Polymer–Micelle Interactions: Physical Organic Aspects

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1 Introduction

Studies of the interaction between non-ionic, water-soluble polymers and micelles have their roots in biochemistry, for they originated from the study of protein–surfactant interaction.[1,2] Polymer–micelle interaction[3] in turn may now serve as a simplified model for biological binding processes, for instance to cell membranes. An important difference between proteins and non-ionic polymers is the complete absence of charged groups in the latter. Consequently polymer–micelle interaction results from an accumulation of relatively weak binding forces, which makes the association process even more intriguing.

At an early stage of the research in this field, it was recognized that in the polymer–micelle complex the properties both of the micelles and of the polymers are mutually modified.[2,4] To mention the most important aspects with respect to industrial applications, the solubilization power as well as the viscosity of an aqueous solution of polymer-bound micelles is higher than that of the separate surfactant and polymer solutions.[2–4] This commercial interest is reflected in the fact that many of the early reports on polymer–micelle interaction originated from industrial research laboratories.[2,5–8] The properties of the polymer–micelle complex are very well appreciated in formulations for paints and coatings, in cosmetic products, and in laundry detergents. Polymer–micelle interaction also plays a role in tertiary oil recovery.

Although the applications of polymer–micelle complexes are numerous, many problems are still unsolved. Particularly, the question of how the precise chemical structure of the surfactant and the morphology of the unperturbed micelle are related to the tendency for association with polymers poses a challenge for chemists. The very limited choice of surfactants as well as dubious generalizations[3] in the study of polymer–micelle interaction certainly obscure this problem. For example, the belief that in general anionic micelles interact with polymers, cationic micelles hardly, and non-ionic micelles not at all was deduced with sodium n-alkylsulfates, predominantly sodium n-dodecylsulfate (SDS), as representatives of anionic surfactants, with n-alkyltrimethyl-ammonium bromides as representatives of cationic surfactants, and with n-alkoxypoly(ethylene oxide) ethers as representatives of non-ionic surfactants. Not only is the generalization unwarranted but also the rationalization behind it is hampered by the limited choice of surfactants.

1.1 The Development of the Polymer–Micelle Model

The recognition of the interaction between non-ionic, water-soluble polymers and surfactants occurred decades later than the notion that surfactants proper form aggregates. But the *morphology* of the micelle attracted minimal comment until the eighties, despite the enormous number of articles devoted to the properties of micelles. In contrast, the morphology of the polymer–surfactant complex puzzled chemists from around 1955, when the pioneering work of Saito[4] was published, till the end of the seventies when an NMR study of the poly(ethylene oxide) (PEO)/SDS system by Cabane[9] firmly established the contemporary model. However, many intriguing questions remain. In particular, the relationship between the chemical structure of surfactant and polymer and their propensity for interaction, and also the dominant driving force for interaction are still debated in the literature.

In 1957, Saito[4] published the first extensive study on polymer–surfactant complexation. Two major observations were (i) an increase in viscosity of an aqueous poly(vinylpyrrolidone) (PVP) solution upon addition of SDS and (ii) an increase in solubilizing power of an SDS solution upon addition of PVP. Though it was suggested that the aggregation of sufactant molecules in the presence of polymer resembled normal micellization, Saito proposed that, at a low surfactant-to-polymer ratio, the surfactant molecules bind individually to the polymer (as in the case for protein–surfactant interactions at low surfactant concentration). This binding was thought to occur by dipolar interaction of the surfactant headgroups with polar sites on the polymer, while the surfactant chain was thought to lie parallel to the polymer chain. At a higher degree of saturation the location of the alkyl chain would be altered. However, Saito[4] wisely stated that the structure of the polymer–micelle or polymer–surfactant complex had not yet been clearly established.

The major concept to emerge in the following decade, summarized in Breuer's and Robb's review article,[2] was the picture of individual molecules along the polymer, with some kind of micellization occurring above the critical micelle concentration (cmc) of the surfactant in pure water.[10,11]

Many details of polymer–micelle interaction were revealed in that period, including the finding that complexation takes place even below the normal cmc.[10] This has long been used as

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support for individual binding[12] It was also found that above a minimum molecular weight (MW) of the polymer, the interaction is independent of MW,[7,8,10] and that a certain saturation takes place at increasing surfactant concentration[5,10] The importance of hydrophobic interactions[2] in polymer–surfactant complex formation was deduced from the stronger interactions obtained as polymer hydrophobicity[4,10] and surfactant alkyl chain length were increased[10] Much later, in 1987, measurements of heat capacities and apparent molar volumes also revealed a shift of these thermodynamic properties, upon addition of polymer, in the direction of enhanced hydrophobic association[13]

Using cmc values for a series of homologous sodium alkyl sulfates, $C_nH_{2n+1}OSO_3Na$ (n = 10, 11, 12), either with or without added PVP, Shinoda[6] derived the Gibbs energy of transferring a CH_2 group from the aqueous solution to either the aggregate (polymer—micelle complex) or the micelle to be in both cases 1 1 kT He deduced from these data that C_nH_{2n+1}-OSO_3Na molecules absorbed on PVP are in contact with each other, and are not uniformly distributed on the PVP macromolecule, right from the initial stages of absorption In the same year, Lange[5] commented on the discrepancy between the increase in viscosity upon polymer–surfactant complexation, which indicates coil expansion, and the increased solubilizing power of the polymer–surfactant complex, which involves a compact structure of the complex He also stressed the cooperative nature of the complex formation, which is apparent from the existence of a critical concentration for its formation These arguments appeared to require the notion that *micelles* bind to the polymer – but initially another explanation was advanced to explain the new results[5]

The idea that surfactants bind to polymers in clusters took hold[7,8] and the next issue gradually became apparent Tokiwa and Tsujii (1973)[7] assumed without any discussion that the surfactant micelles encompass portions of the polymer chain Shirahama,[12] however, in 1976 suggested that a binding of the polymer at the micellar surface (above the cmc) occurs leading to a stabilization through reduction of the core–water contact, but he did not yet believe in the existence of micelles below the unperturbed cmc He also predicted lower aggregation numbers for the polymer-bound micelles[12]

In 1977 Cabane[9] established the polymer–micelle model as it is now quite generally accepted (see, for instance, the excellent review article of Goddard[3]) Figure 1 gives a schematic representation of the model Cabane studied the PEO/SDS system using ^{13}C, ^1H, and ^{23}Na NMR Only the first three carbon atoms of SDS, counted from the SO_4 headgroup, exhibit ^{13}C chemical shifts consistent with the presence of PEO Cabane[9] concluded that in the polymer–micelle complex the major part of the alkyl chain resides in an environment indistinguishable from a normal micelle, which is a micellar core The first three carbon atoms are influenced by the polymer because the polymer binds at the micellar surface, which in an unperturbed micelle (according to Cabane) is one third occupied by $-SO_4^-$ groups The other two thirds of the surface contain primarily the first chain segments The NMR signals of the polymer are barely influenced by complexation with micelles That is interpreted as an indication that only a fraction of the polymer is actually absorbed onto the micellar surface, whereas the rest protrudes as loops in the aqueous surroundings This was anticipated because total absorption and thus a restricted mobility of the polymer chain would be very unfavourable for entropic reasons Cabane[9] also mentions two sound, common sense reasons why PEO should bind at the micellar outer sphere First, PEO does not dissolve in hydrocarbons, and will therefore not penetrate into the hydrophobic micellar interior Second, most probes that have been used to study micellar properties are quite hydrophobic but still bind at the micellar surface Therefore it is likely that even rather hydrophobic polymers like poly(propylene oxide) (PPO), poly(vinylmethylether) (PVME), partially acetylated poly(vinylalcohol) (PVA-Ac), and hydroxypropyl cellulose (HPC) will also seek the outer layer of the micelle

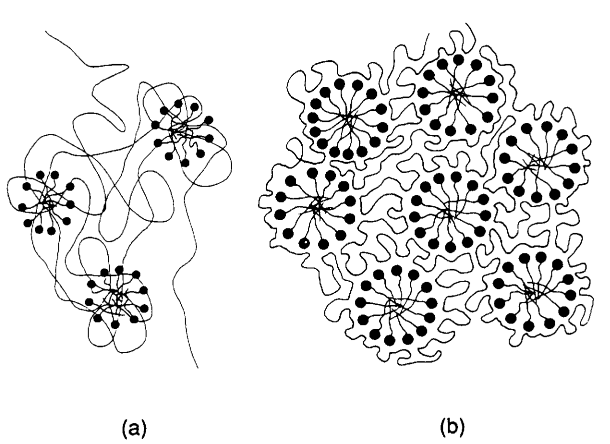


Figure 1 Schematic representation of a polymer–micelle complex according to Nagarajan The probably more realistic representation (a)[15e] from 1985 shows the development of the model Figures (a) and (b), reproduced by permission, from references 15*e* and 15*b* respectively

Very recently, Kwak *et al*[16] published an NMR study on the system ω-phenyldecanoate/PEO and concluded that PEO resides in the interior of the micelle The conclusions were based on ^1H aromatic ring current-induced shifts of the PEO protons However, the argument hinges on the (debatable) assumption that the phenyl moieties do not fold back to the surface of the micelles

Two additional indications that both hydrophilic polymers and relatively hydrophobic polymers bind to the micellar surface are the smaller aggregation numbers of polymer-bound micelles[14,17,20] and the variation in interaction tendency with headgroup charge[4,8,13,21] (*vide supra*) The decrease in aggregation number was initially only documented for the system PEO/SDS,[14,17,21] PVP/SDS,[17,18,20,21] and PVA/SDS[17] but has recently also been reported for PPO/SDS[19,21] and, in our studies, for CTAB in the presence of PPO and PVME (Section 4) This is in accord with the presence of the polymer at the micellar surface, whereas solubilization in the core is expected to lead to an increase in aggregation number The effect of short-chain and long-chain alcohols and alkanes on the aggregation number of micelles supports these considerations[22,23] Short-chain alcohols, which reside at the micellar surface decrease the aggregation number,[23] whereas alkanes which reside in the core increase the aggregation number[22] The finding that cationic surfactants usually interact more weakly with polymers than anionic surfactants do, (which will be discussed in detail below), also points to a location of the polymer in the same region as the headgroups, whatever the origin of the difference is

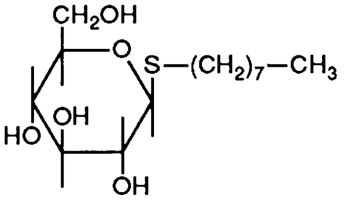
Gilanyi and Wolfram,[17] in 1981, began an endeavour to find a quantitative model for the prediction of binding isotherms and critical concentrations Their model was based on the mass-action law for micellization[17] Like all other models for polymer–micelle interaction[15,24,25] considered so far, the predictions were checked with experimental data on SDS micelles bound to the hydrophilic polymers (PVA, PVP,and PEO) The models of Ruckenstein[24] and Nagarajan[15] were checked on the system PEO/SDS, and the model of Evans[25] on the system PEO/$Cu(DS)_2$[26] Gilanyi and Wolfram[17] also made the important point that the formation of regular (free) micelles may take place at a surfactant concentration below the saturation concentration of the polymer, since the activity of the surfactant rises as the polymer is loaded with micelles[14,15] The activity of the surfactant ions may thus reach the critical value for formation of free micelles before binding of micelles to the polymer is completed

Several authors have studied the influence of polymers on the properties of probe molecules bound to micelles These results indicate a more open and water-penetrated structure of the polymer-bound micelles

Details concerning the polymer–micelle interaction[3] have been provided by techniques like NMR self-diffusion, electric birefringence, ultrasound absorption, and the use of surfactant-ion selective electrodes Nevertheless, a consistent explanation for the influence of the precise chemical structure of surfactant and polymer on the interaction tendency and a quantitative model that is applicable to more systems than PEO/SDS alone are still lacking A clarification of just these problems is of the utmost importance for the further understanding of polymer–micelle interaction and development of the model This review will focus on recent work carried out in our laboratory and is aimed at obtaining a better understanding of the relation between the chemical structure of both surfactant and polymer, and the propensity for polymer–micelle interaction

2 Criteria for Polymer–Micelle Interaction

A reduction of the cmc due to the presence of polymer fails to be the ultimate criterion for polymer–micelle attraction It is certainly decisive in one sense, that is, if a reduction takes place, it definitely points to polymer–micelle association However, one should consider the situation that binding of the polymer does not affect the stability of the micelle significantly, but that only the polymer is stabilized in the binding process For example, it was believed for a long time that polymers do not bind to non-ionic micelles However, our studies[27] on the clouding behaviour and Krafft temperatures of PPO solutions in the presence of micelles formed from n-octyl β-D-thioglucopyranoside (OTG) (1) provide evidence that the micelles do interact with the polymer



n-Octyl β-D-thioglucopyranoside

(OTG)

(1)

This remarkable association between PPO and OTG micelles was definitely confirmed by microcalorimetric measurements When an OTG solution was injected into the PPO solution, the microcalorimetric response curve consisted of an endothermic peak followed by an exothermic peak (Figure 2) This phenomenon is attributed to rapid endothermic polymer–micelle association near the injection point followed by a slower disintegration of the complex and dilution of the surfactant molecules in the entire solution [27] The total dilution enthalpies shown in Figure 3 are summations of the areas of the endothermic and exothermic peaks

The curve for OTG dilution in H_2O can be characterized by three regions In the pre-micellar region I, the injected micelles disintegrate completely and the enthalpy change for de-micellization and loss of intermicellar interactions is recorded Region II is the transition region around the cmc In the post-transition region III, the injected micelles remain intact and only a very small enthalpy change for reduction of intermicellar interaction is measured The enthalpy of micellization, calculated as the difference in dilution enthalpy between region I and II, is + 4 5 kJ mol^{-1} a normal value for a non-ionic surfactant

Comparison of the curve for the PPO solution with the curve for H_2O reveals that PPO exerts only a small endothermic effect on the pre-micellar enthalpy of dilution Furthermore the transition region is located in the same concentration range, indicative of an unchanged cmc However, a clear endothermic effect, + 4 3 kJ mol^{-1}, is observed in the post-transition region of the PPO solution We contend that this value represents the enthalpy of interaction between PPO and OTG micelles

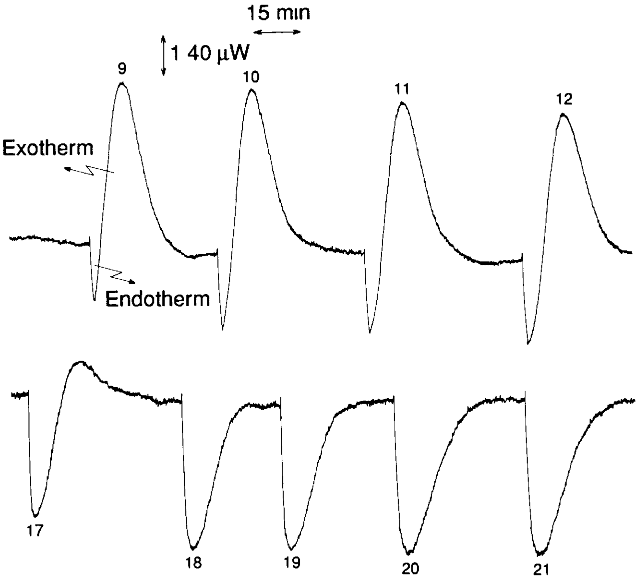


Figure 2 Top Microcalorimetric response curve upon (ref 27) injection of a concentrated OTG solution into a PPO solution with the final OTG concentration remaining below the cmc The numbers refer to the titration steps, *i e* 9 corresponds to the ninth titration step (see also Figure 3) Each response consists of an endothermic and an exothermic peak Bottom similar data but now the final OTG concentration is beyond the cmc Note the increase of the endothermic signal relative to that shown in the top part The exothermic effect has disappeared completely beyond titration step 18 Signal noise is caused by the stirrer Temperature, 25 °C

Since the Gibbs energy of micellization of OTG is unchanged by the presence of PPO, the endothermic interaction enthalpy is apparently compensated by a positive entropy change This $\Delta H/\Delta S$ compensatory behaviour probably originates largely from the release of water molecules from the hydrophobic hydration shells of the polymer upon interaction with the micelles

The different behaviour of PEO and PPO most likely reflects the difference in Gibbs energy of transfer of the polymer from water to a more apolar environment PPO is more soluble in hydrocarbons than in water, contrary to PEO In this context we also refer to subsequent studies on HPC [28]

The question arises whether PPO, interacting with OTG micelles, resides at the micellar surface like PEO in the system PEO/SDS, or deeper in the micellar core The latter possibility is not likely for the reason mentioned previously, but additional evidence is called for Aggregation numbers may give a clue, because if PPO resides in the core an increase in aggregation number is expected instead of the usual decrease found in most polymer–ionic micelle complexes We have made an attempt to measure aggregation numbers of OTG micelles in the absence and presence of PPO using static fluorescence quenching We obtain an aggregation number of 156 ± 10 for OTG micelles, which is rather high compared to the values of 68—84,[29] or 87,[30] for β-D-n-octylglucoside (with an ether instead of a thio linkage) determined by light scattering and sedimentation techniques In the presence of 0 5 g dL^{-1} of PPO, we find a value of 96 ± 3 Although the exact values may be slightly in error, we submit that the trend is obvious, and points to location of PPO in the outer region of the micelle Thus PPO/OTG interaction probably resembles the classical PEO/SDS association The most important conclusion is, however, that polymer–micelle interaction is not necessarily accompanied by a reduction in cmc

It goes without saying that the driving force for polymer–micelle interaction is a reduction in Gibbs energy of the *total* system Still, it is worthwhile to note that both stabilization of

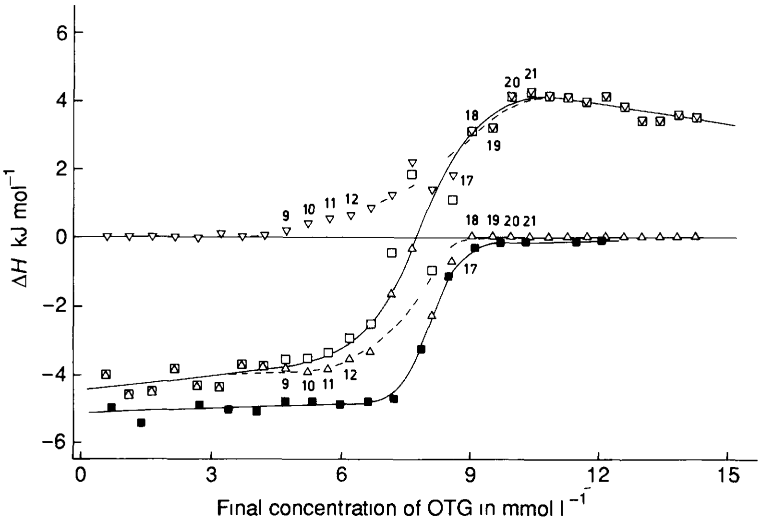


Figure 3 Enthalpy of dilution as a function of the final OTG concentration in water or in an aqueous solution of PPO at 25 °C (■) in water, cmc = 8 05 × 10^{-3}, in PPO solutions (▽) exothermic effect, (▽) endothermic effect, (□) summation of exothermic and endothermic effects The numbers (9—12, 17—21) correspond with the titration steps indicated in Figure 2 (Taken from reference 27)

Table 1 Cmc values[a] of DDAO, at various degrees of protonation, in the absence and presence of polymers

	β^c				
Polymer[b]	0 0	0 24	0 47	0 75	0 98
—	1 7	1 53	1 80	2 54	4 74
PPO	—	1 46	1 33	1 63	—
PVME	—	1 56	1 70	2 08	—
PEO 10 k	—	1 61	1 84	2 55	—

[a] In mM [b] Polymer concentration *ca* 0 9 g dL^{-1} [c] Calculated from the pH at the cmc using $pK_a = 5$ 0

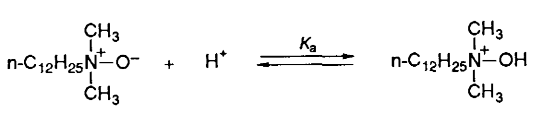
the micelle proper and a reduction in the Gibbs energy of the (hydrated) polymer may provide the major contribution to the total free energy for the formation of polymer-bound micelles

3 The Role of the Charge and Structure of the Surfactant Headgroup

Micellar charge, whether positive or negative, definitely promotes micelle *stabilization* upon binding of polymers It is not, however, a prerequisite for association, as has long been propagated [3] The major effects of surfactant charge on the stabilization of polymer-bound micelles are a contribution from the reduction in electrostatic repulsion due to the smaller size of the bound micelles, and the influence of charged groups on the hydration sheaths of polymers The former effect is operative for both negatively and positively charged surfactants The latter effect does, in practice, depend on the sign of the charge, since only a limited choice of charged groups can be used as headgroups of a surfactant

3.1 The Effect of Headgroup Charge on Polymer–Micelle Interaction: n-Dodecyldimethylamine Oxide[31]

Dipolar n-dodecyldimethylamine oxide (DDAO) belongs to an interesting class of non-ionic surfactants, sometimes referred to as the semi-polar class The headgroup charge of DDAO in the micelle can be easily varied between 0 and 1 *via* variation of the pH(equation 1)



$$\text{n-C}_{12}\text{H}_{25}\overset{+}{\text{N}}(\text{CH}_3)_2\text{–O}^- + \text{H}^+ \underset{}{\overset{K_a}{\rightleftharpoons}} \text{n-C}_{12}\text{H}_{25}\overset{+}{\text{N}}(\text{CH}_3)_2\text{–OH} \qquad (1)$$

No drastic change in structure and volume of the headgroup is involved The effect of charge variation on the cmc and other micellar properties has been investigated in some detail [31]

3 1 1 Cmc Values

Cmc values (obtained by the pH-method developed for phosphate surfactants[32]) are listed in Table 1 The degree of protonation (β, ± 0 01) is calculated from pH at the cmc using a pK_A value of 5 0 It can be adjusted by varying the pH of the concentrated DDAO stock solution The pH at the cmc, and thus β, is not noticeably affected by the presence of polymer

The obtained cmc values for DDAO in H_2O, are relatively low in comparison with those reported previously A similar observation was made in case of the phosphate surfactants [32] Presumably the method responds to even the first stage of aggregation

Within the limits of reproducibility (5 % at β = 0 24, 2 % at β = 0 5 and 0 75) the cmc at β = 0 24 is not affected by the presence of polymers At higher degrees of protonation the cmc is decreased in the presence of PPO and PVME, but not influenced by the presence of PEO It is tempting to conclude from the cmc data that the stabilization of the micelles by PPO and PVME increases with increasing micellar charge However, a more quantitative conclusion should be based on a comparison of Gibbs energies of micellization in the presence and absence of polymer In a first approximation, the Gibbs energy of micellization is related to the cmc expressed in mole fraction units according to equation 2 [7 12] The change in standard Gibbs energy of the micelles due to the binding of a polymer is given by equation 3, in which cmc_p represents the cmc in the polymer solution [7 12] The quantity $\Delta G^0_{\text{mic pol}} - \Delta G^0_{\text{mic}}$ denotes the change in standard Gibbs energy when 1 mole of surfactant molecules is transferred from unperturbed micelles to polymer-bound micelles, plus the change in free energy of the polymer induced by this process Values for $\Delta G^0_{\text{mic pol}} - \Delta G^0_{\text{mic}}$ (Table 2) confirm the intuitive conclusion from the cmc data, namely, that polymer-induced stabilization is more pronounced at higher

$$\Delta G^0_{\text{mic}} = RT \ln (\text{cmc}) \qquad (2)$$

$$\Delta G^0_{\text{mic pol}} - \Delta G^0_{\text{mic}} = RT \ln (\text{cmc}_p/\text{cmc}) \qquad (3)$$

Table 2 $\Delta G^{0}_{\mathrm{mic\ pol}} - \Delta G^{0}_{\mathrm{mic}}$ for DDAO micelles,[a] at various degrees of protonation, in the presence of polymers

Polymer[b]	β[c] 0.24	0.47	0.75
PPO	−0.1	−0.8	−1.1
PVME	0.1	−0.2	−0.5
PEO 10 k	0.1	0.1	0.0

[a] In kJ mol^{-1}; estimated error 0.1 kJ mol^{-1}. [b] Polymer concentration *ca.* 0.9 g dL^{-1}. [c] Calculated from the pH at the cmc using pK_a = 5.0.

micellar charge. This seems to agree with current views on polymer-micelle interaction. We contend however, that, although indeed the interaction with the ionic surfactant is stronger than with the non-ionic surfactant, any rationalization based on headgroup volume is misplaced. Protonation will hardly influence the size of the headgroup, but the hydration shell will be affected. This is expected to lead to a larger (hydrated) size of the cationic headgroup. Apparently, the size of the cationic headgroup will not be much different from that of a trimethylammonium group. We propose that the increase in stabilization of the micelles by interaction with polymers at increasing micellar charge stems from an enhanced reduction of electrostatic repulsion. Particularly at higher micellar charge the formation of smaller, polymer-bound micelles will be favoured, since electrostatic repulsion is diminished whereas the increased hydrocarbon–water contact area is stabilized by the polymer. Since hitherto the influence of charge has only been studied by comparing polymer–micelle interaction for SDS, CTAB, and Triton X-100,[3] *i.e.* for surfactants with completely different headgroups, too much emphasis has been placed on headgroup structure and size, instead of on the role of charge proper.

3.1.2 Aggregation Numbers[31]

It should be stressed that one should be careful not to link the *occurrence* of polymer–micelle interaction too heavily to the *stabilization* of the micelles. Therefore, aggregation numbers have been measured to decide whether or not the absence of a reduction of the cmc points to the complete absence of polymer–micelle interaction.

The aggregation numbers of DDAO micelles at various degrees of protonation were determined by static fluorescence quenching.[33,34] Our data (Table 3) on DDAO in the absence of polymer agree with those reported in the literature. The aggregation numbers of DDAO in water show a decreasing trend with increasing β. Enhanced electrostatic repulsion may account for the observation. The slightly higher aggregation number at β = 0.47 compared to those at β = 0.24 and 0.75 would be in accord with inter-headgroup hydrogen-bonding being maximal. The effect is too small, however, to exclude the possibility of an experimental artifact. We emphasize that the possibility of systematic errors that may obscure a comparison is appreciably higher within a horizontal row of Table 3 than within a vertical column.

Table 3 Aggregation numbers of micelles of DDAO, at various degrees of protonation, in the absence and presence of polymers

Polymer[a]	[surfactant], mM	β[b] 0.0	0.24	0.47	0.75	0.98
—	30	75	70	72	70	66
—	20	76	70	73	73	67
PPO	20	55[c]	46	43	38	—
PVME	20	57[c]	46	42	37	—
PEO 10 k	20	73[c]	67	71	73	—

[a] Polymer concentration *ca.* 0.5 g dL^{-1}. [b] Calculated from the pH at the cmc using pK_a = 5.0. [c] Calculated on the assumption that the cmc in the presence of polymer equals that in H_2O.

The data in Table 3 nicely illustrate that an unperturbed cmc may have different origins. In the case of DDAO/PEO at various degrees of protonation, the unperturbed numbers (within confidence limits) obviously indicate the absence of interaction. In the case of DDAO/PPO and DDAO/PVME at low degree of protonation, in contrast, the reduction in aggregation number definitely suggests polymer–micelle association. Interestingly, this interaction does not lead to stabilization of the micelle (because of the negligible effect on the cmc), most likely because of counteracting contributions to the total Gibbs energy from the changes in Gibbs energy of surfactant molecules and polymer upon transferring a mole of surfactant molecules from normal to polymer-bound micelles.

Steric hindrance between the hydrated non-ionic headgroups and polymer segments will be unfavourable, whereas in the case of PPO or PVME the transfer of polymer segments to the micellar phase will be favourable. Furthermore, there will be no favourable loss of electrostatic repulsion like at higher β.

The decrease in aggregation number in the presence of PPO and PVME becomes more pronounced at higher β. This is anticipated since a reduction in electrostatic repulsion by increasing the surface-to-volume ratio of the micelles will be more important at higher micellar charge. The influence of PPO and PVME on the aggregation number is, within the confidence limits, equal, even though $\Delta G^{0}_{\mathrm{mic\ pol}} - \Delta G^{0}_{\mathrm{mic}}$ is clearly more negative for PPO than for PVME. This may be rationalized in terms of stronger hydrophobic interaction for PPO compared to PVME. A slight difference in morphology of the polymer–micelle complex due to the lower molecule weight of PPO (MW 1000) compared to that of PVME (MW 27000) should also be taken into account.

4 The Influence of Polymers on the Micellar Architecture of Cetyltrimethylammonium Salts[35]

Cetyltrimethylammonium salts (CTAX), particularly the bromide and chloride, are by far the most widely studied cationic surfactants. The formation of viscoelastic solutions at extremely low concentrations (*ca.* 10^{-4} M) in the presence of salicylate anions is an especially fascinating phenomenon. Notwithstanding these interesting properties, CTAX salts as well as the relatively few other cationic surfactants that have been investigated, have a poor reputation in the field of polymer–micelle chemistry.[3] This stems from the fact that they give only significant interaction with rather hydrophobic polymers, though recently a modest propensity for binding to more hydrophilic polymers has been detected.[36]

Three explanations have been advanced for the origin of the weakness of the interactions between polymers and cationic surfactants: (i) the bulkiness of the cationic headgroup, (ii) a positive charge (*vide infra*) on the polymer, and (iii) a difference in interaction of cations and anions with the hydration sheath of the polymer. The first explanation was suggested by Saito,[4] and later adopted by Nagarajan.[15] The bulkiness of the headgroup of most cationic (and non-ionic) surfactants is assumed to hamper the presence of a polymer at the hydrocarbon–water interface. Furthermore, a bulky headgroup quite effectively shields the hydrophobic core. Thus, the stabilization of the core–water interface by the polymer is less relevant in that case than for micelles having a core less shielded by headgroups. Small angle neutron scattering studies indeed reveal that the trimethylammonium headgroup in micelles of n-tetradecyltrimethylammonium bromide does not even leave enough space for penetration of water molecules between the headgroups.[37] There are, however, several observations which cannot be reconciled with bulkiness playing a major role. These include: (i)

DAC and protonated n-dodecyldimethylammineoxide ($DDAOH^+$) micelles (*vide supra*) do not interact with PEO, PVP, and PVA or only very weakly and (ii) the finding that the bulkiness of the hydrophobic polymers does not prevent interaction with, for instance, CTAB, which has a voluminous trimethylammonium headgroup.

The second explanation [8,38] involves electrostatic repulsion with a proposed slightly positive charge on the polymers. This charge is thought to originate from protonation of the ether oxygens in the case of polyethers and the amide moiety in the case of PVP. The pH dependence of the interaction between SDS and PEO was used by Schwuger[8] to support this view. Moroi and Saito[38] used the same concept to explain the difference between DTAB and SDS in mixed micelle formation with non-ionic micelles of the poly(oxyethylene)alkylether type. The very low pK_a value of an ether or amide [pK_a $(CH_3CONH_2)H^+ = 0.3$], however, raises serious doubts about the importance of protonation at neutral pH.

The third explanation is based on the different influence of cations and anions on the hydration sheath of the polymer, and thus of headgroup–polymer interaction. To support this view Witte[19] refers to the work of Napper,[39] who studied the role of electrolytes in the flocculation behaviour of polymers. The decrease in clouding temperature of PEO by the addition of salts also indicates the more pronounced influence of anions compared to cations. The ion–polymer interactions are usually thought to occur *via* hydration shell overlap effects.

Probably the size of the headgroup and the interaction of the headgroup with the hydration sheath of the polymer are the main reasons for weak interaction of cationic micelles with polymers. The electrostatic repulsion between polymer and micelles may modify interactions at low pH, but does not seem to be decisive under neutral conditions. Overall, only an appreciably hydrophobic polymer can overcome these factors by a favourable Gibbs energy of transfer of polymer segments from the aqueous to the micellar phase and interact also with cationic (and non-ionic) micelles.

4.1 The Sphere-to-Rod Transition of CTATs[35]

So far, only the interaction of spherical cationic micelles with polymers has been discussed, but certain cetyltrimethylammonium salts are well known for the formation of rodlike (or wormlike) micelles. Using the salicylate salt, Hirata *et al.*[40] have published electron micrographs of these rods. Although their results have been criticized and are most likely artifacts associated with chemical staining, the use of cryo-transmission electron microscopy avoids these artefacts and direct imaging of the rods has become feasible.[41] From these direct images of the rods it appears that the diameter (45 to 60 Å) is an agreement with expectations.[42]

Surprisingly, Nagaragan[15c] is the only author previously to have considered rodlike micelles in the study of polymer–micelle interactions. He predicted theoretically that rodlike micelles of SDS formed in the presence of NaCl would be transformed to polymer-bound ellipsoidal micelles in the presence of PEO.

One of the counterions that is able to induce the formation of rod-like micelles from cetyltrimethylammonium surfactants is tosylate (Ts). Sepulveda and co-workers[43] first introduced CTATs for the measurement of the degree of dissociation of CTAX, in which X represents inorganic counterions. Later they studied the rheology of solutions of CTATs and of other CTAX surfactants. They also reported cmc values, degees of dissociation, and the transfer Gibbs energy for the counterion from water to the micelle.[43]

The tosylate ion is less rod-inducing than the salicylate (Sal) ion. As a result globular micelles of CTATs are initially formed above the cmc (2.6×10^{-4} M).[43b] These micelles start to grow at a critical rod concentration (crc) of around 15 mM. Thus, CTATs provides the possibility of studying the sphere-to-rod transition and the influence of polymers on the concentration at which this transition takes place. In the case of CTASal, rod-like micelles are formed directly above the cmc.

We have used viscosity measurements to obtain the concentration at which the sphere-to-rod transition of CTATs micelles occurs, in the absence and presence of PVME. For these rheological measurements we used a shear-viscometer that can be equipped with different measuring devices, one having cone-and-plate geometry and the other cylindrical geometry. Provided that the rheometer is also equipped with a special sensor, the former device allows the measurement of first normal stress differences, indicating viscoelasticity, as well as shear stress, from which the apparent viscosity can be calculated according to equation 4.

$$\text{apparent viscosity} = \text{shear stress/shear rate} \qquad (4)$$

The latter device only allows the measurement of shear stress but produces more accurate data.

Usually the apparent viscosity of a solution of rod-like micelles drops rapidly when the shear rate is increased. Only at low shear rates (or at very high shear rates) is the viscosity Newtonian, that is, independent of shear rate. In Table 4 these low shear (Newtonian) viscosities are listed for solutions containing various concentrations of CTATs in H_2O, and in the presence of 0.25 and 0.5 $g\,dL^{-1}$ of PVME (measured with cylindrical geometry).[35] For the highly viscous solutions, shear rates as low as $6 \times 10^{-3}\ s^{-1}$ have been used. It is hard to associate the sphere-to-rod transition to a well-defined concentration, since the viscosity increases non-linearly with the CTATs concentration (Figure 4). The viscosity of a 15 mM CTATs solution in H_2O is already four times as high as that of water (1 cP). At 18 mM CTATs, a first normal stress difference, indicating viscoelastic behaviour and thus the presence of rods, can be observed above a shear rate of 476 s^{-1} (using cone-and-plate geometry). Such viscoelastic behaviour can also be observed visually as the recoil of trapped air bubbles when a swirling motion of the solution is abruptly stopped. From 20 mM CTATs onwards, thixotropic behaviour is definitely displayed using a cone-and-plate measuring device (between 119 s^{-1} and 476 s^{-1}) and from 25 mM CTATs onwards using a cylindrical measuring device (between 60 s^{-1} and 119 s^{-1}). Thixotropic behaviour is the occurrence of a decrease in apparent viscosity with increasing time under shear and is revealed in this case after a stepwise increase in shear rate. The thixotropy as well as the viscoelasticity and non-Newtonian behaviour are indicative of changes in the internal structure of the solution. These changes originate from alignment and disruption of the rod-like micelles by shear forces.[44]

Although the transition concentration for CTATs cannot be clearly defined it seems obvious from Figure 4 that the presence of PVME shifts the sphere-to-rod transition to higher concentrations. However, there may be a pitfall in this alluring conclusion. In 1985 Hoffmann *et al.*[45] stated 'that all theories which try to explain the viscoelastic properties of micellar solutions on

Table 4 Apparent viscosities of CTATs in aqueous solutions in the absence and presence of PVME at 25 °C

[CTATs] mM	η_{app}, Pa s H_2O	 0.25 $g\,dl^{-1}$ PVME	 0.5 $g\,dl^{-1}$ PVME
10	0.0017	0.0016	0.0017
15	0.0046		
20	0.016	0.0047	0.0040
25	0.047	0.013	
30	0.53	0.081	0.021
35	5.09	0.24	0.067
40		1.28	0.32
45		3.55	1.25
50		10.01	2.54

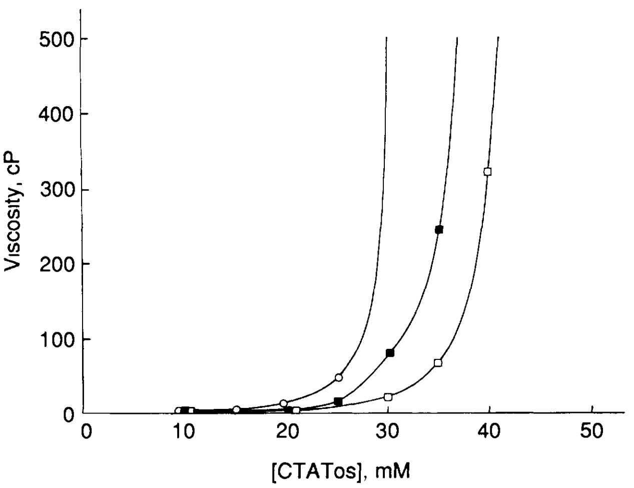


Figure 4 The viscosity at low shear rates (Newtonian behaviour) of CTATs in H_2O (○), 0 25 g dL^{-1} PVME (■), and 0 5 g dL ^{1} PVME (□) at 25 °C, measured with cylindrical geometry (Extrapolation of the lines is based on the data from Table 4)

models that are based on the existence of well-defined rods, without taking into account the transient nature of the micelles, sooner or later must fail' He illustrated this statement with the behaviour of n-tetradecylpyridinium salicylate and n-tetradecylammonium salicylate These compounds have similar cmc values, critical rod concentrations, and light scattering behaviour, suggesting that the micellar structures and the interactions between them should also be similar In fact, the viscosities of aqueous solutions of these two compounds differ by almost two orders of magnitude The differences between the structural relaxation times of the micelles was shown to lie at the origin of this difference For these surfactants the relaxation time stems from the kinetics of formation and dissociation of the micelle, whether stepwise per monomer or *via* coalescence or fragmentation of the entire micelle, and not from the rotation of the rods Since this relaxation time may be influenced by the presence of additives[42] such as n-butanol or n-pentanol, it is conceivable that the shift in concentration where the viscosity increase of the CTATs solution takes place, caused by PVME, is also due to these kinds of effects and not to a shift in concentration of the sphere-to-rod transition However, we submit that this is not the case (*vide infra*) and that indeed a shift in transition concentration upon PVME addition takes place We propose that PVME preferentially binds to spherical micelles of CTATs, for which the surface-to-volume ratio is more favourable for interaction with the polymer Headgroup–headgroup repulsion and headgroup–absorbed polymer repulsion will be less compared to those for polymer-bound rod-like aggregates, while the extra hydrocarbon core–water contact is stabilized by PVME When the CTATs concentration exceeds the saturation concentration of PVME, free micelles will be formed, which grow into rods upon increasing the concentration [46]

4.2 The Polymer-induced Transition from a Non-Newtonian to a Newtonian Fluid[46,47]

Cetyltrimethylammonium salicylate (often prepared by addition of sodium salicylate to CTAB solutions) is the archetype of a cationic surfactant[42] that forms rod-like micelles even in dilute (*ca* 10^{-4} M) solutions At higher concentrations CTASal solutions become viscoelastic and behave in a strongly non-Newtonian manner The maximum in viscosity lies at a $[\text{Sal}^-]/[\text{CTA}^+]$ ratio below one[44] A second maximum in viscosity is observed in the presence of an excess of salicylate ions for n-tetradecylpyridinium micelles [44]

One does not need special apparatus to observe the high viscosity and viscoelasticity of such a curious mixture It is also easily seen that the presence of 0 5 g dL^{-1} PVME or PPO completely eliminates the gel-like properties and reduces the viscosity to about that of water Addition of the more hydrophilic polymers PEO or PVP does not induce such a transition Although the change in the properties of the CTASal solutions induced by PVME or PPO strikes the eye, rheological measurements were performed to quantify the effect

The same shear viscometer as used in the study of CTATs was used The (apparent) viscosities of micellar CTAB solutions in the absence and presence of sodium salicylate, polymers, and low molecular weight additives are listed in Table 5 These values have been obtained using a measuring device with cylindrical geometry The CTAB/NaSal solutions, whether or not in the presence of PVP, ethanol, or t-butanol, and, to a slightly lesser extent, CTAB/NaSal/PEO (20k), exhibit genuine non-Newtonian behaviour, *i e* the apparent viscosities vary dramatically with changing shear rate (Table 5)

Table 5 The effect of sodium salicylate and several monomeric and polymeric additives on the viscosity of a micellar CTAB solution[47]

[CTAB], mM	[NaSal], mM	additive[a]	viscosity, cP
25			1 08 ± 0 02
25		PVME	1 510 ± 0 0006
25		PEO	1 26 ± 0 02
25	15		2771,[b] 8 8[c]
25	15	PVME	1 630 ± 0 006
25	15	PPO	1 080 ± 0 006
25	15	PEO	274,[b] 16 9[c]
25	15	PVP	2817,[b] 15 4[c]
25	15	EtOH	3055,[b] 8 1[c]
25	15	t-BuOH	2213,[b] 8 9[c]

[a] [Additive] = 0 5 g dL ^{1} [b] Shear rate = 0 2985 s ^{1} [c] Shear rate = 477 6 s ^{1}

By contrast, the apparent viscosities of CTAB/NaSal in the presence of PVME or PPO, and of CTAB solutions without NaSal, are orders of magnitude lower and are independent of shear rate, indicative of Newtonian behaviour

This polymer-induced transition from a non-Newtonian to a Newtonian fluid is, like in the case of CTATs, attributed to preferential binding of *spherical* rather than *rod-like* micelles onto the hydrophobic polymers This is completely consistent with the reduction in aggregate size of CTAB micelles in the presence of PVME and PPO, and the shift to higher surfactant concentrations for the sphere-to-rod transition of CTATs by PVME The hydrophilic polymers PEO and PVP do not bind CTAX micelles and, therefore, do not exert dramatic effects on the rheology of a solution of these aggregates

5 Conclusion

Polymer–micelle interaction depends on several properties of the surfactant molecule, such as the chemical nature, geometry, and charge Unfortunately, an arbitrary combination of these factors is not easily obtained For instance, it is hard to find an anionic surfactant without an oxygen-rich headgroup or a cationic surfactant with many oxygen atoms and without a quaternary nitrogen atom Therefore, it is not yet possible to formulate general rules concerning the relative importance of the properties, mentioned above Cationic, anionic, and non-ionic surfactants have all been shown to undergo polymer–micelle interaction on the premise that the polymer is sufficiently hydrophobic The first non-ionic and cationic surfactant that interacts substantially with, for instance, PEO has still to be reported For cationic micelles, a betaine, like $\overset{+}{\text{R}}\text{N}(\text{Me}_2)\text{CH}_2\text{COOH}$, may be found to interact with PEO, in view of the favourable interaction between the ether linkage and the COOH moiety

6 References

1 L M Klotz, in 'The Proteins', Vol I, Part B, ed H Neurath and K Bailey, Academic Press, New York, 1953, p 727
2 M M Breuer and I D Robb, *Chem Ind (London)*, 1972, **13**, 530
3 E D Goddard, *Colloids Surf*, 1986, **19**, 255
4 S Saito, *Kolloid Z*, 1957, **154**, 1g
5 H Lange, *Colloid Polym, Sci*, 1971, **243**, 101
6 H Arai, M Murata, and K Shinoda, *J Colloid Interface Sci*, 1971, **37**, 223
7 F Tokiwa and K Tsujii, *Bull Chem Soc Jpn, 1973,* **46**, 2684
8 M J Schwuger, *J Colloid Interface Sci*, 1973, **43**, 491
9 B Cabane, *J Phys Chem*, 1977, **81**, 1639
10 M N Jones, *J Colloid Interface Sci*, 1967, **23**, 36
11 (*a*) S Saito and M Yukawa, *J Colloid Interface Sci*, 1969, **30**, 211 (*b*) S Saito and M Yukawa, *Kolloid Z-Z Polym*, 1969, **234**, 1015
12 K Shirahama and N Ide, *J Colloid Interface Sci*, 1976, **54**, 450
13 G Perron, J Françoeur, J E Desnoyers, and J C T Kwak, *Can J Chem*, 1987, **65**, 990
14 B Cabane and R Duplessix, *Colloids Surf*, 1985, **13**, 19
15 (*a*) R Nagarajan and B Kalpakci, in 'Microdomains in Polymer Solutions', ed P Dubin, Plenum Press, New York, 1985, p 369 (*b*) R Nagarajan, *Colloids Surf*, 1985, **13**, 1 (*c*) R Nagarajan, *Adv Colloid Interface Sci*, 1986, **26**, 205 (*d*) R Nagarajan and B Kalpacki, *Polym Prepr (Am Chem Soc, Div Polym Chem)*, 1982, **23(1)**, 41 (*e*) R Nagarajan, *J Chem Phys*, 1989, **90**, 1980
16 Z Gao, R E Wasylishen, and J C T Kwak, *J Colloid Interface Sci*, 1990, **137**, 137
17 (*a*) T Gilyani and E Wolfram, *Colloids Surf*, 1981, **3**, 181 (*b*) T Gilyani and E Wolfram, in ref 15(*a*), p 383
18 (*a*) R Zana, J Lang, and P Lianos, in ref 15(*a*), p 357 (*b*) R Zana, J Lang, and P Lianos, *Polym Prep (Am Chem Soc, Div Polym Chem)*, 1982, **39(1)**, 39
19 (*a*) F M Witte and J B F N Engberts, *Colloids Surf*, 1989, **36**, 417 (*b*) F M Witte, Ph D Thesis, University of Groningen, 1988
20 E A Lissi and E Abuin, *J Colloid Interface Sci*, 1985, **105**, 1
21 F M Witte and J B F N Engberts, *J Org Chem*, 1987, **52**, 4767
22 A Malliaris, *J Phys Chem*, 1987, **91**, 6511
23 R Zana, S Yiv, C Strazielle, and P Lianos, *J Colloid Interface Sci*, 1981, **80**, 208
24 E Ruckenstein, G Huber, and H Hoffmann, *Langmuir*, 1987, **3**, 382
25 D F Evans, D J Mitchell, and B W Ninham, *J Phys Chem*, 1984, **88**, 6344
26 C Treiner and D Nguyen, *J Phys Chem*, 1990, **94**, 2021
27 J C Brackman, N M van Os, and J B F N Engberts, *Langmuir*, 1988, **4**, 1266
28 F M Winnik, *Langmuir*, 1990, **6**, 522
29 H Hoffmann and G Huber, *Colloid Surf*, 1989, **40**, 181
30 K Kameyama and T Takagi, *J Colloid Interface Sci*, 1990, **137**, 1
31 J C Brackman and J B F N Engberts, *Langmuir*, 1992, **8**, 424
32 J C Brackman and J B F N Engberts, *J Colloid Interface Sci*, 1989, **132**, 250
33 N J Turro and A Yekta, *J Am Chem Soc*, 1978, **100**, 5951
34 G G Warr and F Grieser, *Chem Phys Lett*, 1985, **116**, 505
35 J C Brackman and J B F N Engberts, *Langmuir*, 1991, **7**, 2097
36 K Shirahama, A Himuro, and N Takisawa, *Colloid Polym Sci*, 1987, **265**, 96
37 S S Berr, E Caponetti, J S Johnson, Jr, R R M Jones, and L J Magid, *J Phys Chem*, 1986, **90**, 5766
38 Y Moroi, H Akisada, M Saito, and R Matuura, *J Colloid Interface Sci*, 1977, **61**, 233
39 D H Napper, 'Polymeric Stabilisation of Colloidal Dispersions', Academic Press, London, 1983, p 141
40 H Hirata, Y Kanda, Y Sakaiguchi, *Bull Chem Soc Jpn*, 1989, **62**, 2461
41 P K Vinson and Y Talmon, *J Colloid Interface Sci*, 1989, **133**, 288
42 H Hoffmann and G Ebert, *Angew Chem, Int Ed Engl*, 1988, **27**, 902
43 (*a*) D Bartet, C Gamboa, and L Sepulveda, *J Phys Chem*, 1980, **84**, 272 (*b*) C Gamboa and L Sepulveda, *J Phys Chem*, 1989, **93**, 5540 (*c*) C Gamboa and L Sepulveda, *J Colloid Interface Sci*, 1986, **113**, 566
44 H Rehage and H Hoffmann, *J Phys Chem*, 1988, **92**, 4712
45 H Hoffmann, H Lobl, H Rehage, and I Wunderlich, *Tenside Deterg*, 1985, **22**, 6
46 J C Brackman, Ph D Thesis, University of Groningen, 1990
47 J C Brackman and J B F N Engberts, *J Am Chem Soc*, 1990, **112**, 872