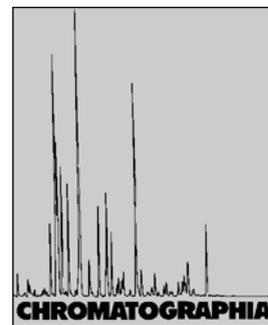


HPLC Study of the Physicochemical Characteristics of Reverse-Osmosis Separation on a Polyamide Membrane Material



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Key Words

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Summary

The fundamental characteristics of reverse osmosis on a polymer membrane have been correlated with HPLC experimental conditions by using the membrane material as a column packing. Twelve formulas were used to calculate the physicochemical characteristics of the reverse-osmosis separation process and it was found that these characteristics can be determined on the basis of retention (t_R , V_R) and partition coefficient (K) of the solute in HPLC. It seems that HPLC is an effective tool for studying the physicochemical nature of reverse-osmosis separations and the characteristics of the polymer membrane.

Introduction

Reverse osmosis is a new field of applied chemistry and chemical engineering, and its application potential is very important in industrial development. The membrane separation technology of reverse osmosis is a common means of separating substances in solution, and is used widely in the chemical industry. The more effective utilization of reverse-osmosis separation technology requires the better understanding of its mechanism and of the physicochemical characteristics of polymer membrane materials.

Reverse osmosis is controlled by two factors, an equilibrium effect and a dynamic effect. The equilibrium effect depends on adsorption by the polymer mem-

brane surface whereas the dynamic effect depends on the movement of solute and solvent molecules in the pores of the membrane. The mechanism of the reverse-osmosis separation process, as expounded elsewhere [1, 2], is very similar to that of HPLC and a few fundamental studies have been conducted to investigate the reverse-osmosis process by HPLC simulation [2, 3].

In the research described in this paper the reverse-osmosis process on the membrane has been simulated by HPLC. The affinity of the polymer for the solute, as reflected directly by the retention time (t_R), and the partition coefficient (K) of the solute, is used to characterize adsorption at the membrane-solution interface. We have also derived some formulas cor-

relating the experimental conditions in HPLC with the terms in the basic transport equation for reverse osmosis with the polymer membrane material. Thus the fundamental reverse osmosis characteristics of the polymer membrane material can be easily obtained and used to describe its physicochemical properties.

Experimental

Apparatus

HPLC experiments were performed with a Gilson high-performance liquid chromatograph equipped with a refractive index (RI) detector (4×10^{-5} RI units full-scale). The system was equipped a six-way injection valve, with 20- μ L loop.

Chromatographic Conditions

The analytical column was prepared from stainless steel tubing (30 cm \times 0.4 cm i. d.) packed with polyamide membrane material. The particle size and specific surface area of the polyamide material were $10 \pm 1 \mu\text{m}$ and $5.98 \pm 0.05 \text{ m}^2 \text{ g}^{-1}$, respectively. The effective membrane area (S), or the total surface area of the polyamide material in the HPLC column was $24.5 \pm 0.5 \text{ m}^2$. The mobile phase was double-distilled water, at a flow rate of 0.5 mL min^{-1} . The operating pressure was 5 \pm 0.1 MPa. Experiments were performed at temperatures in the range 20–30 °C. The sample injection volume was 10 μ L.

Table I. Characteristics of reverse osmosis on polyamide membranes.

<i>PWP</i>	8.36×10^3
<i>PR</i>	8.33×10^4
N_A	3.69×10^7
N_B	1.64×10^9
<i>k</i>	0.16
<i>A</i>	9.48×10^{14}
m_1	1.09×10^3
m_3	1.69×10^6
X_{A1}	1.00
X_{A3}	0.996
<i>f</i>	99.8
$D_{AM}/K\delta$	5.73×10^9

Ascorbic acid was used as a solute unadsorbed by the polyamide column; the retention of D₂O was used as the retention of water.

Chemicals and Reagents

NaCl, Na₂CO₃, KBr, CH₃COONa, phenol, acetone, diethyl ether, glycerol, methanol, deuterated water (D₂O), sucrose, ascorbic acid, and pyridine were purchased from Lanzhou Reagent Company, and were analytical-reagent grade.

Sample solutions were prepared in doubly distilled water; concentrations were 0.0159 mol · L⁻¹ for inorganic solutes and 10% mass concentration for organic solutes.

Results and Discussion

The Basic Transport Equation of Reverse Osmosis

Some common symbols used in this paper have been defined elsewhere [2, 3]. As Sourirajan suggests [2], Eqs (1)–(4) are the basic transport equations of the reverse-osmosis process in which water molecules are adsorbed by the membrane surface before the solute molecules.

$$A = \frac{PWP}{M_B \times S \times 3600 \times P} \quad (1)$$

$$N_B = A(P - \pi X_{A2} + \pi X_{A3}) \quad (2)$$

$$N_B = c \times \frac{D_{AM}}{K\delta} \times \frac{1 - X_{A3}}{X_{A3}} \times (X_{A2} - X_{A3}) \quad (3)$$

$$N_B = c \times k \times (1 - X_{A3}) \times \ln \left(\frac{X_{A2} - X_{A3}}{X_{A1} - X_{A3}} \right) \quad (4)$$

Under the operating pressure *P*, *PWP* and *PR* are the rates of osmosis (g · s⁻¹) through the effective membrane area for a column of pure water and for sample li-

quid, respectively. If *f* is the rate of separation of a solute (%) which can be obtained from a reverse osmosis experiment, *PWP*, *PR*, and *f* are the basic data of a reverse-osmosis separation and express the fundamental characteristics of the separation. N_A and N_B are flux of solute and solvent through the membrane (mol · cm⁻² · s⁻¹), *k* is the mass-transfer coefficient at the high-pressure side of the membrane (cm · s⁻¹), which can be calculated from the experimental conditions used for the reverse osmosis, and *L* is the length of the chromatographic column (cm). c_W , c_M , and c_A , t_W , t_M , and t_R , and V_W , V_M , and V_R are the primary solution concentrations (mol · L⁻¹), retention times, and retention volumes of D₂O, unretained compound and solute, respectively, and X_{A1} , X_{A2} , and X_{A3} are the mole fractions of solute in the parent fraction, in the thick boundary layer and in the liquid. m_1 and m_3 are the concentrations of solute in the parent fraction and the liquid (mol · L⁻¹) and M_A and M_B are molecular masses of the solute and solvent (water). *c* is the concentration of the solution (mol · L⁻¹) and π is osmotic pressure (MPa). *A* is the permeability constant of pure water (mol · cm⁻² · s⁻¹ MPa⁻¹), and $D_{AM}/K\delta$ is the transport parameter of the solute (cm · s⁻¹), in which D_{AM} is the diffusion coefficient of the solute in the membrane phase (cm² · s⁻¹), *K* is the partition coefficient of the solute, and δ is the effective membrane thickness (cm). *A* and $D_{AM}/K\delta$ are used to describe the nature of the membrane; in reverse osmosis it is only necessary to obtain the total value of $D_{AM}/K\delta$, rather than those of each of its components. The nature of the polymer membrane is, therefore, specified by this term.

The following equations were obtained by correlating the experimental conditions used for HPLC with the basic transport equations of reverse osmosis with the polymer membrane material (Eqs 1–4).

$$PWP = \frac{c_W \times V_W}{t_W} \quad (5)$$

$$PR = \frac{c_M \times V_M}{t_M} \quad (6)$$

$$N_A = \frac{c_A \times V_R}{S \times t_R} \quad (7)$$

$$N_B = \frac{c_W \times V_W}{S \times t_W} \quad (8)$$

$$k = \frac{L}{t_R} \quad (9)$$

$$X_{A3} = \frac{N_A}{N_A + N_B} \quad (10)$$

$$m_3 = \frac{c_A \times V_R}{1000 \times M_A} \quad (11)$$

$$f = \frac{m_1 - m_3}{m_1} = 1 - \frac{X_{A3}}{1 - X_{A3}} \times \frac{1 - X_{A1}}{X_{A1}} \quad (12)$$

In addition, the value of $D_{AM}/K\delta$ can be computed from the conditions used for the HPLC experiment, because of its definition. Thus the fundamental RO data *PWP*, *PR*, *f*, N_A , N_B , *k*, X_{A1} , X_{A3} , *A*, m_1 , and m_3 can be evaluated by use of Eqs (1)–(12).

In this research we performed HPLC on polyamide under these chromatographic conditions with glycerol as reference solute. The experimental data were used to calculate the physicochemical characteristics of the reverse-osmosis separation on polyamide membrane material, by use of the equations given above. The results, are listed in Table I, can be used to predict the physicochemical properties of the membrane.

Definition of Equation for Polymer Membrane Interface

The equations defined in Refs [1]–[3] are:

$$V_S = V_W - V_{\min} \quad (13)$$

$$t_i = \frac{V_S}{S} \quad (14)$$

$$K = \frac{V_R - V_{\min}}{V_W - V_{\min}} \quad (15)$$

$$\frac{\Gamma}{c_{Ab}} = (K - 1) \times t_i \quad (16)$$

where V_S is the volume of solid phase in the chromatographic column, V_{\min} is the minimum retention volume, t_i is the interfacial water layer thickness, *K* is the partition coefficient of the solute, Γ is the surface excess concentration of solute (mol · m⁻²), and c_{Ab} is the concentration of the parent fraction (mol · L⁻¹).

Γ/c_{Ab} , t_i , and *K* can be obtained from the HPLC experiment, and reflect the equilibrium effect of reverse osmosis and indicate the strength of the interaction between the solute and the membrane material. When $\Gamma/c_{Ab} < 0$ or $K < 1$, water mole-

cules will be adsorbed on to the membrane surface before solute molecules. When $\Gamma/c_{Ab} > 0$ or $K > 1$, the opposite is true. When $\Gamma/c_{Ab} > 1$ or $K \gg 1$, solute molecules will be strongly adsorbed by the membrane surface whereas water molecules will be repelled. Our previous experimental results [3] show that K and Γ/c_{Ab} for each solute are related to the chemical properties of both the membrane material and the solvent. Thus, the experimental data K and Γ/c_{Ab} can be used to determine the properties of the membrane interface in reverse osmosis.

The membrane interfacial equilibrium condition in reverse osmosis has been simulated by the HPLC experiment. As mentioned above, the affinity of the polymer for the solute can be reflected directly by the retention time t_R . The larger t_R for a solute, the stronger its affinity for the polymer. The smaller the value of t_R , the weaker the affinity. The experimentally measured values of t_R , K , and Γ/c_{Ab} are listed in Table II and can be used to describe reverse-osmosis equilibrium conditions at the polymer membrane interface.

Adsorption at the membrane-solution interface is dependent on solute-solvent-membrane material interactions. Obviously, the larger the value of t_i and the lower the value of K the greater is the separation efficiency of the membrane. It is found that solute separation in reverse osmosis correlates with the chemical properties of the solute, if the solvent and mem-

Table II. Data from HPLC experiments with polyamide as column-packing material.

Solute	t_R (min)	V_R (L)	K	$\Gamma/c_{Ab} (\times 10^8 \text{ m})$
NaCl	3.07	1.54	0.59	-1.16
Na ₂ CO ₃	3.04	1.52	0.57	-1.21
KBr	3.28	1.64	0.74	-0.73
CH ₃ COONa	2.84	1.42	0.42	-1.64
Phenol	2.93	1.47	0.49	-1.44
Acetone	3.70	1.85	1.04	0.11
Ethanol	3.10	1.55	0.61	-1.10
Ether	4.11	2.06	1.35	0.99
Glycerol	3.12	1.56	0.62	-1.07
Methanol	3.48	1.74	0.88	-0.34
Sucrose	2.87	1.44	0.45	-1.55
D ₂ O	3.63	1.82	1.00	0
Pyridine	7.23	3.62	3.61	7.36
Ascorbic acid	2.26	1.13	0	-2.82

V_{\min} is the retention volume of ascorbic acid; t_i for polyamide is 2.82×10^{-8} m.

brane material are unchanged. This result agrees with Sourirajan's suggestions [4, 5].

Conclusions

Dynamic and equilibrium effects have definitive influence on reverse osmosis. The basic transport equation terms express the effects of the former, whereas the latter can be determined from the properties of the membrane interface. Because of their similarities, HPLC can be used to simulate adsorption and transport in reverse osmosis. As a result, values of these fundamental characteristics of reverse osmosis can be computed from HPLC data. HPLC seems, therefore, to be a very effective tool for study of the physicochemical nature of

reverse-osmosis separations and the properties of polymer membranes.

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