



# Effects of the hydrophobicity of adsorbate on the adsorption of salicylic acid and 5-sulfosalicylic acid onto the hydrophobic-hydrophilic macroporous polydivinylbenzene/polymethylacrylethylenediamine IPN



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## ABSTRACT

Hydrophobic-hydrophilic macroporous polydivinylbenzene/polymethylacrylethylenediamine IPN (PDVB/PMAEM IPN) was synthesized indirectly through the strong forced compatibility. The effects of the hydrophobicity of adsorbate on the adsorption of salicylic acid and 5-sulfosalicylic acid onto the hydrophobic-hydrophilic PDVB/PMAEM IPN were investigated. PDVB/PMAEM IPN exhibited greater adsorption capacity of salicylic acid than that of 5-sulfosalicylic acid. The absolute values of  $\Delta H$ ,  $\Delta G$  and  $\Delta S$  of the adsorption of salicylic acid onto PDVB/PMAEM IPN were greater than those of 5-sulfosalicylic acid, indicating the adsorption of salicylic acid onto PDVB/PMAEM IPN was more welcome. Adsorption mechanism proved that greater adsorption capacity of salicylic acid onto PDVB/PMAEM IPN than that of 5-sulfosalicylic acid was attributed to the stronger hydrophobicity of salicylic acid.

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## 1. Introduction

Both salicylic acid (denoted as SA) and 5-sulfosalicylic acid (denoted as SSA) are the important raw material or intermediate in the manufacture of medicine, dye and surfactant [1,2]. In the manufacturing process of menthyl salicylate, menthyl salicylate can be synthesized by SA and methanol [3]. The technique produces a large amount of waste water including the unreacted SA and the by-products of SSA [3]. The waste water brings about a severe environmental problem because of its' high levels of toxicity [4]. Many disposal techniques, such as photo catalytic degradation [5], advanced oxidation [6] and biodegradation [7], are developed to remove SA and SSA from the waste water. For the high additional value of SA and SSA, it is very interesting that adsorption is used to recover them.

Interpenetrating polymer network (IPN) is a new type of polymer materials, which is consisted of two or more entangled and cross-linked polymer networks [8]. The characteristics of interface interpenetration, strong forced compatibility and low swelling

degree make IPN developed rapidly as an effective modification of polymer [9]. Most polymers are composed of similar or identical hydrophobic characters or hydrophilic characters networks. So far there are few studies related to hydrophobic-hydrophilic IPN [10]. Resin adsorption is getting more and more attention as an effective treatment of organic pollutants [11–13]. Polystyrene is a kind of typical non-polar adsorption resin. Its' extreme hydrophobic surface reduces its' ability to adsorb polar organic acids from waste water. In the view of the hydrophobic benzene ring of SA and SSA, the first network of polydivinylbenzene (PDVB) is synthesized, which has hydrophobic adsorption ability. In the view of the hydrophilic  $-\text{OH}-\text{COOH}$  and  $-\text{SO}_3\text{H}$  of SA and SSA, the second network of polymethylacrylethylenediamine (PMAEM) is synthesized, which has hydrophilic adsorption ability.

The hydrophobic-hydrophilic IPN can't be synthesized directly because of strong phase-separation between a hydrophobic network and a hydrophilic network [14]. In this paper, the similar hydrophobic polydivinylbenzene/polymethylmethacrylate IPN (PDVB/PMMA IPN) is synthesized by suspension polymerization, and then is transformed into hydrophobic-hydrophilic PDVB/PMAEM IPN by converting the polymethylmethacrylate (PMMA) to PMAEM through aminolysis with ethylenediamine. From their molecular structure, SA has stronger hydrophobicity than SSA

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because of its' lack of the hydrophilic  $-\text{SO}_3\text{H}$ . SA and SSA are selected as model molecules to evaluate the effects of the hydrophobicity of adsorbate on the adsorption of SA and SSA onto the hydrophobic-hydrophilic macroporous polydivinylbenzene/poly-methylacrylethylenediamine IPN.

## 2. Experimental

### 2.1. Material and chemicals

Methyl methacrylate (MMA) was purchased from Tianjin Damao Chemical Plant (Tianjin, China) and purified by vacuum distillation before used. 2, 2-Azobisisobutyronitrile (AIBN) and benzoperoxide (BPO) were obtained from Shanghai Zhongli Chemical Plant (Shanghai, China) and recrystallized before use. Divinylbenzene (DVB, 50%) was purchased from Gray-west Chemical Plant (Sichuan Province, China) and eluted by 5% NaOH. Triallyl isocyanurate (TAIC, 98%) was obtained from Liu-yang Chemical Plant (Hunan Province, China). SA and SSA applied as the adsorbates were analytical reagents and used directly. The other chemicals were all analytical reagents.

### 2.2. Synthesis of the hydrophobic-hydrophilic PDVB/PMAEM IPN

As described in Scheme 1, macroporous crosslinked PDVB was synthesized according to the literature [8]. 20 g PDVB beads were firstly swollen in the mixture of MMA, butyl acetate, TAIC, *n*-heptane and AIBN for 24 h. The mixture of *n*-heptane and butyl acetate (1:4, w/w) was applied as porogens. The ratios of the monomers (MMA and TAIC) to the porogens, TAIC to MMA were 1:2.5 (w/w), 1:9 (w/w) respectively. Then, the swollen PDVB beads were separated out of the above mixture and added into the aqueous solution (300 parts) of 1% PVA (w/w) and 3% NaCl (w/w). The mixture was stirred and heated at 358 K for 12 h. The beads (PDVB/PMMA IPN) were filtered out and extracted with petroleum ether for 12 h, and then dried at 318 K. PDVB/PMMA IPN was swollen in excess ethylenediamine for 24 h, and then reacted with ethylenediamine for 12 h at the condition of refluxing to convert the PMMA to PMAEM. The dried sample of the beads was named as PDVB/PMAEM IPN.

### 2.3. Characterization of the hydrophobic-hydrophilic PDVB/PMAEM IPN

FT-IR spectroscopy of all samples was recorded on the Nexus 870 Fourier transformed infrared instrument with a resolution of  $1.0\text{ cm}^{-1}$ . Weak basic exchange capability was measured using acid-base neutralization titration method described in the literature [15]. BET surface area and pore volume of all samples were determined using  $\text{N}_2$  adsorption-desorption isotherms at 77 K with the Micrometics ASAP 2010 surface area and porosity analyzer.

### 2.4. Adsorption assay

Adsorption experiments of SA and SSA onto the PDVB/PMAEM

IPN were conducted at the scheduled temperature respectively for 24 h. About 0.2 g PDVB/PMAEM IPN and 50 mL solution with known concentrations of SA and SSA were introduced into 100 mL glass flasks. The flasks were capped and shaken in a rotary shaker to ensure equilibrium. The adsorption capacity of adsorbate ( $q$  mg/g) was calculated as the following equation:

$$q = \frac{V(C_0 - C_e)}{m} \quad (1)$$

where  $V$  (mL) represented the volume of the solution of SA and SSA,  $m$  (g) was the weight of PDVB/PMAEM IPN,  $C_0$  (mg/mL) and  $C_e$  (mg/mL) represented the initial and the equilibrium concentration of adsorbate, respectively.

### 2.5. Dynamic adsorption and desorption

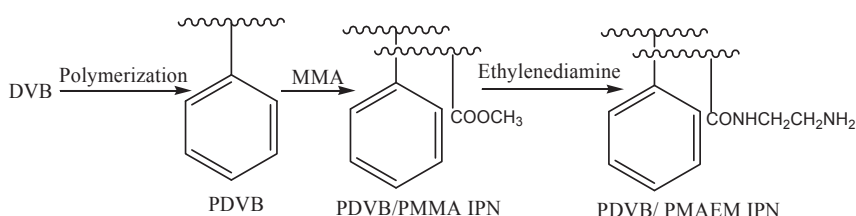
Dynamic adsorption was performed with a glass column (inner diameter 10 mm) filled with 10 mL PDVB/PMAEM IPN at 298 K. The initial concentration of SA and SSA solution was 5.1 mmol/l. The flow velocity was 4 BV/h (BV is bed volume). The concentration of the effluent SA and SSA from PDVB/PMAEM IPN was monitored until the effluent concentration approached the same as the initial concentration. Then the column was rinsed with 3 BV deionized water. PDVB/PMAEM IPN was desorbed with 6% NaOH (w/w) at a flow rate of 2 BV/h and the desorbed concentration of SA and SSA was determined.

## 3. Results and discussion

### 3.1. Characterization of the resins

Fig. 1 shows the FT-IR spectra of PDVB, PDVB/PMMA IPN and PDVB/PMAEM IPN. The IR spectrum of PDVB characterizes its benzene ring adsorption peaks at  $1600\text{ cm}^{-1}$  and  $1450\text{ cm}^{-1}$ . Compared with the IR spectrum of PDVB, the spectrum of PDVB/PMMA IPN continues to have the primary characteristic spectrum of PDVB, and a new characteristic peak attributed to the carbonyl group at  $1735\text{ cm}^{-1}$  is presented. After aminolysis reaction of the PMMA of PDVB/PMMA IPN with ethylenediamine, a strong adsorption peak is found at  $3100\text{--}3500\text{ cm}^{-1}$  in the spectrum of the obtained PDVB/PMAEM IPN and the peak can be assigned to the N–H of PMAEM.

Water content and weak basic exchange amount of PDVB, PDVB/PMMA IPN and PDVB/PMAEM IPN are listed in Table 1. Extreme hydrophobic surface makes PDVB with low water content, while hydrophilic ester groups in PMMA improve the water content of PDVB/PMMA IPN greatly. Amino groups can form hydrogen bond with water, which can improve the water content of PDVB/PMAEM IPN further compared with PDVB/PMMA IPN. Weak base exchange amounts of PDVB and PDVB/PMMA IPN are 0 mmol/g, while the weak base exchange amount of PDVB/PMAEM IPN is 1.15 mmol/g. The change of the weak base exchange amount of PDVB/PMMA IPN and PDVB/PMAEM IPN suggests that the second network PMMA of



Scheme 1. Synthesis of the PDVB/PMAEM IPN.

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