%	40% MeOH	80% MeOH	40% EtOH	80% EtOH
0.1	3.46	3.72	4.33	3.98	4.70
0.2	2.83	3.11	3.67	3.39	4.07
0.4	2.21	2.49	2.92	2.64	3.24
1.0	1.36	1.68	2.01	1.77	2.43
2.0	0.73	1.06	1.36	1.15	1.70

Concentration of HClO ₄ [mol dm ⁻³]	0%	80% EtOH
0.1	3.52	4.90
0.2	2.92	4.24
0.4	2.31	3.64
1.0	1.55	2.56
2.0	0.94	1.88

Table 3

Dependence of the distribution coefficient of Mn^{2+} ($\log D_g$) on the concentrations of acid and organic solvent

Concentration of HCl [mol dm ⁻³]	0%	40% MeOH	80% MeOH	40% EtOH	80% EtOH
0.1	3.48	3.76	4.32	3.95	4.70
0.2	2.85	3.16	3.68	3.37	4.04
0.4	2.24	2.55	3.02	2.67	3.28
1.0	1.39	1.72	2.12	1.81	2.42
2.0	0.78	1.09	1.46	1.20	1.78

Concentration of HClO ₄ [mol dm ⁻³]	0%	80% EtOH
0.1	3.56	4.95
0.2	3.00	4.41
0.4	2.39	3.68
1.0	1.68	2.95
2.0	1.18	2.32

the stronger interaction between M^{2+} and Ac^- ions in the aqueous phase [9] decrease the sorption.

Solvents with low permittivity facilitate electrostatic interactions and the formation of ionic pairs between counterions and R-SO_3^- groups of the ion exchanger. A decrease of concentration of osmotically active ions in the ion-exchanger phase results in the

increase of selectivity. Swelling of the ion exchanger as well as changes in the selectivity depend mainly on the permittivity of the medium and polarity of the solvent.

The dissolution of the electrolyte MB in mixed medium is accompanied by the dissociation and solvation of ions. When the permittivity of the medium is high and the solution diluted, the dissociation is nearly complete. A decrease in the permittivity of the solvent reflects in the increase of pK_{dis} by the formula [10]:

$$pK_{\text{dis}} = (e^2/2.303 k T) (1/r_M + 1/r_B) 1/\epsilon = A/\epsilon. \quad (5)$$

The relationship (5) is valid if the distance of ions r_M , r_B and the nature of solvent remain unchanged. On this assumption, the quantity A is constant for a given electrolyte and the dependence of pK_{dis} upon $1/\epsilon$ is linear. The validity of eqn (5) was observed for many electrolytes both in pure and in mixed solvents [11, 12].

Fig. 2 shows a dependence of the distribution coefficients of Mg^{2+} and Mn^{2+} on the permittivity of the mixed media (HCl—MeOH, EtOH, and HCl—HAc). Instead of $\log D_g$ vs. $1/\epsilon$, the dependence of $\Delta \log D_g$ (a difference of logarithms of the distribution coefficients of the given cation in the mixed and aqueous media) upon $100/\epsilon$ is outlined there, for ease of comparison. The values of $\Delta \log D_g$ represent averages in 0.1—2 M-HCl. In solutions with 0—80% of MeOH, EtOH, and HAc, the dependence deviates only slightly from a linear course.

The increase of the distribution coefficients of cations in a homologous series of solvents (e.g. MeOH, EtOH) appears to depend only on the $1/\epsilon$ value, in the first approximation. It holds if the formation of the negatively charged complexes is negligible under the given conditions.

For the studied group of cations, relations between the distribution coefficients found in aqueous media remain valid also in mixed media. The solvent polarity, changes in solvation and interactions of cations with the solvent may affect the ion-exchange equilibria in such a degree that the increase of the distribution coefficients would not be so high as should correspond to the permittivity decrease of the medium.

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