Structural interpretation of the interfacial properties of aqueous solutions of methylcellulose and hydroxypropyl methylcellulose

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(Received 25 March 1983; revised 23 May 1983)

Interfacial properties of aqueous solutions of methyl and hydroxypropyl methyl ethers of cellulose are important in foam and emulsion stability, detergency and many other applications involving surface activity of these cellulose ethers. Interfacial tensions of aqueous solutions of these cellulose ethers are measured using a spinning drop interfacial tensiometer. A general correlation is found between interfacial tension and the degree of substitution of methoxyl and hydroxypropyl groups. From thermodynamic considerations it is proposed that these cellulose ethers, for a constant degree of substitution, should exhibit the lowest interfacial tension values for a polymer having the most uniform distribution of substituent groups along the backbone. Other factors which influence the interfacial tension values are surface gelation of adsorbed polymer, molecular weight, concentration of cellulose ether in water phase, ageing time, temperature, and the type of organic phase.

Keywords Methylcellulose; hydroxypropyl methylcellulose; interfacial tension; surface activity; substituent distribution

INTRODUCTION

Methylcellulose (MC) and hydroxypropylmethylcellulose (HPMC) are water-soluble polymers derived from cellulose that contains a basic repeating structure of anhydroglucose units. Methylcellulose is produced by reacting cotton linters or wood pulp, pretreated with a caustic solution (NaOH), with methylchloride yielding methyl ether of cellulose. In the manufacture of HPMC, propylene oxide is used in addition to methyl chloride to obtain hydroxypropyl substitution on the anhydroglucose units. Each anhydroglucose ring of the cellulose molecule contains three hydroxyl groups. The average number of hydroxyls in the anhydroglucose units that are substituted with methyl ether groups is known as the degree of substitution (DS). In the case of the reactions of propylene oxide with cellulose the hydroxyl group of the pendant hydroxypropyl ether chain [$-O-CH_2CH(OH)CH_3$] may react with more propylene oxide, either resulting in propylene oxide chain, or may react with methyl chloride resulting in 2-methoxyl propyl ether substitution. Under these circumstances it is not known how many of the hydroxyls of the anhydroglucose units have been substituted. The term molar substitution (MS) was used, therefore, to describe the total number of moles of propylene oxide reacted per anhydroglucose unit.

These polymers are known to have the ability to lower surface and interfacial tensions of an aqueous solution. Because of this surface active property, these polymers find use in many diverse applications, such as foam and emulsion stability, protective colloid action as in suspension polymerization, detergency as a antiredeposition agent, lubrication, controlled flocculation as in latex paint, and adhesion as in leather manufacture, cosmetics etc. Many applications are also based on the ability of these polymers to alter bulk properties such as flow behaviour and gelation. There is voluminous literature on these bulk properties. Although many commercial applications of these polymers depend on their surface activity, the number of studies reported on this subject is very limited[1-3].

It is well known that surface activity of a solute molecule arises primarily due to the ability of the adsorbed solute molecule to alter the attractive interactions between two dissimilar molecules (air–water or oil–water) at the interface[4]. When an adsorbed surfactant molecule orients itself in such a way at the interface that the hydrophilic and lipophilic ends reside at the water and oil side of the interface, respectively, the attractive interaction of both the oil and water molecules towards the interface is maximized resulting in a lowering of interfacial tension. This simple model of interfacial tension becomes extremely complicated in the case of polymeric surfactants, such as methylcellulose and hydroxypropyl methylcellulose, which do not have any well defined hydrophilic and lipophilic ends as in the case of simple surfactants.

It is necessary initially to understand the mode of polymer adsorption at the flat two-dimensional homogeneous interface as encountered at the oil–water or air–water interface. Several theories on this subject have been proposed previously[5-10]. Like many other polymers, MC and HPMC occur in dilute solution in the form of three-

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dimensional random coils, the configuration of which depend on temperature and solvent. When these molecules adsorb at a surface, it is believed[11-13] that they retain their size and the three-dimensional coil configuration with loops protruding into the solvent phases. This is because the unfolding of the coil is extremely slow due to the high internal potential energy barrier. The hydrodynamic adsorbed layer thickness is slightly greater[13] than the hydrodynamic diameter of a polymer molecule in solution. This is apparently due to some deformation of the random coil after adsorption at the interface. The adsorption isotherm is found[10] to be primarily a function of a partition function for adsorbed segments and the stiffness of the chain, both of which can be regarded as the function of the chemical nature of the solvent and the polymer. Lowering of interfacial tension will occur only when the polymer segments have hydrophilic and lipophilic groups distributed in such a way that they are attracted towards both oil and water. The hydrophilic and lipophilic groups will prefer to be in the water and oil phases, respectively. However, because of the restrictions imposed by the stiffness of the backbone and the internal potential energy barrier towards reorientation at the interface, the hydrophilic and lipophilic sites although preferring the water and oil phases, respectively, may sometimes be pulled into the oil and water phases, respectively. Interfacial tension, therefore, will depend not only on the number of hydrophilic and lipophilic sites, but also their distribution along the backbone. This paper examines the influence of different factors, such as degree of substitution, distribution of substituent groups along the backbone, molecular weight, surface gelation, etc. of the cellulose ether in determining the interfacial tension of their aqueous solution.

EXPERIMENTAL

Materials

Methylcellulose and hydroxypropyl methylcellulose used for this study were Methocel* brand cellulose ethers, produced by the Dow Chemical Company, Midland, Michigan 48640, USA. Organic solvents were all chemically pure reagent grades which were equilibrated with water. Water used was distilled in glass.

Procedures

All the glassware and other surfaces that came in contact with the oil–water system were either cleaned with chromic acid/or alcoholic-NaOH cleaning solution followed by 0.5N nitric acid cleaning and finally rinsed with deionized water.

Interfacial tensions were measured with a spinning drop interfacial tensiometer[14] purchased from University of Texas at Austin. The relative precision at the 95% confidence level for this method was less than $\pm 2\%$.

The degree of substitution of Methocel samples was measured by the GC–Zeisel technique[15]. Viscosity of solutions during enzymatic degradation studies were measured using Ubbelohde capillary viscometers at 20°C.

RESULTS AND DISCUSSION

Interfacial tension at the liquid–liquid interface with adsorbed polymer will depend on the detailed structure of the interfacial region separating the two bulk phases. Quantitative interpretation of the interfacial tension data of such a system is extremely difficult. For surfactants, an HLB (hydrophilic–lipophilic balance) concept was developed by Griffin and later quantified by Davies[13] based on structural group contributions. Although this HLB concept may not be absolutely valid for polymers, a qualitative interpretation of the dependence of the degree of substitution of MC and HPMC may be obtained based on this HLB concept. Cellulose molecules are hydrophilic in nature with the anhydroglucose units having an HLB of 9.9. However, cellulose is not soluble in water because of the crystalline nature of the polymer. Introduction of the methyl or hydroxypropyl groups into the cellulose backbone essentially breaks down the crystallinity of the molecules. The water solubility of the molecule is imparted by the hydrophilic groups such as the residual hydroxy group and the oxygen at the ether and acetal linkages. In the process, however, lipophilic groups such as methyl and propyl groups have been added thus reducing the HLB of the polymer. As propyl groups have three times the contribution towards lipophilicity, by virtue of having three carbon atoms, as that of the methyl groups, surface activity of MC and HPMC can be expected to increase with increase in (DS+3MS) values. *Figure 1* shows that for a wide range of substitution values, the interfacial tension of 0.05% aqueous solution of HPMC-1,2 dichloroethane system, decreases initially relatively sharply followed by a gradual decrease as a function of (DS+3MS). All these data were obtained using samples having 2% solution viscosity at 20°C

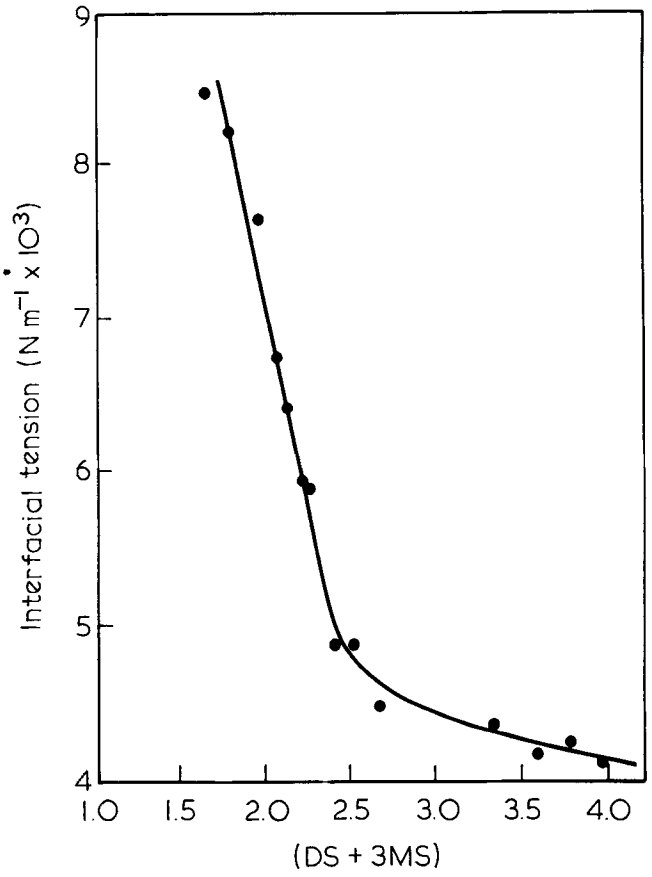

Figure 1 Relation between interfacial tensions of aqueous HPMC solution–1,2 dichloroethane system and (DS+3MS) of the polymer. HPMC conc., 0.05%; temperature, 30°C; equilibration time, 30 min

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between 15 and 100 mN s m^{-2}. As discussed later, interfacial tension does not vary appreciably within this molecular weight range.

Figure 2 shows the effect of temperature on the interfacial tension of 0.05% aqueous HPMC solution–1,2-dichloroethane system for different types of HPMC. It is noteworthy that for some products, the interfacial tension decreases first with the increase in temperature and then shows an increase. However, some products show a decrease, and then level off. This phenomenon can be related to the gelation and/or precipitation behaviour of HPMC products on increasing the temperature. In all these experiments, although the bulk concentration of HPMC is low, the surface concentration could be several orders of magnitude higher. It is known[16] that at high concentrations, aqueous solutions of HPMC can gel on increasing the temperature beyond a critical gelation temperature. The strengths or the yield values of these gels are highly dependent on type and degree of substitution and molecular weight. The gel strengths of different HPMC products of similar molecular weight decrease with the decrease in DS or with the increase in MS. Measurement of interfacial tension appears to be influenced by this surface gelation phenomenon of aqueous HPMC.

As, according to the theory of the spinning drop interfacial tension measurement[17], at sufficiently high speed at 'equilibrium', the tube, the liquid, and the drop are all rotating at the same angular velocity, there is no shear stress at the interface. Therefore, viscosity or viscoelasticity does not enter into the theory. However, for very viscous systems, it may take longer for the drop to reach its equilibrium shape because of the inertial effects. If the interfacial layer behaves like an elastic gel with high yield value, the drop may resist deformation if the yield value is large compared to the centripetal force.

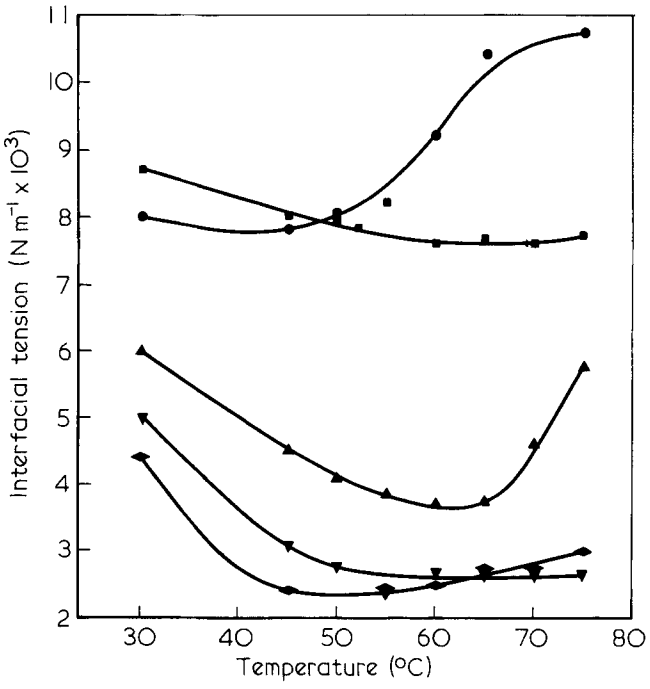

Figure 2 Interfacial tensions of 0.05% aqueous HPMC solution–1,2-dichloroethane systems as a function of temperature at 30 min of equilibration for different types of HPMC. ●, A (DS=1.78, MS=0; ■, B (DS=1.49, MS=0.24); ▲, C (DS=1.84, MS=0.16); ▼, D (DS=1.9, MS=0.23); ◆, E (DS=1.06, MS=0.84)

In the interfacial tension measurements here, data were collected after 30 min equilibration. For the measurements at 30°C, all the values attained at least 95% of the steady-state value. However, at higher temperatures this may not be true and the interfacial tension values will, therefore, reflect the interfacial gelation behaviour.

It is seen from *Figure 2*, that HPMC cellulose ether products having high gel strength[16], i.e., sample A and C, show considerable increase in interfacial tension values on increasing temperature beyond a critical temperature. Sample B and D exhibiting low gel strength show a levelling off effect. Sample E, however, does not exhibit much gelation, yet shows a slight increase in interfacial tension above ≈45°C. This is probably due to the fact that Sample E molecules precipitate out without exhibiting any gelation, thus becoming less surface active. This results in the increase in interfacial tension on increasing temperature beyond the critical precipitation temperature.

Steady-state interfacial tension was found to be time dependent as shown in *Figure 3*, for Methocel F50 and F4M having 2% solution viscosity at 20°C of 50 and 4000 mN s m^{-2}, respectively, corresponding to weight-average molecular weights of 70 000 and 800 000, respectively. The rate of approach to a steady-state value appears to follow a sigmoidal curve. The higher molecular weight sample appears to be slower in attaining a steady-state value than the low molecular weight sample. This suggests that the diffusion of molecules to the interface controls the rate of decrease in interfacial tension. As the larger molecules are expected to diffuse slower, it also shows a slower rate to attain steady state as compared to the smaller molecules.

It is also evident from *Figure 3* that although Methocel F4M and F50 have similar chemical nature, the product with higher molecular weight exhibits considerably higher interfacial tension in the water/octane system than the lower molecular weight product. This can be rationalized if it is assumed that as at the interface layer molecules may have a tendency to form loops[11] extending into the bulk phase, the relative density of surface active groups at the interface will be low. This will result in lower attractive interaction between the adsorbed molecules and the solvent molecules, leading to higher interfacial tension for HPMC having higher molecular weight.

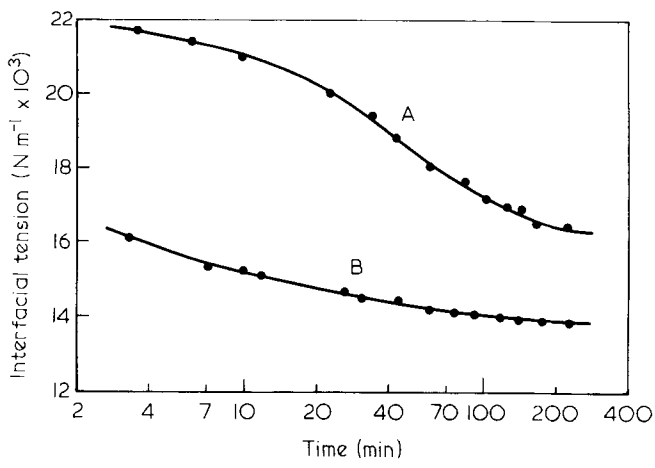

Figure 3 Interfacial tensions of 0.05% aqueous HPMC (DS=1.84, MS=0.16) solution–*n*-octane system as a function of time at 30°C for two different molecular weight samples. $\bar{M}_w$=A, 800 000; B, 70 000

Dependence of interfacial tension on molecular weight is also shown in *Table 1*, for different types of Methocel in the water–1,2-dichloroethane system. In this experiment, Methocel samples of different molecular weight with the same substitution levels and distribution of substituent groups along the backbone were used. In all these cases, interfacial tension decreases slightly on decreasing molecular weight appears to eventually level off.

Evaluation of the effect of the distribution of substituent groups along the backbone is extremely difficult. This is primarily due to the fact that no analytical technique exists at present to determine directly the distribution or the sequence of the different monomeric units along the backbone of cellulose ether. It is necessary, therefore, to depend on indirect methods. One such method is the measurement of the enzymatic degradation of cellulose ether. It is generally believed[18–20] that degradation of cellulose ethers by enzymes (cellulase) in solution depends on the presence of unsubstituted glucose units. Unsubstituted glucose units arise due to either lower total degree of substitution or non-uniform distribution of substituent groups along the backbone. If the degree of substitution is kept constant, faster rate of enzymatic degradation of the polymer would mean non-uniform distribution of the substituent groups. Unfortunately, enzymes cannot distinguish[24] between mono-, di- or tri-substituted glucose units, which may have a pronounced effect on interfacial tension. An enzymatic degradation study can only show broad differences.

As most Methocel products are relatively high in degree of substitution, enzymatic action is relatively slow. Samples of cellulose ethers were prepared, therefore, with low levels of methoxy substitution and water solubility of these samples were imparted by substituting a very small amount of carboxymethyl groups. The initial rate of enzymatic degradation was followed by measuring viscosity of 0.1% solutions in water at 20°C in the presence of a cellulase enzyme. Sample pairs of cellulose ethers were chosen which had different interfacial tension values but very close substitution values.

Results shown in *Table 2* indicate that for the same level of substitution the sample with higher interfacial tension exhibit a faster rate of enzymatic degradation. This suggests that the non-uniform substitution leads to higher interfacial tension. To understand how this is possible, the following explanations are proposed.

If the molecules were a perfect block polymer, with the hydrophilic and lipophilic block lengths large enough to allow the polymer to re-orient at the interface so that all the lipophilic and hydrophilic groups will be in the oil and water phases, respectively, as shown in *Figure 4a*, the attractive interactions will be maximized and the interfacial tension will be extremely low. However, in reality, formation of such a block polymer of MC or HPMC under the current processing conditions is highly unlikely. It is believed the polymers have relatively

Table 1 Interfacial tension of 0.05% aqueous methocel solution—1,2-dichloroethane system at 30°C and 30 min of equilibration for methocel products of different molecular weights

Cellulose ether type	Viscosity for 2% solution at 20°C (mN s m^{-2})	Approximate weight-average molecular weight	Interfacial tension (N m^{-1} x 10^3)
Methocel J	5000	1 000 000	5.0
(Methoxy = 25.6%	106	105 000	4.4
Hydroxypropyl = 18.7%)	53.1	70 000	4.3
	29.2	55 000	4.3
Methocel F	7780	1 200 000	5.6
(Methoxy = 29.3%	62.8	80 000	4.4
Hydroxypropyl = 7.3%)	53.7	70 000	4.3
	41.4	64 000	4.1
Methocel HB	10 000	1 500 000	12.0
(Methoxy = 32.0%	100	100 000	7.0
Hydroxybutyl = 2.1%)			

Table 2 Enzymatic degradation of carboxymethyl methylcellulose sample pairs exhibiting identical substitution values but different interfacial tensions of 0.2% aqueous cellulose ether solution—hydrocarbon oil system at 25°C

Methocel sample pair	Interfacial tension (N m^{-1} x 10^{-3})	Methoxy DS	Carboxymethyl DS	Initial rate of intrinsic viscosity loss (dl g^{-1} min^{-1})
A	14.9	1.32	0.137	0.996
	12.1	1.35	0.137	0.674
B	14.2	1.42	0.140	1.031
	11.8	1.42	0.141	0.827
C	14.0	1.34	0.140	0.996
	10.4	1.30	0.140	0.789
D	12.9	1.31	0.145	1.03
	13.2	1.34	0.145	1.02
E	14.7	1.35	0.104	0.90
	12.5	1.32	0.104	0.80

random distribution of substituted groups along the cellulose backbone. Within this random distribution, there could be relatively uniformly or non-uniformly distributed lipophilic and hyprophilic sites as shown in *Figures 4b* and *4c*. The difference between *Figures 4b* and *4c* is the relative lengths of the hydrophilic and lipophilic blocks. In both the cases the lengths of the blocks are so small that the restrictions imposed by the rigidity of the molecule and internal potential energy barrier towards re-orientation at the interface will force some lipophilic and hydrophilic groups into the water and oil phases, respectively, along with the polymer chain against their will. Now the problem is to establish which one of the situations, *Figure 4b* or *4c*, will have the lower interfacial tension.

Consider a segment of polymer in either the water or oil phase in the vicinity of the interface, as idealized in *Figure 5*, showing the cases of uniform and short block distribution of lipophilic and hydrophilic sites. The circles of the polymer segment depict the sites similar in nature to the solvent molecules, and the squares depict sites unlike the solvent molecules.

In the case of uniformly distributed substituents, as idealized by the polymer segments having alternating lipophilic and hydrophilic sites, all the solvent molecules are strongly attracted by the polymer. For example, molecule B although situated over a dissimilar site, is attracted by the neighbouring sites of the polymer. Molecules A and C are attracted strongly towards the polymer by virtue of their being in the close vicinity of the similar sites of the polymer. Under this situation all the water and oil molecules on two sides of the interface are strongly attracted towards the adsorbed polymer molecule, thus maximizing lowering of interfacial tension.

In the case of the short block distribution of the functional sites, as idealized in *Figure 5b*, the attractive interactions along the polymer backbone are discontinuous. For example, solvent molecules A, B, and C are all situated over dissimilar sites. Molecules A and C are only weakly attracted towards the neighbouring sites and molecule B has hardly any attraction towards the polymer segment. Because of this discontinuity in attractive interactions on both sides of the interface, the overall decrease in free energy or the interfacial tension will be lower than in the case of uniform distribution.

These situations are analogous to the cases of 'condensed', 'expanded' and 'gaseous' films. The uniform distribution case will be similar to an 'expanded' or 'gaseous' film formation and the short block distribution case will be similar to the 'condensed' film formation. In thermodynamic terms the difference in interfacial tensions between the two cases, therefore, is expected to be due, primarily, to the difference in surface entropy. As the two cases have been assumed to have the same degree of substitution, the sum of the total attractive interaction, and so the surface enthalpy, between these two cases will be identical.

It was stated previously that when the lengths of the hydrophilic and lipophilic blocks are large enough so that polymer segments can re-orient themselves at the surface to maximize attractive interactions, as shown in *Figure 4a*, the interfacial tension will be extremely low. However, it is proposed here that when the lengths of the block are at a minimum so that the polymer is termed uniformly distributed, the interfacial tension is going to be lower than the short block distribution. This stipulates that the interfacial tension must pass through a maximum corresponding to a critical block length, as a function of the length of the block or some distribution function. This critical block length will also be a function of the flexibility of the chain. As the polymer chain becomes more flexible, the critical block length for maximum interfacial tension is expected to decrease. However, it can be predicted that the interfacial tension in the case of *Figure 4a* will be much lower than the case of *Figure 4b* by virtue of the higher attractive interactions and lower entropy state of the *Figure 4a* compared to *Figure 4b*.

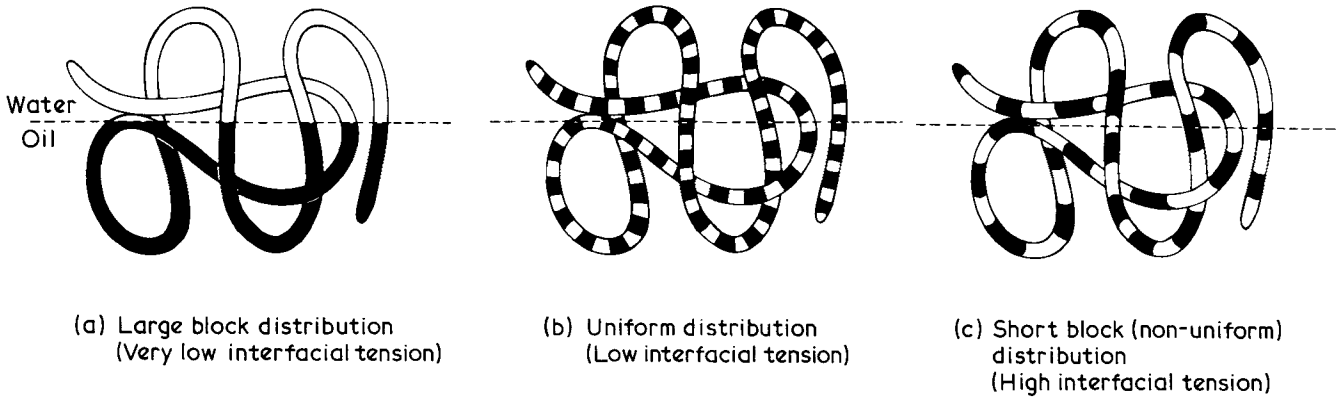

Figure 4 Idealized hydrophilic (white area)–lipophilic (black area) group distribution of polymers at a water–oil interface

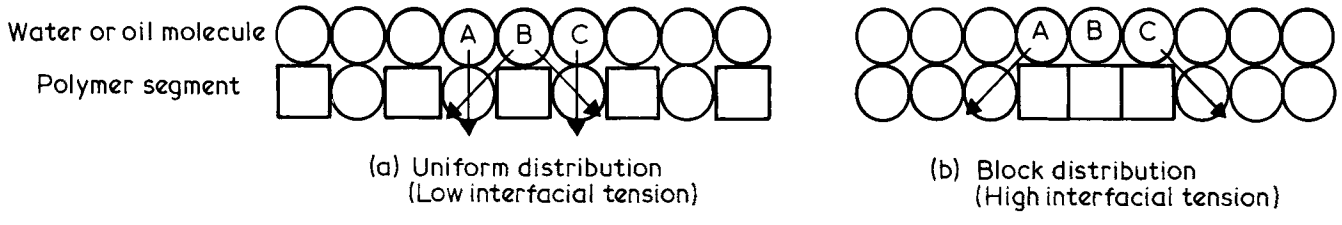

Figure 5 Attractive interactions between polymer segments and solvent molecules

CONCLUSIONS

Interfacial tension of methylcellulose and hydroxypropylmethylcellulose solution–oil systems depends on several factors. Interfacial tension decreases with the increase in total degree of methoxyl and hydroxypropyl substitution. Interfacial tension decreases first with increase in temperature and then increases again for samples exhibiting gelation or precipitation. Interfacial tension increases slightly with the increase in molecular weight of cellulose ether. Higher molecular weight polymers attain steady state interfacial tension values slower than lower molecular weight polymers due to differences in the diffusivity of the macromolecules. From a detailed analysis of the structure of adsorbed cellulose ethers at an aqueous solution–organic liquid interface, it has been proposed that the more uniform the distribution of the substituents along the cellulose ether backbone the lower the interfacial tension. Qualitative agreement of this proposal is found from the results that cellulose ethers exhibiting faster enzymatic degradation in solution, which is an indication of non-uniform substituent distribution, give higher interfacial tension, and *vice versa*.

ACKNOWLEDGEMENTS

The author wishes to thank Barbara Seliskar, Gilbert Ellerby, and Cletus T. Krueger, of the Dow Chemical Company for some of the experimental data included in this paper. The author also wishes to thank Dow Chemical Company for permission to publish this paper.

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