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ORIGINAL CONTRIBUTION

Wetting properties of aqueous solutions of hydrophobically modified inulin polymeric surfactant

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Abstract The contact angles of aqueous solutions of a polymeric surfactant namely hydrophobically modified inulin (INUTEC®SP1) were measured on hydrophilic and hydrophobised quartz glass surfaces using the sessile drop technique. These measurements showed a large difference (>10°) between the advancing contact angle θ_1 (that is measured immediately after placing the drop on the surface) and the constant contact angle θ_2 (that is measured 30 minutes after placing the drop). In all the results only the contact angle θ_2 was subsequently measured. θ versus INUTEC®SP1 concentration C_s curves were obtained at various NaCl concentrations both on hydrophilic and hydrophobic glass surfaces. On hydrophilic glass surface the θ versus C_s curves showed a maximum at a concentration range of 10^{-6} to 2×10^{-5} mol dm^{-3} INUTEC®SP1. These curves were shifted to lower values as the NaCl concentration was increased. On such hydrophilic surface the INUTEC®SP1 molecule adsorbs with the polyfructose loops and tails oriented towards the surface leaving the alkyl chains in solution. Saturation adsorption with this orientation occurs at 2×10^{-5} mol dm^{-3} INUTEC®SP1. However, the contact angles remain quite small (<18°) indicating the presence of several hydrophilic glass patches uncovered by surfactant molecules. At $C_s>2\times10^{-5}$ mol dm^{-3} θ decreases with further increase of the INUTEC®SP1 concentration reaching 5° at the Critical Association Concentration (CAC) of the polymer. This indicates the formation of a bilayer of INUTEC®SP1 molecules with the alkyl chains hydrophobically attached to those of the first layer. On a hydrophobic glass surface, adsorption of INUTEC®SP1 occurs by multi-point attachment with the alkyl chains on the surface leaving the hydrophilic polyfructose loops and tails dangling in solution. This results in a gradual decrease of the contact angle with increase in INUTEC®SP1 concentration, reaching a plateau value (>85°) between 2×10^{-5} and 2×10^{-4} mol dm^{-3}. The large contact angles obtained on adsorption of the polymeric surfactant on a hydrophobic surface indicate the presence of several uncovered hydrophobic patches. These results give a reasonable picture of the adsorption and orientation of the INUTEC®SP1 molecules on both hydrophilic and hydrophobic solid surfaces.

Keywords Wetting · Contact angles · Polymeric surfactant · Hydrophobically modified inulin

Introduction

The adsorption and conformation of polymeric surfactants at various surfaces, namely air/liquid, liquid/liquid, and solid/liquid, are of vital importance in application in foam, emulsion and dispersion stability [1]. For fundamental understanding of the role of polymeric surfactants in these systems it is essential to carry out direct measurements of the interaction forces in the liquid films between the

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surfaces involved. For foam and emulsion films measurement of the disjoining pressure as a function of film thickness [2, 3] gives such information. For the solid/liquid dispersions atomic force microscopy (AFM) measurements can provide an accurate method for such investigation [4, 5]. However, the adsorption and conformation of the polymer at the solid/liquid interface can also be obtained from wetting contact angle measurements. This is particularly important for distinguishing between hydrophilic and hydrophobic surfaces.

In this paper, we have applied wetting contact angle measurements for a novel non-ionic polymeric surfactant, namely hydrophobically modified inulin (INUTEC®SP1) [6] on both hydrophilic and hydrophobic surfaces. The results obtained can give direct information on the conformation of the polymeric surfactant on both surfaces. This can be related to the stabilization of solid/liquid dispersions which is important in many technological applications. INUTEC®SP1 was used in the preparation and stabilization of latex dispersions [7]. In addition the stability of many dispersions was carried out under conditions of high temperature and high electrolyte concentration and this showed the enhanced stability obtained using INUTEC®SP1. Direct measurement using the AFM illustrated the strong steric repulsion between hydrophobic surfaces containing adsorbed polymeric surfactant molecules [8].

The above mentioned non-ionic polymeric surfactant is an AB_n graft copolymer with a linear polyfructose backbone (A) with degree of polymerization greater than 23 on which several alkyl (C_{12}) B-chains are attached [9]. On a hydrophilic surface, one would expect adsorption with the polyfructose loops and tails pointing to the surface leaving an alkyl group in the medium. It is also possible to have a second layer with hydrophobic bonding of the alkyl groups and now leaving the polyfructose loops and tails in solution. On a hydrophobic surface, one would expect adsorption with multi-point attachment with several alkyl chains leaving loops and tails of polyfructose chains dangling in the aqueous solution. Such adsorption behavior should have a direct influence on the wetting contact angle on the surface, and this is the main objective of the present paper.

Experimental section

Materials

The polymeric surfactant was the non-ionic inulin on which several alkyl groups have been grafted [9] (INUTEC®SP1, ORAFTI, Belgium). Its average molecular mass is approximately 4500 g.mol^{-1}. The inulin backbone (linear polyfructose) has a degree of polymerization greater than 23. Grafting was carried out using alkyl isocyanates in a nonaqueous solvent. The polymer was purified either by solvent precipitation or by supercritical CO_2 extraction. The chemical structure of the polymeric surfactant [9] is presented in Fig. 1. The chemical composition of the modified polymer is not completely characterized there, since no such data have been provided by the producer ORAFTI. Aqueous INUTEC®SP1 solutions were prepared in the presence and absence of electrolyte. NaCl (from Merck) was heated for 2 hours at 500 °C to remove any organic impurities. Twice distilled water has been used for preparation of all solutions.

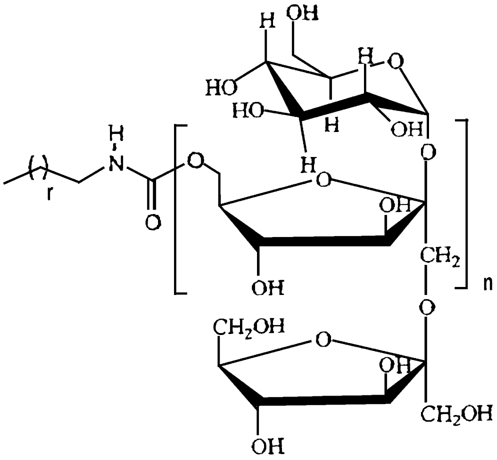

Fig. 1 Structure of inulincarbamates

A series of aqueous solutions of INUTEC®SP1 with different concentrations in the range 5×10^{-8}–2×10^{-4} mol dm^{-3} have been prepared. Each series of solutions were also prepared in the presence of NaCl at the following concentrations: 0, 10^{-4}, 10^{-2}, 10^{-1} and 1 mol dm^{-3}. In total five series of INUTEC®SP1 aqueous solutions have been studied.

Two different solid substrates have been used: (i) A quartz glass smooth flat plate which was very carefully washed with acid mixtures and rinsed several times with twice distilled water to obtain a substrate with a hydrophilic surface. A drop of twice distilled water placed on this surface completely spreads giving a zero contact angle. (ii) A second identical quartz glass flat plate was carefully

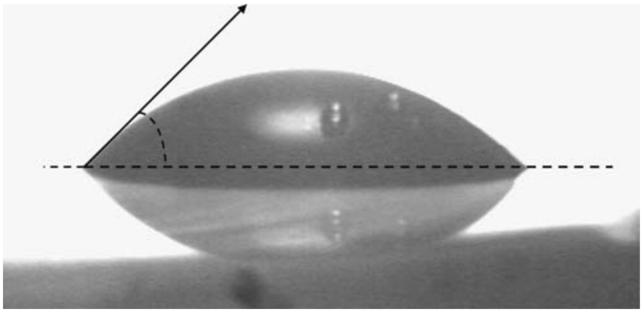

Fig. 2 Image of a sessile drop on a solid surface; the contact angle is determined using image analysis

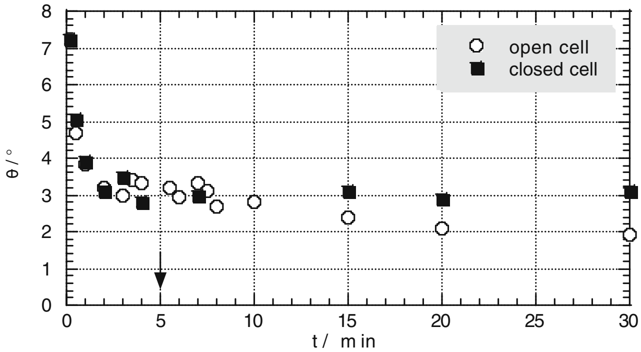

Fig. 3 Time dependence of the contact angle on the hydrophilic solid surface in open or closed cell for 5×10^{-5} mol dm^{-3} INUTEC®SP1+0.1 mol dm^{-3} NaCl aqueous solution

hydrophobised by immersion in a solution of trimethylchlorosilane in dichloromethane for 12 hours. The plate was removed from the solution and rinsed several times with dichloromethane and finally dried at 95 °C to obtain a substrate with a hydrophobic surface. A 0.5 μl drop of twice distilled water placed on the plate and immediately measured (see below), gave a contact angle of 102° (this should be the advancing contact angle).

Methods of measurement

The contact angle θ was measured using the sessile drop technique [10] that is suitable for a solid surface. The latter was placed on a horizontal table that was attached to a mechanical device which allows one to move it up and down. The whole plate was covered by a glass cuvette with plane-parallel optical walls. The polymer solution used for the contact angle measurements was carefully placed near the glass plate using a pipette in order to obtain a saturated vapor. A micro-pipette containing the aqueous polymer solution is fixed normal to the solid substrate using another mechanical device that can also move it up and down. A micro-drop (volume of 0.5 μl) of the solution under investigation is placed on the solid surface using the micro-pipette.

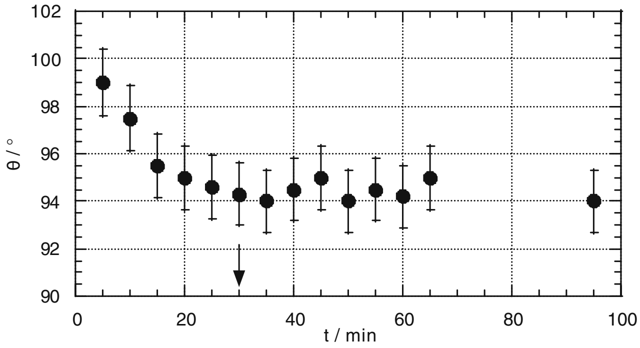

Fig. 4 Time dependence of contact angle on the hydrophobic solid surface for 2×10^{-7}mol dm^{-3} INUTEC®SP1 + 10^{-4} mol dm^{-3} NaCl aqueous solution

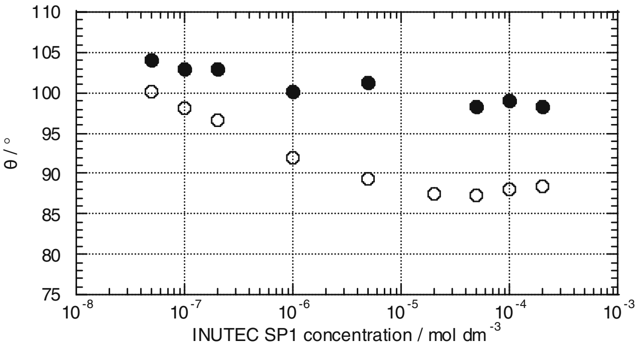

Fig. 5 Dependence of the contact angles θ_1 (●) and θ_2 (○) on INUTEC®SP1 concentration for hydrophobic solid surface (solutions without salt)

The drop on the solid surface is illuminated using white diffuse light. This drop was observed through the optical cuvette walls using a telemicroscope. The powerful objective used, produced a clear image of the drop (Fig. 2) which was directly transferred through a CCD-camera to show the drop profile that can be analyzed using the computer program. The contact angle solid/liquid/gas is determined from the tangent to the drop at the three phase contact line. A special computer program (IMAQ Vision Builder) was used for image analysis.

The surface tension γ of all the solutions studied was measured using the Wilhelmy plate method (using a microbalance, Techniport, Poland). All measurements of the θ and γ were carried out at a temperature of 22°±0.5 °C. The accuracy of γ is±0.2 mN.m^{-1} and that of the contact angle measurements is±0.3° in the range of 1°–5°, ±1.0° in the range of 5°–20°, and ±1.5° in the range of 75°–100°.

Results and discussion

Time dependence of the contact angles

Figure 3 shows the variation of the contact angle with time for a 0.5 μl drop of an INUTEC®SP1 solution (5×

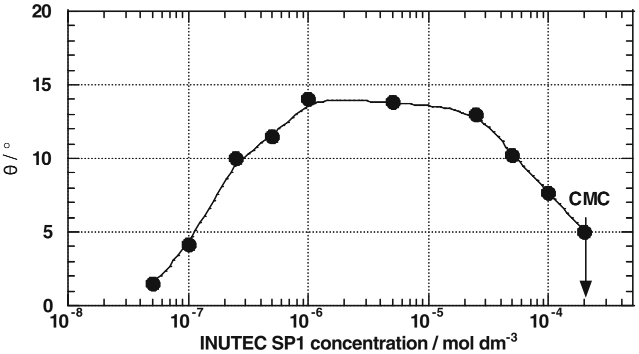

Fig. 6 Dependence of the contact angle on the INUTEC®SP1 concentration for hydrophilic solid surface (solutions without salt)

10^{-5} mol dm^{-3}+10^{-1} mol dm^{-3} NaCl) for both an open cell and a closed cell using a saturated atmosphere of the vapour of the same solution. For the open cell, there is a continues reduction of contact angle with time, which continued even after 30 minutes and this must be due to the evaporation of the INUTEC solution. However, when using a closed cell, the contact angle decreases with time and became constant after 5 minutes. On a hydrophobised surface and using a saturated atmosphere the contact angle became only constant after 30 min (Fig. 4). Based on these results, all

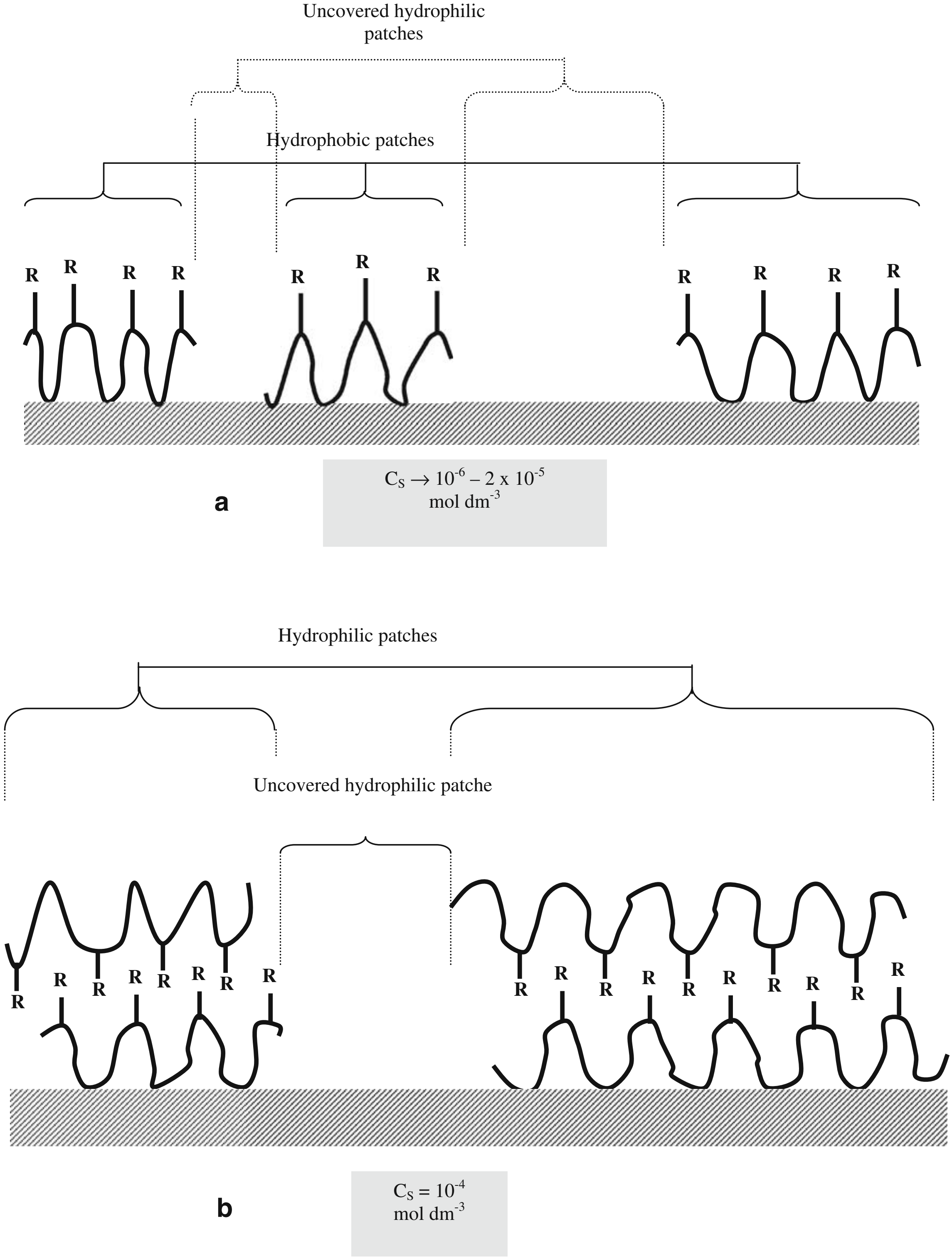

Fig. 7 Schematic representation of the adsorption of INUTEC®SP1 (including the formation of a bilayer) on a hydrophilic surface

Table 1 Surface tension γ as a function of surfactant (C_s) and electrolyte (C_{el}) concentrations and the CAC-values obtained

C_{el} mol dm^{-3}	C_s mol dm^{-3}						CAC mol dm^{-3}
	10^{-6} γ, mN m^{-1}	5×10^{-6}	2×10^{-5}	5×10^{-5}	10^{-4}	2×10^{-4}	
10^{-4}	67.0	61.1	56.1	52.5	50.5	50.8	10^{-4}
10^{-2}	63.5	58.0	54.5	52.0	50.5	50.8	7×10^{-5}
10^{-1}	60.0	55.0	52.5	50.2	50.3	-	5×10^{-5}
1	57.2	54.5	51.0	51.5	50.1	50.9	3×10^{-5}

subsequent measurements were carried out after 30 min from placing the drop on the substrate.

Hysteresis of the contact angles

It is well known that on any real solid surface there is a static hysteresis of the contact angles of the three-phase contact gas/liquid/solid [10]. The advancing contact angle θ_1 can only be obtained immediately after placing the drop on the substrate. However, even in a saturated atmosphere one cannot completely avoid some evaporation since the vapor pressure of the small drop (with a large curvature) is slightly higher than that of the equilibrated vapor pressure of the surrounding atmosphere. For this reason the contact angle continues to decrease with time and the constant angle θ_2 obtained after 30 min should be close to the receding contact angle. The reduction of the drop volume during the 30 min evaporation (stabilization) time, calculated from the initial and final drop images, was less than 2%.

Figure 5 illustrates the dependence of θ_1 (that was immediately obtained after placing the drop on the substrate) and the constant value θ_2 (obtained after 30 min) for INUTEC®SP1 solutions with various concentrations on a hydrophobic surface. It can be seen from this figure that the difference between θ_1 and θ_2 can be higher than 10°, particularly at higher INUTEC®SP1 concentrations. In all subsequent results θ is simply the value of θ_2.

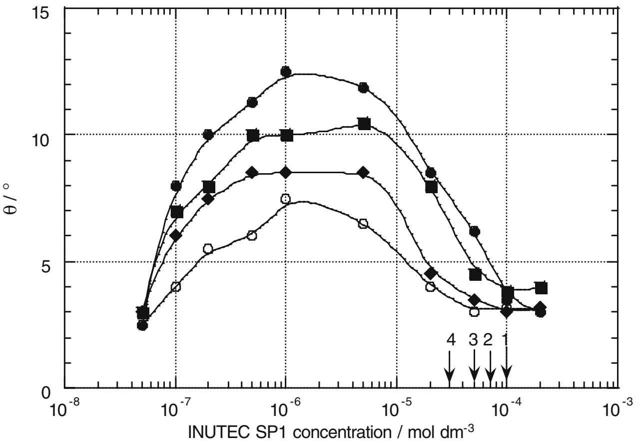

Fig. 8 Dependence of the contact angle on the INUTEC®SP1 concentration for hydrophilic solid surface in the presence of different NaCl concentrations: 10^{-4} (●), 10^{-2} (■), 10^{-1} (♦), and 1 (○) mol dm^{-3}

Contact angles on hydrophilic glass surface

Figure 6 shows a plot of θ versus INUTEC®SP1 concentration (C_S) on hydrophilic glass surface. All values are quite small (1 - 15°), but they clearly show initial increase in the contact angle reaching a maximum at about 10^{-6} mol dm^{-3} and then θ starts to decrease at about 2×10^{-4} mol dm^{-3} INUTEC®SP1. The value of θ at the lowest C_S (5×10^{-8} mol dm $^{-3}$) that is equal to 1° is close to that of pure water (0°). At such surfactant concentration very low coverage of the surface with the surfactant molecules occurs. With increase in C_S more surfactant adsorption occurs with the hydrophilic polyfructose chain oriented to the surface and hence the surface becomes more and more hydrophobic resulting in an increase of the contact angle. Although not too large, the change of the contact angle with respect to the complete wetting (θ=0°) is significant and reliable. It can be due only to the adsorption of INUTEC®SP1 on both solid/liquid and liquid/air interfaces. The following qualitative picture could be drawn up on basis these data.

It is quite likely that saturation adsorption with this orientation occurs between 10^{-6} and 2×10^{-5} mol dm^{-3} INUTEC®SP1. The decrease of contact angle above this concentration may be due to formation of a bilayer now with alkyl chains hydrophobically attached to the first INUTEC®SP1 layer leaving the polyfructose hydrophilic chain oriented to the solution. A schematic picture of this

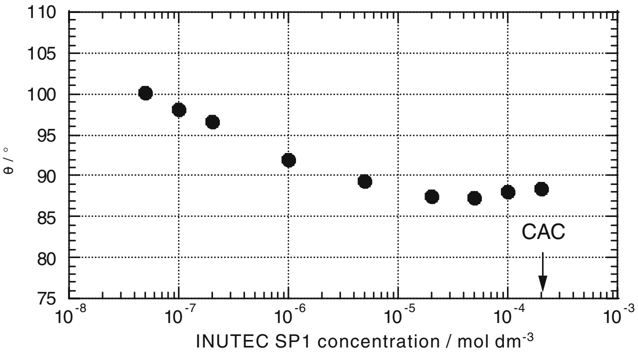

Fig. 9 Dependence of the contact angle on INUTEC®SP1 concentration for hydrophobic solid surface (solutions without salt)

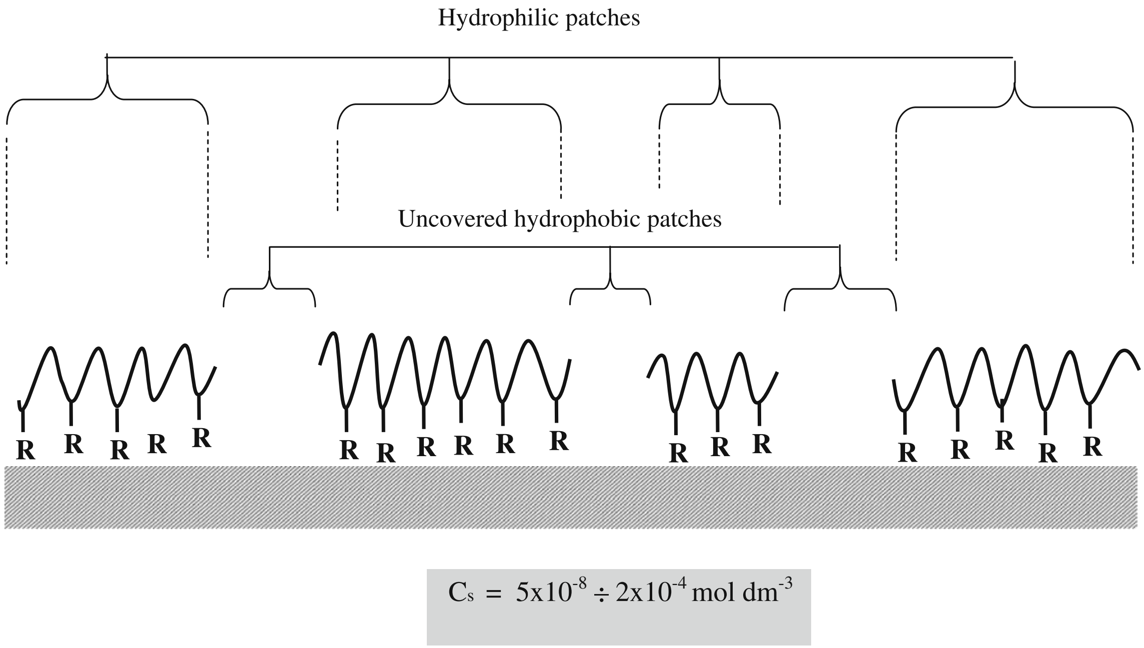

Fig. 10 A schematic picture of the adsorption of INUTEC®SP1 on hydrophobically modified glass surface

bilayer on a hydrophilic surface is shown in Fig. 7, which also shows the presence of hydrophilic patches on the surface that accounts for the low contact angle observed. This low θ value obtained at 2×10^{-4} mol dm^{-3} INUTEC®SP1 is equal to the critical association concentration (CAC) of the polymer.

The CAC was obtained from the γ-log C_S curves. A summary of the measured surface tension γ as a function of surfactant and electrolyte concentration as well as the CAC-values obtained at various NaCl concentrations is given in Table 1.

The influence of addition of electrolyte (NaCl) on the θ-C_S curves is shown in Fig. 8. Several NaCl concentrations were used namely 10^{-4}, 10^{-2}, 10^{-1}, and 1 mol dm^{-3}. The general trend of the variation of θ with C_S is roughly the same as that obtained in aqueous solution without salt (Fig. 6). However, there seems to be a gradual shift in the θ-C_S curves to lower values with increase of NaCl concentration. The CAC value (Table 1) of the polymer at each NaCl concentration is indicated by an arrow in Fig. 8. It is clear that the CAC decreases with increase in NaCl concentration. This can be accounted for by the reduction

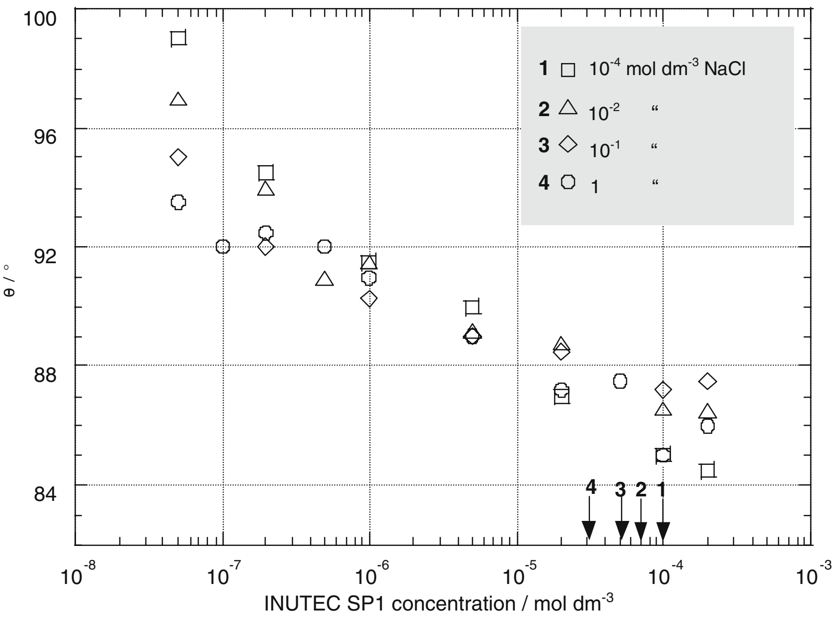

Fig. 11 Dependence of the contact angle on the INUTEC®SP1 concentration for hydrophobic solid surface in the presence of different NaCl concentrations

of the hydration of polyfructose chain with increase of NaCl concentration. This reduction of hydration is also reflected in the reduction of contact angle with increase of NaCl concentration. Evidence for this dehydration on addition of electrolyte was obtained from AFM measurements [6] which showed a systematic reduction in the adsorbed layer thickness of the polymeric surfactant with increase of Na_2SO_4 concentration.

Contact angles on hydrophobic glass surface

Figure 9 shows the θ-C_S curve on hydrophobised glass surface. The trend in this case is completely different from that for hydrophilic surface. The θ at low C_S (5×10^{-8}mol dm^{-3}) is quite large (100°) and it showed a gradual decrease with increase of C_S reaching values between 85 and 90° at a concentration range of 2×10^{-5}–2×10^{-4} mol dm^{-3}. This reduction in contact angle with increase in C_S can be attributed to the adsorption of the polymer surfactant on a hydrophobic surface with the alkyl groups pointing to the surface leaving the loops and tails of polyfructose dangling in solution. However, the large contact angle obtained (>85°) at the CAC implies incomplete coverage of the surface with hydrophilic loops and tails. It is quite likely that the adsorption of the polymeric surfactant does not completely cover the surface with the chains leaving some hydrophobic patches in between. A schematic picture of the adsorption of INUTEC®SP1 on hydrophobically modified glass surface is shown in Fig. 10, which illustrates the presence of the above mentioned hydrophobic patches.

The influence of addition of NaCl to the INUTEC®SP1 solution on the contact angle of the θ-C_S curves is shown in Fig. 11. The CAC values are also indicated by arrows on the figure. The general trend is the same but in this case the θ-C_S curves do not shift much from the values obtained for the aqueous solution without salt (Fig. 9). All the values seem to be very close to each other (within experimental error). This behavior is consisted with the patches shown in Fig. 10. Addition of electrolyte will cause some dehydration of polyfructose loops and tails but since the θ-values are determined by the hydrophobic patches such reduction in hydration will not cause a significant increase in θ-values.

Conclusions

Contact angle measurements of drops of hydrophobically modified inulin (INUTEC®SP1) aqueous solutions on both hydrophilic and hydrophobic glass surfaces give valuable information on the adsorption and conformation of the polymeric surfactant on these surfaces. On hydrophilic glass surface the INUTEC®SP1 molecule adsorbs with the hydrophilic loops and tails of polyfructose oriented towards the glass surface leaving the alkyl chains in solution. Saturation adsorption with this orientation occurs at an INUTEC®SP1-concentration between 10^{-6} and 2×10^{-5} mol dm^{-3}. However, the measured contact angle does not exceed 18° indicating the presence of patches of uncovered hydrophilic glass surface. On increasing the INUTEC®SP1 concentration above 2×10^{-5} mol dm^{-3} the contact angle decreases reaching a value of 5° at the Critical Association Concentration (CAC) of the polymer. This indicates the formation of a bilayer with the alkyl chains of the polymer hydrophobically attached to the alkyl chains of the first layer leaving the hydrophilic polyfructose loops and tails pointing to the solution. On a hydrophobic glass surface adsorption occurs with multi-point attachment of the alkyl chains on the surface leaving the hydrophilic polyfructose loops and tails in solution. However, the contact angle reached at the CAC is still above 85° indicating the presence of hydrophobic patches on the glass surface. These contact angle measurements can be used for interpretation of the wetting film studies that will be reported in a subsequent publication.

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