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Reverse Osmosis Separations of Free Radicals in Aqueous Solutions

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Abstract

The reverse osmosis separations of two piperidinooxy radicals from aqueous solutions were studied at operating pressures of 1724 to 6895 kPag. Both radicals are stable during the reverse osmosis experiment and positively separated by using cellulose acetate membranes. The liquid chromatography data indicates that piperidinooxy radicals are weakly adsorbed to cellulose acetate polymer, while their electrolyte analogues are rejected, and undissociated piperidine solute (also a structural analogue of the radicals) is strongly adsorbed.

Reverse osmosis is a versatile separation process. It has been successfully applied to the separations of inorganic and organic solutes in aqueous (*1a, 2*) and nonaqueous (*1c, 3, 4*) solutions, and also to the separations of liquid–liquid (*1a, 3*) liquid–gas (*5*), and gas–gas (*6, 7*) mixtures. However, reverse osmosis separations of free radicals in aqueous or nonaqueous solutions have not been reported so far; such membrane separations should be of interest in biomedical research (*8*). This communication reports the results of the study on reverse osmosis separations of two piperidinooxy radicals in aqueous solutions. Both radicals are positively separated in reverse osmosis using cellulose acetate membranes. Experimental reverse osmosis and the corresponding liquid chromatography data indicate that the preferential sorptions of the piperidinooxy radicals at the cellulose acetate material–aqueous solution interface lie intermediate between those of undissociated piperidine solute and dissociated hydrochloride solutes of structurally similar compounds, and are closer to those of the latter compounds.

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The combination of free radicals and membranes is not new to chemical literature. For example, nitroxide biradicals were used to study the structure and properties of biological membranes (*9*). Also, destruction of biomembrane lipids by free radical oxidants was related to the aging process (*10*). However, the use of synthetic membranes for reverse osmosis (RO) separations of free radicals in aqueous solutions have not been reported before; such separations are of interest in biomedical research and applications (*8*). A fundamental feature governing such separations is illustrated in this report, for which purpose a cellulose acetate (CA) membrane and two piperidinooxy free radicals, which are stable in aqueous solutions, were chosen as examples.

It is known (*1a, 11*) that preferential sorption of either solvent or solute at the membrane–solution interface is a major factor governing RO separations. Consequently, two kinds of experiments were carried out. RO experiments using very dilute aqueous solutions (solute concentration in feed, 100 ppm) were carried out with a CA membrane to obtain relative data on solute separations, defined as (solute ppm in feed – solute ppm in membrane permeated product)/solute ppm in feed. Liquid chromatography (LC) experiments were carried out to obtain information on the nature of preferential sorption at the membrane–solution interface.

Some of the other experimental details are as follows. The CA membrane used was of the Batch 316(10/30)-type described in the literature (*12*), and its specifications (*1b*) are given in Table 1 in terms of RO data for a reference $NaCl–H_2O$ feed solutions. The RO experiments were carried out at 25 ± 1°C in the operating pressure range 1724 to 6895 kPag (250 to 1000 psig). The organic solutes used were 2,2,6,6-tetramethyl-4-piperidone hydrochloride (I), 4-hydroxy-2,2,6,6-tetramethyl piperidine hydrochloride (II), 4-oxo-2,2,6,6-tetramethyl piperidinooxy free radical (III), 4-hydroxy-2,2,6,6-tetramethyl piperidinooxy free radical (IV), and 4-hydroxy-2,2,6,6-

TABLE 1

Specification of Cellulose Acetate Membrane Used[a]

Pure water permeability constant, $A^b \times 10^6$, kg·mol/m^2·s·kPa	0.2759
Solute transport parameter, $(D_{AM}/K\delta)_{NaCl}{}^b \times 10^8$, m/s	40.21
Solute separation, %	86.0
Pure water permeation rate, g/h[c]	29.60
Product rate, g/h[c]	20.00

[a] Sodium chloride concentration in feed solution, 0.06 molal; operating pressure, 1724 kPag (250 psig).

[b] Solute transport parameters, A and $(D_{AM}/K\delta)_{NaCl}$, are defined in the literature (*1b*).

[c] Effective area of membrane surface, 9.6 cm^2.

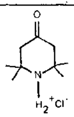
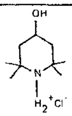
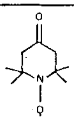
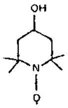
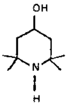
tetramethyl-piperidine (V), all of which were recrystallized in methanol prior to use in RO experiments. The structures of the above organic solutes are shown in Table 2. A total carbon analyzer (Beckman model 915A) was used to determine the concentration of the organic solutes in feed and membrane permeated product solutions, and the stability of the free radicals during membrane permeation was confirmed by their detection in the product solution by electron spin resonance. The adsorption characteristics of the organic solutes, relative to D_2O (*13*), were obtained in terms of their retention volumes using a liquid chromatograph (Waters Associates, model ALC 202). A 60-cm stainless steel column (0.032 cm o.d.) packed with CA powder (particle size, 38–53 μm) was used as the chromatography column. Ten microliters of sample solutions (10% for D_2O and 1% for the organic solutes) were injected into the mobile phase water stream (flow rate, 0.27 cm^3/min), and the solute eluted was detected by a differential refractometer.

The results of RO experiments are given in Table 2, and those of LC experiments are given in Fig. 1.

The RO data on membrane performance given in Table 2 represent only those for the particular membrane tested under the specified operating conditions; in particular, the data do not represent limits for all CA membranes. This discussion is concerned with the relative variations in solute separation and product rate data given in Table 2. In view of the very

TABLE 2

Results of Reverse Osmosis Experiments[a]

Solute number	I	II	III	IV	V
Solute structure					
Operating Pressure, 1724 kPag					
Solute separation, %	91.8	85.7	87.7	87.0	85.7
Product rate, g/h[b]	28.8	28.0	29.1	28.8	29.4
Operating Pressure, 3448 kPag					
Solute separation, %	90.2	87.1	88.6	87.5	75.0
Product rate, g/h[b]	57.5	56.5	53.5	59.3	59.3
Operating Pressure, 6895 kPag					
Solute separation, %	90.2	88.0	87.6	90.0	60.0
Product rate, g/h[b]	107.0	104.0	106.0	109.6	109.6

[a] Solute concentration in feed solution, 100 ppm.

[b] Effective area of membrane surface, 9.6 cm^2.

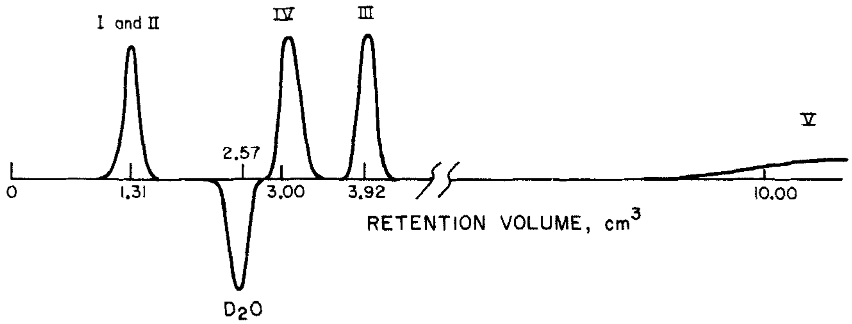


FIG. 1. Chromatograms of organic solutes used and deuterium oxide.

low solute concentration in the feed solutions, osmotic pressure effects can be considered negligible; hence the variations in product rate reflect mainly the effects of fluctuations in operating temperature during the experiment and compaction of the membrane substructure at high operating pressures. The RO data on solute separations are, however, of fundamental significance. From Table 2, one makes the following observations:

(a) All the five solutes are positively separated.
(b) The variation in the separations of the ionized solutes (I and II), the free radicals (III and IV), and the nonionized solute (V) is in a very narrow range at the lowest operating pressure.
(c) Increase in operating pressure has very little effect on solute separation with respect to both the ionized solutes (I and II) and the free radicals (III and IV).
(d) Increase in operating pressure decreases separation for the nonionized solute (V) significantly.

All the above observations are understandable on the basis of the results of LC experiments given in Fig. 1 which show that the retention volumes of the ionized solutes (I and II) are only slightly lower, and those of the free radicals (III and IV) are only slightly higher than the retention volume of D_2O, while the retention volume of the nonionized solute (V) is far higher than that of D_2O. Thus the LC data indicate that the ionized solutes I and II are weakly repelled away from, and the free radical solutes III and IV are weakly attracted toward the surface of the CA membrane material, whereas the nonionized solute (V) is relatively strongly adsorbed at the CA material–aqueous solution interface (*11, 14, 15*). These results explain the RO data given in Table 2. It has been established (*14, 16*) that the transport of polar organic solutes through reverse osmosis membranes is governed by electrostatic repulsion, polar (hydrogen bonding) attraction or repulsion, steric repulsion, and nonpolar (van der Waals) attraction of the solute at the membrane–solution interface. On the basis of the similarity of chemical structure, the extent of steric repulsion for all the five organic solutes studied may be considered to be quite close to each other. The observations (a) and (b) on solute separation listed above are understandable on the basis that solute separations are governed predominantly by steric repulsions; the weakly respulsive forces on ions and the weakly attractive forces on the free radicals explain the observation (c), and the relatively strong attractive force on the nonionized solute and the increase in the mobility of the preferentially sorbed solute at higher operating pressures explain observation (d).

That the preferential sorptions of the free radicals at the CA material–aqueous solution interfaces lie intermediate between those of undissociated and dissociated solutes of similar chemical structure, and much closer to that of the dissociated species, is of fundamental interest in the study of the permeation of free radicals through porous polymeric membranes. A detailed quantitative study (*15*) of the magnitude and intensity of the interfacial forces involved in free radical–water–polymer systems through RO and LC experiments can contribute significantly to the application of free radicals and synthetic membranes in biomedical research.

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