ADSORPTION OF GALLIUM WITH N_{503} LEVEXTREL RESIN①

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ABSTRACT

The adsorptivity of N_{503} (N, N-di(sec-octyl) acetamide) levextrel resin to gallium in the HCl medium was studied. The adsorption rate and adsorption isotherm of the resin to gallium were measured. The results show that the adsorption of the resin to gallium is carried out in pseudo first order reaction and follows Freundlich isothermal adsorption equation. The adsorption equilibrium and infrared spectrum study show that the adsorption reaction of N_{503} levextrel resin to gallium obeys the following equation:

$$2\overline{N}_{503}+H^{+}+Ga^{3+}+4Cl^{-}=\overline{(N_{503})_2H^{+}GaCl_4^{-}}$$

Key words: gallium adsorption N_{503} levextrel resin

1 INTRODUCTION

Gallium was once extracted by neutralization and replacement reaction with the disadvantages of long procedure and low recovery rate. Recently, the solvent extraction has found wide applications in the separation and extraction of gallium. The extractants in common use are methyisobutyl ketone, tributyl phosphate, trioctylamine. The disadvantages possessed by these solvents, such as large water solubility and bad selectivity, limit their application range[1]. The N_{503} of weak basicity is a substitute extractant of the acylamide. The N_{503} has high stability, nontoxicity and good selectivity. Therefore it is an ideal extractant[2]. The levextrel resin has the advantages of low extractant loss, high column load capacity and good mass transfer property etc[3].

This paper studied the adsorptivity and mechanism of the extraction of the N_{503} levextrel resin to gallium in the HCl medium. And the results show that this kind of resin will find application in extracting gallium.

2 EXPERIMENTAL

2.1 *Reagents And Apparatuses*

The N_{503} levextrel resin was synthesized according to ref. [4] and its grain size is 40 — 60 mesh. The concentration of the N_{503} is 840umol/g-resin. The standard gallium solution was prepared with Ga_2O_3 using routine method. The concentration of the 5-Br-PADAP alcohol solution was 5×10^{-4} mol/L. The other reagents were all analytically pure. The instruments used were 721 spectrophotometer, isothermal flask-shaking machine, AA-670 atomic absorption spectrophotometer and PE-683 infrared spectrophotometer.

2.2 *Adsorption Test of N_{503} Levextrel Resin and Method*

The ratio of levextrel resin to standard gallium solution was 500 mg/20 mL (of which there is 4.0

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mL HCl). The mixture was vibrated for 3 h while the pretest shows that the equibibrium could be reached after vibration for 150 min. Taking proper amounts of the eqilibrium solution for measurements, the difference method was used to calculate the adsorption ratio($E\%$) and the distribution ratio(D):

$$E\% = (C^0 - C)/C^0 \times 100\%$$

$$D = (C^0 - C)V/(WC)$$

where C^0 and C are the initial and equilibrium concentrations of gallium in the aqueous phase; V is the solution volumn, mL; W is the resin amount used, g.

The measurement of gallium: took a proper amount of gallium ($\leqslant$20 μg) and put it into a 25 mL color comparison tube; added one drop of 2,4 —dinitrophenol and adjusted the solution with ammonia solution until the appearance of yellow colour. Then added 2.5 mL HAc-NaAc buffer solution(pH4.0) and 20 mL 5-Br-PADAP alcohol solution. Diluted to volume and mixed. Ten minutes later, measured the absorbance at 570 nm against a reagent blank with 1 cm cell and obtained the gallium concentration from the calibration curve. The concentrations of the other metallic ions were determined by atomic absorption spectrophotometry.

3 RESULTS AND DISCUSSION

3.1 *Adsorptivity of Resin*

(1) Adsorption equilibrium in HCl Medium

Changing the HCl concentration according to the experimental method, we tested the adsorption of the resin to gallium ions and other metallic ions, see Fig. 1. It is clear from Fig. 1 that when the HCl concentration is in the range 3.5 — 5.0 mol/L, the adsorptivity of gallium approaches 100%. When the HCl concentration is 4.0 mol/L, the gallium ions can be completely adsorbed; part of the Fe^{3+} and In^{3+} ions can be adsorbed; and the Cu^{2+}, Ni^{2+} ions and major part of the Zn^{2+} ions can be separated from the gallium ions.

(2) Adsorption Equilibrium in Mixed H_2SO_4 and HCl Medium

Kept the NaCl concentration in the solution at 4.0 mol/L. Changed the H_2SO_4 concentration and measured the adsorptivities of the resin to gallium ions and various other metallic ions, see Fig. 2. With increasing H_2SO_4 concentration, the adsorption ratios of the resin to various metallic ions increased. Under the condition of adding 4.0 mol/L NaCl to the 0.5 mol/L H_2SO_4 solution, the gallium ions can almost completely be adsorbed and can be separated from most of the other metallic ions. The selectivity of the gallium ions in this medium is better than in the 4.0 mol/L HCl medium.

(3) Influence of Salting out Agent on Adsorption.

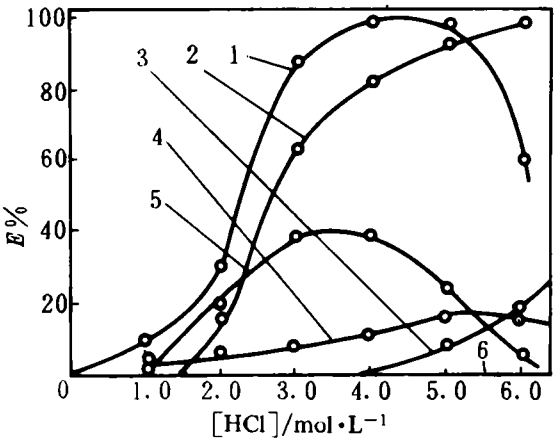

Fig. 1 Adsorptivity of N_{503} levextrel resin in HCl medium ($[M^{n+}]$ = 100 μg/20 mL)
1—Ga^{3+}; 2—Fe^{3+}; 3—Cu^{2+}; 4—Zn^{2+}; 5—In^{3+}; 6—Ni^{2+}

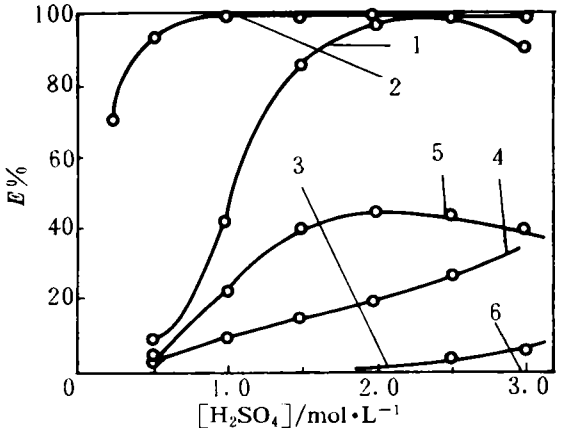

Fig. 2 Adsorptivity of N_{503} levextrel resin in mixed H_2SO_4 and NaCl medium
[NaCl] = 4.0 mol/L; the other conditions are the same as in Fig. 1.

Kept the HCl concentration at 1.0 mol/L, tested the influences of the salting out agents, namely NaCl and $MgCl_2$, on the adsorption of the resin to gallium, see Fig. 3. With increasing NaCl and $MgCl_2$ concentrations, the adsorption ratios increased because of the common ion effect. When the Cl concentration is larger than 4.0 mol/L, the adsorption ratio of the gallium ions reduced due to the competitive adsorption of the Cl^- ions.

3.2 *Adsorption Kinetics*

(1) Adsorption Rate

Weighed 200 mg N_{503} levextrel resin and put it into a triangular flask with a stopper, then added 6.0 mg gallium; kept the HCl concentration at 4.0 mol/L and the total volume at 100 mL; vibrated the solution on the isothermal flask-shaking machine; sampled at given intervals to calculate the adsorption amount Q of the resin to gallium; plotted the Q versus t curve, as shown in Fig. 4(1) and obtained the equilibrium adsorption amount of gallium to be 310 μmol/g-resin.

In light of the pseude first order reaction equation[5]:

$$(a_i - a_t)/a_i \cdot \ln[(a_i - a_\infty)/(a_t - a_\infty)] = k_f \cdot t$$

where k_f is apparent reaction rate constant; a_i and a_∞ are initial and equilibrium gallium concentrations; a_t is the gallium concentration at time t, the k_f value calculated from Fig. 4(2) is 2.31×10^{-1} s^{-1}.

(2) Adsorption Isotherm

Weighed 8 shares of the resin and added different amounts of the standard gallium solution, plotted Q versus C (equilibrium) curve, as shown in Fig. 5(1).

According to Freundlich isothermal adsorption reaction equation:

$$Q = K \cdot C^{1/n}$$

or $$\lg Q = 1/n \lg C + \lg K$$

plotted Fig. 5(2), where K and $1/n$ are Freundlich constants. The straight line of Fig. 5(2) shows that in the experimental range, the adsorption of the resin to gallium follows the Freundlich isothermal adsorption equation. The Freundlich constants are calculated to be $n = 2.40$, $K = 37.2$. It is generally considered that when n equals 2～10, the adsorption reaction is easy to occur[6].

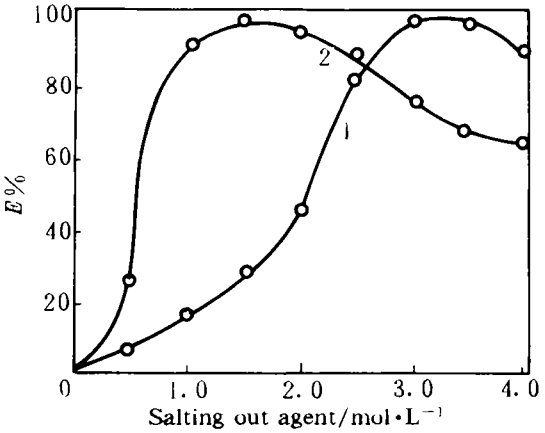

Fig. 3 Influence of salting out agents on adsorption of N_{503} levextrel resin to gallium ions
1—NaCl; 2—$MgCl_2$

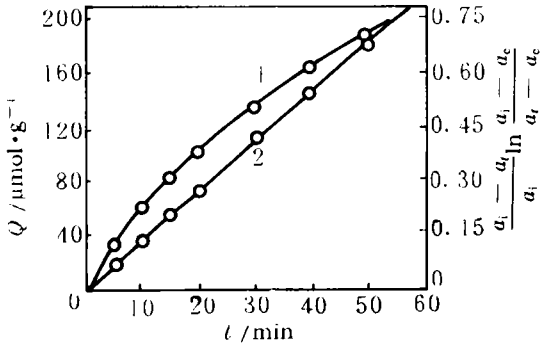

Fig. 4 Adsorption rate of N_{503} levextrel resin to gallium

3.3 *Adsorption Mechanism of N_{503} Levextrel Resin to Gallium*

(1) Isomolar Series Method

Kept the total amount of gallium and N_{503} at 50 μmol, plotted the gallium adsorption amount Q versus the mole fraction of gallium $[Ga]/([Ga] + [\overline{N_{503}}])$ curve as shown in Fig. 6. The largest adsorption amount of gallium occurs when the mole fraction of gallium equals 0.32. This indicates that the adsorption mole ratio of N_{503}/gallium is 2:1.

(2) Saturation Method

Added extra amount of gallium and measured the saturated adsorption amount of the N_{503} levex-

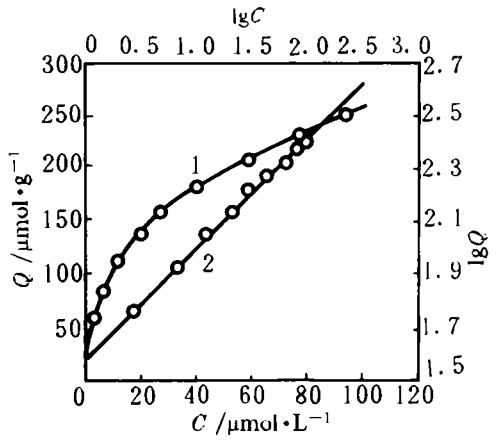

Fig. 5 Adsorption isotherm of N_{503} levextrel resin to gallium

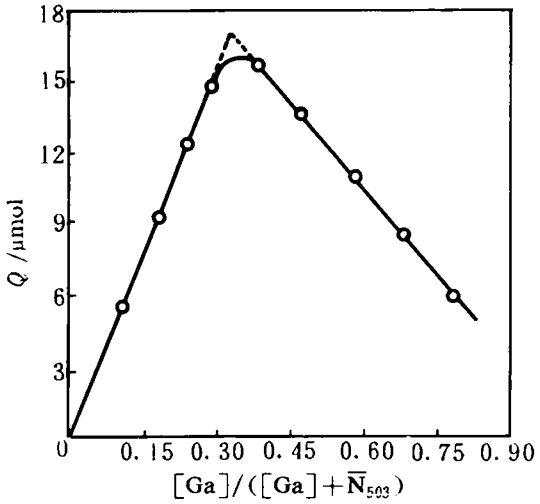

Fig. 6 Dependence of Q on $[Ga]/([Ga]+[\overline{N_{503}}])$ in isomolar series method

trel resin to gallium to be 371 μmol/g; the ratio of this value to the N_{503} concentration in the resin (8.10 μmol/g) is 1:2.26, which approaches 1:2. There fore the results obtained by both the above method agree with each other.

(3) Determination of H^+ Number in Each Absorbed Molecule

Added 100 μg gallium, changed $[H^+]$ to keep the $[Cl^-]$ at 4.0 mol/L by using NaCl, then plotted the lg$D$ versus lg$[H^+]$ curve, see Fig. 7. The obtained curve is a straight line with a slope of 1.06. This indicates that each absorbed molecule contains one H^+.

(4) Determination of Cl^- Number in Each Absorbed Molecule

Added 100 μg gallium, kept the $[H^+]$ at 1.0 mol/L, and used NaCl to adjust the $[Cl^-]$. Plotted lg$D$ versus lg$[Cl^-]$ curve, as shown in Fig. 8, obtained the slope to be 4.08. This indicates that each absorbed molecule contains four Cl^- ions.

(5) Infrared Spectrum of Resin

In order to further determine the bonding types of the absorbed molecules, the infrared adsorption spectra of the resin before and after adsorbing gallium. From Fig. 9, it is clear that before adsorbing gallium, $\nu_{C=O}$ and ν_{C-N} of the N_{503} in the resin are situated at 1 640 cm^{-1} and 1 340 cm^{-1} respectively. After adsorbing gallium, $\nu_{C=O}$ moves to 1 620 cm^{-1}, but the displacement of ν_{C-N} is not clear. This indicates that in the process of adsorption, the carbonyl plays the role of protonation. In

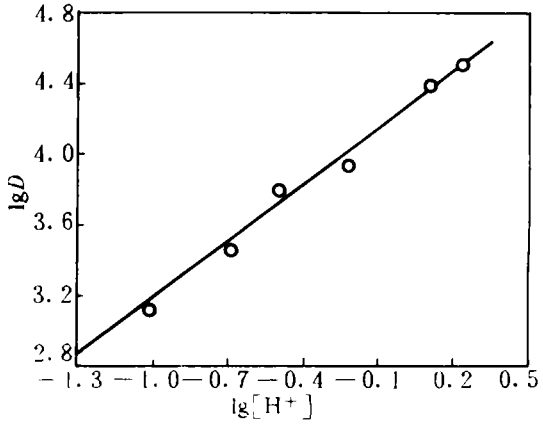

Fig. 7 Dependence of lg$D$ on lg$[H^+]$

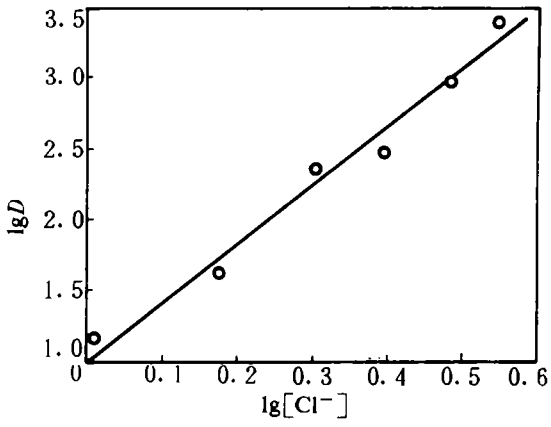

Fig. 8 Dependence of lg$D$ on lg$[Cl^-]$

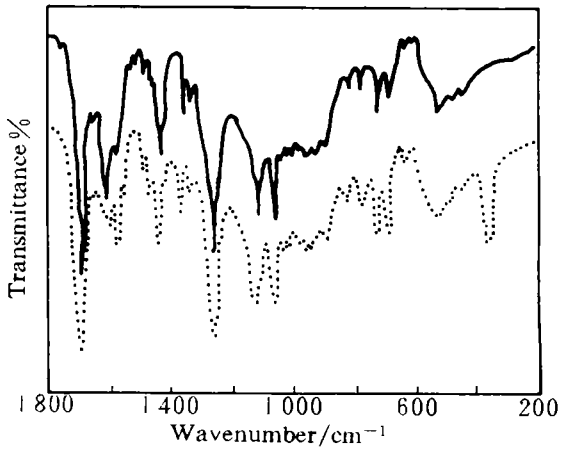

Fig. 9 Infrared spectra of resin
solid line—before adsorbing gallium;
dash line-after adsorbing gallium

addition, after the resin adsorbs galliuln, there appears at 370 cm^{-1} a characteristic adsorption peak of Ga — Cl bond. This shows that there exist $GaCl_4^-$ ions.

According to the above experimental results, it can be believed that the adsorption reaction of the N_{503} levextrel resin to gallium is carried out as follows:

$$2\overline{N_{503}} + H^+ + Ga^{3+} + 4Cl^- = \overline{(N_{503})_2H^+GaCl_4^-}$$

$$K = \frac{\overline{[(N_{503})_2H^+\,GaCl_4^-]}}{\overline{[N_{503}]}^2 \cdot [H^+] \cdot [Ga^{3+}] \cdot [Cl^-]^4} = \frac{D}{\overline{[N_{503}]}^2 \cdot [H^+] \cdot [Cl^-]^4}$$

where K is adsorption equilibrium constant; D is distribution ratio; $\overline{[N_{503}]}$ is the N_{503} concentration in the resin.

Taking the logarithm of the above equation, we have:

$$\lg D = \lg K + \lg[H^-] + 2\lg\overline{[N_{503}]} + 4\lg[Cl^-]$$

The above experimental results all demonstrate this relation.

4 SUMMARY

In HCl or mixed NaCl and H_2SO_4 medium, the N_{503} levextrel resin has good adsorptivity to gallium. It is hopeful to become an effective extractant for gallium. On-column dynamic method is in the process of further study.

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