

Water-Swellable Hydrophobic Porous Copolymer Resins Based on Divinylbenzene and Acrylonitrile. II. Pore Structure and Adsorption Behavior

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ABSTRACT: By using purified divinylbenzene (DVB, 98.8%) or technical DVB (79.3%), the hydrophobic, but water-wettable or swellable porous copolymer resins based on DVB and acrylonitrile (AN) could be prepared with a wide range of pore structures under certain conditions. The specific surface area for the resulting AN/DVB resin, with an AN/DVB ratio of 40/60 (by mole), could reach a value of 704 m²/g, while such a resin is still water wettable or swellable by direct contact with water. The adsorption behavior of the AN/DVB resins was investigated by focusing on the comparison between the resins with and without prewetting, using caffeine and phenol as model adsorbates.

Adsorption behavior of the AN/DVB resins, without prewetting, correlates well with the wetting ability of the resins in water, suggesting that a well water-wettable hydrophobic porous AN/DVB resin could be directly applied, in a dry state, to the adsorption in an aqueous medium, almost without diminishing the ability of the resin to adsorb the solutes. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 94: 2050–2056, 2004

Key words: divinylbenzene–acrylonitrile; hydrophobicity; swelling; structure; adsorption behavior

INTRODUCTION

We have shown that hydrophobic porous resins based on divinylbenzene (DVB) and acrylonitrile (AN) could be prepared as water-wettable or swellable by using purified DVB (98.8%) or technical DVB (79.3%) in the presence of 1,2-dichloroethane (DCE) as porogen.¹ Because of the stronger polarity of AN than methyl acrylate (MA), the AN/DVB resins thus obtained are water wettable in a wider range of copolymer compositions compared with the resins based on DVB and MA² and will be more valuable from the point of practical application.

In recent years, numerous attempts have been made to increase the hydrophilicity of the hydrophobic polymer adsorbents, especially the resins based on styrene (ST) and DVB.^{3,4} The polymer adsorbents thus obtained should exhibit excellent hydrophilicity and are therefore less dependent on prior wetting with a water-miscible organic solvent prior to their use in an aqueous medium. However, all these reported methods are based upon the approaches to introduce a hydrophilic component, such as carboxylic and sul-

fonic acid groups, or a hydroxyl-containing monomer.^{3–7}

Compared with above methods, our finding provides a new, unique approach to obtain a water-wettable or water-swellable polymer adsorbent mainly based on DVB, in which the hydrophobic monomer units, for example, MA or AN, could be incorporated, instead of the hydrophilic monomer 2-hydroxyethyl methacrylate⁶ or *n*-vinylpyrrolidone.⁷ This paper reports the pore structure and adsorption behavior of the water-wettable porous AN/DVB resins.

EXPERIMENTAL

Resins synthesis

Copolymer resins were prepared, as described in the previous paper,¹ by using purified DVB (98.8%) or technical DVB (79.3%), through a usual suspension copolymerization method.^{8,9} For all resin samples the contents of DVB and AN in the starting reaction mixture are expressed as a mole percentage of the total amount of monomers. Except for additional illustration the DCE was used as porogen at a 2 : 1 ratio (vol/vol) to the monomers.

Characterization

The apparent density (d_a , g/mL) of resins in a dry state was determined by an improved mercury pyc-

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nometric method as described in our previous paper, with a relative error of measurement less than 1%.^{1,10} The true density (d_t , g/mL) was also measured by the pycnometric method but with *n*-heptane as the confining fluid.¹⁰ From d_a and d_t the porosity (P , vol %) and pore volume (V_p , mL/g) were calculated using the equations $P = (1 - d_a/d_t) \times 100$ and $V_p = 1/d_a - 1/d_t$, respectively. The specific surface area (S , m²/g) was determined by a conventional nitrogen adsorption BET technique using a ST-03 instrument, and the average pore diameter (D , nm) can be calculated by the equation: $D = 4 \times 10^3 V_p/S$ (nm).

Adsorption experiment

The adsorption behavior of the AN/DVB resins was investigated by focusing on the comparison of the adsorption isotherms for the resins with and without prewetting. The prior wetting was carried out by first immersing the resin in methanol for 24 h and then washed with water thoroughly to remove the methanol. Caffeine and phenol were used as model adsorbates, and the adsorption isotherms were determined in aqueous solutions with the initial concentration (C_0 , mg/L) of 25, 50, 75, 100, and 125 mg/L for caffeine and 100, 150, 200, 250, and 300 mg/L for phenol. The equilibrium adsorption was performed in a flask at a constant temperature of 30°C. In each case 0.12 g dry resin (nonprewetted resin) or the wet resin (prewetted resin) corresponding to the 0.12 g dry resin was contacted with 25 mL aqueous solution of known concentration. After shaking for 24 h the resin was separated and the equilibrium concentration (C_e , mg/L) of the solution was measured using an UV spectrophotometer at 272 nm for caffeine and at 270 nm for phenol. The caffeine or phenol adsorbed on the resins (adsorption capacity), q_e (mg/g), was calculated according to

$$q_e = V(C_0 - C_e)/W$$

where V (L) is the volume of solution and W is the weight of dry resin (g). The adsorption isotherms were correlated with the Freundlich equation, and from the obtained parameters K and n the adsorption capacities toward caffeine at $C_e = 25$ mg/L and toward phenol at $C_e = 100$ mg/L were calculated.

RESULTS AND DISCUSSION

Porous structure of AN/DVB resins derived from purified and technical DVB

Figure 1 shows the dependence of specific surface area and porosity of the AN/DVB resins on the DVB content. The resins were prepared by using purified DVB (98.8%), with DVB content ranging from 10 to 70% (or AN/DVB ratio from 90/10 to 30/70). It is seen that,

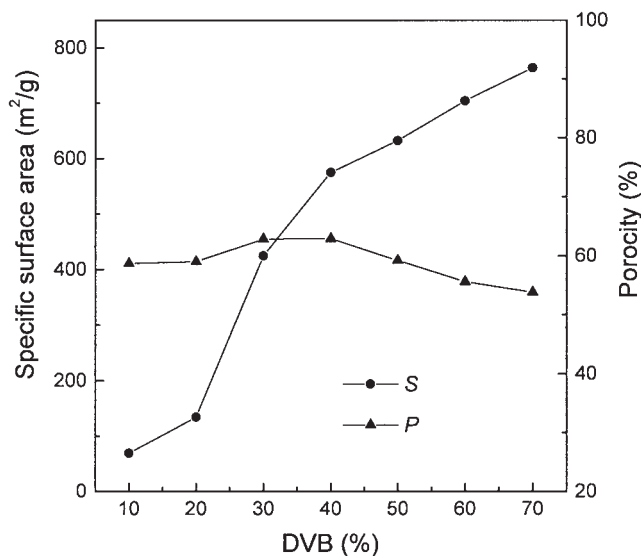


Figure 1 Dependence of specific surface area (S) and porosity (P) of AN/DVB resins on the DVB content. The resins were prepared by using purified DVB (98.8%).

while the specific surface area increases significantly with an increase in DVB content, the porosity does not change importantly at different DVB levels. As a result, the average pore diameter calculated based on the specific surface area and pore volume decreases monotonously from 74 to 5.4 nm, with increasing the DVB content from 10 to 70%.

The DVB dependence of specific surface area in Figure 1 is similar to that for ST/DVB resins synthesized with toluene as porogen, but the dependence of porosity on DVB content is apparently different from the case of ST/DVB resins.^{11,12} For ST/DVB resins, they appear as glassy (i.e., porosity = 0) around 10% DVB, and beyond about 20% DVB the porosity increases rapidly with raising DVB content up to 50–60% DVB.^{8,11} The difference in DVB dependence of the porosity between AN/DVB and ST/DVB resins could be mainly ascribed to the different thermodynamic properties between the monomers AN and ST or DVB and between the polymers of poly(acrylonitrile) (PAN) and poly(styrene) (PST) or poly(divinylbenzene) (PDVB). For ST/DVB copolymers, when a solvating solvent toluene was used as a porogen, the driving force for pore formation was mainly crosslinking-induced phase separation.^{13–15} In this case, the phase separation occurs at a relatively high critical value of the DVB content, and beyond that the extent of phase separation increases with raising the DVB level. Accordingly, the porosity of ST/DVB resins increases with increasing the amount of DVB beyond a certain DVB level. For AN/DVB resins, even with DCE as porogen, the situation is more complicated. While the monomer DVB and porogen DCE are good solvents for DVB units and are poor solvents for AN

TABLE I
Porous Properties of AN/DVB Resins Prepared by Using
Technical DVB (79.3%) and in the Presence of Different
Porogens of DEC and Toluene

AN/DVB	DCE as porogen			Toluene as porogen		
	<i>S</i> (m ² /g)	<i>P</i> (%)	<i>D</i> (nm)	<i>S</i> (m ² /g)	<i>P</i> (%)	<i>D</i> (nm)
87/10	73	51.7	51.4	/	70.8	/
75/20	135	50.0	26.4	77	70.3	108.6
63/30	343	54.1	11.4	260	70.4	30.4
50/40	507	51.8	7.0	418	57.1	11.0
37/50	550	38.2	4.0	561	57.7	8.6

S, specific surface area; *P*, porosity; *D*, average pore diameter.

units in the AN/DVB resins, the monomer AN is a poor solvent for the whole copolymer of the AN/DVB resins. Then, at lower DVB levels, with a higher proportion of AN than DVB in the reaction mixture, and with more AN unit than DVB unit incorporated into the copolymer during the copolymerization, the compatibility between the monomers–porogen mixture and the forming polymer networks is very poor. The incompatibility, in this case, will cause an earlier phase separation that should be responsible for the higher porosity of the AN/DVB resins at lower DVB levels. With an increase in DVB content, the number of the DVB units in the forming copolymer networks increase and the number of the AN units decrease, which improves the compatibility between the polymer and other components in the copolymerization system and reduces the extent of phase separation induced by the incompatibility. On the other hand, however, the phase separation induced by the crosslinking reaction increases with raising the DVB content, and in consequence the total porosity of the resulting AN/DVB resins does not change greatly. Therefore, it is the combination of these two pore-forming mechanisms that causes the DVB dependence of the porosity of AN/DVB resins presented in Figure 1.

In a previous paper we have shown that by copolymerization of purified DVB and AN with DCE as porogen, the resulting AN/DVB resins with DVB contents up to 60% (79% by weight) are water wettable or swellable.¹ In Figure 1, the specific surface areas for the 40, 50, and 60% DVB resins are 575, 632, and 704 m²/g, with a porosity (pore volume) of 62.9% (1.38 mL/g), 59.2% (1.23 mL/g), and 55.6% (1.08 mL/g), respectively. These data indicate that the water-swallowable AN/DVB resins could also be prepared with a wide range of pore structures.

Table I presents the porous properties of the AN/DVB resins prepared by using technical DVB (79.3%), with either DCE or toluene used as porogen for the preparation. Since the main impurity in technical DVB is EVB, the other part of the monomer unit in the AN/DVB resins, besides the DVB and AN, is EVB. As

can be seen in this table, with either DCE or toluene as porogen, the DVB dependence of both specific surface area and average pore diameter is very similar to the case of AN/DVB resins prepared by using purified DVB (98.8%) in Figure 1. That is, the specific surface area increases and the average pore diameter decreases with an increase in DVB content. On the other hand, however, the dependence of porosity on the DVB content in Table I is somewhat different from that in Figure 1. While the difference between the porosities at various DVB levels is not great in Figure 1, the decrease of the porosity at high DVB levels in Table I, for both kinds of resins with DCE and toluene as porogen, is profound. This phenomenon is somewhat similar to the observation reviewed in literature¹⁶ and is probably in consequence of an increase in EVB units in the copolymer resins. An increased portion of EVB in resins improves the compatibility between the monomers–porogen mixture and the forming polymer networks, but does not increase the crosslinking density of the copolymer resins; as a result, the porosity decreases.

The comparison between the resins in Table I prepared with two different solvents as porogen shows that the porosity and average pore diameter for resins with toluene as porogen are much greater than the corresponding resins with DCE as porogen. Obviously, this is because the DCE is a polar solvent and its solubility parameter is closer to that of AN/DVB copolymer. For the same reason, when toluene was used as porogen, the resulting AN/DVB resins could swell or be wetted in water with DVB contents up to 30%, whereas with DCE as porogen the DVB content at which the resins are water wettable or swellable could reach a higher value of 40%.¹ From the above results we can see that the AN/DVB resins could also be prepared with a rather high surface area, e.g., 507 m²/g for 50/40 AN/DVB resin with DCE as porogen, by using commercially available DVB, while the resins are wettable or swellable in water.

Effect of resin composition on pore structure

Pore structure of AN/DVB resins described above and reported in the literature^{16,17} was investigated on the resin samples that were synthesized by simply changing the proportion of DVB to AN as is the case in Figure 1. Because in that way changing one component must cause other components to be changed, the situation is very complicated. To make the effects of DVB and AN contents on the pore structure of the resins clear, we prepared the AN/DVB resins by changing DVB content at a fixed AN level or by changing AN content at a fixed DVB level, and in all cases the purified DVB (98.8%) was used for the preparation. Tables II and III present the results.

TABLE II
Porous Properties of AN/DVB Resins with
Different DVB Contents

AN/DVB	S (m ² /g)	d_a (g/mL)	P (%)	V_p (mL/g)	D (nm)
50/30	2.0	0.861	19.5	0.227	/
50/35	76	0.671	41.4	0.617	32.6
50/40	396	0.565	53.1	0.939	9.4
50/43	504	0.546	52.7	0.965	7.6
50/46	573	0.494	58.0	1.174	8.2
50/50	632	0.480	59.0	1.229	7.8

The AN/DVB resins were prepared by using purified DVB (98.8%), with AN content fixed at 50% and DVB content varied from 30 to 50% by incorporating EVB. S , specific surface area; d_a , apparent density; P , porosity; V_p , pore volume; D , average pore diameter.

Table II presents the porous properties of AN/DVB resins with AN content fixed at 50% and the DVB content varied from 30 to 50% by incorporating EVB. As can be seen, with AN content fixed at a constant level, the porosity or pore volume increases together with the specific surface area, as the DVB content of the resins is increased. This is different from the DVB dependence of the porosity in Figure 1 and is opposite to the observation in literature where the porosity of AN/DVB resins decreases with increasing the DVB content.¹⁶ However, the DVB dependence of the porosity presented in Table II is very similar with the case of ST/DVB resins.^{11,12} Clearly, this is because, with AN content fixed at a constant level, the change of the pore structure for AN/DVB resins is dominated by the only factor of the DVB content. For resins with high DVB levels between 40 and 50% DVB (57 and 71% DVB by weight), because of the parallel increase in pore volume and surface area, the average pore diameters of these resins are close to each other, with the values of 7.6–9.4 nm. The resins with DVB content in this range possess rather high specific surface area of 396–632 m²/g, while all these AN/DVB resins are water wettable or water swellable as judged by water uptake measurement or by float–sink test.

Table III presents the porous properties of AN/DVB resins with DVB content fixed at 40% and the AN content varied from 30 to 60% also by incorporating EVB. It is seen that, with DVB content fixed at a constant level, both the specific surface area and porosity or pore volume increase with raising the AN content. For the resins with AN content between 50 and 60%, the average pore diameter is nearly the same, with the values of 9.0–9.6 nm. In the same range of AN levels the specific surface area reaches rather high values between 415 and 575 m²/g, and the resins are wettable or swellable by direct contact with water. The AN dependence of the porosity can easily be explained by an increased incompatibility of the copolymerization system with raising the AN content, since the AN portion in both monomers or forming

polymer network actually acts as an intrinsic nonsolvating porogen.¹⁵

The AN dependence of the specific surface area presented in Table III is interesting. One of the reason for such a relationship between surface area and AN content can probably be ascribed to the high polarity of the AN units in AN/DVB copolymer resins. It is known that the copolymers containing AN units have, similar to the case of PAN, a semicrystalline structure in which the ordered regions can act as additional physical crosslinks.¹⁸ Then, just as with the case of increasing DVB content, an increase in AN content results in an increased crosslinks, which is in favor of the formation of the pores with smaller size, therefore a larger surface area of the resulting resin products.

Adsorption behavior of AN/DVB resins

For hydrophobic porous polymer resins, especially the resins derived from ST and DVB, their application as adsorbent in aqueous mediums is often restricted by the problem associated with the hydrophobic surface of the resins.^{3–5} Without prior wetting of the resins with a water-miscible organic solvent such as methanol, most of the interior surface area of the porous resins is inaccessible to water and hence to solutes present in aqueous solution. Accordingly, the usual hydrophobic porous resins, without prewetting, fail to adsorb the solutes from water.

The hydrophobic porous AN/DVB resins, when prepared under certain conditions,¹ are water wettable or swellable, therefore it is interesting to know the adsorption behavior of these kinds of resins. Using caffeine and phenol as model adsorbates, the adsorption behavior of the AN/DVB resins in aqueous solutions was investigated by focusing on the comparison of the adsorption isotherms of the resins with and without prewetting.

TABLE III
Porous Properties of AN/DVB Resins with
Different AN Contents

AN/DVB	S (m ² /g)	d_a (g/mL)	P (%)	V_p (mL/g)	D (nm)
30/40	78	0.879	24.2	0.276	/
35/40	85	0.850	25.8	0.303	/
40/40	323	0.750	34.8	0.463	5.7
46/40	410	0.640	44.6	0.697	6.8
50/40	415	0.565	53.1	0.939	9.1
53/40	501	0.457	58.3	1.167	9.4
56/40	523	0.486	59.8	1.231	9.4
60/40	575	0.456	62.9	1.379	9.6

The AN/DVB resins were prepared by using purified DVB (98.8%), with DVB content fixed at 40% and AN content varied from 30 to 60% by incorporating EVB. S , specific surface area; d_a , apparent density; P , porosity; V_p , pore volume; D , average pore diameter.

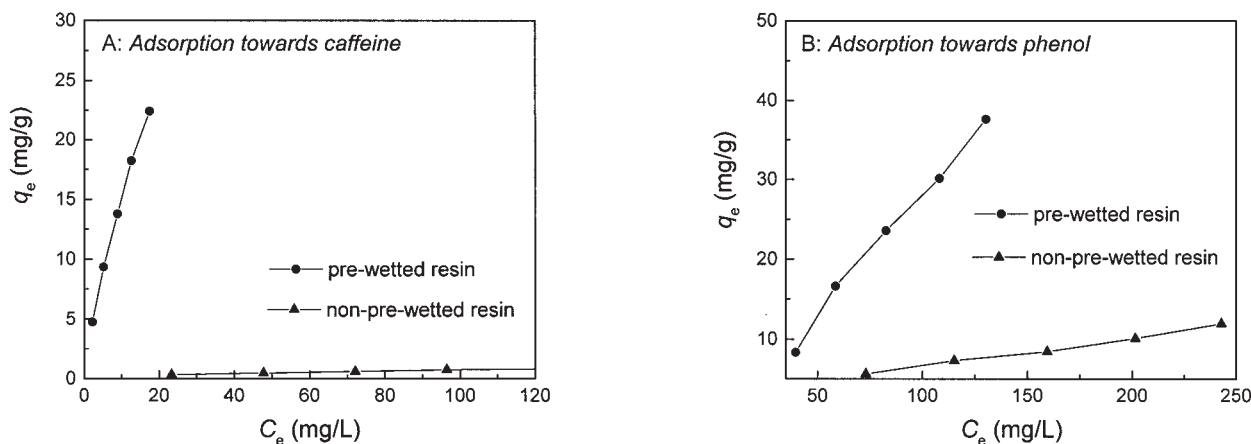


Figure 2 Adsorption isotherms of caffeine and phenol on XAD-4 resin with and without prewetting (prewetted and nonprewetted resin). (a) adsorption toward caffeine; (b) adsorption toward phenol.

First, as a comparison, the adsorption isotherms of caffeine and phenol on the Amberlite XAD-4 resin, a well-known ST/DVB polymer adsorbent possessing a specific surface area about $750 \text{ m}^2/\text{g}$, is presented in Figures 2(a) and (b). The resin was prewetted or not prewetted before use. It is seen that, in both cases of the caffeine and phenol adsorption from aqueous solution, the adsorption of solute on the nonprewetted resin is very limited as opposed to the adsorption on the prewetted one. Obviously, the interior surface of the hydrophobic XAD-4 resin without prewetting is essentially inaccessible to water.

The AN/DVB resins in Figure 1 with DVB contents of 30–60% are water wettable, the water uptake, measured by direct contact with water, for 70/30, 60/40, 50/50, and 40/60 AN/DVB resins is 2.08, 2.04, 1.83, and 1.53 mL/g, respectively. As a result, for all these resins, the adsorption isotherms in the prewetted and nonprewetted cases become close to each other. As an example, the adsorption isotherms of 50/50 AN/DVB

resin toward caffeine and phenol are shown in Figures 3(a) and (b). As can be seen, both the caffeine and phenol adsorption isotherms in Figure 3 exhibit almost no difference for the prewetted and nonprewetted ones, indicating that there is no need for this resin to be prewetted in the application as an adsorbent in the aqueous solutions.

A further investigation has been done on the effect of the resin composition on the adsorption behavior by changing DVB or AN content of the AN/DVB resins, with either AN or DVB content fixed at a constant level.

Table IV presents the Freundlich parameters (K , n), along with the correlation coefficient (R^2) for the caffeine and phenol adsorption on the AN/DVB resins. The resins were prepared with AN content fixed at 50% and DVB content varied from 30 to 50% by incorporating EVB. As can be seen, the values for R^2 in this table are all above 0.99, showing that the Freundlich equation is applicable to the caffeine and phenol ad-

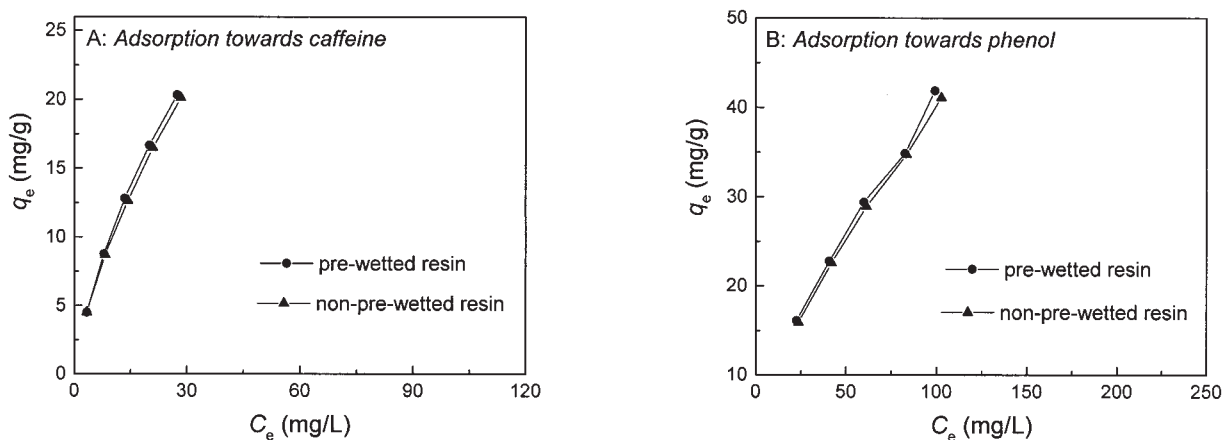


Figure 3 Adsorption isotherms of caffeine and phenol on 50/50 AN/DVB resin with and without prewetting (prewetted and nonprewetted resin). (a) adsorption toward caffeine; (b) adsorption toward phenol.

TABLE IV
Freundlich Parameters K , n , and Correlation Coefficients R^2 for Caffeine and Phenol Adsorption on the AN/DVB Resins with Different DVB/Contents

AN/DVB	Caffeine adsorption			Phenol adsorption		
	K	n	R^2	K	n	R^2
50/30						
Nonprewetted	/	/	/	0.128	1.154	0.998
Prewetted	0.158	1.967	1.000	1.100	1.362	0.997
50/35						
Nonprewetted	0.122	1.459	0.993	0.369	1.072	0.997
Prewetted	0.717	1.217	0.994	1.236	1.405	0.998
50/40						
Nonprewetted	0.961	1.296	0.998	1.408	1.452	0.998
Prewetted	1.123	1.315	0.999	1.559	1.475	0.999
50/50						
Nonprewetted	1.963	1.430	1.000	1.982	1.535	0.992
Prewetted	1.940	1.393	0.999	2.058	1.540	0.992

The resins are the same as those in Table II. The values for K and n were obtained by correlating the adsorption isotherms of the resins with Freundlich equation: $\log q_e = \log K + 1/n \log C_e$, where q_e is the adsorption capacity and C_e is the equilibrium concentration of caffeine or phenol in the aqueous solution.

sorptions on the AN/DVB resins with and without prewetting. For 50/40 and 50/50 AN/DVB resins, which are water wettable, as will be seen in Table V, the values of n in both prewetted and nonprewetted cases are close to each other. Since the parameter n is related to the magnitude of the adsorption driving force, this fact indicates that, for a water-wettable AN/DVB resin, the affinity of both prewetted and nonprewetted resins toward solutes in water is almost the same.

From the parameters K and n , the adsorption capacities (mg/g) of caffeine and phenol on the AN/DVB resins in Table IV were calculated at $C_e = 25$ and $C_e = 100$ mg/L, respectively, and summarized in Table V. The experimental results on the water-wetting properties, assessed by water uptake measurement and float-sink test,^{5,19} are also presented in the same table. As can be seen, the 50/30 or 50/35 AN/DVB resin with DVB content of 30 or 35% is not water wettable, with the water uptake at a very low level. As

a result, the caffeine adsorption on the nonprewetted 50/30 resin is undetected and on the nonprewetted 50/35 resin is very small compared with the adsorption on the prewetted one. Probably because of the partially wetting of the resin, and because of the vapor adsorption of the phenol, which is more volatile compared with caffeine, onto the internal surface of the resin without prewetting, the difference in phenol adsorption between the prewetted and nonprewetted 50/35 AN/DVB resins is small. The weak vapor adsorption of, e.g., acetic acid, on to the nonprewetted XAD-4 resin was reported before,¹⁹ through an equilibrium between the vapor and the solid surface. However, on the other hand, for 50/30 AN/DVB resin with a very limited water uptake of 0.01 mL/g, the phenol adsorption on the prewetted and nonprewetted resins is greatly different in this table, as is the case with XAD-4 resin shown in Figure 2(b).

With only a 5% increase in DVB content, the 50/40 AN/DVB resin in Table V becomes water wettable,

TABLE V
Adsorption Capacities of Caffeine and Phenol on AN/DVB Resins with Different DVB Contents

AN/DVB	Wettability	Water uptake (mL/g)	Caffeine adsorbed (mg/g)		Phenol adsorbed (mg/g)	
			Nonprewetted resin	Prewetted resin	Nonprewetted resin	Prewetted resin
50/30	F	0.010	/	0.8	6.9	32.4
50/35	F	0.306	1.1	10.1	27.1	32.8
50/40	S	1.394	11.5	13.0	33.6	35.4
50/50	S	1.827	18.6	19.3	39.8	41.0

The resins are the same as those in Table II. The water uptake was measured by direct contact of the resin with water,¹ and the wettability of the resin in water was checked by the float-sink test,^{5,19} in this case a water-wettable sample will sink into the water (denoted by S), whereas a nonwettable sample retains air in pores and thereby remains on the surface of the water (denoted by F). The adsorption capacities (solute adsorbed by resin, mg/g) of caffeine and phenol were calculated at $C_e = 25$ and $C_e = 100$ mg/L, respectively, from the Freundlich parameters K and n .

TABLE VI
Adsorption Capacities of Caffeine and Phenol on AN/DVB Resins with Different AN Contents

AN/DVB	Wettability	Water uptake (mL/g)	Caffeine adsorbed (mg/g)		Phenol adsorbed (mg/g)	
			Nonprewetted resin	Prewetted resin	Nonprewetted resin	Prewetted resin
30/40	F	0.093	/	/	8.5	27.0
40/40	F	0.157	0.4	13.5	28.5	33.7
50/40	S	1.380	11.5	13.0	33.6	35.4

The resins are the same as those in Table III. The water uptake was measured by direct contact of the resin with water,¹ and, F and S represent float and sink as is the case in Table V. The adsorption capacities (solutes adsorbed by resin, mg/g) of caffeine and phenol were calculated at $C_e = 25$ and $C_e = 100$ mg/L, respectively, from the Freundlich parameters K and n .

with a water uptake of 1.394 mL/g. Consequently, the adsorption of both caffeine and phenol on the nonprewetted 50/40 resin increases significantly and is getting close to the adsorption on the prewetted one. With a further improvement in water-wetting property of the 50/50 AN/DVB resin, the adsorption capacities of caffeine or phenol become almost the same for the prewetted and nonprewetted resin, suggesting that a hydrophobic porous polymer resin could be applied directly, in a dry state, to the adsorption in an aqueous medium, almost without diminishing the ability of the resins to adsorb the solutes.

In Table VI, the adsorption experiment toward caffeine and phenol has been done on a series of AN/DVB resins with DVB content fixed at 40% and the AN content varied from 30 to 50% also by incorporating EVB. The resin samples are the same as those in Table III.

It is seen that the resins with AN content of 40% or less are not water wettable, but between 40 and 50% AN a transition in wettability occurs, and the 50/40 AN/DVB resin is therefore water wettable with a much higher water uptake than that of 40/40 resin. In this case, the caffeine adsorption on the nonprewetted 40/40 AN/DVB resin is negligible in comparison with the prewetted one, whereas the caffeine adsorption on the nonprewetted 50/40 resin is close to that on the prewetted one. For the phenol adsorption on the 40/40 AN/DVB resin, on the other hand, the difference between the prewetted and nonprewetted resins is not very great. This can also be explained as before, by the vapor adsorption of phenol onto the interior surface of the resin and the partial wetting of the resin. Then, with a decrease in AN content from 40 to 30%, the adsorption capacity toward phenol of the nonprewetted 30/40 resin decreases together with the water uptake, from 28.5 to 8.5 mg/g, which is much smaller than the value of 27.0 mg/g for the prewetted 30/40 resin. On the contrary, with increasing the AN content from 40 to 50%, the phenol adsorption on the nonprewetted 50/40 resin becomes closer to that on the prewetted one. Here again, the results in Table VI suggest that the prior wetting is less important for a well water-wettable AN/DVB resin to be applied to the adsorption in an aqueous medium.

CONCLUSION

Water-wettable or swellable hydrophobic porous AN/DVB resins could be prepared with a wide range of pore structures. With DCE as porogen, the specific surface area for AN/DVB resins prepared by using either purified DVB (98.8%) or technical DVB (79.3%) could reach high values, while these resins are wettable by direct contact with water. The adsorption behavior of the AN/DVB resins, without prewetting, correlates well with the wetting ability of the resins in water, and therefore, for the first time a hydrophobic porous copolymer resin could be applied directly, in a dry state, to the adsorption in an aqueous medium, almost without diminishing the ability of the resins to adsorb the solutes. In this way, our results provide a new, unique approach to obtain a water-wettable or swellable polymer adsorbent.

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