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Extraction of Naphthenic Acid from Kerosene Using Porous and Nonporous Polymeric Membranes

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ABSTRACT

A systematic study of membrane-assisted extraction of naphthenic acids from hydrocarbon fractions by aqueous caustic soda using both porous and nonporous membranes is reported. The effects of hydrodynamic factors, concentration of naphthenic acids and caustic soda, and temperature on the transmembrane flux are discerned. The film model is used to determine the intrinsic mass transfer characteristics of the membranes.

Key Words. Membrane; Extraction; Naphthenic acids; Hydrocarbon fractions

INTRODUCTION

Solvent extraction is widely used in the chemical industry for a variety of applications. In general, solvent extraction consists of two stages: 1) dispersion of one phase in the other for efficient contact and 2) separation of the two phases. The efficiencies of these two stages depend upon such system properties as the interfacial tension and the viscosities of the two

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phases. Systems which are easy to disperse are difficult to coalesce/separate and vice versa. There are a number of situations in which the second stage of separation poses serious problems because of a tendency to form stable emulsions. In such cases a nondispersive solvent extraction (NDSE) procedure has been suggested (1, 2). In NDSE the two phases are separated by a membrane which allows the transfer of solute without physical contact. The membrane used can be nonporous (1) or porous (2).

Crude oil contains a number of contaminants [naphthenic acids (NA), mercaptans, etc.] which require chemical treatment for their removal. Naphthenic acid is the generic name for a family of compounds that belong to the broad category of carboxylic acids where one or a combination of saturated ring hydrocarbons have the organic acid (COOH) group attached to one of the carbon atom. Acidity of the crude oil is mainly due to the NA present in the crude. Crudes from many sources contain substantial amounts of NA, which create several processing difficulties in refineries (3, 4). The acidity of the crude leads to corrosion problems in such refinery operations as vacuum distillation or hydroprocessing of gas oil fraction. The middle distillate fractions derived from the crude oil contain a major portion of the original NA in the crude. Turbine or jet fuel is a rapidly growing refinery product. Jet fuel must meet very stringent international specifications, one of which is the maximum acidity of the fuel.

The chemical treatment of the crude or any fraction for removal of NA involves alkali wash; the process is called Napfining (5). However, direct alkali contact results in emulsions which are difficult to break. Also, some of the sodium naphthenate formed and water are carried over to the organic phase, leading to several difficulties. This is an ideal application for NDSE. Both porous and nonporous membranes can be used for NDSE. Porous membranes are expected to yield higher extraction rates than nonporous membranes because to the higher diffusion coefficients in the organic solvent filling the pores as compared to the diffusion coefficient in the polymer matrix of the nonporous membrane. However, porous membranes are prone to solvent seepage across the membrane if an interface immobilizing pressure is not carefully maintained (6). In this event, the porous membrane can lead to emulsion formation. Such a situation can be avoided by using nonporous membranes (7). Thus, although nonporous membranes yield lower fluxes, they may be preferred over porous membranes when solvent carry-over must be totally avoided.

This study deals with a membrane-based extaction, Perstraction, of NA in aqueous sodium hydroxide. Both porous and nonporous membranes were employed for this purpose in order to determine the relative reduction in the flux in a nonporous membrane below that for a porous membrane.

THEORY

Extraction with Porous Membranes

Kiani et al. (2) extensively discussed the mechanism of extraction using porous membranes. The steps involved in the overall extraction process have been delineated. Using the flux equations for the individual steps and the resistance in a series model, Kiani et al. (2) derived expressions for the overall mass transfer coefficients in terms of the individual mass transfer coefficients and relevant system properties for a variety of cases including hydrophobic and hydrophilic membranes. This approach allows the calculation of intrinsic membrane tortuosity. The expression developed by Kiani et al. for a hydrophobic membrane is

$$\frac{1}{K_o} = \frac{m}{k_w} + \frac{1}{k_m} + \frac{1}{k_o} \tag{1}$$

The intrinsic membrane mass transfer coefficient, k_m, can be determined once the liquid film resistances on either side of the membrane are eliminated. In the present case, liquid film resistances can be eliminated by increasing the speed of agitation in both phases (discussed later). Equation (1) under these condition reduces to

$$\frac{1}{K_o} = \frac{1}{k_m} \tag{2}$$

The flux expression is then

$$J = k_m(C_{bo} - C_{bw}) \tag{3}$$

The flux across the membrane is determined experimentally. C_{bw} is the concentration of dissolved NA in the bulk aqueous phase. In the presence of a finite concentration of NaOH in the aqueous phase, $C_{bw} = 0$, since NA reacts irreversibly with the alkali:

$$J = k_m C_{bo} \tag{4}$$

Thus, by knowing J and C_{bo}, the intrinsic membrane mass transfer coefficient, k_m, can be determined using Eq. (4).

Extraction with Nonporous Membranes

Figure 1 shows the concentration profile of the diffusing solute. The transport process is similar to that described by Kiani et al. (2) with a few minor differences arising out of the nonporous nature of the membrane. The following distinct steps, which comprise the overall process, can be discerned:

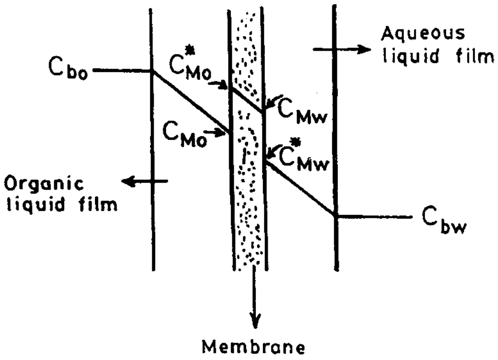

FIG. 1 Concentration profiles with liquid film mass transfer resistances.

1. Transfer of solute from the bulk organic phase to the membrane surface
2. Sorption of solute by the membrane
3. Diffusion of the solute across the membrane
4. Partitioning of solute from the membrane surface to the aqueous phase
5. Transfer of the solute from the membrane surface to the bulk aqueous phase

The sorption and the partitioning steps, Steps 2 and 4, respectively, are assumed to occur at equilibrium and therefore do not contribute to the overall resistance. The only difference between the present case and the porous membrane situation of Kiani et al. is that Step 2 or 4 is additional, depending upon whether the porous membrane is hydrophobic or hydrophilic, respectively. The rate expressions for the individual transport steps for the case of transfer from organic phase to aqueous phase can be written in a manner similar to Kiani et al. (2):

$$\text{Step 1:} \quad J_1 = k_o(C_{bo} - C_{mo}) \tag{5}$$

$$\text{Step 3:} \quad J_3 = k_m(C^*_{mo} - C_{mw}) \tag{6}$$

$$\text{Step 5:} \quad J_5 = k_w(C^*_{mw} - C_{bw}) \tag{7}$$

The equilibria for Steps 2 and 4 are described by

$$\text{Step 2:} \quad S_o = C^*_{mo}/C_{mo} \quad \text{or} \quad C^*_{mo} = S_oC_{mo} \tag{8}$$

$$\text{Step 4:} \quad S_w = C_{mw}/C^*_{mw} \quad \text{or} \quad C^*_{mw} = C_{mw}/S_w \tag{9}$$

By using Eq. (8), Eq. (6) can be written as

$$J_3 = k_m S_0 (C_{m0} - C'_{mo}) \tag{10}$$

where C'_{mo} is a fictitious organic phase concentration in equilibrium with the water side membrane phase concentration, C_{mw}.

Similarly, by using Eq. (9), Eq. (7) can be written as

$$J_5 = \frac{k_w}{S_w}(C_{mw} - C'_{mw}) \tag{11}$$

where C'_{mw} is a fictitious membrane phase concentration in equilibrium with the bulk aqueous phase concentration, C_{bw}. Equation (11) can be converted to an organic phase concentration basis by using the equilibrium relationship for Step 2. Thus:

$$J_5 = k_w \frac{S_o}{S_w}(C'_{mo} - C'_{bo}) \tag{12}$$

where C'_{bo} is a fictitious organic phase concentration in equilibrium (through the membrane phase) with the bulk water phase concentration, C_{bw}.

Equations (5), (10), and (12) can be written as

$$J_1/k_o = C_{bo} - C_{mo} \tag{13}$$

$$J_3/k_m S_o = C_{mo} - C'_{mo} \tag{14}$$

$$J_5 S_w/k_w S_o = C'_{mo} - C'_{bo} \tag{15}$$

At steady state, $J_1 = J_3 = J_5 = J$. J can be defined in terms of an overall concentration gradient and mass transfer coefficient. Thus:

$$J = K_o(C_{bo} - C'_{bo}) \tag{16}$$

Combining Eqs. (13) through (16), the following relationship between the overall mass transfer coefficient and the individual mass transfer coefficients is obtained:

$$\frac{1}{K_o} = \frac{1}{k_o} + \frac{1}{k_m S_o} + \frac{S_w}{S_o k_w} \tag{17}$$

In the present study the downstream phase NA concentration is essentially zero because NA reacts irreversibly with the alkali on the downstream side of the membrane. k_o and k_w take into account the solute diffusion through the liquid film on the upstream and downstream sides of the membrane, respectively. The mass transfer resistance for diffusion across the liquid films can be eliminated by increasing the speeds of agitation in the two vessels (described later). Thus, when the organic and aqueous film resistances are eliminated, Eq. (17) becomes

$$\frac{1}{K_o} = \frac{1}{k_m S_o} \tag{18}$$

The flux in this case is given by

$$J = k_m S_o C_{bo} \tag{19}$$

In the present work the experiments were conducted in a batchwise manner. For this case a differential mass balance gives the following expression for k_m:

$$k_m = \frac{V}{At} \ln \frac{C_{oi}}{C_{of}} \tag{20}$$

Equation (20) was used for calculating k_m from the experimental data for porous as well as nonporous membranes.

EXPERIMENTAL

Permeation Studies

Figure 2 shows the experimental setup employed for the study. Two glass vessels of 300 cm^3 capacity provided with baffles were connected by a bridge in which the membrane was located. The two vessels were provided with stirrers for agitation. The speeds of agitation in the two vessels could be varied independently. This assembly was kept in a constant temperature water bath. Commercial kerosene and NA having an acid value (AV) of 180 and commercial grade caustic soda were used in the experiments. Two types of membranes, porous and nonporous, were used. Tetratex, porous poly(tetrafluoroethylene) film, supplied by Tetratec Corporation, USA, was used as the porous hydrophobic membrane. The nonporous membrane used was a silicone rubber membrane, poly(dimethylsiloxane) (PDMS). The silicone rubber and crosslinker, supplied by Wacker Chemie, Germany, were mixed in the proportion of 9:1 and then spread on a Perspex sheet with the help of a bar coater. The resulting membrane was then annealed at 80°C for 8 hours.

The membrane was equilibrated with kerosene containing NA before the start of each experiment. Experiments were conducted over a wide range of NA concentrations (1000 to 3500 ppm), alkali concentrations (0.1 to 2 kg·mol/m^3), and varying speeds of agitation in the two vessels. The effective membrane area for extraction was 5.04×10^{-4} m^2. The kerosene phase was analyzed for NA before and after the experiments in accordance

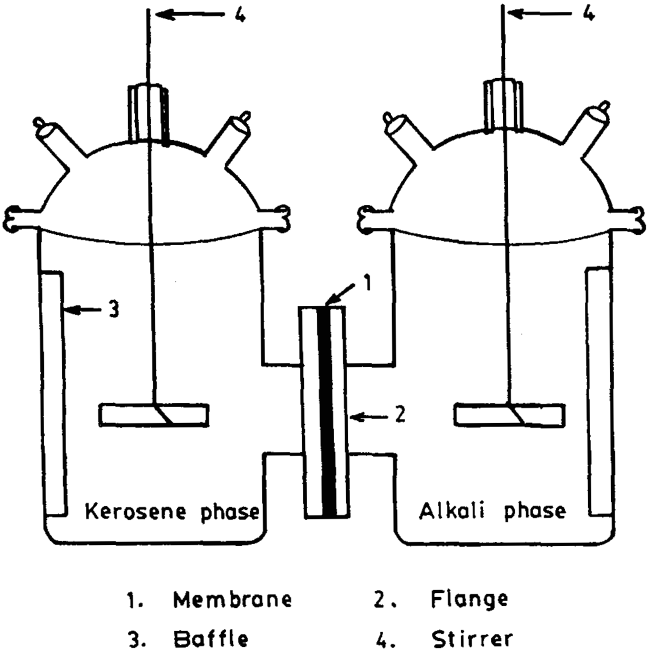

FIG. 2 Experimental setup used in the work.

with UOP method 587-71 (8). Experiments were carried out at 30, 40, and 50°C with a silicone rubber membrane and at 30°C with Tetratex film.

Sorption Studies

Silicone rubber films of known weight were immersed in a known volume of kerosene of differing NA concentration. These films were allowed to equilibrate over a period of 1 week at constant temperature. The films were removed and weighed after the superfluous liquid was wiped with tissue paper. The increase in weight of the film is due to the NA and kerosene sorbed by the film. In order to find out the amount of NA uptake of the films, these films were dipped in a known volume of 0.005 N sodium hydroxide solution and left for 2 days. The alkali solution was then titrated against 0.005 N sulfuric acid. For finding out the sorption of NA from water, a similar procedure was followed with varying concentrations of NA in water.

RESULTS AND DISCUSSION

Sorption

Figure 3 gives the sorption plots of solute concentration in the membrane against the feed concentration. It is evident that the sorption behavior of NA in silicone rubber film can be described by Henry's law.

Effect of Speed of Agitation in the Organic Phase

Figure 4 shows the variation of flux of NA with speed of agitation in the organic phase for nonporous and porous membranes. It can be seen that for all three membranes, there is initially a steep increase in the flux of NA with an increase in the speed of agitation. However, above a certain speed, termed the critical speed, N_{co}, the flux remains constant. It can be concluded that the organic phase resistance has been eliminated at the corresponding N_{co}.

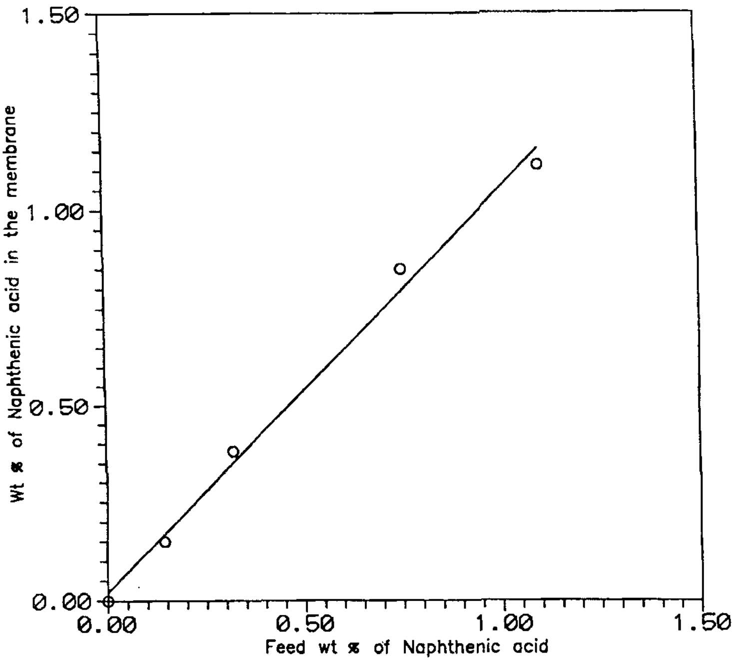

FIG. 3 Variation of membrane phase concentration with feed concentration: (O) silicone rubber membrane.

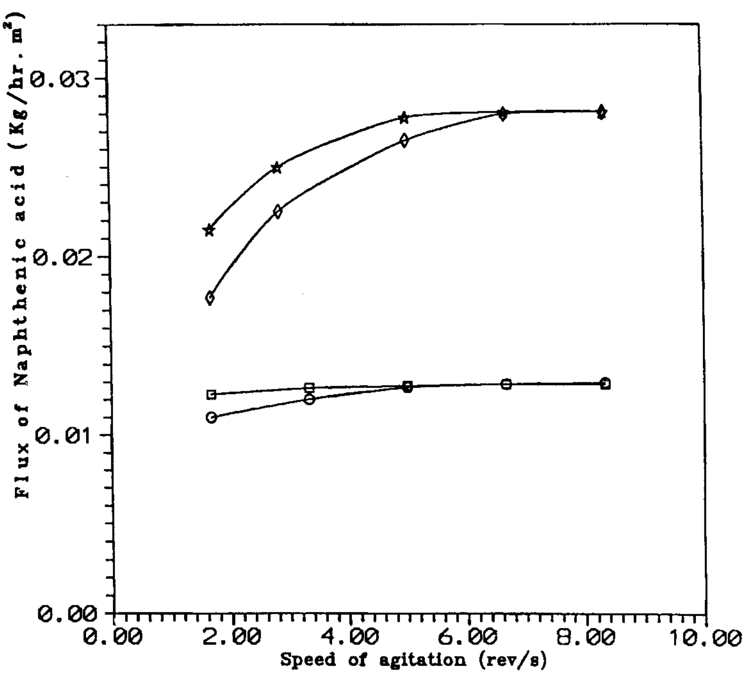

FIG. 4 Variation of NA flux with speed of agitation: (○) alkali phase/silicone rubber membrane, (□) organic phase/silicone rubber membrane, (◇) alkali phase/porous membrane, (☆) organic phase/porous membrane.

Effect of Speed of Agitation in the Alkali Phase

The behavior in this case is similar to that described above for the case of variation in the speed of agitation in the organic phase (Fig. 4). Above N_{cw}, the mass transfer resistance on the alkali side is eliminated.

From the above results it can be concluded that the organic and aqueous phase resistances are eliminated at lower speeds of agitation for the nonporous membranes compared to the porous membrane. The porous membrane is expected to offer less resistance compared to the nonporous membrane. Hence, the mass transfer resistance are eliminated at a higher speed of agitation for a porous membrane.

Effect of Alkali Concentration

The concentration of caustic soda in the aqueous compartment was varied while keeping the speeds of agitation in both compartments at relatively high levels. Figure 5 shows the variation of flux obtained at different alkali concentrations for porous as well as nonporous membranes.

Nonporous Membrane

It is evident from Fig. 5 that flux increases with an increase in alkali concentration up to 1.5 kg·mol/m^3 for a silicone rubber membrane.

Porous Membrane

It can be seen from Fig. 5 that flux increases with increasing alkali concentration up to 2 kg·mol/m^3, beyond which it remains constant.

The extraction of NA in the aqueous compartment is accompanied by a chemical reaction between NA and OH$^-$ ions. Thus, k_w is actually $(k_w)_R$, mass transfer coefficient with reaction. $(k_w)_R$ depends upon the concentration of OH$^-$. The reaction between the carboxylic group and OH$^-$ is unlikely to be different than an instantaneous reaction. For this

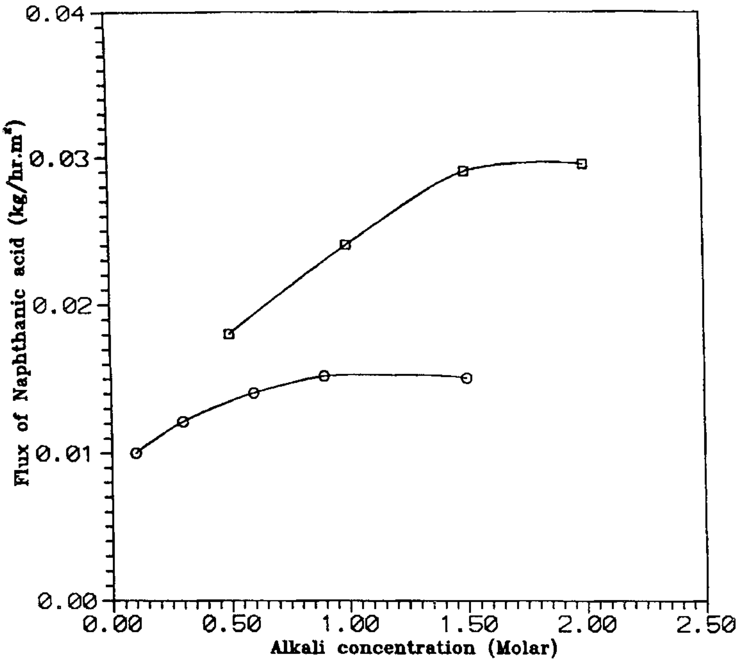

FIG. 5 Variation of NA flux with alkali phase concentration: (□) porous membrane, (○) silicone rubber membrane.

case, $(k_w)_R$ varies linearly with OH^- concentration (9). Thus, when OH^- concentration is initially low, $(k_w)_R$ is low and the aqueous phase resistance contributes significantly to the overall resistance. With increasing OH^- concentration, $(k_w)_R$ increases. Finally, at higher OH^- concentration, $(k_w)_R$ is relatively so large as to have a negligible effect on the flux.

Effect of NA Concentration in the Organic Phase

NA concentration in the organic phase was varied while using relatively high speeds of agitation (12 rev/s) in both compartments as well as using alkali concentrations of 2 kg·mol/m^3 in order to ensure that the membrane resistance is the chief contributor to the overall resistance. The fluxes for the porous and the nonporous membranes are given by Eqs. (4) and (19), respectively. Both these equations indicate that the flux is a linear function of the NA concentration in the organic phase. The experimental results shown in Fig. 6 also show a linear dependence of flux with NA concentration in the feed.

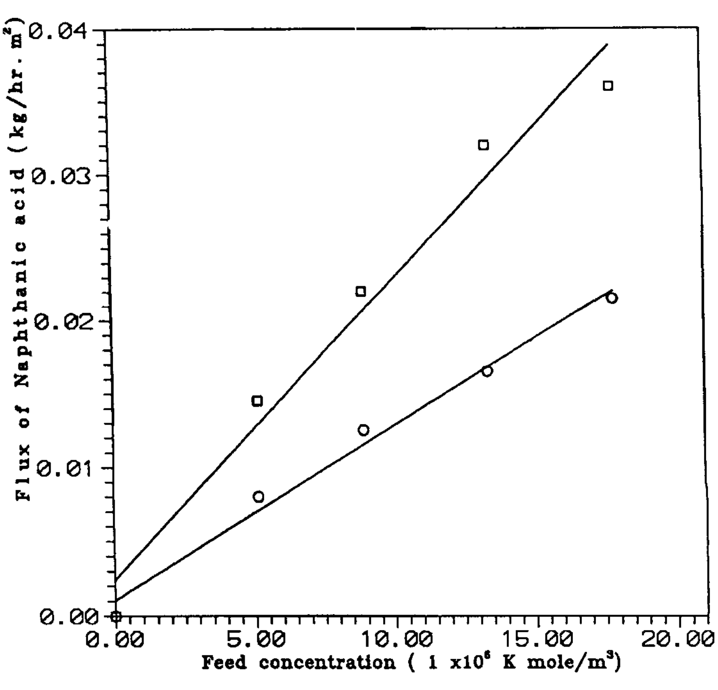

FIG. 6 Variation of NA flux with NA concentration: (□) porous membrane, (○) silicone rubber membrane.

Estimation of Membrane Characteristics

Porous Membrane

The intrinsic membrane mass transfer coefficient, k_{m}, is related to the physicochemical properties and membrane characteristics (2):

$$k_{\mathrm{m}} = D_{\mathrm{L}}\epsilon/\tau\delta \tag{21}$$

For the Tetratec membrane used in this work, $\epsilon = 0.85$ and $\delta = 38 \times 10^{-6}$ m. D_{o} for NA in kerosene was estimated by employing the Wilke–Chang (10) equation as 6.23×10^{-10} m^2/s and $k_{\mathrm{m}} = 4.17 \times 10^{-6}$ m/s (from Eq. 20). Using these values, τ for the Tetratec membrane was found to be 3.35, which is comparable to the value of 2 obtained by Kiani et al. (2) for the Celgard 2400 membrane.

Nonporous Membrane

k_{m} is related to the physicochemical parameters by

$$k_{\mathrm{m}} = D_{\mathrm{m}}/\delta \tag{22}$$

For the PDMS membrane, $k_{\mathrm{m}} = 1.7 \times 10^{-6}$ m/s (from Eq. 20), $\delta = 40 \times 10^{-6}$ m. Using these values, the diffusivity of NA in PDMS was found to be 6.778×10^{-11} m^2/s.

Comparison of Membrane Performance

The performance of the various membranes can be compared by using the membrane transfer coefficient, k_{m}, for each. k_{m} values obtained are listed in Table 1, which shows the following performance order: Porous membrane > silicone rubber membrane. This order reflects the fact that the diffusivity of the solute is greater in the organic phase as compared to the polymer phase.

TABLE 1
Calculated Membrane Properties

Property	Silicone rubber membrane (40 μm)	PTFE (porous) (38 μm)
τ	—	3.35
k_{m}(m/s)	4.3×10^{-6}	7.37×10^{-6}
D_{m}(m^2/s)	6.778×10^{-11}	—

CONCLUSIONS

A detailed study of the extraction of naphthenic acid from kerosene was carried out using both porous and nonporous membranes. An attempt was made to determine the intrinsic membrane mass transfer characteristics.

NOMENCLATURE

A	area of membrane, m^2
C_{bo}	bulk solute concentration in the organic phase, $kmol/m^3$
C'_{bo}	fictitious organic phase concentration in equilibrium (through the membrane phase) with the bulk water phase concentration, $kmol/m^3$
C_{bw}	bulk solute concentration in the aqueous phase, $kmol/m^3$
C_{mo}	solute concentration in the organic phase at the organic–membrane interface, $kmol/m^3$
C^*_{mo}	solute concentration in the membrane in equilibrium with the organic phase, $kmol/m^3$
C'_{mo}	fictitious organic phase concentration in equilibrium with the aqueous side membrane phase concentration, $kmol/m^3$
C_{mw}	solute concentration in the aqueous phase at the aqueous–membrane interface, $kmol/m^3$
C'_{mw}	fictitious membrane phase concentration in equilibrium with the bulk aqueous phase concentration, $kmol/m^3$
C^*_{mw}	solute concentration in the membrane in equilibrium with the aqueous phase, $kmol/m^3$
C_{0i}	initial feed concentration, $kmol/m^3$
C_{0f}	final feed concentration, $kmol/m^3$
D_L	diffusivity in the liquid phase, m^2/s
D_m	diffusivity in the membrane phase, m^2/s
J	molar flux, $kmol/m^2{\cdot}s$
k_o	organic side liquid film mass-transfer coefficient, m/s
k_w	aqueous side liquid film mass-transfer coefficient, m/s
k_m	membrane phase mass-transfer coefficient, m/s
$(k_w)_R$	mass-transfer coefficient with reaction, m/s
K_o	overall mass-transfer coefficient, m/s
m	distribution coefficient of solute, dimensionless
N_{co}	critical speed of agitation in the organic phase, rev/s
N_{cw}	critical speed of agitation in the aqueous phase, rev/s
S_o	membrane sorption coefficient in equilibrium with the organic phase, dimensionless

S_w	membrane sorption coefficient in equilibrium with the aqueous phase, dimensionless
t	experiment time, seconds
V	volume of the organic phase in the vessel, m^3

Greek Symbols

δ	thickness of the membrane, m
ϵ	porosity of the membrane, dimensionless
τ	membrane tortuosity factor, dimensionless

Subscripts

b	bulk phase
f	final value
i	initial value
m	membrane phase
o	organic phase
R	reaction
s	critical point
w	aqueous phase

Superscripts

$*$	equilibrium value
$'$	fictitious value

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