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Effect of crosslinking on sorption, diffusion and pervaporation of gasoline components in hydroxyethyl cellulose membranes

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ABSTRACT

The effect of crosslinking on desulfurization mechanism was investigated by the study of sorption and diffusion behaviors of typical gasoline components through the hydroxyethyl cellulose (HEC) membranes with different crosslink density. The sorption, diffusion and permeation coefficients of gasoline components were calculated in the membranes. The results showed that the diffusion mode of typical gasoline components *n*-heptane and cyclohexane in the HEC membranes tended to non-Fickian, but the diffusion kinetic of thiophene, toluene and cyclohexene was typical Fickian. The increasing crosslink density did not change the transport mode of gasoline components in HEC membranes but severely reduced the HEC–gasoline components interaction. Although the sorption and diffusion rates decreased, the difference of sorption/diffusion rates between sulfur and non-sulfur compounds increased with increasing crosslink density, predicting that permeation flux decreased but sulfur enrichment factor increased. The effect of crosslinker content on pervaporation performance of HEC membrane was studied, and the change regularity of flux and sulfur enrichment factor corresponded to the theory analysis results on dynamic sorption curves. Thiophene species had higher sorption and diffusion rates in the HEC membranes than other hydrocarbon components and were the preferential permeation components. These were verified by gas chromatography analysis results of feed and permeate samples of real gasoline.

1. Introduction

Sulfur species in gasoline are primary contributors of SO*x* air pollution, and sulfur in gasoline is a well-known poison for the catalytic converters used for the processing of motor smokes, too. Ultra-deep desulfurization from gasoline has become a very important subject in petroleum refining industry worldwide. The requirement of clearer burning fuels has resulted in a continuing worldwide effort to reduce the sulfur levels in gasoline [1–3]. Gasoline desulfurization by pervaporation (PV) process is a newly emerged technology, which has a number of potential advantages over traditional sulfur removal process and has attracted the increasing attentions of researchers and refiners worldwide [4,5].

In this technique, polymer membrane is the core and key of the research and development. Up to now, many polymer membranes for gasoline desulfurization such as Nafion.RTM.-type ionic membranes [6], polyimide membranes [7], polyurea/urethane membranes [8], crosslinked fluorinated polyolefin [9] and crosslinked poly(dimethyl siloxane) (PDMS) membranes [10–15] had been developed. Our previous work also reported the excellent desulfurization performance of crosslinked polyethylene glycol (PEG) polymer membranes [16–18]. According to the above described, most of the polymer membranes used in gasoline desulfurization have been crossslinked since crosslinking is a simple and effective method of modified membrane. The effect of crosslinking on PV performance has been also studied in detail.

However, little was reported about the effect of crosslinking on transport mechanism of gasoline components through the polymer membranes. Gasoline is a complex mixture composed of hundreds of compounds. Studying transport mechanism of gasoline components through polymer membrane is of great technological importance, and deep understanding of the mechanism will contribute to the research and development of a high separation performance membrane as well as the improvement of PV separation efficiency. In general, the transport of small molecules through polymer membrane is explained by a solution–diffusion mechanism, which divided into three consecutive stages: sorption–diffusion–desorption [19,20]. According to the mechanism, the whole separation effect is based on the selective sorption and diffusion [21]. Therefore, it can obtain the

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Nomenclature

A	effective membrane area (m^2)
C_F	total sulfur content of feed sample (μg/g)
C_P	total sulfur content of permeate sample (μg/g)
D	diffusion coefficient (m^2/s)
E	sulfur enrichment factor
J	total flux (kg/(m^2 h))
L	initial thickness of membrane (m)
M_t	solvent mass sorbed at time t (g)
M_∞	solvent mass sorbed at equilibrium (g)
m_0	mass of dry membrane sample (g)
m_1	mass of wet membrane at equilibrium (g)
M_c	molecular weight between crosslinks (g/mol)
P	permeability (m^2/s)
Q	amount permeated (kg)
S	sorption coefficient (g/g)
t	PV experimental time interval (h)
Greek letter	
γ	crosslink density (mol/g)

transport mechanism of gasoline components into polymer membranes and further judge the separation potential of a membrane towards a gasoline mixture just rely on the sorption and diffusion behaviors. In the other separated system, it has been extensively used to study the transport mechanism and separation capability of PV membrane by the sorption and diffusion behaviors.

Some investigators determined the dynamic sorption curves of water, ethanol, chloroform, acetic acid and the organic–water mixtures into different polymer membranes. By the dynamic sorption curves determined, they successfully predicted the separation potential of various polymer towards these water–organic mixtures [22–26]. The sorption of different substituted benzene into a series of natural rubber blends membranes was studied [27–29]. The study results showed that transport properties were greatly influenced by the nature of interacting solvent molecule, the structural variation of polymer blends and temperature. In the meantime, the increasing concerns were focused on the transport process in crosslinked membrane [28–30]. Wang described that the dynamic sorption and desorption behaviors of benzene, cyclohexane and *n*-hexane in crosslinked poly(ethylene oxide imide) segmented copolymer membrane were Fickian diffusion [31]. The impacts of crosslink type and crosslink density on the swelling behavior of styrene–butadiene rubber membranes in alkanes were detailed investigated by George et al. [32]. They stated that crosslink density significantly affects the maximum solvent uptake rather than crosslink type. Park et al. [33] investigated the effect of the crosslinked chain length in sulfonated polyimide membranes on water sorption, proton conduction and methanol permeation properties. They found these parameters decreased with the increasing crosslink density. In our previous work, the temperature dependence of sorption behaviors of gasoline components in PEG membrane was investigated, but the sorption data about the impact of crosslink density on the transport behaviors were still insufficient [34]. The previous researches [32,33] had presented that crosslink density greatly influenced the sorption and transport of small molecule in polymer membrane. Therefore, the effect of crosslink density on mass transfer mechanism of gasoline components through the membranes must be further studied in detail.

In this paper, the impact of crosslink density on the desulfurization mechanism of hydroxyethyl cellulose (HEC) membrane was studied and further analyzed in theory. The effect of crosslinker content on PV performance of HEC membrane was investigated and the gas chromatography (GC) of feed and permeate samples of real gasoline was analyzed, too. The mass-transfer mechanism determined was verified by PV experiments and GC analysis results.

2. Experimental

2.1. Materials

In real gasoline, the typical hydrocarbon functional groups are alkanes, cycloalkanes, aromatics and alkenes, and the primary sulfur compounds are thiophene species (about 80%) [18,34]. Real gasoline is a complex mixture and it is difficult to carry out detailed investigations for all gasoline components. Therefore, typical gasoline components, including thiophene, *n*-heptane, cyclohexane, cyclohexene and toluene, were selected as model compounds (organic solvents). All chemicals used were of analytical reagent (A.R.) grade from Tianjin Chemical Reagent Factory and used without further purification. HEC, 1,6-hexanediol diacrylate (HDDA) and benzoyl peroxide (BPO) were all purchased from the Shanghai Reagent Factory. The model gasoline was composed of *n*-heptane and thiophene, and the sulfur content was about 1200 μg/g by adjusting the content of thiophene. Real gasoline feed was obtained from Shenghua Refinery (China) and the gasoline was cleaned by alkali to remove most of thiols.

2.2. Membrane preparation

The technology of membrane preparation divided into four stages, i.e. dissolving polymer, degassing, coating and post treating. The detailed process was described as follows. The polymer HEC, crosslinker HDDA and initiator BPO were dissolved in N,N-dimethylformamide to form a homogenous solution of 15 wt.% polymer at room temperature. To investigate the effect of crosslinking on sorption and diffusion behaviors besides PV performance, the HEC membranes with different content of crosslinker were prepared. After degassing under vacuum, the solution was cast onto the glass plate with a scraper. The cast film was placed in an oven at 363 K for some time to crosslink and to evaporate the solvent, and then the membrane was dried at the room temperature in vacuum drying oven for at least 24 h. All membrane samples were stored in dust-free and dry environment before used in the sorption and PV experiments.

2.3. FTIR characterization

The membrane structure was analyzed based on Fourier transform infrared (FTIR) spectra determined by a Nicolet-8700. 32 scans were taken with 4 cm^{-1} resolution. FTIR spectra were recorded within the range of 4000–400 cm^{-1}.

2.4. Sorption experiments

The process of sorption experiment included preparing membrane samples, drying in vacuum drying oven, weighing the mass of dry membrane, immersing in solvent and weighing the mass of wet membrane. Pieces of vacuumed-dried HEC membranes with 5.1 cm diameter were cut. Thickness measurements were made at several points with an accuracy of ±0.0001 cm using a micrometer screw gauge. The samples were weighed using a highly sensitive electronic balance (Mettler, Shanghai, China) with an accuracy of 0.0001 g. The membrane piece was put in a bottle full of solvent to measure single component liquid sorption. After taken from the sealed bottle at certain interval (0.1–10 min), the membrane sample was gently blotted to wipe off the surface liquid and weighed immediately, then replaced in the bottle. This experiment was done as quickly as possible to improve the accuracy. The samples were weighed until the mass of membrane was constant (i.e., sorption equilibrium). The sorption experiments were performed at 298.15 K. The data in this paper are the average values of four to five measurements.

The initial sorption curves were linear. The diffusion coefficient, D, of model compounds (gasoline components) in membrane can be estimated [30,35].

$$\frac{M_t}{M_\infty} = 4\left[\frac{Dt}{\pi L^2}\right]^{0.5} \tag{1}$$

Here, M_t and M_∞ refer to the solvent mass sorbed at time t and at equilibrium, respectively. L is initial thickness of membrane.

The weight gained during sorption, i.e. sorption coefficient (S), is defined as

$$S = \frac{m_1 - m_0}{m_0} \tag{2}$$

where m_0 is the mass of dry membrane sample, and m_1 is the mass of wet membrane at equilibrium.

Hence, the permeability

$$P = D \times S \tag{3}$$

2.5. *PV experiments*

The PV apparatus and experiments followed our previous published introduction [17,18]. The test temperature was 85 °C and 105 °C for model gasoline and real gasoline, respectively. The total flux was determined gravimetrically with an experimental error of 1–2%. The total flux (J) was obtained by

$$J = \frac{Q}{At} \tag{4}$$

Here, Q is the total amount permeated through the effective membrane area (A) during the experimental time interval (t) at steady state.

The sulfur enrichment factor, E, is defined as

$$E = \frac{C_P}{C_F} \tag{5}$$

where C_F and C_P are the total sulfur content of feed and permeate samples, respectively. The total sulfur level was determined by Micro-Coulometric Analysis Instrument. The sulfur enrichment factor for model gasoline feed and real gasoline feed means E of thiophene and E of all sulfur species, respectively.

Hydrocarbon composition analysis of real gasoline was carried out by Varian3800 gas chromatography (GC) equipped with CB-8 quartz capillary column and pulsed flame photometric detector (PFPD).

3. Results and discussion

3.1. *FTIR characterization*

The spectrum of pure HEC shows two sharp peaks at wave numbers 3473 and 1105 cm^{-1}, indicating the presence of hydroxyl group and ether group (characteristic group of HEC). In the spectrum of the crosslinked HEC membrane, the appearance of a new absorbance peak at 1749 cm^{-1} is due to the formation of saturated aliphatic carbonyl group (Fig. 1). This meant that a crosslinking reaction occurred between HDDA and HEC.

3.2. *Effect of crosslink density on transport behaviors of typical gasoline components*

The crosslink densities of the HEC membranes were calculated according to Flory–Rehner relation [28,36] using the maximum solvent uptake values measured in thiophene. The calculated crosslink density (γ) and molecular weight between crosslinks (M_c) are given in Table 1. The effect of crosslink density on sorption and transport behaviors of gasoline components was investigated.

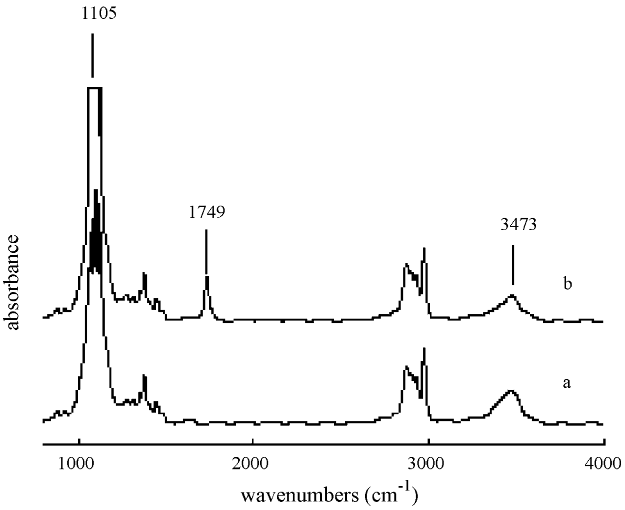

Fig. 1. FTIR spectrums of pure and crosslinked HEC membranes (a: pure HEC membrane; b: crosslinked HEC membrane).

Table 1
The calculated results of crosslink density (γ) (298.15 K, solvent: thiophene).

Membrane no.	Mass ratio of crosslinker and HEC	M_c (g/mol)	γ ($\times 10^4$ mol/g)
0#	0.00	–	0.0
1#	0.13	533	9.4
2#	0.20	330	15.2
3#	0.60	171	29.3
4#	1.00	168	29.8

3.2.1. *Effect of crosslink density on sorption kinetics*

During sorption experiments, it is found that the swelling degree (S) of unmodified HEC membrane in thiophene and toluene is infinite; meaning that the above species can dissolve the unmodified HEC membrane. Therefore, the sorption curves of thiophene and toluene into unmodified HEC membrane cannot be obtained.

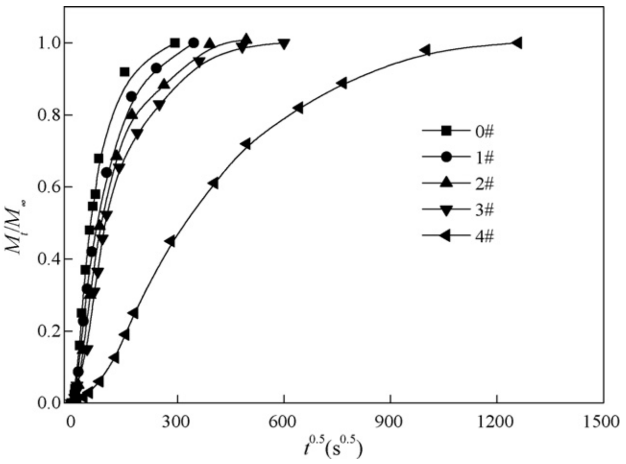

Fig. 2. Fitting curves of dynamic sorption for n-heptane in the HEC membranes with different crosslink density (0#: γ = 0.0 mol/g, 1#: $\gamma = 9.4 \times 10^{-4}$ mol/g, 2#: $\gamma = 15.2 \times 10^{-4}$ mol/g, 3#: $\gamma = 29.3 \times 10^{-4}$ mol/g, 4#: $\gamma = 29.8 \times 10^{-4}$ mol/g; time of reaching sorption equilibrium: 292^2, 345^2, 493^2, 600^2, 1260^2).

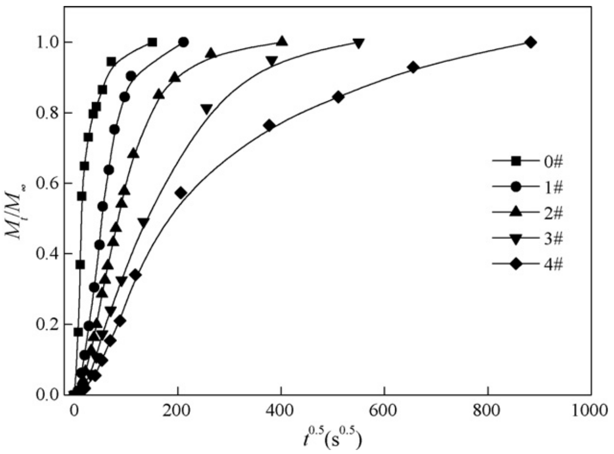

Fig. 3. Fitting curves of dynamic sorption for cyclohexane in the HEC membranes with different crosslink density (0#: $\gamma = 0.0$ mol/g, 1#: $\gamma = 9.4 \times 10^{-4}$ mol/g, 2#: $\gamma = 15.2 \times 10^{-4}$ mol/g, 3#: $\gamma = 29.3 \times 10^{-4}$ mol/g, 4#: $\gamma = 29.8 \times 10^{-4}$ mol/g; time of reaching sorption equilibrium: 150^2, 221^2, 401^2, 550^2, 883^2).

Fig. 2 presents the effect of crosslink density on dynamic sorption curves of *n*-heptane. The sorption equilibrium for *n*-heptane reaches first in membrane 0# whereas it reaches last in membrane 4#, and the time to reach equilibrium gradually increases with the increasing crosslink degree. The same results are seen from the dynamic sorption curves of cyclohexane, cyclohexene, toluene and thiophene in the HEC membranes with different crosslink density as well (Figs. 3–6). All of these results indicated that the increasing crosslinking density reduced the sorption and diffusion rates of solvent in HEC membrane and further hindered the membrane swelling. By the comparison of Figs. 2–6, it is seen that the time order of the typical gasoline components reaching sorption equilibrium is thiophene > toluene > cyclohexene > cyclohexane > *n*-heptane. Obviously, HEC membranes reached sorption equilibrium in thiophene quicker than in the other types of hydrocarbon components, meaning that thiophene showed strong preferential sorption and diffusion properties into HEC membrane. The preferential sorption and diffusion led to the excellent selectivity of HEC membrane for thiophene species, fulfilling the separation of thiophene/hydrocarbon mixture.

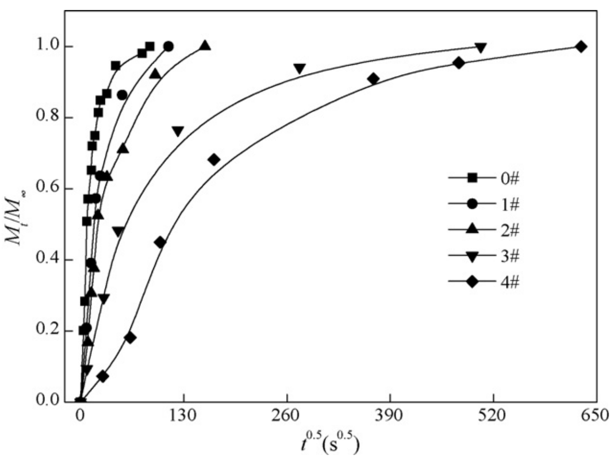

Fig. 4. Fitting curves of dynamic sorption for cyclohexene in the HEC membranes with different crosslink density (0#: $\gamma = 0.0$ mol/g, 1#: $\gamma = 9.4 \times 10^{-4}$ mol/g, 2#: $\gamma = 15.2 \times 10^{-4}$ mol/g, 3#: $\gamma = 29.3 \times 10^{-4}$ mol/g, 4#: $\gamma = 29.8 \times 10^{-4}$ mol/g; time of reaching sorption equilibrium: 87^2, 110^2, 156^2, 503^2,630^2).

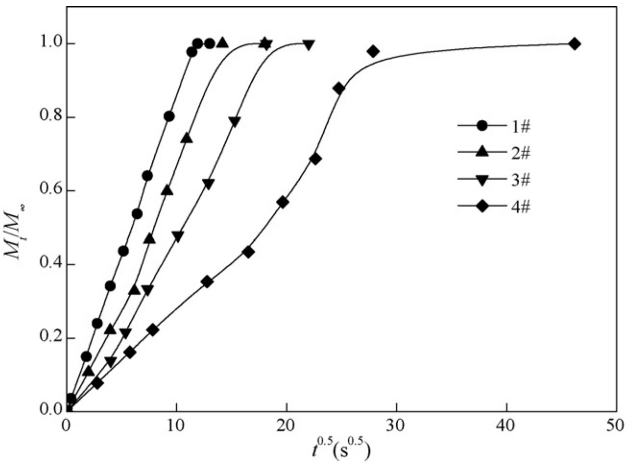

Fig. 5. Fitting curves of dynamic sorption for toluene in the HEC membranes with different crosslink density (1#: $\gamma = 9.4 \times 10^{-4}$ mol/g, 2#: $\gamma = 15.2 \times 10^{-4}$ mol/g, 3#: $\gamma = 29.3 \times 10^{-4}$ mol/g, 4#: $\gamma = 29.8 \times 10^{-4}$ mol/g; time of reaching sorption equilibrium: 19^2, 50^2, 71^2, 176^2).

The transport mechanism of gasoline components in HEC membranes can be analyzed using the formula.

$$\log\left(\frac{M_t}{M_\infty}\right) = K + n \log t \tag{6}$$

The constant *K*, depends on the structural characteristics of the polymer and offers information about interaction of polymer and solvent. The value of *n* indicates the transport mode. The Fickian diffusion is characterized as $n = 0.5$, and non-Fickian or anomalous diffusion by *n* varying between 0.5 and 1 [26–29,32,34,35]. The values of *n* and *K* were obtained by regression analysis of $\log(M_t/M_\infty)$ versus $\log t$ plot using the initial linear sorption data, i.e. before the attainment of 50% equilibrium solvent uptake. The optimized values of *n* and *K* for the sorption processes are summarized in Table 2. The regression coefficients (R^2) are close to 1 and the goodness of fit is very good, meaning the values of *n* can be used for the analysis of transport mechanism. The values of correlated parameter *n* for the typical gasoline components *n*-heptane and cyclohexane calculated are 0.74–0.98, for thiophene, toluene and cyclohexene 0.43–0.53. Evidently, the diffusion mode of typical gasoline components *n*-heptane and cyclohexane in HEC membranes tended to be non-Fickian. This resulted from that the solubility of *n*-heptane

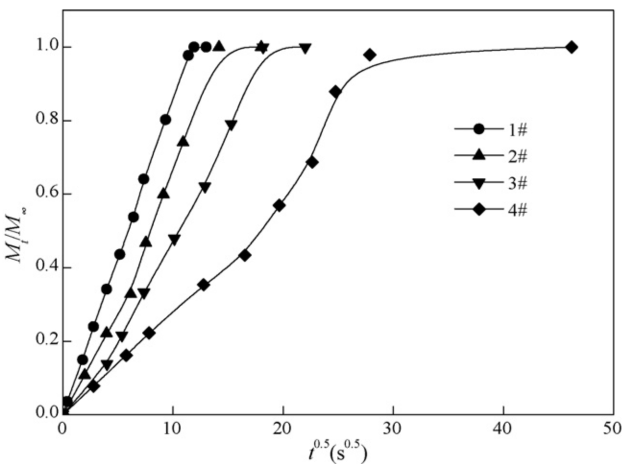

Fig. 6. Fitting curves of dynamic sorption for thiophene in the HEC membranes with different crosslink density (1#: $\gamma = 9.4 \times 10^{-4}$ mol/g, 2#: $\gamma = 15.2 \times 10^{-4}$ mol/g, 3#: $\gamma = 29.3 \times 10^{-4}$ mol/g, 4#: $\gamma = 29.8 \times 10^{-4}$ mol/g; time of reaching sorption equilibrium: 12^2, 14^2, 18^2, 46^2).

Table 2
Parameters *n* and *K* for crosslinked HEC membrane obtained from sorption curves.

Gasoline components	Membrane no.	n	K ($\times 10^4$ g/g s^n)	R^2
n-Heptane	0#	0.74	14.60	0.99
	1#	0.91	3.45	0.99
	2#	0.90	2.52	0.99
	3#	0.75	2.15	0.99
	4#	0.74	0.99	0.99
Cyclohexane	0#	0.94	38.50	1.00
	1#	0.98	3.44	0.99
	2#	0.95	2.68	0.99
	3#	0.93	1.85	0.99
	4#	0.89	0.95	0.99
Cyclohexene	0#	0.47	612.60	0.98
	1#	0.48	328.00	0.98
	2#	0.43	295.30	1.00
	3#	0.46	95.80	1.00
	4#	0.50	19.70	0.96
Toluene	0#	–	–	–
	1#	0.49	737.30	1.00
	2#	0.47	298.70	0.99
	3#	0.49	204.30	0.99
	4#	0.50	111.90	0.99
Thiophene	0#	–	–	–
	1#	0.47	952.20	1.00
	2#	0.50	590.00	1.00
	3#	0.53	421.40	0.96
	4#	0.51	350.39	1.00

and cyclohexane in membrane was very poor and the chain relaxation of HEC was slow. For thiophene, toluene and cyclohexene, *n* values are close to 0.5, and their diffusion kinetic in HEC membranes is typical Fickian. The above result attributed to thiophene, toluene and cyclohexene had stronger affinity with polymer HEC, and uptake velocity in membrane was quicker. As preferential sorption component, thiophene has higher *K* values than other gasoline components, meaning stronger HEC–thiophene molecule interaction.

According to the comparison of the *n* values between typical gasoline components in different HEC membranes, it is seen that the *n* values for *n*-heptane and cyclohexane are always between 0.74 and 0.98 and for thiophene, toluene and cyclohexene 0.43–0.53. The *n* values of every component did not change substantially with the increasing crosslink density. This indicated the little effect of crosslink degree on the transport mode of gasoline components in HEC membranes. However, the significant effect of crosslink degree on *K* values was observed. From Table 2, *K* values greatly decrease for all gasoline components probe molecule systems, indicating that the HEC–probe molecule interactions decrease with the increasing crosslink density. The reason was that increasing crosslink density limited the swelling of membrane samples. Although *K* value decreased, *K* ratio of thiophene and other hydrocarbons increased. The increase of *K* ratio made possible an increase in selectivity of HEC membranes for sulfur-bearing.

3.2.2. Effect of crosslink density on diffusion, sorption and permeation coefficients

Diffusion coefficient (D), sorption coefficient (S) and permeation coefficient (P) can more directly reflect the effect of crosslink density on transport mechanism and the mass transfer rate difference between small molecules in the membrane. Table 3 shows S, D and P values of typical gasoline components in the HEC membranes with different crosslink degree. The sorption coefficients of typical gasoline components greatly decrease with the increasing crosslink degree, especially for thiophene and toluene. When the crosslink densities of HEC membranes increase from 0 to 2.980×10^{-3} mol/g, the swelling degrees of thiophene and toluene decrease from infinite to 0.238 and 0.151, respectively. Evidently, this supported the viewpoint that crosslinking modification of HEC improved the solvent resistant performance and lengthened the application life of HEC membranes.

It is obvious that the diffusion and permeation coefficients of gasoline components also decrease severely with the increasing crosslink density (Table 3), implying a decrease in permeation flux. Crosslinking affected the structure of HEC membrane since the chemical crosslinking occurred among polymer-molecules. The reticular spatial structure formed due to the addition of crosslinker. And then the mobility of macromolecular chain segment weakened

Table 3
D, *S* and *P* for typical gasoline components in crosslinked HEC membranes.

Gasoline components	Membrane no.	D ($\times 10^{14}$ m^2/s)	S ($\times 10$ g/g)	P ($\times 10^{15}$ m^2/s)
n-Heptane	0#	1.67	3.97	6.63
	1#	0.39	1.32	0.51
	2#	0.23	1.21	0.28
	3#	0.16	0.91	0.15
	4#	0.04	0.39	0.02
Cyclohexane	0#	49.90	15.35	765.97
	1#	5.57	2.17	12.09
	2#	0.95	1.37	1.30
	3#	0.27	1.01	0.27
	4#	0.07	0.43	0.03
Cyclohexene	0#	291.79	22.59	6591.54
	1#	31.86	3.66	116.61
	2#	23.97	1.98	47.46
	3#	2.40	1.57	3.77
	4#	0.55	0.91	0.50
Toluene	0#	–	∞	–
	1#	368.73	4.70	1733.03
	2#	21.97	3.39	74.48
	3#	16.26	1.35	21.95
	4#	12.56	1.21	15.20
Thiophene	0#	–	∞	–
	1#	388.98	8.55	3325.78
	2#	173.75	6.98	1212.78
	3#	142.00	3.12	443.04
	4#	102.06	2.38	242.90

Table 4
GC results for sulfur species distribution in feed and permeate samples.

Sulfur species	Feed sample (μg/g)	Permeate sample (μg/g)	Enrichment factor
Thiol	52.16	34.43	0.66
Sulfide	100.01	42.00	0.42
Disulfide	7.24	6.75	0.51
Thiophene	114.37	646.19	5.65
2-Methyl thiophene	150.44	278.31	1.85
3-Methyl thiophene	218.81	632.36	2.89
Dimethyl thiophene	304.78	947.87	3.11
Isopropyl thiophene	12.53	45.61	3.64
Trimethyl thiophene	103.14	313.55	3.04
C4 thiophene	10.91	14.51	1.33

leading to a decrease in the free volume, and this was very unfavorable for the diffusion and permeation of small solvent molecules through polymer networks. However, the permeation coefficient ratio of sulfur species and hydrocarbon species increased with the increasing crosslink density, indicating an increase in sulfur enrichment. The same as *K* values, the *D* and *S* values for thiophene are highest whereas those of *n*-heptane are lowest. But *S* and *D* values more intuitively showed the desulfurization mechanism and transport mechanism through the HEC membrane. That was to say, thiophene species were preferential permeation components, and the difference of sorption rate as well as diffusion rate between hydrocarbon and sulfur components resulted in the removal of sulfur-bearing compounds from gasoline through the HEC membrane. Moreover, *S* and *D* gave the effect of crosslinking on the transport and desulfurization mechanism, i.e. the sorption and diffusion rates of gasoline components decreased with increasing crosslink density but the permeate ratio between thiophene and hydrocarbon species increased to make the preferential selectivity of HEC membrane for sulfur-bearing compounds increase. As a result, flux decreased but enrichment factor increased with increasing crosslink density.

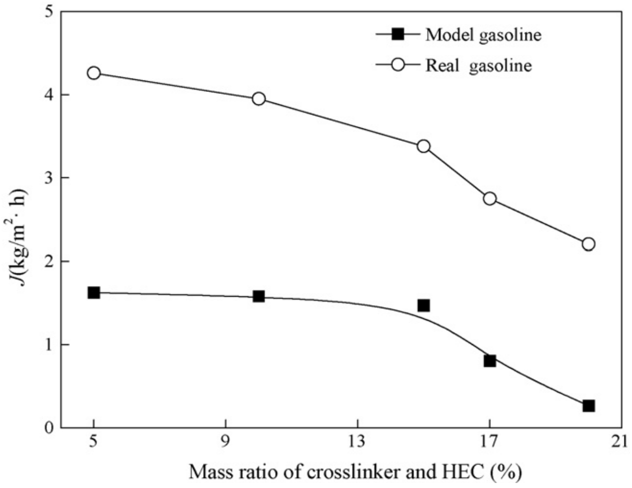

Fig. 7. Effect of content of crosslinker on permeation flux.

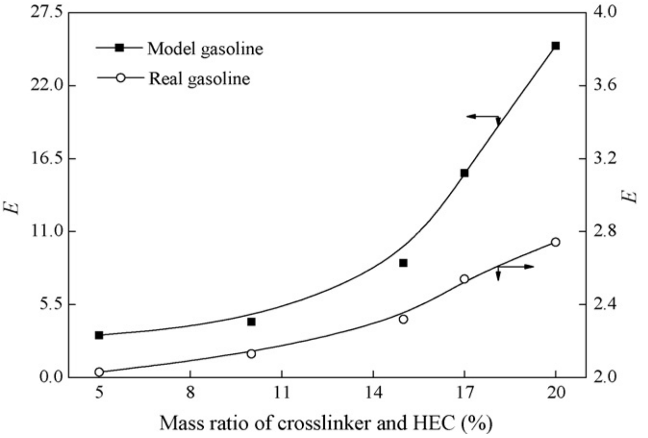

Fig. 8. Effect of content of crosslinker on sulfur enrichment factor.

3.3. Comparison on sorption and PV experiments results

In order to verify the desulfurization and transport mechanism obtained from the above theory analysis, PV experiment of HEC membranes with different crosslinker content was done. Since the exorbitant addition of crosslinker caused lower flux and poor membrane mechanical intensity, the content of crosslinker was no more than 20% in the PV experiment.

As predicted, permeation flux decreases and sulfur enrichment factor increases with the increasing content of crosslinker (Figs. 7 and 8). As crosslinker content increased, crosslink density increased as well. Hereby, the diffusion rate and maximum uptake of gasoline components in HEC membranes both decreased, so did permeation flux. Because the sorption rate and diffusion rate of thiophene species were higher than other hydrocarbon components through any membranes, sulfur enrichment factor still increased when sulfur and hydrocarbon species flux both decreased.

It is also found from Fig. 8 that the sulfur content for real gasoline is enriched about threefold by the HEC membrane (mass ratio of crosslinker and HEC 0.20:1). The distribution of sulfur and hydrocarbon functional group of the feed and permeate samples is analyzed, and the analysis results is presented in Tables 4 and 5. Comparison of Tables 4 and 5, concentration level of sulfur species (mainly thiophene species) is higher than other hydrocarbon compounds, demonstrating that thiophene species are preferential permeate components. Secondly,

Table 5
GC hydrocarbon functional group analysis of feed and permeate samples for real gasoline.

Hydrocarbon functional groups	Feed sample (wt.%)	Permeate sample (wt.%)	Enrichment factor
Aromatics	14.83	28.13	1.89
Alkenes	42.56	37.61	0.88
Alkanes	35.62	25.86	0.72
Cycloalkanes	7.00	6.27	0.89

Table 5 shows that part of aromatics can be removed at the same time of desulfurization by HEC membrane. This partly attributed to the similar aromaticity and solubility parameter between aromatics and thiophene species. To sum up, the PV experimental results and GC experimental results corresponded to the desulfurization mechanism concluded on the dynamic sorption curves.

4. Conclusions

The transport and desulfurization mechanism through the HEC membrane was obtained by investigating the dynamic sorption behaviors of typical gasoline components. The diffusion mode of *n*-heptane and cyclohexane in the HEC membranes tended to non-Fickian; but thiophene, toluene and cyclohexene had stronger affinity with polymer HEC and their diffusion kinetic was typical Fickian. By analyzing the dynamic sorption curves of typical gasoline components permeating the membranes with different crosslinking degree, it was found that the transport mode of these gasoline components did not change essentially with the increasing crosslink density. However, the interaction between HEC–gasoline components (*K* values) remarkably decreased with the increasing crosslinking density.

The same as *K* values, the sorption and diffusion coefficients obviously decreased with the increasing crosslinking density, too. The increasing crosslink density apparently reduced the sorption and diffusion rates of gasoline components into the membranes, while heightened the difference of solubility/diffusion between thiophene/hydrocarbon components. This predicted that permeation flux decreased but sulfur enrichment factor increased with the increasing crosslink density. Moreover, according to dynamic sorption curves of typical gasoline components, thiophene species showed higher sorption and diffusion rates in HEC membranes than other hydrocarbon compounds and were preferential permeation components.

To verify the transport mechanism and desulfurization mechanism obtained through the above theory analysis, PV experiments and GC experiments were conducted. The changing trend of permeation flux and sulfur enrichment factor corresponded to the above theory analysis results, and the removal trend of HEC membrane for gasoline components also agreed with the theory analysis results. All these investigations will provide helpful suggestions for the newly emerged membrane desulfurization technology and complex organic mixture separation by PV.

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