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Inversion of Selectivity in the Liquid Membrane Permeation Process

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Abstract

The dependence on different operative techniques of the separation factor obtained through liquid membrane permeation process is studied. An interpretation of inversion of selectivity is proposed by taking into account the different configurations of the liquid membranes.

INTRODUCTION

In order to justify the data obtained in the separation of hydrocarbons through liquid membrane permeation, Li (*1*, *2*) considered the process as based on diffusion and solubility of the components in the aqueous solution of surfactants.

Casamatta (*3*) considered the influence of the solubility of the components in water as the parameter which governs the separation.

Our results show the complexity of the phenomenon connected with permeation and its noticeable dependence on the different operative techniques employed. This paper reports some experimental results obtained at different operating conditions; in addition, an attempt at interpretation is made. This interpretation takes into account the configuration of the aqueous phase in the different runs so that the inversion of selectivity values with a change of the methodology employed can be explained.

EXPERIMENTAL SECTION

Materials

The compounds used in the runs as surfactants were: di"octyl" sodium sulfossuccinate (DOS) (Schuchardt, Munchen RFT); Saponin (Sap) (BDH Chemicals); and polyoxyethylene nonionic ethers $RO(CH_2\text{-}CH_2O)_nH$ (Marl Kreis Rechelinghausen, RFT); where R is either a lauryl group and $\bar{n}$ (degree of polymerization) = 15 (PL 15) or a *p-tert*-nonyl phenyl group with $\bar{n} = 5.4$ (PNP).

Commercially available hydrocarbons (Fluka 98% purity) were employed as the feed and the extractive solvent.

Procedures

The runs were carried out with two different methodologies. First, in the single drop technique (SD) the test tubes were closed at both ends with pierceable gaskets so the introduction of the feed and the sampling of the solvent for analysis and evaluation of the permeation could be performed. Second, in the emulsion technique the emulsion of the feed with the aqueous surfactant solution was achieved in suitable vessels (*4*) by mixing (intensity of mixing, 300 rpm) for variable times (5 to 30 min); the solvent was then added to the vessels and, according to the methodology used, the secondary mixing was or was not effected (intensity of mixing, 30 rpm for 30 sec). The permeation process was controlled by analysis of the solvent at different times so that the change of the concentration of the permeates could be evaluated.

RESULTS

The experimental data reported are expressed as a separation factor β' defined as $\beta' = (x_A/x_B)(y_B/y_A)$ where x_A and x_B, and y_A and y_B are, respectively, the molar concentration of Components A and B in the feed and in the solvent.

β' is a conservative parameter; as y_B/y_A increases with the time, x_A/x_B must also vary, so that values higher than those reported have to be expected.

TABLE 1

Separation Factors Evaluated for the Separations of Styrene (A)–Ethylbenzene (B) Using Various Surfactant Solutions (*n*-pentane as extractive solvent) with Different Techniques

	β'		
Surfactant solution	SD	EPS M	EWS M
DOS 1% wt	0.94	1.59	0.83
PL 15 1.5%–DOS 1%	0.86	1.61	—
Saponin 1%–DOS 0.5%	0.91	1.61	—
PNP 0.01%–DOS 1%	0.88	1.69	0.80

TABLE 2

Separation Factors Evaluated for the Separation of *n*-octane (A)–Ethylbenzene (B) Using Various Surfactant Solutions (*n*-pentane as extractive solvent) with Different Techniques

	β'		
Surfactant solution	SD	EPS M	EWS M
DOS 1% wt	11.92	0.67	18.91
DOS 1%–PL 15 2.5%	1.96	0.82	3.08
PL 15 2.5%–Saponin 10%	10.22	0.86	24.38
PL 15 2.5%–PNP 0.01%	1.57	0.74	—
DOS 1%–PNP 0.01%	1.38	0.78	2.56

In Table 1 the separation factors obtained for styrene (A)–ethylbenzene (B) mixtures, using different surfactant solutions and the three procedures above mentioned [single drop (SD), emulsion plus secondary mixing (EPS M), emulsion without a secondary mixing with the solvent (EWS M)], are reported.

Table 2 reports the values obtained with the same procedures for the *n*-octane–ethylbenzene mixture (*4*). From these data and other similar data obtained for other hydrocarbon systems it can be seen that the separation factors vary according to the methodology employed. The attainment of these different results, apparently in contrast with the different techniques, means that the "physical phenomenon" is quite complex.

INTERPRETATION

The above-mentioned experimental results emphasize that a change of the operating method may yield an inversion of selectivity. Indeed, for the styrene–ethylbenzene mixture (Table 1) we have a preferential transfer of styrene (more water-soluble component) in the SD runs and in the EWS M runs, while a preferential transfer of ethylbenzene is obtained when the emulsion undergoes a secondary stirring with the extraction solvent. The same behavior can be observed for the separation of the *n*-octane–ethylbenzene mixture (see Table 2).

According to Li (*1*, *2*), the selectivity difference between the SD runs and the diffusion column runs should be due to a different thinning rate of the liquid membrane. If the membrane is schematized by taking into account the various resistances in series (*3*), such an interpretation can also be extended to the emulsion case. That is, the flux of a component, in terms of the overall driving force existing between the feed and the solvent, should be (*3*)

$$N_A = K_A(c_{Af} - c_{As}) \tag{1}$$

where the overall exchange coefficient

$$\frac{1}{K_A} = \frac{1}{k_{A1}} + \frac{s}{H_A D_A} + \frac{1}{k_{A3}} \tag{2}$$

takes into account:

(1) The resistance offered by the boundary layer between a feed drop and the liquid membrane, together with the permeability of the first layer of surfactant, i.e.,

$$\frac{1}{k_{A1}} = \frac{1}{k'_1} + \frac{1}{P_{A1}} \tag{3}$$

(2) The resistance of the aqueous layer included between the two layers, internal and external, of oriented molecules of surfactant.

(3) The resistance offered by the second layer of surfactant and by the boundary layer between membrane and solvent, which can be expressed in the form of Eq. (3).

According to Eq. (2), the instantaneous selectivity of the process

$$\beta_i = \frac{K_A}{K_B} = \frac{N_A(c_{Bf} - c_{Bs})}{N_B(c_{Af} - c_{As})} \tag{4}$$

seems to be regulated (*3*) by the transport of the two components in the aqueous phase:

$$\beta_i = \frac{\dfrac{1}{k_{B1}} + \dfrac{s}{H_B D_B} + \dfrac{1}{k_{B3}}}{\dfrac{1}{k_{A1}} + \dfrac{s}{H_A D_A} + \dfrac{1}{k_{A3}}} \cong \frac{H_A D_A}{H_B D_B} \cong \frac{H_A}{H_B} \tag{5}$$

and consequently by their solubility in water, unless the aqueous layer is so thin that the other terms in Eq. (2) become significant, as might be the case in the emulsion runs.

The interpretation of the selectivity in terms of solubility, even if it is in agreement with the results obtained by Casamatta et al. (*3*, *5*), is not fully satisfactory, as has already been emphasized by Steele and Halligan (*6*). Moreover, some objections also remain when the permeabilities of the surfactant layers are taken into account in addition to the solubilities.

In the first place, Eq. (5), which is acceptable for a liquid membrane with a spheric symmetry, does not take into account the quite different geometric configuration assumed by the aqueous phase in the emulsion runs.

In the second place, by this interpretation it is not possible to give a clear explanation of the inversion of selectivity which occurs when the emulsion is stirred with the extraction solvent. Without doubt the secondary stirring favors the drainage of the excess surfactant solution (*2*) and, consequently, the thinning rate of the aqueous phase surrounding the feed droplets, but this drainage can be made small by working with surfactant/feed ratios close to the critical values for a stable emulsion (*2*, *7*). In any case, this drainage is not likely to be the only cause of so marked an effect on the selectivity; if it were so, we could expect a more regular variation of selectivity with an increase of the secondary stirring time instead of the abrupt transition occurring when we pass from the runs without secondary stirring to those carried out with a very short secondary stirring.

If we make reference to the geometric configuration of the system, it is evident that, in the emulsion runs without secondary stirring (see Fig. 1A1), the mass transfer conditions are quite similar to those occurring in the single drop runs (see Fig. 1A). The mass exchange with the solvent principally involves the droplets of the upper emulsion layer; each of them is largely submerged in the solvent phase from which they are separated by a spheric, cap-shaped liquid membrane. The remaining part of the interfacial surface between the surfactant solution and the solvent is formed by the spaces existing among the droplets, which contribute very

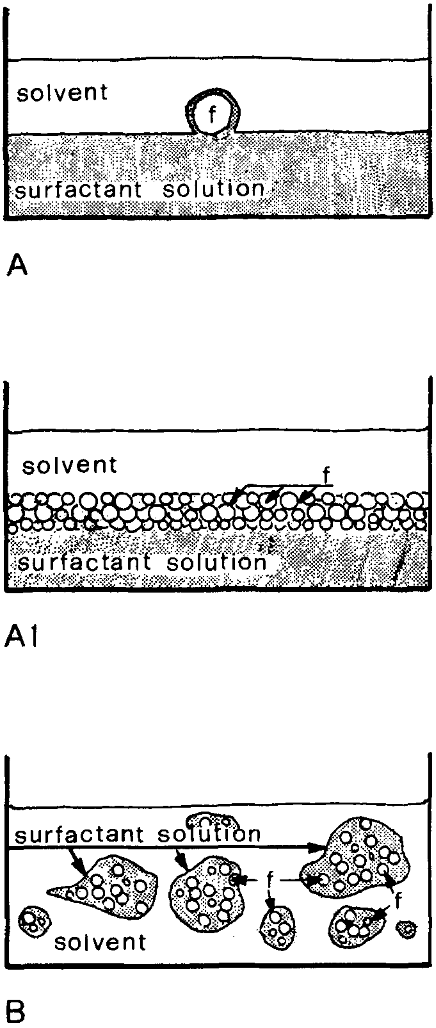

FIG. 1. Schematic diagram of liquid membrane system. (A) Single drop technique (f = feed). (A1) Emulsion technique without secondary mixing. (B) Emulsion technique with secondary mixing.

little (about 10% with reference to the semispheric emerging caps) to the overall interfacial surface and even less to the flux, since these spaces correspond to higher resistance paths.

Therefore, in the single drop runs as well as in the emulsion runs without secondary stirring, the fluxes can be expressed by Eqs. (1) and (2), and the selectivity is likely controlled by the solubilities in water. For the ethylbenzene–styrene system, the solubility ratio is about 0.5, in agreement with the value (lower than 1) of the separation factor.

Even with very little secondary stirring, the geometric configuration of the system changes greatly; the feed–surfactant emulsion, obtained with the primary stirring, results in a subdivision of the aggregates (*2*, *5*, *8*), each of them containing many feed droplets which remain suspended in the solvent phase (see Fig. 1B). In this case the reference to a simple liquid membrane with constant thickness is no more acceptable; rather each aggregate can be considered, in a first approximation, as a continuous spheric system in which simultaneous generation and diffusion phenomena occur with the same schematization adopted for a sinterized particle subjected to a gas–solid reaction (*9*, *10*).

The total flux coming out of a feed droplet

$$S_d N_{Ad} = \frac{d(V_d c_{Af})}{dt} = S_d k_{A1}\left(c_{Af} - \frac{c'_A}{H_A}\right) \tag{6}$$

can be considered as the generation rate inside the aggregate, so that the distribution of the concentration c'_A in the aqueous solution can be described by the differential equation

$$\frac{\partial c'_A}{\partial t} - D_A \varepsilon_d \frac{1}{R^2}\frac{\partial}{\partial R}\left(R^2 \frac{\partial c'_A}{\partial R}\right) = \frac{3(1-\varepsilon_d)k_{A1}}{r_d}\left(c_{Af} - \frac{c'_A}{H_A}\right) \tag{7}$$

with the boundary conditions:

$$t = 0: \qquad c'_A = H c^\circ_{Af}; \qquad c_{Af} = c^\circ_{Af} \tag{8}$$

$$R = R_p: \qquad -\varepsilon_d D_A \frac{\partial c'_A}{\partial R} = k_{A3}\left(\frac{c'_A}{H_A} - c_{As}\right) \tag{9}$$

$$R = 0: \qquad \frac{\partial c'_A}{\partial R} = 0 \tag{10}$$

where in the first of the conditions of Eq. (8) we have supposed that the feed and the aqueous solution have attained equilibrium during the primary stirring.

If only the initial instants of the process are taken into account, in Eq. (7) we can put $c_{Af}(R) = c_{Af}^{\circ} = \text{const}$, instead of expressing the change of $c_{Af}(R)$ as a function of time according to Eq. (6). Moreover, the accumulation term of Eq. (7) can be neglected in front of the diffusion and generation terms, since the concentration c'_{A} in the aqueous solution is always quite a bit lower than the concentration in the feed. Then, with reference to a quasi-stationary initial condition, we have:*

$$\frac{1}{\rho^2}\frac{\partial}{\partial\rho}\left(\rho^2\frac{\partial\gamma_A}{\partial\rho}\right) = \phi_A{}^2\gamma_A \tag{11}$$

where

$$\rho = \frac{R}{R_p}; \qquad \gamma_A = \frac{c'_A - H_A c_{Af}^{\circ}}{c_{Af}^{\circ}} \tag{12}$$

and

$$\phi_A = R_p\sqrt{\frac{3k_{A1}(1-\varepsilon_d)}{\varepsilon_d r_d H_A D_A}} \tag{13}$$

is a parameter quite similar to the Thiele modulus.

Therefore, the overall transfer coefficient to be introduced into Eq. (1) results (*12*) in

$$\frac{1}{K_A} = \frac{1}{k_{A3}} + \frac{r_d}{\eta_A(1-\varepsilon_d)R_p k_{A1}} \tag{14}$$

where

$$\eta_A = \frac{3}{\phi_A}\left(\frac{1}{\operatorname{tgh}\phi_A} - \frac{1}{\phi_A}\right) \tag{15}$$

The initial instantaneous selectivity should consequently depend on the permeabilities, on the solubilities, and on the geometric parameters in a much more complicated way than in Eq. (5). In particular, if ϕ_A and ϕ_B are much lower than unity, we have $\eta_A \cong \eta_B \cong 1$ and the selectivity results are independent of the component solubilities in water. As we have seen,

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*The above simplifying hypothesis is fully acceptable only for

$$\frac{r_d}{3k_{A1}H_A(1-\varepsilon_d)} \ll t \ll \frac{r_d}{3k_{A1}}$$

In fact, the time range during which the concentration c_{Af} can be considered as a constant is defined by the relaxation time of Eq. (6), a short initial interval excepted during which the system attains quasi-stationary conditions (*11*).

the same result is obtained from Eq. (5) by assuming a very low value for the film thickness s. From this point of view, the aggregate model is equivalent to the liquid membrane model.

However, as is more probable, if ϕ_A and ϕ_B are much higher than unity, i.e., if the diffusion through the aqueous phase is to be considered as the slowest phenomenon, Eq. (15) degenerates (*12*) into the asymptotic form $\eta_A = 3/\phi_A$, from which, neglecting the term $1/k_{A3}$, we obtain

$$N_{Ap} = \sqrt{3\varepsilon_d(1 - \varepsilon_d)r_d k_{A1} H_A D_A}(c_{Af} - c_{As}) \tag{16}$$

$$\beta_i^\circ = \sqrt{\frac{k_{A1} D_A H_A}{k_{B1} D_B H_B}} \tag{17}$$

Consequently, the initial selectivity should depend on the root of the solubility ratio as well as on the ratio k_{A1}/k_{B1}. In this last parameter we have to pay attention in explaining the inversion of the separation factor in the emulsion runs.

In a first approximation, the ratio k_{A1}/k_{B1} can be identified with the ratio P_{A1}/P_{B1} between the permeabilities of the surfactant layer with respect to the two components. When the components pass through the ordered molecules of the surfactant which separate the feed from the aqueous phase, they interact with the layer in a different way. In the case of the ethylbenzene–styrene mixture, the molecular structure of the surfactant might present an affinity with the ethylenic double bond and then offer to styrene a lower permeability with respect to ethylbenzene. Taking into account the measured values of the separation factor, the permeability ratio should be about 5 or more, so that the solubility ratio ($\simeq 0.5$) is counterbalanced. This behavior can be observed in a more remarkable way for the *n*-octane–ethylbenzene mixture where the structures of the components are totally different and will influence the permeability ratio.

In this regard the remarkable influence of composition and of the type of surfactant in the emulsion runs is significant. The surfactant mixture DOS 1% + PNP 0.01%, which forms very stable liquid membranes, also seems to be particularly permeable to ethylbenzene.

We should add that the permeation rate referred to the unit volume of the stirred emulsion–solvent system

$$W_A = \frac{3}{R_p}\varepsilon_p N_{Ap} \tag{18}$$

depends on the aggregate sizes which are very likely to decrease with an increase of the intensity and length of secondary stirring. On the other hand, the primary stirring affects the sizes of the feed droplets, i.e., r_d. Taking into account that the separation factor as a function of time passes through a maximum, and making reference to Eqs. (14) and (15) instead of to the asymptotic solutions, it is possible to give a qualitative explanation of the effects of primary and secondary stirring on selectivity. The effect of secondary stirring on the permeation rate (*2*) can be directly explained on the basis of Eq. (18) alone.

CONCLUSIONS

The experimental results relative to styrene–ethylbenzene and *n*-octane–ethylbenzene mixtures show that selectivity in the permeation process can be inverted by passing from an operative methodology to another methodology. This is a new fact which cannot be neglected in the extrapolation of laboratory data.

In order to explain these inversions it is necessary to thoroughly examine the current interpretations of the phenomenon of selective permeation by supposing, for instance, that the slower phenomenon is always diffusion in the aqueous phase and by ascribing the diversity of the values to a different configuration of this phase.

In the single drop runs and in the emulsion runs without secondary mixing, the permeation phenomenon is performed through a true liquid membrane, and this can be interpreted with Eqs. (1)–(5). In the case of the emulsion technique with secondary mixing, we have a subdivision of the emulsion in aggregates for which the permeation can be described by Eqs. (6)–(17).

SYMBOLS

c_A	volumetric concentration of the Component A in the oily phases (mole/m^3)
c'_A	volumetric concentration of the Component A in the aqueous phase (mole/m^3)
D_A	diffusion coefficient of the Component A in the aqueous phase (m^2/sec)
H_A	equilibrium coefficient for the Component A (distribution between oily phase and aqueous phase) (dimensionless)
K_A	overall transfer coefficient between feed and solvent (m/sec)
k_{A1}	transfer coefficient between feed and aqueous phase (m/sec)

k_{A3}	transfer coefficient between aqueous phase and solvent (m/sec)
k'_1	transfer coefficient through the feed boundary layer (m/sec)
N_A	unitary molar flux of the Component A (mole/m^{2}sec)
P_{A1}	permeability of the surfactant layer between feed and aqueous phase (m/sec)
r_d	average radius of the feed droplets dispersed in emulsion (m)
R	spatial variable in the aggregates (m)
R_p	average radius of the aggregates (m)
s	thickness of the aqueous phase in the liquid membrane (m)
S	surface (m^2)
t	time (sec)
V	volume (m^3)
x_A	molar fraction of the Component A in the feed (dimensionless)
y_A	molar fraction of the Component A in the oily phase (dimensionless)
W_A	permeation rate (mole/m^{3}sec)
β'	separation factor (dimensionless)
β_i	instantaneous selectivity, defined by Eq. (4) (dimensionless)
ε_d	volumetric ratio between aqueous phase and feed in the aggregates (dimensionless)
ε_p	volumetric ratio between solvent and aggregates (dimensionless)
γ_A	dimensionless concentration defined by the second of Eq. (12)
η_A	effectiveness factor (dimensionless)
ρ	dimensionless radius
ϕ_A	Thiele modulus defined by Eq. (13)

Indices

A, B,	components
d	feed droplet in emulsion
f	feed
p	aggregate
s	solvent
0	initial value

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