

SYNTHESIS , STRUCTURE AND PROPERTIES OF INTERPENETRATING SULFONIC ACID RESINS WITH HIGH CAPACITY

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ABSTRACT

Two series of interpenetrating sulfonic acid resins (ISAR), $10 \times n$ and $n \times 10$, were prepared by means of the wet method, and the physicochemical, thermodynamic and kinetic properties of the ISAR were measured. The results show: $10 \times n$ resins exhibit better properties than $n \times 10$ ones, mainly in higher apparent degree of crosslinking and larger conformational entropy effect, among which, 10×1 resin exhibits the best thermodynamic and kinetic properties. In the DTA graphs of $n \times 10$ resins, there are two T_g and two T_{ox} , but in those of $10 \times n$, only one T_g and one T_{ox} . This result well supports the conclusion that $10 \times n$ resins have much better interpenetrating structural aspects.

INTRODUCTION

Millar et al.^[1] at first in the early 1960's and Xu et al.^[2,3], in the recent years, reported that the sulfonic acid resins with interpenetrating network structure possess better properties than the ordinary gel resins, mainly better physicochemical properties, higher selectivities and higher interdiffusion coefficients. However, Millar's study almost only concentrated on 4.5×4.5 ISAR, of which the degrees of crosslinking of the two networks are the same, whereas the influence of changing the degree of crosslinking at the first and the second polymer network on the properties of ISAR was seldom concerned, which is just the main aspect showing why the properties of ISAR are much different.

The keys for obtaining the ISAR with high capacity are low degree of swelling and high degree of sulfonation of it. Raising degree of crosslinking of ISAR is for lowering its degree of swelling, but when degree of crosslinking is too high, it is unfavourable to increase degree of sulfonation. Moreover, it will markedly lower interdiffusion rate of ions. In referene [4], we have indicated that 12, the degree of crosslinking of the first polymer network of the ISAR, is good for obtaining ISAR with high capacity, and a good result has been achieved when this kind of ISAR is used for the treatment of wastewater containing Zn^{2+} . However, if the size of ions to be absorbed is larger, the efficiency of the treatment will obviously decline because of low diffusion rate inside the ISAR. In this paper, the relationship between structures and properties of ISAR with high capacity is studied. We designed two series of interpenetrating resins with nearly equal saturated penetrating degree. It shows that the resins with the high crosslinking first network are penetrated with less amount of the monomer for the second polymerization and those with the low crosslinking first network penetrated with larger amount of that. The two series of resins have the same

weight ratio of the high crosslinking polymer networks to the low ones, which makes the two series of resins have the same average DVB% amount. Only in the above-mentioned case, we are able to compare exactly the properties of the two series of ISAR with each other and thus able to confirm that the difference of the properties between the two series of ISAR is just due to the difference of interpenetrating structure between them. Based on above-mentioned considerations, we selected the degree of crosslinking of the two series of ISAR being $10 \times n$, which means that the degree of crosslinking of the first and the second polymer network is 10% and $n\%$ respectively (or 10×1 , 10×2 , 10×4), and $n \times 10$ (or 1×10 , 2×10 , 4×10).

EXPERIMENTAL

1. Synthesis of the ISAR

The two series of interpenetrating St-DVB resins were synthesized by means of the wet method^[5] as follows: let the first polymer beads obtained by usual copolymerization method absorb the monomer mixture containing initiator in the water medium and then, under heating, the second polymerization takes place in situ. Such prepared interpenetrating resins were sulfonated by using concentrated H_2SO_4 six times the weight of the polymer beads at first and then adding twice of fuming H_2SO_4 in the later period of sulfonation to increase the degree of sulfonation.

2. Determination of properties of the ISAR

(1) Physicochemical properties of the ISAR were measured by the method of American ion exchange resin test^[6].

(2) The measurement of DTA was carried out with CDR-1 type of DSC instrument.

(3) The equilibrium constants K_B^A of ion exchange were calculated by means of graphic integral^[2] according to $\text{Ln} K_B^A = \int_0^1 K_B^A d\bar{X}_A$, and the thermodynamic functions

ΔG^0 , ΔH^0 and ΔS^0 were calculated respectively according to the equations $\Delta G^0 = (-RT/Z_A Z_B) \text{Ln} K_B^A$, $(\partial \text{Ln} K_B^A / \partial T) = Z_A Z_B \Delta H^0 / RT$ and $\Delta S^0 = (\Delta H^0 - \Delta G^0) / T$.

(4) The reaction degree F of ion exchanges concerned with time t was measured with shallow beds^[7]. The function relation between F and t is as follows: $F = [1 - \exp(-\bar{D}\pi^2 t / r_0^2)]^{1/2}$. In the equation $\bar{D}$ is the interdiffusion coefficient and r_0 is the average radius of the polymer beads. Let $B = \bar{D}\pi^2 / r_0^2$, and it can be seen that there is a corresponding value of Bt to each F . Thereby, B was obtained and then $\bar{D}$ was calculated. According to Arrhenius equation $\bar{D} = \bar{D}_0 e^{-E_a/RT}$, the interdiffusion activation energy E_a was obtained.

RESULTS AND DISCUSSION

1. Physicochemical properties of the ISAR

Table 1 shows that the physicochemical properties mainly depend on the degree of

crosslinking of the first polymer network of the resin. $10 \times n$ and $n \times 10$ series of resins contain the same amount of DVB, but their physicochemical properties are very different. For example, the water regain of 10×1 is 114 g/eq, but that of 1×10 is 224 g/eq, and the $\text{Na}^+ \rightarrow \text{H}^+$ swelling percentage of 10×1 is 1.8%, but that of 1×10 is 7.4%. All of those prove that $10 \times n$ resins have higher apparent degree of crosslinking than $n \times 10$ resins do. For the $n \times 10$ resins, the properties markedly change with the change of " n ", for the $10 \times n$, however, the properties do not change in the like manner with the change of " n ". Besides the amount of DVB, the degree of interpenetrating of the two networks also quite largely contributes on apparent degree of crosslinking of ISAR. It can be deduced that the degree of interpenetrating of the two networks of $10 \times n$ series is larger than that of $n \times 10$ series. The two networks of $10 \times n$ penetrate into a whole interpenetrating network and entangle each other, which exhibits, therefore, high apparent degree of crosslinking. The results of DTA to the $10 \times n$ and $n \times 10$ resins also well prove the above conclusion (see Fig. 1).

Table 1 Physicochemical properties of the ISAR

Two net . crosslink . deg .	Two net . wt . ratio (g : g)	Water regain (g/eq)	Apparent crosslink . deg .	$\text{Na}^+ \rightarrow \text{H}^+$ swel . %	Capacity (meq/ml)	Strength (g/bead)
1×10	1 : 1.6	224	6.5	7.44	1.85	250
2×10	1 : 1.6	193	7.7	7.04	1.96	270
4×10	1 : 1.6	152	10.0	6.87	2.22	300
10×1	1.6 : 1	114	15.2	1.81	2.34	370
10×2	1.6 : 1	110	15.8	3.06	2.34	340
10×4	1.6 : 1	109	16.3	2.95	2.39	340

In the DTA graphs of $n \times 10$ resins, there are two T_g and two T_{ox} , but in the graphs of $10 \times n$, only one T_g and one T_{ox} . It further proves that the structural aspects of the two series of resins are very different. Because the crosslinking degree of the first polymer network of $n \times 10$ resins is low and that of the second is high, the first network is just only filled with the second one. Their DTA graphs exhibit, therefore, two T_g and two T_{ox} , and the T_{g1} and T_{ox1} markedly rise with increasing " n ", but the T_{g2} and T_{ox2} do not change similarly. The degree of interpenetrating of the $10 \times n$ resins is very high. The two polymer networks penetrate and entangle each other very well, and thus their DTA graphs exhibit only one T_g and one T_{ox} , and they are just between T_{g1} and T_{g2} of the $n \times 10$ as well as T_{ox1} and T_{ox2} respectively, hardly changing with changing " n " which is due to the intersection of the two networks of the $10 \times n$ resins.

2. Thermodynamic properties of the ISAR

Table 2 shows : $K_{\text{H}^+}^{\text{Na}^+}$ and $K_{\text{H}^+}^{\text{Zn}^{2+}}$, the equilibrium constants of the ion exchanges, of the $10 \times n$ resins are markedly larger than those of $n \times 10$ ones, and the former

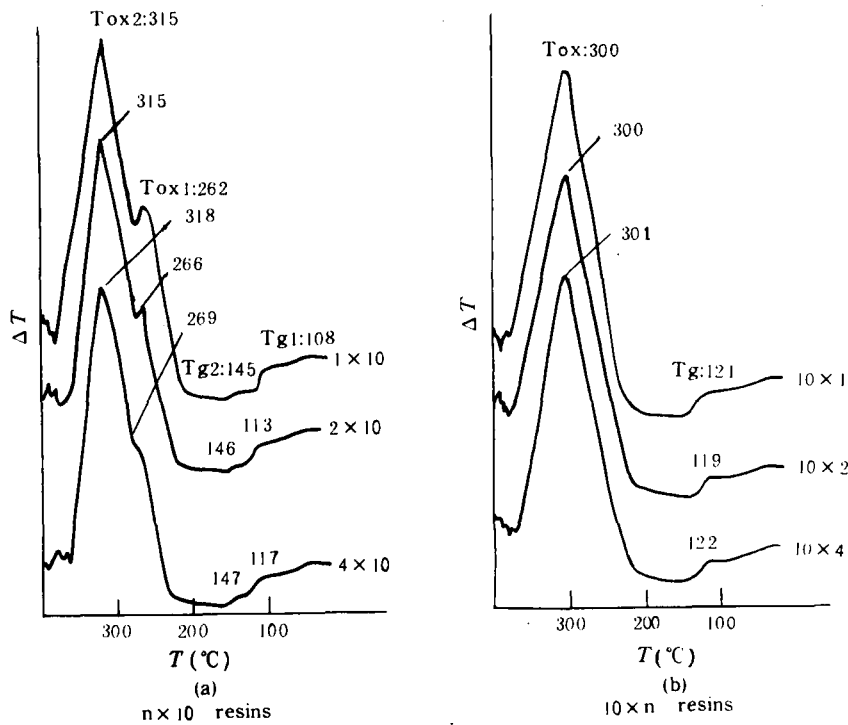


Fig.1 DTA graphs of the ISAR

Table 2 $K_{H^{+}}^{Na^{+}}$ & $K_{H^{+}}^{Zn^{2+}}$ of the ISAR at different temperature

Resins	$K_{H^{+}}^{Na^{+}}$		$K_{H^{+}}^{Zn^{2+}}$	
	30 $^{\circ}\text{C}$	60 $^{\circ}\text{C}$	30 $^{\circ}\text{C}$	60 $^{\circ}\text{C}$
10×1	1.915	1.743	4.179	5.155
10×2	1.940	1.725	4.076	4.879
10×4	1.883	1.647	3.745	4.630
1×10	1.650	1.389	3.032	3.239
2×10	1.750	1.439	3.435	3.606
4×10	1.823	1.497	3.743	3.912

change with the “ n ” less than the latter do . Obviously , it results in that the two networks of the $10 \times n$ resins interpenetrate much better than those of the $n \times 10$ ones . Comparing with K of $n \times 10$, $K_{H^{+}}^{Na^{+}}$ of the $10 \times n$ resins decrease in less extent and $K_{H^{+}}^{Zn^{2+}}$ increase in larger extent with temperature rising . The property exhibited by the $10 \times n$ resins is just that the property of the interpenetrating resins whose two

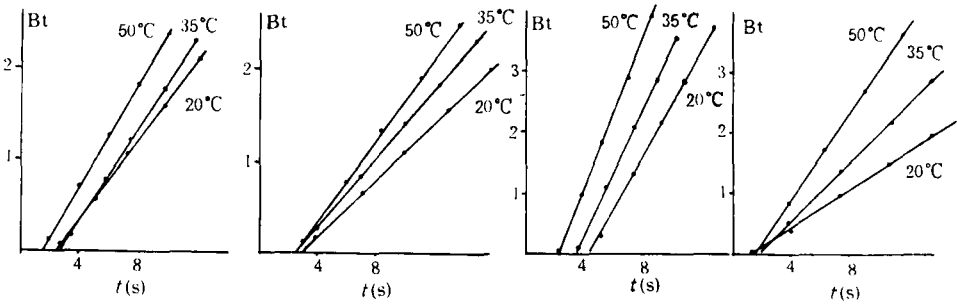
Table 3 ΔG^0 (cal/eq), ΔH^0 (cal/eq) & ΔS^0 (cal/eq deg.) of Na^+/H^+ & $\text{Zn}^{2+}/\text{H}^+$ ion exchanges of the ISAR

Resins	Na^+/H^+ exchange				$\text{Zn}^{2+}/\text{H}^+$ exchange			
	$\Delta G_{30^\circ\text{C}}^0$	$\Delta G_{60^\circ\text{C}}^0$	ΔH^0	ΔS^0	$\Delta G_{30^\circ\text{C}}^0$	$\Delta G_{60^\circ\text{C}}^0$	ΔH^0	ΔS^0
10×1	-390	-367	-606	-0.72	-859	-1085	1355	7.33
10×2	-398	-361	-761	-1.20	-844	-1049	1161	6.64
10×4	-380	-330	-866	-1.61	-824	-1015	1033	6.15
1×10	-301	-218	-1109	-2.68	-666	-782	424	3.61
2×10	-336	-241	-1264	-3.07	-743	-849	313	3.50
4×10	-361	-268	-1297	-3.09	-795	-903	284	3.57

polymer networks interact very well. It can be seen from Table 3 that the $10 \times n$ resins exhibit larger positive entropy effect of ion exchange, but the entropy effect for the $n \times 10$ resins is much less. This is the reason why $10 \times n$ resins exhibit different regularity of $K_{\text{H}^+}^{\text{Na}^+}$ and $K_{\text{H}^+}^{\text{Zn}^{2+}}$ changing with temperature from $n \times 10$ ones. Although the second polymer network of $10 \times n$ resins penetrates into and entangles to the first one well, the two networks can relatively move in the swelling state. When Na^+ or Zn^{2+} spontaneously replaces H^+ , the two networks relatively move to suit the change of electricity tension and others due to the ion exchange, which makes the resin enter into the suitable and stable state. Therefore, $10 \times n$ resins exhibit large conformational entropy effect of the resin skeleton during ion exchange reaction. Among the $10 \times n$ resins, the lower the degree of crosslinking of the second polymer network is, the softer its network and the better its entanglement to the first one, so that the larger the conformational entropy effect is. Thereby, it can be indicated that the high degree of interpenetrating of the two networks of the resins and fine entangling result in not only marked increase of apparent degree of crosslinking but also the enhancement of conformational entropy effect.

3. Kinetics properties of the ISAR

Fig. 2 exhibits that the relationships between Bt and t of concerning ion exchanges are linear. It proves that the rates of the ion exchanges are controlled by particle diffusion rates. Some interesting results can be seen from Table 4: (1) Though $n \times 10$ series of resins have the same amount of DVB as $10 \times n$ series, the former's interdiffusion coefficients are larger than the latter's, and the former's diffusion activation energies are smaller than the latter's; (2) At lower temperature $\overline{D}_{\text{Na}^+ - \text{H}^+}$ of the 10×1 resin is smaller than that of the 10×2 resin, but at higher temperature the former is larger than the latter. Generally, among the $10 \times n$ resins, $\overline{D}$ of the 10×1 resin is the largest, and E_a of the 10×1 is the largest, too; (3) $\overline{D}_{\text{Zn}^{2+} - \text{H}^+}$ of the $n \times 10$ resins are larger than $\overline{D}_{\text{Na}^+ - \text{H}^+}$, and those of the $10 \times n$ resins are just on the contrary, but at higher temperature $\overline{D}_{\text{Zn}^{2+} - \text{H}^+}$ of the 10×1 resin is larger than $\overline{D}_{\text{Na}^+ - \text{H}^+}$.



a. $1 \times 10, \text{Na}^+/\text{H}^+$ b. $10 \times 1, \text{Na}^+/\text{H}^+$ c. $1 \times 10, \text{Zn}^{2+}/\text{H}^+$ d. $10 \times 1, \text{Zn}^{2+}/\text{H}^+$
Fig.2 Curves of Bt versus t of particle diffusion

Table 4 $\bar{D}$ & E_a of Na^+/H^+ & $\text{Zn}^{2+}/\text{H}^+$ exchanges of the ISAR

Resins	$\bar{D}_{\text{Na}^+ - \text{H}^+} \times 10^6$			$E_a(\text{Na}^+/\text{H}^+)$ (cal/eq)	$\bar{D}_{\text{Zn}^{2+} - \text{H}^+} \times 10$			$E_a(\text{Zn}^{2+}/\text{H}^+)$ (cal/eq)
	20 °C	35 °C	50 °C		20 °C	35 °C	50 °C	
10×1	2.80	3.33	4.27	2649	2.02	3.18	4.66	5186
10×2	2.83	3.12	3.50	1779	2.02	2.51	3.13	2880
10×4	2.01	2.36	2.78	1892	1.12	1.63	2.18	4126
1×10	4.06	4.52	5.17	1490	7.50	8.41	10.29	1954
2×10	3.20	3.72	4.20	1735	3.95	5.02	6.06	2557
4×10	2.79	3.25	3.79	1863	2.97	3.77	4.43	2815

Although the DVB amount in the $10 \times n$ series is the same as that in the $n \times 10$ series, there is a big difference between conformational aspect of the $10 \times n$ and that of the $n \times 10$ series of resins . In addition to chemical crosslinkage in the polymer networks, the $10 \times n$ resins have high degree of entangling and penetrating between the first and the second network , which increases the resistance to the ion diffusion and thus lowers the rate of the ion diffusion. The diffusion activation energy of the 10×1 resin is the largest, which indicates that the two networks of the 10×1 resin entangle each other very well , and the degree of interpenetrating is very much higher . However , diffusion activation energy is not the only factor that affects the rate of interdiffusion . In addition to that , there is other important factor or activation entropy of interdiffusion . The second polymer networks of the 10×1 resin are rather soft because of their low degree of crosslinking , so that the mobility of its interpenetrating networks is high . Therefore , the inner environment of the resin will be easily disturbed (or the conformation comes into change) during ion diffusion . The vibration rate and amplitude of the interpenetrating networks of the 10×1 resin markedly increase with temperature rising , so that the resistance of the resin skeleton to ion diffusion greatly decreases . Thus , interdiffusion rate in the 10×1 resin rapidly rises with temperature rising . Since $\text{Zn}^{2+}/\text{H}^+$ exchange is a reaction of bivalent ion replacing monovalent ion , the probability of Zn^{2+} that effectively collide with sulfonic acid groups is larger than that of Na^+ . Thus , it is possible that the rate of $\text{Zn}^{2+}/\text{H}^+$ exchange is larger than that of Na^+/H^+ exchange when the resistance of

resin skeleton is low enough. But the radius of hydrated ion of Zn^{2+} is larger, so that the rate of the particle diffusion of Zn^{2+} rapidly lowers with the increase of the apparent degree of crosslinking. In this case, the rate of Na^+/H^+ exchange will advance ahead that of $\text{Zn}^{2+}/\text{H}^+$. The results of $\overline{D}_{\text{Na}^+ - \text{H}^+}$ and $\overline{D}_{\text{Zn}^{2+} - \text{H}^+}$ for various resins listed in Table 4 further indicate the difference between the degrees of interpenetrating of the $10 \times n$ resins and that of the $n \times 10$ ones.

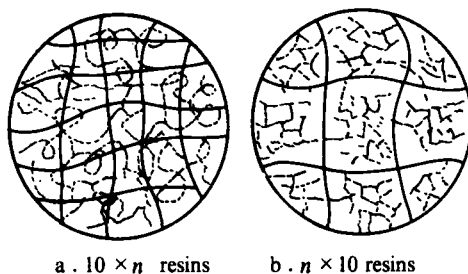


Fig.3 Structural aspect model of the ISAR

According to previous discussions, we can summarize that the two series of interpenetrating resins of the $10 \times n$ and $n \times 10$ as two kinds of structural aspect models shown in Fig.3a, b. Fig.3a indicates that the low crosslinking second polymer network exhibits a high degree of entangling and penetrating into the first one. The two networks interact with each other to form interpenetrating network. The resins with such an interpenetrating structure exhibit very large positive entropy effect including large activation entropy of interdiffusion in the ion exchange reaction. It makes this kind of resins have good thermodynamic and kinetic properties. If the resins are used in the ion exchange of bivalent ion replacing monovalent ion at higher temperature, a good result can be achieved. On the other hand, Fig. 3b shows that the high crosslinking second polymer network seems to fill in the chemical pores of the low crosslinking first network. The two networks are independent of each other. So the resins have large degree of swelling. Their apparent degree of crosslinking is just slightly larger than the average degree of chemical crosslinking. It is the difference of the structural aspects between $10 \times n$ and $n \times 10$ series of resins that leads to the large difference of properties between the two series of resins.

CONCLUSION

(1) The ISAR with a high crosslinking first network and a low crosslinking second network have much larger apparent degree of crosslinking than those with a low crosslinking first network and a high crosslinking second network which leads to that the former have much better physicochemical properties than the latter do.

(2) Comparing with the $n \times 10$ resins, the $10 \times n$ ones exhibit better thermodynamic properties because the two networks of the $10 \times n$ resins have higher degree of entangling and penetrating and good mobility. Therefore, this kind of ISAR exhibits large positive entropy effect of ion exchange reactions and high selectivity.

(3) The $n \times 10$ resins have larger $\overline{D}_{\text{Na}^+ - \text{H}^+}$ and $\overline{D}_{\text{Zn}^{2+} - \text{H}^+}$ than the $10 \times n$ resins do, which further proves that the latter have better interpenetrating structural aspect.

(4) It is necessary to indicate that, among the two series of ISAR, the 10×1 resin exhibits a series of especially good properties. It is because that the degree of crosslinking of the second network of it is lower than that of any other else, and its two networks have very high degree of entangling. It is such a structural character of 10×1 makes it fully exhibit good properties of interpenetrating resins, or well-distributed structural character, and large conformational entropy and activation entropy of ion exchange.

Keywords :

Interpenetrating networks, Sulfonic acid resin, Selectivity, Degree of crosslinking.

REFERENCES

- [1] Millar, J. R., *J. Chem. Soc.*, 1960, 3, 1311-1317.
- [2] 刘萍书, 徐和德, 高分子通讯 (*Polym. Commun.*), 1984, 5, 369-374.
- [3] 刘萍书, 黄爱东, 徐和德, 华南师范大学学报 (*J. South China Normal Univ.*), 1983, 1, 108-114.
- [4] 李国明, 郑章福, 徐和德, 华南师范大学学报 (*J. South China Normal Univ.*), 1987, 2, 49-54.
- [5] 丁峻峰, 华南师院学报 (*J. South China Teachers' College*), 1981, 1, 44-55.
- [6] 华东电业管理局中心试验所, 电力技术通讯 (副刊) (*Electricity Power Technology Communication, Supplement*), 1976, 2, 91-110.
- [7] Friedrich Hefferich, "Ion Exchange", McGraw-Hill Book Company, Inc., 1962, 250-322.