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The Effect of Temperature on Accumulation of Lead and Cadmium by Anion Exchange

Štefica Cerjan-Stefanović and Marija Kaštelan-Macan

Department of Analytical Chemistry, Technological Faculty, Marulićev trg 20, Zagreb

and

Maja Blanuša

Institute for Medical Research and Occupational Health, Moše Pijade 158, Zagreb

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Binding conditions for lead and cadmium on Ionenaustauscher III in relation to medium, complexing ions and temperature were determined. Maximal distribution coefficients were obtained for lead in 1 mol/dm^3 HBr at 293 K, and for cadmium in 0.5 mol/dm^3 HBr at 293 K. Satisfactory conditions for separation of lead from cadmium in the mixture were found to be in chloride medium on 303—323 K and in bromide medium at 293 K.

INTRODUCTION

In hard waters with a high salt content and very low concentrations of toxic heavy metals direct determination of lead and cadmium by common analytical techniques is impracticable. Therefore, the metals have to be concentrated or extracted. Toxic metals are easily concentrated by ion exchange resins or chelating cellulose.[14] There are several reports in the literature on the separation of lead and cadmium on anion exchange resins from chloride, bromide or iodide solutions.[5–9] Some authors, however, prefer cation exchange or separation from nonaqueous media.[10–14] The separation on anion exchange resins is based on different stabilities of chloro- or bromo-complexes with lead and cadmium. By varying the concentration of the ligand and the pH of the medium, optimal separation and selectivity are achieved. The coefficient of distribution (D) should be higher for the ion binding on the resin than for the one to be eliminated, whose numerical value should be as low as possible. Under these conditions the latter ion either does not bind on exchange resin at all or is eluted with small volumes of the eluent. To achieve selective sorption, the ratio of distribution coefficients (α) for cadmium and lead should be as high as possible.

In this work we determined parameters for the separation of cadmium from lead in chloride and bromide media by anion exchange. We confirmed our earlier finding[15] that binding efficiency is influenced by temperature. Optimum binding conditions were determined between 293 and 323 K.

EXPERIMENTAL

For the sorption of lead and cadmium on an anion exchange resin, the batch method was used to obtain a static equilibrium. The method consisted of two steps: 1. accumulation of metal ions and temperature equilibration of the working solution and 2. determination of the metal concentration in solution. For the separation of ions, the anion exchange resin Ionenaustauscher III, Merck, was used. This is a basic resin with a polystyrene network, functional group

$^{+}(CH_3)_2$—N—C_2H_4OH and 100 mesh particle size. The resin (0.5 g) was transferred to the working form by 2 mol/dm^3 HCl or 2 mol/dm^3 HBr and regeneration was performed using the same solutions. The chloride or bromide form of the resin was mixed in a flask with 25 cm^3 of cadmium or lead ion solution and 25 cm^3 of acid. Five different concentrations of acid were used for elution to determine the optimum one (Table I). The concentrations of metals varied from 1 to 100 ppm. The solutions were equilibrated for 60 minutes in the ultrathermostat (Type NBE-VEB Prüfgeräte-Werk, DDR). After equilibration, the concentrations of metal ions were determined in aliquot from each batch by an appropriate analytical method. Strelow[7] recommended filtration of the mixture before metal analysis, but we did not consider it necessary. Lead and cadmium analyses were performed in solutions before and after elution on the resin, by complexometric titration with EDTA,[16] by flame AAS or by electrothermal atomization AAS. The details of the methods were described previously.[15]

TABLE I

The Dependence of Distribution Coefficients (D) *for Lead and Cadmium on Medium Concentration (293 K)*

Binding solution c (HCl) mol dm^{-3}	D (Pb)	D (Cd)	Binding solution c (HBr) mol dm^{-3}	D (Pb)	D (Cd)
0.2	100.9	125.1	0.65	52.1	191.7
2.0	212.6	1495.7	0.1	247.0	873.6
3.0	344.1	1255.9	0.5	364.1	2963.8
4.0	121.0	10.5	1.0	620.1	2238.2
8.0	12.1	5.5	2.0	10.1	36.4

TABLE II

Dependence of Distribution Coefficients (D) *on Temperature at Optimum Medium Concentrations*

Temperature (K)	D (Pb) c (HCl) = 3 mol dm^{-3}	D (Cd) c (HCl) = 2 mol dm^{-3}	D (Pb) c (HBr) = 1 mol dm^{-3}	D (Cd) c (HBr) = 0.5 mol dm^{-3}
293	344.4	1495.2	620.1	2963.8
303	303.3	1300.6	316.2	1322.0
313	267.2	1130.4	29.0	89.9
323	193.7	750.0	20.1	38.1

RESULTS AND DISCUSSION

The behaviour of ion exchange resins at high temperatures depends on their structure. According to the manufacturer's recommendations, acid — — cation exchange polymerized resins can be used up to a temperature of 293

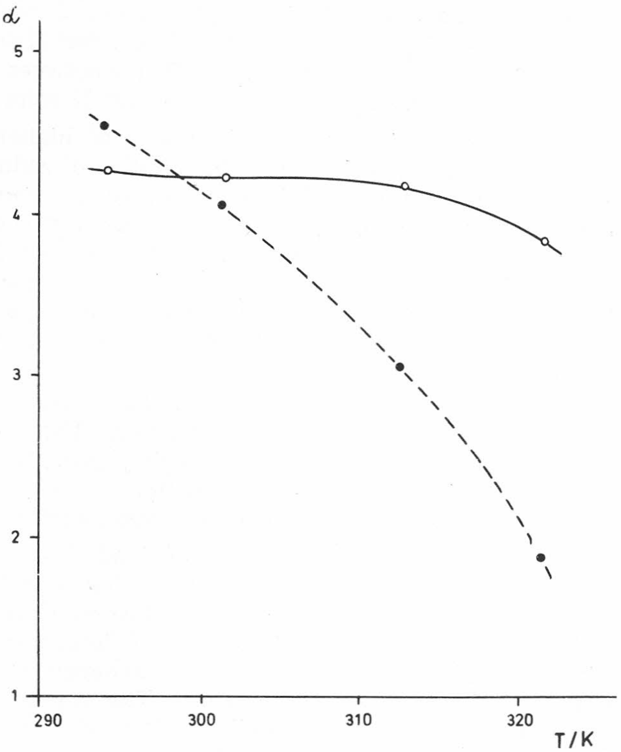

Figure 1. Separation factor (α) in relation to temperature in ○ chloride medium and ● bromide medium.

K. The resin remains stable at higher temperatures and, since ion exchange is a physical reaction, it usually occurs without a change in temperature. However, in the resin — solution system, besides the physical reaction of ion exchange, several chemical reactions occur which depend on temperature. These are: electroselectivity reaction, ion solvation, formation of ion pairs, association and formation of complexes. The thermodynamic dependence of the ion exchange equilibrium is defined by equation:

$$\log \frac{K_2}{K_1} = - \frac{\Delta H}{2.303\,R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

where K_1 and K_2 are thermodynamic constants of ion exchange te temperatures T_1 and T_2, and ΔH is the change in standard enthalpy of ion exchange. Before examining the temperature dependence we calculated the coefficients of distribution (D) for different concentrations of acids at normal temperature (293 K) according to:

$$D = \frac{\text{mass of ions in solution (g)}}{\text{mass of ions on resin (g)}} \cdot \text{mass of resin (g)}$$

The concentration of HCl varied from 0.2 to 8.0 mol/dm^3 and that of HBr from 0.65 to 2.0 mol/dm^3 (Table I).

The optimum concentrations of the media were: 3 mol/dm^3 HCl or 1 mol/dm^3 HBr for lead and 2 mol/dm^3 HCl or 0.5 mol/dm^3 HBr for cadmium. At these media concentrations, four temperature levels between 293 and 323 K were examined (Table II). Temperatures lower than 293 K were not examined.

The distribution coefficients for lead decreased at higher temperatures and were maximum at 293 K in both media. The binding of cadmium depended also on the working temperature and it was optimal at room temperature, 293 K in a bromide solution. Bromide solution is generally considered better for binding metal ions[17] than aqueous solutions. When two ions are to be separated from a mixture, separation factor (α) is the parameter to be considered. This factor was calculated by dividing distribution coefficients of cadmium and lead in chloride or bromide solution and plotted against temperature (Figure 1).

The separation factor in a chloride solution has higher values than in a bromide solution, with a maximum at about 313 K. The separation factor in a bromide solution is highest at 293 K, steeply falling with rising temperature. Hence, the separation of ions is better in chloride medium at higher temperature, because of the higher separation factor value.

These results show that the separation of lead from cadmium in a mixture is possible from the same binding medium but at different working temperatures. In the model of ion exchange described by Gregor,[18] selectivity is explained without considering the influence of temperature. Measuring the accumulation of toxic metals on a cation exchange resin we noticed that ion binding is influenced by temperature. The present measurements on an anion exchange resin show a similar effect of temperature on the binding of metal ions. Selectivity and binding ability are highly dependent on temperature without exhibiting any mutual correlation. This phenomenon could be explained by the dependence of complex stability on temperature.

CONCLUSIONS

The results show that the binding of lead and cadmium on an anion exchange resin depends on temperature. Apart from concentrations of ligands and the pH of the medium, also temperature has bearing on the selectivity of the resin. The calculated parameters show the separation of lead from cadmium in chloride medium to be satisfactory at 303—329 K and in bromide medium at 292 K. When the two metals are eluted separately, satisfactory binding conditions are 293 K and 1 mol/dm^3 HBr for lead, and 293 K and 0.5 mol/dm^3 HBr for cadmium.

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SAŽETAK

Temperaturna ovisnost vezanja olova i kadmija na anionski izmjenjivač

Š. Cerjan-Stefanović, M. Kaštelan-Macan i M. Blanuša

Određeni su uvjeti vezanja olova i kadmija na Ionenaustauscher III, ovisno o mediju, kompleksirajućim ionima i temperaturi. Maksimalni distribucijski koeficijenti izmjereni su za olovo u 1 mol/dm^3 HBr pri 293 K, a za kadmij u 0.5 mol/dm^3 pri 293 K. Zadovoljavajući uvjeti za separaciju olova od kadmija postižu se u kloridnom mediju pri temperaturama 303 do 323 K, a u bromidnom mediju pri 293 K.