306. W. Lang, Papier, 10, Nos. 3–4, 41 (1956).
307. N. Iwanow and R. Scheider, Bull. Inst. Textile France, 63, No. 10, 7 (1956); Rayon, Zellwolle, Chemiefasern, 556 (1957).
308. J. Schurz and R. Kienzl, Svensk Papperstid., 61, 844 (1958); Ref. Zhur. Khim., 59374 (1959).
309. A. B. Sen Gupta, S. K. Majumdar, and W. G. McMillan, Science and Culture, 443 (1960); Ref. Zhur. Khim., 71870 (1960).
310. H. P. Bhattacherjee, Jute and Gunny Rev., 10, 451 (1959); Ref. Zhur. Khim., 29271 (1960).
311. H. M. Ulrich, Prakt. Chemie, 5, 235 (1954).
312. T. Kleinert and V. Mössmer, Textil-Rundschau, 10, 353 (1955).
313. A. Agster, Melliand Textilber., 36, 1 (1955).
314. A. Agster, Melliand Textilber., 35, 1209 (1954).
315. B. C. M. Dorset, Textile Manufacturer, 88, 394 (1962).
316. G. Zaitoun, Compt. rend., 254, 2980 (1962).
317. R. M. Shchegoleva and T. D. Zakharova, Tekst. Prom., No. 10, 61 (1962).
318. F. A. Abadie-Maumert, Norsk Skogind., 2, 28 (1960).
319. S. Claeson, G. Palm, and G. Wettermark, Arkiv Kemi, 17, 579 (1961); Ref. Zhur. Khim., 11P449 (1962).
320. G. S. Egerton and A. G. Roach, Nature, 180, 189 (1957); J. Colloid Sci., 12, 274 (1957); Chem. Abs., 51, 17156 (1957).
321. S. Claeson and G. Wettermark, Arkiv Kemi, 17, 355 (1961).
322. J. Jortner, J. Polymer Sci., 37, 199 (1959).
323. J. Schurz, D. Kaempgen, M. Schlor, and K. Windisch, Papier, 17, 556 (1963).
324. O. B. Zapol'skii, Vysokomol. Soed., 5, 68 (1963).
325. B. C. Bera, S. D. Kapila, and D. A. L. Rao, J. Sci. Ind. Res., India, D21, 444 (1962).
326. P. N. Agarwal, B. C. Bera, and L. K. Chaturvedi, Indian J. Technol., 1, 356 (1963).
327. A. D. Virnik, K. Malikamov, and Z. A. Rogovin, Khim. Volokna, 47 (1963).

The following additional references are given for a more detailed discussion of individual problems.

328. Canad. Chem. Processing, 42, 46 (1962).
329. H. Sihtola and N. E. Virkola, Norsk Skogind, 12, 87 (1958); Paperi Puu, 40, 579, 627 (1958); 41, 35 (1959).
330. H. Sihtola, Paperi Puu, 45, 71 (1963).
331. H. Sihtola, B. Anthoni, Y. Hentola, I. Pelenius, and N. E. Virkola, Paperi Puu, 40, 579 (1958).
332. H. Sihtola, B. Anthoni, Y. Hentola, I. Pelenius, and N. E. Virkola, Paperi Puu, 40, 627 (1958).
333. H. Sihtola and N. E. Virkola, Paperi Puu, 41, 5 (1959).
334. N. A. Jappe and O. A. Kaustinen, TAPPI, 42, 206 (1959).
335. O. P. Koz'mina and V. I. Kurlyankina, Zhur. Prikl. Khim., 31, 601 (1960).
336. F. I. Sadov, "Deistvie Sveta i Atmosfernykh Uslovii na Khlopchatobumazhnye Tkani" (The Effect of Light and Atmospheric Conditions on Cotton Fabric), Gizlegprom, Moscow, 1945.
337. W. Bubser, Z. Ges. Textil-Ind., 65, 108 (1963).
338. F. Schafizeden, M. L. Wolfram, and P. McWain, J. Amer. Chem. Soc., 81, 1221 (1959).

Department of Natural and Synthetic Macromolecules, Iasi Polytechnical Institute, Roumania

U. D. C. 543.542.1 : 661.185.1

THE PHYSICOCHEMICAL PROPERTIES OF OXYETHYLATED NON-IONIC SURFACE-ACTIVE SUBSTANCES

I. A. Gritskova, R. M. Panich, and S. S. Voyutskii

CONTENTS

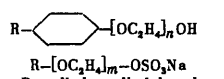
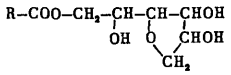
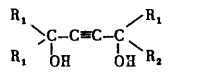
I. Introduction 867
II. Structure of non-ionic surface-active substances (NSAS) 868
III. Solubility and temperature of appearance of turbidity in solutions 868
IV. Surface activity and surface films 870
V. Micelle formation. The shape and dimensions of micelles 871
VI. Formation of mixed micelles. Solubilisation 874
VII. Hydrophilic–lipophilic balance (HLB) 875
VIII. Reasons for the stabilising action of NSAS 879
IX. The use of NSAS for emulsion polymerisation and for increasing the stability of lattices 880

I. INTRODUCTION

The production of non-ionic surface-active substances (NSAS) began in 1929–1935, when for the first time products were obtained by the addition of ethylene oxide to organic compounds containing at least one reactive hydrogen atom, such as the higher aliphatic acids, their amides, higher aliphatic alcohols, thiols, alkylphenols, amines, etc. These products are characterised by the number of ethylene oxide groups attached to one mole of the organic substance. It should be noted that the oxyethylene chains in the compounds are almost never of equal length, their distribution with respect to dimensions being described by a classical Poisson curve[1,2]. At the present time, methods are available for separating a mixture of polymer-homologues into individual products[3] and also for obtaining certain individual NSAS using particular chemical reactions[4].

As a result of the slightly hydrophilic character of ethylene oxide, the addition products usually have a higher solubility in water than the original substances. A significant advantage of oxyethylated substances is the possibility of controlling their hydrophilic nature by altering the quantity of attached ethylene oxide, and also the number of carbon atoms in the hydrophobic chain. This makes it possible to obtain substances with optimal properties for any given field of application. Another important characteristic feature of oxyethylated substances is that they cannot form salts, so that they are stable in hard water and can be used in combination with both anion-active and cation-active SAS.

TABLE 1. Main classes of NSAS.[10]

Type	Chemical structure	Trade name and firm**
Oxyethylated aliphatic acids and products of the oxyethylation of tall oil*	$R-CO[OC_2H_4]_nOH$	Soromine SG Emulsifier A Sterox CD (Monsanto) Prevocel (Buna)
Oxyethylated amides	$R-CON\begin{matrix}[C_2H_4O]_xH\\[C_2H_4O]_yH\end{matrix}$	Dionyl (Hulz)
Oxyethylated alcohols	$R-[OC_2H_4]_nOH$	Peregal O, Bunegal O (Buna)
Oxyethylated alkylphenols		Igepal C and W, Sapal (Buna)
Sulphonated oxyethylated alcohols	$R-[OC_2H_4]_m-OSO_3Na$ R = alkyl or alkylphenyl $m = 2-8$	Alipal Igepal B
Esters of sorbitan and aliphatic acids		Span
Oxyethylated esters of sorbitan and aliphatic acids	the same, polyglycol ester	Tween
Monoethanolamides	$R-CO-NH-C_2H_4OH$	Ninol
Diethanolamides	$R-CON\begin{matrix}C_2H_4OH\\C_2H_4OH\end{matrix}$	Ninol
Oxyethylated poly(propylene glycol)s	$H[OC_2H_4]_x-[OC_3H_6]_n-[OC_2H_4]_y-OH$; $R-[OC_3H_6]_n-[OC_2H_4]_xOH$	Pluronic
Oxyethylated (ethylenediaminopolypropylene glycol)s	$CH_2-N\{[C_3H_6O]_n-[C_2H_4O]_xH\}_2$ $CH_2-N\{[C_3H_6O]_n-[C_2H_4O]_xH\}_2$	Tetronic
Dialkyldihydroxyacetylene		Surfynol
Esters of saccharose and aliphatic acids	R–CO–(saccharose)	Sacrodet
Saccharose alkylurethanes	R–NH–CO–(saccharose)	

* Tall oil is a by-product of sulphate cellulose production, containing chiefly a mixture of aliphatic and resin acids.

** See Ref. 10.

The combination of valuable technical properties shown by NSAS and the continuous decrease in the cost of their production has recently led to their extensive application in many branches of technology, including the textile industry, the manufacture of wetting agents[5], the processing of petroleum[6], etc.

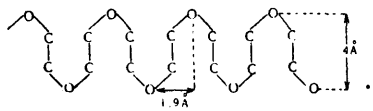
As well as increased production of these substances, the production of oxyethylated substances of the block copolymer type – oxyethylated poly(propylene glycol)s[7,8] and oxyethylated ethylenediaminopoly(propylene glycol)s[8,9] – has been developed in recent years.

Since 1935, NSAS of the sorbitan ester, ethanolamide, saccharose–aliphatic acid ester, dialkyldihydroxyacetylene, etc., type have been prepared in addition to oxyethylated NSAS. Some of the most commonly encountered classes of NSAS are listed in Table 1.

The aim of the present review is to summarise data on the properties of oxyethylated non-ionic surface-active substances and to indicate some of their fields of application.

II. STRUCTURE OF NON-IONIC SURFACE-ACTIVE SUBSTANCES (NSAS)

In a study of the structure of polyoxyethylene chains, Staudinger[11] suggested that the retarded increase in chain length with increase in the number of oxyethylene groups can be explained by assuming that the polyoxyethylene chain has a winding shape (caterpillar shape):



The winding shape of the polyoxyethylene chain is generally assumed to be due to the mutual attraction of the oxygen atoms in the chain to one another. The chain strives to become shorter under the influence of the forces of attraction. At a low degree of polymerisation, these forces are insufficiently strong to lead to a decrease in the length of the chain, and the chain retains its usual zigzag shape[12].

Comparison of the observed and calculated specific viscosities of polyoxyethylene diacetates established that the chains have a zigzag shape up to a degree of polymerisation of 9 and that they acquire a winding shape only at higher degrees of polymerisation.

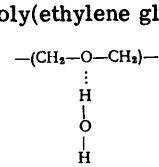
Many studies have been made of the structure of the polyoxyethylene chain[13-16]. Rösch[16] explains the winding shape of the polyoxyethylene chain on the basis of the general concepts of valency theory. He represents the structure of the polyoxyethylene chains as a zigzag structure, in which, because of the presence of CH_2-CH_2-O and CH_2-O-CH_2 groups, oblique-angled and equilateral triangles alternate in the ratio 2:1. Each ethylene oxide group forms a dipole with a moment of 1.88, in which the CH_2 is the positive pole and the O the negative pole. The distance between the dipoles is 2.3 Å. The CH_2 groups of the ethylene oxide repel one another and the oxygen atoms attract neighbouring CH_2 groups. This produces stresses which increase with increase in the length of the zigzag chain. When the degree of oxyethylation reaches 9–11, the magnitude of the stresses becomes sufficiently high to produce a change in structure, and the zigzag shape is converted into the winding shape. The change in the structure leads to contraction of the oxyethylene chain.

In aqueous solutions of oxyethylated substances, as a result of the formation of polyoxonium complexes, an increase in the polarisation of the CO bond takes place and this may also lead to a change in structure.

Uchida and coworkers[17], on the basis of the dipole moments in dioxan solution, established that the polyoxyethylene chain consists of a mixture of both structures, although the winding shape of the chain predominates in aqueous solution.

III. SOLUBILITY AND TEMPERATURE OF APPEARANCE OF TURBIDITY IN SOLUTIONS

The solubility of oxyethylated substances in water is due to the formation of hydrates as a result of the production of hydrogen bonds between the water molecules and the ether oxygen atoms of the poly(ethylene glycol) residue:



With increase in the number of oxyethylene groups, there is an increase in the number of water molecules attached to the ether oxygen atoms, and the hydrophilic

nature of the oxyethylated substance increases. Thus the polyoxyethylene chain can be regarded as "sheathed" with water molecules throughout its length. One or more of these water molecules may take up a proton from the surrounding solvent, with the formation of a hydroxonium ion. When this is so, each molecule of the oxyethylated substance is surrounded by an electrical double layer of ions. The ethylene oxide oxonium group can be represented as follows:

$$[-(CH_2-\underset{\displaystyle H_3O}{\underset{|}{O}}-CH_2)]^+OH^- .$$

The formation of charged groups increases the hydration of the substance. The presence of the charge was confirmed indirectly by the analytical studies of Wurzschmidt[18], who showed that in aqueous solutions, oxyethylated substances behave as weakly cation-active polyoxonium compounds. Only a small proportion of the ether oxygen atoms usually form oxonium salts. Studies by Schick[19], however, showed that oxonium salt formation increases on acidification, and that in strongly acidic media every ether oxygen atom forms an oxonium ion.

Scheller[5] established a rule which makes it possible to find the relationship between the number of carbon atoms in the hydrophobic fraction of oxyethylated substances and the number of oxyethylene groups necessary to make these substances soluble in water. If the hydrophobic fraction contains n carbon groups, $n/3$ oxyethylene groups are required to give minimum solubility in water, $n/2$ oxyethylene groups are required to give moderate solubility in water, and between n and $3n/2$ oxyethylene groups are required to give ready solubility in water.

According to the ideas of Cohen and Smith[20], one hydroxyl group or one ether oxygen atom is sufficient to overcome the hydrophobic character given to a substance by three methylene groups. Since the ethylene oxide molecule contains two CH_2 groups, the oxyethylated substance should contain one oxyethylene group in the hydrophilic fraction for every CH_2 group in the hydrophobic fraction if the substance is to dissolve in water. Thus a substance with general formula $H[CH_2]_x[OCH_2CH_2]_yOH$ is soluble in water if $y \geq x - 3$.

Shakhovskii[5] prepared oxyethylated C_4-C_{12} alcohols and established that the substances obtained dissolved in water when they contained $M/44.05$ oxyethylene groups, where M is the molecular weight of the aliphatic alcohol.

The solubility of oxyethylated substances in water decreases with increase in temperature, and since the energy of the hydrogen bond is low (7 kcal mole^{-1}), dehydration takes place so that the non-ionic substance loses its ability to dissolve in water. With decrease in temperature, the hydrate is reformed and the substance dissolves. The solubility of oxyethylated substances in water at elevated temperatures is characterised by the temperature at which turbidity appears in the solution (the cloud point). This temperature provides an important analytical indication of the degree of polyoxyethylation of the product and to some extent makes it possible to characterise NSAS. If the poly(ethylene glycol) residue contains a sufficiently large number of CH_2-CH_2-O groups, the ability of these compounds to undergo hydration is so great that their aqueous solutions do not become cloudy even on boiling. Table 2 gives the cloud points of aqueous solutions of polyoxyethylated poly(propylene glycol)s.

TABLE 2. Cloud points (t_c) of 10% aqueous solutions of Pluronics[6].

Pluronic symbol	Characteristics of Pluronic	Mean molecular weight of polyoxypropylene taken for oxyethylation	% polyoxyethylene in Pluronic molecule	t_c, °C
L-62	liquid	1750	20	20
L-64	liquid	1750	40	70
L-44	liquid	1200	40	78
F-68	flakes	1750	80	100

Table 2 shows that the longer the oxyethylene chain, the greater the degree of hydration and the higher the temperature necessary for dehydration of the non-ionic molecules of the substance. The properties of Pluronics have been described in detail[21].

Raphael[5] determined the dependence of the cloud points of oxyethylated alcohols and octylcresols on the degree of oxyethylation at different concentrations. He showed that increase in the degree of oxyethylation leads to a linear increase in the cloud point, and that for a given degree of oxyethylation the cloud points are higher in concentrated solutions.

The cloud point depends on the chain-length distribution of the oxyethylene chains. If the oxyethylated substance contains a large proportion of low-molecular-weight products, the cloud point is low, whereas substances with a narrow distribution are more hydrophilic and have high cloud points[22].

The addition of certain electrolytes to solutions of oxyethylated substances leads to a marked decrease in the solubility and cloud points. Thus Knowles and Krupin[23], in a study of the cloud points of aqueous solutions of nonylphenols with different degrees of oxyethylation in the presence of electrolytes, obtained the results given in Table 3.

The influence of electrolytes involves chiefly a dehydrating action resulting from rupture of the hydrogen bonds. Sometimes, however, electrolytes exhibit a stabilising action related to the cation-active nature of the oxyethylated substances. Hydrochloric acid raises the cloud point (Table 3). This is due to the fact that in acid medium there is an increase in the possibility of formation of oxonium ions and hence in the hydration. Sulphuric acid has a very weak dehydrating action, since the increase in hydration resulting from oxonium ion formation is compensated by the desolvating action of the bivalent SO_4^{2-} anion. Bases bring about particularly extensive dehydration. The cation-active nature of NSAS is also shown by the fact that the solubility is little influenced by the nature of the cation but is influenced to a marked extent by the nature of the anion[24].

TABLE 3. Influence of electrolytes on the cloud point of oxyethylated nonylphenols[28].

Degree of oxyethylation of nonylphenol	Cloud point, °C						
	distilled water	3% NaCl	3% Na_2CO_3	3% NaOH	3% HCl	3% H_2SO_4	3% Na_3PO_4
9	55	45	32	31	60.5	51	43
10.5	72	61	48	45.5	78	69	60
15	98	84.5	70	67	100	96	83.5
20	100	95	78	73	100	100	92

Doscher and coworkers[25] showed that salts of the alkaline earth metals, for example, calcium, have no dehydrating action and even facilitate the dissolution of NSAS. The Ca^{2+} ions are strongly hydrated and the dipoles of the water are orientated around the Ca^{2+} ions with their positive pole directed outwards. This orientation favours the formation of a coordinate bond between the hydrated ions and the negative ether oxygen atoms, leading to an increase in the hydration of the NSAS. This may explain the high efficiency of non-ionic wetting agents in hard water.

The addition of small quantities of anionic surface-active substances increases the cloud point by 10–20 deg. Maclay[26] attributed this phenomenon to the formation of mixed micelles of anionic and non-ionic SAS. At the cloud points, the non-ionic detergents are solubilised in these micelles.

The addition of aromatic or polar aliphatic substances (benzene, phenol, aniline) leads to a marked lowering of the cloud point[26–28]. The lowering of the cloud point in the presence of polar additives is attributed to the fact that these substances are solubilised in the micelles of non-ionic detergent and, as it were, increase the relative part played by the hydrophobic fraction of the detergent, with a consequent decrease in hydration and lowering of the cloud point.

IV. SURFACE ACTIVITY AND SURFACE FILMS

It has been shown for the case of oxyethylated aliphatic alcohols[5,29], alkylphenols[5,30], and Pluronics[31] that within a given series, the minimal surface tension of the aqueous solutions increases with increase in the degree of oxyethylation and decreases with increase in the number of carbon atoms in the hydrophobic chain. The change in surface activity shows qualitative agreement with Traube's rule, that is, the surface activity increases with increase in the number of carbon atoms in the hydrophobic chain. The surface activity decreases with increase in the degree of oxyethylation. Data for Pluronics, confirming these general features, are given in Table 4.

With increase in temperature, the minimal surface tension of aqueous solutions of NSAS decreases and the surface activity of the non-ionic substances increases. This characteristic feature is related to the dehydration of the NSAS molecules with increase in temperature.

Crook and coworkers[30] recorded the surface tension isotherms for *p*-t-octylphenols with normal distribution and for individual *p*-t-octylphenols prepared by special methods[4]. Using these isotherms, they determined the dependence of the minimal surface tension σ_{c_k} and the areas occupied by the molecules in a layer with maximum

TABLE 4. Dependence of the surface tension (dyn cm^{-1}) of a series of Pluronics at 30° on the concentration of the aqueous solutions[31].

Pluronic symbol	Concentration, %			
	1	0.1	0.01	0.001
L-44	41.2	45.2	47.2	52.5
L-62	34.5	37.1	42.0	45.6
L-64	36.0	40.0	43.8	48.6
F-68	43.6	46.6	47.4	64.0

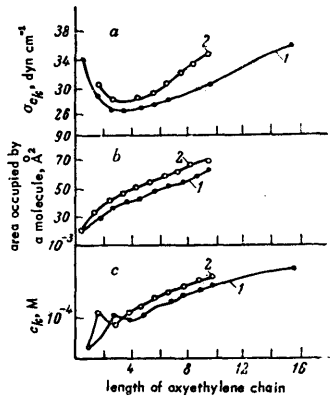


Fig. 1. Dependence of the surface tension at c_k (*a*), area occupied by a molecule (*b*), and c_k (*c*) on the chain length of individual OP SAS (2) and mixtures with normal distribution (1).[39]

saturation on the degree of oxyethylation (Figs. 1*a* and 1*b*). It can be seen from Fig. 1*a* that the surface tension corresponding to c_k for the individual products is greater than that for the mixtures with normal distribution, since in the latter case preferential adsorption of the more highly surface-active components with lower degree of oxyethylation takes place at the solution–air boundary.

On the basis of a comparison of the surface activity of oxyethylated substances of different classes, Schönfeldt concluded that oxyethylated alcohols and phenols exhibit the highest surface activity. Wrigley and coworkers[31] studied the surface tension of 1% solutions of oxyethylated aliphatic acids and aliphatic alcohols with oxyethylated chains of different length. With equal numbers of carbon atoms in the hydrophobic fraction and equal numbers of oxyethylene groups in the hydrophilic fraction, the surface tension is greater for the oxyethylated alcohols. For example, the values of the surface tension (dyn cm^{-1}) for hexadecanol specimens with degree of oxyethylation equal to 15, 20, and 30, are 36.4, 38.2, and 40.2 respectively, whereas the values for palmitic acid specimens with the same degree of oxyethylation are 34.2, 35.8, and 38.4.

To determine the nature of the orientation of non-ionic surface-active substances at an air–water boundary, a number of workers have studied surface films of aqueous solutions of polyoxyethylated aliphatic alcohols[32] and alkylphenols[19,28,33–36].

The nature of the packing and orientation of the polar groups in these surface films was established from the surface tension and surface potentials, and also by recording two-dimensional phase diagrams for the films[32]. Schick[33] used the Gibbs equation and surface tension isotherms to establish the dependence of the area of the adsorbed surface film on the surface pressure π for two homologous series of oxyethylated NSAS.

The areas occupied by the molecules in the adsorbed films at $\pi = 20$ dyn cm^{-1} are given in Table 5. This table also gives the data obtained by Lange[35] for a saturated adsorbed film, and Schick's data for insoluble surface films of the same NSAS. It can be seen from Table 5 that the area occupied by a molecule of oxyethylated n-dodecanol and n-octadecanol is much greater than the cross-sectional area of aliphatic hydrocarbons (20 Å²) or the benzene

TABLE 5. Areas occupied by the molecules in the surface films of non-ionic detergents.

Hydrophobic group	Degree of oxyethylation	Area occupied by a molecule, Å²		
		adsorbed film		insoluble film
		π=20 dyn cm^{-1}	π_{max}	π=20 dyn cm^{-1}
n-Dodecanol	0	—	—	25
	4	44	—	—
	5	—	54	—
	7	48	59	65
	9	—	71	—
	12	—	77	—
	14	65	—	160
	23	82	—	—
	30	107	—	265
n-Octadecanol	0	—	—	20
	5	42	—	70
	14	94	—	160
	100	150	—	960

ring (25 Å²) and increases with increase in the length of the oxyethylated chain. Thus vertical orientation of the oxyethylene chain is excluded. Changes in the structure of the hydrophobic groups at constant molar concentration of ethylene oxide have little influence on the area occupied by the molecule. On the basis of these results, two possible configurations can be suggested for the NSAS molecules in adsorbed surface films: the molecules are orientated in such a way that the hydrophobic groups lie above the interface, and the oxyethylene groups either lie on the surface of the phases or form coils in the aqueous phase. In order to select one of the two possible orientations, a comparison was made of the molecular areas occupied by the molecules of non-ionic detergents in adsorbed surface layers and the corresponding molecular areas in insoluble surface films[35]. In the latter, the substrate consisted of a saturated solution of sodium nitrate or 29% sodium chloride solution.

In both homologous series, the areas occupied by the molecules at comparable surface pressures increase with increase in the length of the oxyethylene chain, whereas the difference in the structures of the hydrophobic groups at constant degree of oxyethylation has little influence on the areas of the molecules in the saturated films. From this it should have followed that the hydrophobic groups are orientated above the interface, and the oxyethylene chains lie on the surface. The molecular areas in insoluble surface films, however, are very much greater than the corresponding values in adsorbed surface films, so that the horizontal orientation is also excluded. These considerations led the authors to the conclusion that the molecules of the surface-active substance are orientated at the air–water interface with their hydrophobic groups above the interface and with the oxyethylene chains forming coils in the aqueous phase. The dimensions of the coils increase with increase in the number of segments in the oxyethylated chain.

These conclusions were confirmed and extended in a study of the surface potentials for polyoxyethylated n-dodecanols and n-octadecanols containing oxyethylated chains of different length[19].

It was found that the increase in surface potential and hence the increase in the dimensions of the coils decreases with increase in the degree of oxyethylation. This is related to the polymeric nature of the oxyethylene chain. Figure 1*b* gives the dependence of the area occupied by a molecule of *p*-t-octylphenol on the length of the oxyethylene chain. The increase in area is non-linear, although

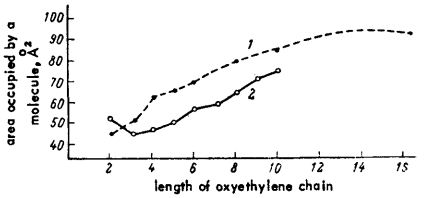


Fig. 2. Dependence of the area occupied by a molecule at the solution–isooctane boundary on the chain length of individual OP SAS (2) and mixtures with normal distribution (1).[39]

the deviation from linearity is slight in the range from 3 to 10 oxyethylene groups. On the basis of the assumption that the hydrated molecules of oxyethylated substances in adsorption layers form statistical configurations, Van Voorst-Vader[37] concluded that the area of the molecule at saturation is proportional to $\sqrt{m}$, where m is the degree of oxyethylation. This was confirmed for the case of oxyethylated alkylphenols. Lange[32] obtained the same relationship for oxyethylated dodecanol.

By measuring the interfacial tension at the interface between isooctane and an aqueous solution of NSAS, Crook[30] determined the dependence of the area occupied by a molecule at the interface on its degree of oxyethylation (Fig. 2). For individual substances, the areas occupied by a molecule on the solution–hydrocarbon boundary are close to the corresponding values for a solution–air boundary. For mixtures with normal distribution, the area of the molecule at the solution–air boundary (Fig. 1*b*) is smaller, and the area at the solution–hydrocarbon boundary (Fig. 2) greater, than the value for the corresponding individual products. As already described, the former is due to the preferential adsorption of the more highly surface-active components of the mixture at the solution–air boundary. The second result is due to the fact that for mixtures with normal distribution it is necessary to make allowance for the specific solubility of the different components of the mixture in isooctane. Since the components with lower degree of oxyethylation are more soluble in isooctane, they are concentrated in the hydrocarbon phase, so that the average molecular weight of the NSAS dissolved in water increases, leading to an increase in the area of the molecule at the interface. Becher[34] put forward suggestions regarding the orientation of non-ionic surface-active substances at an oil–water interface for the polyoxyethylated lauryl alcohols and nonylphenols, and the part played by hydrogen bonds in this orientation.

V. MICELLE FORMATION. THE SHAPE AND DIMENSIONS OF MICELLES

Micelle formation by NSAS has been fairly fully studied. The studies have been carried out chiefly using oxyethylated aliphatic alcohols and alkylphenols. Several methods have been used to determine the critical concentration of micelle formation (c_k) of non-ionic surface-active substances: the surface tension method[38–43], the dye solubilisation method, a method based on the change in the absorption spectrum[40,43–50], the light scattering method[40,41,50–55], and the viscosity method[51,55].

Unlike the case of ionogenic surface-active substances, in which the hydrophilic fraction of the molecule is much

TABLE 6. c_k and the micellar weights of non-ionic detergents in aqueous solutions[56].

Hydrophobic groups	Degree of oxyethylation	Number of C atoms in the hydrophobic fraction	c_k, μmole litre^{-1}	Micellar weight × 10^{-3}, M_m	Degree of association (n)
Nonylphenol (branched)	10	10.5	75	182	276
	15		110	70	80
	20		140	68	62
	30		185	67	44
	50		280	48	20
n-Dodecanol	7	12	50		
	14		55	100	125
	23		60		
	30		80	82	55
n-Octadecanol	14	18	60	330	370
	100		20	465	100

smaller than the hydrophobic fraction, the hydrophilic fraction may be greater than the hydrophobic fraction in non-ionic oxyethylated substances. With non-ionic substances, the absence of electric charge facilitates micelle formation, so that c_k for NSAS is much lower than c_k for ionic surface-active substances, as can be seen from Table 6, which gives the values of c_k for several homologous series of non-ionic detergents in aqueous solutions. For comparison, it may be noted that for sodium dodecyl sulphate, c_k = 8100 μmole litre^{-1}.[5]

From the results obtained it follows that c_k increases with increase in the length of the oxyethylene chain, that is, increase in hydration or solubility hinders the aggregation of the non-ionic surface-active substances. The low values of c_k for n-octadecanol-100, compared with those for n-octadecanol-14, can be attributed to the decrease in the solubility of the oxyethylene fraction of the chain at very high degrees of oxyethylation. Thus with increase in the length of the oxyethylene chain, the overall solubility of non-ionic detergents passes through a maximum. It has been shown[38,39] that the increase in c_k with increase in the length of the oxyethylene chain is given by the equation

$$\ln c_k = BR + K \qquad (1)$$

where R is the average number of oxyethylene groups in the chain, B a constant which depends on the nature of the hydrophobic group and decreases with increase in the length of the hydrophobic chain, and K a constant which depends on the nature and concentration of the electrolyte present.

For oxyethylated nonylphenols in water, B = 0.056 and K = 3.87. It then follows from formula (1) that the value of c_k is doubled when R increases by 12. Approximately the same relationship is applicable for oxyethylated substances of other classes (Fig. 1c)[39].

For oxyethylene chains of constant length, the values of c_k for NSAS, like those for ionogenic detergents, decrease with increase in the length of the hydrocarbon chain, due to the increase in the interaction between the hydrocarbon chains, facilitating aggregation. According to recent work by Schinoda[57], the influence of the length of the hydrocarbon chain on c_k is given by the formula

$$\log c_k = -\frac{m\omega}{kT} + \text{const}, \qquad (2)$$

where m is the number of carbon atoms in the chain and ω the change in cohesion energy for the transfer of one methylene group from aqueous solution into the micelle.

The values of c_k are approximately doubled when the hydrophobic chain is reduced by one CH_2 group. Thus the influence of 12 ethylene oxide groups on c_k is equivalent to that of one methylene group.

The influence of temperature on c_k for NSAS solutions is opposite to the usual influence of temperature on micelle formation. Since thermal movement hinders micelle formation, the latter should decrease with increase in temperature, and the values of c_k should increase. This is the usual relationship observed, with certain exceptions, in solutions of ionogenic SAS. For NSAS, c_k decreases with increase in temperature, that is, micelle formation shows negative thermal effects.

Schick[58] used the Clausius–Clapeyron equation to determine the enthalpy change on micelle formation (ΔH_m) from the temperature dependence of c_k. The dependence of $\log c_k$ on $1/T$ for oxyethylated alcohols is shown in Fig. 3. As shown in Fig. 3 and in other papers[41,59,60], this relationship is strictly linear for NSAS, and the enthalpy increases on micelle formation. The fact that the Clausius–Clapeyron equation is applicable to micelle formation means that in NSAS solutions this process must be regarded as involving phase separation. This approach is also applicable to ionic detergents in the presence of salting-out electrolytes[60,61]. From the conditions for equilibrium at c_k, it follows that the free energy change $\Delta\bar{G}_m$ is equal to zero, and the entropy of micelle formation can be calculated from the equation

$$\Delta\bar{S}_m = \frac{\Delta\bar{H}_m}{T}. \qquad (3)$$

The quantity $\Delta\bar{H}_m$ is positive, so that the entropy change on micelle formation in NSAS solutions is also positive. A positive entropy change means an increase in disorder. Since it cannot be that aggregation of monomeric detergent molecules to form micelles is accompanied by an increase in the disorder of the system, it is necessary to find other reasons for the positive change in entropy. Studies have shown[33,56,58,62] that the chief reason for the increase in entropy on micelle formation may be the desolvation of the NSAS molecules on aggregation. This is confirmed by the data in Table 7.

The greater the concentration of electrolyte and hydration of the anion ($CNS^- < Cl^- < SO_4^{2-}$), the greater the increase in entropy. The part played by dehydration can

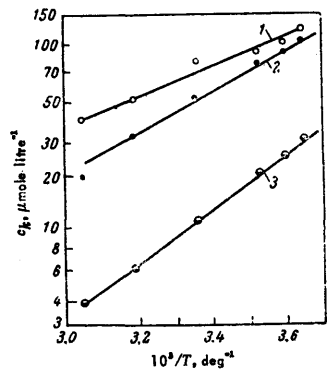


Fig. 3. Straight lines obtained by plotting $\log c_k = f(1/T)$ for aqueous solutions of non-ionic detergents[68]:
1) n-$C_{12}H_{25}(OC_2H_4)_{30}OH$; 2) n-$C_{12}H_{25}(OC_2H_4)_7OH$;
3) n-$C_{16}H_{33}(OC_2H_4)_{30}OH$.

TABLE 7. Partial values of the enthalpy and entropy of micelle formation for non-ionic detergents*.[58]

Hydrophobic group	Degree of oxyethylation	Solvent	$\Delta\bar{H}_m$, kcal mole^{-1}	$\Delta\bar{S}_m$, cal × ×mole^{-1} deg^{-1}
n-Dodecanol	30	H_2O	3.7	12.3
n-Dodecanol	7	H_2O	5.0	16.6
n-Hexadecanol	30	H_2O	6.6	21.9
n-Dodecanol	30	0.43 M NaCl	6.0	19.9
n-Dodecanol	30	0.86 M NaCl	6.5	21.6
n-Dodecanol	30	0.86 M NaCNS	4.1	13.6
n-Dodecanol	30	0.86 M $^1/_2Na_2SO_4$	9.1	30.2

* Values obtained in the range 1–55°.

also be seen by comparing the values of $\Delta\bar{S}_m$ for substances with different hydrophilic character (n-dodecanol-30, n-dodecanol-7, and n-hexadecanol-30). The greater the hydrophilic character, the more difficult the process of dehydration and the smaller the increase in entropy on aggregation.

In addition to desolvation, another factor increasing the entropy may be an increase in the configurational entropy of the hydrocarbon chain of the detergent molecule inside the micelle[36,64]. To counterbalance this, the configurational entropy of the oxyethylene chain in the outer sheath of the micelle is smaller than its entropy in solution. Since the experimentally-observed entropy change is positive, the decrease in entropy taking place on aggregation of the molecules of non-ionic detergents is compensated by desolvation and to some extent by an increase in the entropy of the hydrocarbon chain.

Tables 6 and 8 give values of the micellar weights and corresponding values of c_k for non-ionic detergents in aqueous solutions, obtained by the light scattering and ultracentrifuge methods[54]. Similar results were obtained by Mankowich[65], Dwiggins and coworkers[66-68], and Elworthy and Macfarlane[55].

Low values of c_k correspond to the highest values of the micellar weights, and vice versa, as is usually the case in micellar solutions. The degree of association or the number of molecules in the micelle is defined as the ratio of the micellar weight to the molecular weight of the surface-active substance. No allowance is made for the degree of hydration since this is unknown.

It can be seen from Table 6 that when the degree of oxyethylation is constant (for example, 14 or 15 CH_2-CH_2-O groups), the micellar weights and degree of aggregation increase with increase in the chain length of the hydrophobic fraction of the molecule. With increase in the number of oxyethylene groups, however (Tables 6 and 8), the micellar weights decrease, and for substances with a low degree of oxyethylation, small changes in the ethylene oxide content bring about the most marked changes in the micellar weights. Study of a mixture of fractions with different degree of oxyethylation showed that the change in the micellar weight for fractions with high ethylene oxide content is much greater than that for fractions with low degree of oxyethylation. Thus change in the conditions of preparation of polyoxyethylated surface-active substances may have a marked influence on their micellar weight in solutions.

TABLE 8. Average micellar weights and degree of association of oxyethylated lauryl alcohol and nonylphenols[53].

Hydrophobic fraction	Degree of oxyethylation	$10^3 c_k$, g litre^{-1}	Micellar weight × 10^{-3}, M_m	Degree of association, n
Lauryl alcohol	8	59	68.2	123
	12	65	58.9	81
	18	80	50.6	51
	23	110	48.9	40
Nonylphenol	10	64	66.3	100
	15	77	45.0	52
	30	236	29.7	19

The degree of association decreases with increase in the length of the oxyethylene chain. With n-octadecanols (Table 6), the degree of association also decreases with increase in the length of the oxyethylated chain, but the micellar weight increases, due to an increase in the molecular weight of the surface-active substance. Becher[53] found a linear relationship between the degree of association and the degree of oxyethylation. For derivatives of lauryl alcohol and nonylphenol, the equations for the straight lines are of the form

$$n = 1025/R - 5.1 \quad (4)$$

and

$$n = 1215/R - 22.5 \quad (5)$$

respectively, where n is the degree of association and R the number of oxyethylene groups in the chain.

A decrease in the degree of association with increase in the length of the oxyethylene chain was also observed by Kushner et al.[69] for polyoxyethylated isooctylphenols and by Stauff and Rasper[70] for polyoxyethylated dodecanol. This work[69,70] was carried out with fractionated specimens, however, and since the polymer distributions are different in the fractionated specimen and in the industrial product with the same average molecular weight, these results are of mainly theoretical importance.

Work by Balambra and coworkers[54] and Mankowich[47] showed that the micellar weights increase exponentially with increase in temperature.

A number of authors have put forward suggestions regarding the shape of the micelles in NSAS solutions[53,56,71-74]. As for ionic detergents, the existence of spherical, lamellar, and cylindrical micelles has been suggested. On the basis of calculations of the surface area of micelles of different types for oxyethylated nonylphenols and lauryl alcohol, Becher[53] showed that the cylindrical shape is the most probable.

Ermilov[48] suggests that there exist two critical concentrations for micelle formation: c'_k, at which small spherical micelles are formed, and c''_k, at which large lamellar micelles are formed. Levitskii and coworkers[49], however, consider that only the spherical micelles postulated by Hartley exist at c'_k and c''_k, but that the quantity of these micelles is smaller at c'_k and greater at c''_k. The final equilibrium distribution of the structural units of different type (molecules and micelles), both in the bulk of the micellar solutions and between the bulk and the adsorption layers, is established at c''_k, and this distribution remains unchanged over a wide concentration range until another form of micelle is produced in the solution.

Schick and coworkers[56] determined the shape of micelles formed by non-ionic surface-active substances, by the light-scattering method and from the rate of sedimentation. They suggest that in the micellar weight range 45 000–100 000 the micelles are most probably spherical, whereas

at higher micellar weights they have the shapes of discs and rods. Similar results were obtained by Gorkill[74].

The addition of electrolytes influences c_k and the dimensions of the micelles in solutions of non-ionic detergents. This influence is analogous to the influence of electrolytes on c_k for ionic SAS, established by Corrin and Harkins[75] and Klevens[76]. Addition of electrolytes leads to a decrease in c_k and an increase in the micelle dimensions. The influence of electrolytes on c_k for non-ionic detergents has been studied in detail by Hsiao and coworkers[39], Becher[38], Kuriyama[77], and Schick[33].

It can be seen from Table 9 that increase in the NaCl concentration leads to a marked increase in c_k for solutions of polyoxyethylated nonylphenols in water (the increase is greater than that for ionic surface-active substances).

In a study of the influence of added electrolytes on micelle dimensions for oxyethylated derivatives of lauryl alcohol, nonylphenol, and tridecanol in the presence of Na and Ca chlorides, Na sulphate, and Na citrate $Na_3C_6H_5O_7$, Becher[38] showed that replacement of the univalent Na^+ cation by the bivalent Ca^{2+} cation has no significant influence on the micelle dimensions or degree of association; change in the anion, however, has a more marked influence on these quantities. The anions can be arranged in the following order of decreasing activity:

sulphate > citrate > chloride.

TABLE 9. Influence of electrolyte concentration on c_k for solutions of polyoxyethylated nonylphenols[33].

NaCl concentration, M	Decrease in c_k, μmole litre^{-1}	
	nonylphenol + $+15CH_2CH_2O$	nonylphenol + $+50CH_2CH_2O$
0.43	45	80
0.86	55	130
1.29	65	180

The data which they obtained on the influence of electrolytes are given in Table 10. The micellar weights M_m were calculated from the Debye equation, and the degree of association n was calculated from the micellar weight and the average molecular weight of the surface-active substance. The increase in the degree of association is due to the decrease in the hydration of the oxyethylene chain resulting from the desolvating action of the electrolytes. It can be seen from Table 10, however, that this influence of electrolytes is shown only in solutions of substances with low degree of oxyethylation. For substances with a high degree of oxyethylation, the addition of electrolytes sometimes leads to a decrease in the degree of association, although the addition of electrolytes leads to a decrease in c_k even at high degrees of oxyethylation, as can be seen from Table 9. Becher suggests that the effect of electrolytes involves not only their action on the hydrophilic nature of the polyoxyethylene chain but also their action on the charge of the micelles resulting from the formation of the hydroxonium ion.

VI. FORMATION OF MIXED MICELLES. SOLUBILISATION

Kuriyama and coworkers[78] determined the micellar weight for mixtures of non-ionic and ionic surface-active substances in 0.2 M sodium chloride solution at different temperatures. The results are given in Table 11.

The micellar weight of non-ionic surface-active substances increases with increase in temperature, whereas that of ionic surface-active substances decreases.

In mixtures of non-ionic and ionic surface-active substances, the increase in the micellar weight of the non-ionic detergents is suppressed with increase in the quantity of ionic SAS added. When the quantity of added ionic SAS exceeds a definite value (~20%), the micellar weights decrease with increase in temperature. This relationship was explained as follows[78]. The formation of micelles in solutions of non-ionic surface-active substances is determined by two factors: the forces of cohesion between the oleophilic groups and the affinity of the hydrophilic groups

TABLE 10. Influence of electrolytes on the micellar weight (M_m) and average degree of association (n).[38]

Original products	$10^{-3}M_m$, degree of oxyethylation								n, degree of oxyethylation							
	8	10	12	15	18	22	23	30	8	10	12	15	18	22	23	30
Polyoxyethylated lauryl alcohol without electrolytes	68.2	—	58.9	—	50.6	—	48.8	—	123	—	81	—	51	—	40	—
NaCl 0.30 *N*	70.0	—	57.6	—	52.9	—	42.2	—	127	—	79	—	53	—	35	—
0.50 *N*	77.0	—	50.0	—	45.4	—	40.3	—	140	—	69	—	46	—	33	—
$CaCl_2$ 0.30 *N*	66.1	—	52.4	—	45.0	—	40.2	—	120	—	72	—	45	—	33	—
0.50 *N*	82.0	—	46.9	—	43.2	—	38.8	—	149	—	63	—	44	—	32	—
$Na_3C_6H_5O_7$ 0.30 *N*	97.0	—	46.3	—	38.3	—	34.5	—	176	—	64	—	39	—	28	—
0.50 *N*	87.2	—	48.0	—	40.2	—	34.3	—	158	—	66	—	40	—	28	—
Na_2SO_4 0.30 *N*	171	—	53.5	—	45.8	—	47.2	—	310	—	73	—	46	—	39	—
0.50 *N*	472	—	53.5	—	49.5	—	45.0	—	856	—	73	—	50	—	37	—
Polyoxyethylated nonylphenol without electrolytes	—	66.3	—	45	—	—	—	29.7	—	100	—	52	—	—	—	19
NaCl 0.30 *N*	—	75	—	51	—	—	—	30.7	—	113	—	58	—	—	—	20
0.50 *N*	—	82.9	—	46.5	—	—	—	24.0	—	126	—	53	—	—	—	16
Polyoxyethylated tridecanol without electrolytes	—	58.7	—	32.8	—	32.5	—	—	—	92	—	38	—	28	—	—
NaCl 0.30 *N*	—	70.0	—	40.5	—	33.5	—	—	—	110	—	47	—	29	—	—
0.50 *N*	—	90.3	—	40.0	—	32.8	—	—	—	141	—	47	—	28	—	—

for water molecules. At a given temperature, a corresponding balance is established between the forces of hydration and cohesion, and micelles with definite dimensions are formed. In the case of ionic SAS, the formation of micelles is associated with a balance between the electric forces of the ionised groups and the forces of cohesion of the hydrocarbon chain.

In mixtures of ionic and non-ionic detergents in solution, mixed micelles are formed. The balance between the electric forces and the forces of cohesion and hydration may be altered in either direction with increase in temperature, depending on the ratio of the quantities of ionic and non-ionic detergents. It follows from the results obtained (Table 11) that the micellar weights increase with increase in temperature until a definite composition is reached in the mixture of ionic and non-ionic SAS, after which the micellar weights decrease.

The ionogenic substances added to a solution of non-ionic detergents may influence the equilibrium between the forces of cohesion and the electric forces in two ways: (1) by penetrating into the micelle and altering its structure, and (2) by dissolving in the aqueous phase and thus altering the medium surrounding the micelles[25].

The solubilisation of n-decane and n-decanol in solutions of oxyethylated decanols with general formula $C_{10}H_{21}[OC_2H_4]_nOCH_3$, where n = 8 or 12, at different temperatures, was studied by Kuriyama[79,80]. The solubilisation was estimated from the change in micellar weights, as shown in Table 12.

TABLE 11. Micellar weights of mixed micelles of sodium dodecyl sulphate and methoxypoly(oxyethylene)-dodecyl ether[78].

Temperature, °C	Wt. % of sodium dodecyl sulphate in the detergent mixture						
	0	5	20	40	60	80	100
30	61 000	60 200	53 600	45 500	40 000	37 600	31 800
50	71 000	66 900	54 000	41 700	36 200	31 700	26 600
70	92 200	86 100	57 300	43 900	33 800	28 300	23 100

TABLE 12. Influence of substance being solubilised on the structure of micelles[80].

Surface-active substance (S)	Substance being solubilised (H)	H/S, wt. %	Critical concentration of micelle formation, $c_k \times 10^4$, g per 100 ml	Micellar weights $\times 10^{-3}$, M_m	Number of molecules of NSAS in the micelle	Number of molecules of substance being solubilised in the micelle
$C_{10}H_{21}[OC_2H_4]_8OCH_3$	n-decane	0	6.0	43.1	83	0
		1.32	5.7	45.6	87	4
		2.33	5.4	47.8	90	8
		3.16	5.2	50.5	94	11
		3.78	5.1	52.0	96	13
		4.93	4.8	57.5	105	19
		(12.0)	4.0	88.5	158	46
		(150)	4.0	90.7	162	47
	n-decanol	3.40	5.2	47.8	89	10
		6.19	4.5	51.3	93	19
		8.50	4.0	61.3	109	30
		11.42	3.3	90.9	157	59
		16.61	2.0	21.3	351	192
$C_{10}H_{21}[OC_2H_4]_{12}OCH_3$	n-decane	0	9.5	42.9	65	0
		1.4	9.2	44.8	67	4
		2.58	9.0	51.5	76	9
		3.31	8.8	54.3	80	12
	n-decanol	5.67	8.4	52.6	75	18
		10.18	7.5	62.9	86	37
		17.12	6.3	12.2	158	113

With n-decane, the micellar weights increase with increase in its solubilisation up to a definite saturation limit and then remain unchanged. The data obtained indicate that the increase in micellar weights is due not to simple introduction of the molecules of the substance being solubilised into existing micelles but also to an increase in the number of molecules of surface-active substance making up the micelle. Thus the solubilisation process is associated with a change in the structure of the micelles. These results agree with data given by Mattoon[81].

Mankowich[47], in a study of the micellar solubilisation of oxyethylated alkylphenols, found that the temperature dependence of this process is exponential.

VII. HYDROPHILIC-LIPOPHILIC BALANCE (HLB)

Of decisive importance for the surface and bulk properties of the non-ionic SAS described in the preceding sections and hence for their application, is the relative efficiency of the two opposed groups of the molecule — the hydrophilic and hydrophobic (or lipophilic) groups — the so-called hydrophilic-lipophilic balance (HLB). Unlike the case of ionic SAS, whose HLB depends to a marked extent on the concentration of electrolytes in the medium, the HLB of non-ionic SAS is comparatively constant and depends only on the structure of the molecule.

An empirical quantitative characterisation of the HLB was derived in 1949 by Griffin[82] and this has been used extensively in the last decade as a guiding principle in the preparation of emulsions and for other applications of SAS. The HLB system was described briefly by Schönfeldt[5] and in more detail by Jalina and Goǒjila[83]. According to Griffin's classification, each SAS is characterised by a definite value for the HLB number, which may vary from 1 to 40. The higher the HLB number, the greater the hydrophilic character of the SAS. The smallest HLB number, 1, is shown by oleic acid, and the highest, 40, by Na lauryl sulphate. The HLB number determines the range of application of the SAS, as follows:

HLB number	Application
3–6	water/oil emulsions
7–9	wetting agents
8–18	oil/water emulsions
13–15	wetting agents
15–18	solubilising agents

It should be emphasised that the value of the HLB number, which determines the range of application of the SAS, does not characterise its efficiency sufficiently completely. SAS with different chemical structures, some of which are more effective than others, may have the same HLB number. The HLB system makes it possible to define the parameter required for a given process and thus to limit the range of substances studied. The HLB number is determined from the emulsifying action. Here it must be borne in mind that the HLB number characterises not only the emulsifier but also the "oil" being emulsified. The so-called necessary HLB number of the "oil" is taken as the value of the HLB number of the emulsifier which forms the most stable emulsion with this oil. To determine the necessary HLB number of the "oil", use is made of the fact that the change in HLB number, when a mixture of two SAS is used, is additive. If a series of emulsions of a given "oil" is prepared, using as emulsifiers a mixture of two SAS for both of which the HLB numbers are known, and the stability of the resulting emulsions is determined, it

is possible to calculate the HLB number of the optimal mixture (the necessary HLB number of the "oil") using the formula:

$$HLB_1X + HLB_2(1-X) = HLB_0\dagger, \quad (6)$$

where X is the weight fraction of the first emulsifier in the mixture.

By emulsifying an "oil" with known necessary HLB number HLB_o, using a mixture of two emulsifying agents, for one of which the value of the HLB number HLB_1 is known, while that of the other requires to be determined, it is possible to find the optimal ratio of these emulsifying agents and to calculate from formula (6) the value of the HLB number HLB_2 in which we are interested. The values of the experimentally determined HLB numbers for various emulsifying agents and oils are given in Table 13.

Griffin's procedure for determining HLB numbers is very tedious, so that a method for the rapid determination of the HLB numbers of emulsifying agents and the necessary HLB of "oils", using a centrifuge, has been proposed[84].

In the experimental determination of HLB numbers by these methods, use is made of a high concentration of emulsifying agent (5% of the total volume of the disperse phase and dispersion medium) so that this number makes allowance for the influence of the structure of the molecule of the emulsifying agent and the nature of the disperse phase on the stability of the emulsion but it does not characterise the influence of the emulsifying agent concentration.

In later work, using different pairs of NSAS for the emulsification of the same oil, Griffin[85] was able to show that in all the experiments, maximum stability is observed at the same weight percentage of hydrophilic substance in the mixture. Thus the HLB of NSAS is essentially a function of the weight fraction of the hydrophilic part of the molecule. On the basis of this observation, it was possible to derive formulae for calculating HLB numbers; these were found to be different for substances of different chemical character. For example, the HLB number of esters is calculated from the formula

$$HLB = 20\left(1-\frac{s}{A}\right), \quad (7)$$

where s is the saponification number and A the acid number.

TABLE 13. HLB numbers[82].

Emulsifying agent	HLB No.	Oil	HLB No.
Na oleate	18	Carbon tetrachloride	9
K oleate	20	Paraffin	9
Oleic acid	1.8	Kerosene	12.5
Span 80	4.3	Cetyl alcohol	13
Span 60	4.7	Dimethyl phthalate	15
Span 20	8.6	*o*-Phenylphenol	15.5
Tween 81	10.0	Stearic acid	17.0
Tween 60	14.9		
Tween 80	15.0		
Tween 20	16.7		
Oxyethylated nonylphenol-7	9.9		
Oxyethylated nonylphenol-15	16.1		

† In this and all subsequent formulae, the symbol HLB denotes the HLB number of the corresponding substances.

For oxyethylated products, whose hydrophilic fraction consists of ethylene oxide, the following formula is applicable:

$$HLB = \frac{E}{5}, \quad (8)$$

where E is the wt. % of ethylene oxide groups.

A paper by Davies[86] gave a convenient method proposed by Griffin for calculating HLB numbers from chemical composition by means of so-called group numbers. The calculation uses the formula

$$HLB = \Sigma N_{\text{hydrophilic}} - nN_{CH_2} + 7, \quad (9)$$

where $\Sigma N_{\text{hydrophilic}}$ is the sum of the group numbers of the hydrophilic groups, n the number of CH_2 groups in the molecule, and N_{CH_2} the group number for CH_2. The values of the group numbers are given in Table 14.

The numbers given are not suitable for very large molecules of oxyethylated substances; in practice, a degree of oxyethylation equal to 20 represents the upper limit of the value of the HLB number for these molecules. The values of the HLB number calculated from formula (9) for a number of substances show good agreement with the values found experimentally. Sometimes[87], instead of the HLB numbers, the so-called approximate HLB number is calculated. The approximate HLB number is the ratio of the number of ethylene oxide groups in the hydrophilic chain to the number of carbon atoms in the straight chain of the hydrophobic group. In these calculation a benzene ring is taken as equivalent to 3.5 carbon atoms. It should be borne in mind that an unsatisfactory feature of all the formulae used for the calculations is that they are based on the stoichiometric composition and make no allowance for isomerism.

A large number of papers have been devoted to establishing the relationship between the empirical HLB number characterising the range of application of SAS, and their physicochemical properties, such as the solubility in water and other solvents[5], the distribution between the two phases of an emulsion[86], the formation of insoluble complexes[88], the cloud point[4], the surface tension and interfacial tension[89,90], c_k,[42] the hydration energy, and the electric potential[86].

Table 15 shows that the solubility in water is an extremely approximate characteristic of the HLB. It has been pointed out[90] that there is no direct relationship between solubility and the HLB number. Two emulsifying agents with the same HLB number may exhibit different solubilities.

TABLE 14. Group numbers for calculating HLB numbers[86].

Groups	Group No.	Groups	Group No.
Hydrophilic groups		Lipophilic groups	
$-SO_4Na^+$	38.7	$-CH-$	−0.475
$-COOK^+$	21.1	$-CH_2-$	−0.475
$-COONa^+$	19.1	CH_3-	−0.475
N (tertiary amines)	9.4	CH−	−0.475
Ester group (sorbitan ring)	6.8		
Ester group	2.4	Complex groups	
−COOH	2.1		
Hydroxyl	1.9	$-(CH_2-CH_2-O)-$	0.33
−O−	1.3	$-(CH_2-CH_2-CH_2-O)-$	−0.15
Hydroxyl (sorbitan ring)	0.5		

TABLE 15. Approximate values for the HLB numbers of SAS with different solubilities in water.

Solubility in water	HLB No.
Not dispersed	1–4
Slightly dispersed	3–6
Milky dispersion formed after vigorous shaking	8–10
Spontaneous formation of milky dispersion	10–13
Transparent solutions	13

‡ The solubility of water in a mixture of organic solvents, for example, dioxan and benzene, is altered in the presence of NSAS. The water number characterises the number of millilitres of distilled water which must be added to a mixture of solvents containing NSAS until a permanent turbidity is produced. The water numbers of SAS mixtures are algebraically additive and directly proportional to the HLB numbers for the given class of substance. The coefficients in the equations of the straight line are different for different classes of substance.

The HLB of individual SAS can also be characterised by the distribution constant R_f for distribution between a stationary aqueous phase and a mobile organic phase for chromatography on paper or on paper which has been made hydrophobic[90]. There is a direct relationship between R_f and the HLB number. Unfortunately, this method is not suitable for a mixture of emulsifying agents, since separation into individual components takes place[2].

In an examination of the relationship between the rate of coalescence of an emulsion of oil in water and an emulsion of water in oil, the HLB number, and the solubility of the emulsifying agent in each of the emulsion phases, Davies[86] concluded that the HLB number is related to the distribution of the emulsifying agent between the two phases by the expression

$$\text{HLB} - 7 = 0.36 \ln \frac{c_w}{c_o}, \qquad (10)$$

where c_w and c_o are the solubilities of the emulsifying agent in water and oil.

If the emulsifying agent dissolves preferentially in water, the HLB number is greater than 7, and if the emulsifying agent dissolves preferentially in the oil, the HLB number is less than 7.

The methods used by Karabinos and Jutaka Tanaka to characterise the HLB, described in a paper by the latter[88], are based on the fact that when aqueous or alcoholic solutions of NSAS are titrated with a phenol solution, an insoluble complex of these two substances is formed and the solution becomes cloudy. The quantity of phenol solution used up at the end of the titration is called the cloud number. The cloud numbers increase with increase in the length of the oxyethylene chain. An interesting feature is that Jukata Tanaka's cloud number is directly proportional to the HLB number, irrespective of the class of compound. The equation of the corresponding straight line is

$$\text{HLB} = 0.89A + 1.11, \qquad (11)$$

where A is the cloud number.

‡ The beginning of this paragraph is missing from the Russian text (first two lines of preceding paragraph repeated instead) (Ed. of Translation).

For a given class of compounds, the HLB may be characterised by the cloud point, which is higher, the greater the hydrophilic character of the substance.

It might be suggested that the necessary HLB number of an oil is equal to the HLB number of the emulsifying agent which produces the greatest decrease in the interfacial tension. Wachs and Reusche[90] studied the stability of emulsions of undecane in water in the presence of mixtures of emulsifying agents with HLB from 2 to 17 and the interfacial tension at the boundary between the undecane and solutions of the corresponding mixtures of emulsifying agents, and found that the optimal value of the HLB number was equal to 9.5, irrespective of the composition of the mixture of emulsifying agents. In some systems the interfacial tension at this value of the HLB number passes through a minimum. In others, however, the interfacial tension changes continuously with change in the HLB, without passing through extreme values. Becher[34] obtained the same results in a study of the dependence of the interfacial tension on the degree of oxyethylation. Thus the interfacial tension is not the only factor determining the stability of an emulsion and the necessary HLB number of the oil. Ross and coworkers[89] concluded that the influence of the interfacial energy on the energetic balance in the formation of emulsions cannot be denied. Low interfacial tension, however, is a necessary but insufficient condition for stability. Another condition for stability in an emulsion of the type formed by oil in water is that the spreading coefficient S_1 should have a low negative value (from 0 to -5). The spreading coefficient indicates the way in which the oil spreads over the surface of a 1% solution of the emulsifying agent in water, and is calculated from the formula

$$S_1 = \sigma_{\text{solution}} - (\sigma_o + \sigma_{i.f.}), \qquad (12)$$

where σ_{solution} is the surface tension of the solution of the emulsifying agent in water, σ_o the surface tension of the oil, and $\sigma_{i.f.}$ the interfacial tension at the boundary between the oil and the solution of the emulsifying agent in water.

It follows from Ross's data that the spreading coefficient is directly proportional to the HLB number of the emulsifying agent. The results for the boundary between castor oil and an aqueous solution of an emulsifying agent are given in Fig. 4. This makes it possible to replace

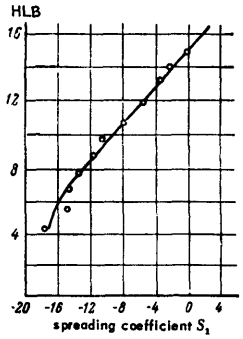


Fig. 4. Spreading coefficient S_1 for castor oil on the surface of 1% solution of SAS with different HLB.[99]

the tedious and sometimes inaccurate method of determining the HLB number of an emulsifying agent by measurements of the physicochemical constants of the system formed by the disperse phase with a solution of the emulsifying agent in the dispersion medium.

Wachs and Hyano[42] found experimentally for the monoesters of saccharose and saturated aliphatic acids that the HLB of this class of compound is directly proportional to the logarithm of c_k. These authors derived the same equation by calculation based on a comparison of the above equations used by Griffin[85] for calculating the HLB, on the one hand, with the empirical equation (2) giving the dependence of c_k on the length of the hydrocarbon chain, on the other hand. This showed the applicability of Griffin's equation. The observed relationship between the HLB number and c_k makes it possible to determine the HLB numbers of the stereoisomers of the monoesters; as pointed out above, this cannot be done using the calculation formulae.

In a paper presented at the Second Congress on Surface-Active Substances in London, Davies[86] tried to provide a quantitative kinetic basis for the HLB system. Davies' conclusion was based on the suggestion put forward by Rebinder[92] that both oil/water and water/oil emulsions are formed during emulsification, the nature of the final emulsion depending on which of the emulsions formed undergoes more rapid coalescence. Davies considered the rate of coalescence (R_1) of two drops of oil separated by water, and the rate of coalescence (R_2) of two drops of water separated by oil in the presence of the emulsifying agent. He assumed that the rate R_1 depends on a hydrodynamic factor A_1, an energy barrier related to the electric potential ψ_0, and an energy barrier $\Sigma\epsilon_h$, equal to the sum of the energies of hydration of the polar groups, which must be overcome in order to remove the hydration layers of water from the surface. In general, the rate of coalescence of oil drops decreases both as a result of charging and as a result of hydration, and the equation is of the form

$$R_1 = A_1 e^{-\frac{0.24\psi_0^2 - \theta\Sigma\varepsilon_h}{RT}}, \qquad (13)$$

where θ is the fraction of the surface occupied.

The opposite system consisting of two drops of water in a non-polar oil will undergo coalescence if the intermediate layer of oil is squeezed out as the drops of water approach one another. The rate of coalescence R_2 will depend on a hydrodynamic factor A_2, the barrier created by each CH_2 group on movement into water (equal to 300 cal[93]), the number n of CH_2 groups, and the proportion θ of the surface occupied by the emulsifying agent

$$R_2 = A_2 e^{-2n\theta\frac{300}{RT}}. \qquad (14)$$

By combining Eqns. (13) and (14) and assuming that $A_1 = A_2$ (i.e. that the viscosities and phase volumes of the oil and water are equal), we obtain the equation

$$RT\ln\frac{R_2}{R_1} = 0.24\psi_0^2 + \theta\Sigma\varepsilon_h - 600n\theta. \qquad (15)$$

Separating n from Eqns. (9) and (15) and comparing the right-hand sides of the resulting equations term by term, Davies arrived at a system of three equations:

$$\ln\frac{R_2}{R_1} = 2.2\theta(\mathrm{HLB} - 7), \qquad (16)$$

$$\Sigma N_{\substack{\text{hydrophilic}\\ \text{hydrated}}} = \frac{\Sigma\epsilon_h}{1260}, \qquad (17)$$

$$\Sigma N_{\substack{\text{hydrophilic}\\ \text{charged}}} = 1.9\times10^{-4}\frac{\psi_0^2}{\theta}, \qquad (18)$$

where $\Sigma N_{\substack{\text{hydrophilic}\\ \text{hydrated}}}$ is the sum of the group numbers of the hydrophilic hydrated groups, and $\Sigma N_{\substack{\text{hydrophilic}\\ \text{charged}}}$ the sum of the group numbers of the hydrophilic charged groups.

These equations show that the HLB system has a firm kinetic basis. The HLB determines the rate of coalescence. For oil/water emulsions the HLB numbers are greater than 7 and for water/oil emulsions the HLB numbers are less than 7. For an HLB number equal to 7 or values of θ close to zero, neither of the emulsions is stable. Eqns. (17) and (18) show the part played by the hydration energy and charge in the characterisation of the HLB of surface-active substances. It can be seen from Eqn. (18) that the HLB of a charged group depends on ψ_0, and the latter changes with even a small change in the concentration of electrolytes in the system. Thus the contribution made by the charged groups to the HLB numbers of anion-active and cation-active SAS, as already noted, is not strictly constant, so that the HLB numbers are not constant. In the case of non-ionic SAS, the values of the HLB numbers are less dependent on the electrolyte concentration.

Deryagin[94], in the discussion of Davies' paper, pointed out that it is incorrect to express the influence of the hydrophilic groups of the emulsifying agents on the stability of an emulsion of oil in water as the simple sum of the hydration energies of these groups. In actual fact, the action of the hydrophilic groups is determined by the forces of repulsion produced under the general influence of these groups in the aqueous polymolecular layers surrounding the surface of the drops.

These studies make it possible to estimate the part played by the HLB as a factor characterising the relationship between the structure of the molecule of the emulsifying agent and its affinity for the disperse phase and the dispersion medium of the emulsion. It should be emphasised that the HLB numbers of SAS, as shown at the start of the present section, play an important part not only in emulsification, but also in other processes taking place in dispersion systems. For example, Schick and Beyer[87] showed that the HLB number of a non-ionic stabiliser characterises the stability of foams. In each homologous series of NSAS, the stability of the foams passes through a maximum at a certain critical value of the HLB number. This is due to the fact that the resistance to rupture shown by the film of stabiliser depends on the magnitude of the cohesion of the adsorbed molecules, and the latter passes through a maximum with increase in the degree of oxyethylation.

Examples of the use of HLB numbers for the selection of emulsifying agents for emulsion polymerisation have been given[95]. A study was made of the dependence of the stability of the latices, the dimensions of the particles, the viscosity, and the rate of conversion on the HLB numbers for the emulsion polymerisation of styrene and vinyl acetate. An anionic emulsifying agent (an alkyl aryl sulphonate), non-ionic emulsifying agents (polyoxyethylated esters of oleic, lauric, steric, palmitic, and other acids), and their mixtures were used for this purpose. A high rate of conversion and the most stable polystyrene emulsions were obtained using polyoxyethylated stearate, with HLB

number equal to 15. With mixtures of anionic and non-ionic SAS, the greatest stability of the emulsions lies at HLB numbers of about 14–15. With vinyl acetate, this range is broader and extends from 16.2 to 17.5.

VIII. REASONS FOR THE STABILISING ACTION OF NSAS

When NSAS are used, the stabilising action cannot be due to the electrical double layer. In this case, other thermodynamic stability factors are operating, such as hydration of the molecules of stabiliser, the entropy factor[96], and the associated splitting pressure. In addition to these thermodynamic factors, the structural-mechanical properties of the adsorption layer may be of considerable importance for the aggregate stability[97,98].

It has been shown[99,100] that dispersion systems stabilised by non-ionic SAS may exhibit a small electrokinetic potential. For example, 1% polychloroprene latices stabilised by the oxyethylated products OP-4, OP-7, and OP-10, at pH 9, had electrokinetic potentials from -35 mV to -55 mV. The magnitude of the electrokinetic potential decreased with increase in the degree of oxyethylation. Butadiene–styrene latices stabilised with the SAS OP-7, OP-10, and OP-18, and prepared with precautions to reduce the concentration of electrolytes in the system, showed much smaller electrokinetic potentials. The potential varied from -9 mV for the latex stabilised by OP-7 to -5 mV for the latex stabilised by OP-18. These results show that here the electrokinetic potential is due to the selective adsorption of anions which are present, for one reason or another, in the system. The negative charge produced by the adsorption of anions may be partly neutralised by adsorbed molecules of oxyethylated SAS, exhibiting cation-active character. The longer the chain, the greater the extent to which the negative charge of the globules is reduced. None of the resulting latices coagulated when electrolytes were added, although the electrokinetic potential decreased to zero. The aggregative stability of the polychloroprene latices in the isoelectric state decreased slightly relative to that of the original latices. These results confirm the part played by non-electric stability factors, for example, according to the authors cited, hydration of the adsorption layers.

The importance of hydration of the stabiliser and its affinity for the dispersion phase of the emulsion was examined by Davies[86] and was reflected in the HLB system. As shown above, however, this examination did not make allowance for the possibility that hydration of the hydrophilic groups of the stabiliser molecules leads to the formation of polymolecular hydrate sheaths and the production of a splitting pressure when the particles approach one another. The splitting pressure is positive, that is, it prevents approach, if the interaction between the hydrophilic groups of the stabiliser molecules and the molecules of the solvate layer is greater than the interaction between the molecules of the solvate layer and the molecules of the medium, Duyvis and Overbeek[101] showed that for foam films formed by solutions of NSAS of the type OP-7, OP-10, and OP-20 in the presence of an electrolyte (NaCl), there exist two ranges of equilibrium film thickness: one very small, of the order of 100 Å, which is close to twice the length of the stabiliser molecule, and the other much greater, observed only at NaCl concentrations less than 10^{-4} *N*. The first thickness corresponds to the repulsion caused by steric hindrance, whereas the second is related to the splitting pressure. Analogous results were obtained by Sheludko and coworkers[102], who also worked with free liquid films. On the basis of the existence of equilibrium film thicknesses of the order of 100 Å, with stability related to the steric hindrance arising in the interaction of the adsorption layers, it was concluded that in order to obtain thermodynamically stable films, it is necessary that the adsorption monolayer have a sufficiently high stability (an arbitrary term denoting the presence of adequate tangential forces of cohesion in the monolayer).

Deryagin and coworkers[103] studied free films of solutions of the NSAS OP-10 and oxyethylated di-t-butylphenol at an NaCl concentration of 10^{-2} *N*. The equilibrium film thickness, equal to approximately 120 Å, is independent of the electrolyte concentration and temperature. The observed splitting pressure, which prevents further decrease in the thickness of the film, was attributed to interaction between the adsorbed monolayers and adjoining water layers with a thickness of 10–20 molecules. If, however, these results are compared with the results obtained by Duyvis and Overbeek, the phenomena observed by Deryagin and coworkers must be attributed not to the splitting pressure but to steric hindrance provided by the adsorbed molecules of the monolayer. The splitting pressure associated with the polymolecular hydrate layers apparently could not be observed in this work because of the relatively high concentration of electrolytes in the system. The absence of a splitting pressure due to hydration is also confirmed by the fact that the observed effects were independent of temperature, whereas increase in temperature should have a dehydrating action.

The existence of a splitting pressure in stabilisation by non-ionic SAS can be related not only to hydration in the true sense of the term, but also to osmotic forces developing during the swelling of the adsorbed layer of stabiliser, as suggested for protective colloids by Bromberg[104]. This possibility is confirmed by the above results obtained by Schick[58], from which it follows that the oxyethylated chains are present in the form of a coil in the dispersion medium, so that they exhibit the properties of a flexible polymeric chain capable of undergoing micro-Brownian movement. The micro-Brownian movement, which causes the dispersion medium to be forced into the space between approaching particles, can also be regarded as the entropy component of the splitting pressure (the entropy stability factor). The mobility of a chain usually increases with increase in temperature, but here the mobility decreases with increase in temperature, since dehydration takes place, causing the oxyethylene chains to adhere to one another with a consequent loss of mobility. Thus increase in temperature should lead to a decrease in both the hydration and the entropy components of the splitting pressure. The same influence on the splitting pressure should be shown by the addition of electrolytes. The part played by hydration as a factor influencing the stability of dispersion systems in the presence of NSAS is confirmed by the fact that dehydration, produced for example by an increase in temperature, leads to separation of the phases and, in the case of latices, to gelatinisation. This last result was shown by Panich and coworkers[100] for the case of butadiene–styrene latices stabilised by the non-ionic oxyethylated products OP-7, OP-10, and OP-18. Work by Orr and coworkers[105,106] showed that the addition of a non-ionic stabiliser to latices containing an anion-active soap leads to a decrease in the area occupied by a molecule of the latter. This was attributed to a decrease in the electrostatic repulsion of the soap ions as a result of the presence of the molecules of

the non-ionic stabilising agent between the ions in the adsorption layer. Sometimes, however, non-ionic soaps produce the opposite effect. Van Voorst-Vader[37], in a study of a solution—air interface, showed that the area occupied by the molecule of an ionic soap increases in the presence of non-ionic soaps. He attributed this phenomenon to the fact that in the presence of two different hydrophilic groups, the water molecules may be orientated in such a way that the ionic soap is more readily hydrated. This leads to attraction of the ionic soap into the water, increases the area occupied by the molecule, and thus decreases the affinity of the soap for the surface. Thus the addition of NSAS to disperse systems containing ionic soaps may either increase or decrease the affinity of the ionic soap for the dispersion phase with a corresponding influence on the aggregative stability of the system.

Neiman and coworkers[107] showed that the addition of NSAS of the OP type to an adsorptively unsaturated latex stabilised by an ionic soap increases its stability to the action of electrolytes until saturation of the adsorption layer takes place. Further addition of NSAS has no influence on the stability. The results obtained are readily explained by the fact that on the addition of NSAS, an important part begins to be played by the non-electric latex--stability factor, and the influence of electrolytes becomes less marked.

Aleksandrova and coworkers[108] studied the influence of NSAS on the stability to mechanical treatment shown by adsorptively saturated and unsaturated polystyrene latices stabilised by an ionic emulsifying agent (sodium oleate) and found that the addition of non-ionic emulsifying agents leads to an increase in the aggregative stability only for the adsorptively saturated latex. With the unsaturated latices, the addition of non-ionic surface-active substances is accompanied by a decrease in the aggregative stability until adsorptive saturation of the surface of the latex globules takes place, after which the stability increases, as for the adsorptively saturated latices. The observed phenomena were explained as follows. When small quantities of NSAS are added to adsorptively unsaturated latices, the molecules of the non-ionic emulsifying agents are distributed on the free areas of the surface of the polymeric globules, screening the sodium oleate molecules and leading to a deterioration in the protective properties of the adsorption monolayer. Increase in the quantity of NSAS leads to an even sharper decrease in stability as a result of the formation of a fragile saturated monolayer consisting of alternating associates of NSAS and sodium oleate. A sharp increase in stability is observed only when the excess of NSAS is sufficient for the formation of a single--layer protective sheath. The theory that a polymolecular protective sheath is formed on the surface of the latex globules is not undisputed. Kuznetsov and Lebedev[109] showed, on the basis of viscosity measurements, that soaps of aliphatic acids form a monomolecular interfacial layer on the surface of globules of butadiene–styrene latex.

Shits and Trapeznikov[110] studied the structural-mechanical properties of adsorption layers of the NSAS Xylital O-10, OP-7, OP-10, OP-20, Tween-20, and OS-20 at the boundaries with air and styrene. They found that only OS-20 forms a stable adsorption film at the boundary with air. At the boundary with styrene, in the initial period of existence of the interfacial surface, the SAS studied do not produce a high surface viscosity. The process of solubilisation, accompanied by the spontaneous formation of a styrene micro-emulsion, takes place gradually and facilitates structure-formation in the volume adjoining the interface on the aqueous-solution side.

Taubman and coworkers[111] studied the stability of adsorption layers of non-ionic stabilisers (OP-10 and Pluronic L-64) at the boundary with xylene, and also the stability of emulsions of xylene in water and the stability to freezing shown by polystyrene latices in the presence of the same substances. The stability of the emulsions and latices was greatest when protective layers of high stability were formed. High stability of the protective layers is associated with the formation, at the interface, of two liquid phases consisting of complex supermolecular structures in the form of fairly thick multi-layer films. It has been shown[112-114] that these structures are formed as a result of a hydrodynamic effect associated with the surface turbulence and convection leading to unidirectional transfer of the hydrocarbon phase into the aqueous phase in the form of an ultramicro-emulsion. It can be seen that Taubman and coworkers[111] studied not the structural--mechanical properties of the adsorbed films but the structure-mechanical properties of the supermolecular structures. The formation of the latter represents a particular case and cannot be taken into account in the development of a general theory of the stability of disperse systems. This was confirmed by Sonntag and Klare[115], who pointed out particularly that in the characterisation of the specific protective action of SAS, it is necessary to consider only those concentrations at which the interfacial tension is greater than the critical value, and at which spontaneous emulsification does not take place.

IX. THE USE OF NSAS FOR EMULSION POLYMERISATION AND FOR INCREASING THE STABILITY OF LATICES

As noted in the Introduction, extremely varied use is made of NSAS in the modern economy. The use of NSAS in various branches of technology was examined in detail in the well-known monograph by Schönfeldt[5], to which the reader is referred. In this section we shall review briefly only the application of NSAS as stabilisers in emulsion polymerisation and for increasing the stability of latices — the fields which are of greatest interest to the authors of the present review.

Polymerisation in emulsions has found extensive application in industry, since it has a number of important advantages over other methods of polymerisation under the influence of free radicals. The high rates of the processes compared with those in homogeneous systems, the wider temperature range in which the polymerisation processes can be carried out, and the possibility of varying the nature and concentration of emulsifying agents are of considerable importance for the control of the polymer properties.

A large number of papers[116-120] have been devoted to the problems of studying the complex heterogeneous process represented by emulsion polymerisation. Several recently published papers have dealt with the problems of studying the characteristic features of the mechanism of emulsion polymerisation in the presence of non-ionic emulsifying agents. Thus French[121] studied the emulsion polymerisation of vinyl acetate with the non-ionic emulsifying agent Pluronic F-68 (a block copolymer of ethylene oxide and propylene oxide) in the presence of potassium persulphate. Parts and Moore[122] studied the polymerisation of

vinyl stearate with oxyethylated octylphenol as emulsifying agent. Neither of these papers, however, give any conclusions regarding the characteristic features of this process.

The problems of selecting different emulsifying agents (anionic, cationic, and non-ionic) for emulsion polymerisation were examined by Helin and coworkers[123], who recommended a number of emulsifying agents and their mixtures on the basis of a study of the kinetics of polymerisation and stability of latices.

Gritskova and coworkers[124-126] studied the emulsion polymerisation of styrene in aqueous solutions of non-ionic emulsifying agents (Pluronic F-68 and oxyethylated octylphenol and octadecanol) and point out a number of characteristic features distinguishing these processes from the analogous processes taking place "in bulk" and in the presence of ionic emulsifying agents.

NSAS are often used as additives to latices for increasing their stability to the action of electrolytes. This is particularly important in the production of latex pigments. Many grades of NSAS are produced especially for this purpose[5]. It has been shown[5,110] that NSAS added to latices increase their stability to low temperatures. Finally, NSAS can be used for the thermo-sensitisation of latex mixtures[127]: the NSAS give the latices stability at low temperatures, whereas with increase in temperature they separate as an individual phase, are solubilised in the adsorption layers of the ionogenic stabiliser and decrease their protective properties, leading to gelatinisation of the latices.

1. R.L.Mayhew and R.C.Hyatt, J.Amer.Oil Chemists' Soc., 29, 357 (1952).
2. J.Kelly and H.L.Greenwald, J.Phys.Chem., 62, 1096 (1958).
3. H.P.Kaufmann and G.Walter, Fette u.Seifen, 61, 9, 782 (1959).
4. B.A.Gingras and C.H.Bayley, Canad.J.Chem., 35, 599 (1957).
5. N.Schönfeldt, "Oberflächenaktive Anlagerungsprodukte des Äthylenoxyds. Ihre Herstellung, Eigenschaften und Anwendung", Stuttgart, 1959.
6. P.A.Rebinder, G.A.Babalyak, and I.I.Kravchenko (Editors), "Primenenie Poverkhnostno-Aktivnykh Veshchestv v Neftyanoi Promyshlennosti" (The Use of Surface-Active Substances in the Petroleum Industry), Gos.Nauchno-Tekhn. Izd.Neftyanoi i Gorno-Toplivnoi Lit., Moscow, 1961.
7. T.H.Vaughn, H.R.Suter, L.G.Lundsted, and M.G.Kramer, J.Amer.Oil Chemists' Soc., 28, 7 (1951).
8. L.G.Lundsted, U.S.P. 2674619 (1950).
9. K.G.Mizuch and R.A.Lapina, Khim.Nauka i Prom., 4, 592 (1959).
10. F.Püschel, Z.Chem., 3, 9, 338 (1963).
11. H.Staudinger, "Die hochmolecularen organischen Verbindungen", Springer, Berlin, 1932.
12. V.V.Korshak, "Khimiya Vysokomolekulyarnykh Soedinenii" (The Chemistry of Macromolecular Compounds), Izd.Akad. Nauk SSSR, Leningrad, 1950.
13. K.Hess and H.Kiessig, Chem.Ber., 81, 327 (1948).
14. J.H.Schulman, R.Matalon, and M.Cohen, Discuss.Faraday Soc., No.11, 117 (1951).
15. M.Kehren and M.Rösch, Fette u.Seifen, 59, 1, 80 (1957).
16. M.Rösch, Kolloid Z., 150, 153 (1957).
17. T.Uchida, T.Kurita, N.Koizumi, and M.Kubo, J.Polymer Sci., 21, 313 (1956).
18. B.Wurzschmidt and M.Fresenius, Z.analyt.Chem., 130, 105 (1950).
19. M.Schick, J.Colloid Sci., 18, 4, 378 (1963).
20. M.Cohen and C.C.Smith, Nature, 165, 613 (1950).
21. Chem.Products, 25, 9, 386 (1962).
22. L.Raphael, Chemistry and Manufacture, 29, 105 (1958).
23. C.M.Knowles and F.Krupin, Proc.Chem.Specialities Manuf. Assoc., p.175 (December 1953).
24. F.E.Balley and R.W.Gallard, J.Appl.Polymer Sci., 1, 56 (1959).
25. T.M.Doscher, G.E.Myers, and D.C.Atkins, J.Colloid Sci., 6, 223 (1951).
26. W.N.Maclay, J.Colloid Sci., 11, 272 (1956).
27. M.H.I.Weiden and L.B.Norton, J.Colloid Sci., 8, 606 (1953).
28. H.K.Livingston, J.Colloid Sci., 9, 365 (1954).
29. H.Lange, Fette u.Seifen, 64, 457 (1962).
30. E.H.Crook, D.B.Fordyce, and G.F.Trebbi, J.Phys.Chem., 67, 1987 (1963).
31. A.N.Wrigley, F.D.Smith, and A.J.Stirton, J.Amer.Oil Chemists' Soc., 34, 39 (1957).
32. H.Lange, Kolloid Z., 182, 123 (1962).
33. M.J.Schick, J.Colloid Sci., 17, 801 (1962).
34. P.Becher, J.Colloid Sci., 18, 665 (1963).
35. M.J.Schick, J.Amer.Oil Chemists' Soc., 40, 680 (1963).
36. F.Tokiwa, Bull.Chem.Soc.Japan, 36, 222 (1963).
37. Van Voorst-Vader, Trans.Faraday Soc., 56, 1078 (1960).
38. P.Becher, J.Colloid Sci., 17, 325 (1962).
39. L.Hsiao, H.N.Dunning, and P.B.Lorenz, J.Phys.Chem., 60, 657 (1956).
40. A.Mankowich, Ind.Eng.Chem., 47, 2175 (1955).
41. J.M.Gorkill, J.F.Goodman, and R.H.Ottewill, Trans. Faraday Soc., 57, 1627 (1961).
42. W.Wachs and S.Hyano, Kolloid Z., 181, 139 (1962).
43. P.Becher, J.Phys.Chem., 63, 1675 (1959).
44. P.Becher and N.K.Clifton, J.Colloid Sci., 14, 519 (1959).
45. S.Ross and J.P.Oliver, J.Phys.Chem., 63, 1671 (1959).
46. M.E.Ginn, F.B.Kinney, and J.C.Harris, J.Amer.Oil Chemists' Soc., 37, 4 (1960).
47. A.M.Mankowich, J.Amer.Oil Chemists' Soc., 37, 11 (1960).
48. P.I.Ermilov, Uch.Zap.Yaroslav.Tekhnol.Inst., 6, 53 (1961).
49. L.M.Levitskii, S.A.Nikitina, and A.B.Taubman, Dokl. Akad.Nauk SSSR, 149, 633 (1963).
50. L.M.Kushner and W.D.Hubbard, J.Phys.Chem., 58, 1163 (1954).
51. P.Becher, J.Phys.Chem., 64, 1221 (1960).
52. A.B.Taubman and S.A.Nikitina, Dokl.Akad.Nauk SSSR, 135, 1179 (1960).
53. P.Becher, J.Colloid Sci., 16, 49 (1961).
54. R.R.Balambra, J.S.Clunic, J.M.Gorkill, and J.F.Goodman, Trans.Faraday Soc., 58, 8 (1962).
55. P.H.Elworthy and C.B.Macfarlane, J.Chem.Soc., 907 (1963).
56. M.J.Schick, S.M.Atlas, and F.R.Eirich, J.Phys.Chem., 66, 1326 (1962).
57. K.Schinoda, Bull.Chem.Soc.Japan, 34, 237 (1961).
58. M.J.Schick, J.Phys.Chem., 67, 1796 (1963).

59. K.W.Herman, J.Phys.Chem., 66, 295 (1962).
60. K.Shinoda and E.Hutchinson, J.Phys.Chem., 66, 577 (1962).
61. S.Matijevič and B.A.Pethica, Trans.Faraday Soc., 54, 587 (1958).
62. P.White and G.Benson, J.Colloid Sci., 13, 584 (1958); Trans.Faraday Soc., 55, 1025 (1959); J.Phys.Chem., 64, 599 (1960).
63. E.D.Goddard, A.J.Hoeve, and G.Benson, J.Phys.Chem., 61, 593 (1961).
64. J.M.Gorkill, J.F.Goodman, and S.P.Harrold, Trans. Faraday Soc., 60, 202 (1964).
65. A.M.Mankowich, J.Phys.Chem., 58, 1027 (1954).
66. C.W.Dwiggins, R.J.Bolen, Jnr., and H.N.Dunning, J.Phys. Chem., 64, 1175 (1960).
67. C.W.Dwiggins and R.J.Bolen, Jnr., J.Phys.Chem., 65, 1787 (1961).
68. C.W.Dwiggins and R.J.Bolen, Jnr., J.Phys.Chem., 66, 3 (1962).
69. L.M.Kushner, W.D.Hubbard, and A.S.Doan, J.Phys. Chem., 61, 371 (1957).
70. J.Stauff and J.Rasper, Kolloid Z., 151, 148 (1957).
71. C.A.J.Hoeve and G.C.Benson, J.Phys.Chem., 61, 1149 (1957).
72. S.Kuroiwa, K.Shimizu, and J.Yano, J.Chem.Soc.Japan, Ind.Chem.Sect., 58, 859 (1955).
73. C.D.Deston, Hexagon Digst., 13, 3 (1953).
74. Y.M.Gorkill, J.Phys.Chem., 67, 4 (1963).
75. A.L.Corrin and W.D.Harkins, J.Amer.Chem.Soc., 69, 683 (1947).
76. H.B.Klevens, J.Phys.Colloid Chem., 52, 130 (1948).
77. K.Kuriyama, Kolloid Z., 181, 44 (1962).
78. K.Kuriyama, H.Inoue, and T.Nakagawa, Kolloid Z., 183, 68 (1962).
79. K.Kuriyama, Kolloid Z., 180, 55 (1962).
80. T.Nakagawa, K.Kuriyama, and H.Lnoue, J.Colloid Sci., 15, 268 (1960).
81. R.W.Mattoon, R.S.Stearus, and W.D.Harkins, J.Chem. Phys., 16, 644 (1948).
82. W.G.Griffin, J.Soc.Cosmetic Chemists, 1, 311 (1949).
83. J.Jalina and R.G.Gobjilă, Petrol Gaze (Bucharest), 11, 207 (1960).
84. J.E.Robbers and V.N.Bhatia, J.Pharm.Sci., 50, 708 (1961).
85. W.G.Griffin, J.Soc.Cosmetic Chemists, 5, 249 (1954).
86. J.T.Davies, "Proceedings of the Second International Congress on Surface Activity, London, 1957, Vol.1. Gas/Liquid and Liquid/Liquid Interface" (Edited by J.H.Schulman), Butterworth, London, p.426.
87. M.J.Schick and E.A.Beyer, J.Amer.Oil Chemists' Soc., 40, 66 (1963).
88. Jutaka Tanaka, "Proceedings of the Second International Congress on Surface Activity, London, 1957, Vol.1. Gas/Liquid and Liquid/Liquid Interface" (Edited by J.H.Schulman), Butterworth, London, p.132.
89. S.Ross, E.S.Cheu, P.Becher, and H.Y.Ranauto, J.Phys. Chem., 63, 1681 (1959).
90. W.Wachs and W.Reusche, Fette u.Seifen, 9, 803 (1960).
91. H.L.Greenwald, G.L.Brown, and M.N.Fineman, Analyt. Chem., 28, 1693 (1956).
92. P.A.Rebinder and T.Venstrem, Kolloid Z., 23, 145 (1930); P.A.Rebinder, Kolloid.Zhur., 8, 157 (1946).
93. M.Archer and V.K.La Mer, Ann.Acad.Sci., 58, 807 (1937).
94. B.V.Derjaguin, "Proceedings of the Second International Congress on Surface Activity, London, 1957, Vol.1. Gas/Liquid and Liquid/Liquid Interface" (Edited by J.H.Schulman), Butterworth, London, p.477.
95. G.Greth and J.E.Wilson, J.Appl.Polymer Sci., 5, 135 (1961).
96. S.S.Voyutskii, Uspekhi Khim., 30, 1237 (1961) [Russ.Chem. Rev., 556 (1961)].
97. P.A.Rebinder and A.A.Trapeznikov, Zhur.Fiz.Khim., 12, 573 (1938).
98. P.A.Rebinder, Kolloid.Zhur., 17, 149 (1955).
99. R.M.Panich, V.V.Kireitsev, D.M.Sandomirskii, and S.S.Voyutskii, Kolloid.Zhur., 24, 733 (1962).
100. R.M.Panich, N.V.Konovalova, T.B.Gonsovskaya, D.M.Sandomirskii, and S.S.Voyutskii, Kolloid Zhur., 27, 589 (1965).
101. E.M.Duyvis and J.Overbeek, Proc.k.ned.Akad.Wetenschap., 65, 26 (1962).
102. A.Sheludko, D.Ekserova, and D.Platikanov, Kolloid.Zhur., 25, 606 (1963).
103. B.V.Deryagin, A.S.Titievskaya, and V.Kh.Vybornova, Kolloid Zhur., 22, 393 (1960).
104. A.V.Bromberg, Kolloid.Zhur., 8, 117, 199 (1946); 9, 13 (1947).
105. R.Orr and L.Breitmann, Canad.J.Chem., 38, 668 (1960).
106. R.Orr, Rubber Plastics Age, 41, 1027 (1960).
107. R.E.Neiman and O.G.Kiseleva, Kolloid.Zhur., 25, 35 (1963).
108. E.M.Aleksandrova, A.A.Shits, and Ts.P.Romm, Dokl. Akad.Nauk SSSR, 148, 637 (1963).
109. V.L.Kuznetsov and A.V.Lebedev, Kauchuk i Rezina, 22, (7), 7 (1963).
110. L.A.Shits and A.A.Trapeznikov, Kolloid.Zhur., 35, 613 (1963).
111. S.A.Nikitina, A.B.Taubman, N.V.Kuligina, and V.A.Spiridonova, Dokl.Akad.Nauk SSSR, 149, 4 (1963).
112. C.Sternling and L.Scriven, Amer.Inst.Eng.Chem., 6, 514 (1959).
113. H.Linde, Monatsber.Deut.Akad.Wiss.Berlin, 1, 7, 586 (1959); 2, 699 (1959).
114. A.Kaminski and J.W.McBain, Proc.Roy.Soc., A198, 447 (1949).
115. H.Sonntag and H.Klare, Z.phys.Chem.(Frankfurt), 1–2, 223 (1963).
116. P.M.Khomikovskii, Uspekhi Khim., 27, 1025 (1958).
117. P.M.Khomikovskii, Uspekhi Khim., 28, 547 (1959).
118. S.S.Medvedev, Doklad na Simpoziume v Prage, 1957 (Paper Presented at the Symposium in Prague, 1957).
119. G.D.Berezhnoi, Candidate's Thesis, Lomonosov Moscow Institute of Fine Chemical Technology, Moscow, 1962.
120. S.S.Medvedev, P.M.Khomikovskii, A.P.Sheinker, E.V.Zabolotskaya, and G.D.Berezhnoi, "Problemy Fizicheskoi Khimii" (Problems in Physical Chemistry), Vol.1, Goskhimizdat, 1958.
121. D.M.French, J.Polymer Sci., 32, 395 (1957).
122. A.G.Parts and D.E.Moore, J.Oil Colour Chemists' Assoc., 45, 9 (1962).
123. A.F.Helin, J.M.Gyenge, and D.A.Beadell, Ind.Eng.Chem., 45, 1330 (1953).
124. I.A.Gritskova, S.S.Medvedev, and M.F.Margaritova, Kolloid.Zhur., 26, 168 (1964).
125. I.A.Gritskova, Z.M.Ustinova, and N.M.Fodiman, Kolloid. Zhur., 27, 338 (1965).
126. I.A.Gritskova, S.S.Medvedev, and M.F.Margaritova, Vysokomol.Soed., 10, 1880 (1964).
127. D.M.Sandomirskii, I.D.Pil'menshtein, and M.L.Lebedinskaya, Kolloid.Zhur., 24, 679 (1962).

Lomonosov Institute of
Fine Chemical Technology