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Reverse Osmosis Separation of Hydrocarbons in Aqueous Solutions Using Porous Cellulose Acetate Membranes

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Synopsis

A physicochemical parameter, represented by the symbol Σs^*, based on molar solubility in water and molar attraction constants of Small, has been developed to express quantitatively the relative hydrophobicity, or nonpolar character, of the hydrocarbon molecule. The value of Σs^* can be calculated for a hydrocarbon from its chemical structure. The scale of Σs^* is consistent within each group of aromatic, cyclic, and noncyclic hydrocarbons. Reverse osmosis data have been obtained at 250 psig for single-solute aqueous feed solution systems involving low concentrations of 39 different hydrocarbons (including 13 aromatics, 10 cyclic, and 16 noncyclic compounds) and several samples of cellulose acetate membranes of different surface porosities. The effect of operating pressure on membrane performance has also been studied for two aromatic hydrocarbon solutes. The values of Σs^* for the solutes used were in the range of 425 to 924 for aromatic hydrocarbons, 521 to 931 for cyclic hydrocarbons, and 369 to 960 for noncyclic hydrocarbons. The reverse osmosis data have been correlated with Σs^* for each group of hydrocarbons studied. In all cases, positive solute separations were obtained, and the ratio $[PR]/[PWP]$ was less than 1. With respect to each film, solute separation increased with increase in Σs^*, and decreased with increase in operating pressure. Also, solute separation decreased in the order aromatic hydrocarbon > cyclic hydrocarbon > noncyclic hydrocarbon at any given value of Σs^*. At a given operating pressure, for low values of Σs^* ($\sim$500 or less) solute separation increased with progressive decrease in average pore size on the membrane surface. For high values of Σs^* ($\sim$800 or more), solute separation initially increased with decrease in average pore size, then passed through a maximum and minimum with further decrease in average pore size, and again increased with still further decrease in average pore size. The results are discussed on the basis of preferential sorption of solute at the membrane–solution interface under the experimental conditions studied.

INTRODUCTION

Physicochemical criteria for the reverse osmosis separations of different classes of polar organic solutes (including alcohols, phenols, acids, aldehydes, ketones, ethers, esters, and amines) in aqueous solutions using Loeb-Sourirajan-type porous cellulose acetate membranes have been extensively discussed.[1–5] This paper is concerned with the development of appropriate physicochemical criteria for the reverse osmosis separations of hydrocarbons in aqueous solutions using the above membranes. The

TABLE I

Nonpolar Parameters and Other Data for Hydrocarbons

Solute no.	Solute: Name	Solute: Formula	Solute: Molecular weight	Solubility in water at 25°C: ppm	Solubility in water at 25°C: g-mole/l. × 10³	Solute concn. in feed, ppm	Small's number	Modified Small's number Σs^*
		Aromatic Hydrocarbons						
1	Benzene	C_6H_6	78.11	1780	22.79	63.0	825	425
2	Toluene	$C_6H_5CH_3$	92.13	515	5.59	51.2	949	549
3	Styrene	$C_6H_5CH{=}CH_2$	104.14	300	2.88	28.5	1061	561
4	Ethylbenzene	$C_6H_5C_2H_5$	106.16	152	1.43	34.4	1082	682
5	*o*-Xylene	$C_6H_4(CH_3)_2$	106.16	175	1.65	46.9	1086	686
6	*m*-Xylene	$C_6H_4(CH_3)_2$	106.16	196	1.85	46.3	1086	686
7	*p*-Xylene	$C_6H_4(CH_3)_2$	106.16	198	1.87	40.4	1086	686
8	Cumene	$C_6H_5CH(CH_3)_2$	120.19	50	0.42	23.0	1191	791
9	Propylbenzene	$C_6H_5C_3H_7$	120.19	55	0.46	16.1	1215	815
10	Mesitylene	$C_6H_3(CH_3)_3$	120.19	—	—	18.8	—	823
11	*t*-Butylbenzene	$C_6H_5C(CH_3)_3$	134.12	34	0.25	9.9	1284	884
12	*s*-Butylbenzene	$C_6H_5CH(CH_3)C_2H_5$	134.12	—	—	4.0	1324	924
13	Isobutylbenzene	$C_6H_5CH_2CH(CH_3)_2$	134.12	—	—	10.4	1324	924
		Cyclic Hydrocarbons						
14	Cyclopentene	$\underline{CH{=}CHCH_2CH_2CH_2}$	68.11	535	7.85	26.9	731	521
15	Cycloheptatriene	$\underline{CH{=}CH{-}CH{=}CH{-}CH}$ $\underline{{=}CH{-}CH_2}$	92.13	620	6.73	80.1	924	524
16	Cyclohexene	$\underline{CH{=}CHCH_2CH_2CH_2CH_2}$	84.14	213	2.59	121.3	854	654

17	Cyclopentane	$CH_2CH_2CH_2CH_2CH_2$	70.13	156	2.22	72.7	774	665
18	4-Methylcyclohexene	$CH{=}CHCH_2CH(CH_3)CH_2CH_2$	96.17	—	—	—	963	763
19	Methylcyclopentane	$CH(CH_3)CH_2CH_2CH_2CH_2$	84.16	42	0.50	31.6	884	774
20	1-Methylcyclohexene	$C(CH_3){=}CHCH_2CH_2CH_2CH_2$	96.17	52	0.54	43.3	976	776
21	Cycloheptene	$CH{=}CHCH_2CH_2CH_2CH_2CH_2$	96.17	66	0.69	43.0	987	787
22	Cyclohexane	$CH_2CH_2CH_2CH_2CH_2CH_2$	84.16	55	0.65	30.0	898	798
23	Cycloheptane	$CH_2CH_2CH_2CH_2CH_2CH_2CH_2$	98.18	30	0.31	4.0	1031	931
		Noncyclic hydrocarbons						
24	1,6-Heptadiyne	$CH{\equiv}CCH_2CH_2CH_2C{\equiv}CH$	92.13	1650	17.91	16.4	989	369
25	1,2-Pentadiene	$CH_2{=}C{=}CHCH_2CH_3$	68.11	—	—	53.7	—	517
26	2,3-Pentadiene	$CH_3CH{=}C{=}CHCH_3$	68.11	—	—	54.0	—	519
27	Isoprene	$CH_2{=}C(CH_3){-}CH{=}CH_2$	68.11	642	9.43	89.6	724	524
28	1-Hexyne	$CH{\equiv}CCH_2CH_2CH_2CH_3$	82.14	360	4.38	159.0	898	598
29	1,5-Hexadiene	$CH_2{=}CHCH_2CH_2CH{=}CH_2$	82.14	169	2.06	94.6	868	668
30	1-Heptyne	$CH{\equiv}CCH_2CH_2CH_2CH_2CH_3$	96.17	94	0.97	39.0	1031	731
31	2-Heptyne	$CH_3C{\equiv}CCH_2CH_2CH_2CH_3$	96.17	—	—	62.9	1049	749
32	4-Methyl-1-pentene	$CH_2{=}CHCH_2CH(CH_3)CH_3$	84.16	48	0.57	28.1	890	790
33	*cis*-4-Methyl-2-pentene	$CH_3CH{=}CHC(CH_3)CH_3$	84.16	—	—	33.0	892	792
34	*trans*-4-Methyl-2-pentene	$CH_3CH{=}CHC(CH_3)CH_3$	84.16	—	—	48.3	892	792
35	1,6-Heptadiene	$CH_2{=}CHCH_2CH_2CH_2CH{=}CH_2$	96.17	44	0.46	19.5	1001	801
36	Isopentane	$CH_3CH(CH_3)CH_2CH_3$	72.15	47.8	0.66	29.7	803	803
37	2-Methyl-1-pentene	$CH_2{=}C(CH_3)CH_2CH_2CH_3$	84.16	78	0.93	32.8	903	803
38	1-Hexene	$CH_2{=}CHCH_2CH_2CH_2CH_3$	84.16	50	0.59	20.7	914	814
39	*n*-Hexane	$CH_3CH_2CH_2CH_2CH_2CH_3$	86.17	9.5	0.11	7.9	960	960

hydrocarbon solutes are essentially hydrophobic, or nonpolar, in character. Since the cellulose acetate membrane material has both polar and nonpolar characters, the extent of solute separation in reverse osmosis using the above membranes may be expected to be governed by both the polar and the nonpolar characters of the solute and solvent molecules. This has already been pointed out.[4-6] With respect to hydrocarbon solutes in aqueous solutions in conjunction with porous cellulose acetate membranes, the relative hydrophobicity, or nonpolar character, of the solutes may be expected to govern their relative separations in reverse osmosis. A direct measure of hydrophobicity of a hydrocarbon molecule is given by its molar solubility in water. A physicochemical parameter based on such solubility data[7-9] and the molar attraction constants of Small[10] is presented in this paper to express quantitatively the relative hydrophobicity, or nonpolar character, of the hydrocarbon molecule. The above nonpolar parameter is called "modified Small's number." Reverse osmosis data have been obtained at 250 psig for single-solute aqueous feed solution systems involving low concentrations of 39 different hydrocarbons (including 13 aromatic, 10 cyclic, and 16 noncyclic compounds) and several samples of membranes of different surface porosities. These data are correlated and discussed with the modified Small's numbers for the respective hydrocarbon molecules. The effects of operating pressure on the reverse osmosis separations of two aromatic hydrocarbons are also briefly studied and discussed in this paper.

EXPERIMENTAL

Reverse Osmosis Experiments

Hydrocarbon solutes listed in Table I and laboratory-made batch 316-type[11] porous cellulose acetate membranes specified[12] in Table II were used. The apparatus and experimental procedure were the same as those reported in earlier papers.[1-5] All experiments were of the short-run type and were carried out at the laboratory temperature (23–25°C). The solute concentration used for each hydrocarbon is given in Table I. Clear, homogeneous solutions were used in all cases. In each experiment, the per cent solute separation, defined as

$$\left(\frac{\text{solute ppm in feed} - \text{solute ppm in product}}{\text{solute ppm in feed}}\right) \times 100,$$

the product rate [PR], and the pure water permeation rate [PWP], in grams per hour per given area of films surface (7.6 cm^2 in these experiments), were determined at the specified operating conditions of pressure, feed concentration, and feed flow rate. In all experiments the terms "product" and "product rate" refer to membrane-permeated solutions. The reported [PR] and [PWP] data are those corrected to 25°C using the relative viscosity and density data for pure water. A feed flow rate of

TABLE II
Specifications and Some Performance Data for the Cellulose Acetate Membranes Used[a]

Film no.	$A \times 10^6$, g-mole/cm^2-sec-atm	$(D_{AM}/K\delta) \times 10^5$, cm/sec	Membrane performance Solute sepn., %	Product rate, g/hr-7.6 cm^2 of film area
1	2.48	3.22	94.7	19.1
2	3.53	9.50	90.4	27.4
3	5.35	16.89	87.0	41.2
4	6.80	34.16	79.0	52.3
5	9.73	144.4	63.3	73.5
91	3.11	4.21	93.8	23.8
92	3.71	5.91	92.2	28.2
93	4.42	10.71	89.7	34.0
94	5.87	24.85	83.5	45.5
95	6.72	44.32	75.5	52.2
96	7.96	105.5	63.0	63.1
101	3.52	8.00	86.2	26.1
102	3.68	19.07	83.4	28.9
103	4.14	23.55	79.6	32.3
104	4.50	28.29	76.8	35.0
105	4.35	40.34	73.1	34.3
106	4.80	60.50	70.4	38.4

[a] Operating pressure: 250 psig; feed system: 1500 ppm NaCl–H_2O; mass transfer coefficient: 57×10^{-4} cm/sec; A: pure water permeability constant; $(D_{AM}/K\delta)$: solute transport parameter.

~400 cc/min was used in each experiment; at this feed rate, the mass transfer coefficient[12] on the high-pressure side of the membrane was 57×10^{-4} cm/sec for the reference solution system 1500 ppm NaCl–H_2O. All reverse osmosis data are for single-solute systems. The solute numbers in all figures in this paper are the same as those listed in Table I. Under the experimental conditions used, the osmotic pressure effects on reverse osmosis transport were negligible in all cases.

Analysis

Beckman total carbon analyzer (Model 915) was used to measure concentrations of aromatic hydrocarbons when the feed concentrations were greater than 30 ppm; the analytical procedure was the same as that used before.[1,2] All other hydrocarbon analyses were carried out using a gas chromatograph (Tracor, Model 160). The chromatographic column used was a 6-ft-long, 0.25-in.-diameter stainless steel tubing packed with 20–30 mesh ascarite for the initial 4.5 in., and with 5% OV1 on 80–100 mesh Chromosorb W(HP) for the remaining length. Helium flow through the column was 64 cc/min, and the entire effluent passed into a hydrogen flame ionization detector. The column was operated at 100°C. The accuracy and consistency of the carbon analyzer and the gas chromatograph data were confirmed by measuring the hydrocarbon concentrations in saturated aqueous solutions of ethyl benzene and *o*-xylene, and comparing the results with literature data. The results obtained were as follows.

	Hydrocarbon conc. in saturated soln., ppm		
	Carbon analyzer	Gas chromatograph	Literature data[7]
Ethyl benzene	160.6	158.0	152
o-Xylene	178.3	174.1	175

The above results showed reasonable agreement between the carbon analyzer and gas chromatograph data and between the experimental and literature data.

RESULTS AND DISCUSSION

Nonpolar Character and Membrane Performance

Polymer–Solute–Solvent Interactions. The cellulose acetate polymer material has both polar and nonpolar character. One may consider that the polar character, which represents the hydrogen-bonding ability of the polymer molecule, arises out of the hydroxyl and oxygen linkages in the molecule, and the nonpolar character arises out of the hydrocarbon backbone and the hydrocarbon group in the ester part of the molecule. Consequently, the cellulose acetate polymer material may be expected to attract both the polar solvent (water) and the nonpolar solute (hydrocarbon). The relative extent of such attractions determines whether solvent or solute or neither is preferentially sorbed at the membrane–solution interface.

With reference to aqueous hydrocarbon solution systems and porous cellulose acetate membranes, when the attraction for water is more than for the hydrocarbon solute, water is preferentially sorbed at the membrane–solution interface; in this case, membrane performance in reverse osmosis may be expected to be similar to that reported earlier[1,4] for aqueous solutions of alcohols whose Taft numbers are negative. When the attraction for water is the same as that for the hydrocarbon solute, neither solute nor solvent is preferentially sorbed at the membrane–solution interface; in this case, no solute separation in reverse osmosis is possible, whatever the porous structure of the membrane may be. When the attraction for water is less than that for the hydrocarbon solute, the latter is preferentially sorbed at the membrane–solution interface; this case, discussed below, is of particular relevance in this work.

Preferential Sorption of Hydrocarbon Solute and Membrane Performance. This case is analogous to the case of phenol–water and *p*-chlorophenol–water systems discussed earlier.[3] In the latter case, the preferential sorption of solute at the membrane–solution interface is due to the relative polar character of the solute and the membrane material; in the present case of the hydrocarbon–water system, preferential sorption of solute at the membrane–solution interface is due to the relative nonpolar character of the solute and the membrane material, the solvent being the same in both cases. Even though the reason for the preferential sorption of solute at the membrane–solution interface is different in each case, the effect of such preferential sorption on membrane performance in reverse osmosis should be similar in both cases.

Therefore, the data on membrane performance for the hydrocarbon–water system can be considered on the same basis as that stated earlier[3] for the phenol–water and *p*-chlorophenol–water systems. Following the previous discussion, the above basis may be stated explicitly as follows with reference to the hydrocarbon–water system:

1. The hydrocarbon solute is preferentially sorbed at the membrane–solution interface.
2. In the sorbed layer, the mobility of water is more than that of the hydrocarbon solute.
3. The mobility of the preferentially sorbed hydrocarbon decreases progressively as the membrane surface is approached; thus, in general, the preferentially sorbed layer consists of both immobile and less-mobile (compared to water) solute molecules.
4. Increase of operating pressure increases the sorption of both hydrocarbon and water at the interface.
5. Increase of operating pressure also increases the degree of mobility of the preferentially sorbed layer, i.e., a greater proportion of the preferentially sorbed layer is mobile at higher operating pressures.

In terms of membrane performance in reverse osmosis, the following are some of the results obtainable as a consequence of the above basis.

a. The overall solute separation may be positive, negative, and/or zero, depending on the extent of preferential sorption, number of immobile layers at the interface, relative mobility of the sorbed species, pore structure on the membrane surface, and other operating conditions of the experiment.

b. With a given membrane, an increase in operating pressure decreases solute separation.

c. At a given operating pressure, depending on its magnitude, solute separation can increase or decrease, with decrease in average pore size on the membrane surface.

d. Since the immobile layer at the interface tends to block the pore area available for fluid flow, the ratio $[PR]/[PWP]$ is significantly less than 1, even when osmotic pressure effect on transport is insignificant. Further, the magnitude of the above ratio tends to decrease with increase in operating pressure for any given membrane.

All the above results have been experimentally established for the system *p*-chlorophenol–water, and they were shown to be consistent with the foregoing basis for reverse osmosis transport.[3]

Results (b) and (d) itemized above are particularly significant because they offer some *a priori* experimental criteria to determine whether or not solute is preferentially sorbed at the membrane–solution interface in any particular membrane–solution-operating system.

Nonpolar Parameter for Hydrocarbons

Molar Solubility in Water and Data on Membrane Performance. Data on molar solubility in water offer a direct measure of hydrophobicity, or nonpolar character, of hydrocarbon compounds. Within hydrocarbon series of similar chemical structure, the higher the hydrophobicity of the hydrocarbon molecule, the lower is its solubility in water. Figure 1 illustrates the plots of data on solubility[7–9] versus solute separation and $[PR]/[PWP]$ ratio obtained with film 1 in reverse osmosis experiments at 250 psig for 30 different hydrocarbon–water systems. These plots illustrate some important aspects with respect to the reverse osmosis systems involved.

In all the cases studied, the $[PR]/[PWP]$ ratio was less than 1; in most cases, the value of the above ratio was in the range of 0.85 to 0.95. Further, reverse osmosis data on the effect of operating pressure on membrane performance for the benzene–water system, given later in this paper (Fig. 9), showed that, for the above system, solute separation decreased with increase in operating pressure for any given membrane, and the ratio $[PR]/[PWP]$ was less than 1 and showed a tendency to decrease with increase in operating pressure for any given membrane. These data are in accordance with the *a priori* criteria stated earlier for the case of preferential sorption of solute at the membrane–solution interface. Since benzene has the highest molar solubility in water among the hydrocarbon solutes studied, membrane performance in reverse osmosis may be expected to be similar with aqueous solutions of other hydrocarbon solutes which are even more hydrophobic than benzene. Consequently, one may conclude that in all the cases studied in this work, solute was preferentially sorbed at the membrane–solution interface.

In all the cases studied, positive solute separations to different extents were obtained with the membrane used. This result showed that, in each case, the preferentially sorbed layer consisted of different extents of both immobile and less-mobile solute molecules (compared to water) under the operating conditions used for the experiment.

When the chemical structure of the hydrocarbons used was reclassified into aromatic, cyclic, and noncyclic series, there was good correlation between molar solubility of solute in water and solute separation in reverse osmosis within each series. Further, the correlation showed that solute separation tended to increase with decrease in solubility of solute in water. These results showed that, with reference to the reverse osmosis systems studied, molar solubility of solute in water was a relavent physicochemical parameter to express quantitatively the hydrophobic or nonpolar character of the hydrocarbon molecule. Within each series of hydrocarbons, classified as aromatic, cyclic, and noncyclic, solubility data offered a consistent scale of expressing the nonpolar character of the hydrocarbon molecule.

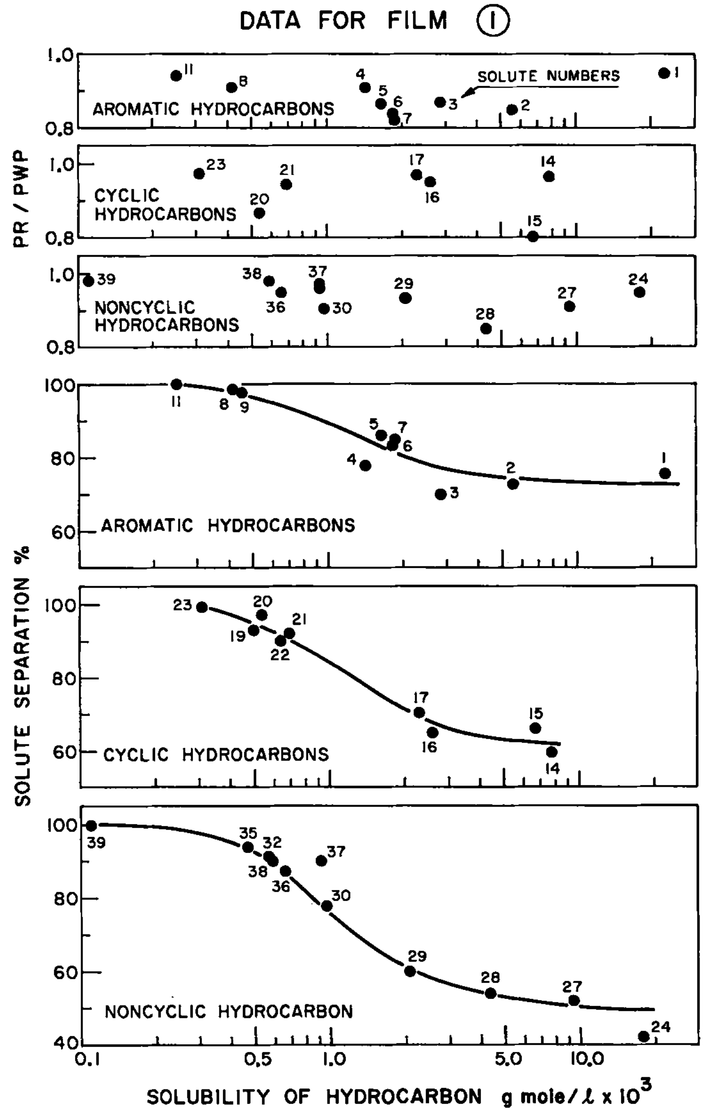


Fig. 1. Molar solubility of hydrocarbon in water vs. data on membrane performance. Solute numbers same as in Table I; operating pressure, 250 psig.

The affinity of the membrane surface for the solute molecule increased with increase in the nonpolar character of the molecule, which in turn decreased the relative mobility of the solute in the preferentially sorbed layer resulting in higher solute separation in reverse osmosis.

The correlations also showed that at a given molar solubility in water, solute separation in reverse osmosis was in the order aromatic > cyclic > noncyclic. Data on [*PR*]/[*PWP*] ratio appear scattered in the correlation presented in Figure 1. This result is understandable on the basis that differences in solute concentrations in the feed solution may be expected to affect the pore area available for fluid flow as a result of the blocking effect of the preferentially sorbed solute on the membrane surface.

Small's Number. All the hydrocarbon solutes studied in this work are liquids. The concept of cohesive energy of a liquid is discussed extensively in the literature.[10,13,14] The molar cohesive energy of a liquid is defined as the energy necessary to break all intermolecular contacts in a mole of the liquid and thus overcome all intermolecular forces holding the molecules together as a liquid. The molar cohesive energy E is given by the expression

$$E = \Delta U_{\text{vap}} + \int_{V_{\text{vap}}}^{\infty} \frac{\partial U}{\partial V_T} dV \qquad (1)$$

$$\approx \Delta H_{\text{vap}} - RT \qquad (2)$$

where U = internal energy, V = molar volume, H = heat of vaporization, R = gas constant, T = absolute temperature, and the subscript vap refers to the vapor state. The integral in eq. (1) is the correction for the imperfection of the vapor; when the latter can be assumed to be a perfect gas, E is simply the internal energy of vaporization.

When the cohesion between molecules is due to dispersion forces, as is essentially the case for nonpolar molecules, E is related to heat of mixing per cc (ΔH_{cc}) by Scatchard's semiempirical relation

$$\Delta H_{\text{cc}} = \varphi_1\varphi_2[(E_1/V_1)^{1/2} - (E_2/V_2)^{1/2}]^2 \qquad (3)$$

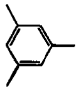
where φ is the volume ratio and the subscripts 1 and 2 represent a set of two dissimilar molecules. Scatchard's relation eq. (3), assumes additivity of the energies of molecular pairs, and randomness and no volume change in mixing. Though these assumptions are not strictly true, eq. (3) has proved eminently successful in solution theory.[14] Consequently, the basis of eq. (3) has practical significance. Equation (3) is equivalent to the statement that the cohesive energy E of a mixture of n_1 moles of liquid 1 and n_2 moles of liquid 2 can be given by the expression[10,14]

$$E^{1/2}(n_1V_1 + n_2V_2)^{1/2} = n_1(E_1V_1)^{1/2} + n_2(E_2V_2)^{1/2} \qquad (4)$$

which shows that $(EV)^{1/2}$ is an additive property. Assuming that this property might add in compounds on an atomic and constitutive basis, Small[10] derived a set of additive constants for the commoner groups of organic molecules, which allowed the calculation of $(EV)^{1/2}$ for different organic compounds. These constants (called "molar attraction constants" by Small[10] and "Small's numbers" in this paper) are given in Table III. The values of $(EV)^{1/2}$ calculated for 72 hydrocarbons from Small's numbers agreed very well with those calculated from thermodynamic data available in the literature.[10] Therefore, Small's numbers have a firm thermodynamic and experimental basis.

The relevance of Small's number to reverse osmosis arises from the following considerations. Small's number gives a quantitative measure

TABLE III
Small's Number and Modified Small's Number for Structural Group in Hydrocarbons at 25°C

Structural group		Small's number, $cal^{1/2}cc^{1/2}$	Modified Small's number (s^*), $cal^{1/2}$ $cc^{1/2}$
$-CH_3$	single-bonded	214	214
$-CH_2-$		133	133
$-\overset{\vert}{\underset{\vert}{C}}H$		28	28
$-\overset{\vert}{\underset{\vert}{C}}-$		−93	−93
$CH_2=$	double-bonded	190	140
$-CH=$		111	61
$>C=$		19	−31
$CH\equiv C-$		285	−15
$-C\equiv C-$		222	−78
Phenyl		735	335
Phenylene (*o*, *m*, *p*)		658	258
Ring, 5-membered		105–115	0
Ring, 6-membered		95–105	0
Conjugation		20–30	25
H		80–100	90
		—	181
$=C=$		—	−31

of the relative mutual attraction of organic molecules to one another as a result of dispersion forces. Consequently, Small's number offers a basis for expressing quantitatively the nonpolar character of different hydrocarbons on a relative scale. Further, Small's number for a hydrocarbon can be calculated entirely from its chemical structure, and such calculation is not limited by the physical state (gas, liquid, or solid) of the compound. An increase in Small's number signifies an increase in hydrophobicity or nonpolar character for the hydrocarbon.

The Small's number for each of the hydrocarbon solutes used in this work is given in Table I, and the above number was obtained from the corresponding number given by Small (Table III) for different structural groups.

Small's Number for Hydrocarbon, Its Molar Solubility in Water, and Solute Separation in Reverse Osmosis. Since both Small's number and molar solubility in water reflect the nonpolar character of a hydrocarbon solute, some correlation must exist between the above two properties. This is confirmed by the data presented in Figure 2 for 33 different hydrocarbons, including five compounds (A, B, C, D, and E) which were not used in reverse osmosis experiments in this work. The latter compounds are included in Figure 2 only to establish the correlations shown. Figure 2 shows that Small's number versus logarithm of solubility is a straight line which is different for different reactive series of compounds of similar chemical structure; the above straight-line correlations are essentially parallel to each other; and within each series, solubility decreases with increase in Small's number. Figure 2 gives the correlations for seven series, of compounds including paraffins, cycloparaffins, olefins, cycloolefins, diolefins, acetylenes, and aromatics. The correlations for cycloparaffins and olefins are essentially identical within the accuracy of the solubility data; such is also the case for cycloolefins and diolefins. Consequently, five different straight-line correlations are given in Figure 2 for the seven series of hydrocarbon compounds examined. For a given Small's number,

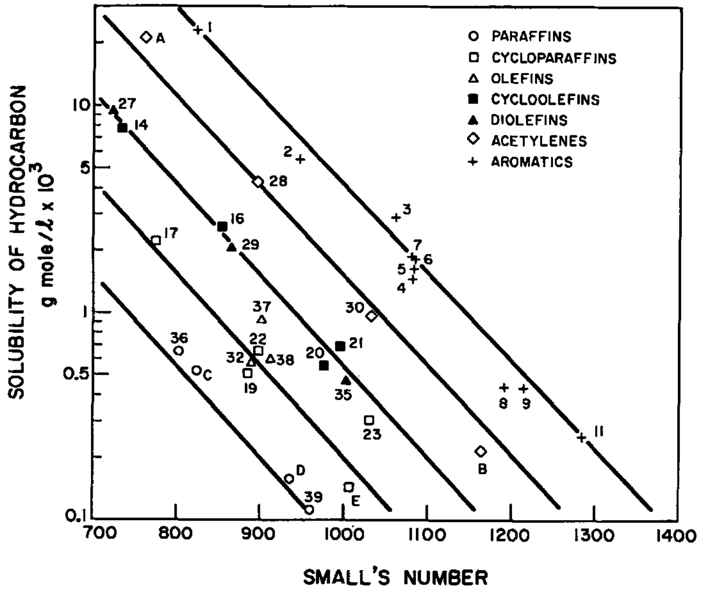


Fig. 2. Small's number vs. molar solubility of hydrocarbon in water. Solute numbers same as in Table I.

molar solubility in water is in the order paraffins < cycloparaffins, ≈ olefins < cycloolefins ≈ diolefins < acetylenes < aromatics.

Figure 3 gives the plots of Small's number versus solute separation data for a number of hydrocarbon solutes tested in reverse osmosis experiments. The reverse osmosis data are the same as those given in Figure 1. Figure 3 illustrates that solute separation data can be correlated with Small's number for hydrocarbons. These correlations are different for different reactive series of compounds tested. Thus there are seven correlations in Figure 3 for the seven series of compounds tested. Within each series, solute separation tends to increase with increase in Small's number. With the exception of aromatic hydrocarbons, the order of solute separation at a given Small's number is the same as the order of solubility of the hydrocarbons, solute separation being higher for the hydrocarbon whose solubility is lower.

Modified Small's Number. From the foregoing discussion, it is evident that both molar solubility in water and Small's number can serve as parameters to express the hydrophobicity or nonpolar character of hydrocarbons for purposes of correlation of reverse osmosis data. In either mode of expression, hydrocarbons have to be classified into several groups of similar chemical structure and the scale of relative nonpolar character is consistent only within each such group. These groups, however, are more broad (such as aromatic, cyclic, and noncyclic) and hence lesser in number when solubility is used as the nonpolar parameter; whereas these groups are more narrow (such as paraffins, cycloparaffins, olefins, cycloolefins, diolefins, acetylenes, and aromatics) and hence larger in number when Small's number is used as the nonpolar parameter. On the other hand, one can calculate Small's number just from the chemical structure of the hydrocarbon molecule, whereas one needs experimental solubility data for the use of the latter as the nonpolar parameter. From a practical point of view, it is desirable to have a nonpolar parameter which can be calculated from the chemical structure of the hydrocarbon molecule and which involves the least number of classified groups in terms of relative scale of hydrophobicity. By combining the solubility data and Small's number appropriately, a modified nonpolar parameter which combines the advantages of both the above parameters can be obtained for purposes of correlation of reverse osmosis data. This modified nonpolar parameter may be called "modified Small's number" represented by the symbol s^* for the structural group and Σs^* for the hydrocarbon molecule.

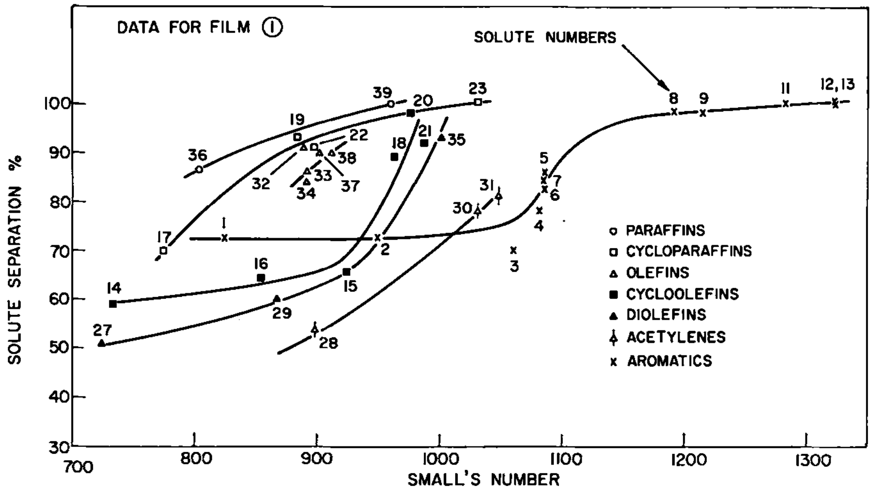


Fig. 3. Small's number vs. solute separation. Solute numbers same as in Table I; operating pressure, 250 psig.

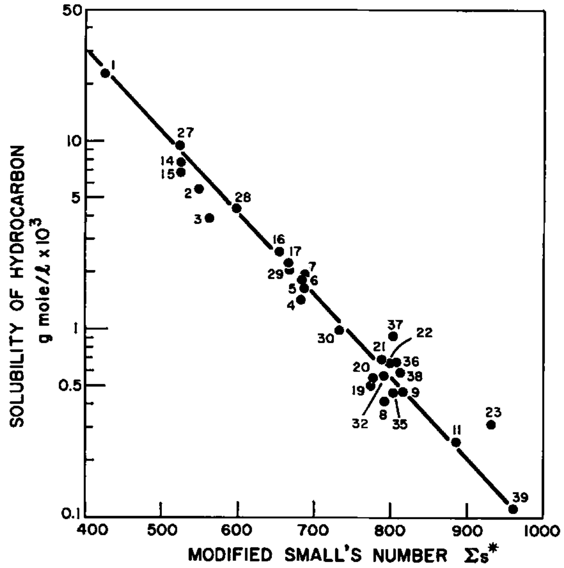


Fig. 4. Modified Small's number (Σs^*) vs. molar solubility of hydrocarbon in water.

Figure 2 shows that a given molar solubility corresponds to different Small's numbers depending on the chemical structure of the hydrocarbon series. Figure 4 is a replot of Figure 2 on the basis that a given solubility corresponds to a single value of Σs^* obtained by adjusting the value of Small's number to correspond to a reference correlation of solubility versus Small's number. The latter correlation for paraffins given in Figure 2 is arbitarily chosen as reference for obtaining the values of Σs^* for the other series of hydrocarbons. The choice of the reference correlation is based on the reported excellent agreement between the experimental and calculated values for Small's number for paraffins and olefins.[10] Thus, the straight-line correlation of solubility versus Σs^* given in Figure 4 is identical to the correlation of solubility versus Small's number for paraffin hydrocarbons given in Figure 2. Figure 2 shows that the five parallel straight-line correlations given therein are each 100 units apart in terms of Small's number for a given solubility. By simply subtracting the required number of units from the correponding Small's number, the numerical values of Σs^* applicable for all the series studied were obtained. These values are given in Tables I and III for the hydrocarbons (Σs^*) and the structural groups (s^*) respectively studied in this work.

The advantages of Σs^* as a nonpolar parameter for hydrocarbons are immediately obvious. The value of Σs^* can be calculated for a hydrocarbon from its chemical structure using the additivity principle. The scale of Σs^* may be expected to be consistent within each of the groups of aromatic cyclic, and noncyclic hydrocarbons.

Other Parameters. There are other methods of expressing the hydrophobicity of organic molecules. These methods are also essentially based on solubilities and involve data on free energies of transfer of the organic molecule from water to a nonaqueous phase, or data on partition coefficients between water and a nonaqueous phase.[15–20] Such methods of expressing the hydrophobicity of a hydrocarbon do not have either the convenience or the generality of the Σs^* parameter developed above.

Modified Small's Number (Σs^*) and Membrane Performance

Data for Hydrocarbons. Figure 5 gives solute separation data as a function of Σs^* for the 13 aromatic hydrocarbons, 10 cyclic hydrocarbons, and 16 noncyclic hydrocarbons listed in Table I for films 1, 3, and 4 specified in Table II. The values of Σs^* for the solutes used were in the range 425 to 924 for aromatic hydrocarbons, 521 to 931 for cyclic hydrocarbons, and 369 to 960 for the noncyclic hydrocarbons. Figure 5 also gives the corresponding $[PWP]$ and $[PR]$ data in terms of ω (*l.*/g-mole) defined as

$$\omega = \frac{[PWP] - [PR]}{[PWP](\text{feed concn.})}$$

which gives a relative measure of the decrease in fluid permeation rate through the membrane, brought about by the pore-blocking effect of the preferentially sorbed hydrocarbon solute at the membrane–solution interface under the specified operating conditions of the experiment. The data on film specifications given in Table II show that the average pore size on the membrane surface increased in the order film 1 < film 3 < film 4. Though there is some scatter in the experimental data presented in Figure 5, the results lead to several conclusions of general significance, which are discussed below. The scatter in experimental data may be attributed to inherent errors involved in using very low solute concentrations in the feed solutions and also to the differences in mass transfer coefficients for the solutes used under the conditions of the experiments.

Effect of Σs^* on ω. Figure 5 shows that with respect to each class of hydrocarbons studied, the value of ω was smaller for the film whose average pore size on membrane surface was bigger. This is understandable because the blocking effect must be less when the pore size on the membrane surface is bigger. The differences in the values of ω for films 1, 3, and 4 were far more for the aromatic hydrocarbons than for the cyclic and noncyclic hydrocarbons. These data show that the thickness of the preferentially sorbed layer is significantly more for aromatic hydrocarbons than for the cyclic and noncyclic hydrocarbons; this is confirmed by the corresponding solute separation data.

For each film, the value of ω decreased in the order aromatic hydrocarbons > cyclic hydrocarbons > noncyclic hydrocarbons in the entire range of Σs^* values studied. The above order is the same as that obtained for the corresponding solute separations which shows that blocking effect and solute separation are directly related. Further, for aromatic hydrocarbon, ω increased with increase in Σs^*. This increase was relatively steep in the

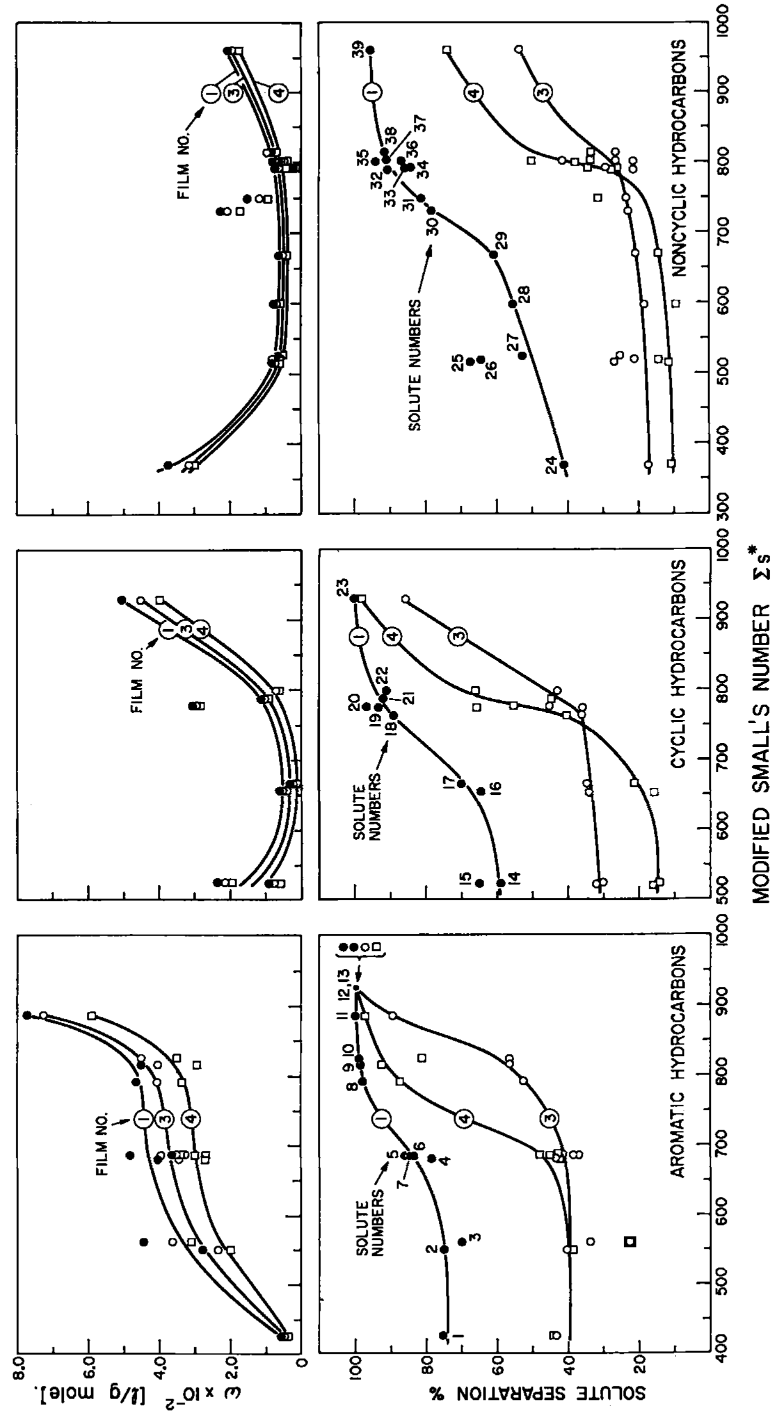


Fig. 5. Modified Small's number (Σs^*) vs. data on membrane performance. Solute numbers same as in Table I; operating pressure, 250 psig.

Σs^* ranges of 425 to 550 and 800 to 924; in the intermediate region of Σs^* ω values changed very little. For cyclic hydrocarbons, ω passed through a minimum at a Σs^* value of $\sim$700; and for noncyclic hydrocarbons, ω passed through a minimum in the Σs^* region of $\sim$500 to 800. These data seem to indicate the changes in blocking effect caused by changes in the extent and mobility of the preferentially sorbed solute at the membrane–solution interface.

Effect of Σs^* on Solute Separation. Figure 5 shows that, with respect to each film, solute separation tended to increase with increase in Σs^*, and this increase was relatively steep in the Σs^* range of 650 to 850 for all the hydrocarbon solutes studied; further, solute separation decreased in the order aromatic hydrocarbon > cyclic hydrocarbon > noncyclic hydrocarbon at any given value of Σs^*.

With respect to each class of hydrocarbons, solute separations were the highest for film 1 (whose average pore size on membrane surface was the smallest) in the entire range of Σs^* values studied. For films 3 and 4, however, the order of solute separation was not the same for all the solution systems studied. With respect to aromatic hydrocarbons, solute separations were essentially the same for films 3 and 4 when Σs^* values were less than 650; at higher Σs^* values, solute separations were higher for film 4 whose average pore size on membrane surface was bigger. With respect to cyclic and noncyclic hydrocarbons, solute separations were lower for film 4 at Σs^* values lower than 750, and higher for the same film at Σs^* values lower than 750.

The above results are more explicity described by Figure 6, which gives solute separation as a function of pore size on membrane surface expressed in an arbitrary scale for Σs^* values of 500, 750, and 850 chosen just for illustration. Figure 6 shows that in the range of average pore sizes between those represented by films 4 and 1 (which range includes the average pore size represented by film 3), solute separation could increase, remain unchanged and then increase, or pass through a minimum depending on the class of hydrocarbons considered and their Σs^* values. For all the three classes of hydrocarbons studied, solute separation increased with decrease in average pore size when the latter was in the range of small values between those represented by films 3 and 1. In the case of cyclic and noncyclic hydrocarbons, solute separation increased when Σs^* was 500, remained unchanged when Σs^* was 750, and decreased when Σs^* was 850, with decrease in pore size in the range of intermediate pore sizes between those represented by films 4 and 3. In the same range of pore sizes, in the case of aromatic hydrocarbons, solute separation remained unchanged when Σs^* was 500 and decreased when Σs^* values were 750 and 850, with decrease in pore size.

The foregoing results are understandable on the following basis. As Σs^* increases, preferential sorption of solute at the membrane–solution interface increases resulting in an increase in the thickness of either (a) the part of the preferentially sorbed layer containing the less-mobile solute mole-

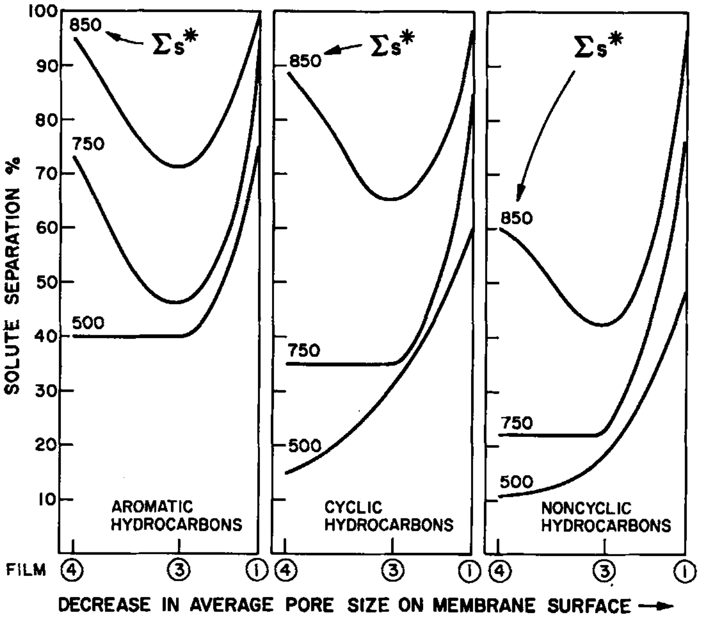


Fig. 6. Effect of decrease in average pore size on membrane surface and Σs^* of hydrocarbon on solute separation in reverse osmosis, data for films 4, 3, and 1 at 250 psig.

cules, (b) the part of the preferentially sorbed layer containing the immobile solute molecules, or (c) both the above parts of the preferentially sorbed layer. The change (a) is predominant at relatively low values of Σs^*, the change (b) is predominant at high values of Σs^*, and the change (c) is predominant at intermediate values of Σs^*.

Since positive solute separation in reverse osmosis is the result of lower mobility of the solute molecules compared to that of water in the interfacial layer, an increase in Σs^* tends to increase solute separation, and this tendency is greatest at the intermediate range of Σs^* values where the change (c) is predominant.

Since the pore-blocking effect is more due to immobile solute molecules than the mobile ones, it is reasonable to expect ω to be affected very little by change (a) above and to increase steeply by changes (b) and (c) above. This is confirmed by the data given in Figure 5 for the change in ω with increase in Σs^* for all solutes except cyclopentene, cycloheptatriene, and 1,6-heptadiyne (solutes 14, 15, and 24), whose Σs^* values are 521, 524, and 369 respectively. The high values of ω obtained for the above three solutes whose Σs^* values are relatively low indicate the possible existence of additional factors affecting ω and hence the need for further investigations with the above solutes.

The effect of pore size on solute separation for a given value of Σs^* is particularly interesting as illustrated in Figure 7. Solute separation is a function of the relative transport of solute and solvent through the pore

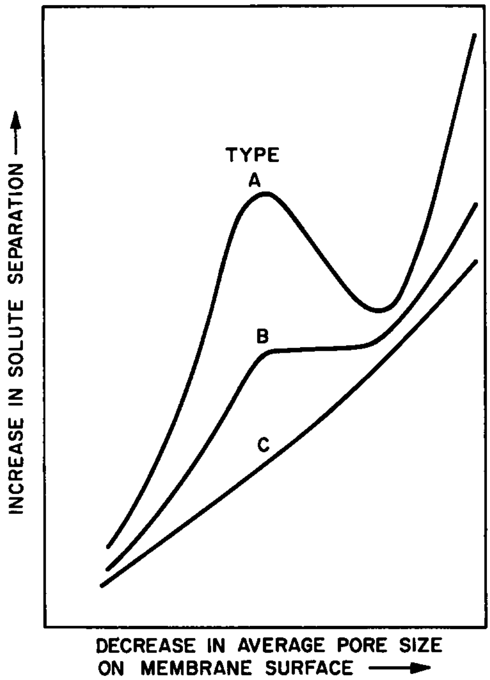


Fig. 7. General correlation of decrease in average pore size on membrane surface and Σs^* of hydrocarbon on solute separation in reverse osmosis.

area on the membrane surface. In the general case, the above pore area may be considered to consist of three distinct regions, namely, (i) the "bulk solution region" in the middle of the pore unaffected by the interfacial forces, (ii) the "less-mobile solute region" consisting of a part of the interfacial region where the preferentially sorbed solute molecules are less mobile than water, and (iii) the "immobile solute region" immediately next to the membrane surface consisting of the remaining part of the interfacial region where the preferentially sorbed solute molecules are far less mobile than water or practically immobile. In the bulk solution region, the velocity of solute through the pore is the same as that of water and no solute separation results by fluid permeation through this region of the pore. In the less-mobile and immobile solute regions, the solute concentration is higher than in the bulk solution region, but the average velocity of solute through the above regions of the pore is less than that of water. When the above average velocity of solute is sufficiently low (more than enough to compensate for the increased solute concentration in the preferentially sorbed region), fluid permeation through the less-mobile and immobile solute regions of the pore results in positive solute separation in reverse osmosis. This is obviously the case with respect to all the hydrocarbon solution systems studied in this work. The effect of size of pores (on membrane surface) on solute separation in such a case is best understood by considering separately the effect of variation in the magnitude of the above three regions on overall solute separation.

First consider solute separation in reverse osmosis with respect to an aqueous solution of a hydrocarbon whose Σs^* value is high. Let the total thickness t of the preferentially sorbed interfacial layer consist of an immobile solute layer of thickness t_{im}, and a less-mobile solute layer of thickness $(t - t_{im})$. Assuming, for simplicity, circular pores of average diameter d on the membrane surface, the effect of progressive decrease in d on solute separation may be considered for three typical cases:

Case 1: $d > 2t$. In this case, the bulk solution region controls solute separation. A progressive decrease in pore size results in a rapid decrease in the contribution of bulk solution flow to total flow through the membrane. Consequently, solute separation increases with decrease in pore size on membrane surface.

Case 2: $2t > d > 2t_{im}$. In this case, the less-mobile solute region controls solute separation. In the pore area, the above region overlaps each other resulting in an increase in solute concentration in the pore. A progressive decrease in pore size results in a corresponding increase in such overlap and hence solute concentration in the pore. The permeation of this concentrated solution through the pore tends to decrease overall solute separation in reverse osmois. Consequently, solute separation decreases with decrease in pore size on the membrane surface.

Case 3: $d < 2t_{im}$. In this case, the immobile solute region controls solute separation. In the pore area, the above region overlaps each other resulting in a concentration of immobile solutes in the pore and a consequent increase in pore-blocking effect. Even though solute concentration is higher in the pore area, the relative immobility of the solute molecules decreases their permeation through the pore, which results in higher solute separation. Consequently, solute separation increases with decrease in pore size on the membrane surface.

On the basis of the above controlling factors, one can conclude that for the hydrocarbon solute under consideration, a progressive decrease in average pore size on the membrane surface should result in an initial increase in solute separation with decrease in pore size, followed by a decrease in solute separation with further decrease in pore size and an increase in solute separation with still further decrease in pore size. This is illustrated by the type-A curve in Figure 7 which shows the existence of both a maximum and minimum in solute separation with progressive decrease in pore size on the membrane surface.

Next, consider the correlation of solute separation versus decrease in pore size on membrane surface for a hydrocarbon solute whose Σs^* value is much smaller compared to that considered above. For such as solute, both t and the difference in average mobility of solute and that of water in the less-mobile solute region may be expected to be smaller. For such a case, solute separation should be less for any given pore size, and the effect of the less-mobile solute region on solute separation should also be small. Consequently, solute separation may be expected to increase continuously with decrease in average pore size on membrane surface. Such a correlation is represented by the type-C curve in Figure 7. From similar considerations, the corresponding correlation for a hydrocarbon solute with an intermediate Σs^* value may be given by the type-B curve in Figure 7, which type is intermediate between the types A and C in the same figure.

Comparing Figures 6 and 7, it is clear that the form of the correlations given in Figure 6 is similar to part (right side) of the type-A, B, and C curves shown in Figure 7. These results indicated the possibility that correlations more fully similar to those given in Figure 7 could be expected if only solute separation data were available for an extended range of average pore sizes on the membrane surface. This possibility was then tested.

For the purpose of this test, two solutes (one with a high Σs^* and another with a low Σs^*) were chosen from each of the three groups of the hydrocarbons studied, and reverse osmosis experiments at 250 psig were carried out with five samples of cellulose acetate membranes of different surface porosities. The solutes chosen were cumene ($\Sigma s^* = 791$) and toluene ($\Sigma s^* = 549$) representing aromatic hydrocarbons, methyl cyclopentane ($\Sigma s^* = 774$) and cycloheptatriene ($\Sigma s^* = 524$) representing cyclic hydrocarbons, and 1,6-heptadiene ($\Sigma s^* = 801$) and 1,5-hexadiene ($\Sigma s^* = 668$) representing noncyclic hydrocarbons. The membranes used were films 1, 2, 3, 4, and 5 whose average pore sizes were represented by sodium chloride separations of 94.7, 90.4, 87.0, 79.0, and 63.3, respectively, obtained with a 1500-ppm $NaCl-H_2O$ feed solution at 250 psig. The solute separation data obtained for the hydrocarbons with the above films are given in Figure 8.

Figure 8 shows that solute separation passed through a maximum and then a minimum with progressive decrease in average pore size on membrane surface for all the three high Σs^* solutes, namely cumene, methylcyclopentane, and 1,6-heptadiene; for each of these hydrocarbons, the solute separation-versus-decrease in pore size correlation was similar to the type-A curve shown in Figure 7. With respect to the low Σs^* solutes, the corresponding correlation for toluene was similar to the type-B curve, and the correlations for cycloheptatriene and 1,5-hexadiene were similar to the type-C curve shown in Figure 7. Thus the results given in Figure 8 offer firm experimental evidence for the validity of transport mechanism discussed above for the reverse osmosis separations of hydrocarbons in aqueous solutions using porous cellulose acetate membranes.

Effect of Σs^*, Operating Pressure, and Average Pore Size on Membrane Performance. The effect of operating pressure on membrane performance for the system *p*-chlorophenol–water has been discussed earlier.[3] On the basis of this discussion and the solute separation-versus-decrease in pore size correlations presented in the foregoing section, some interesting results may be expected by a study of the combined effect of Σs^*, operating pressure, and average pore size on overall membrane performance. This is illustrated in Figures 9 and 10 for two typical hydrocarbon solutes, namely,

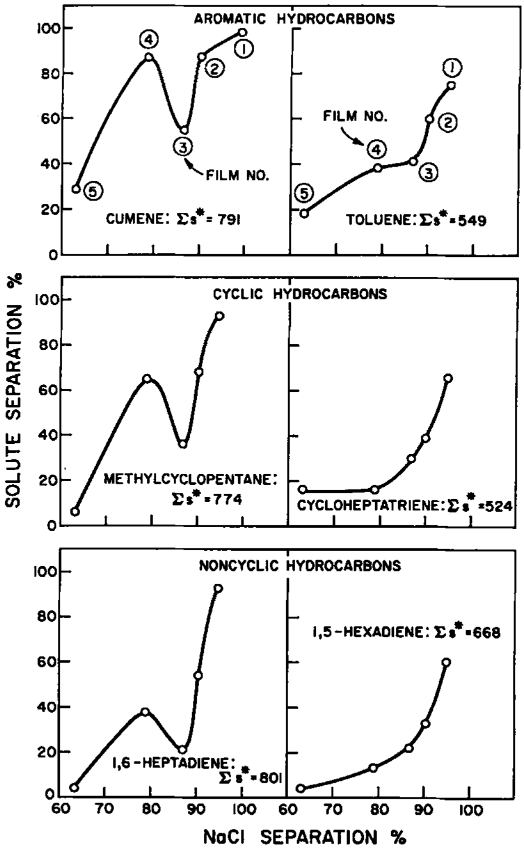


Fig. 8. Data on the effect of decrease in average pore size on membrane surface on reverse osmosis separation of different hydrocarbon solutes. Operating pressure, 250 psig.

benzene and cumene. Benzene was chosen because of its low Σs* value (425), and cumene, because of its high Σs* value (791).

Reverse osmosis data on solute separation, product rate, and [*PR*]/[*PWP*] ratio for aqueous benzene feed solutions are presented in Figure 9. In these experiments, the solute concentrations used in the feed solutions were in the range of 0.00046 to 0.00082 g-mole/l. (36 to 64 ppm). The operating pressures used varied in the range of 50 to 500 psig. Six different samples of cellulose acetate membranes (films 91, 92, 93, 94, 95, and 96) of different surface porosites were used. The average pore sizes on the membrane surface for each of these films are represented in Figure 9 in terms of their respective data on sodium chloride separations obtained with 1500 ppm $NaCl-H_2O$ feed solutions at 250 psig; the latter sodium chloride separations varied in the range of 63.0% to 93.8%.

Similar reverse osmosis data for aqueous cumene feed solutions are presented in Figure 10. In these experiments, the solute concentrations used

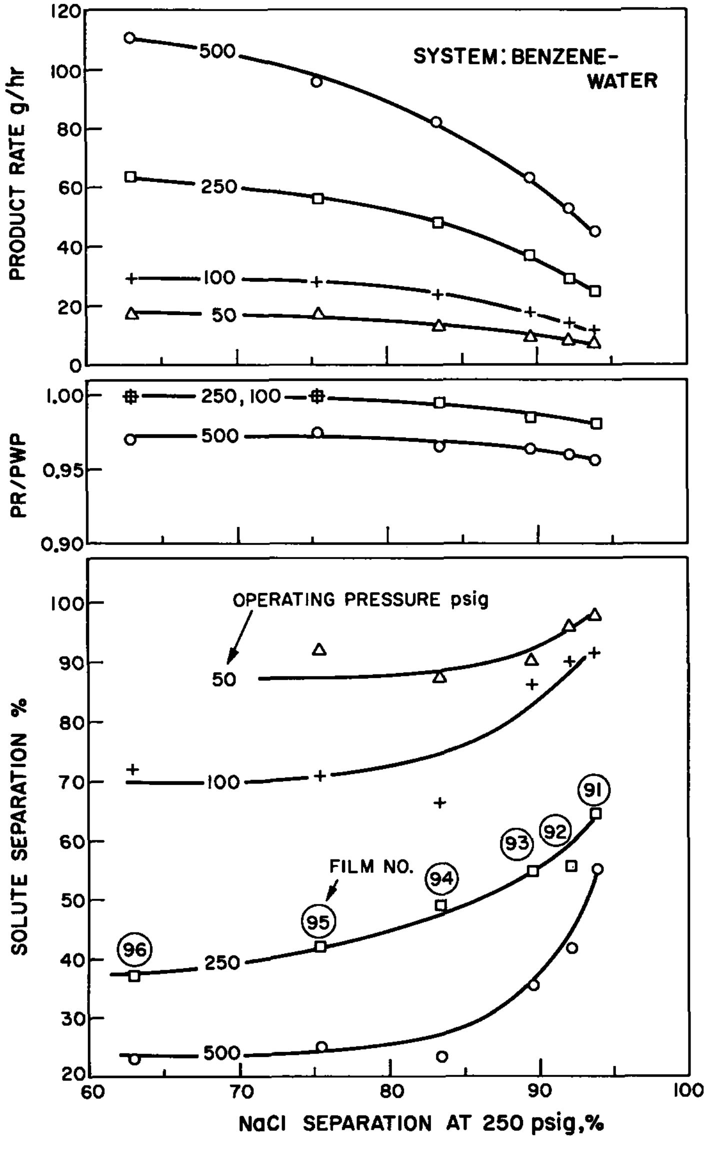


Fig. 9. Effect of operating pressure and decrease in average pore size on membrane surface on membrane performance for the reverse osmosis separation of benzene in aqueous solutions. Film area, 7.6 cm^2.

in the feed solutions were in the range of 0.00016 to 0.00044 g-mole/l. (19 to 53 ppm). The operating pressures used varied in the range of 100 to 1500 psig. Six different samples of cellulose acetate membranes (films 101, 102, 103, 104, 105, and 106) of different surface porosities were used. The average pore sizes on the membrane surface for each of these films are represented in Figure 10 in terms of their respective data on sodium chloride

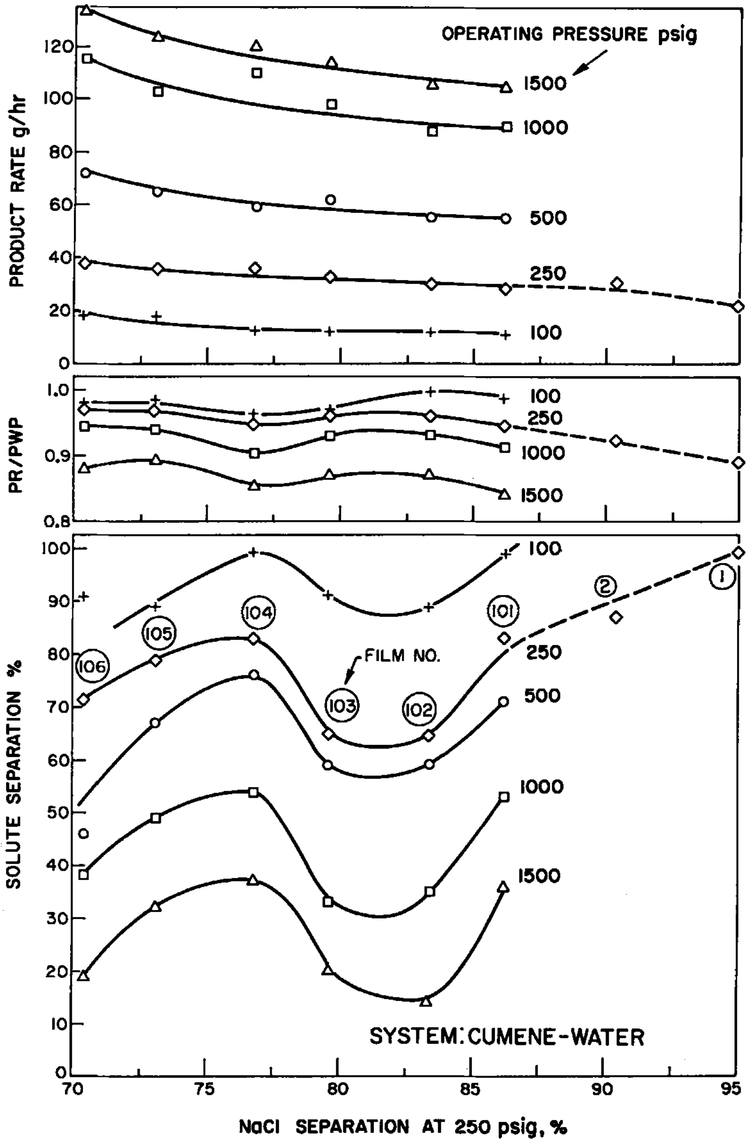


Fig. 10. Effect of operating pressure and decrease in average pore size on membrane surface on membrane performance for the reverse osmosis separation of cumene in aqueous solutions. Film area, 7.6 cm^2.

separations obtained with 1500 ppm NaCl–H_2O feed solutions at 250 psig; the latter sodium chloride separations varied in the range of 70.4% to 86.2%. Reverse osmosis data for films 1 and 2 at 250 psig given in Figure 2 are also included in Figure 10 to illustrate the effect of extension of the above range.

The experimental results given in Figures 9 and 10 are of both fundamental and practical interest. Since the data on solute separation cover a wide range both for benzene (22% to 98%) and cumene (14% to 99%), the mechanism of reverse osmosis transport representing the above data has a firm experimental basis.

At each of the operating pressures studied, whereas solute separation for benzene increased progressively with decrease in average pore size on the membrane surface, solute separation for cumene passed through a maximum and a minimum with progressive decrease in average pore size on the membrane surface. Thus, at each pressure, the solute separation-versus-decrease in pore size correlation for benzene is similar to the type-C curve in Figure 7, which is characteristic of low Σs^* solutes; and the corresponding correlation for cumene is similar to the type-A curve in Figure 7, which is characteristic of high Σs^* solutes. These data indicate that the mechanism of reverse osmosis transport discussed above is valid for the entire range of operating pressures studied.

With each film tested, solute separation decreased with increase in operating pressure both for benzene and cumene. These data confirm the basic experimental criterion showing the preferential sorption of solute at the membrane solution interface under the conditions of reverse osmosis operation.

For both the benzene and cumene systems, at each operating pressure, the $[PR]/[PWP]$ ratio decreased with increase in solute separation in the entire range of membrane pore sizes studied; further, the $[PR]/[PWP]$ ratio decreased with increase in operating pressure for each membrane. These data are similar to those reported earlier[3] for the *p*-chlorophenol–water system, and they show that the pore blocking effect of the preferentially sorbed solute is higher at higher solute separations and at higher operating pressures. This result emerges as a direct consequence of the transport mechanism discussed above.

Finally, referring to solute separation data for both benzene and cumene, the results illustrate the possibility that the same level of solute separation is obtainable by different combinations of average pore size on membrane surface and operating pressure. This possibility is of practical interest especially for the reverse osmosis separation of high Σs^* hydrocarbon solutes in aqueous solutions using porous cellulose acetate membranes. For example, Figure 10 shows that 99% separation for cumene was obtained with films 104 and 101 at 100 psig, and also with film 1 at 250 psig. From a practical point of view, it is obviously advantageous to use the membrane with the biggest average pore size (film 104) at the lowest operating pressure (100 psig) to obtain the highest solute separation (99%) with the lowest pore-blocking effect ($[PR]/[PWP]$ ratio) and hence highest product rate at the operating pressure.

CONCLUSIONS

The modified Small's number has proved to be a useful parameter to express the hydrophobicity, or nonpolar character, of hydrocarbons for purposes of correlation of reverse osmosis data. The above parameter offers a basis for the development of necessary transport equations applicable for the reverse osmosis separation of nonpolar solutes in aqueous solutions using porous cellulose acetate membranes. The correlations presented in this paper open new avenues of reverse osmosis research and development particularly relevant to food processing and waste water treatment applications involving nonpolar solutes in aqueous solutions.

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