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Preliminary Exploration of Polyvinyl Alcohol/Ionic Liquids Hybrid Membrane in Desulfurization of Model Gasoline

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Recently, the exploration of using ionic liquid in gasoline desulfurization has attracted extensive attentions^[1-5]. Directly using ionic liquid as an extractant for liquid/liquid extraction^[1-3] or as solvent for the oxidative desulfurization of model oil, commercial diesel and light oils, etc, were reported and perfect results were obtained^[4,6]. In order to make the operation more practically usable, herein, we present our new attempt to prepare a Polyvinyl alcohol (PVA) supported ionic liquid membrane and its possibility to be used in gasoline desulfurization.

The PVA supported ionic liquid membrane was prepared as following procedure. Firstly, suitable amount of PVA powder (87-89% hydrolyzed; M_w : 85000-124000; Aldrich Chemical Co.) and ionic liquid^[7] were dissolved in deionized water and stirred for 4 h at 80 °C. Then the homogeneous solution was poured onto a stainless steel plate and the solvent was evaporated at room temperature in air for 12 hours. So a PVA supported ionic liquid membrane with around 25 μm thickness (by SEM analysis) was achieved. All the membranes with or without ionic liquid were characterized by FT-IR (Nicolet Nodule 5700), DSC (Mettler Toledo 822) and SEM (JSM-5600LV).

The typical FT-IR spectra of PVA membrane, pure ionic liquid and PVA supported [EMIm][BF₄] ionic liquid membrane were shown in Fig. 1. Although

the FT-IR spectra of PVA itself and ionic liquid were

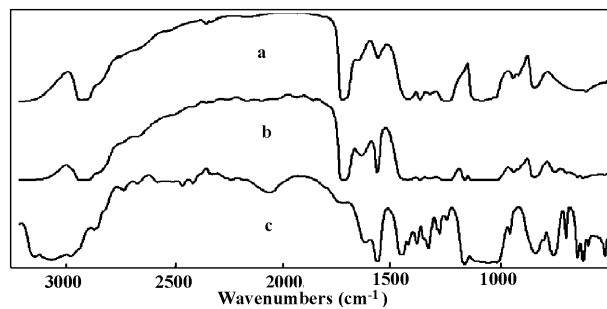


Fig. 1 FT-IR spectra of PVA membrane (a), PVA supported 30wt% [EMIm][BF₄] (b) and (c) pure [EMIm][BF₄]

overlapped with each other, the characteristic peaks of ionic liquid [EMIm][BF₄] at 1573 cm^{-1} and 1171 cm^{-1} were still observable after immobilization. Therefore, it was clear that the ionic liquid was successfully immobilized on/in the PVA membrane. The SEM photographs of different membranes were shown in Fig. 2,

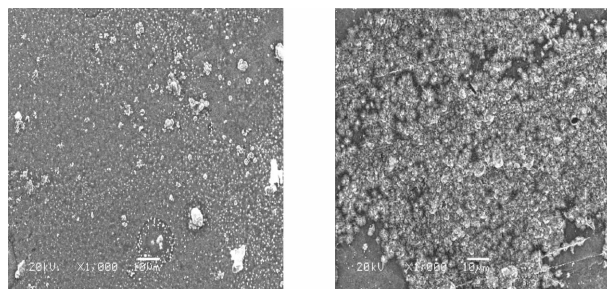


Fig. 2 SEM pictures of PVA membrane (left) and 30% [EMIm][BF₄]/PVA (right, 20 kV, 1 000)

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and the thickness of the membranes was determined to be about 25 nm. The morphology of the pure PVA membrane is relatively flat and uniform but the PVA supported ionic liquid membrane was very coarse and porous. Results of DSC measurement of pure PVA membrane, PVA supported ionic liquid membrane and pure ionic liquids were given in Table 1. It could be found that for PVA supported ionic liquid membrane the T_g , T_{cc} and T_m were all unobservable between -100 °C and 150 °C. The reason might be that the PVA and ionic liquid were well mixed with each other and therefore they lost their own specific properties.

Table 1 Melting (T_m), cold crystallization (T_{cc}) and glass-transition (T_g) temperatures for PVA/ionic liquids hybrid membranes^a

compound	$T_g/^\circ\text{C}$	$T_{cc}/^\circ\text{C}$	$T_m/^\circ\text{C}$
PVA membrane	85	---	---
[EMIm][BF ₄]	-87.87	-16.73	-3.95
30% [EMIm][BF ₄]/PVA	---	---	---
[BMIm][BF ₄]	-86.94	---	---
30% [BMIm][BF ₄]/PVA	---	---	---

^a [EMIm] = 1-ethyl-3-methyl imidazolium; [BMIm] = 1-butyl-3-methyl imidazolium.

The treatment of the model gasoline was illustrated in Fig. 3. The effective area of the membrane was $2.78 \times 10^{-3} \text{ m}^2$. About 10 ml of n-octane/thiophene mixture was added into the feed compartment and vacuum treated ($\sim 133 \text{ Pa}$) under stirring for 5 hours. The materials that passed the membrane were collected with liquid nitrogen cooling trap and further analyzed by

GC-FID. Model gasolines of different thiophene concentrations were firstly tested with 30% [EMIm][BF₄]/PVA membrane, Table 2. The corresponding thiophene mass fractions in the feed were varied between 7.33×10^{-4} and 0.497 g/g . It was clear that the variation of thiophene concentration has great influence on the flux of thiophene itself and n-octane. As imagined, the flux of thiophene increased with the increasing of the thiophene concentration but the selectivity decreased. For the flux of n-octane, it decreased at the same time. As to the stability testing of the membrane, it was reused over sample with thiophene concentration $13.3 \times 10^{-4} \text{ g/g}$. However, the final concentration of thiophene increased to $4.95 \times 10^{-4} \text{ g/g}$ from $3.15 \times 10^{-4} \text{ g/g}$ in the second run. Hence the preparation method should be further improved in order to get applicable membrane.

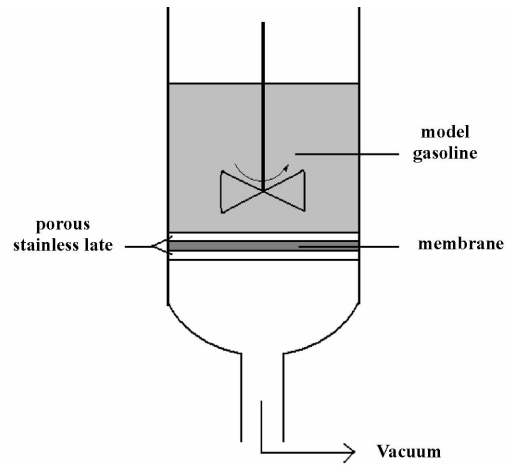


Fig. 3 An illustration for the treatment of thiophene containing model gasoline

Table 2 The treatment of model gasolines contain different amount of thiophene with 30% [EMIm][BF ₄]/PVA membrane ^a					
Original concentration (g/g)	$J_{\text{n-octane}}$ (g/m ² h)	$J_{\text{thiophene}}$ (g/m ² h)	$J_{\text{n-octane + thiophene}}$ (g/m ² h)	Sele. (%) ^b	Final concentration (g/g)
7.33×10^{-4}	90.4	0.2	90.6	10	$2.59 \text{ E} - 4$
13.3×10^{-4}	58.5	0.5	59.0	26	$3.15 \text{ E} - 4$
13.3×10^{-4}	29.1	0.4	29.5	15	$4.95 \text{ E} - 4^c$
29.3×10^{-4}	67.8	1.0	68.8	20	$7.61 \text{ E} - 4$
0.302	24.3	25.2	49.5	3.1	0.250
0.410	31.2	23.1	54.3	4.7	0.315
0.497	20.2	56.3	76.5	4.7	0.435

^a the model gasoline was prepared with n-octane and thiophene; $J = Q/At(\text{g/m}^2 \text{ h})$, J is the flux ($\text{g/m}^2 \text{ h}$), Q is the total amount of mixtures that passed the membrane during the experimental time interval, t , at steady state and A is the effective membrane area. ^bselectivity $\alpha_{\text{thiophene/n-octane}} = (y_{\text{thiophene}}/y_{\text{n-octane}})/(x_{\text{thiophene}}/x_{\text{n-octane}})$, $x_{\text{thiophene}}$, $y_{\text{thiophene}}$, $x_{\text{n-octane}}$ and $y_{\text{n-octane}}$ are the weight fractions of thiophene and n-octane in the feed and in the permeated liquid mixture. ^c The membrane was reused for the second time.

In consideration of the flux and selectivity to thiophene together, it indicated that our membrane system is more suitable for low concentration thiophene gasoline treatment. Therefore, we further test the function of several readily available ionic liquids supported in/on PVA membrane using 200 ppm thiophene model gasoline. As it was shown in Table 3, [BMIm][H₂PO₄], [BMIm][N(CN)₂] and [C₂OHMIm][BF₄] exhibited relatively good selectivity to thiophene. The concentration could be reduced to ~ 120 ppm. If use PVA supported [C₃

CNMIm][BF₄], [BPy][BF₄], [BMIm][NO₃] and [C₃CNmmorpholine][NTf₂] membranes, the final concentration of thiophene was still maintained at 170-180 ppm. The reason for this difference was still unclear at this stage. Elemental analysis of PVA supported [BMIm][NO₃] membrane showed that the nitrogen contents in the membrane were 5.8% and 6.0% before and after using. Therefore the ionic liquid could be immobilized inside the membrane effectively.

Table 3 Results of model gasoline treatment with different ionic liquid/PVA membranes^a

Membranes	Original concentration (g/g)	J n-octane (g/m ² h)	J thiophene (g/m ² h)	Sele. (%) ^a	Final concentration (g/g)
30% [BMIm][H ₂ PO ₄]/PVA	200 ppm	56.8	0.09	12	123 ppm
30% [BMIm][N(CN) ₂]/PVA	200 ppm	53.6	0.08	12	127 ppm
30% [C ₂ OHMIm][BF ₄]/PVA	200 ppm	71.2	0.07	7.7	133 ppm
30% [C ₂ OHMIm][NO ₃]/PVA	200 ppm	42.8	0.05	8.5	150 ppm
30% [C ₃ CNMIm][BF ₄]/PVA	200 ppm	45.1	0.03	3.3	181 ppm
30% [BPy][BF ₄]/PVA	207 ppm	16.2	0.006	2.0	176 ppm
30% [BMIm][NO ₃]/PVA	200 ppm	94.2	0.04	2.4	175 ppm
30% [C ₃ CNmmorpholine][NTf ₂]/PVA	200 ppm	47.56	0.04	4.40	172 ppm

^a the same condition as used in Table 2. [C₂OHMIm] = 1-hydroxyethyl-3-methyl imidazolium; [C₃CNMIm] = 1-Butyronitrile-3-methyl imidazolium; [Bpy] = N-butyl pyridinium; [C₃CNmmorpholine] = 1-Butyronitrile-3-methyl morpholine.

In conclusion, the desulfurization of model gasoline containing thiophene with ionic liquid modified PVA membrane was investigated. The preliminary results showed that the ionic liquid modified PVA membrane was suitable for the treatment of low thiophene concentration gasoline. The further improvement and the detailed characterization of the membrane system are undergoing.

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聚乙烯醇担载离子液体薄膜的制备、表征及其
模拟汽油脱硫性能的初步研究

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摘 要: 本文合成了一系列聚乙烯醇担载离子液体薄膜, 并进行了 FT-IR, SEM 以及 DSC 表征. 通过对模拟汽油脱硫性能的初步研究发现, 这一类薄膜对于较低硫含量的体系具有较好的脱硫性能.

关键词: 聚乙烯醇膜; 离子液体; 担载; 噻吩; 脱硫

《分子催化》2006 年影响因子在国内化学类期刊中的排名

No.	期刊名称	影响因子	总被引频次	No.	期刊名称	影响因子	总被引频次
1	燃料化学学报	1.106	871(16)	18	化学通报	0.557	1129(13)
2	化学进展	0.978	737(17)	19	应用化学	0.520	1454(7)
3	催化学报	0.977	1462(6)	20	分析科学学报	0.517	669(19)
4	化学学报	0.968	2510(3)	21	结构化学	0.508	557(20)
5	分析化学	0.960	3423(2)	22	感光科学与光化学	0.503	281(29)
6	物理化学学报	0.957	1587(5)	23	高分子通报	0.469	516(21)
7	分子科学学报	0.925	251(30)	24	分子催化	0.408	457(24)
8	高分子学报	0.865	1452(8)	25	电化学	0.373	332(27)
9	无机化学学报	0.851	1597(4)	26	合成化学	0.366	414(26)
10	高等学校化学学报	0.785	4192(1)	27	化学研究与应用	0.340	685(18)
11	有机化学	0.715	1175(10)	28	化学研究	0.329	190(32)
12	分析测试学报	0.712	979(15)	29	化学试剂	0.287	498(22)
13	中国科学 B 辑	0.705	1276(9)	30	<i>Chin J Polym Sci</i>	0.263	149(34)
14	分析试验室	0.698	1113(14)	31	<i>Chem Res Chin Univ</i>	0.250	179(33)
15	环境化学	0.692	1173(11)	32	化学与粘合	0.242	315(28)
16	煤炭转化	0.614	469(23)	33	化学与生物工程	0.206	223(31)
17	色谱	0.608	1130(12)	34	<i>Chin Chem Lett</i>	0.151	448(25)

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