Preparation and Behavior of Calix[4]arene-containing Organosilicone Resins (I)

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ABSTRACT: Two organosilicone resins (PCSN and PCSNN) were prepared from 1,3-bis-glycidyl-*p*-*tert*-butyl-calix[4]arene(BGC) via condensation with triethoxyaminopropyl-silane or triethoxy-4-azo-6-aminohexylsilane, followed by copolymerization with tetrae-thoxysilane, respectively. The resins exhibit high thermostability and adsorb nitrogen under elevation temperature. The adsorption capacity of PCSN and PCSNN toward Mg(II), Cu(II), Pb(II), Hg(II), and Au(III) cations was determined and the thermodynamic parameter of the resins toward Au(III) ion was deduced. Human serum protein was also adsorbed on the resins. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 80: 58–64, 2001

Key words: organosilicone resin; calix[4]arene; silicone monomer; condensation polymerization; adsorption

INTRODUCTION

Functionalized polysiloxanes were widely used as stationary phases or adsorbents in analytical chemistry and separational science, as catalyst supports in catalysis and organic synthesis.[1–5] These materials have good diffusivity of solutes, excellent thermal stability, and can be recovered and reused easily. Calixarenes (Fig. 1) are the third-generation host molecules after crown ethers and cyclodextrins. Because the calixarene possess special cavity composed of phenyl moieties and cyclic hydroxyl array, they exhibit good complexation ability either with ions or neutral molecules.[6] Calixarene modified polysiloxanes were used as station phases in GC and HPLC.[7,8]

However the calixarene content in the above-mentioned polymer is low. In this article we wish to report the synthesis of two calix[4]arene-containing organosilicone monomers (CSN, CSNN) and their copolymer with tetraethoxysilane (PCSN, PCSNN). The synthetic route is shown in Figure 2. It was found that these calix[4]arene-containing organosilicone resins possess high thermostability and special adsorption behavior toward nitrogen. Their adsorption ability toward metal cations ions and human serum protein was also explored.

EXPERIMENTAL

Materials

1-Chloro-2,3-epoxypropane was purified by treating with a molecular sieve and distilling before use, supplied by the Resin Factory of the Hunan Yueyang Chemical Industry Co.
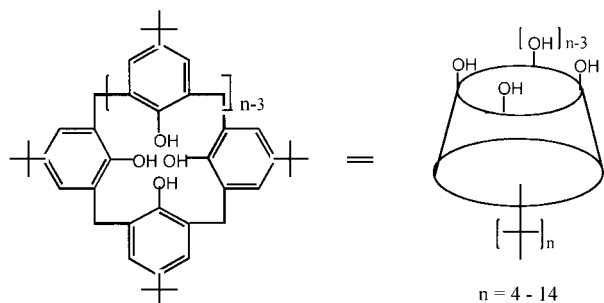

Figure 1 Structure of calixarenes.

(China). γ-Aminopropyl-triethoxysilane, 4-azo-6-aminohexyl-triethoxysilane and tetraethoxysilane were supplied by the Chemical Plant of Wuhan University. *p-tert*-Butyl-calix[4]arene (Fig. 1, $n = 4$) was synthesized by the reaction of *p-tert*-butyl-phenol with formal-aqueous solution in the presence of potassium hydroxide and nitrogen atmosphere, yield: 55%, m.p. > 300°C; [lit. [11], 50%]. Other reagents were supplied by the Shanghai Chemical Reagents Co. (Shanghai, China). They were laboratory grade chemicals.

Measurements

Elemental analysis carried out by a 1106 elemental autoanalysis apparatus (Carlo-Erba, Italy). The IR spectra were recorded on a Nicolet 170SX FTIR spectrometer (Hitachi, Japan). ^{1}H-NMR spectra were obtained on a EM-360L spectrometer (Varian, USA). Mass spectra were recorded on a ZAB 3FHF Mass Spectrometer by fast atom bombardment (FAB-MS, VG, UK). The TG and DSC were carried out on a STA 409C thermal analyzer (Netzsch, Germany). The runs were performed at a heating rate of 20°C/min from 40 to 700°C in an atmosphere of dry nitrogen (80 mL/min). The concentrations of metal ions were determined by titration or by a 180–80 atomic absorption spectrometer (AAS, Hitachi, Japan). The concentrations of human serum protein was determined by a 1061 ultraviolet absorption spectrometer (UV, Hitachi, Japan).

Synthesis of 1,3-Bisglycidyl *p-tert*-butyl calax[4]arene

The 1,3-bis-glycidyl calix[4]arene (BGC, Fig. 2) was synthesized referring to the literature,[12,13] by etherifying *p-tert*-butyl calix[4]arene with 1-chloro-2,3-epoxypropane in dry toluene at reflux for 6 h in the

presence of anhydrous potassium carbonate as the base. After filter and evaporation of the solvent under reduced pressure, the residue was washed with water and purified by column chromatotograph(silica, CH_2Cl_2/petroleum ether, 1 : 2). 1,3-Diglycidyl-calix[4]arene (BGC) was obtained in 60% yield, m.p. 278–281°C. Anal. calcd (%) for $C_{50}H_{64}O_6$: C, 78.91; H, 8.48. Found (%): C, 78.51; H, 8.34. FAB-MS: *m/z* 760 (*RI* 70, M$^+$).

Synthesis of Calix[4]arene-Containing Silicone Monomer

1,3-Bisglycidyl *p-tert*-butyl calix[4]arene (7.6 g, 10 mmol), γ-aminopropyl-triethoxysilane (4.4 g, 20 mmol), anhydrous acetonitrile (50 mL) were added to a 100-mL round-bottomed flask equipped with a magnetic stirrer, and stirred at 50°C for 38 h under nitrogen atmosphere. After evaporation of the solvent under reduced pressure, the residue was purified by fast-column chromatograph (100–200 mesh silica gel, eluant: chloroform ratio acetone equal 5 : 1) to give calix[4]arene-containing silicone monomer (CSN) in 85.0% yield, a colorless viscous liquid. Calix[4]arene-containing silicone monomer (CSNN) was similarly prepared but using 4-azo-6-aminohexyl triethoxysilane instead of γ-aminopropyl tri-
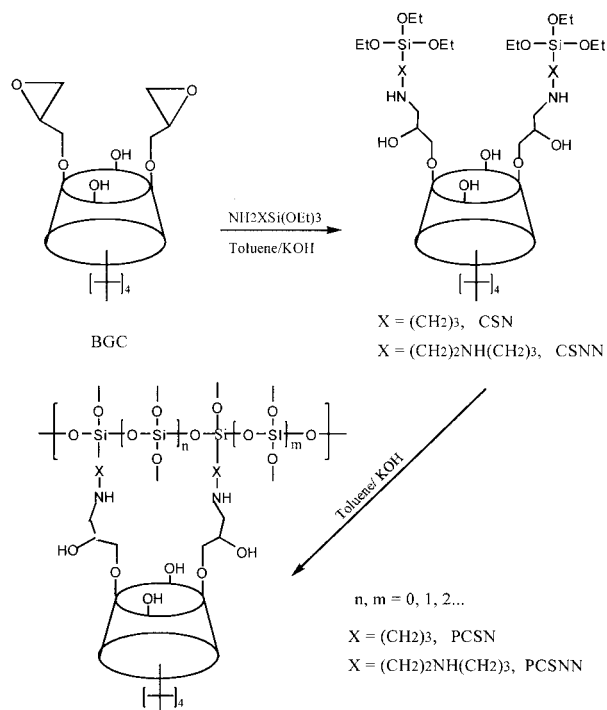

Figure 2 Synthetic route of two calix[4]arene-containing organosilicone resins.

CSN	Yield: 85.0%. ^{1}H-NMR: 0.58 (t, 4H CH$_2$Si); 1.08, 1.12 (s, 9H each, ArCCH$_3$); 1.21–1.33 (over lapped, 36H, ArCCH$_3$ + OCH$_2$CH$_3$); 1.59 (m, 4H, CH$_2$CH$_2$Si); 2.9–3.5 (over lapped, 16H, NCH$_2$ + ArCH$_2$Ar + NH + CHOH); 3.8–4.5 (over lapped, 22H, ArCH$_2$Ar + CHOH, ArOCH$_2$, + SiOCH$_2$); 6.98, 7.02 (bs, 4H each, ArOH); 8.5 (b, 2H ArOH). Anal. Calcd for C$_{68}$H$_{110}$N$_2$O$_{12}$Si$_2$(%): C, 67.85; H, 9.21; N, 2.33. Found (%): C, 67.52; H, 9.49; N, 2.10.
CSNN	Yield: 82.2%. ^{1}H-NMR: 0.58 (t, 4H CH$_2$Si); 1.09, 1.11 (s, 9H each, ArCCH$_3$); 1.22–1.35 (over lapped, 36H, ArCCH$_3$ + OCH$_2$CH$_3$); 1.60 (m, 4H, CH$_2$CH$_2$Si); 2.9–3.4 (over lapped, 26H, NCH$_2$ + ArCH$_2$Ar + NH + CHOH); 3.8–4.5 (over lapped, 22H, ArCH$_2$Ar + CHOH, ArOCH$_2$, + SiOCH$_2$); 7.00, 7.03 (bs, 4H each, Ar-H), 8.35 (b, 2H ArOH). Anal. Calcd for C$_{72}$H$_{120}$N$_4$O$_{12}$Si$_2$ (%): C, 67.09; H, 9.38; N, 4.34. Found (%): C, 66.74; H, 9.06; N, 4.11.

oxysilane, yield: 82.2%, a light yellow viscous liquid. The structure of CSN and CSNN was characterized by ^{1}H-NMR spectrum and elemental analysis (Table I).

Preparation of Organosilicone Resins

CSN (4.8 g, 4 mmol), tetraethoxy-sillican (1.7 g, 8 mmol), toluene (20 mL) and potassium hydroxide (0.3 mL, 1.0 mol/L) were added to a 50-mL round-bottomed flask equipped with a magnetic stirrer, and stirred at room temperature for 5 h under nitrogen atmosphere, and then reflux for 5 h. After 2 mL distilled water was dropped in to the flask, the reactant was stirred continuously at reflux for 3 h under nitrogen atmosphere. The viscosity of the reactant increases slowly and turned into light yellow solid after cooling. The solid was washed with distilled water until the filtrate remained neutral and dried at 110°C under reduced pressure. Then resin was ground and extracted by acetone for 12 h, dried at 110°C under reduced pressure to constant weight. Calix[4]arene-containing organo-

silicone resin (PCSN) 4.6 g was obtained as a light yellow powder; yield: 79.8%.

The PCSNN resin was prepared similarly but using CSNN instead of CSN, a light yellow powder; yield: 82.7%. The analysis result and IR spectra data of PCSN and PCSNN were shown in Table II.

Adsorption of Organosilicone Resin for Metal Ions[14]

Adsorption behavior of PCSN and PCSNN resins toward metal ions was examined. 0.02 g (W) of resin and 10 mL (V) of metal ion solution with known concentration (Ci) were placed in a 25 mL closed flask. A series of such flask were shaken at a constant speed (120 times/min) and a specified constant temperature for 2 h. The metal ion concentration (Ce) of the liquid phase was determined by titration with EDTA for Hg(II), Cu(II), Pb(II), and by AAS for Mg(II), Au(III). The adsorption capacity (Q) was calculated as follows:

$$Q = (Ci - Ce)V/W \text{ (mmol/g)} \tag{1}$$

Adsorption of Organosilicone Resin for Human Serum Protein

Adsorption ability of PCSN and PCSNN resins for human serum protein was examined by the adsorption experiment of 0.02 g (W) of resin and human serum protein solution with known concentration (Ci). The flask was shaken at a constant temperature (20°C) and speed (120 times/min) for 24 h. The protein concentration (Ce) remained in the solution was determined by ultraviolet absorption spectrometer.[15] The adsorption capacity (Q) was calculated by above equation.

RESULTS AND DISCUSSION

Analysis of CSN and CSNN

The structure of CSN and CSNN was characterized by ^{1}H-NMR spectra and elemental analysis. The obtaining result was shown in Table I. The

Table II Elemental Analysis (%) and IR (cm^{-1}) of PCSN and PCSNN

PCSN	C, 56.36; H, 7.78; N, 2.28.	IR (cm^{-1}): 3050, 1590, 1485, 1645, 1263.
PCSNN	C, 54.17; H, 8.06; N, 4.43.	IR (cm^{-1}): 3052, 1594, 1483, 1645, 1265

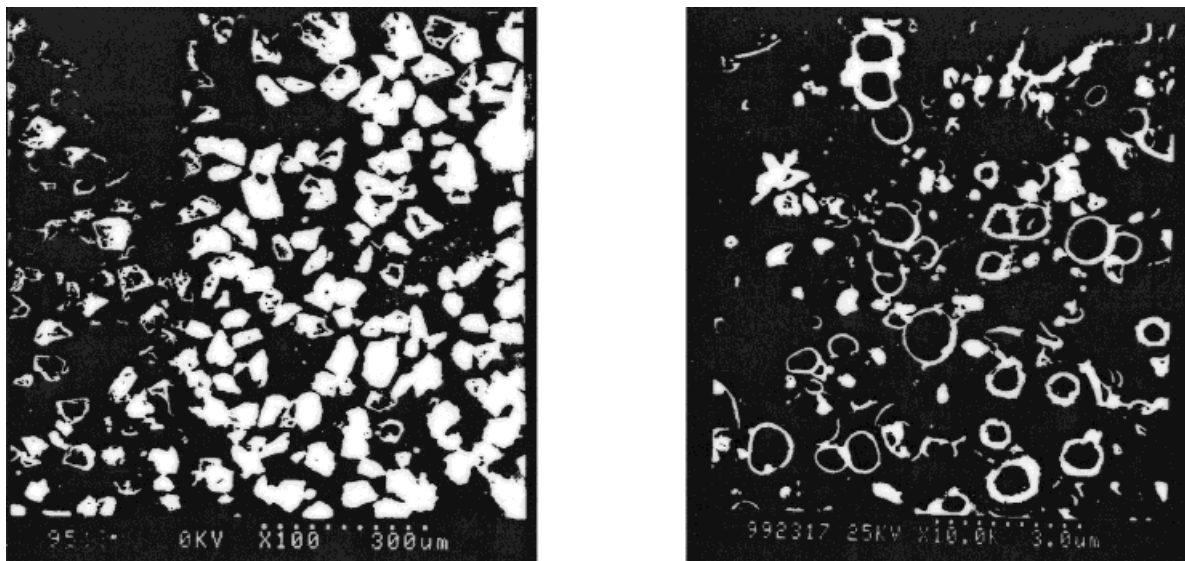**Figure 3**   SEM of organosilicone resin (PCSN).

data of ^{1}H-NMR and elemental analysis confirms the structure of calix[4]arene-containing silicone monomer as shown in Figure 2.

Analysis of Organosilicone Resin

The elemental analysis and IR characterization of calix[4]arene-containing silicon resins (PCSN and PCSNN) were shown in Table II. Table II shows that characteristic bands of calixarene phenyl group presented at about 3050, 1590, 1485, and 805 cm^{-1}; produced by aromatic rings C—H stretching vibration, vibration of aromatic rings skeletons and the out-of-plane aromatic rings C—H bending vibrations, respectively. C—N stretching vibration is at 1263 cm^{-1}. The loaded amount of CSN and CSNN are 0.85 and 0.75 mmol/g resin, respectively.

SEM Characterization

Scanning electron micrographs (SEM) of the surface morphology of calix[4]arene-containing organosilicone resin (PCSN) are presented in Figure 3. Figure 3 shows that the organosilicone resin is particles of unregular shape, and has abundant porous structure on the surface. The size of particle is about 500 to 800 μm. The size of porous on the surface is about 3 to 6 μm.

Thermal Analysis

Thermal analysis curves of BGC, PCSN, and PCSNN are presented in Figure 4(a), 4(b) and 4(c), respectively. TG and DTG curves of BGC, PCSN, and PCSNN show that there is not loss of weight until 380, 478, and 481°C, respectively. The starting weight-lose temperature of BGC is lower than that of the organosilicone resins, PCSN and PCSNN. DTG curves also indicate that the temperature of fastest weight loss rate is at 433, 540, and 542°C, respectively. This implied that the thermal stability of organosilicone resin with calix[4]arene units is higher than that of 1,3-bisglycidyl *p-tert*-butyl calix[4]arene (BGC). It is worth notice that weight increase was observed in Figure 4. TG curves show that weight is increased by raising temperature until 321, 224, and 227°C for BGC, PCSN, and PCSNN, respectively. The weight increase by 7.4% at 321°C, 20.7% at 224°C, and 21.2% at 227°C over the initial weight in nitrogen ambience (80 mL/min) for BGC, PCSN, and PCSNN, respectively. The result shows that both 1,3-bisglycidyl *p-tert*-butyl calax[4]arene (BGC) and organosilicone resins can adsorption nitrogen at an elevated temperature. The adsorption ability of PCSN and PCSNN toward nitrogen is higher than that of BGC, which implies that the network structure of organosilicone resins is favorable to adsorb nitrogen. The result was not observed in network crown ether resin [lit. [14]]. TG and DTG curves show that the thermal decomposition temperature of PCSN and PCSNN was almost the same, and the ability of adsorption nitrogen was close.
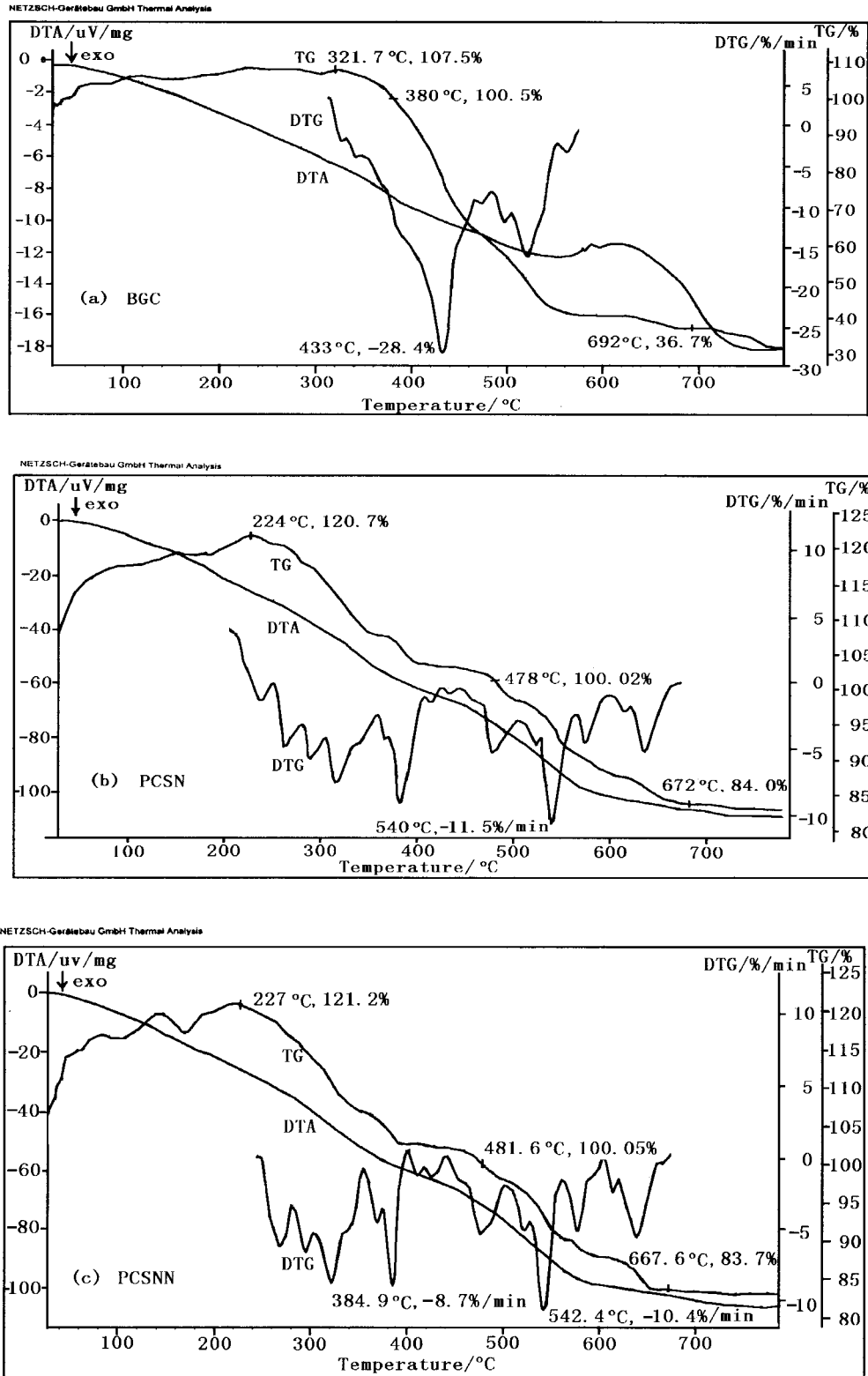
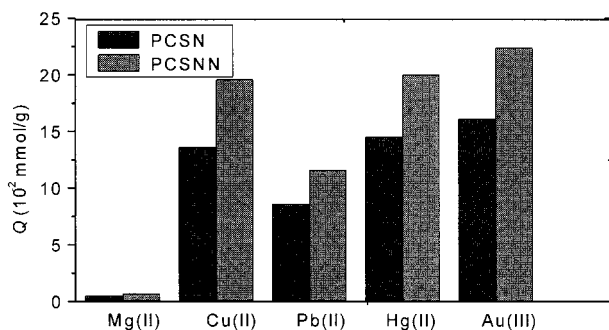**Figure 4**   TG and DTG analysis of (a) BGC, (b) PCSN, and (c) PCSNN.

Figure 5 Adsorption capacity of PCSN and PCSNN (30°C, 24 h, Ci 2 mmol/L).

Figure 6 Effect of temperature for distribution ratio (2 h, Ci 2 mmol/L).

Adsorption Behavior of Resins for Metal Ions

The adsorption capacity of PCSN and PCSNN for divalent magnesium, copper, lead, mercury ions, and trivalent auric ion was determined, respectively. The experimental results are plotted in Figure 5. It shows that the two organosilicone resins have poor adsorption ability towards alkali−earth metal ion as Mg(II); the adsorption ability for divalent copper, lead, mercury ions, and trivalent aurum ion is higher than that for Mg(II). The adsorption capacity for trivalent auric ion is the highest among all these metal ions. The adsorption capacity of PCSNN for all these metal ions is higher than that of PCSN. This can be attributed to the contribution of nitrogen existed in the spacers of calix[4]arene moieties.

Adsorption Behavior of Resin for Trivalent Auric Ion

Effect of Temperature

In the temperature range of 30 to 60°C, the adsorption capacity of two organosilicone resins for trivalent auric ion was determined. $1/T$ vs. $\lg D$ (D: distribution ratio, $D = Q/Ce$) is plotted in Figure 6. The results indicate that the distribution ratio is increased with the increase of the solution temperature. This shows that the adsorption process is an endothermal process and a chemical adsorption process. It also can be caused by the enhancement of swelling ability of resins and ionic diffusivity in aqueous solution with the increase of the solution temperature.[15]

In Figure 6, for PCSN and PCSNN, the linear slope is -1.589×10^3 and -0.928×10^3; respectively; the correlation coefficient (r) is 0.996 and 0.998; respectively. According to $\lg D = -\Delta H/2.303RT + C$, ΔH can be found for PCSN and
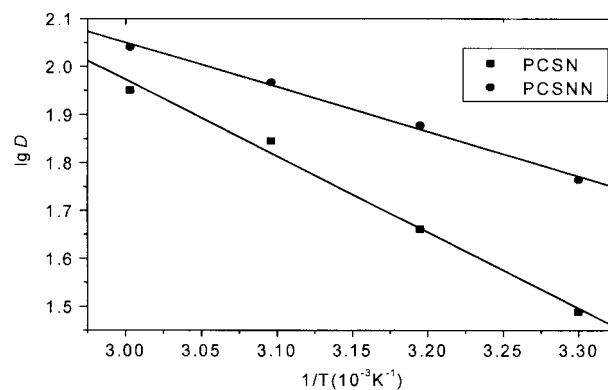
PCSNN as follows: ΔH equals 30.42 (kJ/mol), and 17.77 (kJ/mol), respectively.

Effect of the Amount of Resin Used

Using the constant concentration of the auric ion (Ci 2 mmol/L) and the changing amount of PCSN or PCSNN from 0.25 to 2.0 g/L, the concentration of the auric ion in solution was determined. The results are plotted in Figure 7. It is obvious that the lower amount of organosilicone resin used has the higher adsorption capacity.

Adsorption of Human Serum Protein on Organosilicone Resin

The adsorption capacity of human serum protein in various initial concentrations (1.4–7.0 mg/mL) on a constant amount of PCSN and PCSNN was determined. The experimental data plotting in Figure 8 indicate that the adsorption capacity of human serum protein on PCSNN is higher than that of
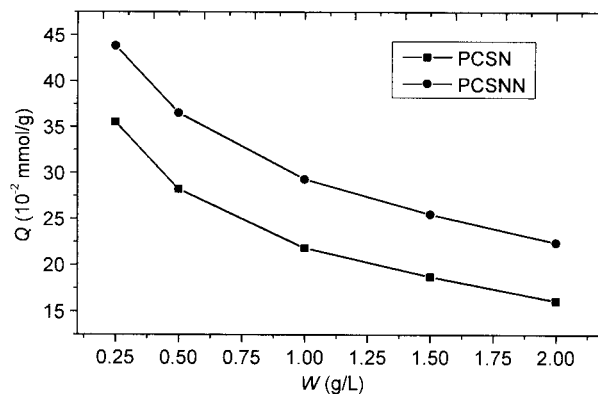

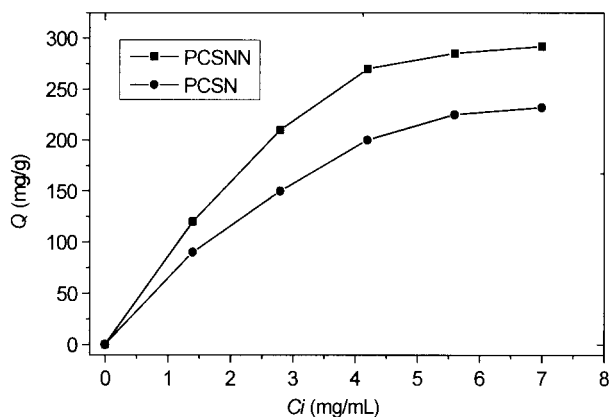**Figure 7** Effect of the amount of resin used.

Figure 8 Adsorption capacity of resins for human serum protein.

PCSN. This may be attributed to the contribution of nitrogen atoms that existed in the spacers of calix[4]arene moieties. The adsorption behavior of human serum protein on calix[4]arene-containing organosilicone resins is in agreement with that of hydrophobic group modified silica adsorbents.[16]

CONCLUSION

Calix[4]arene-containing organosilicone resins (PCSN and PCSNN) were prepared from 1,3-bis-glycidyl-*p-tert*-butyl-calix[4]arene(BGC) via condensation with triethoxyaminopropylsilane or triethoxy-4-aza-6-aminohexylsilane, followed by copolymerization with tetraethoxysilane, respectively. The resins were characterized by elemental analysis, IR spectra, SEM, and thermal analysis. PCSN and PCSNN exhibit high thermal stability and the ability of adsorption nitrogen in the experimental condition. The adsorption capacity of PCSN and PCSNN towards divalent copper, lead, mercury ions, and trivalent aurum ion is higher than that towards divalent Magnesium ion. The thermody-

namic parameters were deduced from the experimental data of resins towards trivalent aurum ion. The adsorption behavior of PCSN and PCSNN toward human serum protein is similar to that of hydrophobic group-modified silica adsorbents.

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