Synthesis and Adsorption Property of Two Polymeric Adsorbents with Pendent Ether Bonds

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Abstract: Two polymeric adsorbents, poly(methyl *p*-vinylbenzyl ether) and poly(phenyl *p*-vinylbenzyl ether), were synthesized from chloromethylated polystyrene. Their adsorption property for phenol in hexane solution was investigated. The results showed that the two adsorbents adsorb phenol from hexane solution through hydrogen-bonding and π-π stacking interaction.

Keywords: Poly(methyl *p*-vinylbenzyl ether), poly(phenyl *p*-vinylbenzyl ether), adsorption, hydrogen-bonding, π-π stacking interaction.

Adsorption selectivity in adsorptive separation can be enhanced by limiting solute-sorbent binding interaction to a single or a few special mechanisms[1]. In recent years, we have focused our attention on hydrogen-bonding as an appropriate adsorption mechanism. Hydrogen-bonding is a useful mechanism for adsorptive separation because the low energy of hydrogen bond ensures reversibility, whilst the directionality and the short range of this bond confer selectivity[2]. We have synthesized a series of hydrogen-bonding adsorbents and examined their adsorption property for some organic compounds especially certain natural products[3, 4]. If ether bonds are introduced into polymeric adsorbents, they will act as hydrogen-bonding acceptor and adsorb compounds with hydrogen-bonding donor. However, polymeric adsorbents with ether bonds have not been reported so far.

In this letter, two polymeric adsorbents with pendent ether bond, poly(methyl *p*-vinylbenzyl ether) and poly(phenyl *p*-vinylbenzyl ether), were synthesized by reacting chloromethylated macroporous crosslinked polystyrene with sodium methylate or sodium phenolate in N, N-dimethylformamide at 368 K for 20 h.

Adsorption studies were conducted in which phenol was adsorbed from hexane solution onto the two adsorbents. Equilibilium data for phenol were generated at four different temperatures in the range from 295 K to 307 K. In each case, weighed amounts of the adsorbent (A) were added to a dilute solution of phenol (c_0). After equilibration at a fixed temperature the liquid-phase phenol concentration (c) was

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measured by UV spectrometry at the wavelength of peak absorbance for phenol (270.2 nm). The adsorption capacity (q) was calculated using the following equation:

$$q = (c_0-c)V/A \qquad (1)$$

where V is the volume of hexane solution of phenol.

Adsorption enthalpy was calculated by using the Van't Hoff method as follows:

$$\ln(q/c) = -\Delta H/(RT) + \Delta S/R + K \qquad (2)$$

where $\Delta H, \Delta S$ is standard enthalpy and entropy change of adsorption, respectively; R is the universal gas constant; T is the absolute temperature in degree Kelvin; K is a constant when the study was confined to a dilute concentrations; q/c is adsorption affinity. Since our studies were confined to a low phenol concentration, adsorption was limited to the linear region of the adsorption isotherm, the adsorption affinity is the slope of the adsorption isotherm, then equation (2) suggested that a plot of ln(q/c) *versus* 1/T should yield a straight line with a slope of $-\Delta H/R$.

Figure 1 and **Figure 2** listed adsorption isotherms of phenol onto poly(methyl *p*-vinylbenzyl ether) and poly(phenyl *p*-vinylbenzyl ether) from hexane solution at different temperature. The adsorption affinity was calculated according to the adsorption isotherms, the plot of ln(q/c) *versus* 1/T should yield a straight line with a slope of $-\Delta H/R$ as described in equation (2). Thus the adsorption enthalpy calculated was -31.19kJ/mol and -46.84kJ/mol for phenol onto poly(methyl *p*-vinylbenzyl ether) and poly(phenyl *p*-vinylbenzyl ether), respectively. Adsorption mechanism between adsorbents and adsorbates is often based on hydrophobic interaction, hydrogen-bonding and π-π stacking interaction[5]. Since the adsorption experiments were conducted in hexane solution, the hydrophobic interaction was not existed. Thus, the adsorption might be based on hydrogen-bonding between the oxygen atoms in the adsorbents and the hydroxyl hydrogen atoms of phenol, and π-π stacking interaction between the benzene rings of the adsorbent and the benzene ring of phenol.

In order to distinguish hydrogen-bonding from the π-π stacking interaction, adsorption isotherms of methyl phenyl ether onto the two adsorbents from hexane were measured. The results indicated that no methyl phenyl ether was adsorbed onto the two adsorbents, which implied that the π-π stacking interaction was not the main interaction between phenol molecules and the adsorbents.

Hydrogen-bonding acceptor of the two adsorbents are the same, which are the oxygen atoms, while the adsorption enthalpies for phenol are quite different, the adsorption enthalpy of phenol onto poly(phenyl *p*-vinylbenzyl ether) is -15.45kJ/mol more negative than that onto poly(methyl *p*-vinylbenzyl ether). In common case, hydrogen-bonding basicity of the oxygen atoms in poly(phenyl *p*-vinylbenzyl ether) is weaker than that in poly(methyl *p*-vinylbenzyl ether), and the hydrogen-bonding of phenol with poly(phenyl *p*-vinylbenzyl ether) should be weaker than that with poly(methyl *p*-vinylbenzyl ether), which is in contrast with our results. Comparing the structure of the two adsorbents, it can be found that the phenolic phenyl groups of poly(phenyl *p*-vinylbenzyl ether) are replaced by methyl groups of poly(methyl *p*-vinylbenzyl ether), and this resulted in the difference of adsorption enthalpies. When phenol was adsorbed onto poly(phenyl *p*-vinylbenzyl ether), in addition to hydrogen-bonding, there existed corporative π-π stacking interaction between the

phenolic phenyl groups of poly(phenyl *p*-vinyl benzyl ether) and the phenyl groups of phenol molecules. However, for adsorption of phenol onto poly(methyl *p*-vinylbenzyl ether), there was no corporative π-π stacking interaction, and thus the adsorption enthalpy was less negative.

Figure 1   Adsorption isotherms of phenol poly-(methyl *p*-vinylbenzyl ether) from hexane solution at different temperature
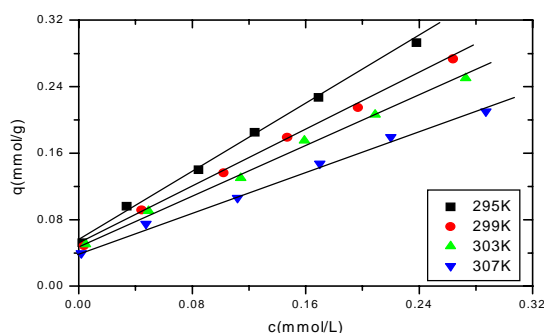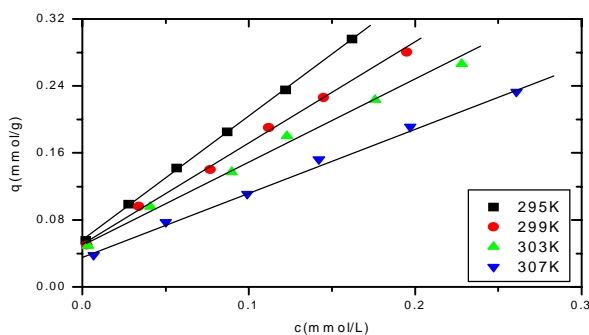

Figure 2   Adsorption isotherms of phenol onto poly(phenyl *p*-vinylbenzyl ether) from hexame solution at different temperature

Acknowledgment

References

1.   J. A. Kolehler, K. K. Wallance, P. J. Smith, *Ind. Eng. Chem. Res*., **1999**, *38*, 3076.
2.   N. Maity, G. F. Payne, J. L. Chipchosky, *Ind. Eng. Chem. Res.*, **1991**, *30*, 2456.
3.   Z. Q. Shi, M.C. Xu, X. Lin, M. C. Xu, Y. G. Fan, *Chinese. J. React. Polym.*, **2000**, *9*, 34.
4.   M.C. Xu, Z. Q. Shi, X. L. Xie, M. C. Xu, Y. Zeng, *Chinese. J. React. Polym.*, **2000**, *9*, 10.
5.   N. Maity, G. F. Payne, *Reactive Polymers.*, **1992**, *17*, 273.