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Explanation of the Zn/Cu Dual Temperature Separation on Amberlite IRC-718 Ion-Exchange Resin

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ABSTRACT

The earlier temperature ion-exchange separation of copper and zinc with temperature variations on Amberlite IRC-718 iminodiacetic resin was physicochemically described. Contrary to conventional double temperature ion-exchange separation methods, the temperature dependence of ion-exchange selectivity was not found to be a main driving force of the process. Separation of the two metals is controlled by formation of HSO_4^- complexes in the surrounding solution.

INTRODUCTION

Conventional ion exchange is widely used for the selective separation of ions from different solutions. However, its application is accomplished with the production of large quantities of wastes at the elution/regeneration steps. In many cases double temperature ion-exchange processes can solve this problem. This technique usually explores the temperature dependence of an ion-exchange resin selectivity toward the desired ions. A most successful process based on the double temperature separation is “sirotherm” desalination (1). This process has its specific area of application and can not be easily extended to other separation needs. The reason is that the specially designed “sirotherm” resin does not provide a selectivity toward transition metals and many other ions which have to be treated. The resin has a narrow work interval of pH that limits its applicability even more. Many carboxylic cation exchangers provide

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fairly good temperature-dependent selectivity for alkali earth metal ions (2–4). However, the low selectivity to a majority of other ions also limits their applicability. A special technique that allows exploration of low selective sorbents in double temperature processes is parametric pumping. Most studies on double temperature ion exchange over a wide range of time have been devoted to this method (5, 6). The method provides a high separation efficiency; however, it is not practically applicable beyond a laboratory scale. Some studies were conducted to find selective temperature-sensitive ion exchangers for some particular systems (7–10). All these works explore the temperature dependence of resin selectivity toward the separated ions.

The double temperature separation of copper and zinc was investigated recently (10, 11). The system is based on the Amberlite IRC-718 chelating ion-exchange resin. Separation was found to be highly successful despite to absence of any significant dependence of the Cu–Zn ion-exchange constant on temperature. This phenomenon can not be explained in the traditional way. An approach based on the variation of the total metal loading capacity of the ion exchanger was employed to describe the phenomenon (10). This simple approach can be successfully used for practical needs. The variations of the total metal loading capacity should, however, have a physicochemical driving force, which was not found before. This communication is written to explain the phenomenon from the physicochemical point of view. Different chemical processes present in the system are taken into consideration. The driving force found occurred in the solution surrounding the ion-exchange resin.

EXPERIMENTAL

Resin and Reagents

The iminodiacetic resin Amberlite IRC-718 was received from Rohm & Haas, USA. The resin was preconditioned prior to use. Details of the preconditioning were described earlier (12). Air-dried samples intended for experiments were weighed simultaneously with samples intended for a water content determination. The water content in the resin was measured separately by drying it in vacuum over P_2O_5 until constant weight was attained. The dry weight of the resin was used for all calculations.

$CuSO_4 \cdot 5H_2O$ and $ZnSO_4 \cdot 7H_2O$ (Kebo Lab, Sweden) and H_2SO_4 (Merck, Germany) of analytical grade were used as received. All solutions were prepared using deionized water.

Analysis

The concentrations of Cu and Zn were determined by AAS (Perkin-Elmer 603) and ICP (ARL 3520B) techniques. The error of the spectrochemical analysis was less than 1% for Cu and 2% for Zn. pH was measured using a glass electrode (Orion 92-02).

Determination of the Total Exchange Capacity

The total exchange capacity was determined from Cu^{2+} since the resin has the highest selectivity for this ion. The validity of this method was proved earlier (12, 13). A precisely weighted sample of the resin (10 g of the air-dried H^+-form) was placed in a glass column. The amount of water in the resin was determined separately. The resin was totally loaded with Cu^{2+} using 0.1 M $CuSO_4$ and was then washed with deionized water until copper was absent in the effluent. The copper was eluted from the resin by 1 M H_2SO_4. The total exchange capacity (Q_r) was calculated from analysis of the eluate:

$$Q_r = \frac{C_{Cu}V_{el}}{m_{d.r.}} = 5.08 \text{ meq/g dry resin} \tag{1}$$

where C_{Cu} is the concentration of the eluate (meq/mL), V_{el} is the volume of the eluate (mL), and $m_{d.r.}$ is the weight of the dry resin (g).

Selectivity Characteristics of the Ion-Exchange Equilibria

The equilibrium measurements were done by the dynamic method at different temperatures (10). The glass columns providing the temperature control of both resin and solution phases were used. Two grams (air-dried H^+-form) of the resin was used in each experiment. The composition of the feed solution was: $C_{Zn} = 102$ mM, $C_{Cu} = 12$ mM, $C_{SO_4} = 140$ mM, pH = 1.8 (H_2SO_4). The solution was passed through each column at a constant velocity of 0.37 m/h (the value is based on the column cross-section area). The achievement of ion-exchange equilibrium was monitored by a comparison of the concentration of each cationic species in the effluent with that of the feed solution. Then the feed solution residual was removed by vacuum suction. 1 M H_2SO_4 was applied for elution of sorbed ions. The amount of metal ions eluted was used for the calculation of the selectivity characteristics. The amount of hydrogen in the resin phase was calculated as the difference between the total exchange capacity and the amount of metal ions in the resin phase

$$[RH_2] = \frac{Q_r}{2} - [RZn] - [RCu]$$

It was assumed that the ion exchanger phase included both the resin network and the internal solution.

RESULTS AND DISCUSSION

Consider the reactions taking place in the system described. Three different 1-1 complexes are formed in the Cu^{2+} and Zn^{2+} containing acidic sulfate solutions:

$$Cu^{2+} + SO_4^{2-} = CuSO_4, \qquad \beta_{CuSO_4} = \frac{[CuSO_4]}{[Cu^{2+}][SO_4^{2-}]} \tag{2}$$

$$Zn^{2+} + SO_4^{2-} = ZnSO_4, \qquad \beta_{ZnSO_4} = \frac{[ZnSO_4]}{[Zn^{2+}][SO_4^{2-}]} \tag{3}$$

$$H^{+} + SO_4^{2-} = HSO_4^{-}, \qquad \beta_{HSO_4^-} = \frac{[HSO_4^-]}{[H^{+}][SO_4^{2-}]} \tag{4}$$

Corresponding complex formation constants (β) relate to each complex formation reaction. Concentration of all other possible associates between Cu^{2+}, Zn^{2+}, H^+, SO_4^{2-}, and OH^- ions are insignificant at the selected experimental conditions (Fig. 1).

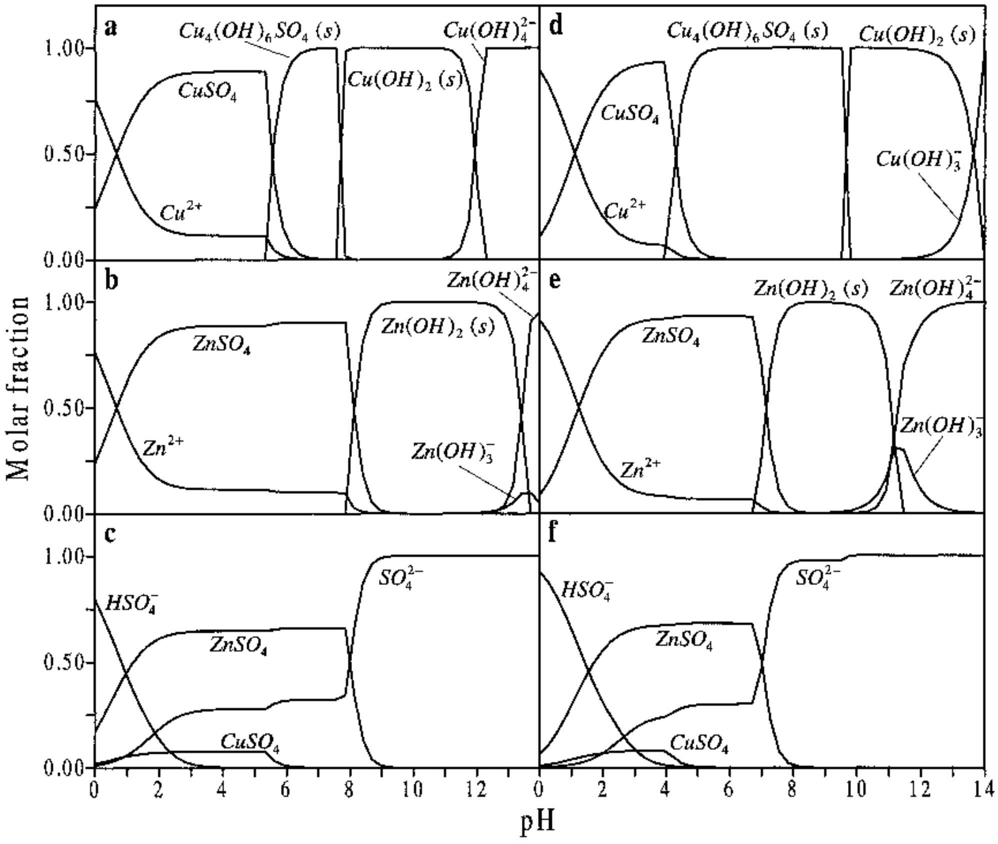


FIG. 1 Complex formation at different temperatures. The solution contains 0.012 M Cu^{2+}, 0.102 M Zn^{2+}, and 0.14 M SO_4^{2-}. (a, b, c) Temperature 15°C; (d, e, f) temperature 75°C. (a, d) Molar fraction distribution of Cu^{2+}; (b, e) molar fraction distribution of Zn^{2+}; (c, f) molar fraction distribution of SO_4^{2-}. Reference data (14, 15) were used for the model calculations.

Three different ion-exchange processes take place in the system:

$$\mathrm{RZn} + \mathrm{Cu}^{2+} = \mathrm{RCu} + \mathrm{Zn}^{2+}, \qquad \tilde{K}^{\mathrm{Cu}}_{\mathrm{Zn}} = \frac{[\mathrm{RCu}][\mathrm{Zn}^{2+}]}{[\mathrm{RZn}][\mathrm{Cu}^{2+}]} \tag{5}$$

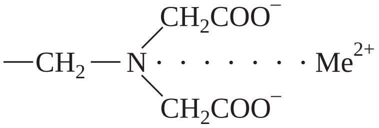
$$\mathrm{RH}_2 + \mathrm{Cu}^{2+} = \mathrm{RCu} + 2\mathrm{H}^{+}, \qquad \tilde{K}^{\mathrm{Cu}}_{\mathrm{H}} = \frac{[\mathrm{RCu}][\mathrm{H}^{+}]^2}{[\mathrm{RH}_2][\mathrm{Cu}^{2+}]} \tag{6}$$

$$\mathrm{RH}_2 + \mathrm{Zn}^{2+} = \mathrm{RZn} + 2\mathrm{H}^{+}, \qquad \tilde{K}^{\mathrm{Zn}}_{\mathrm{H}} = \frac{[\mathrm{RZn}][\mathrm{H}^{+}]^2}{[\mathrm{RH}_2][\mathrm{Zn}^{2+}]} \tag{7}$$

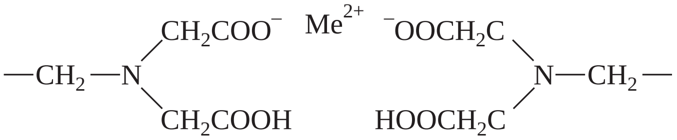
Corresponding selectivity coefficients ($\tilde{K}$) are written for each ion-exchange reaction. We have to note that the H^{+}–Me^{2+} exchange on iminodiacetic groups is often described by the formal Reaction (8) instead of Reactions (6) and (7):

$$2\mathrm{RH} + \mathrm{Me}^{2+} = \mathrm{R}_2\mathrm{Me} + 2\mathrm{H}^{+} \tag{8}$$

An identity of all hydrogen ions in the resin is assumed in Reaction (8). This approach is convenient for practical calculations but not physically correct. The reasons are the following. The iminodiacetic group reacts as a single unit, forming the well-known coordination complex (16, 17).



A bonding of Me^{2+} by two functionalities



would be extremely weak if possible. Another proof of the irrationality of Reaction (8) is the double-step dissociation of the iminodiacetic group. Thus, Reaction (8) describing the independent reactivity of each hydrogen has only a formal meaning and can not be used to explain the real physicochemical process.

The selectivity coefficients $\tilde{K}$ (Eqs. 5–7) describe the corresponding ion exchange reactions. However, the practical separation should be characterized by the corresponding equilibrium coefficients (α):

$$\alpha^{\mathrm{Cu}}_{\mathrm{Zn}} = \frac{[\mathrm{RCu}]C_{\mathrm{Zn}}}{[\mathrm{RZn}]C_{\mathrm{Cu}}} \tag{9}$$

$$\alpha^{\mathrm{Cu}}_{\mathrm{H}} = \frac{[\mathrm{RCu}]C^{2}_{\mathrm{H}}}{[\mathrm{RH}_2]C_{\mathrm{Cu}}} \tag{10}$$

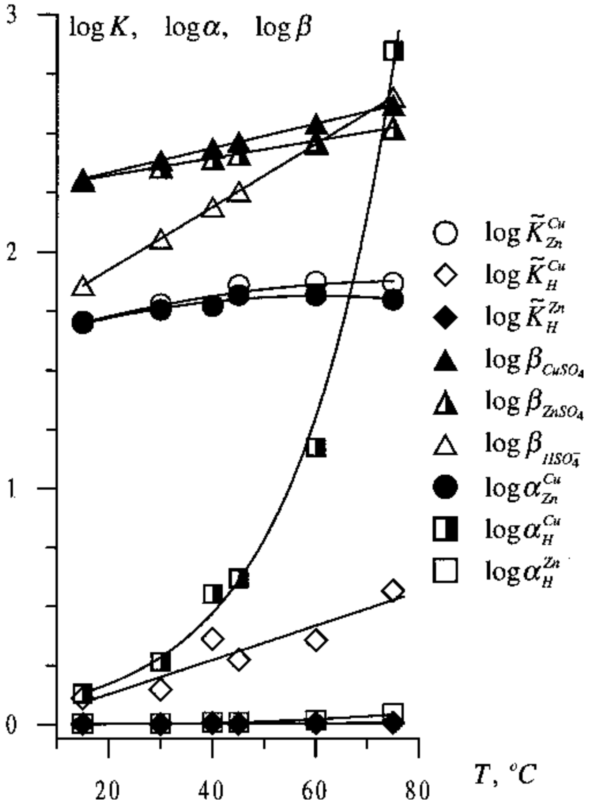


FIG. 2 Temperature dependence of the equilibrium parameters studied.

$$\alpha_{\mathrm{H}}^{\mathrm{Zn}} = \frac{[\mathrm{RZn}]C_{\mathrm{H}}^{2}}{[\mathrm{RH_2}]C_{\mathrm{Zn}}} \tag{11}$$

where $C_{\mathrm{Ion}} = [\mathrm{Ion}] + [\mathrm{IonSO_4}]$ is the total concentration of one ion in solution. $C_{\mathrm{Ion}} \neq [\mathrm{Ion}]$ for systems including complex formation, hence $\alpha \neq \tilde{K}$.

The experimental results on the equilibrium parameters study are plotted on Fig. 2. Consider the temperature dependencies of different equilibria existing in the system. We have found that copper and zinc can be successfully separated on Amberlite IRC-718 using the temperature variations (10, 11, 13). Thus, our attention is first attracted to the ion exchange between Cu^{2+} and Zn^{2+} (Eq. 5). However, neither the equilibrium coefficient ($\alpha_{\mathrm{Zn}}^{\mathrm{Cu}}$) nor the selectivity coefficient ($\tilde{K}_{\mathrm{Zn}}^{\mathrm{Cu}}$) of this reaction exhibits a significant temperature dependence (Fig. 2). The selectivity coefficients of the reactions, including the exchange of hydrogen, $\tilde{K}_{\mathrm{H}}^{\mathrm{Cu}}$ and $\tilde{K}_{\mathrm{H}}^{\mathrm{Zn}}$, have a moderate temperature dependence. However, these dependencies have the same direction and compensate each other. This means that no one of the ion-exchange reactions can be responsible for the existing sufficient separation. The equilibrium coefficients $\alpha_{\mathrm{H}}^{\mathrm{Cu}}$ and $\alpha_{\mathrm{H}}^{\mathrm{Zn}}$, however, depend on temperature significantly. The cause can be found by considering interactions in the solution. The formation of $CuSO_4$ and $ZnSO_4$ complexes has some temperature dependence (14, 15). The same direction of these dependencies [a slow increase of the complex formation constants (2, 3) as the temperature increases], however, results in their compensation of each other. Only the formation of the HSO_4^- complex depends on temperature significantly (14, 15) and it is not compensated for by any other phenomenon. The dependence between the equilibrium coefficients (10) and (11) and the corresponding selectivity coefficients (6) and (7) can be expressed as

$$\alpha_{H}^{Me} = \tilde{K}_{H}^{Me} \frac{[Me^{2+}]}{C_{Me^{2+}}} \left(\frac{C_{H^+}}{[H^+]} \right)^2 \tag{12}$$

This is obtained by combining Eqs. (6), (7) and (9), (10). The formation of HSO_4^- affects the ratio between C_{H^+} and $[H^+]$. According to Eq. (12), this results in a square power dependence of the equilibrium coefficient on the strongly temperature-dependent hydrogen complex formation.

Thus, the variation of the total metal loading capacity described earlier (10) is initiated by the H^+–Me^{2+} ion exchange (6, 7). The process is controlled, however, by hydrogen complex formation in the surrounding solution (4). This principle is illustrated by Fig. 3. The separation is possible because the resin exhibits a high selectivity to Cu^{2+} in comparison with Zn^{2+}. The total

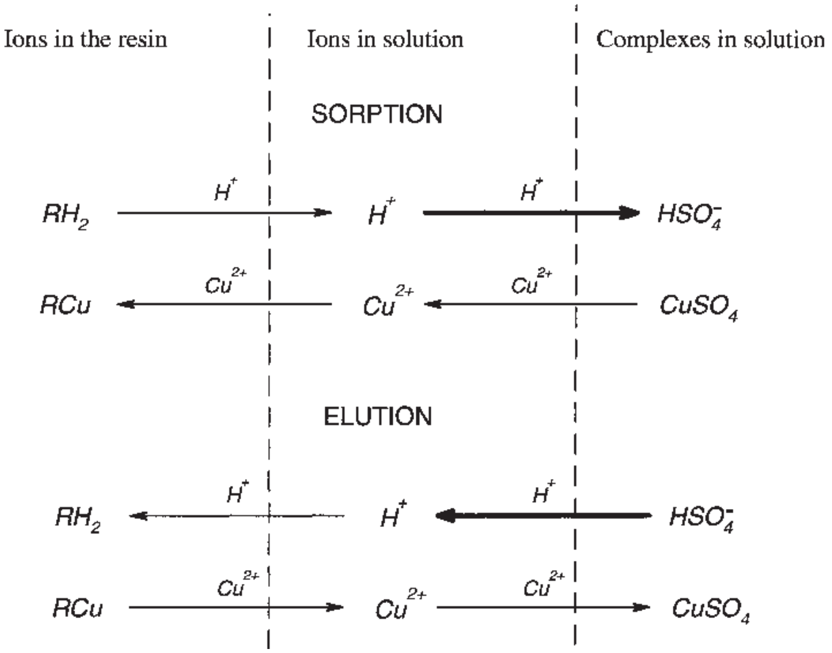


FIG. 3 Chemical background of separation in the system considered. The processes including Zn^{2+} are not reported in the illustration because the zinc redistribution is insignificant. The bold arrows indicate the temperature-controlled processes.

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concentration of Cu and Zn in the work solution increases at one temperature and decreases at another temperature, but the expressive changing of the Cu concentration is accompanied by insignificant shifts in the Zn concentration, thus providing the successful separation.

CONCLUSIONS

The double temperature ion-exchange separation of copper and zinc on iminodiacetic resin Amberlite IRC-718 is physicochemically explained. Contrary to conventional double temperature ion-exchange separation methods, the temperature dependence of ion-exchange selectivity was not found to be the main driving force of the process. The separation is controlled by HSO_4^- complex formation in the surrounding solution.

SYMBOLS

C	total concentration of ion in solution (eq/L or M)
Ion	any cation: metal (Cu^{2+} or Zn^{2+}) or hydrogen (H^+) ion
$\tilde{K}$	ion-exchange selectivity coefficient
$m_{\text{d.r.}}$	weight of dry resin (g)
Q_r	ion-exchange capacity of the resin (meq/g of dry resin)
R	the resin matrix
V	volume of solution (mL)
α	equilibrium coefficient
β	constant of the complex formation in solution

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