Interfacial Properties of Ethyl Cellulose/Cellulose Acetate Blends by HPLC

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Abstract: The high performance liquid chromatography method (HPLC) with ethyl cellulose/cellulose acetate (EC/CA) blends and EC as column packing material, and small molecular weight compound as probe molecules was employed to measure the retention volume (V_R) and equilibrium distribution coefficient (K) of both inorganic and organic solutes. The interfacial separation properties of EC/CA blends were characterized by the HPLC data. The effects of the blends on the interfacial adsorption properties, hydrophilicity, affinity, polar and non-polar parameters of EC membrane materials were studied subsequently. The research results indicate that the interfacial adsorption properties and hydrophilicity of EC have been improved by solution blending with CA. The alloys are superior to EC in the separation efficiency for non-dissociable polar organic solute. The EC/CA alloy (80:20, ω) is suitable for desalting and desaccharifying.

Key words: ethyl cellulose; cellulose acetate; interfacial property; high performance liquid chromatography

1　INTRODUCTION

In previous research work, the high performance liquid chromatography (HPLC) experiments were used to simulate the equilibrium conditions at the membrane−solution interface of membrane separation technology processes[1,2]. The interfacial properties of membrane material could be identified with the HPLC data. It was an effective and convenient method to understand interfacial properties of membrane material because the interfacial properties of membrane material could be identified with the HPLC data[3,4].

Ethyl cellulose (EC) and cellulose acetate (CA) are the best abundant natural polymer membrane materials. However, application of the EC membrane material is limited in the field of membrane separation due to its worse hydrophilic and membrane-forming performance. The previous studies[5−7] showed that EC was modified with chitosan, CA and PVC, and the compatibility and thermal stability of the EC/CA blends were also studied. As far as we know, there is no report of research on the interfacial properties of EC/CA blends by HPLC.

In this work, the EC/CA blends prepared by the method in Ref.[5] were used as the column packing material of HPLC. The measured HPLC data were used to investigate the effects of the blends on the interfacial separation properties of EC membrane material. The results from this work will be a useful reference for the process of orientational membrane fabrication and expand the applied field of EC.

2　EXPERIMENTAL

2.1　Apparatus

All HPLC experiments were performed with a variant high-performance liquid chromatograph instrument (Model: Prostar 210) equipped with a refractive index (RI) detector (5.12×10^{-4} RI units full scale). The system was connected by a six-channel injection valve with a 20 μL loop. Electronic scale (AB104-N, Mettler Toledo) and grinding machine (DJ-04) were used.

2.2　Materials

Ethyl cellulose [η=8~10 mPa·s, DS (degree of substituent)=2.13], cellulose acetate (M_v=2.1×10^4, percent of acetyl is 39.5%, DS=2.5), NaCl, CaCl$_2$, FeCl$_3$, phenol, benzene β-phenethyl alcohol, benzyl alcohol, ethyl acetate, methanol, ethanol, isopropanol, deuterated water (D$_2$O), formaldehyde, D(+)-xylose, rhamnose, lactose and heavy water were purchased from Shanghai Reagent Company with analytical-reagent grade.

Except doublely-distilled water, sample solutions were prepared in doublely-distilled water, concentrations are 10 mg/mL for inorganic solutes, phenol, D(+)-xylose, rhamnose and lactose and 10% volumetric concentration for else organic solutes.

2.3 Preparation for the Column Packing of Polymer

The EC/CA blends (80:20, 50:50, ω) are prepared by the same method used in the previous study[5]. Those deposits are ground, screened to get the fraction of 37~40 μm. Then they are floated three times with doubly-distilled water in order to remove residual monomer molecules and other impurities, reduce osmosis resistance and raise separation performance of the membrane. Finally they are dried at 50 ℃ and used as the column packing material. A similar procedure is performed for EC. The column is packed with wet method.

2.4 Chromatographic Condition

The analytical column is prepared from a stainless steel tube (150 mm×4 mm i.d) packed with a series of EC/CA blends and EC membrane material, respectively. The mobile phase is doubly-distilled water, at a flow rate of 1.0 mL/min. The operating pressure is 1.0 MPa. The experiments are performed at 30 ℃. The sample injection volume is 10 μL.

2.5 Sample Analysis by HPLC

Under the aforementioned chromatographic conditions, each sample solution is analysed by HPLC. The retention volume (V_R) for each solute is calculated from the retention time (t_R) and carrier flow rate (F), and the data are listed in Table 1.

Table 1　Data from HPLC experiments with EC and its blends as column-packing material

Solute	EC		EC/CA (80:20, ω)		EC/CA (50:50, ω)	
	V_R (mL)	K	V_R (mL)	K	V_R (mL)	K
NaCl	1.489	0.581	1.466	0.495	1.415	0.673
CaCl$_2$	1.473	0.452	1.424	0.087	1.358	0.293
FeCl$_3$	1.437	0.161	1.418	0.029	1.333	0.127
Phenol	22.736	171.927	30.538	282.748	20.346	126.880
Benzene	10.273	71.419	14.006	122.243	9.898	57.227
β-Phenethyl alcohol	6.506	41.040	6.386	48.262	6.200	32.573
Benzyl alcohol	6.404	40.218	5.647	41.087	5.329	26.767
Ethyl acetate	1.753	2.710	1.671	2.485	1.630	2.107
Isopropanol	1.767	2.823	1.707	2.835	1.888	3.827
Ethanol	1.724	2.476	1.637	2.155	1.700	2.573
Methanol	1.699	2.274	1.601	1.806	1.611	1.980
D$_2$O	1.541	1.000	1.518	1.000	1.464	1.000
Formaldehyde	1.529	0.903	1.501	0.835	1.420	0.707
D(+)-xylose	1.458	0.331	1.422	0.068	1.353	0.260
Rhamnose	1.444	0.218	1.419	0.039	1.333	0.127
Lactose	1.417	0	1.415	0	1.314	0

Note: The amounts of EC, EC/CA (80:20, ω), EC/CA (50:50, ω) in column were 0.989 1, 0.727 7 and 0.893 4 g, respectively. The retention volume of D$_2$O was used as the retention volume of water V_w, V_{min} was the retention volume of lactose and V_R the retention volume of solute in Eqs.(1) and (2).

3　RESULTS AND DISCUSSION

3.1 Interfacial Adsorption of EC/CA Blends

Quantitatively, interaction force at the membrane–solution interface depends on the value of equilibrium distribution coefficient (K) of solute. The lower the value of K, the greater the repulsive force between solute and membrane interface, and the higher efficiency the membrane wipes off solute. Whereas, the larger the value of K, the greater the adsorption force between them. The value of K is defined in Refs.[2,3] by the following formula:

$$K=(V_R-V_{min})/(V_w-V_{min}). \tag{1}$$

Thus, the K values of solutes are calculated by Eq.(1) and listed in Table 1. Obviously, solutes of aromatic annulus such as phenol, benzene and benzyl alcohol are strongly adsorbed on the membrane surface because their corresponding values of K are far larger than 1. Single functional non-dissociable polar organic solutes, such as methanol and ethanol, are also adsorbed. Whereas multi-functional organic solutes, such as rhamnose, lactose and inorganic solutes, are strongly repulsed on the membrane surface because their K values are lower than 1. Additionally, inorganic solutes of larger valence state receive stronger repulsion than those of lower one. For example $K_{FeCl_3}<K_{CaCl_2}<K_{NaCl}$. Comparing EC with EC/CA alloys in the separation, the EC/CA alloy (80:20, ω) is the best membrane material for desalting and desaccharifying.

3.2 Hydrophilicity of EC/CA Blends

As suggested by Matsuura et al.[8], hydrophilicity of polymer could be characterized by interfacial water per unit weight of polymer (V_s/m) in the HPLC column, which is expressed by the following formula

$$V_s/m=(V_w-V_{min})/m. \tag{2}$$

Thus, the V_s/m values of EC and EC/CA blends are obtained, $[V_s/m]_{EC}=0.1254$ mL/g, $[V_s/m]_{EC/CA(80:20,\omega)}=0.1415$ mL/g, $[V_s/m]_{EC/CA(50:50,\omega)}=0.1679$ mL/g. Obviously, the hydrophilicity of EC/CA is improved with increasing the percent of CA increasing. It is indicated that the hydrophilicity of EC can be effectively improved by the solution blended with CA.

3.3 Interfacial Polar and Non-polar Parameters of EC/CA Blends

The interfacial polar (α_p) and non-polar (α_n) parameters are used to describe the polar and non-polar nature at polymer−solution interfaces, respectively. Increasing of the α_p and α_n values can improve separation performance of non-dissociable polar organic solute. In Refs.[9−11], the following formulae have been obtained:

$$\gamma=K_{s1}/K_{s2}, \tag{3}$$

$$\ln\gamma_1=\alpha_p+\alpha_n, \tag{4}$$

$$\ln\gamma_2=\chi\alpha_p+\alpha_n, \tag{5}$$

where γ is the ratio of the equilibrium distribution coefficient K of two samples, and in Ref.[9] χ can be estimated by the polymer solubility parameters. The χ values of EC, EC/CA (80:20, ω) and EC/CA (50:50, ω) are estimated as −0.232, −0.232 and −0.231, respectively. Here we choose methanol, ethanol and isopropanol as the reference solutes in the present experiment, then $\gamma_1=K_{ethanol}/K_{methanol}$ and $\gamma_2=K_{isopropanol}/K_{ethanol}$. The γ_1, γ_2, α_p and α_n values are finally calculated and summarized in Table 2.

Table 2　Parameters of EC and its blends

EC:CA (ω)	γ_1	γ_2	α_p	α_n	γ_{s1}	γ_{s2}	β
100:0	1.089	1.140	−0.037	0.122	4.664	1.554	0.991
80:20	1.193	1.316	−0.080	0.256	5.020	1.687	1.068
50:50	1.299	1.487	−0.110	0.372	3.131	1.051	0.596

The EC/CA blends are superior to EC in the separation efficiency for non-dissociable polar organic solute.

3.4 Affinity of EC/CA Blends

Parameter β characterizes the difference between the affinity of polymer for non-dissociable polar organic compounds and that dissociable inorganic compounds. Polymer with large β has higher affinity for organic solute than inorganic solute. The value of β is in the range from 1.37 to 0.5, the lower the value of β, the greater separation efficiency for organic solute.

By selective rule of reference solute expounded in Ref.[9], equilibrium distribution coefficients of three reference solutes of ethyl acetate, formaldehyde and NaCl are used to determine β. Therefore, the equations have been obtained as follow:

$$\gamma_{s1}=K_{ethyl\ acetate}/K_{NaCl}, \tag{6}$$

$$\gamma_{s2}=K_{formaldehyde}/K_{NaCl}, \tag{7}$$

$$\beta=(\ln\gamma_{s1}+\ln\gamma_{s2})/2. \tag{8}$$

The values of β, γ_{s1} and γ_{s2} can be evaluated by using Eqs.(6~8) and are listed in Table 2. So the EC/CA blends have the greater separation efficiency than EC material.

4　CONCLUSIONS

The present research results show that HPLC data can reflect quantitatively the property and magnitude of interaction force between solute and interface of membrane. The results would guide the process of orientational membrane fabrication.

The interfacial adsorption properties and hydrophilicity of EC have been improved by solution blending with CA. The alloys are superior to EC in the separation efficiency for non-dissociable polar organic solute. The EC/CA alloy (80:20, ω) is suitable for desalting and desaccharifying.

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