第 12 期
2003 年 12 月

无 机 化 学 学 报
CHINESE JOURNAL OF INORGANIC CHEMISTRY

Vol. 19, No. 12
Dec., 2003

研究简报

亚氨基二乙酸树脂吸附钇(Ⅲ)的研究

熊春华*,[1] 吴香梅[2]

([1] 杭州商学院食品、生物技术和环境工程学院, 杭州 310035)

([2] 丽水师范专科学校化学系, 丽水 323000)

关键词: 亚氨基二乙酸树脂 钇 吸附 机理

分类号: O614.32+2

Study on the Adsorption of Iminodiacetic Acid Resin for Yttrium (Ⅲ)

XIONG Chun-Hua*,[1] WU Xiang-Mei[2]

([1] *College of Food Science, Biotechnology and Environmental Engineering, Hangzhou University of Commerce, Hangzhou* 310035)

([2] *Department of Chemistry, Lishui Teachers College, Lishui* 323000)

The adsorption behavior and mechanism of a novel chelate resin, iminodiacetic acid resin (IDAAR) for Y (Ⅲ) were investigated. The statically saturated adsorption capacity is 102mg · g^{-1} resin at 298K in HAc-NaAc medium at pH 5.7. Y (Ⅲ) adsorbed on IDAAR can be reductively eluted by 1.0 ~ 4.0mol · L^{-1} HCl used as eluant and the elution percentages are almost as high as 100%. The resin can be regenerated and reused without apparent decrease in adsorption capacity. The apparent adsorption rate constant is $k_{298} = 3.36 \times 10^{-5} s^{-1}$. The adsorption behavior of IDAAR for Y (Ⅲ) conforms to Freundlich's model reasonably. The thermodynamic adsorption parameter, enthalpy change ΔH of IDAAR for Y (Ⅲ) is 18.6kJ · mol^{-1}. The complex molar ratio of the functional group of IDAAR to Y (Ⅲ) is about 3∶1. The adsorption mechanism of IDAAR for Y (Ⅲ) was examined by using chemical method and IR spectrometry.

Keywords: iminodiacetic acid resin yttrium adsorption mechanism

0 Introduction

Chelate resin that possesses atoms such as oxygen, nitrogen, sulphur and phosphorous has the ability of coordinating directly with metal ions and in this area more and more research is involved recently[1~7]. Iminodiacetic acid resin (IDAAR) is a novel chelate resin and contains a functional group of [-N(CH_2COOH)$_2$] which possesses not only proton that can exchange with cation, but also oxygen atom that can coordinate directly with metal ions. What's more, it has quite a lot of advantages such as high adsorption capacity, easy regeneration and convenient operation etc. So IDAAR can be effectively used in the adsorption of metal ions. The present paper aims at studying the adsorption behavior and mechanism of IDAAR for Yttrium (Ⅲ). The basic adsorption parameters were determined. The ex-

收稿日期: 2003-06-24。收修改稿日期: 2003-08-26。

浙江省高校中青年学科带头人基金资助项目, 浙江省自然科学基金资助项目(No. 200072)。

*通讯联系人。E-mail: xiongch@163.com

第一作者: 熊春华, 男, 44 岁, 教授; 研究方向: 配位化学。

perimental results may provide a basis for concentrating Yttrium (Ⅲ) in hydrometallurgy and further studying in coordination chemistry.

1 Experimental

1.1 Materials

IDAAR: iminodiacetic acid resin (provided by East China University of Science and Technology, H-type, activated before use), standard solutions of Y (Ⅲ), La (Ⅲ), Sm (Ⅲ) and Ho (Ⅲ) were prepared from Y_2O_3, La_2O_3, Sm_2O_3 and Ho_2O_3 with a purity of 99.99%, buffer solution with pH 3.0 ~ 6.0 were prepared from KCl ~ HCl and HAc ~ NaAc, other reagents were of A. R. grade.

1.2 Experimental Method

1.2.1 Adsorption Equilibrium Experiment[7]

A desired amount of treated resin was weighed up and added to a conical flask, and then a desired volume of the buffer solution with pH 5.7 was added to it. After 24h, a required amount of standard solution of Y (Ⅲ) was added to the flask. The flask was shaken in a SHZ-B temperature constant shaking machine at the constant temperature. The upper layer of the clear solution was taken for analysis until the adsorption equilibrium was reached. The concentration of Y (Ⅲ) in the aqueous phase was quantitatively determined by using a Shimadzu UV-2401PC UV/VIS spectrophotometer at 570nm[8]. The adsorption capacity (Q), distribution coefficient(D) and separating coefficient(β) were calculated as follows.

$$Q = \frac{(C_0 - C_e) \cdot V}{W}$$

$$D = \frac{Q}{C_e}$$

$$\beta_{RE^{3+}/Y^{3+}} = \frac{D_{RE^{3+}}}{D_{Y^{3+}}}$$

C_0: initial concentration of metal ion in solution (mg Y (Ⅲ) · mL^{-1})

C_e: equilibrium concentration of metal ion in solution (mg Y (Ⅲ) · mL^{-1})

V: total volume of solution (mL)

W: resin weight (g)

RE: rare earth (La, Sm, Ho)

1.2.2 Elution Test

20.0mg resin was added to a mixed solution composed of pH 5.7 buffer solution and a desired amount of the standard solution of Y (Ⅲ). After the equilibrium was set up, the concentration of Y (Ⅲ) in the aqueous phase was determined, and then the adsorption capacity of the resin for Y (Ⅲ) was obtained.

The resin separated from the residual was washed three times with the pH 5.7 buffer solution. The resin adsorbed Y (Ⅲ) was shaken with the eluant. After the equilibrium was set up, the concentration of Y (Ⅲ) in aqueous phase was determined and then the percentage of elution was obtained.

2 Results and Discussion

2.1 Effect of pH on the Distribution Coefficient and Separating Coefficient

The test was carried out according to the above-mentioned method. The effect of pH on the adsorption behavior of IDAAR for Y^{3+} was shown in Fig. 1. The results indicate that the distribution coefficient increases with the increase of pH but when pH is above 5.7, it keeps nearly steady. So all the following experiments were performed at pH 5.7. With the same method, the experiments on the adsorption for La (Ⅲ), Sm (Ⅲ) and Ho (Ⅲ) were conducted individually. When $[RE^{3+}]_0$ is 4.0mg/30.0mL, pH is 5.7, the separating coefficients of $\beta_{La^{3+}/Y^{3+}}$, $\beta_{Sm^{3+}/Y^{3+}}$ and $\beta_{Ho^{3+}/Y^{3+}}$ are 3.04, 3.82 and 5.02, respectively. The results indicate that La^{3+}, Sm^{3+}, Ho^{3+} and Y^{3+} can be separated to a certain degree.

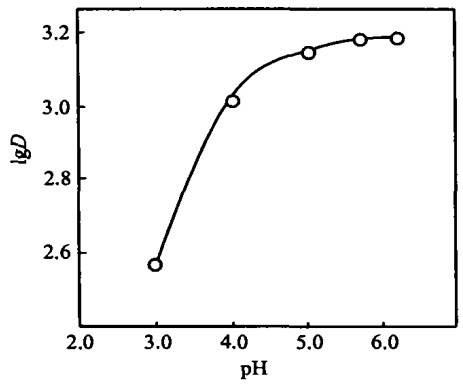

Fig. 1 Effect of pH on distribution coefficient
resin 20.0mg $[Y^{3+}]_0$ = 4.0mg/30.0mL T = 298K

2.2 Isotherm Adsorption Curve

20.0mg, 25.0mg, 30.0mg, 35.0mg, 40.0mg of the resin were weighed and put into conical flasks individually. The other experimental conditions were shown in Fig. 2. When the adsorption equilibrium arrived, the equilibrium concentration C_e(mg · mL^{-1}) was determined and its corresponding adsorption capacity Q(mg · g^{-1} resin) was calculated. As we all know, the empirical Freundlich adsorption equation has the general form:

$$Q = aC_e^{1/b} \quad \text{i.e.} \quad \lg Q = 1/b(\lg C_e) + \lg a$$

where b and a are the isotherm parameters to be determined. The regression equation at 298K is $\lg Q = 0.253 \lg C_e + 2.32$ with a correlation coefficient 0.9971, which indicates that adsorption on the IDAAR fits Freundlich's model reasonably (Fig. 2). So, b is equal to 3.9 and a is 207. The fact that b value is between 2 and 10 means that the adsorption of IDAAR for Y (Ⅲ) is a favorable adsorption process[9].

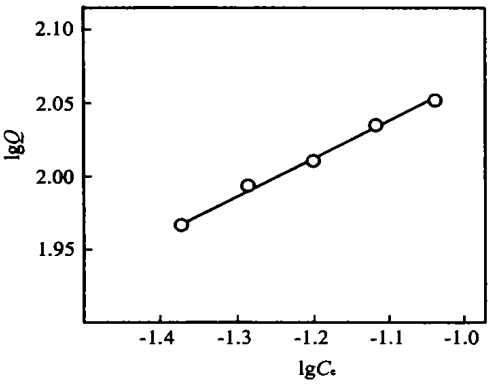

Fig. 2 Freundlich isotherm curve
$[Y^{3+}]_0 = 5.0$mg/30.0mL $T = 298$K pH = 5.7

2.3 Determination of Adsorption Rate Constant

According to the experimental condition shown as Fig. 3 and the above-mentioned method, 0.30mL of upper layer clear solution was taken out at intervals for the determination of residual concentration, after the remains kept constant and volume was corrected, a series of data was obtained. When the adsorption amount is a half of that at equilibrium, the required time is $t_{1/2} = 11$h. According to Brykina method[10],

$$-\ln(1 - F) = kt,$$

where $F = Q_t/Q_\infty$, Q_t and Q_∞ are the adsorption amounts at certain time and at equilibrium time, respectively. The experimental results are accorded with the equation and a straight line is obtained by plotting $-\ln(1 - F)$ against t. Therefore, the adsorption rate constant which is $k_{298} = 3.36 \times 10^{-5}$s^{-1} can be found out from the slope of the straight line.

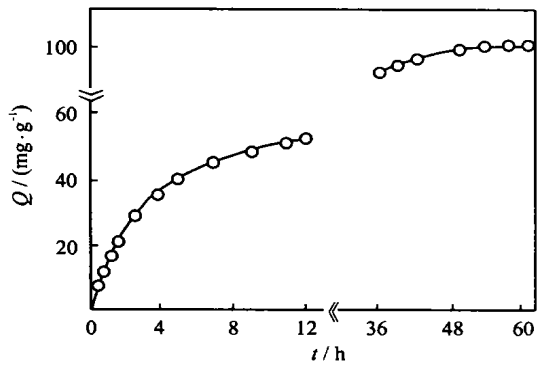

Fig. 3 Adsorption capacity Q in different adsorption time
resin 20.0mg $[Y^{3+}]_0 = 4.0$mg/40.0mL pH = 5.7 $T = 298$K

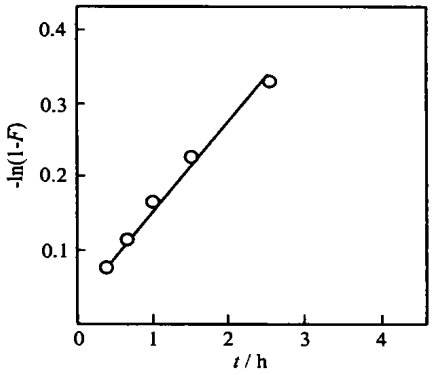

Fig. 4 Determination of adsorption rate constant
resin 20.0mg $[Y^{3+}]_0 = 4.0$mg/40.0mL pH = 5.7 $T = 298$K

2.4 Effect of Adsorption Temperature on Distribution Coefficient and Determination of Thermodynamic Parameter

Under the experimental condition shown in Fig. 5, the distribution coefficient D of the resin for Y^{3+}, over the range of temperature 291 ~ 317K, was measured. A straight line was obtained by plotting $\lg D$ against $1/T$ with a correlation coefficient 0.9976. The result obviously indicates that it is favorable for the adsorption if the temperature rises, ie, under the experimental range of temperature, the adsorption ability of the resin increases with the rise in temperature. It implies that the adsorption process is an endothermic process.

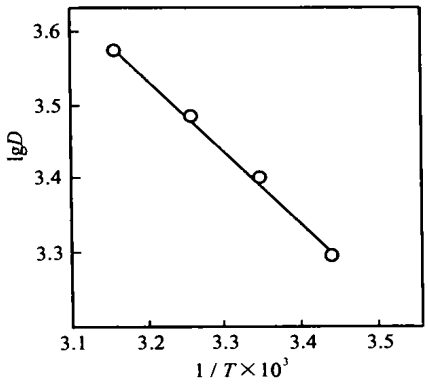

Fig. 5 *Effect of temperature on distribution coefficient*
resin 20.0mg $[Y^{3+}]_0 = 3.0mg/30.0mL$ pH = 5.7

Therefore, the adsorption reaction is a chemical adsorption. According to

$$\lg D = -\Delta H/2.30RT + \text{constant}$$

ΔH can be found out from the slope of the line and the result is 18.6kJ · mol^{-1}.

2.5 Determination of the Complex Molar Ratio

2.5.1 Saturated Method

The nitrogen content of IDAAR was determined by using EA 1110 Elemental Analyzer[6]. The result was shown in Table 1.

Table 1 Complex Molar Ratio of IDAAR Functional Group to Y (Ⅲ)

N% of IDAAR/%	functional group capacity of IDAAR /(mmol FG · g^{-1})	adsorption capacity of IDAAR /(mmol Y (Ⅲ) · g^{-1})	complex molar ratio FG/Y (Ⅲ)
4.66	3.33	1.15	2.90:1

Under the experimental condition of $T = 298K$, $[Y^{3+}]_0 = 5.0mg/30.0mL$, the experiment was performed by using the above-mentioned method. The adsorption capacity of the resin for Y^{3+} is 102mg · g^{-1} resin. The amount of the functional group and the capacity of the resin for Y^{3+} are calculated and listed in Table 1, which indicates that the molar ratio of the functional group to Y (Ⅲ) is approximately 3:1.

2.5.2 The Effect of Na^+ on Adsorption Capacity of IDAAR

Na^+ can also be adsorbed by IDAAR resin. But according to 2.6, we can know that it just exchanges with H of -COOH instead of coordinating with them. In order to find out the adsorption ability of resin for Y^{3+}, we also conducted an investigation into the experiment when Na^+ was added into the solution and the other conditions were the same as 2.5.1. The result indicates that the capacity of the resin for Y (Ⅲ) changes little with the increase of Na^+ in the solution. So, it might be concluded that IDAAR resin has a certain selectivity and that the coordination with it is strong in Na^+ solution.

2.5.3 Equimolar Method[5]

Seven parts of different amount of resin were accurately weighed, and added into the conical flasks, respectively, and then mixed with different amount of Y (Ⅲ). The total mole of IDAAR and Y (Ⅲ) was kept a constant 145.0μmol, whatever the molar ratio may be. That was carried out with the same method mentioned before. The adsorption amount vs $[R]/([Y^{3+}] + [R])$ yields a curve as shown in Fig. 6. The expected adsorption amount is the maximum as the molar fraction of resin is 0.72 shown on the abscissa. It means that the complex molar ratio of the functional group to Y (Ⅲ) is about 3:1, which is consistent with the result of the saturated method.

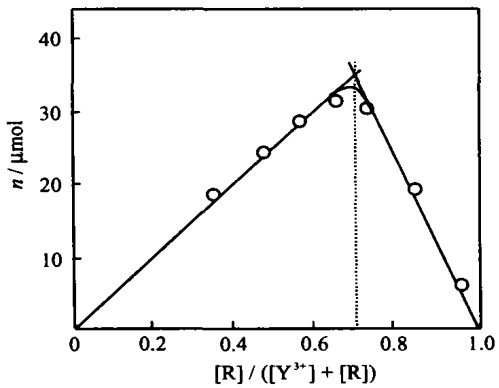

Fig. 6 Equimolar series method
$T = 298K$ pH = 5.7

2.6 Analysis of Infrared Spectra[6]

From the above result, it can be concluded that the adsorption of Y (Ⅲ) by IDAAR ($\Delta H > 0$) belongs to chemical adsorption. Therefore, in the functional groups of IDAAR, -COOH and Y (Ⅲ) are supposed to form chemical bonds. In order to confirm this, we carried out IR(KBr) spectra experiment by using a Perkin-Elmer 683 FT-IR spectrophotometer in the 400 ~ 4000cm^{-1} region and compared the spectra of the resin before and after Y (Ⅲ) is adsorbed. It is easy to discover that the characteristic adsorption peaks of the bond C = O (1728cm^{-1}) has disappeared, but the new

Table 2 Effect of Na^+ on Adsorption Capacity of IDAAR

concentration of NaCl/(mol · L^{-1})	0	2.28×10^{-3}	4.56×10^{-3}	6.84×10^{-3}	9.12×10^{-3}	1.82×10^{-2}
adsorption capacity of IDAAR/(mg Y(Ⅲ) · g^{-1})	102	101	102	100	102	101

peaks 1607cm^{-1} and 1407cm^{-1} have formed. The newly-formed peaks can be assigned to the $\nu_{as(COO^-)}$ and the $\nu_{s(COO^-)}$ vibration of the COO^- and the $\Delta\nu$ is 200 cm^{-1}. We also investigated the spectra of the Na-type resin and found that the $\nu_{as(COO^-)}$ appeared at 1631cm^{-1} and $\nu_{s(COO^-)}$ at 1394cm^{-1} and the $\Delta\nu$ was 237cm^{-1}. Those data further support these the two facts: the formation of the coordination bonds of oxygen atoms and Y(Ⅲ); the consistence with a bidentate mode[11].

2.7 Elution and Recovery of Resin

When HCl was used as an eluant, HCl aqueous solution with different concentration were studied in this experiment. Experimental results listed in Table 3 show that the percentages of elution are almost up to 100% when the concentration of HCl varies from 1.0mol · L^{-1} to 4.0mol · L^{-1}. So Y(Ⅲ) adsorbed on the resin can be recovered quantitatively.

Table 3 Elution Test of Y(Ⅲ)

concentration of HCl/(mol · L^{-1})	adsorption capacity of IDAAR /(mg Y(Ⅲ)/20.0mg)	elution amount/mg	elution percentage/%
1.0	2.04	2.04	100.0
2.0	2.04	2.04	100.0
3.0	2.04	2.03	99.5
4.0	2.04	2.03	99.5

In order to examine the practical value of HCl as an eluant, the elution rate of 1.0mol · L^{-1} HCl was determined by using the same method mentioned before. The results show that $t'_{1/2}$ is equal to 8min and t'_∞ is 40min. Here $t'_{1/2}$ and t'_∞ are the time required to reach 50% and 100% of elution. Therefore, the elution of Y(Ⅲ) is practical from the point of kinetic view.

2.8 Regeneration and Reuse of IDAAR

After Y(Ⅲ) was adsorbed and eluted by 1.0mol · L^{-1} HCl, the resin was washed several times by redistilled water. Three times of regeneration test were carried out. The results listed in Table 4 show that the adsorption capacity is almost unchangeable and that IDAAR has a good ability to regenerate. So the resin can be used repeatedly.

Table 4 Results of Reuse of IDAAR

reuse times	1	2	3
adsorption capacity Q/(mg · g^{-1})	102	102	101

The IR spectrum of the regenerated resin is exactly the same as that of IDAAR and N content of the regenerated IDAAR equals to that of the original IDAAR too. The results show that the quality of regenerated IDAAR is good.

References

[1] CHEN Yi-Yong, CAI Guo-Ping, WANG Nai-Dong *Macromol Sci-chem*, **1990**, **A27**(9 ~ 11), 1321.

[2] CHEN Yi-Yong, LIANG Chao, CHAO Yan *Reactive Polymers*, **1998**, **36**, 51.

[3] Alexandratos S. D. *Proceedings of IUPAC 9th International Conference on Polymer Based Technology*, Tianjin China, **2000**, 4.

[4] XIONG Chun-Hua(熊春华), WANG Yong-Jiang(王永江), SHI Lin-Mei(施林妹) *Chemistry Research in Chinese Universities*, **2003**, **19**(3), 366.

[5] XIONG Chun-Hua(熊春华), WU Xiang-Mei(吴香梅) *Huanjing Kexue Xuebao*(*Acta Scientiae Circumstantiae*), **2000**, **20**(5), 627.

[6] XIONG Chun-Hua(熊春华), SHU Zeng-Nian(舒增年) *Youse Jinshu*(*Nonferrous Metals*), **2000**, **52**(2), 61.

[7] WANG Nai-Dong(王耐冬), XIONG Chun-Hua(熊春华), JI Fu-Gend(计福根), ZHU Guo-Hua(朱国华) *Gaodeng Xuexiao Huaxue Xuebao*(*Chemical Journal of Chinese Universities*), **1986**, **7**(9), 765.

[8] Translated by SUN Shu-Yuan(孙淑媛), SUN Ling-Gao(孙龄高) *The Organic Reagent in Metal Analysis*(金属分析中的有机试剂), Beijing: Beijing Normal University Press, **1983**, p208.

[9] Translated by LU Zheng-Li(鹿政理) *Adsorption Basis and Design*(吸附的基础与设计), Beijing: Chemical Industry Press, **1983**, p33.

[10] Brykina G. D., Marchak T. V., Krysina L. S., Belyavskaya T. A. *Zhi. Anal. Khim.*, **1980**, **35**(12), 2294.

[11] Nakamoto K. (中本一雄), Translated by HUANG De-Ru (黄德如), WANG Ren-Qing(汪仁庆) *Infrared and Raman Spectra of Inorganic and Coordination Compounds, Third Edition*(无机和配位化合物的红外和拉曼光谱, 第三版), Beijing: Chemical Industry Press, **1986**, p235.