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THE SEPARATION OF *Zn* AND *Cu* USING CHELATING ION EXCHANGERS AND TEMPERATURE VARIATIONS

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ABSTRACT

This paper reports the results of a study on the ion-exchange equilibrium of Cu^{2+} and Zn^{2+} at different temperatures on chelating ion-exchange resins: Amberlite IRC-718 (iminodiacetic acid based functional groups), VPC-1 (picolinic acid based) and thiourea-based resins. The separation factors and the conditional equilibrium constants of the ion-exchange reaction were determined in temperature range from 15 to 75 °C. An estimation of thermodynamic functions has also been carried out. Possibility of the separation of *Cu* and *Zn* mixture by dual temperature ion-exchange method has been demonstrated.

INTRODUCTION

Chelating ion exchangers are designed for selective sorption of complex-forming metal ions. These resins contain as a rule one or more donor atoms which can form a coordination bond with metal ions [1,2]. Selectively coefficients of chelating resins are usually characterized by a strong *pH* dependence, that allows one to enhance the selectivity of separation by modulating acidity/alkalinity of the feed solution. The *pH* dependency of ion exchange equilibria for chelating resins of different types was reported in a number of

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publications [3-12]. However, the practical application of this fractionation technique is complicated by the use of large acid and/or alkali volumes needed for the *pH* adjustment and for the further neutralization of resulting wastes.

Another type of ion-exchange separation technique is based on applying ion-exchange resins with distinct temperature dependence of their selectivity towards the desired ions [13-18]. Most of the work in this area has been performed with sulfonic and carboxylic resins, which are characterized by relatively low selectivity, while chelating ion exchangers have not been practically used in dual-temperature separation.

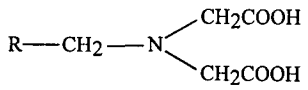
In the parallel study, it has been shown that iminodiacetic asid based resin (Lewatit TP-207) can be successfully applied for the separation of metal ions by the dual-temperature ion-exchange technique [19]. The present study was undertaken mainly to obtain information on temperature dependencies of *Cu-Zn* exchange equilibrium on thiourea based ion exchangers and on picolinic acid-based resin from sulfate solutions at $pH = 1.8$. For comparison the behavior of iminodiacetic acid-based resin Amberlite IRC-718 under the same experimental conditions was also investigated.

EXPERIMENTAL

Amberlite IRC-718 resin was received from *Rohm & Haas* (USA). Experimental resin VPC-1 was synthesized in the *Institute of Chemical Technology* (Moscow, Russia). Thiourea based resins (BTU) were synthesized as described elsewhere [20]. The active groups of the resins are shown in Figure 1. Every ion exchange resin was washed alternately with *HCl* and *NaOH* solutions three times to remove organic matter present from the resin's manufacture.

$CuSO_4 \cdot 5H_2O$ and $ZnSO_4 \cdot 7H_2O$ (*KEBO Lab*, Sweden) and H_2SO_4 (*MERK*, Germany) of analytical grade were used as received. All solutions were prepared using deionized water. The composition of the stock solution remained constant in all series of experiments. *Zn* to *Cu* molar ratio was 102:12 . The total concentration of SO_4^{2-} was kept constant at 0.14 mol/L. The *pH* was maintained to 1.8 with H_2SO_4.

The concentrations of *Cu* and *Zn* were determined by AAS technique using (*Perkin Elmer 603*). *pH* was measured using a glass electrode. The error of spectrochemical analysis was less then 1 % for *Cu* and 2 % for *Zn*.



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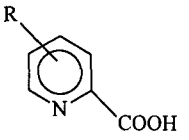

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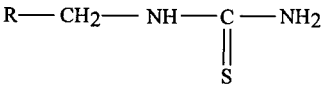

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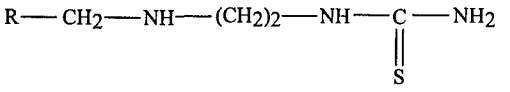

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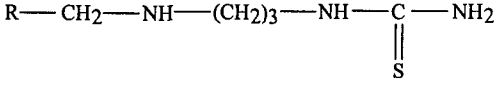

(e)

FIGURE 1. The functional groups of used ion exchange resins: a - IRC-718, b - VPC-1, c - BTUO-1, d - BTUL-1, e - BTUL-2.

The ion exchange equilibria were studied under dynamic conditions in thermostatic glass columns providing the heating / cooling of both resin and solution phases. Each column was loaded with a specified amount of air-dried resin usually approximately 2 g of H^+-form. The amount of water in the resin was determined separately by drying the resin in vacuum over P_2O_5 (until the weight was constant). The feed solution was passed through each column at a constant flow rate of 0.5 ml/min, corresponding to a velocity 0.37 m/h in the column. Achieving ion-exchange equilibrium was monitored by a comparison of the concentration of each cationic specie in the effluent with that in the feed solution. Then the resins (except Amberlite IRC-718) were washed with 10 ml H_2O to remove the stock solution from the interbed space. In the case of the IRC-718 resin, the

feed solution residual was removed by applying vacuum suction because the fast kinetics of IRC-718 resin allows hydrolysis of *Zn*-form during the washing stage. 1 M H_2SO_4 was used for elution of sorbed ions. 2 M H_2SO_4 was used to remove *Cu* residual from the VPC-1 and BTU sorbents. Concentration of *Cu*, *Zn* and *pH* in the eluate obtained were determined. We made a correction for the IRC-718 resin [21] because the solution residual cannot be totally removed from the resin bed by the suction.

The examples of the typical breakthrough curve are shown in Figure 2. It appears that the macroporous absorbent IRC-718 has better kinetic properties (for *Cu* and *Zn*) then the other sorbents. The minima on VPC-1 curve were caused by breaks in the solution pumping rate. This effect was used for an additional control to test for equilibrium. (The equilibrium is reached if there is no concentration decrease in the effluent after the break in the pumping.)

The separation experiment was carried out in the same column as the equilibria experiments. The column was loaded with 4 g of air-dried resin IRC-718. The feed solution was passed through the column at 0.5 ml/min of flow rate. The operating temperature was switched in turn between 15 and 75 °C. The volume passed at each half-cycle was 150 ml. The effluent was collected in 25 ml fractions. Every fraction was analyzed for *Cu*, *Zn* and *pH*.

DATA TREATMENT

Figure 3 shows that *Cu* and *Zn* do not form positive charged complexes in sulfate solutions under the experimental conditions studied. Hence, $M_{Cu}=[RCu]$ and $M_{Zn}=[RZn]$, where M_{Me} and $[RMe]$ are a total metal concentration and the concentration of its ion in the resin phase, respectively. Thus there is only one ion exchange reaction between *Cu* and *Zn*, which is described by following equation

$$RZn + Cu^{2+} = RCu + Zn^{2+} . \quad (1)$$

First the separation factor for *Zn-Cu* exchange reaction (1) can be calculated as follows:

$$\alpha = \frac{[RCu] \cdot C_{Zn}}{[RZn] \cdot C_{Cu}} , \quad (2)$$

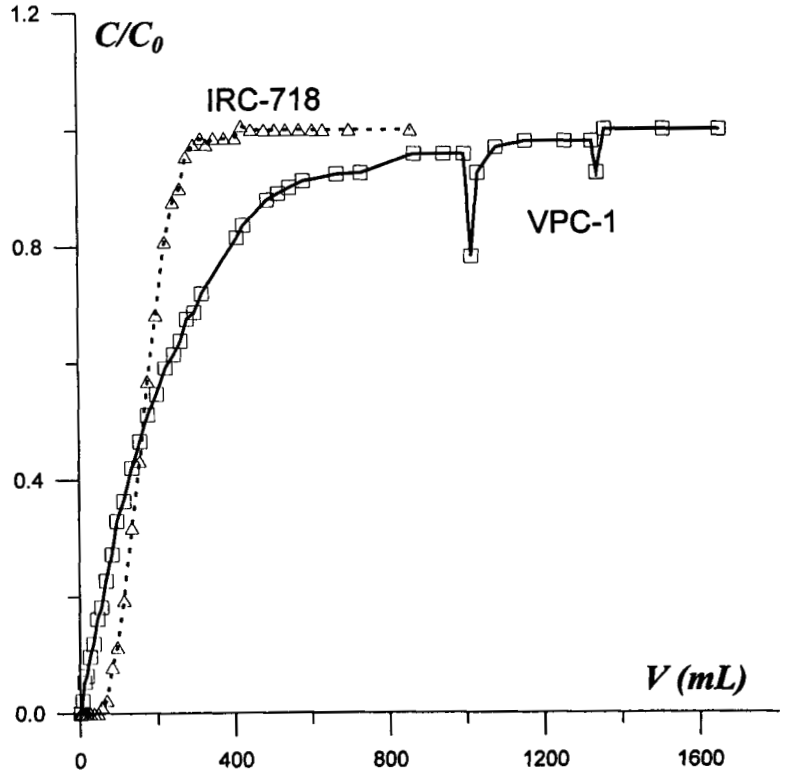

FIGURE 2. *Cu* concentration in effluent history. The sorption by IRC-718 and VPC-1 at 75 °C.

where C_{Me} is a total concentration of metal in the solution phase, which can be expressed as follows:

$$C_{Me} = [Me_{ion}] + [Me_{fixed\ in\ complexes}] \tag{3}$$

One can write the possible complex formation reactions which may proceed in the solution containing Cu^{2+}, Zn^{2+} and SO_4^{2-} under the experimental conditions as follows:

$$Cu^{2+} + SO_4^{2-} = CuSO_4 \ ; \tag{4}$$

$$Zn^{2+} + SO_4^{2-} = ZnSO_4 \ ; \tag{5}$$

$$H^{+} + SO_4^{2-} = HSO_4^{-} \ . \tag{6}$$

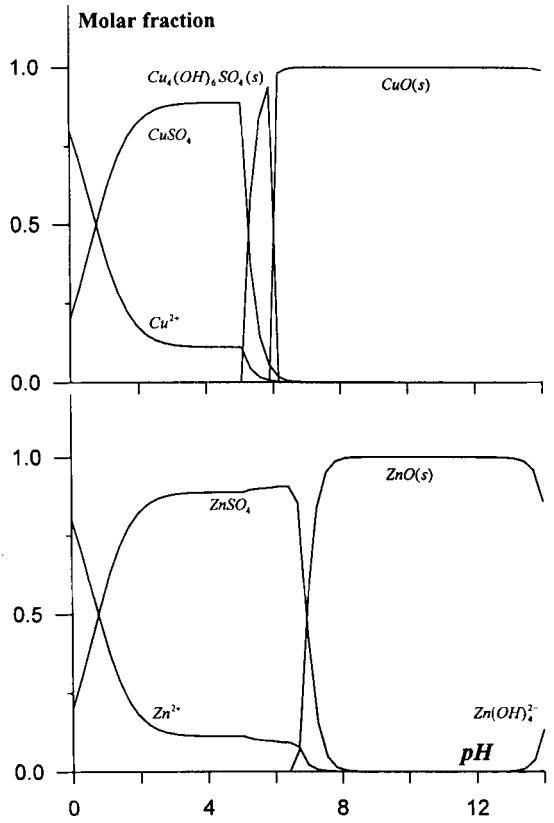

FIGURE 3. Equilibrium calculation for the formation of different complexes in a solution containing 12 mmol/L *Cu* ($CuSO_4$), 102 mmol/L and *Zn* ($ZnSO_4$). (*s*) represents a solid phase.

Concentrations of free metal and complex ions in solution can be calculated from the respective complex formation constants:

$$\beta_{CuSO_4} = \frac{[CuSO_4]}{[Cu^{2+}][SO_4^{2-}]} \quad ; \tag{7}$$

$$\beta_{ZnSO_4} = \frac{[ZnSO_4]}{[Zn^{2+}][SO_4^{2-}]} \quad ; \tag{8}$$

$$\beta_{HSO_4} = \frac{[HSO_4^-]}{[H^+][SO_4^{2-}]} , \quad (9)$$

from the electroneutrality equation

$$2[Cu^{2+}] + 2[Zn^{2+}] + [H^+] = 2[SO_4^{2-}] + [HSO_4^-] + [OH^-] , \quad (10)$$

from the water dissociation equation,

$$K_W = [H^+][OH^-] , \quad (11)$$

and from the expressions for the analytical concentrations of the compounds:

$$C_{Cu} = [Cu^{2+}] + [CuSO_4] ; \quad (12)$$

$$C_{Zn} = [Zn^{2+}] + [ZnSO_4] ; \quad (13)$$

$$C_{SO_4} = [SO_4^{2-}] + [HSO_4^-] + [CuSO_4] + [ZnSO_4] . \quad (14)$$

The complex formation constants (eq. (7)-(9)) were taken from [22]. Analytical concentrations of the different components were analyzed. The system of equations (7)-(14) was solved numerically.

The conditional constant of reaction (1) was calculated as follows

$$\tilde{K}_{ex} = \frac{[RCu][Zn^{2+}]}{[RZn][Cu^{2+}]} . \quad (15)$$

$\tilde{K}_{ex}$ is characteristic of the ion exchange reaction (1). It does not depend on the complex formation processes in solution. For our system under chosen conditions, the relationship between $\tilde{K}_{ex}$ and α is given by

$$\tilde{K}_{ex} = \alpha \cdot \frac{1 + \beta_{CuSO_4}[SO_4^{2-}]}{1 + \beta_{ZnSO_4}[SO_4^{2-}]} . \quad (16)$$

This expression is obtained from the equations (7), (8), (12) and (13).

The error of determinations was examined at 40 °C in the system including IRC-718 resin. The confidence limit was found to be ± 6 % for α determination and ± 1.5 % for $\log \tilde{K}_{ex}$ determination at 90% probability.

RESULTS

The capacities of resins studied for *Cu* and *Zn* exchanged at different temperatures are shown in Table 1. The equilibrium parameters are collected in Table 2. IRC-718 and VPC-1 resins demonstrate a far higher selectivity towards *Cu* than BTU resins. $\widetilde{K}_{cx}$ values for IRC-718 depend slightly on temperature, while those for VPC-1 increase significantly when the temperature rises. The selectivity parameters of the BTU resins also depend on temperature, but low ion-exchange capacities of these resins towards *Cu* and *Zn* (see Table 1) limit their use in practice. From the results given in Table 2, the length of the spacer influences the *Zn/Cu* equilibrium parameters of BTU resins. Indeed, the functional groups of BTUO-1 resin are attached to PS-DVB matrix via one methylene unit. In BTUL-1 resin the length of the spacer increases due to two additional methylene- and one imino- chain units. The further increase of the spacer length does not influence the selectivity of BTU resins significantly (see Table 2).

The thermodynamic functions of the reaction (1) may by estimated through the use of following base equations:

$$\Delta\widetilde{G} = -RT\ln\widetilde{K}_{ex} \quad ; \tag{17}$$

$$\Delta\widetilde{H} = -R\frac{d\ln\widetilde{K}_{ex}}{d(1/T)} \quad ; \tag{18}$$

$$\Delta\widetilde{G} = \Delta\widetilde{H} - T\Delta\widetilde{S} \quad . \tag{19}$$

Although $\widetilde{K}_{ex}$ is not a thermodynamically meaningful parameter, it can be connected with the thermodynamic equilibrium constant K_{ex} of reaction (1) as follows [23]

$$\log K_{ex} = \int_0^1 \widetilde{K}_{ex}\, d\bar{x} \quad , \tag{20}$$

where $\bar{x}$ is the molar fraction of the better sorbed ion (*Cu* in our case) in the resin phase. When $\widetilde{K}_{ex}$ does not depend on the resin composition, one can substitute K_{ex} in equations (17) and (18). From the results in Table 1 and Figure 4, it is shown that the composition of

TABLE 1. THE LOADING CAPACITIES OF RESINS STUDIED TOWARDS Cu AND *Zn* AT DIFFERENT TEMPERATURES MMOL PER 1 g OF DRY RESIN IN H^+ FORM
(equilibrium solution: 0.75 g/L *Cu*, 7.5 g/L *Zn*, *pH* 1.8 (H_2SO_4))

Resin	15 °C		30 °C		40 °C		45 °C		60 °C		75 °C	
	[RCu]	[RZn]	[RCu]	[RZn]	[RCu]	[RZn]	[RCu]	[RZn]	[RCu]	[RZn]	[RCu]	[RZn]
IRC-718	1.12	0.10	1.35	0.10	1.53	0.10	1.56	0.12	1.68	0.12	1.93	0.16
VPC-1	1.64	0.10	1.97	0.07	-	-	2.02	0.06	1.99	0.05	2.10	0.05
BTUO-1	0.02	0.03	-	-	-	-	-	-	-	-	0.20	0.08
BTUL-1	0.04	0.02	-	-	-	-	-	-	-	-	0.35	0.10
BTUL-2	0.03	0.02	-	-	-	-	-	-	-	-	0.06	0.02

TABLE 2. α, $\tilde{K}_{ex}$ AND $\log \tilde{K}_{ex}$ VALUES FOR *Zn-Cu* EXCHANGE ON DIFFERENT CHELATING RESINS
(equilibrium solution: 0.75 g/L *Cu*, 7.5 g/L *Zn*, *pH* 1.8 (H_2SO_4))

	15 °C			30 °C			40 °C			45 °C			60 °C			75 °C		
Resin	α	$\tilde{K}_{ex}$	$\log \tilde{K}$	α	$\tilde{K}_{ex}$	$\log \tilde{K}$	α	$\tilde{K}_{ex}$	$\log \tilde{K}$	α	$\tilde{K}_{ex}$	$\log \tilde{K}$	α	$\tilde{K}_{ex}$	$\log \tilde{K}$	α	$\tilde{K}_{ex}$	$\log \tilde{K}$
IRC-718	110	111	2.05	129	136	2.13	134	144	2.16	123	135	2.13	129	147	2.17	111	131	2.12
VPC-1	153	154	2.19	242	255	2.41	-	-	-	307	336	2.53	337	382	2.58	352	415	2.62
BTUO-1	5	5	0.73	-	-	-	-	-	-	-	-	-	-	-	-	24	28	1.45
BTUL-1	13	13	1.12	-	-	-	-	-	-	-	-	-	-	-	-	32	37	1.57
BTUL-2	14	14	1.15	-	-	-	-	-	-	-	-	-	-	-	-	31	36	1.56

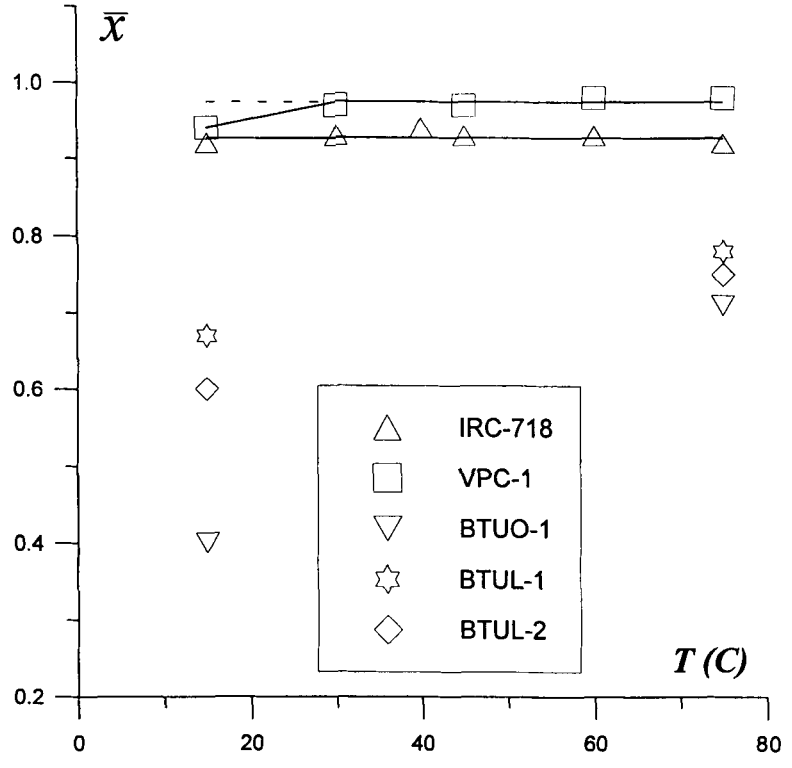

FIGURE 4. Dependencies of copper mole fraction in ion exchangers on temperature.

IRC-718 resin remains constant within the temperature range studied, whereas that of VPC-1 ion exchanger composition is constant in the temperature interval from 30 to 75 °C. Hence, variations of $\tilde{K}_{ex}$ are caused by the temperature changes and $\tilde{K}_{ex} \neq f(\bar{x})$ in these intervals. Plots of $\ln \tilde{K}_{ex} = f(1/T)$ for two resins are given in Figure 5. The results of $\Delta\tilde{H}$ estimation made from the slopes of the straight lines shown in Figure 5 give the following values:

$$\Delta\tilde{H}_{IRC-718} = 2.32 Kj / mol \quad ;$$

$$\Delta\tilde{H}_{VPC-1} = 9.41 Kj / mol \quad .$$

The calculated temperature dependencies of $\Delta\tilde{G}$ and $T\Delta\tilde{S}$ are shown in Figure 6 as well.

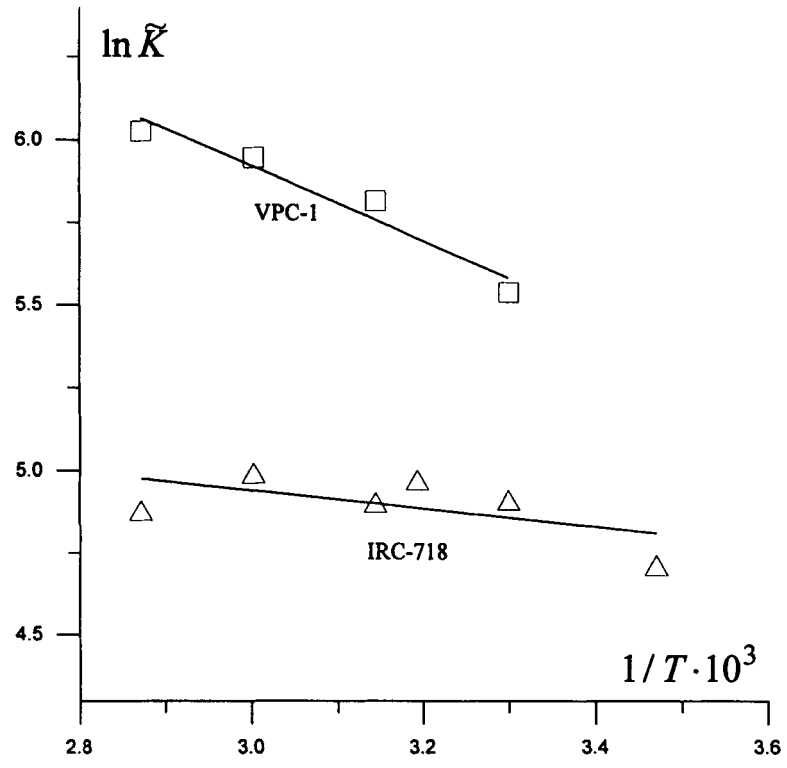

FIGURE 5. The approximation of $\ln \tilde{K}$ dependencies on *1/T* for the thermodynamic calculations.

DISCUSSION

The strong temperature dependence of α and $\tilde{K}$ allows one to use the resins including the picolinic acid groups for the separation of *Cu-Zn* mixtures. The separation was done by passing a solution containing *Cu* and *Zn* continuously through the resin bed. No regeneration solution is used. The temperature of the column was changed between 15 and 75 °C ("low" and "high" temperature), for example. Two eluate fractions were collected according to the temperatures. The concentration of *Cu* in the effluent increases during contact with the resin at "low" temperature and decreases at "high" temperature.

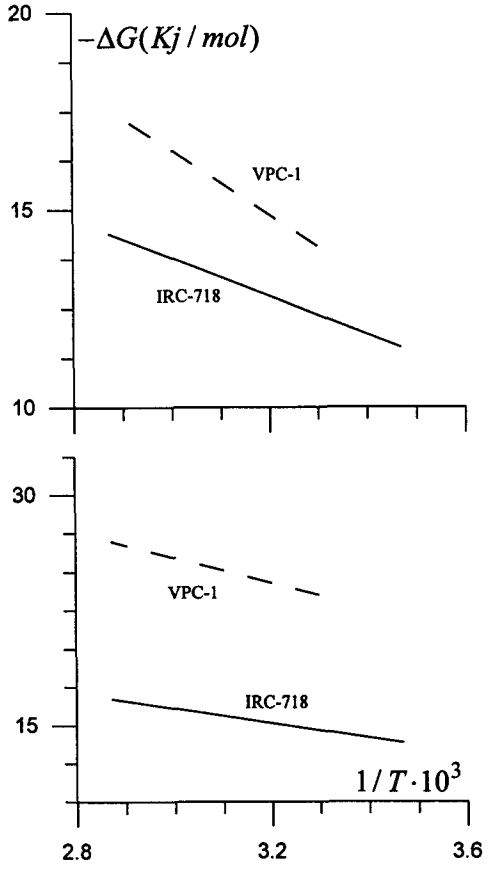

FIGURE 6. Results of thermodynamic calculations.

However, the practical separation by VPC-1 resin is impaired by the slow kinetics of this resin.

The IRC-718 resin has a weak temperature dependence of α and $\tilde{K}_{ex}$ but the strong dependence of the total loading exchange capacity (for *Cu* and *Zn*) on temperature (Figure 7) may be exploited. This is possible because this resin has a high selectivity to *Cu*. The total concentration of *Cu* and *Zn* in the work solution increases at "low" temperature and decreases at "high" temperature, but the big shifts in the *Cu*

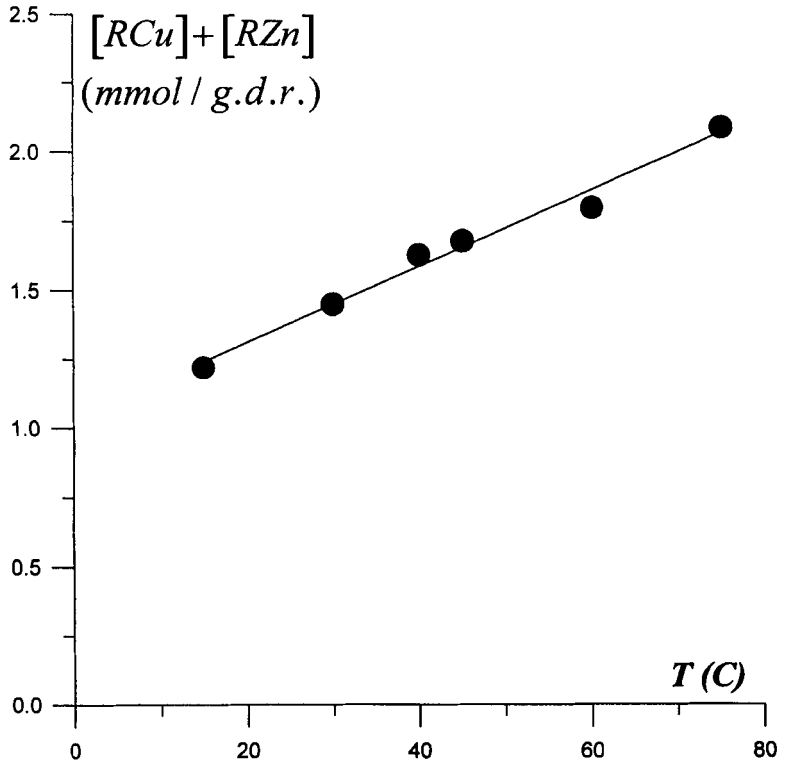

FIGURE 7. The temperature dependence of the total loading exchange capacity *([RZn]+[RCu]*) for Amberlite IRC-718 resin.

concentration are accompanied by the insignificant shifts in *Zn* concentration. The ratio C_{Cu}/C_{Zn} in the concentrated solution is much more than in feed solution.

Figure 8 shows the result of separation experiment on IRC-718 resin, where metal concentrations and *pH* are plotted as a function of the volume passed from the beginning of one cycle. The *Cu* maximal concentration in the effluent increases 88% at "low" temperature and decreases at "high" temperature. Consequently "high-temperature" fraction is a purified solution of *Zn* which contains only 3.7 times less initial concentration of *Cu* in the most purified fraction. The *Cu* concentration difference between two fractions is 7.6 times.

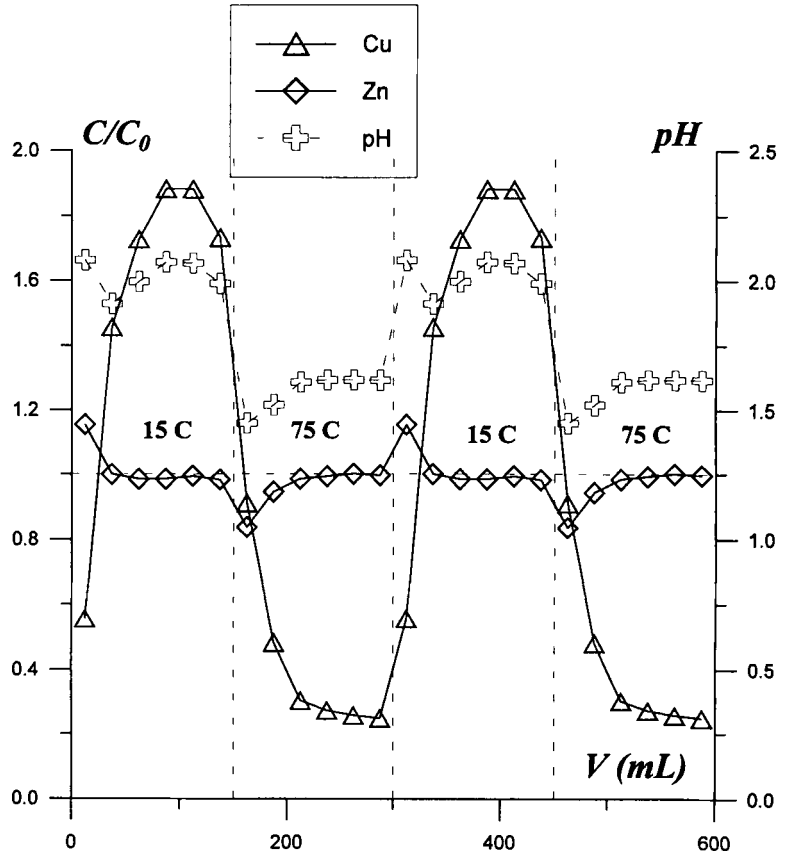

FIGURE 8. Concentration profiles of *Cu*, *Zn* and *pH* as function of volume of feed solution passed for the separation experiment on IRC-718 resin. Zero of the volume axes accords to the beginning of the cycle.

CONCLUSIONS

The possibility of the temperature dependent separation of *Cu* and *Zn* was investigated iminodiacetic acid based, picolinic acid based and thiourea-based resins. The results of equilibria study indicated a better *Cu* and *Zn* separation by VPC-1 resin. The IRC-718 resin has better kinetic properties and may be used for separation and / or concentration of the ion mixture. Earlier studies on dual temperature ion exchange

processes [13-18] indicate that the separation efficiency is dependent on the variation of the separation factor with temperature. Our results indicate that the variation of the total metal loading capacity (of both metal ions) on the ion exchange resins is the determining factor for the separation efficiency. This can be easily understood in view of the fact that the loading capacity of chelating resins is more temperature dependent than non chelating resins. In this case, better separation is obtained when the resins have a much higher selectivity for one of the ions (Cu^{2+}).

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