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USE OF ADDITIVES TO ENHANCE THE SELECTIVITY OF LIQUID SURFACTANT MEMBRANES

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Summary

This study is aimed at attempting to improve both the selectivity and the permeation rates for the separation of 1-methylnaphthalene from dodecane using aqueous surfactant membranes. This enhancement is achieved by adding various water-soluble chemical compounds ("additives") to the water phase. Seven different additives were tried in this study and their efficacy was determined by carrying out mass transfer permeation experiments to determine both the rates of transfer and the selectivity of separation. In line with our previous work (Sharma et al. [5]; Krishna et al. [6]), we have corrected the mass transfer coefficients for emulsion breakage, and found these coefficients, and the selectivity, to correlate well with the work of transfer of the additive-containing surfactant system. The increase in selectivity in the presence of the additive has been shown to be due to the relative increase in the activity coefficient of 1-methylnaphthalene in the aqueous solution with respect to that of dodecane. The presence of the additive increases the selectivity by about one order of magnitude, and the present study should aid in the development of a viable liquid membrane separation process for the selective removal of aromatics from kerosene, a process which is required for the production of aviation turbine fuel from crudes having a high aromatic content in the lighter distillates.

Introduction

The separation of aromatic hydrocarbons from mixtures with non-aromatics can be achieved using liquid surfactant membranes formed by dispersing an oil–water (O/W) emulsion of the feed mixture being separated in a non-aqueous receiving phase [1–4]. Selective transfer of aromatics from feed phase to receiving phase is believed to occur by a simple solution–diffusion mechanism [4]. In addition, non-selective transfer can occur due to emulsion breakage as well as by solubilisation and transfer in surfactant micelles [5]. The overall transfer rates are rather low, especially for hydrocarbon mixtures in the kerosene boiling range. Effective enhancement of transfer rates for such systems would be important, as it would make this process an attractive alternative to

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conventional liquid extraction for kerosene dearomatisation, required for aviation turbine fuel and superior kerosene production.

The inert nature of hydrocarbons offers very limited scope for using complexing agents (like LIX 64N for metal ions) as carriers in the membrane phase to increase transfer rates. The postulated solution–diffusion mechanism suggests that the transfer rates may be increased by increasing the solubility of hydrocarbons in the aqueous phase, possibly through the use of chemical additives. In this communication we report the results of an investigation on the effect of various water-soluble additives in the aqueous phase on transfer rates of hydrocarbons. The additives tried are typical polar solvents in which aromatics are known to have preferential solubilities over non-aromatics.

In an earlier publication [6], we modelled the permeation process as a parallel step process consisting of (i) selective trans-membrane diffusional transport; and (ii) non-selective transport due to emulsion breakage.

A schematic diagram of this model is shown in Fig. 1. We have shown that the composition change in the extract phase can be written as a sum of the contributions due to diffusive trans-membrane transport and non-selective emulsion breakage as

$$\frac{\mathrm{d}y_1}{\mathrm{d}\xi}=\frac{(1-\epsilon_\mathrm{b})\rho K_1 aV\tau(x_1-y_1)}{E}-\frac{\epsilon_\mathrm{b}(x_1-y_1)}{E}\frac{\mathrm{d}R}{\mathrm{d}\xi} \tag{1}$$

The variation of mass of raffinate with time was expressed as:

$$R=R^0 f(\xi) \tag{2}$$

and eqn. (1) was integrated to yield an expression for the overall volumetric mass transfer coefficient for 1-methylnaphthalene as

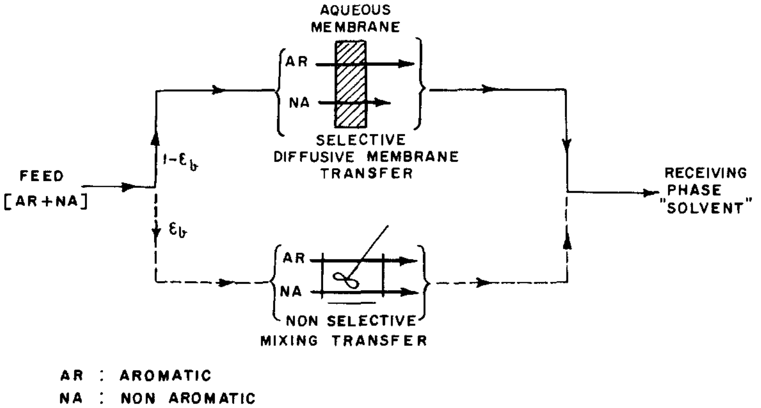

Fig. 1. Schematic diagram of parallel transport mechanism in liquid membranes.

$$K_1 a = \frac{\frac{1}{(1+m)} \ln\left[\frac{m x_1^0}{m x_1^0 - y_1(1+m)}\right] + \epsilon_b \int_0^1 \frac{f'(\xi)\mathrm{d}\xi}{f(\xi)[1+m-mf(\xi)]}}{\frac{\tau(1-\epsilon_b)}{m} \int_0^1 \frac{\mathrm{d}\xi}{f(\xi)[1+m-mf(\xi)]}} \tag{3}$$

with a similar expression for K_2a, the mass transfer coefficient for dodecane. In the present investigation we have used this expression to calculate the volumetric mass transfer coefficients from experimental mass transfer and emulsion breakage data. We have also made surface chemical measurements to investigate the effect of additives on micellisation characteristics of the surfactant used. Micellisation characteristics, as we have shown earlier [5], can affect the mass transfer coefficients, especially for the non-aromatic components.

Experimental

A mixture of 38% by weight 1-methylnaphthalene and 62% by weight dodecane was used as a model hydrocarbon feed representative of a straight run kerosene, while an alkylphenol polyoxyethylene compound, Noigen DK-30, supplied by Dai-Ichi Karkaria Ltd., Bombay, was used as emulsifier. The physical properties of the additives investigated are given in Table 1. These additives were taken in the aqueous surfactant solution prior to emulsification of the feed.

The mass transfer permeation measurements were made at 30°C in a thermostated glass mixer–settler unit of 300 ml capacity, as shown in Fig. 2. Details of the experimental procedure have been published previously [5].

TABLE 1

Physical and surface-chemical properties of additive–surfactant solutions

Additive	Density of additive (kg-m^{-3})	C_{cmc} of additive -surfactant solution (mol-l^{-1})	Work of transfer of additive-surfactant solution (kJ mol^{-1})	Surface tension of additive-surfactant solution (mN m^{-1})
Morpholine	1002.0	0.00040	12.0	42.0
N-Methylpyrrolidone	1039.0	0.00080	16.9	40.0
N-Formylmorpholine	1152.8	0.00038	9.2	41.5
Sulpholane	1260.6	0.00045	9.5	40.0
Dimethyl sulphoxide	1099.0	0.00034	8.0	42.5
Tetraethylene glycol	1124.7	0.00014	7.4	42.5
Triethylene glycol	1125.4	0.00028	7.2	45.0

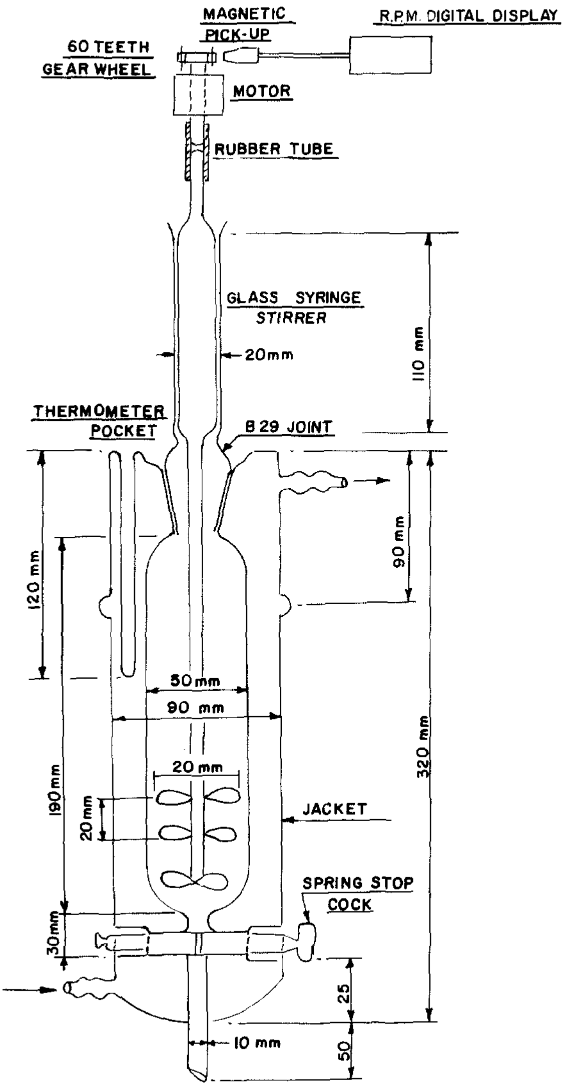

Fig. 2. Diagram of glass mixer-settler unit.

Independent measurements of emulsion breakage in presence of additives could not be made by the dye tracer technique followed earlier [6], owing to appreciable solubility of the dye in the aqueous phase containing the additive. If we consider the situation where transfer of one of the feed components, say dodecane, through the liquid membrane has been effectively prevented by some means, transfer of this component into the solvent can then occur only by emulsion breakage. Physically this situation may arise by keeping the initial concentrations of dodecane equal in the feed and solvent. The change in extract phase composition due to emulsion breakage has been shown [6] to be given by:

$$\frac{dy_2}{d\xi} = -(x_2 - y_2)\frac{dE}{d\xi} \tag{4}$$

The fractional breakage of the emulsion under these conditions will be:

$$\epsilon_b = \frac{y_2 E}{R^0 x_2^0} \tag{5}$$

and, by using appropriate material balance relationships discussed in Ref. [6], eqn. (4) can be integrated to yield an expression for fractional breakage:

$$\epsilon_b = \frac{m[E^0 + R^0 - R^0 g(\xi)]}{(1+m)R^0}\left[1 - \exp\left\{(1+m)\int_0^1 \frac{g'(\xi)d\xi}{g(\xi)[1+m-mg(\xi)]}\right\}\right] \tag{6}$$

Here the variation of mass of raffinate with time is expressed empirically as

$$R = R^0 g(\xi) \tag{7}$$

The form of the function $g(\xi)$ with each additive under conditions of zero dodecane diffusive transfer was evaluated from a curve fit of experimentally measured data, and eqn. (6) was used to calculate the fractional breakage. The form of the function $g(\xi)$ for sulpholane as additive, for example, is $g(\xi) = (1 - 0.08\xi)$.

Results and discussion

In Table 2 we report the experimentally measured compositions of 1-methylnaphthalene and dodecane in the extract phase obtained in the permeation runs with each additive in the surfactant membrane phase at its optimum concentration. The fractional breakage of the emulsions determined independently, as discussed above, along with the overall volumetric mass transfer coefficients calculated by using eqn. (3) are also included in Table 2. The form of the function $f(\xi)$ in eqn. (3) was evaluated from a curve fit of actual measured data and is given by:

$$f(\xi) = 1 - 0.125\,\xi \tag{8}$$

The selectivities reported in Table 2 have been calculated from the ratio of mass transfer coefficients as

$$\beta = K_1 a / K_2 a \tag{9}$$

The plots of surface tension vs. log concentration for the surfactant solution with each additive are given in Figs. 3–6, from which the critical micelle con-

TABLE 2

Experimental mass transfer and emulsion breakage data and calculated transfer coefficients and selectivities

Additive	Concentration of additive (wt%)	Mass fraction 1-methyl-naphthalene in extract phase, y_1	Mass fraction dodecane in extract phase, y_2	Fractional breakage of emulsion, ϵ_b	Volumetric overall mass transfer coefficient for 1-methyl-naphthalene, K_1a (sec^{-1})	Volumetric overall mass transfer coefficient for dodecane, K_2a (sec^{-1})	Selectivity, β
Morpholine	20	0.1144	0.0028	0.025	0.00230	0.0000097	237.1
N-Methyl-pyrrolidone	10	0.1006	0.0025	0.056	0.00176	0.0000015	1173.0
N-Formyl-morpholine	10	0.0770	0.0025	0.025	0.0010	0.0000081	123
Sulpholane	10	0.0971	0.0062	0.060	0.0016	0.000022	72
Dimethyl sulphoxide	20	0.0856	0.0056	0.025	0.0012	0.000025	48
Tetraethylene glycol	20	0.0887	0.0064	0.035	0.0014	0.000027	51
Triethylene glycol	25	0.0646	0.0034	0.036	0.00079	0.000011	71

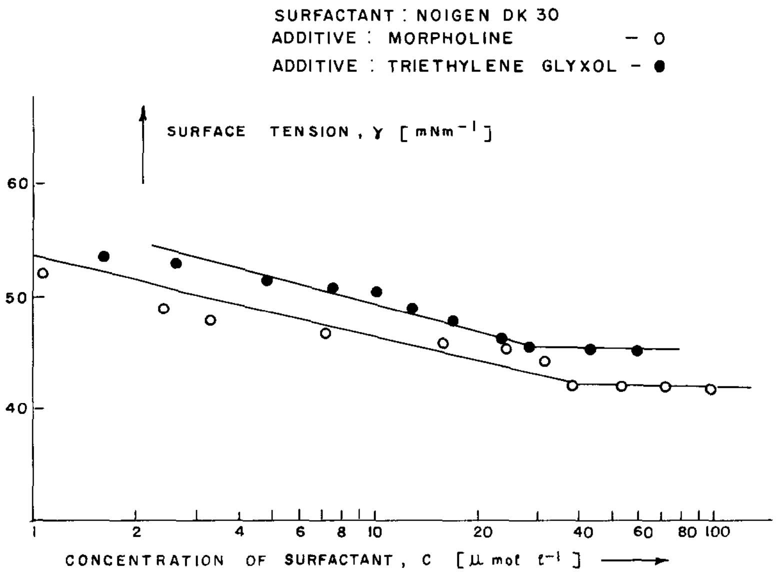

Fig. 3. Surface tension vs. logarithm of concentration of surfactant in aqueous solution containing additive.

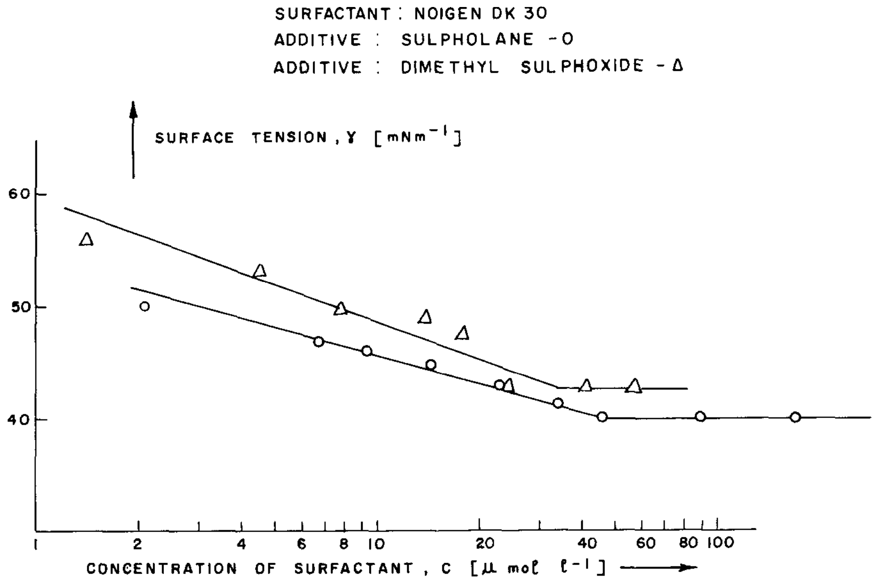

Fig. 4. Surface tension vs. logarithm of concentration of surfactant in aqueous solution containing additive.

centrations, C_{cmc}, have been evaluated as the concentration corresponding to the sharp break in the curves [7]. The slope of the linear portion of the curve below C_{cmc} was determined by a least-squares fit of experimental data, from which the maximum surface excess concentration, Γ, was calculated as [8]:

$$\Gamma = -\frac{1}{\mathscr{R}T}\frac{\partial \gamma}{\partial \ln C}\Bigg|_{T} \tag{10}$$

The area per molecule at the interface at C_{cmc} is given by:

$$A_{\mathrm{cmc}} = 1/N\Gamma \tag{11}$$

The standard free energy of micellisation is written as [7]:

$$\Delta G^{0}_{\mathrm{mic}} = \mathscr{R}T \ln C_{\mathrm{cmc}} \tag{12}$$

Here a hypothetical state of non-micellar surfactant at unit mole fraction with individual molecules behaving as at infinite dilution is chosen as standard initial state, and the micelle itself is chosen as standard final state. By choosing for the standard state of adsorbed surfactant a hypothetical monolayer at its minimum surface area per molecule but at zero surface pressure, and including a term expressing the surface work involved in going from zero surface pressure to surface pressure at C_{cmc}, the standard free energy of adsorption has been written as:

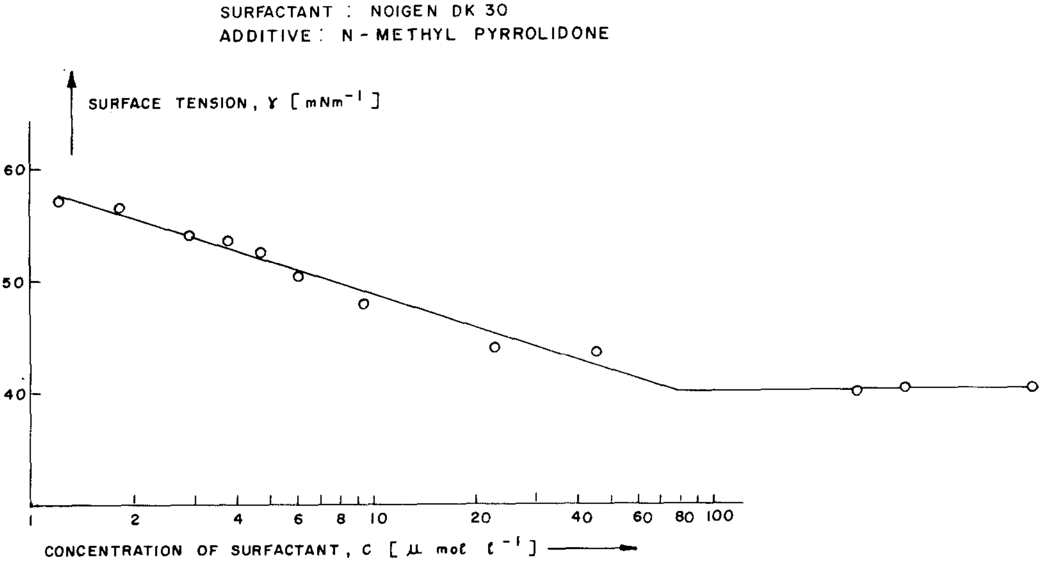

Fig. 5. Surface tension vs. logarithm of concentration of surfactant in aqueous solution containing additive.

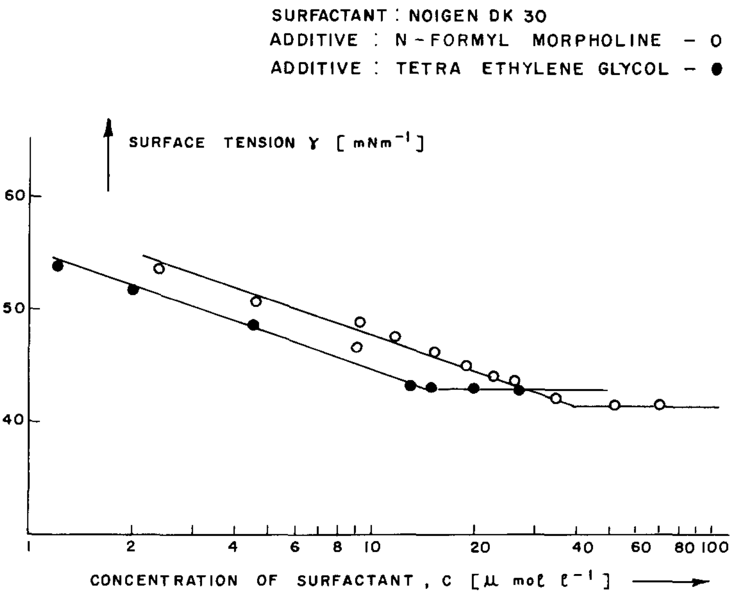

Fig. 6. Surface tension vs. logarithm of concentration of surfactant in aqueous solution containing additive.

$$\Delta G^0_{\mathrm{ad}} = \mathscr{R}T \ln C_{\mathrm{cmc}} - \pi_{\mathrm{cmc}} A_{\mathrm{cmc}} N \tag{13}$$

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

$$W = \Delta G^0_{\mathrm{mic}} - \Delta G^0_{\mathrm{ad}} \tag{14}$$

The work is a measure of the ease of adsorption to form a monolayer at zero surface pressure relative to the ease of micellisation. The work of transfer values for the surfactant in the presence of each additive investigated are given in Table 1. A high work of transfer value indicates a low micellisation tendency for the surfactant and the concentration of micelles may be expected to be low. We reported earlier [5] that the mass transfer coefficient for dodecane increases, while that for 1-methylnaphthalene remains practically constant, with decrease in work of transfer of the surfactant. This, we suggested, could be due to the preferential solubilisation and transport of dodecane in surfactant micelles which are present in larger concentration in surfactant solutions with low work of transfer. In Figs. 7–8 we have plotted the mass transfer coefficients for 1-methylnaphthalene, K_1a, and dodecane, K_2a, and the selectivities, β, vs. the work of transfer for the additive-containing surfactant systems under investigation. For comparison, we have included data on mass transfer coefficients and selectivities from our earlier studies on different surfactants [5]. The similarity in the two sets of data is strikingly evident. The trends observed earlier on variation of mass transfer coefficients and selectivities with work of transfer remain unaltered. The work of transfer of the surfactant system appears to be a unique parameter characterising the mass transfer behaviour in liquid surfactant membranes.

From the plots depicted in Figs. 7 and 8 it is evident that the additives in general improve the separation characteristics of the aqueous membranes. Thus, mass transfer coefficients for 1-methylnaphthalene are increased considerably (for the additive *N*-methylpyrrolidone, for example, an almost fourfold increase from a value of 0.00065 $\sec^{-1}$ without additive [5] to 0.0024 $\sec^{-1}$ with additive is observed) while transfer coefficients for dodecane are reduced, resulting in an overall increase in selectivity.

The additive probably acts by altering the solvent power of the aqueous

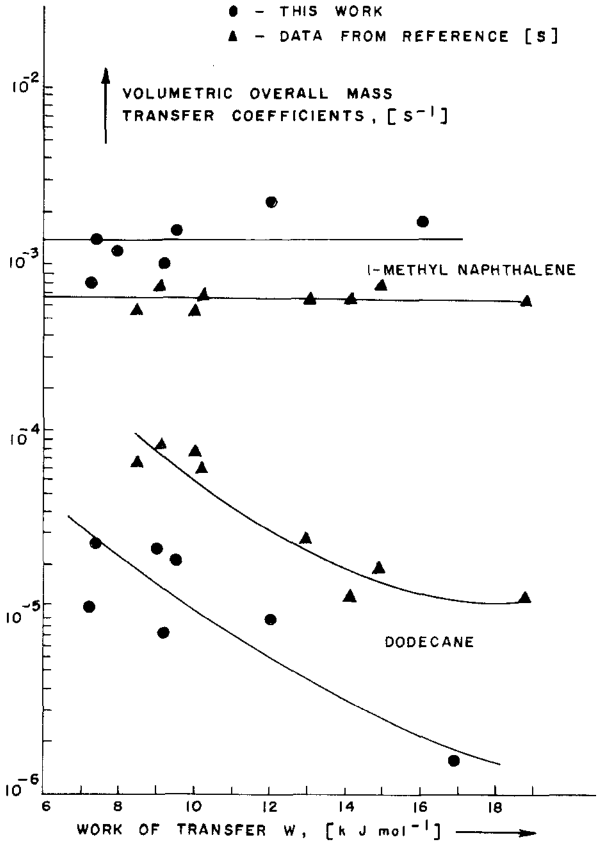

Fig. 7. Relationship between volumetric mass transfer coefficients and work of transfer.

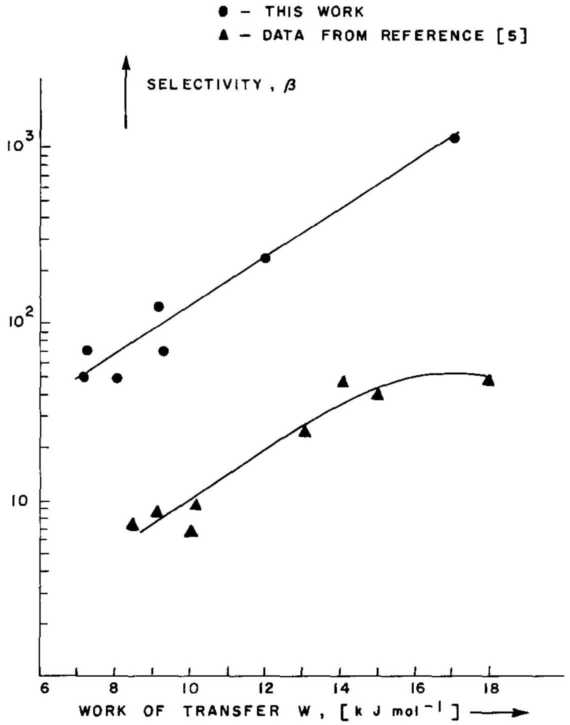

Fig. 8. Relationship between selectivity and work of transfer.

membrane phase. In liquid extraction theory the ratio of the "key" components at infinite dilution in a solvent is often used as a measure of selectivity of the solvent [9]. We considered whether, from such a calculation of this ratio in the aqueous additive-containing surfactant membrane phase, it would be possible to assess the selectivity increase attainable by using a particular additive. As the work of transfer also affects the selectivity, the effect of the additive should be considered under conditions of equal work of transfer. A look at the lower selectivity correlation curve given in Fig. 8 for different surfactant systems shows that, for the surfactant Noigen DK-30 used in this study, with a work of transfer of 14.1 kJ mol^{-1}, the selectivity is 47. The selectivity corresponding to this value of work of transfer to be expected for additive-containing surfactant membrane systems is obtained from the upper correlation curve for additive systems given in the same figure, and is around 430. That is, a selectivity increase of almost 9.1-fold may be expected if an additive-containing surfactant system with the same work of transfer is employed. The additive-containing surfactant system having a work of transfer nearest to this is that of morpholine. It is gratifying to note that the ratio of infinite dilution activity coefficients of 1-methylnaphthalene and dodecane in morpholine–water solution calculated by the UNIFAC equation using interaction parameters reported by Tiegs et al. [10] works out to be 9.6. A broader picture of the role of additive thus appears from these calculations, namely, that by altering the solvent power of the aqueous membrane phase the additive affects both the solubility of surfactant molecules and that of the diffusing species (1-methylnaphthalene and dodecane) in this phase. If the solubility of surfactant molecules in the aqueous phase is altered then surfactant work of transfer, and hence micellar concentration, will change. Therefore, mass transfer coefficients of diffusing species that can become solubilised in micelles and transported across the membrane [5] will be affected. Thus, if surfactant solubility is increased through use of an additive, micellar concentration will be lower, so that we may expect the transfer coefficient of dodecane, the species which gets preferentially solubilised in micelles, to decrease. On the other hand, by selectively affecting the solubility of diffusing species in the aqueous membrane phase, the additive again affects the mass transfer coefficients. Thus, if the additive increases the solubility of 1-methylnaphthalene over that of dodecane, we can expect the mass transfer coefficient for 1-methylnaphthalene to increase. This latter effect can be estimated independently of work of transfer from the infinite dilution activity coefficients of diffusing species in the aqueous surfactant-containing membrane phase.

Conclusion

The effect of water-soluble additives on the transfer rates of 1-methylnaphthalene and dodecane through liquid surfactant membranes has been investigated. It is observed that the additives cause a significant improvement in transfer rates and selectivities. The mass transfer coefficients and selectivities correlate very well with work of transfer, pointing to the uniqueness of this parameter for characterising mass transfer in liquid membrane systems. The additives also influence the solubilities of the diffusing species and, under conditions of equal work of transfer, this effect is measured in terms of infinite dilution activity coefficients.

The results lead us to advocate the use of additives for improving transfer rates in permeation of kerosene-range hydrocarbon mixtures and should aid in selection of the type of additive to be used for such mixtures.

Acknowledgements

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List of symbols

a	interfacial area per unit volume extract phase, m^{-1}
A_{cmc}	area per molecule at interface at C_{cmc}, m^2-molecule^{-1}
C	concentration of surfactant in bulk aqueous phase, mol-m^{-3}
C_{cmc}	critical micelle concentration, mol m^{-3}
E	mass of extract phase, kg
ΔG^0_{mic}	standard free energy of micellisation, J-mol^{-1}
ΔG^0_{ad}	standard free energy of adsorption, J-mol^{-1}
K_1	overall mass transfer coefficient for 1-methylnaphthalene, m-sec^{-1}
K_2	overall mass transfer coefficient for dodecane, m-sec^{-1}
N	Avogadro's number
$\mathscr{R}$	gas constant
R	mass of raffinate, kg
t	time, sec
T	temperature, K
V	volume extract phase, m^3
x	mass fraction of component in raffinate phase, dimensionless
y	mass fraction of component in extract phase, dimensionless

Greek symbols

β	selectivity, dimensionless
γ	surface tension, N-m^{-1}
Γ	surface excess concentration, mol-m^{-2}
ϵ	fractional breakage, dimensionless
ξ	dimensionless time $[=t/\tau]$
π_{cmc}	surface pressure at critical micelle concentration, N-m^{-2}
ρ	density of extract phase, kg-m^{-3}
τ	permeation time, sec

Subscripts

1	denoting 1-methylnaphthalene
2	denoting dodecane
ad	adsorption
mic	micellisation

Superscripts

0	denoting value at $t=0$

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