ORIGINAL ARTICLE

Study on complexation adsorption behavior of dibenzo-18-crown-6 immobilized on CPVA microspheres for metal ions

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Abstract Dibenzo-18-crown-6 (DBC) was immobilized on crosslinked polyvinyl alcohol (CPVA) microspheres, resulting in polymer-supported crown ether DBC–CPVA. The complexation adsorption behaviors of DBC–CPVA microspheres towards diverse metal ions were investigated. The experimental results show that among alkali metal ions, the complexation adsorption ability of DBC–CPVA for K^+ ion is the strongest, and crown ether-metal complex in 1:1 ratio is formed, exhibiting a high adsorption capacity. The adsorption capacities of alkali metal ions on DBC–CPVA are in the order: $K^+ \gg Na^+ > LI^+ > Rb^+ > Cs^+$. Among several divalent metal ions, DBC–CPVA exhibits stronger adsorption ability towards Zn^{2+} and Co^{2+} ions, and a "sandwich"-type complex is formed probably in a molar ratio of 2:1 between the immobilized DBC and Zn^{2+} ion as well as between the immobilized DBC and Co^{2+} ion. The adsorption capacities of the several divalent metal ions on DBC–CPVA are in the order: $Zn^{2+} > Co^{2+} \gg Cd^{2+} > Cu^{2+} > Ni^{2+} > Pb^{2+}$. The complexation adsorption is exothermic physical physisorption process, and raising temperature leads to the decrease of the adsorption capacity. At the same time, the entropy during the complexation adsorption decreases, so the adsorption process is driven by the decrease of enthalpy.

Keywords Dibenzo-18-crown-6 · Immobilization · Complex adsorption · Metal ion · Polyvinyl alcohol microspheres

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Introduction

Crown ethers are an important class of macrocyclic compounds in supramolecular chemistry, and have gained much attention for their ability to form stable complexes with metal ions (including ammonium ions) within their central cavity by right of ion–dipole interaction, and the complexation behaviour of crown ethers usually be described in terms of "host–guest complexation". Furthermore, crown ethers exhibit fine complex selectivity for metal ions, and it is decided by complementary size matching of ionic radii and the ligand cavity and the crown structure, leading to excellent recognition properties for metal ions [1–5]. Just the selective complexing properties of crown ethers towards metal ions have enabled them to be widely used in many areas, such as metal ion adsorption and separation, preconcentration and determination, selective transport, constructing sensors, preparing ion selective electrode, phase-transfer catalysis, and so on [6–10]. However, during the application process of crown ether compounds, there are some obvious drawbacks such as difficult of handling and recoverability. In addition, in general, crown ether compounds are toxic, and the residual crown ethers will cause environment issues. So to date, the widespread use of crown ether compounds has been limited by the difficulties associated with removal of the crown ethers from the resulting reaction mixture [11, 12]. In recent years, the immobilization of crown ether compounds on the surfaces of solid materials has attracted increasing attention [13, 14]. Because polymeric materials are easily chemically modified and so the immobilization of crown ethers using polymeric materials as supports is facile. Now, it is attracts much interest to immobilize crown ethers on polymer supports [12, 14–16]. The polymer-supported crown ethers offer many advantages, including ease of

handling, recoverability and adaption to successive processes as well as effectively avoiding the introduction of crown ether toxicity into environment.

In our previous investigation [17], via a two-step method, chloromethylation of dibenzo-18-crown-6 (DBC) and bonding reaction between the hydroxyl groups of crosslinked polyvinyl alcohol (CPVA) microspheres and the chloromethyl groups of chloromethylated DBC (CMDBC), DBC was immobilized onto CPVA microspheres, and the polymer-supported DBC denoted as DBC–CPVA was obtained. This work focuses on examining the complexation adsorption behavior of DBC–CPVA towards metal ions and investigating the recognition selectivity of DBC–CPVA for different metal ions as well as the combining modes of DBC–CPVA with diverse metal ions. There are some findings in this investigation. For example, for the complex of DBC–CPVA with zinc ion as well as cobalt ion, a sandwich-type complex is easy to form because of the denseness and contiguity of the crown ether macrocycles; the complexation adsorption of DBC–CPVA for metal ions is an exothermic and entropy decrease process. Due to increased concern with the environment remediation, polymer-supported crown ethers have been received increasing interest for the selective removal of targeted metal ions from wastewater, and in this respect, the investigation result in this work offers some valuable theoretical references.

Experimental section

Materials and equipments

Polyvinyl alcohol (PVA, a polymerization degree of 2200, Shanwei Chemical Engineering Ltd., Province Shanxi, China) was received. Glutaraldehyde (50% of aqueous solution, Tientsin Baishi Chemical Engineering Ltd., Tientsin, China) was of analytical grade. 1,4-Bis(chloromethoxy)butane (BCMB), which was use as a chloromethylation reagent without carcinogenic toxicity, was self-synthesized [18]. Dibenzo-18-crown-6 (DBC, Huanyan Gaoshi Chemical Ltd., Province, Hubei China) was of analytical grade. Bromothymol blue (BMB, The Third Chemical Reagent Plant of Shenyang, Province Liaoning, China) was of analytical grade. Other reagents were all commercial chemicals with analytical pure and purchased from Chinese companies.

The instruments used in this study were as follows: Unic-2602 UV/Vis spectrophotometer (Unic Company, Shanghai), Perkin-Elmer 1700 infrared spectrometer (Perkine-Elmer Company, USA), Thermo SOLAAR atomic absorption spectrometer (AA, Thermo Company, USA), TG16-WS high-speed centrifuge with desk type (Changsha Xiangyi Centrifuge Factory, Province Jiangsu, China) and

THZ-92C constant temperature shaker equipped with gas bath (Boxun Medical Treatment Equipment Factory, Shanghai, China).

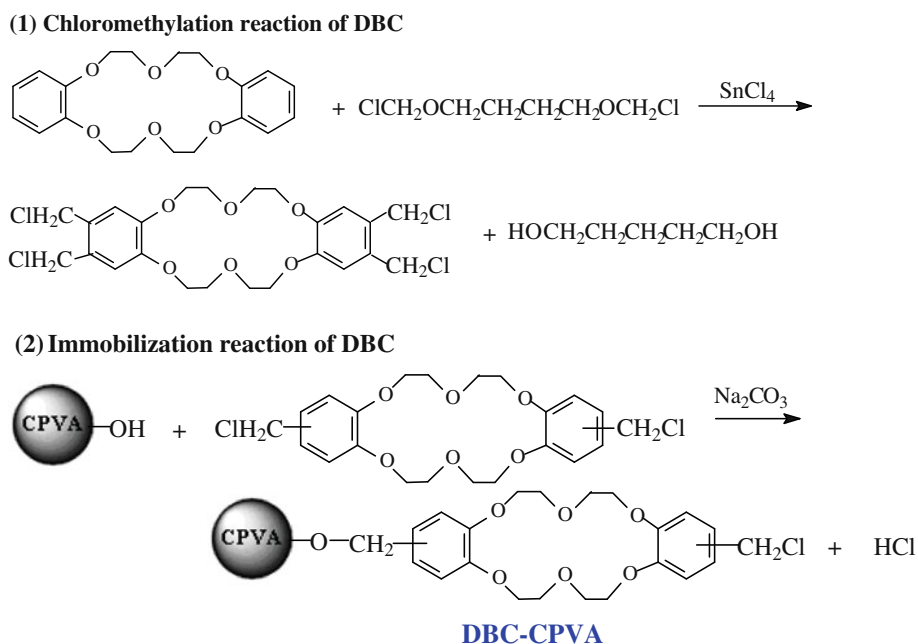### Preparation of DCB–CPVA microspheres

Microspheres DCB–CPVA, on which DCB were immobilized, were prepared according to the procedures described in [17], and the main processes was as follows:

(1) Preparation of CPVA microspheres via directly crosslinking and balling of polyvinyl alcohol in an inverse suspension system: disperser Span 60 (Sorbitan monostearate) was dissolved in liquid paraffin, constituting the oil phase (continuous phase); an aqueous solution of PVA was mixed with glutaraldehyde solution, comprising the water phase (dispersed phase); The water phase was poured into the oil phase, and the system was made to be fully dispersed by stirring, resulting in an inverse suspension system; after adding the catalyst hydrochloric acid, the crosslinking and balling reaction (an aldolization and ether-forming reaction) was allowed to be carried out for 7 h at the constant of 65 °C, obtaining semitransparent microspheres CPVA with excellent sphericity and with a mean diameter of 150 μm.

(2) Chloromethylation of DBC: DBC was chloromethylated in presence of Lewis acid catalyst $SnCl_4$ with BCMB as chloromethylation reagent in chloroform at room temperature, and the chloromethylated DBC (CMDBC) was easy to be obtained; the characterization results of ^1H-NMR and ^{13}C-NMR showed that for the two benzene rings of DBC, the chloromethylation reactions occurred symmetrically at symmetrical four sites probably due to the effect of the crown ether structure, and the chemical structure of CMDBC is presented in Scheme 1.

(3) Immobilization of DBC on CPVA microspheres: the nucleophilic substitution reaction between the chloromethyl groups of CMDBC and the hydroxyl groups of CPVA microspheres was allowed to be carried out with Na_2CO_3 as acid acceptor in N,N-dimethylformamide (DMF) at 70 °C for 9 h, resulting in DBC–CPVA microspheres; the immobilization of DBC on

CMDBC

Scheme 1 Schematic expression of chemical structures of CMDBC

Scheme 2 Schematic expression of preparation process of DBC–CPVA microspheres

(1) Chloromethylation reaction of DBC

(2) Immobilization reaction of DBC

DBC-CPVA

CPVA was confirmed by FTIR; the immobilized amount (mmol/g) of DBC was determined with atom absorption spectrophotometry, and the DBC–CPVA microspheres used in this investigation had a DBC immobilized amount of 0.77 mmol/g. The entire preparation process of DBC–CPVA microspheres can be schematically illustrated in Scheme 2. It needs to be pointed that during the immobilization reaction of DBC, multi-chloromethyl groups of CMDBC probably reacted with hydroxyl groups of CPVA probably, but it will do not affect basically the complexation property of DBC–CPVA.

Complexation adsorption experiments of DBC–CPVA microspheres towards metal ions

Adsorption kinetics experiment

Numbers of 50 mL of Zn(NO$_3$)$_2$ solution of 0.016 M were placed into numerous conical flasks with plug, and 0.1 g of DBC–CPVA microspheres was added into these solutions. These conical flasks were placed in a constant temperature oscillator and were shaken. At different time intervals, the mixtures were taken out, respectively, and after centrifugal separation, the Zn^{2+} concentrations in the supernatants were determined by EDTA complexometric titration with chrome black T as indicators. The corresponding adsorption amounts were calculated, and the adsorption kinetics curve was figured, finally obtaining the equilibrium adsorption time.

Isothermal adsorption experiments

In this work, the adsorption experiments of alkali metal ions and several kinds of bivalent metal ions on DBC–CPVA microspheres were carried out, and the procedure is described by taking Zn^{2+} ion for an example.

Zn (NO$_3$)$_2$ solutions with different concentrations were prepared in a concentration range of 0.8×10^{-3}–16×10^{-3} M. 50 mL of these solutions were taken and transferred into a number of conical flasks with plug, respectively. About 0.1 g of DBC–CPVA microspheres weighted accurately was added into these solutions, and these mixtures were shaken on a constant temperature shaker. After reaching adsorption equilibrium, these mixtures were centrifugally separated. The Zn^{2+} ion concentrations in the supernatants were determined by EDTA complexometric titration, and the equilibrium adsorption amount was calculated according to Eq. 1. The relationship curve between the equilibrium adsorption amount and the equilibrium concentration of Pb^{2+} ion was plotted, namely, adsorption isotherm of DBC–CPVA microspheres for Zn^{2+} ion was obtained.

$$Q_e = \frac{V(C_0 - C_e)}{m} \qquad (1)$$

where Q_e (mmol/1 g) is the equilibrium adsorption amount; V (mL) is the volume of the solution; C_0 (mol/L) is the Zn^{2+} ion concentration in the initial solution; C_e (mol/L) is the equilibrium concentration of Zn^{2+} ion in the supernatant; m (g) is the mass of DBC–CPVA microspheres.

Examining effects of main factors on adsorption property of DBC–CPVA microspheres

Examining effect of metal ion species

For alkali metal ions, Li^+, Na^+, K^+, Rb^{2+} and Cs^+, the solutions with different concentrations were prepared, and the isothermal adsorption experiments were carried out for each alkali metal ion at the same temperature according to the procedure as described in "Isothermal adsorption experiments" section, obtaining corresponding adsorption isotherms. In the adsorption experiments of alkali metal ions, their concentrations in the supernatants were determined with atomic absorption spectroscopy.

Similarly, the solutions with different concentrations for several kinds of bivalent metal ions, Zn^{2+}, Co^{2+}, Cu^{2+}, Ni^{2+} and Pb^{2+}, were prepared, and the isothermal adsorption experiments were carried out for these ions. In the adsorption experiments of these bivalent metal ions, their concentrations were determined by EDTA complexometric titration but with different directors. Chrome black T was used for Zn^{2+} and Pb^{2+} ion determinations, xylenol is used for Cu^{2+} ion determination, and murexide is used for Ni^{2+} ion, respectively.
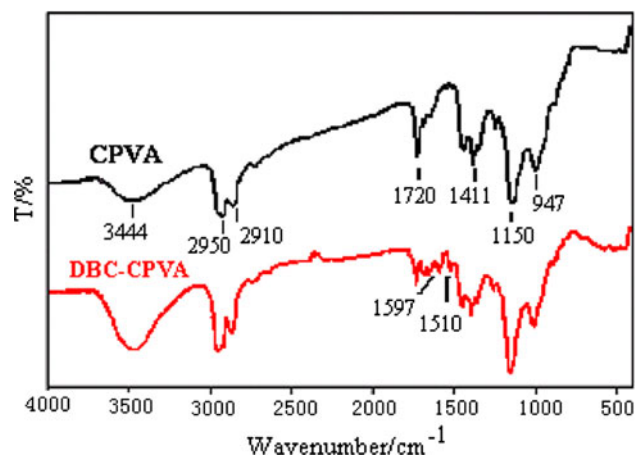
Examining effect of temperature

The isothermal adsorption experiments of DBC–CPVA microspheres were conducted at different temperatures, and the effect of temperature on the complexation adsorption property of DBC–CPVA microspheres towards metal ions was examined and the adsorption thermodynamics was studied.

Results and discussions

Infrared spectrum of DBC–CPVA microspheres

Figure 1 presented the infrared spectra of CPVA and DBC–CPVA microspheres. In the spectrum of CPVA microspheres, except the characteristic absorption bands of polyvinyl alcohol (PVA), the characteristic absorption band of ether bond C–O–C appears at 1150 cm^{-1}, and it comes from the aldolization and ether-forming reaction of PVA with glutaraldehyde. In the spectrum of DBC–CPVA microspheres, the characteristic absorption bands of the benzene ring of the dibenzo of DBC exhibit at 1597 and 1510 cm^{-1}. Furthermore, the characteristic absorption of ether bond C–O–C is strengthened, and it is caused by the ether bond within the crown ether macrocycle of the immobilized DBC. The above spectrum data demonstrate that the nucleophilic substitution reaction between the
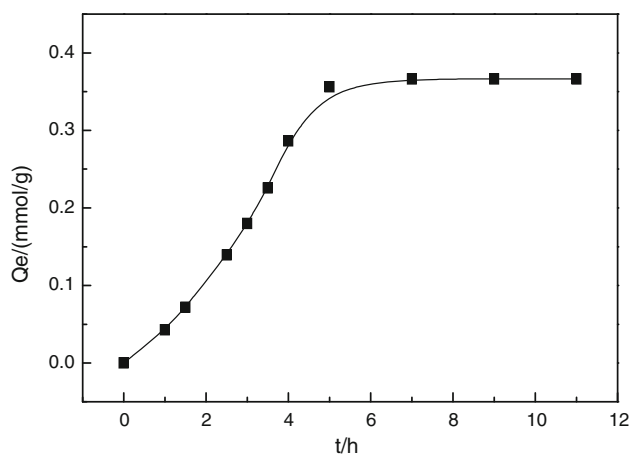

Fig. 1 FTIR spectra of DBC–CPVA microspheres

chloromethyl groups of CMDCB and the hydroxyl groups of CPVA microspheres has been occurred, and DBC has been immobilized on CPVA microspheres.

Adsorption kinetics behavior of DBC–CPVA microspheres towards metal ions

Figure 2 gives the adsorption kinetics curve of DBC–CPVA microspheres towards Zn^{2+} ion. It can be seen from Fig. 1 that in 5 h, the adsorption can reach equilibrium, displaying a faster adsorption rate. There are two reasons for the faster adsorption rate. On one hand, the matrix of DBC–CPVA is hydrophilic CPVA microspheres, and they are easy to be swelled, leading to small diffusion resistance of metal ions; on the other hand, there is a hydrophilic domain inside the caves of the immobilized DBC, and it is also in favor of the metal ion diffusion.
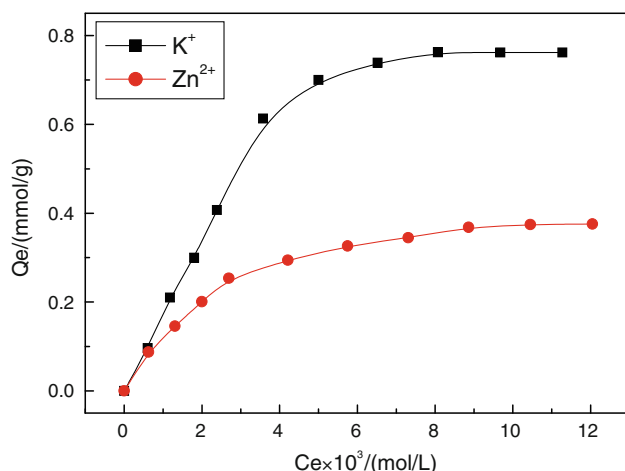

Fig. 2 Adsorption dynamics curve of microspheres DBC–CPVA towards Zn^{2+} ion. Temperature: 25 °C

Adsorption behavior of DBC–CPVA towards K^+ and Zn^{2+} ions as well as combining modes

Figure 3 gives the adsorption isotherms of K^+ and Zn^{2+} ions at 25 °C. The following facts can be found in Fig. 3. (1) The shape of the adsorption isotherms accord with that of Langmuir isotherm, indicating the monomolecular adsorption. (2) The adsorption capacity of DBC–CPVA towards K^+ ion is very high, and the saturated adsorption amount is equal to 0.76 mmol/g, which is completely consistent with the immobilized amount (0.77 mmol/g) of DBC on DBC–CPVA microspheres. (3) The adsorption ability of DBC–CPVA towards Zn^{2+} ion is also higher, and the saturated adsorption amount is 0.38 mmol/g, which is equal to half of the immobilized amount of DBC on DBC–CPVA.

For the above experimental results, the reasonable explanations can be given as follows. The diameter (2.6–3.2 Å) of the hole formed by the disposition of dibenzo-18-crown-6 fits very well the dimensions (2.66 Å) of the potassium ion, and potassium ion can fit the best into the hole of the macrocyclic ligands in a hexagonal arrangement of oxygen donor atoms [19, 20], resulting in the formation of crown ether-metal ion complex in a 1:1 ratio. So the immobilized DBC is highly matching with K^+ ion, and there is strong ion–dipole interaction between them, leading to the highly special complexing of DBC–CPVA for K^+ ion and high adsorption capacity.

The highly complexing of DBC for K^+ ion is very valuable in some science and technology fields. For example, Based on the high binding capacity and selectivity of DBC towards K^+ ion, some researchers used the polymer membrane containing dibenzo-18-crown-6 to constitute the potassium ion-se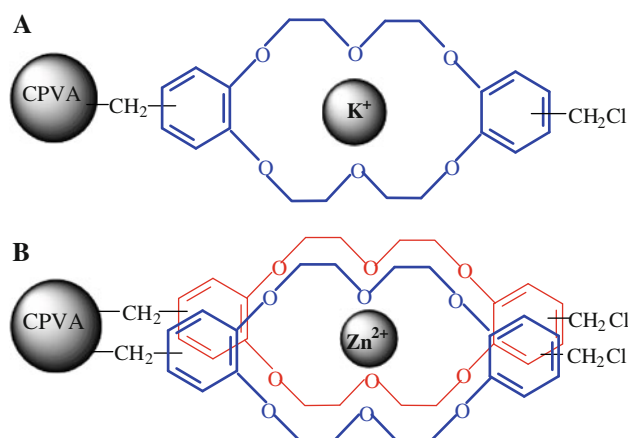nsor [21] and others used the polymer containing the complexes of potassium with DBC as catalysts in some organic reactions [22].

Zn^{2+} ion (1.58 Å) is smaller than the size of the cavity of DBC, and it seems not to be matching with DBC, leading to the lower adsorption capacity in comparison with K^+ ion. Although zinc ion is too small to fit into a single cavity, there is a tendency for Zn^{2+} ion to form a "sandwich" type complex with adjacent crown units of 18-crown-6 cavity [23, 24]. There is a great deal of DBC on the surfaces of DBC–CPVA microspheres, and the adjacent crown units are very dense, so that Zn^{2+} ions are complexed by DBC in sandwich-type and form the crown ether-metal ion complex in 2:1 ratio, leading to higher adsorption capacity. The mode of "sandwich"-type complex between DBC–CPVA and Zn^{2+} ion as well as the mode of the complex in 1:1 ratio between DBC–CPVA and K^+ ion is schematically illustrated in Scheme 3.
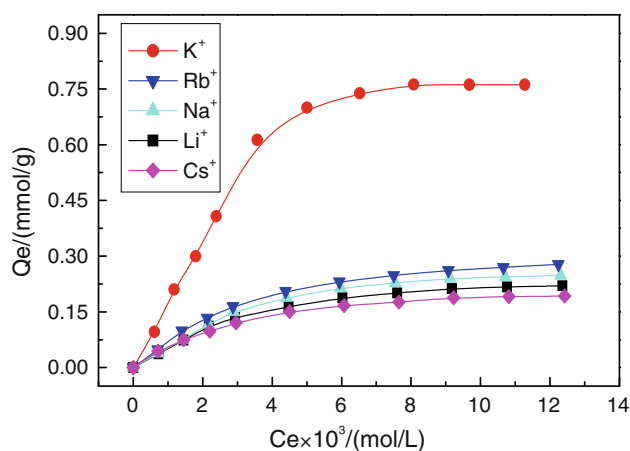
Adsorption properties of DBC–CPVA microspheres for diverse metal ions

The adsorption isotherms of DBC–CPVA microspheres for alkali metal ions are presents in Fig. 4. It can be seen from Fig. 4 that except K^+ ion, the adsorption capacities of other alkali metal ions on DBC–CPVA microspheres are all very low. The reason for this is that the sizes of these ions are not fitted to the cavity (2.6–3.2 Å) of DBC, and the diameters of these ions are 1.2 Å (Li^+), 1.9 Å (Na^+), 2.92 Å (Rb^+) and 3.38 Å (Cs^+), respectively. The adsorption capacities of these ions together with K^+ ion are in the order: $K^+ \gg Rb^+ > Na^+ > Li^+ > Cs^+$, and this adsorption capacity order is consistent with that of these ions on other reported adsorption resins, on which DBC is immobilized [12, 25].
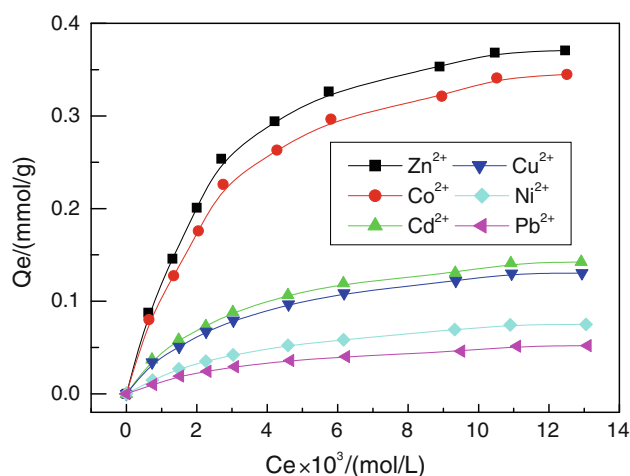
The adsorption isotherms of DBC–CPVA microspheres for several divalent metal ions, Cd^{2+}, Cu^{2+}, Ni^{2+} and

Fig. 3 Adsorption isotherms of microspheres DBC–CPVA towards K^+ and Zn^{2+} ion. Temperature: 25 °C

Scheme 3 Mode of complex between DBC–CPVA and K^+ ion (A) and mode of complex between DBC–CPVA and Zn^{2+} ion (B)

Fig. 4 Adsorption isotherms of DBC–CPVA microspheres for alkali metal ions. Temperature: 25 °C
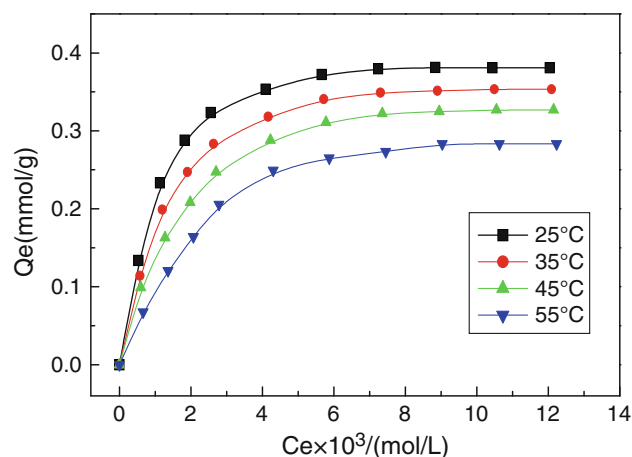

Fig. 5 Adsorption isotherms of DBC–CPVA microspheres for several bivalent metal ions. Temperature: 25 °C

Pb^{2+}, are presents in Fig. 5. It can be found from Fig. 5 that the adsorption capacity of DBC–CPVA microspheres for Co^{2+} ion, whose diameter is also equal to 1.58 Å, is approximate to that of Zn^{2+} ion, and is also higher. Furthermore, the adsorption amount (mmol/g) is also approximate to the half of the immobilized amount (mmol/g) of DBC on DBC–CPVA, suggesting the formation of a "sandwich"-type complex between the immobilized DBC and Co^{2+} ion. And this is an interesting finding, and the reason for this needs to be further probed into. The adsorption capacities of other divalent metal ions are all very small, implying that their dimensions are not matching to the cavity of DBC (the sizes of these ions are 1.94 Å for Cd^{2+} ion, 1.38 Å for Cu^{2+} ion, 1.24 Å for Ni^{2+} ion and 1.68 Å for Pb^{2+} ion, respectively). The adsorption capacity order of the ions together with Zn^{2+} and Co^{2+} ions is: $Zn^{2+} > Co^{2+} \gg Cd^{2+} > Cu^{2+} > Ni^{2+} > Pb^{2+}$. About the

adsorption selectivity of DBC–CPVA for these metal ions, except the matching extent of the ion size for DBC cavity, the Gibbs free energy difference of the hydration process for these ions (the overall result of enthalpy and entropy differences during the hydration process of these ions) also play a major role in the selectivity, and it is up for further investigation.

Effect of temperature on adsorption ability of DBC–CPVA microspheres and adsorption thermodynamics

The isothermal adsorption experiments of DBC–CPVA microspheres towards Zn^{2+} ion were performed at different temperatures, and the corresponding adsorption isotherms are displayed in Fig. 6. It can be observed that the adsorption capacity of DBC–CPVA microspheres towards Zn^{2+} ion decreases with increasing temperature. This result can be analyzed from two aspects. On one hand, the ion–dipole interaction is a weak intermolecular interaction, and the adsorption arisen from such interaction is a physical adsorption process. Physical adsorptions are exothermic, so it is certain that raising temperature leads to the decrease of the adsorption capacity. On the other hand, the entropy in the complexation process of crown ethers with metal ions will decrease ($\Delta S < 0$) because of the fixation of the structure of crown ether–metal ion complex and the loss of randomness, whereas the enthalpy in this process also decreases ($\Delta H < 0$) as described above. According the thermodynamics equation, $\Delta G = \Delta H - T\Delta S$ (ΔG is the Gibbs free energy change in complexation adsorption process), it is inevitable that raising temperature will cause the decrease of the absolute value of the Gibbs free energy change, and it is disadvantageous to the adsorption, leading to the decrease of the adsorption capacity. The above analysis will be further discussed below.

Fig. 6 Adsorption isotherms of microspheres DBC–CPVA towards Zn^{2+} ion at different temperatures

Langmuir equation is shown in Eq. 2, and the straight line-type Langmuir equation obtained by rearranging Eq. 2 can be represented in Eq. 3.

$$Q_e = Q_m \frac{K_a C}{1 + K_a C_e} \qquad (2)$$

$$\frac{C_e}{Q_e} = \frac{C_e}{Q_m} + \frac{1}{K_a Q_m} \qquad (3)$$

where C_e is the equilibrium concentration of metal ions solution (mol/L), Q_e is the adsorbed value of metal ions at equilibrium concentration (mmol/g), Q_m is the is the maximum adsorption capacity (mmol/g), and K_a is the Langmuir adsorption constant (L/mol). The plots of C_e/Q_e versus C_e (the data of C_e/Q_e and C_e were taken from Fig. 6) at different temperatures are given in Fig. 7, and the values of Q_m and K_a at different temperatures can obtained from the slopes and intercepts of these straight lines, respectively.

Thermodynamic parameters of the adsorption process were calculated from the following Van't Hoff equation [26, 27]:

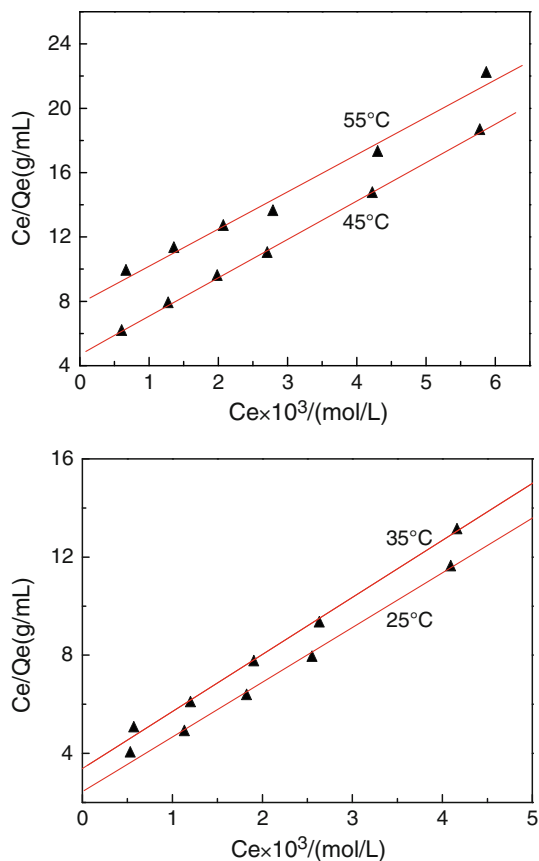$$\ln K_a = -\frac{\Delta H}{R} \times \frac{1}{T} + \frac{\Delta S}{R} \qquad (4)$$

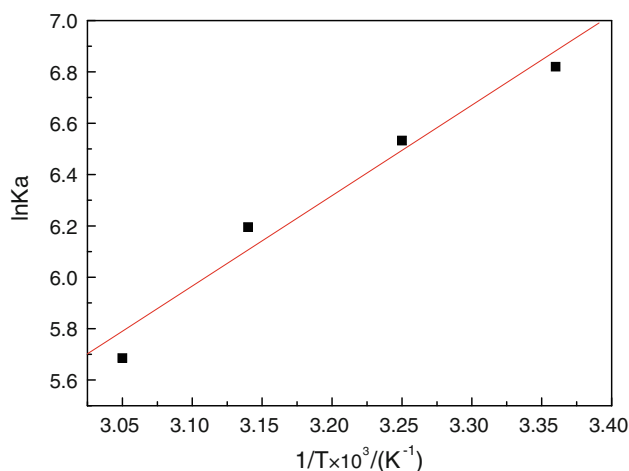**Fig. 7** Langmuir plots of C_e/Q_e against C_e for adsorption of Zn^{2+} ion

Fig. 8 Plot of $\ln K_a$ against $1/T$

Table 1 Thermodynamic parameters of the adsorption of Zn^{2+} ion on DBC–CPVA

T (K)	$-\Delta G$ (kJ mol^{-1})	ΔH (kJ mol^{-1})	ΔS (J K^{-1} mol^{-1})
298.15	16.90	−29.92	−43.71
308.15	16.72	−29.92	−42.84
318.15	16.49	−29.92	−42.26
328.15	15.50	−29.92	−43.96

where ΔH and ΔS are the enthalpy and entropy changes of the adsorption process, R is the universal gas constant (8.314 J/mol K) and T is the absolute temperature (K). Plotting $\ln K_a$ against $1/T$ gives a straight line as shown in Fig. 8. From the slope and intercept of this straight line, the values of ΔH and ΔS were calculated, and are summarized in Table 1.

The Gibbs free energy change ΔG of the adsorption process was calculated from the following relation, and the result is also reported in Table 1.

$$\Delta G = \Delta H - T \Delta S \qquad (5)$$

The negative values of ΔG indicate a spontaneous adsorption process, and furthermore, a more negative ΔG implied a greater driving force of Zn^{2+} ion sorption on DCB–CPVA, resulting in a higher sorption capacity. The negative value of ΔH shows an exothermic adsorption process, and the smaller value (−29.92 kJ mol^{-1}) than −40 kJ mol^{-1} implies that the complexation adsorption of DCB–CPVA towards metal ions is a physisorption process. The negative value of ΔS shows the decreased randomness during the complexation adsorption process, and it originated from the fixation of metal ions. The negative value of ΔS also indicates that the adsorption process is controlled by enthalpy change, and the spontaneous

adsorption process is driven by the stronger complexation with a greater heat release.

Conclusions

In this paper, based on the immobilization of dibenzo-18-Crown-6 on crosslinked polyvinyl alcohol microspheres, the complexation adsorption behaviors of DCB–CPVA microspheres towards diverse metal ions were investigated in depth. The complexation adsorption ability of DCB–CPVA for K^+ ion is far stronger than that for other alkali metal ions, and the crown ether–metal ion complex in 1:1 ratio is formed. The adsorption capacity order of alkali metal ions on DCB–CPVA is: $K^+ \gg Na^+ > LI^+ > Rb^+ > Cs^+$. For the different divalent metal ions, the adsorption capacity order is: $Zn^{2+} > Co^{2+} \gg Cd^{2+} > Cu^{2+} > Ni^{2+} > Pb^{2+}$. Furthermore, the crown ether–metal ion complex in 2:1 ratio, namely, "sandwich"-type complexes, is formed probably between the immobilized DCB and Zn^{2+} ion as well as between the immobilized DCB and Co^{2+} ion. The complexation adsorption process is an exothermic and entropy decrease process, and raising temperature leads to the decrease of the adsorption capacity.

References

1. Saleh, M.I., Kusrini, E., Fun, H.K., Yamin, B.M.: Structural and selectivity of 18-crown-6 ligand in lanthanide–picrate complexes. J. Organomet. Chem. **693**, 2561–2571 (2008)
2. Moriuchi-Kawakami, T., Aoki, R., Morita, K., Tsujioka, H., Fujimori, K., Shibutani, Y., Shono, T.: Conformational analysis of 12-crown-3 and sodium ion selectivity of electrodes based on bis(12-crown-3) derivatives with malonate spacers. Anal. Chim. Acta **480**, 291–298 (2003)
3. Takeda, Y., Yasui, A., Morita, M., Katsuta, S.: Extraction of sodium and potassium perchlorates with benzo-18-crown-6 into various organic solvents. Quantitative elucidation of anion effects on the extraction-ability and -selectivity for Na$^+$ and K$^+$. Talanta **56**, 505–513 (2002)
4. Diao, K.-S., Wang, H.-J., Qiu, Z.-M.: J. Mol. Struct. **901**, 157–162 (2009)
5. Kim, H.-S.: Solvent effect on selectivity of between Na$^+$ and Li$^+$ ion to 18-crown-6: Monte Carlo simulation study. Chem. Phys. **287**, 253–260 (2003)
6. Parat, C., Betelu, S., Authier, L., Potin-Gautier, M.: Determination of labile trace metals with screen-printed electrode modified by a crown-ether based membrane. Anal. Chim. Acta **573–574**, 14–19 (2006)
7. Raut, D.R., Mohapatra, P.K., Ansari, S.A., Sarkar, A., Manchanda, V.K.: Selective transport of radio-cesium by supported liquid membranes containing calix[4]crown-6 ligands as the mobile carrier. Desalination **232**, 262–271 (2008)
8. Seki, A., Motoya, K., Watanabe, S., Kubo, I.: Novel sensors for potassium, calcium and magnesium ions based on a silicon transducer as a light-addressable potentiometric sensor. Anal. Chim. Acta **382**, 131–136 (1999)
9. Heng, L.Y., Hall, E.A.H.: Assessing a photocured self-plasticised acrylic membrane recipe for Na$^+$ and K$^+$ ion selective electrodes. Anal. Chim. Acta **443**, 25–40 (2001)
10. Liu, H., Shao, X.-B., Jia, M.-X., Jiang, X.-K., Li, Z.-T., Chen, G.-J.: Selective recognition of sodium cyanide and potassium cyanide by diaza-crown ether-capped Zn-porphyrin receptors in polar solvents. Tetrahedron **61**, 8095–8100 (2005)
11. Wild, G.P., Wiles, C., Watts, P., Haswell, S.J.: The use of immobilized crown ethers as in-situ N-protecting groups in organic synthesis and their application under continuous flow. Tetrahedron **65**, 1618–1629 (2009)
12. Alexandratosa, S.D., Stine, C.L.: Synthesis of ion-selective polymer-supported crown ethers: a review. React. Funct. Polym. **60**, 3–16 (2004)
13. Zakurdaeva, O.A., Nesterov, S.V., Shmakova, N.A., Feldman, V.I.: Radiation-chemical synthesis of crown-containing poly(ethylene oxide) hydrogels. Swelling behavior and crown ether retention. Radiat. Phys. Chem. **77**, 23–28 (2008)
14. Alexandratos, S.D., Stine, C.L., Sachleben, R.A., Moyer, B.A.: Immobilization of lithium-selective 14-crown-4 on crosslinked polymer supports. Polymer **46**, 6347–6352 (2005)
15. Manzini, B., Hodge, P.: Polymer-supported syntheses of oxo-crown ethers and derivatives containing α-amino-acid residues. React. Funct. Polym. **68**, 1297–1306 (2008)
16. Zakurdaeva, O.A., Nesterov, S.V., Shmakova, N.A., Semenova, G.K., Sozontova, E.O., Feldman, V.I.: Radiation-chemical synthesis of poly(vinyl alcohol) hydrogel containing dicyclohexano-18-crown-6. Nucl. Instrum. Methods Phys. Res. B **265**, 356–361 (2007)
17. Wang S-W, Gao B-J: Immobilizing dibenzo-18-crown-6 on crosslinked polyvinyl alcohol microspheres. J. Funct. Macromol. **22**, 343–358 (2009) (in Chinese)
18. Lü, C.-L., Gao, B.-j., Liu, Q., Qi, Ch.-Sh.: Preparation of two kinds of chloromethylated polystyrene particle using 1,4-bis (chloromethoxy) butane as chloromethylation reagent. Colloid Polym. Sci. **286**, 553–561 (2008)
19. Dapporto, P., Paoli, P., Matijašić, I., Tušek-Božić, L.: Crystal structures of complexes of ammonium and potassium hexa-fluorophosphate with dibenzo-18-crown-6. Molecular mechanics studies on the uncomplexed macrocycle. Inorganica Chim. Acta **252**, 383–389 (1996)
20. Takeda, Y., Endō, K., Yoshiyama, D., Watanabe, K., Fukada, N., Katsuta, S.: Quantitative elucidation of macrocyclic effect on extraction-ability and -selectivity. Benzo-18-crown-6 and its open-ring analog 1,2-bis[2-(2-methoxyethoxy)ethoxy]benzene–alkali metal picrate systems. J. Mol. Liq. **130**, 21–28 (2007)
21. Pandey, P.C., Prakash, R.: Polyindole modified potassium ion-sensor using dibenzo-18-crown-6 mediated PVC matrix membrane. Sens. Actuators B Chem. **46**, 61–65 (1998)
22. Zitsmanis, A., Roska, A., Klyavinsh, M.: Polymer-bound crown ethers. II. Catalysis of several condensation reactions by polymer-bound dibenzo-18-crown-6. React. Polym. Ion Exch. Sorbents **9**, 67–70 (1988)
23. Costero, A.M., Gil, S., Sanchis, J., Peransí, S., Sanz, V., Williams, J.A.G.: Conformationally regulated fluorescent sensors. Study of the selectivity in Zn^{2+} versus Cd^{2+} sensing. Tetrahedron **60**, 6327–6334 (2004)
24. Costero, A.M., Sanchis, J., Peransi, S., Gil, S., Sanz, V., Domenech, A.: Bis(crown ethers) derived from biphenyl: extraction and electrochemical properties. Tetrahedron **60**, 4683–4691 (2004)
25. Favre-Réguillon, A., Dumont, N., Dunjic, B., Lemaire, M.: Synthesis and evaluation of new polyurethane—based material for ion separation. Tetrahedron Lett. **36**, 6439–6442 (1995)

26. Uzun, İ., Güzel, F.: Kinetics and thermodynamics of the adsorption of some dyestuffs and *p*-nitrophenol by chitosan and MCM-chitosan from aqueous solution. J. Colloid Interface Sci. **274**, 398–412 (2004)

27. Bayramoğlu, G., Ekici, G., Beşirli, N., Arica, M.Y.: Preparation of ion-exchange beads based on poly(methacrylic acid) brush grafted chitosan beads: Isolation of lysozyme from egg white in batch system. Colloids Surf. A **310**, 68–77 (2007)