

EFFECT OF SURFACTANT TYPE ON SELECTIVITY FOR THE SEPARATION OF 1-METHYLNAPHTHALENE FROM DODECANE USING LIQUID MEMBRANES

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Summary

The selective removal of aromatics from kerosine for the purposes of smoke-point improvement and to meet the specifications for aviation turbine fuel is an industrially important operation. The present study is part of a programme for developing an energy-efficient aqueous surfactant membrane process with high selectivities for aromatics removal. In the experimental studies, carried out in a batch mixer-settler unit, the kerosine feed was modelled using a synthetic mixture of 1-methylnaphthalene and dodecane. The objective of the experimental study was to study the influence of the surfactant type on the selectivity for removal of 1-methylnaphthalene. Eight different types of surfactants were used in the studies, with HLB (hydrophile-lipophile balance) numbers ranging from 12.8 to 17.8. The selectivity β , defined as the ratio of the mass transfer coefficients for transfer of aromatics to that of the non-aromatics, was determined after correcting for non-selective transport due to emulsion breakage. The selectivity thus obtained correlated very well with W , the work of transfer, which reflects the ease of adsorption of the surfactant to form a monolayer relative to the ease of micellization. For high W (i.e., lower ease of micellization) the selectivities are higher, as might be expected because micelle formation leads to non-selective transport through the membrane barrier. The study sheds light on the appropriate choice of surfactant to obtain increased selectivities.

Introduction

The use of thin aqueous or oil films stabilized by emulsification as selective separation barriers forms the basis of a novel separation technique called Liquid Membrane Permeation. Liquid membranes offer advantages of high separation factors, low energy consumption and simple operation [1] and have been shown capable of handling a variety of separations, such as wastewater treatment [2], hydrocarbon separations [3-6] and hydrometallurgy [7]. With the recent commissioning of an industrial liquid-membrane plant at Lenzing

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AG, Austria, liquid membranes are now poised to make a significant impact on the industrial separation scene.

In the present study, the focus is on the effect of surfactant type on the selective removal of aromatics, using liquid membranes, from mixtures of 1-methylnaphthalene and dodecane, which have been chosen to represent a straight-run kerosine fraction from a crude oil. It may be noted that no work has so far been reported on liquid-membrane separations of hydrocarbon mixtures containing molecules with eight carbon atoms or more.

For meeting specifications of aviation turbine fuel and superior kerosine, selective removal of aromatics from the kerosine fraction may be required. This problem is particularly acute with kerosine from crudes found in India and Indonesia. The existing technology for selective aromatics removal utilizes liquid-liquid extraction with polar solvents, such as liquid sulphur dioxide (as in the Edeleanu process), sulpholane and mono-, di-, tri- and tetraethylene glycols. Liquid membranes offer the promise of an energy-efficient alternative to conventional liquid-liquid extraction.

Liquid-membrane hydrocarbon separations use aqueous surfactant membranes formed by contacting an O/W emulsion of the feed mixture with a non-aqueous "solvent", which may itself be a hydrocarbon boiling well outside the range of the feed mixture to be separated. Ideally, the membrane should be stable and prevent the feed mixture from mixing with the solvent. The selectivity is then governed solely by the relative rates of transfer of the feed components across the aqueous membrane phase and these rates are determined by the ratio of products of solubility and molecular diffusivity of permeating species in the aqueous membrane phase [3]. Selectivity in the transport of aromatics is stated to be primarily due to the much higher solubility of aromatics in the aqueous phase compared with non-aromatics [3]. In practice, however, membrane rupture due to emulsion instability results in non-selective transport of a portion of the feed mixture into the solvent with concomitant loss in selectivity.

Recently, we have developed a theoretical model for the liquid-membrane permeation process which takes this emulsion breakage into account [8]. Briefly, the permeation process has been modelled as a process consisting of two parallel steps:

- (1) selective, diffusional transmembrane transport, and
- (2) non-selective transport due to emulsion breakage.

A schematic diagram of this model is given in Fig. 1. The feed is a mixture of 1-methylnaphthalene (aromatic, AR, denoted by subscript 1 subsequently) and dodecane (non-aromatic, NA, denoted by subscript 2 subsequently). A fraction ϵ_b of this mixture gets transferred to the solvent phase by emulsion breakage. Following the model of Krishna and Goswami [8], the change in composition of the extract phase, due to the contributions of diffusive transmembrane transport and non-selective emulsion breakage, is given by

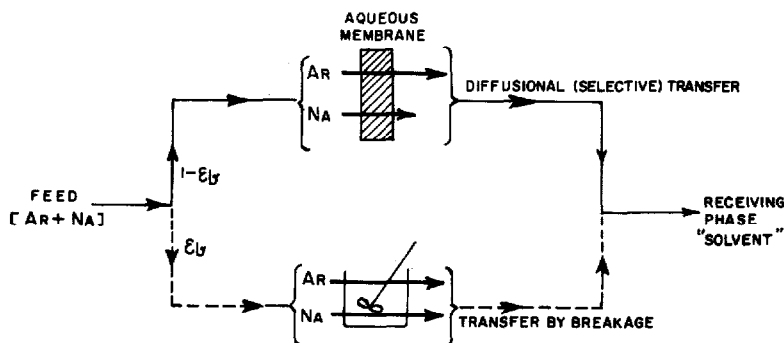


Fig. 1. Schematic diagram of the parallel transport mechanisms in liquid membranes.

$$\frac{dy_1}{d\xi} = \frac{(1 - \epsilon_b) \rho K_1 a V \tau}{E} (x_1 - y_1) - \frac{\epsilon_b (x_1 - y_1)}{E} \frac{dR}{d\xi} \quad (1)$$

where E and R are the masses of extract and raffinate phases, respectively, which will change with time. If the experimental variation of the raffinate phase with time is written as

$$R = R_0 f(\xi) \quad (2)$$

then eqn. (1) can be integrated to yield the overall mass transfer coefficient, corrected for emulsion breakage, for 1-methylnaphthalene

$$K_1 a = \frac{\frac{1}{(1+m)} \ln \left(\frac{mx_1^0}{mx_1^0 - y_1(1+m)} \right) + \epsilon_b \int_0^1 \frac{f'(\xi) d\xi}{f(\xi)[1+m-mf(\xi)]}}{\frac{\tau(1-\epsilon_b)}{m} \int_0^1 \frac{d\xi}{f(\xi)[1+m-mf(\xi)]}} \quad (3)$$

with an analogous expression for the mass transfer coefficient $K_2 a$ for dodecane. The selectivity β may be defined as the ratio of mass transfer coefficients

$$\beta = K_1 a / K_2 a \quad (4)$$

In the present investigation we have used eight non-ionic surfactants of varying hydrophile-lipophile balance (HLB) numbers and studied the permeation of 1-methylnaphthalene-dodecane mixtures through liquid membranes formed with each of these surfactants. The fractional breakage of the emulsions with each surfactant was measured independently using a water-insoluble dye tracer technique. From experimental mass transfer measurements and breakage values, the volumetric overall mass transfer coefficients and selectivities for each membrane were calculated using eqns. (3) and (4),

TABLE 1

Physical and surface-chemical properties of the surfactants

Surfactant	HLB	Molecular weight	γ^* (mN-m ⁻¹)	C_{cmc} (mol-l ⁻¹)	A_{min} (nm ²)	W (kJ-mol ⁻¹)
Hyoxyd AAO	12.8	683	31.5	0.000043	0.37	9.1
Noigen DK120	13.2	692	32.0	0.000043	0.35	8.5
Hyoxyd X150	15.0	780	36.5	0.000066	0.47	10.0
Dai Ichi E0601	15.5	760	38.0	0.00007	0.49	10.2
Hyoxyd X200	16.0	947	39.0	0.000074	0.65	13.0
Dai Ichi E0604	16.5	1630	40.5	0.000076	0.76	14.9
Noigen DK30	17.3	1105	50.0	0.000079	1.10	14.1
Hyoxyd X400	17.8	1420	42.5	0.00015	1.10	18.8

*Surface tension of 0.5 wt% aqueous solution at 30°C.

respectively. The surfactants have been characterized by determining surface-chemical properties like critical micelle concentrations, free energies of adsorption and micellization and "work of transfer". An attempt has been made to interpret the mass transfer data in the light of surface-chemical properties of the surfactants used.

Experimental

All chemicals used were of minimum 99% purity, as verified by gas liquid chromatography.

The surfactants used were supplied by M/s Hico, India and M/s Dai Ichi Karkaria, India. They are non-ionic, of the alkylphenol polyoxyethylene type and were used without further purification. Their physico-chemical properties are given in Table 1.

The mass transfer measurements with each surfactant were made at 30°C in a thermostated glass mixer-settler unit of 300 ml capacity shown in Fig. 2. The model feed mixture of 1-methylnaphthalene-dodecane (27:73 by wt.) was mixed with aqueous surfactant solution in this unit at 4000 rpm for 15 min. The resulting O/W emulsion was then mixed with the "solvent" (n-heptane) at 650 rpm for 5 min, in the same unit. The contents were withdrawn and centrifuged at 1000 rpm for 4 min, during which the emulsion phase separates from the solvent phase. The compositions of these phases were then determined by an azeotropic distillation procedure standardized and reported earlier [9]. The experimental conditions of emulsion formulation, agitation intensities and agitation period have been fixed after a detailed parametric study carried out on this feed mixture. The fractional breakage of the emulsion, under identical conditions, were determined independently by a dye tracer technique following Li [3]. A Du Nouy Tensiometer with a glass plate supplied by M/s White Electric Instrument Co. Ltd., U.K., was used for measurement

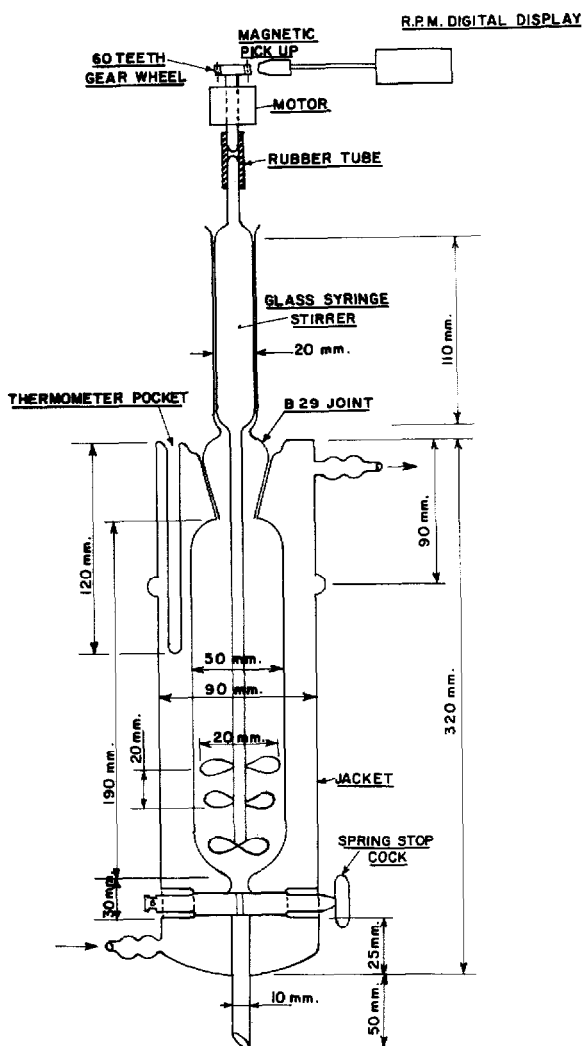


Fig. 2. Diagram of glass mixer-settler.

of surface tensions of aqueous surfactant solutions. Measurements were taken at 15-min intervals until no significant changes occurred.

Results and discussion

The HLB numbers of the surfactants studied range from 12.8 to 17.8. Plots of surface tension vs. log concentration for each surfactant are given in Figs. 3 and 4. As is typical of surfactant solutions [10,11], these curves show a sharp change in slope at a particular concentration — the critical micelle concentra-

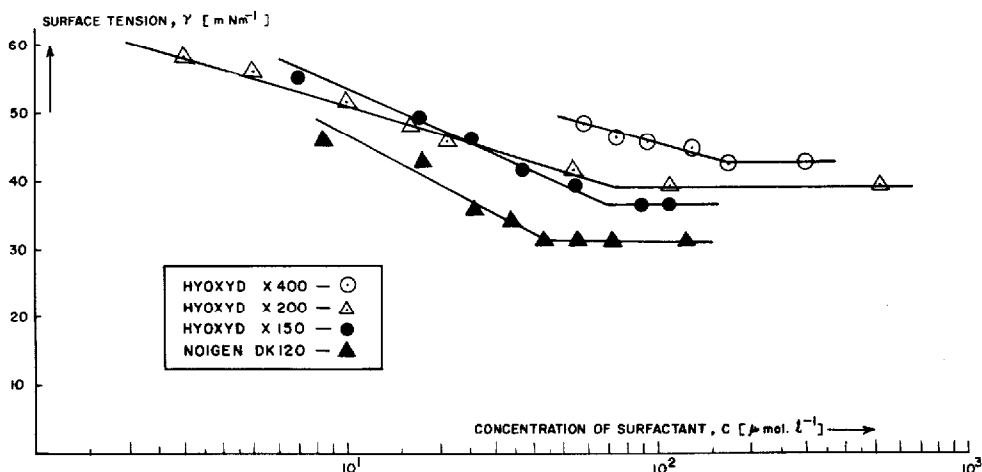


Fig. 3. Surface tension vs. logarithm of the concentration of surfactant in aqueous solution.

tion, C_{cmc} — due to micelle formation. The C_{cmc} was taken as the concentration corresponding to the point of intersection of the straight lines above and below this sharp break [10] and the values thus obtained are reported in Table 1. The slope of the linear portion of the curve below the C_{cmc} was determined by a least-square fit of the experimental data and the maximum surface excess concentration, Γ , was determined by application of the Gibbs equation, which for nonionic surfactants is [12]:

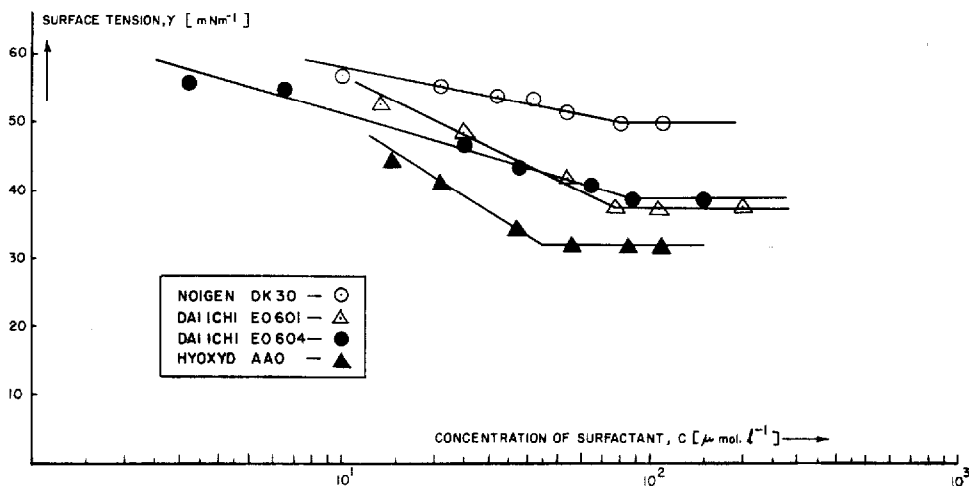


Fig. 4. Surface tension vs. logarithm of the concentration of surfactant in aqueous solution.

$$\Gamma = -\frac{1}{\mathcal{R}T} \left(\frac{\partial \gamma}{\partial \ln C} \right)_T \quad (5)$$

From the maximum surface excess concentration, the area per molecule at the interface at C_{cmc} , A_{cmc} , which also represents the minimum area per molecule at the interface, A_{min} , was calculated from

$$A_{\text{cmc}} = \frac{1}{\mathcal{N}\Gamma} = A_{\text{min}} \quad (6)$$

By choosing for the standard initial state of non-micellar non-ionic surfactant species a hypothetical state at unit mole fraction with individual molecules behaving as at infinite dilution and for the standard final state the micelle itself, the standard free energy of micellization can be written as [10]:

$$\Delta G_{\text{mic}}^{\circ} = \mathcal{R}T \ln C_{\text{cmc}} \quad (7)$$

The standard free energy of adsorption is:

$$\Delta G_{\text{ad}}^{\circ} = \mathcal{R}T \ln C_{\text{cmc}} - \pi_{\text{cmc}} A_{\text{cmc}} \mathcal{N} \quad (8)$$

The standard state for the adsorbed surfactant here is a hypothetical monolayer at its minimum surface area/molecule but at zero surface pressure. The last term in eqn. (8) expressed the surface work involved in going from zero surface pressure to surface pressure π_{cmc} , at constant minimum surface area/molecule $A_{\text{min}} (= A_{\text{cmc}})$.

The work of transfer, W , i.e. the work involved in transferring the surfactant molecule from a monolayer at zero surface pressure to the micelle:

$$W = \Delta G_{\text{mic}}^{\circ} - \Delta G_{\text{ad}}^{\circ} \quad (9)$$

is a measure of the ease of adsorption to form a monolayer at zero surface relative to the ease of micellization.

The values of the work of transfer calculated from eqns. (5)–(9) for each surfactant are given in Table 1.

The variation of the work of transfer with HLB of the surfactant is shown in Fig. 5. The increase in the work of transfer with HLB of the surfactant has been interpreted [13] as indicating that as the surfactant becomes more hydrophilic due to an increase in its polyoxyethylene chain length, steric factors inhibit micellization more than they do adsorption. This is because greater dehydration of polyoxyethylene chains is required for micellization than for adsorption so that the space available to the hydrophilic group is more restricted at the surface of the micelle than at the planar interface. Therefore, it may be

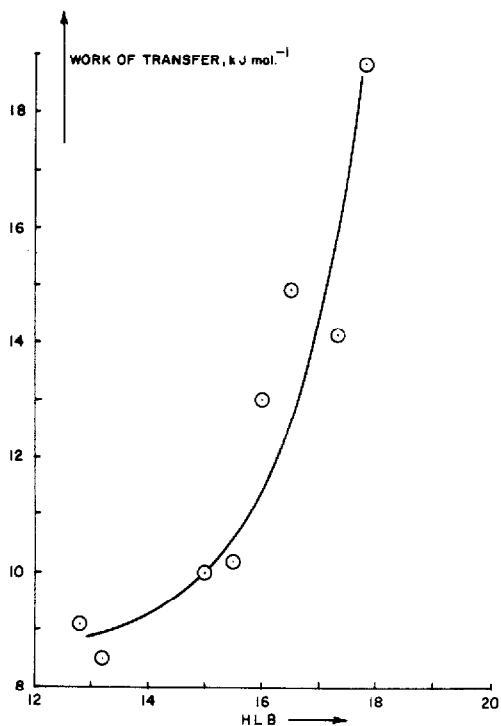


Fig. 5. Relationship between work of transfer and HLB of surfactant.

expected that the extent of micellization will be greater for surfactants with low HLB numbers.

Table 2 shows the experimentally measured compositions of 1-methylna-

TABLE 2

Experimental data on phase composition and fractional breakage of emulsions obtained during permeation and calculated transfer coefficients and selectivities

Surfactant	HLB	y_1	y_2	ϵ_b	$K_1 a$ (sec ⁻¹)	$K_2 a$ (sec ⁻¹)	β
Hyoxyd AAO	12.8	0.0440	0.0231	0.080	0.00077	0.000095	8.2
Noigen DK120	13.2	0.0351	0.0170	0.052	0.00055	0.000071	7.7
Hyoxyd X150	15.0	0.0350	0.0187	0.036	0.00054	0.000081	6.7
Dai Ichi E0601	15.5	0.0400	0.0180	0.087	0.00067	0.000071	9.5
Hyoxyd X200	16.0	0.0402	0.0070	0.022	0.00064	0.000027	23.4
Dai Ichi E0604	16.5	0.0440	0.0081	0.087	0.00077	0.000019	39.6
Noigen DK30	17.3	0.0403	0.0050	0.044	0.00065	0.000014	47.4
Hyoxyd X400	17.8	0.0401	0.0060	0.067	0.00066	0.000014	48.1

For all experiments: $x_1^0 = 0.27$; $x_2^0 = 0.73$; $m = 0.5$.

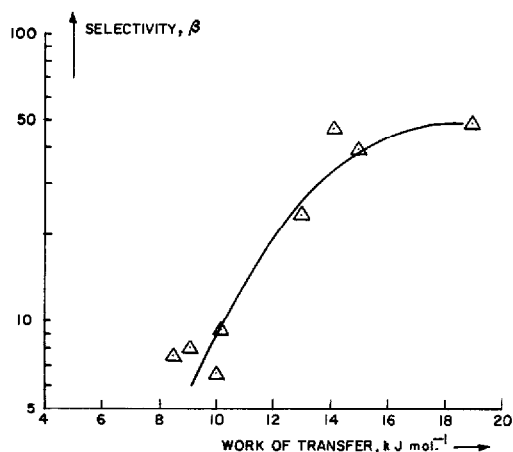


Fig. 6. Relationship between selectivity and work of transfer.

phthalene and dodecane in the extract phase obtained in the permeation runs along with the independently measured fractional breakage of the emulsions. The values of the volumetric overall mass transfer coefficients and selectivities calculated from this data using eqns. (3) and (4) are also given in Table 2. The form of the function $f(\xi)$ in eqn. (2) was evaluated from a curve fit of actual measured data and is given by

$$f(\xi) = 1 - 0.125\xi \quad (10)$$

The variation of selectivity and volumetric overall mass transfer coefficients with work of transfer are presented graphically in Figs. 6 and 7, respectively. For the low-HLB surfactants, for which work of transfer is low, selectivities are low. Selectivities increase sharply as surfactant HLB and work of transfer increase. The volumetric overall mass transfer coefficients for 1-methylnaphthalene do not show any significant variation with work of transfer but the mass transfer coefficients for dodecane show significantly lower values for surfactants with higher work of transfer values.

The increase in selectivity with decrease in micellization tendency of the surfactant (increase in work of transfer) suggests that the presence of surfactant micelles in the aqueous membrane phase may affect the transfer rates of components due to the ability of these micelles to solubilize water-insoluble compounds. In fact, Seno et al. [14] reported a significant increase in the transfer rate of azobenzene when micelles of the surfactant cetyl trimethyl ammonium bromide are present because of solubilization of azobenzene in these micelles. This effect of solubilization and increased transport will be more apparent in case of the low-HLB surfactants studied here because of their increased micellization tendency. The higher value of the mass transfer coef-

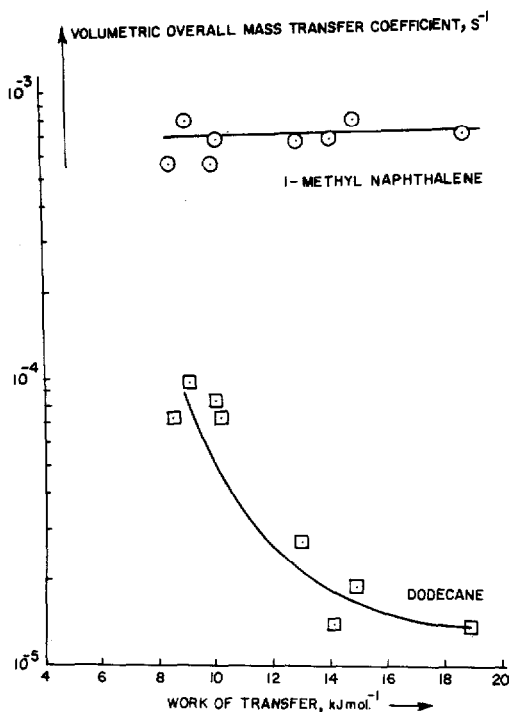


Fig. 7. Plot of volumetric overall mass transfer coefficients vs. work of transfer.

efficient of dodecane at low HLB numbers (see Fig. 7) might be explained on the basis of a "synergistic" mechanism of solubilization. It has been reported [15,16] that polar solubilizes which are solubilized in the micelle interior expand these regions and increase further the solubilization of apolar solubilizes. 1-Methylnaphthalene has readily polarizable electrons so that under the influence of polar constituents it is expected to behave more akin to a polar solubilize. Moreover it has been shown [11] that the locus of solubilization of polycyclics, such as naphthalene or anthracene, is in the micelle interior, in the deep palisade layer. It is possible that during permeation, the initial solubilization of 1-methylnaphthalene in the deep palisade layer of the micelles exerts such a synergistic effect so that solubilization of the apolar dodecane is increased. As this effect will be more pronounced with the low-HLB surfactants with low work of transfer values which micellize to a greater extent, the transfer coefficient for dodecane will increase and selectivities will be low for these surfactants.

Conclusions

The selectivity for transport of 1-methylnaphthalene and dodecane through aqueous surfactant membrane has been found to correlate well with W , the

work of transfer, which expresses the relative ease of adsorption and ease of micellization. The selectivity β increases with increasing W (lower micellization tendency) and this can be rationalized because micelle transport is non-selective. The study aids the choice of surfactant for increased selectivity.

List of symbols

a	Interfacial area per unit volume of extract phase (m^{-1})
A_{cmc}	Area per molecule at interface at C_{cmc} ($\text{m}^2\text{-molecule}^{-1}$)
A_{min}	Minimum area per molecule at interface ($\text{m}^2\text{-molecule}^{-1}$)
C	Concentration of surfactant in bulk aqueous phase ($\text{mol}\cdot\text{m}^{-3}$)
C_{cmc}	Critical micelle concentration ($\text{mol}\cdot\text{m}^{-3}$)
E	Mass of extract phase (kg)
$\Delta G_{\text{mic}}^{\circ}$	Standard free energy of micellization ($\text{J}\cdot\text{mol}^{-1}$)
$\Delta G_{\text{ad}}^{\circ}$	Standard free energy of adsorption of surfactant ($\text{J}\cdot\text{mol}^{-1}$)
K_1	Overall mass transfer coefficient for 1-methylnaphthalene ($\text{m}\cdot\text{sec}^{-1}$)
K_2	Overall mass transfer coefficient for dodecane ($\text{m}\cdot\text{sec}^{-1}$)
m	Initial solvent/feed ratio ($\text{kg}\cdot\text{kg}^{-1}$)
\mathcal{N}	Avogadro's number (6.023×10^{23} molecules $\cdot\text{mol}^{-1}$)
\mathcal{R}	Gas constant ($8.314 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$)
R	Mass of raffinate phase (kg)
t	Time (sec)
T	Temperature (K)
V	Volume of extract phase (m^3)
W	Work of transfer ($\text{J}\cdot\text{mol}^{-1}$)
x	Mass fraction of component in raffinate phase (—)
y	Mass fraction of component in extract phase (—)

Greek symbols

β	Selectivity defined by eqn. (4) (—)
γ	Surface tension ($\text{N}\cdot\text{m}^{-1}$)
γ_{cmc}	Surface tension of solution at critical micelle concentration ($\text{N}\cdot\text{m}^{-1}$)
γ_0	Surface tension of water ($\text{N}\cdot\text{m}^{-1}$)
Γ	Surface excess concentration, eqn. (5) ($\text{mol}\cdot\text{m}^{-2}$)
ϵ_b	Fractional breakage (—)
ξ	Dimensionless time ($=t/\tau$) (—)
π_{cmc}	Surface pressure at critical micelle concentration ($=\gamma-\gamma_0$) ($\text{N}\cdot\text{m}^{-1}$)
ρ	Density of extract phase ($\text{kg}\cdot\text{m}^{-3}$)

τ Permeation time (sec)

Subscripts

- 1 Denoting 1-methylnaphthalene
- 2 Denoting dodecane
- ad Adsorption
- mic Micellization
- min Minimum

Superscripts

- 0 Denoting value at time $t=0$.

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