Surfactant-induced wetting transitions: Role of surface hydrophobicity and effect on oil permeability of ultrafiltration membranes

J.T.F. Keurentjes[a,1], M.A. Cohen Stuart[b], D. Brinkman[a], C.G.P.H. Schroën[a] and K. van 't Riet[a]

[a]*Department of Food Science, Food and Bioengineering Group, Wageningen Agricultural University, P.O. Box 8129, 6700 EV Wageningen (The Netherlands)*
[b]*Department of Physical and Colloid Chemistry, Wageningen Agricultural University, P.O. Box 8038, 6703 HB Wageningen (The Netherlands)*

Abstract

In this study the effect of surface hydrophobicity on adsorption of sodium oleate from a mixture of water and 2-propanol is investigated as well as consequences of this adsorption for wettability by oil or water/2-propanol, respectively. The surface hydrophobicity is varied by the use of compatible mixtures of a hydrophobic (polystyrene) and a more hydrophilic polymer (polyamide or poly(methyl methacrylate)). It appears that for the adsorption onto these surfaces three regions can be distinguished. In the case of a hydrophobic surface adsorption of the surfactant is due to van der Waals and/or hydrophobic interactions between the apolar tails of the surfactant and the surface. Upon an increase of the surface hydrophilicity a large region in which adsorption takes place is followed by a very narrow region of 0.5 mN m^{-1} in which no adsorption is found. A further increase in surface hydrophilicity results in an almost stepwise increase of the amount adsorbed, now due to polar interactions between the polar head groups of the surfactant and the surface, possibly followed by the adsorption of a second layer. The adsorption behavior in the three regions can be explained in a semi-quantitative way, considering interfacial free energies between different components present in the system.

This result can be used in order to design an oil-selective ultrafiltration membrane for the separation of a system of two immiscible liquids (i.e., o/w or w/o emulsions). It was found that only in the region where no surfactant is adsorbed is the surface preferentially wetted by oil and that only then is an ultrafiltration (UF) membrane entirely permeable to oil and not to the aqueous phase.

INTRODUCTION

The presence of amphiphilic molecules in a solution usually affects the hydrophobicity (or wettability) of a surface in contact with this solution [1–3].

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[1]To whom correspondence should be addressed.

In flotation and detergency this effect is used to improve the efficiency of the process. In flotation a surfactant that adsorbs preferentially onto one of the minerals to be separated is added which makes the surface of this mineral more hydrophobic. Air bubbles will preferentially adhere to the more hydrophobic mineral grains, and a separation can be achieved [4–6]. In detergency (washing) adsorption of surfactants with their hydrophobic part onto a fibrous substrate will increase the wettability for water. Subsequently water can penetrate into the pores, thus removing oily materials from the pores by a combined displacement and solubilisation mechanism [7].

Usually, the effect of surfactant concentration on the wetting of a solid substrate is studied [8,9], and little attention is paid to the surface energy of the solid as a parameter in adsorption and wettability of solids. Polymer surfaces may consist of materials with a broad range of surface energies varying from low energy solids like PTFE to rather high energy solids like cellulose, and both dispersive (apolar) and polar or electrostatic interactions may play a role in adsorption and wetting phenomena on those surfaces.

Adsorption and wetting phenomena will play an important role in membrane separation processes. The permeability of hydrophobic membranes for water can be improved by the presence of a surfactant [10] or an alcohol [11]. Two-phase systems can be separated using two membranes of opposite polarity (of which an example is given in Fig. 1). In these systems the polar phase (usually containing water) is allowed to permeate through the hydrophilic membrane, whereas the apolar part (usually containing an organic liquid) permeates through the hydrophobic membrane. In this way, either water-in-oil or oil-in-water emulsions can be separated [12,13].

To alter the membrane surface so as to obtain specified wettability characteristics several modification methods exist. Firstly, surfaces can be treated by radiation induced grafting [14]. However, heavily grafted membranes often exhibit poor mechanical properties compared to ungrafted membranes [15]. Surfaces can also be treated with plasmas, resulting in a coupling of functional
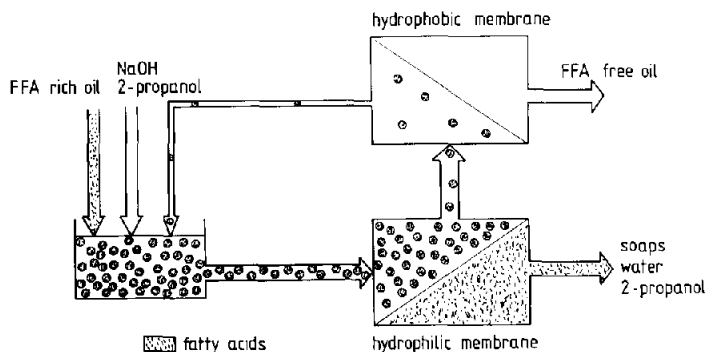

Fig. 1. Two membrane system for the removal of fatty acids from oil [13].

groups to the polymer substrate. In addition, several deposition methods have been proposed. Dip coating [16,17], deposition by plasma polymerization [18,19] and interfacial polymerization [20] are frequently used methods. A particularly practical deposition method was proposed by Franken [21], who simply modified (hydrophobic) membranes by passing a suitable (water soluble) polymer solution over them. After drying, the membrane has the wettability characteristics of the deposited polymer.

In this study the effect of the surface hydrophobicity on the adsorption of a surfactant (sodium oleate) from solution is investigated. Also, the effect of hydrophobicity on wettability by a two-phase system, namely, an emulsion consisting of soybean oil and an aqueous solution of sodium oleate and 2-propanol is investigated. In order to vary the hydrophobicity we used a modification of Franken's method: mixtures of two polymers are deposited on the membranes by passing suitable solutions through them [22]. Finally, we studied the oil selectivity of the modified membranes in the two-phase system described below.

EXPERIMENTAL

Materials

For hydrophobicity measurements, as well as wetting experiments, films consisting of mixtures of two compatible polymers have been prepared. The polymers used are summarized in Table 1. Soybean oil (triesters of glycerol and fatty acids of which more than 95% are C16 and C18) of edible quality was supplied by Rhenus Inc., The Netherlands. All other chemicals were purchased from Merck (F.R.G.) and were reagent grade. The water used was doubly distilled, and the temperature used throughout the study was 20°C. The balance used for surface tension measurements was a Mettler AE 50-S analytical balance.

Wetting behavior and separation characteristics of the different membranes used in this study were tested with an emulsion containing soybean oil as the oil phase, and water containing 2-propanol and sodium oleate (the sodium salt

TABLE 1

Polymers used to produce surfaces with a range in hydrophobicity (Polymers manufactured by Aldrich)

Polymer	M_w (D)
Polyamide (PA)	42 000
Polystyrene (PS)	150 000
Poly(methyl methacrylate) (PMMA)	Unknown

TABLE 2

Membranes used; all membranes are commercially available

Material	Code	Pore size/cut off	Manufacturer
Polypropylene (PP)	Accurel	0.2 μm	ENKA
Polypropylene (PP)	Accurel	0.1 μm	ENKA
PVDF		0.2 μm	Millipore
PVDF	IRIS 3065	10 000 D	Rhone Poulenc
PTFE		0.2 μm	Gore
Polysulfone (PSf)		30 000 D	Amicon

of cis-9-octadecenoic acid) as the water phase. The water/2-propanol/sodium oleate ratio in the water phase was 6.5:3:1 (v/v/v). The ratio between the oil and the water phase in the dispersion was 4:3 (v/v). In a previous paper [13] it was shown, that in this dispersion the oil phase as well as the water phase are present as a continuous phase at water phase contents between 20 and 65%. The transition into a discrete water-in-oil dispersion occurs at 20% water phase. The interfacial tension between the two phases was measured by the spinning-drop technique and was found to be 0.27 mN m^{-1}. This is a relavitely low value but it did not result in the formation of a microemulsion [13].

Several commercially available membranes have been tested for their capability to separate the emulsion. Of those membranes, the 0.1 μm polypropylene has also been used as support material for applied coatings. The membranes used in this study are summarized in Table 2.

Methods

Hydrophobicity

A useful measure of the wettability of a surface is the critical surface tension γ_c, i.e., the surface tension of a liquid that is just capable of giving complete wetting [23]. A good approximation of γ_c is the surface tension γ_d at which air bubble detachment takes place [24]. Since surfaces of low γ_d are hydrophobic, whereas a high value of γ_d indicates a hydrophilic surface, we can use γ_d as a quantitative measure of hydrophobicity.

Measurements of γ_d were carried out using the sticking-bubble technique [24]. A piece of membrane material or polymer film (about 1 cm^2) is placed horizontally at the bottom of a beaker containing a liquid with surface tension γ_L. Water/methanol mixtures used gave a range in γ_L of 23 to 72 mN m^{-1}. Using a 10 μl syringe with a flat ended needle (horizontal), air bubbles were brought into contact with the membrane surface. The surface tension at which the transition from adhesion to detachment takes place (γ_d) has been shown to be a measure of the surface hydrophobicity comparable to the Zisman critical surface tension (γ_c) [23].

Adsorption measurements

Adsorption of surfactant on a ground polymer material was measured from pure water as well as from water/isopropanol mixtures. Films of the different polymer mixtures were prepared by evaporation of the solvent from a 40 g l^{-1} solution in chloroform. The polymer films were then frozen in liquid nitrogen and ground in a Retsch mill with a slit size of 0.5 mm. The specific surface area of each sample was determined by methylene blue adsorption. Adsorption. of sodium oleate onto the surface was measured by the usual depletion method starting from a 3.15·10^{-2} mol l^{-1} solution in water or water/2-propanol solution (6.5:3 v/v). Oleate concentrations were determined by adding 9 ml of 2.5 M HCl to a 1 ml sample, extracting the oleic acid thus formed into hexane, and the concentrations were determined on a Carlo Erba gas chromatograph with a 5 m CP-Sil 5 CB (Chrompack, The Netherlands) capillary column with a cold on-column injection system using caproic acid as an internal standard.

Contact angle measurements

Advancing contact angles of both the oil and water phase on different polymer surfaces were determined. For this purpose the emulsion was separated into its two bulk phases by centrifugation. Glass Wilhelmy plates were dip coated in 40 g l^{-1} polymer solutions in chloroform and air-dried. The surface tension of both the water and the oil phase was determined using these plates (Fig. 2a). Next, the plates were prewetted in one phase, resulting in a thin liquid film on the polymer surface. Thereafter, the force acting on the Wilhelmy plate was measured when the plate was brought into contact with the surface of the other phase. This is shown schematically in Fig. 2b. By measuring the forces F_1 and F_2 for a particular phase (1) on a Wilhelmy plate prewetted with the same phase (1) and with the other phase (2), respectively, one finds the advancing contact angle θ_2 for phase 2 from cos $\theta_2 = F_2/F_1$. The surface tension γ_1 of phase 1 was obtained as usual from $F_1 = L\gamma_1$, where L is the length of the contact line. By measuring both the contact angle of the oil phase on water prewetted plates (θ_o) and of the water phase on oil prewetted plates (θ_w) and taking the difference between the two, one has a measure for the capability of one phase to remove the other phase from the surface.
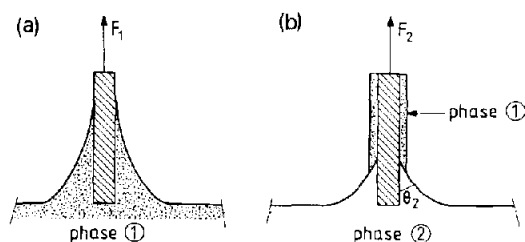

Fig. 2. Measurement of the surface tension of a liquid and the three phase advancing contact angle.

Coating experiments

Membranes were coated using a flat sheet membrane test module (Megaflow TM 100, New Brunswick Scientific Co. Inc., U.S.A.). A polymer solution (40 g l^{-1}) in chloroform was applied as a feed solution at 100 ml min^{-1}, at a starting static pressure of $0.3 \cdot 10^5$ N m^{-2}. Under these conditions only a part of the polymer solution permeated and the pores and the surface were gradually filled with polymer, which resulted in an increase of pressure as a result of an increase in membrane resistance. At a pressure of $1.0 \cdot 10^5$ N m^{-2} circulation of the chloroform solution was stopped and the flow circuit was rinsed with oil to remove the chloroform [22].

Membrane selectivity

To investigate the selectivity of commercially available membranes and coated membranes, the emulsion, described above, was led over the membrane applying a trans-membrane pressure of 10^5 N m^{-2}. The permeate was analysed for the presence of glycerides and oleate by TLC using silica gel F254 TLC sheets purchased from Merck (F.R.G.).

RESULTS

Adsorption of sodium oleate

Mixtures of polystyrene (PS) with polyamide (PA) or with poly(methyl methacrylate) (PMMA), were used to create surfaces varying in hydrophobicity. The results are presented as γ_d (determined by bubble detachment) versus mixture composition in Figs 3 and 4 for PS/PA and PS/PMMA mixtures, respectively. These curves show that γ_d does not depend linearly on the polymer composition of the mixture.

In Figs 5 and 6 the adsorbed amounts of sodium oleate onto PS/PMMA surfaces as a function of hydrophobicity (γ_d) are shown, from water and from water/isopropanol solutions, respectively. The adsorption from water (Fig. 5)
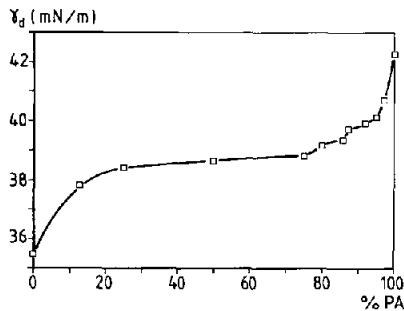
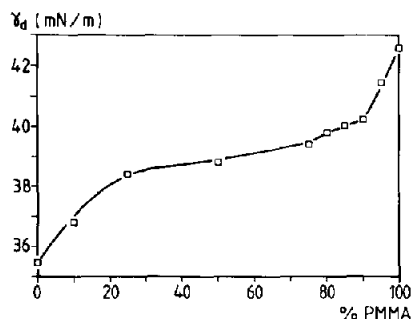Fig. 3. γ_d of PS/PA mixtures versus composition.

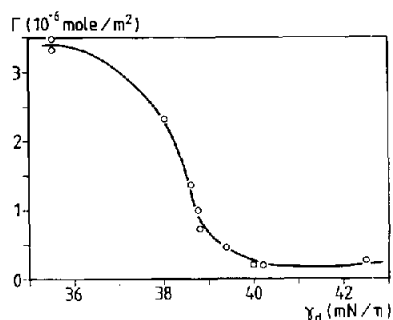Fig. 4. γ_d of PS/PMMA mixtures versus composition.

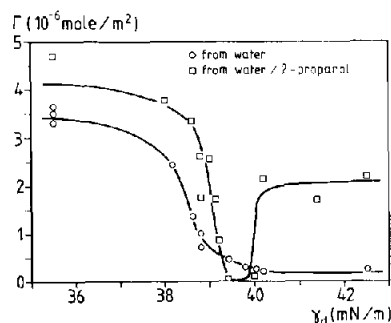Fig. 5. Adsorption of sodium oleate onto PS/PMMA particles from water.

Fig. 6. Adsorption of sodium oleate onto PS/PMMA particles from water/2-propanol (6.5:3 v/v) and water.

decreases with increasing γ_d to almost zero above a γ_d value of 39.5 mN m^{-1}. This result is in agreement with that obtained by Piirma and Chen [25] for the adsorption of sodium dodecyl sulfate (SDS) on PS/PMMA copolymer latex particles. In the case of adsorption from water/isopropanol mixtures (Fig. 6) it can be seen, that the adsorbed amounts at γ_d values below 39 mN m^{-1} are

comparable to those from water. In the region $38.5 < \gamma_d < 39.5$ mN m^{-1} the adsorbed amount drops sharply to zero. However, in contrast to the adsorption from water, a further increase of the surface hydrophilicity results in an almost stepwise increase of the amount adsorbed. Hence, three regions can be distinguished: both at low and at high γ_d we find adsorption, but in between there is a very narrow region where no significant adsorption is detected.

Wetting of the surface

Wettability by each of the liquid phases (oil and water phase, respectively) as a function of γ_d was studied by measuring the advancing contact angle. The surface tension of the water phase and the oil phase against air was determined using dip-coated Wilhelmy plates and appeared to be 28.5 ± 0.1 and 32.5 ± 0.3 mN m^{-1}, respectively. In Fig. 7a and 7b the difference in advancing contact angle ($\Delta\theta = \theta_o - \theta_w$) is plotted against γ_d for PS/PMMA and PS/PA surfaces, respectively. It turns out, that only in a very small region of γ_d did the oil phase exhibit a smaller contact angle than the water phase. This region is almost the same for both polymer mixtures. (The slight discrepancy between the two curves is presumably due to the fact that PS/PA mixtures result in somewhat rougher coatings than PS/PMMA mixtures. From contact angle calculations
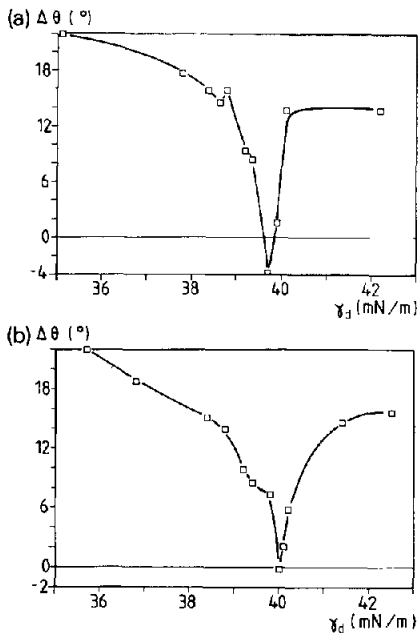

Fig. 7. The difference in advancing three phase contact angles of the water and the oil phase versus surface hydrophobicity: (a) on PS/PA and (b) PS/PMMA.

it was shown [24] that a rougher surface will result in a γ_d value that is slightly lower than that obtained on a smooth surface with the same hydrophobicity.) These results imply, that only in this small region of γ_d, is the surface better wetted by oil than by water/2-propanol. A simple analysis shows that the difference in interfacial tension ($\Delta\gamma$) between the water-wet and the oil-wet polymer surface can be related to the contact angles θ_o and θ_w and the surface tension γ_o and γ_w

$$\gamma_o\cos\theta_o - \gamma_w\cos\theta_w = \Delta\gamma + (\gamma_w - \gamma_o) \qquad (1)$$

Since $\gamma_o \approx \gamma_w$ it follows that $\cos\theta_o - \cos\theta_w \approx \Delta\gamma/\gamma_o$ (provided $\gamma_w - \gamma_o$ is negligible as compared to $\Delta\gamma$). When $\theta_o - \theta_w$ changes sign, this must imply that $\Delta\gamma$ (which is nearly equal to the spreading coefficient since $\gamma_{o/w}$ is very small) changes sign also and the oil/water contact angle will change abruptly when this happens.

Comparing Figs 6 and 7, it can be seen that the region in which no adsorption of sodium oleate takes place coincides with the region of preferential wettability for the oil phase. We conclude that the change in wettability is caused by the fact that no adsorption takes place, and that adsorption of the surfactant improves the wettability for the water phase.

Membrane selectivity

Hydrophobicity measurements were carried out on different commercially available membrane materials. For the polysulfone membrane (which is a hollow fibre device) it was not possible to measure the hydrophobicity without damaging the module severely. Therefore, a range is given for the hydrophobicity of polysulfone as it appears from earlier measurements [24]. The results are given in Table 3.

It appears that none of the membranes listed in Table 3 are selective for one of the two phases. However, from the experiments described above, it may be expected that membranes possessing a hydrophobicity (expressed in γ_d) in the

TABLE 3

γ_d of several hydrophobic membranes; the range given for polysulfone is from Ref. [24]

Membrane	γ_d (mN m^{-1})
Polypropylene (0.2 μm)	29.5
Polypropylene (0.1 μm)	29.5
PVDF (0.2 μm)	42.4
PVDF (10 000 D)	47.0
PTFE (0.2 μm)	24.2
Polysulfone (30 000 D)	49–72

narrow range between 39.5 and 40.0 mN m^{-1} should be capable of separating the oil phase from the surfactant and isopropanol containing dispersion, since on these materials no adsorption of the surfactant occurred, resulting in a good wettability for the oil phase. In order to test this hypothesis a microporous polypropylene support was coated with different PS/PA and PS/PMMA mixtures, making membranes with hydrophobicities corresponding with the hydrophobicity of the applied coating. Subsequent permeation experiments clearly
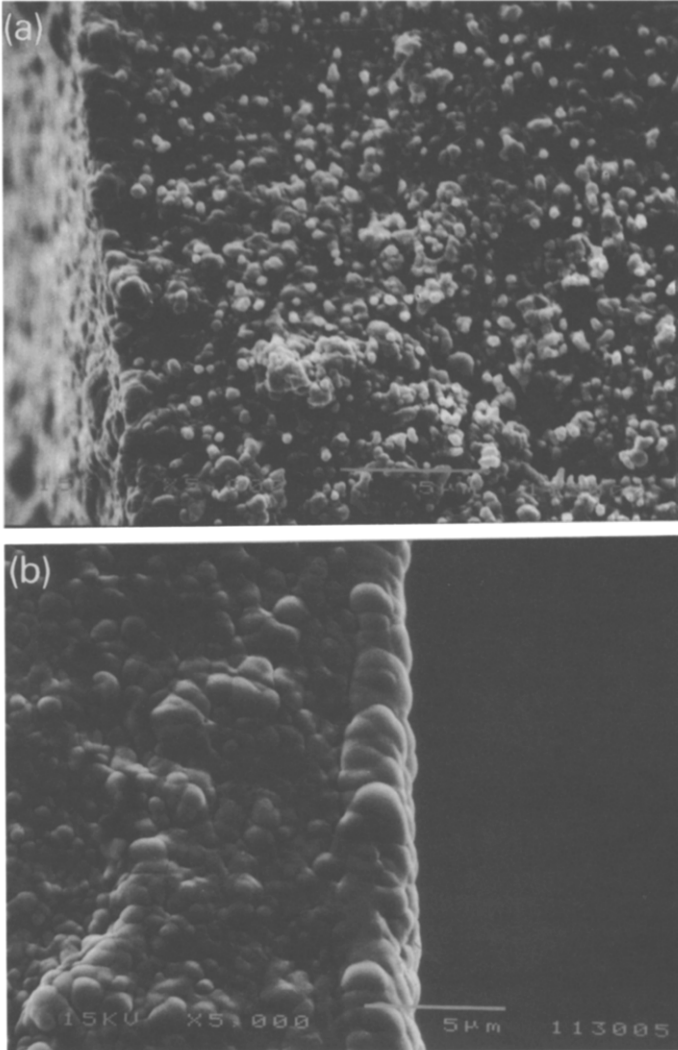

Fig. 8. (a) SEM micrograph of the polypropylene support. (b) SEM micrograph of the coated side of the microporous support.

showed that, indeed, only those coatings on which no surfactant adsorption takes place (i.e., $39.5 < \gamma < 40.0$ mN m^{-1}) are capable of separating the oil phase from the dispersion. Polymer compositions very close to, but not in this composition range are not capable of accomplishing the separation. The measured fluxes for one phase (oil) permeation are between 5 and 50 l/(m^2 h bar). These are common fluxes for ultrafiltration of solutions with comparable viscosities. No significant change in flux or selectivity was observed when experiments were run for several days.

In order to investigate the structure of the coated layer on top of the polypropylene support material, SEM micrographs were taken. From Fig. 8 it can be seen, that the nodular structure of the polypropylene (Fig. 8a) was still present at the coated side of the membrane (Fig. 8b). A layer of the applied coating onto each of the polypropylene nodules was observed, revealing that the polymer was not present as a separate film on top of the microporous support, but as a coating on the nodules of the polypropylene support. Polymer was, therefore, present in the pores, down to about 20 μm from the top surface. For this reason the adhesion between the microporous support and the coated layer was good: it is not possible to peel off the coated layer. An additional factor was the strong interaction between the hydrophobic polymer in the blend (PS) and the polypropylene support. Is has been shown by Franken [21], that strong interactions are a prerequisite for a good adhesion.

DISCUSSION

As shown in Fig. 6, three regions can be distinguished for the adsorption of sodium oleate from the water/2-propanol mixture onto surfaces with different hydrophobicities. Firstly, in the hydrophobic region the surfactant is expected to adsorb with the apolar tails towards the surface. Upon increasing the hydrophilicity of the surface, there is an almost stepwise transition into a region in which no adsorption takes place, followed by another almost stepwise increase in the amount adsorbed. In the latter region the surfactant will presumably adsorb with its polar head group towards the surface, probably followed by the adsorption of a second layer (surfactant or alcohol) on top of this first layer. From the fact that this third region is absent in pure water, it is tempting to conclude that coadsorption of 2-propanol plays also a role here.

The double adsorption transition observed gives rise to two questions. Firstly, one might wonder why the two transitions are so sharp. Secondly, it is important to know what determines their positions and why they are so close. With respect to the first question, it can be said that in general the adsorption of surfactants is a cooperative process because of the tendency of these molecules to associate. Both theoretical [26,27] and experimental [28,29] studies have provided ample evidence of this in the form of sudden jumps in the adsorption isotherm. A change in adsorption energy (at fixed surfactant concentration)

may also give rise to sharp adsorption/desorption transitions. Theoretical models predict this [30] and some evidence comes from neutron scattering studies on nonionic surfactants adsorbed onto SiO_2 where the adsorption energy was varied via pH [31]. Since adsorption/desorption transitions are so sharp it is justified, for a crude description, to consider only either entirely covered or entirely bare surfaces. It is then relatively easy to estimate surface free energies for each of these two cases and find the transition(s) by balancing them.

In order to simplify the matter, the alcohol/water mixture is considered as one component, the solvent (o). On very hydrophobic surfaces the interfacial energy between surfactant molecules adsorbed onto the surface (s) with their tails (t) will be very low, and increasing the surface hydrophilicity, the interfacial free energy will increase also. For adsorption with the head groups (h) the pattern will be reversed compared to adsorption with the tails: the more hydrophilic the surface, the smaller the interfacial free energy will be.

For adsorption with the tails onto the surface, the following requirement has to be fulfilled

$$\gamma_{ts} < \gamma_{so} + \gamma_{to} \tag{2}$$

in which γ_{ij} is the interfacial tension between components i and j; t, s and o refer to components as listed above. The term γ_{to} is a constant since it does not depend on the nature of s, but the other two vary with surface hydrophobicity. It is not necessary to incorporate a term for the head groups of the surfactant, since they remain in the solvent after adsorption. For adsorption of the head groups of the surfactant molecules an equivalent equation can be written

$$\gamma_{hs} < \gamma_{so} + \gamma_{ho} \tag{3}$$

where γ_{ho} is, again, a constant, and the other two vary with γ_d. Each of Eqns (2) and (3) may give rise to a transition; in between, one might even find a region where γ_d of the solid is such that none of them are met, so that the free energy will not decrease by exchanging solvent by heads or tails of the surfactant on the surface, and a negligible adsorption results.

In order to obtain estimates of γ_{ij} we proceed as follows. Surface tensions can be divided into a dispersive and a polar contribution. Following Fowkes [32,33], we write:

$$\gamma = \gamma^d + \gamma^p \tag{4}$$

where γ is the surface tension of the liquid, and γ^d and γ^p are the dispersive and polar components of the surface tension of the liquid, respectively. Interfacial tensions between two phases (γ_{12}) can be determined from the geometric mean of the polar and the dispersive intermolecular interactions [34,35]

$$\gamma_{12} = \gamma_1 + \gamma_2 - 2(\gamma_1^d \gamma_2^d)^{1/2} - 2(\gamma_1^p \gamma_2^p)^{1/2} \tag{5}$$

in which the subscripts 1 and 2 denote the two different liquid phases. For an estimate of interfacial tensions, surface tensions of each of the different species have to be divided into a dispersive and a polar part. For our system, tentative estimates are given in Table 4.

Surface tension components for water/alcohol mixtures have been reported by Janczuk et al. [35]. Although 2-propanol has not been investigated, it can be seen from the data for ethanol and n-propanol that the dispersive component for these two substances is almost the same; namely 20 and 21 mN m^{-1} for a 30% solution of ethanol and n-propanol in water, respectively. Therefore, a dispersive component of 21 mN m^{-1} for 30% 2-propanol in water is a reasonable estimate. The tails of the surfactant will be rather apolar. However, they contain a double bond, which gives rise to a small polar part in the surface tension. The estimate for the head group is more difficult, and although head groups usually are considered as hydrophilic, a significant part will still be due to dispersive intermolecular interactions. For the polymer surfaces we used the values reported by Wu [34], although the γ values used by this author differ slightly from γ_d as determined by us.

Using Eqns (4) and (5) and the values of Table 4, we find interfacial tensions between the different components as plotted in Fig. 9. We can locate the intersection points and determine regions of 'tail down' and 'head down' adsorption as defined by Eqns (2) and (3). It is gratifying to note that the region in which adsorption with the tails towards the surface occurs does not overlap with that in which adsorption with the head groups towards the surface occurs. As a consequence, a region of surface hydrophobicity occurs in which no adsorption takes place. Moreover, our analysis predicts transitions nearly where they are found experimentally. We should note, however, that the calculation of the interfacial tensions is rather sensitive to differences in the chosen values for γ, γ^d and γ^p. Most values in Table 4 are reasonably reliable, but the value for the head groups is perhaps less certain.

With help of Fig. 9 it is now possible to estimate the effect of changes in one or more of the components. The effect of a change in the solvent can be predicted: reducing the amount of alcohol will result in an increase of the polar

TABLE 4

Estimates of surface tension components of the different components in the system

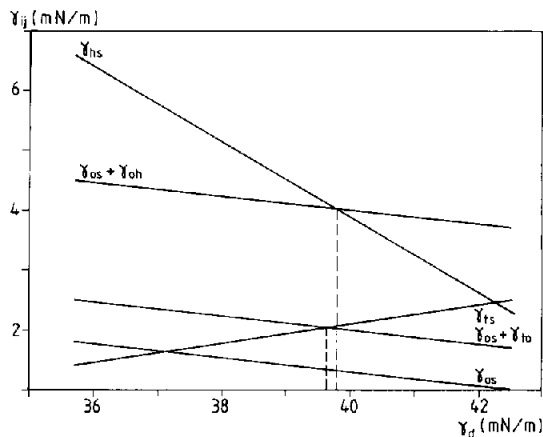| Component	γ	γ^d	γ^p	Ref.
Solvent (o)	29	21	8	[35]
Tails (t)	25	21	4	
Heads (h)	40	20	20	
Surface PS	38	33	5	[34]
PMMA	41	30	11	[34]

Fig. 9. Calculated interfacial tensions between the different constituents of the system versus the surface hydrophobicity.

part of the surface tension of the solvent, while the dispersive part will remain the same. In this region of γ_d this causes an increase in γ_{os} and γ_{to} and a decrease in γ_{ho}. This will narrow down the range in which no adsorption takes place. Eventually, the non-adsorption region may even completely disappear. The ultimate case, in which the solvent merely consists of water, clearly does not obey this rule, as is shown in Fig. 5. This can perhaps be explained by the uptake of surfactant molecules in micelles which occurs in pure water, but not in the water/2-propanol mixture. According to our simple model, cooperative adsorption from water onto a not too hydrophobic surface is possible due to polar interactions. If the molecules already associate in the bulk solution as micelles, the tendency to adsorb will be much reduced.

For a surfactant with a saturated hydrocarbon tail, the polar part of its surface tension will almost vanish, which results in an increase in γ_{to}. Similarly, in this region of γ_d, γ_{ts} will increase, and it will be the ratio of the two terms that determines whether the range in which no adsorption takes place will be broadened or reduced. The fact that a change in one component affects two or three curves at the same time makes it difficult to give precise predictions of the effects, and it will therefore be necessary that values for γ, γ^d and γ^p are known exactly to give real quantitative predictions.

CONCLUSIONS

In this study the effect of surface hydrophobicity on adsorption of sodium oleate from a water/2-propanol solution is investigated. It appears that adsorption of the surfactant takes place in three regions. On a more hydrophobic surface the surfactant will adsorb with the hydrophobic tails onto the surface;

increasing the surface hydrophilicity leads to a narrow region in which virtually no adsorption occurs, followed by a region in which adsorption occurs again, presumably by interactions between the head groups of the surfactant and the surface. From wetting studies it follows that in the regions where adsorption takes place the surface appears to be rather hydrophilic. Surfactant adsorbed onto the hydrophobic solid will expose its polar head groups to the solution, whereas in the case of the more polar solid, a second surfactant or alcohol layer will adsorb on top of the first layer, also rendering the surface more hydrophilic. These adsorption phenomena can be explained in a semiquantitative way by taking the cooperative nature of surfactant adsorption into account and making estimates of free energies for various conceivable interfaces in the system.

It appeared that surfaces in the region where no adsorption of sodium oleate occurs are preferentially wetted by the oil phase of a two-phase system consisting of soybean oil as the oil phase and a sodium oleate solution in water/2-propanol as the water phase. These results have been used to develop a membrane material with the required wetting properties for the separation of such a mixture. Since the range in hydrophobicity in which no adsorption occurs is only 0.5 mN m^{-1} wide, it is not surprising that no commercially available membrane is capable of separating the oil phase from this two-phase system. However, it should be realized that a change in the composition of the mixture to be separated can induce significant changes in the adsorption and wetting behavior. In order to obtain guidelines, it is necessary to have estimates of the different contributions to the surface tension of each of the components of the mixture to be separated and to use these to predict adsorption/desorption transitions of the system.

ACKNOWLEDGEMENTS

LIST OF SYMBOLS

F_1 Force acting on Wilhelmy plate wetted by phase 1 (N).
F_2 Force acting on Wilhelmy plate wetted by phase 2 (N).
h   Head groups of surfactant.
o   Solvent.
s   Surface.
t   Tails of surfactant.
γ Surface tension (mN m^{-1}).
γ_c Zisman critical surface tension (mN m^{-1}).

γ_d Surface tension at air bubble detachment $(\mathrm{mN\ m^{-1}})$.

γ_L Liquid surface tension $(\mathrm{mN\ m^{-1}})$.

γ_{12} Interfacial tension $(\mathrm{mN\ m^{-1}})$.

γ_{ij} Interfacial tension between two components $(\mathrm{mN\ m^{-1}})$.

$\gamma_{o/w}$ Oil/water interfacial tension $(\mathrm{mN\ m^{-1}})$.

γ^d Dispersive component of surface tension $(\mathrm{mN\ m^{-1}})$.

γ^p Polar component of surface tension $(\mathrm{mN\ m^{-1}})$.

$\Delta\gamma$ Difference in interfacial free energy between oil-wetted and water phase-wetted surface $(\mathrm{mN\ m^{-1}})$.

θ_1 Phase 1 advancing contact angle $(°)$.

θ_2 Phase 2 advancing contact angle $(°)$.

θ_o Oil phase contact angle $(°)$.

θ_w Water phase contact angle $(°)$.

$\Delta\theta$ Difference in contact angle between oil and water phase $(=\theta_o-\theta_w)$ $(°)$.

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