Physical Chemistry of Nonionic Detergents

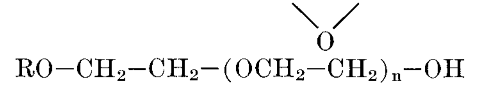
M. J. SCHICK, Lever Brothers Co., Research Center, Edgewater, New Jersey

RELATIVELY FEW papers on the physico-chemical properties of nonionic detergents have appeared so far in the literature, in contrast to the numerous papers published on ionic detergents. This delay in exploring a field of growing industrial importance must be attributed to the fact that monodisperse materials are difficult to prepare. Their synthesis by the Williamson method has been reported for a chain length of one to six ethylene oxide units only (9,34, 35,50). Nonionic detergents, which have been prepared by the condensation of ethylene oxide with aliphatic alcohols, carboxylic acids, amides, mercaptans and alkylphenols, yield products in which the chain length of the hydrophilic portion has a Poisson distribution (14,15,20). In order to cover a wide range of molecular structures, these ethylene oxide condensates have been used in the last decade to elucidate the physico-chemical properties of nonionic detergents in aqueous solutions. In many instances, these samples were molecularly distilled in order to remove unreacted components and reduce the width of molecular weight distribution. The inverse temperature solubility relation of nonionic detergents indicates that the overall solubility of these materials depends on the extent of hydration of the hydrophilic portion; the water molecules being affixed to the ether oxygens by hydrogen bonding. At least four to six ethylene oxide units per molecule are required, depending on the nature of the hydrophobic group, in order to produce a surfactant with distinctly hydrophilic characteristics.

Let us first briefly review the methods of preparation of nonionic detergents and the analytical procedures for the determination of the average ethylene oxide chain length. Homogeneous samples of n-alkyl polyoxyethylene monoethers have been prepared by means of the Williamson ether synthesis, wherein n-alkyl bromide was reacted with the monosodium salt of the appropriate homogeneous polyoxyethylene glycol (9,34,35,50), e.g.,

$$\mathrm{RBr + Na\,O\,(CH_2CH_2O)_6H \longrightarrow RO\,(CH_2CH_2O)_6\,H + NaBr}$$

A large excess of glycol assured formation of the monosodium salt. The condensation of ethylene oxide with compounds containing an active hydrogen atom, such as aliphatic alcohols, alkylphenols, etc., is unique in that it is an addition reaction without termination. For example, ethylene oxide adds to hydroxyl radicals by ring cleavage with the regeneration of the hydroxyl group (14,15,20,32,52):



$$\mathrm{RO{-}CH_2{-}CH_2{-}OH + n\,\underset{\diagdown\ \diagup \atop O}{CH_2{-}CH_2} \longrightarrow RO{-}CH_2{-}CH_2{-}(OCH_2{-}CH_2)_n{-}OH}$$

In a mechanism of this kind, the growth of all the ethylene oxide condensates proceeds under conditions affording equal opportunities for all; and the resulting distributions follow the Poisson formula, which is extremely narrow. This has been shown by Flory in a study of polyethylene glycols (14). If the number of monomers added to each chain is n,

$$\frac{\bar{x}_w}{\bar{x}_n} = 1 + \frac{n}{(n+1)^2}$$

which approaches unity as n becomes large. $\bar{x}_w$ signifies the weight average degree of polymerization and $\bar{x}_n$ the number average degree of polymerization. So far, sufficiently high degrees of polymerization have not been achieved experimentally to demonstrate these unique properties. Mayhew and Hyatt have shown in a study of polyoxyethylated nonylphenol that the distribution of the ethylene oxide chain lengths follows a Poisson distribution in a manner analogous to the polyoxyethylene glycols (14,32). The importance of the amount and type of catalyst in this polycondensation reaction has been demonstrated by Tischbirek (52). The width of the ethylene oxide chain length distribution in polycondensations of primary aliphatic alcohols decreases in the following order of catalysts used: $\mathrm{Li > Na > K > BF_3 > SnCl_4 > SbCl_5}$. Results with $SbCl_5$ conform exactly with a Poisson distribution. It is worth noting that the influence of these catalysts on the rate of the polycondensation reaction follows the same order.

The average chain length of the ethylene oxide adducts is generally determined from their hydroxyl values; this method involves either acetylation or treatment with hydriodic acid (39,49). The corresponding results for polyoxyethylene alkylphenols can also be obtained from their ultraviolet absorption spectra in 1% ethanol solutions (21,43). In a homologous series of polyoxyethylene nonylphenols, the molar absorbancy index and the wave length of maximum absorption, 276 $m\mu$, did not change when the assigned ethylene oxide content varied from 1–30 units. The accuracy of the spectrophotometric procedure can be inferred from its demonstrated conformity to Beer's law. Thus, molecular weights of a homologous series of polyoxyethylene nonylphenols, with n in the region of 1–30, are in close agreement when determined by either method. The homogeneity of the ethylene oxide chain length distribution in nonionic detergents may easily be assessed from the sharp breaks in the surface tension vs. logarithm of concentration plots, which correspond to the critical micelle concentration, as shown in Figure 1 of references (43) and (44). It is worth noting that equimolar mixtures of nonylphenol + 10 EO with 20 EO or 50 EO exhibited no sharp breaks in these plots, in contrast to the sharp breaks observed in the plots of the individual components. Fractionation of polyoxyethylene alkylphenols and aliphatic alcohols by molecular distillation, column chromatography, and thin layer chromatography have shown so far limited success (21,32).

Surface Films

Surface film studies of aqueous solutions of polyoxyethylene aliphatic alcohols and alkylphenols have led to the determination of the configuration of nonionic detergents at the air/water interface (19,27, 28,44,45). The mode of packing and the orientation of the polar groups in these surface films have been determined from surface tension and surface potential measurements respectively. The surface pressure (π) vs. area (A) curves of adsorbed surface films of nonionic detergents have been evaluated by the Gibbs' equation from the slopes of the surface tension vs. logarithm of concentration curves, and by way of illustration the molecular areas (A) at

TABLE I
Molecular Areas in Surface Films of Nonionic Detergents (Lange-27*, Schick-44)**

Hydrophobic group	n EO	Molecular area, Å²		
		Adsorbed film		Insoluble film $\pi = 20$ dynes/cm
		$\pi = 20$ dynes/cm	π max. dynes/cm	
		**	*	**
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-Octadeconal	0			20
	5	42		70
	14	94		160
	100	150		960

specific surface pressures for two homologous series are listed in Table I (27,44). It is evident that the molecular areas are considerably larger than the cross-sectional area of the aliphatic hydrocarbon chain, 20 Å², and increase with increasing length of the ethylene oxide chains in each homologous series. Hence, a vertical orientation of the ethylene oxide chains is ruled out. Variations in the structure of the hydrophobic group at constant ethylene oxide mole ratio have a small effect on the molecular areas in contrast to variations in the length of the ethylene oxide chains. From these results two possible configurations may be assigned to nonionic detergents in adsorbed surface films: either the amphipathic molecules orient with the hydrophobic groups above the interface and the ethylene oxide chains in the air/water interface, or with the hydrophobic groups above the interface and the ethylene oxide chains forming coils in the aqueous phase. In order to distinguish between these two possibilities the molecular areas in adsorbed surface films have been compared with the corresponding molecular areas in insoluble surface films and the results are also listed in Table I (44).

The surface pressure (π) vs. area (A) curves of insoluble surface films have been determined on a 95% saturated sodium nitrate substrate, which effectively prevented dissolution of the surface films. Related results have been obtained by Lange on a 29% sodium chloride substrate (27). In each homologous series the molecular areas at a comparable surface pressure increase with increasing length of the ethylene oxide chains. Variations in the structure of the hydrophobic group at constant ethylene oxide mole ratio have a small effect on the molecular areas in contrast to variations in the length of the ethylene oxide chain. From this it follows that in insoluble surface films the hydrophobic groups orient above the interface and the ethylene oxide chains lie horizontally in the interface. The molecular areas in insoluble surface films exceed by far those in the corresponding adsorbed surface films, and, hence, a horizontal orientation of the ethylene oxide chains in adsorbed surface films is ruled out. It is concluded that the amphipathic molecules orient at the air/water interface with the hydrophobic groups above the interface and the ethylene oxide chains forming coils in the aqueous phase. The size of the coils increases with increasing number of chain segments.

TABLE II
Equilibrium Surface Moments in Surface Films of Nonionic Detergents (Schick-45)

Hydrophobic group	n EO	μ, millidebyes	$\mu_{\text{Det.}} - \mu_{\text{Alc.}}/\text{n EO}$, millidebyes [a]
n-Dodecanol	0	200	–
	1	270	70
	4	390	48
	7	360	23
	14	490	21
	23	560	16
	30	680	16
n-Octadecanol	0	225	–
	5	420	39
	14	600	27
	100	1580	14

[a] Change in surface moment per ethylene oxide unit.

In order to complement these conclusions on the mode of packing in adsorbed surface films, the orientation of the polar group has been defined (45). This has been achieved by a surface potential study. From the combined surface tension and surface potential data, the surface moments in adsorbed surface films have been evaluated by the Gibbs and Helmholtz equations and the results for two homologous series are given in Table II (45). Let us examine these data in order to distinguish among the three possible configurations, which may be assigned to nonionic detergents in adsorbed surface films. Firstly, a vertical orientation of the polar groups would require a linear increase of the surface moments with increments corresponding to that of a single ethylene oxide unit on increasing the length of the ethylene oxide chains in a homologous series. Secondly, formation of a coil by the polar groups would require an increase of surface moments with increasing number of ethylene oxide units. However, since it is known that in a polymeric coil of sufficient length the contribution of individual dipoles is cancelled out by the completely random orientation, it would be expected that the increments per ethylene oxide unit decrease progressively with increasing number of ethylene oxide units as the randomness of the coil increases. Thirdly, a horizontal orientation of the polar groups would require a constant value of the surface moments per ethylene oxide unit with increasing number of ethylene oxide units. It is evident from the results of Table II that in both homologous series the surface moments increase with increasing length of the ethylene oxide chains, and the increments per ethylene oxide unit diminish with increasing length of the hydrophilic group. Hence, a vertical or horizontal orientation of the polar groups is ruled out, and it is concluded that the ethylene oxide chains form coils in the aqueous phase; the size of the coils increases with increasing number of chain segments without reaching complete randomness even with the longest hydrophilic groups. Consequently, the configuration assigned to nonionic detergents in adsorbed surface films from the surface tension and surface potential studies are in agreement (44,45).

Micelle Formation

Among the investigations of the physico-chemical properties of nonionic detergents in aqueous media, micelle formation has been studied more extensively than any other phenomenon (2,4–9, 11–13, 19, 22–27, 29, 30, 38, 42–44, 47,51). The materials generally used in these investigations were ethylene oxide condensates of aliphatic alcohols and alkylphenols; in contrast, homogeneous alkyl hexaoxyethylene glycol monoethers have only been used in two investigations (2,9). General theories of micelle formation have been published by Debye, Ooshika, Reich, and Hoeve and Benson (10,18,40,41). These theories intended to explain why micelles do not grow indefinitely and do not lead to phase separation. Until quite recently, only published data on ionic detergents were avail-

TABLE III

c.m.c. of Polyoxyethylene n-Dodecanols in Aqueous Solutions (Lange-19)

n	c.m.c., μ M/l	
	Surface tension method	Iodine method
5	57	
7	80	71
9	100	83
12	140	108

able to verify these theories. Therefore, investigations complementary to those obtained with conventional ionic detergents were undertaken to increase our experimental knowledge of the factors determining the critical micelle concentration (c.m.c.) and micellar size in aqueous and in electrolyte solutions of nonionic detergents. The findings of these investigations are more amenable to theoretical treatment, because of the nonionic character of the materials used.

Several methods, viz., surface tension, iodine complex, and spectral change of a dye, have been found suitable for the determination of the c.m.c. of nonionic detergents (4,8,19,27,42,44). Among these, the surface tension method gives the most reliable results. The c.m.c., which corresponds to the maximum concentration of molecular dispersion, is indicated by the sharp breaks in the surface tension vs. logarithm of concentration curves (19,27,44), by changes in the absorption spectrum of iodine (4,42), or by the spectral change of eosin (19) and benzopurpurin 4B dye (8). Results of the iodine method generally are lower in comparison to those of the surface tension method as shown in Table III. The c.m.c. values of several homologous series of nonionic detergents in aqueous solutions, listed in Tables III and IV, are seen to be considerably lower than those of ionic detergents with comparable hydrophobic groups (19, 43). This may be attributed to the absence of electrical forces which resist the growth of ionic micelles at a smaller size level. For comparison, the c.m.c. of sodium laurylsulfate is referred to, which is 8,100 μ M/1. The c.m.c. values in the homologous series of polyoxyethylene n-dodecanol and nonylphenol increase with increasing ethylene oxide chain length in the range studied. From this, it follows that increased hydration or solubility resists the aggregation of nonionic detergents. The low c.m.c. value of n-octadecanol + 100 EO as compared to n-octadecanol + 14 EO may be attributed to decreasing solubility of the ethylene oxide portion with increasing molecular weight; i.e., the overall solubility of a nonionic detergent passes through a maximum with increasing ethylene oxide chain length. The c.m.c. values in each homologous series approximately follow the relation ln c.m.c = A + Bn, where n is the number of ethylene oxide units, and A,B are constants (4,19,27,44). According to Becher, B depends on the nature of the hydrophobic group and decreases with increasing chain length of the hydrophobic group (4). Thus, the effect of hydration on aggregation diminishes with increasing hydrophobic chain length. Lange's results, listed in Table III, obtained from surface tension measurements on the most carefully-prepared homologous series adhere best to this empirical relation with A=0.128 and B=3.45 (19). The effect of the chain length of the hydrophobic group on the c.m.c. of nonionic detergents with comparable ethylene oxide chain length of six units is shown in Table V (9). In line with other results reported on ionic detergents, the c.m.c. values decrease markedly with increasing hydrophobic chain length. The hydrocarbon-chain attraction rises at constant hydration of the ethylene oxide chain and enhances aggregation. Finally, the effect of temperature on the c.m.c. of n-dodecanol + 6 EO is given in Table V (9). The c.m.c. values decrease on increasing the temperature. This is in line with the inverse temperature solubility relation of nonionic detergents; and indicates that increased hydration or solubility resists the aggregation of nonionic detergents.

TABLE IV

c.m.c. and Aggregate Molecular Weight of Nonionic Detergents in Aqueous Solutions (Schick, Atlas, Eirich-43)

Hydrophobic group	n EO	No. of C. atoms in hydrophobic chain	c.m.c., μ M/l	Agg. Mol wt	Agg. No.
				(M)	(m_0)
Nonylphenol (branched)	10	10.5	75	182,000	276
	15		110	70,000	80
	20		140	68,000	62
	30		185	67,000	44
	50		280	48,000	20
n-Dodecanol	7	12	50		
	14		55	100,000	125
	23		60		
	30		80	82,000	55
n-Octodecanol	14	18	60	330,000	370
	100		20	465,000	100

$$\text{Nonylphenol} + \text{n EO } m_0 = \frac{1330}{n} - 11.3 \quad \text{(Schick, Atlas, Eirich-43)}$$

$$\text{Nonylphenol} + \text{n EO } m_0 = \frac{1215}{n} - 22.5 \quad \text{(Becher-6)}$$

$$\text{n-Dodecanol} + \text{n EO } m_0 = \frac{1025}{n} - 5.1 \quad \text{(Becher-6)}$$

TABLE V

c.m.c. and Aggregate Molecular Weights of n-Alkyl Hexaoxyethylene Glycol Monoethers in Aqueous Solutions [a]

(Corkill, Goodman and Ottewill-9, Balmbra, Clunie, Corkill, Goodman-2)

Hydrophobic group	Temp., °C.	c.m.c., μ M/l	Agg. mol. wt.	Agg. No.
			(M)	(m_0)
n-Octanol	18		12,450	32
	25	9,800		
n-Dodecanol	15	108	63,000	140
	18		84,000	187
	25	87	180,000	400
	30		320,000	711
	35	72	630,000	1400
	42		1,000,000	2220
	45		1,800,000	4000
n-Hexadecanol	25	1		

[a] A related study by P. H. Elworth and C. B. Macfarlane J. Chem. Soc. 907 (1963) has come to the author's attention after completion of the manuscript.

The corresponding aggregate molecular weights of nonionic detergents in aqueous solutions are given in Tables IV and V (9,43). Related results have been reported by Becher (6) and Dwiggins et al. (11–13). These aggregate molecular weights were determined from light scattering measurements, whereas Dwiggins et al. used the transient state method in an analytical ultracentrifuge. It is worth noting that a low c.m.c. value corresponds to a high aggregate molecular weight, and vice versa, a phenomenon generally observed with micellar solutions.

The degree of association, or the aggregation number, is defined as the ratio of the aggregate molecular weight to the molecular weight of the monomeric detergent. Water of hydration in the aggregate, which is unknown, has not been taken into account. In a homologous series of a nonionic detergent, the aggregation numbers m_0 and the aggregate molecular weights M follow an intricate pattern. This is due to the fact that m_0 decreases as a result of increasing hydrophilicity, while M rises relatively because of the increasing molecular weight of the monomeric detergent. Thus, we see, for example in Table IV, that M increases for n-octadecanol + n EO, while m_0 falls.

TABLE VI

Effect of Electrolyte Concentration on the c.m.c. of Polyoxyethylene Nonylphenol Solutions (Schick-44)

NaCl conc., M/l	△ c.m.c., μ M/l (lowering)	
	NP + 15 EO	NP + 50 EO
0.43	45	80
0.86	55	130
1.29	65	180

TABLE VII

Effect of Electrolyte Type on the c.m.c. of Polyoxyethylene Nonylphenol Solutions (Schick-44)

Electrolyte, 0.86 M/l	Lyotropic number		△ c.m.c., μ M/l (lowering)	
	(Cation)	(Anion)	NP + 15 EO	NP + 50 EO
LiCl	115		45	80
NaCl	100		55	130
KCl	75		60	
TMACl*	<75		65	180
½ $CaCl_2$			53	
½ $MgCl_2$			57	
½ $SrCl_2$			60	
½ $BaCl_2$			60	
NaCNS		13.3	25	55
NaI		12.5	27	
$NaNO_3$		11.6	30	
NaBr		11.3	30	
NaCl		10.3	55	130
$NaBrO_3$		9.6	58	
NaF		4.8	78	
⅓ Na_2SO_4		2.0	87	273
$\sqrt{3}$ Na_3 citrate			85	

* Tetramethylammonium chloride.

The aggregate molecular weights and aggregation numbers increase together with increasing chain length of the hydrophobic group at comparable ethylene oxide chain length of 14 or 15 units as listed in Table IV or of 6 units in Table V (9,43). These results show that the hydrocarbon-chain attraction rises at constant hydration of the ethylene oxide chain. The effect of ethylene oxide chain length on micelle formation for homologous series of nonionic detergents is also given in Table IV (43). Here the hydrocarbon-chain length, and therefore, the attraction, is maintained constant while the length of the ethylene oxide chain increases. Let us first consider nonionic detergents with short hydrophobic groups, i.e., nonylphenol + n EO and n-dodecanol + n EO. Increasing the length of the ethylene oxide chain results in decreased aggregation numbers. Analogous results were found by Becher (6). The same is true for n-octadecanol + n EO, but here on increasing the length of the ethylene oxide chain, the aggregate molecular weight increases, in contrast to nonylphenol + n EO and n-dodecanol + n EO, because of the large molecular weight of the monomeric unit. Finally, the effect of temperature on micelle formation of n-dodecanol + 6 EO, listed in Table V, shows an increase in aggregate molecular weight and aggregation number with increasing temperature (2). This increase in aggregate molecular weight is exponential, reaching a value of nearly two million close to the lower consolute temperature. As stated previously, these thermal effects must be attributed to decreasing hydration of the hydrophilic group with increasing temperature.

The results given so far show that the length of the ethylene oxide portion of the monomeric detergent determines the aggregation in aqueous solution. This indicates hydration as an important stabilizing influence. To elucidate this further, the effect of electrolyte on micelle formation will be discussed and the pertinent results are given in Tables VI, VII and VIII (44). Related results have been reported by Hsiao et al. (19), Becher (7) and Kuriyama (23). An increase in NaCl concentration results in a significant lowering in c.m.c. values of polyoxyethylene nonylphenols containing 15 or 50 ethylene oxide units as shown in Table VI, in a way comparable with electrolyte effects on ionic detergents (44). This decrease in c.m.c. values is more pronounced with the more hydrophilic nonylphenol + 50 EO than with nonylphenol + 15 EO. Since it is generally recognized that the overall solubility of nonionic detergents depends on the extent of hydration of the hydrophilic portion through the formation of hydrogen bonds between the ether oxygens and water molecules, these results imply that the hydrated nonylphenols are salted out on addition of electrolyte.

The mechanism of this "salting out" process may be elucidated from examination of the specific and nonspecific ion effects on the c.m.c. of polyoxyethylene nonylphenols in equivalent electrolyte solutions as shown in Table VII (44). It is well known that specific (uni-univalent) ion effects are related to the size of the hydrated ion, namely, a decrease in the lyotropic number corresponds to a decrease in hydrated ionic radius. The order of effectiveness in lowering the c.m.c. is in line with a decrease in the lyotropic number (Hofmeister series) of the ions, and is more pronounced with the more hydrophilic nonylphenol + 50 EO than with nonylphenol + 15 EO. It is worth noting that a change in the lyotropic number of the anions has a larger effect on the lowering of the c.m.c. than of the cations (19). Thus, the anions may be referred to as "counter" ions in analogy with ionic detergents. From this, it follows again that "salting out" is a plausible mechanism for the observed phenomena. It is generally recognized that nonspecific ion(or valence effects) are the determining factor in the flocculation of charged colloids by electrolytes; the flocculation increases markedly if the valence of the electrolyte, particularly the valence of the "counter" ions, increases. To achieve the same degree of flocculation, the concentration of divalent "counter" ions necessary is only one hundredth of that for the monovalent ions, and the corresponding fraction for trivalent ions is one thousandth. In order to confirm that the electrolyte effect in this problem follows a "salting out" rather than a "flocculation of charged colloid" mechanism, the nonspecific ion effects on the c.m.c. of nonylphenol + 15 EO in equivalent electrolyte solutions are included in Table VII (44). Firstly, the replacement of sodium sulfate by sodium citrate has no observable effect on the c.m.c., and differences between sodium sulfate and sodium univalent-anion salts are small compared to those generally observed in flocculations of charged colloids (7). Secondly, the replacement of an uni-

TABLE VIII

Effect of Electrolyte on the Aggregate Molecular Weight of Polyoxyethylene Nonylphenols (Schick,Atlas,Eirich-43)

Solvent	Lyotropic number		Agg. mol wt		Agg. number	
	(Cation)	(Anion)	NP + 15 EO	NP + 50 EO	NP + 15 EO	NP + 50 EO
H_2O			70,000	48,000	80	20
0.43 M NaCl				46,000		19
0.86 M NaCNS		13.3		46,000		19
0.86 M LiCl	115			46,000		19
0.86 M NaCl	100	10	73,000	62,000	83	26
0.86 M TMACl*	<75			59,000		24
0.86 M ½ Na_2SO_4		2		77,000		32
1.29 M Nacl				62,000		26

* Tetramethylammonium chloride.

TABLE IX

Aggregate Molecular Weight in Mixed Micelles of Sodium Dodecyl Sulfate and Methoxydodecyloxyethylene Dodecyl Ether (Kuriyama,Inoue,Nakagawa-24)

Temp., °C.	% W. SDS in solution						
	0	5	20	40	60	80	100
30	61,100	60,200	53,600	45,500	40,000	37,600	31,800
50	71,000	66,900	54,100	41,700	36,200	31,700	26,600
70	96,200	86,100	57,300	43,900	33,800	28,300	23,100

valent cation by a divalent one maintaining a constant anion has no significant effect on the c.m.c. These findings show that the valence of the ions is not the determining factor in the electrolyte effects and confirm "salting out" as the most plausible mechanism. It is worth noting that the reduction of cloudpoints follows the same order as the lowering of the c.m.c. values.

The corresponding aggregate molecular weights of nonionic detergents in electrolyte solutions are given in Table VIII (43). A low c.m.c. value again corresponds to a high aggregate molecular weight, and vice versa. The aggregate molecular weight and the aggregation number increase only moderately for nonylphenol + 15 EO on addition of NaCl, but both these quantities increase considerably for the more hydrophilic nonylphenol + 50 EO with increasing NaCl concentration. The specific ion effects on the aggregate molecular weight and aggregation number of nonylphenol + 50 EO are included in Table VIII (43). In equivalent electrolyte solutions, the aggregate molecular weights and the aggregation numbers increase with decreasing lyotropic number of the cation or anion, respectively, i.e., decreasing hydration of the ions. This phenomenon is more pronounced with changes in the lyotropic number of the anions than of the cations.

The following mechanism has been postulated for these "salting out" phenomena of nonionic detergents (43,44). In general, "salting out" of neutral molecules depends on the concentration and ionic radii of the electrolyte, and on the dielectric constant of the non-electrolyte. Small hydrated ions (low lyotropic number) are more effective in "salting out" neutral molecules than large hydrated ions (high lyotropic number). This also follows from the results on nonionic detergents, where the "salting out" increases with increasing electrolyte concentration and with decreasing radii of the hydrated ions; in this the hydration of the "counter" anions is more important than of the cations. Thus, there is firstly the removal of hydrogen-bonded water molecules from the ether oxygens of the ethylene oxide chain by the increased electrolyte concentration. Secondly, the extent of the dehydration of the ethylene oxide chain is then determined by the closeness of the approach of the cations to the ether oxygens, but is partially counteracted by the tendency of the "counter" anions to be hydrated. In contrast Becher has explained the electrolyte effects in terms of a positive double layer charge in the outer shell of the micelle (7). In addition, the aggregate shapes of nonionic detergents have been determined from light scattering and sedimentation velocity measurements (43). For the aggregate molecular weight region of 45,000–100,000, spheres appear to be the most probable shape, and for larger micelles, disks or rods. By the way of illustration, the dimension of the micellar model of n-dodecanol + 14 EO expressed in terms of the radius of a sphere is r = 34Å (light scat.) or 44Å (sed. vel.), and of n-octadecanol + 14 EO expressed in terms of the half axes (a,b) of a solvent penetrated ellipsoid or the diameter (d) of a rod is a = 250Å, b = 23Å, and d = 37Å.

In conclusion, the findings of these investigations on the micellar properties of nonionic detergents are briefly compared with results reported before on ionic detergents (43). The aggregation numbers of nonionic micelles depend on the length of both the hydrophobic and hydrophilic groups, whereas those of ionic micelles depend on the length of the hydrophobic group and the state of charge. Differences due to variations of the nature of the ionic groups are insignificant in ionic micelles. At constant hydrophilic group, the aggregation numbers of nonionic as well as ionic micelles increase with increasing length of the hydrophobic group. At constant hydrophobic group, the aggregation number of nonionic micelles increases with decreasing ethylene oxide chain length, whereas the corresponding change in aggregation number of ionic micelles is brought about by addition of electrolyte. Thus, reducing the hydrophilic group of nonionic detergents has the same effect as reducing the ionic repulsion of the polar groups in ionic detergents. However, addition of electrolyte also leads to an increased aggregation number for nonionic micelles, suggesting that the ethylene oxide chains undergo a salting out process. This increase of the aggregation number due to extraneous electrolyte for ionic and nonionic micelles depends inversely on the lyotropic number of the "counter ions."

Various treatments of the thermodynamics of micelle formation have offered explanations why micelles do not grow indefinitely and do not lead to phase separation. A recent experimental study of the thermodynamics of micelle formation of nonionic detergents has provided data, which are most amenable to theoretical treatment than previous studies of ionic detergents (47). Values of the change in heat content, $\Delta\overline{H}_m$, associated with micelle formation of nonionic detergents have been estimated from the temperature variation of the c.m.c. using an equation of the Clausius Clapeyron type. For nonionic detergents, the $\Delta\overline{H}_m$ values and the corresponding $\Delta\overline{S}_m$ values under these equilibrium conditions are positive; e.g., the $\Delta\overline{H}_m$ values of aqueous solutions of n-dodecanol + 30 EO, n-dodecanol + 7 EO and n-hexadecanol + 30 EO are 3.7, 5.0 and 6.6 Kcal./mole in the temperature range from 1–55C. These results imply that the entropy loss caused by aggregation of nonionic detergents must be offset by desolvation and, consequently, solvent modification is an important factor stabilizing an equilibrium-size distribution of micellar aggregates of nonionic detergents.

Mixed Micelle Formation

In the preceding section, a comparison of the micellar properties of nonionic and ionic detergents has been given. This is now complemented by a discussion of mixed micelle formation of nonionic and ionic detergents. The nonionic and ionic polar groups may either be part of a single detergent monomer, such as the sodium n-alkyl ether alcohol sulfates, or be part of separate detergent monomers mixed in different ratios. Weil et al. have shown that the c.m.c. values of sodium n-alkyl ether alcohol sulfates, $n{-}C_mH_{2m+1}{-}(OCH_2CH_2)_n{-}SO_4Na$, decreased with increased hydrophobic group chain length at constant hydrophilic group in analogy with both nonionic and ionic detergents (53); the decrease in c.m.c. values in each homologous series with increasing number of

TABLE X

Saturation Concentration of Solubilization of Long Chain Alkyl Compounds in 1% Aqueous Methoxy-decyloxyethylene Decyl Ether Solutions

(Nakagawa and Tori-37)

n-Octane		n-Decane		n-Dodecane	
11C.	7.0 mg/10 cc	10.3C.	3.0 mg/10 cc	10C.	1.3 mg/10 cc
27	9.0	27	3.9	27	1.6
40	11.2	40	5.5	39.5	2.8
n-Octanol		**n-Decanol**		**n-Dodecanol**	
10C.	32.5 mg/10 cc	11C.	22.6 mg/10 cc		
27	31.2	27	23.8	27C.	20.8 mg/10 cc
35.5	29.0	39.3	24.8	40	20.7
n-Decyl chloride		**Capric acid**		**n-Decylamine**	
10.5C.	2.6 mg/10 cc			10C.	33.6 mg/10 cc
27	4.5	27C.	23.0 mg/10 cc	27	37.8
40	7.7			40	39.2

TABLE XI

Effect of Added Solubilizates on Micellar Constitution of Methoxy-octaoxyethylene Decyl Ether

(Nakagawa, Kuriyama and Inoue-38)

Solubilizate	Solubilizate/ surfactant	Aggregate molecular weight x 10^{-4}	Aggre-gation number	No. of oil molecules per micelle
n-Decane	0	4.31	83	0
	1.32	4.56	87	4
	2.33	4.78	90	8
	3.16	5.05	94	11
	3.78	5.20	96	13
	4.93	5.75	105	19
	(12.0)	8.85	158	46
	(150.0)	9.07	162	47
n-Decanol	3.40	4.78	89	10
	6.19	5.13	93	19
	8.50	6.13	109	30
	11.42	9.09	157	59
	16.61	21.3	351	192

incorporated ethylene oxide units is in line with the transition from the high c.m.c. value of an ionic detergent to the low value of a nonionic detergent. It is worth noting that the difference in the temperature dependence of the c.m.c. of ionic and nonionic detergents is reflected in the behavior of the sodium n-alkyl ether alcohol sulfates (47). For a homolog with a short polyether group, the results follow the pattern of an anionic detergent, whereas for a homolog with a long polyether group that of a nonionic detergent. Kuriyama et al. have determined the aggregate molecular weights of mixtures of a nonionic and an ionic detergent at different temperatures, and the results are given in Table IX (24). The two components were methoxy-dodecyloxyethylene dodecyl ether and sodium dodecyl sulfate, which were added to 0.2 M sodium chloride solution in various mixing ratios. The aggregate molecular weight of the nonionic detergent increases with increasing temperature, whereas that of the ionic detergent decreases. With the mixtures, the increase in aggregate molecular weight of the nonionic detergent is progressively suppressed by increasing addition of the ionic detergent. When the addition of the ionic detergent exceeds a certain ratio (ca. 20%), the aggregate molecular weights begin to decrease with the temperature elevation. In other words, when the balance between hydrocarbon-chain attraction and opposing summation of hydration and repulsive forces is shifted to increased repulsive forces by the addition of the ionic detergent, the aggregate molecular weights decrease with the temperature elevation. The corresponding c.m.c. values follow the same pattern (24).

Solubilization and Phase Equilibria

In addition to these investigations of the micellar properties in binary systems of nonionic detergent and solvent, several studies in ternary systems of nonionic detergent, solvent and solubilizate have been reported (22,36,37,38). In ternary systems containing a surfactant, the complete disappearance of the original solid particle or liquid droplet of solubilizate into the micellar aggregate is termed solubilization. Extensive studies of soap solutions have shown that solubilization of hydrocarbons results in swelling of the micellar aggregates. Nakagawa and Tori have investigated the solubilization of long chain alkyl compounds in aqueous solutions of methoxy-decyloxyethylene decyl ether as a function of temperature and the results are given in Table X (37). As anticipated, the saturation concentration of solubilization decreases with increasing length of the alkyl chain of the solubilizate. The discrepancy between the results of hydrocarbons and alcohols may be attributed to differences in the loci of solubilization. Whereas the hydrocarbons and chlorohydrocarbons penetrate into the oil droplet of the micellar core, the alcohols are held in the palisade layer and thus also cause swelling of the micellar aggregates. The anomalous results of n-decylamine have been explained in terms of formation of an ionic detergent owing to carbon dioxide absorption. The micellar sizes of these systems have also been studied as a function of solubilizate/surfactant ratio and temperature (22,38).

The aggregate molecular weights, aggregation numbers, and number of oil molecules solubilized per micelle increase with increasing amount of added solubilizate within the saturation limit as shown in Table XI (38). These maximum increases are more pronounced in solubilization of n-decanol than of n-decane. It is deduced from the parallel increase of aggregate molecular weight and aggregation number that the increase of aggregate molecular weight does not originate from simple incorporation of solubilizate into the micellar aggregate of definite composition but also from an increase of the aggregation number on swelling by the solubilizate. Thus, the solubilization process is accompanied by the reconstitution of the micelles (38). The aggregate molecular weights of the solubilized systems increase with increasing temperature in line with the behavior of solubilizate-free micelles (22).

Mulley and Metcalf have determined the c.m.c. in ternary systems of a homogeneous nonionic detergent, water, and either benzene, n-octanol or 4-chloro-3,5-xylenol (36). The shifts in the c.m.c. of these ternary systems are small compared to those of corresponding systems containing an ionic detergent.

Detergency and Dispersion

Investigations of the mechanism of detergency in solutions of nonionic detergents have clarified some of the existing hypotheses with respect to the role played by solubilization. Natural soils may be divided into two major classes; nonparticulate soils, such as fatty and oily matter, and particulate soils, such as carbonaceous matter and clay. The usual concept of fatty soil removal is by preferential displacement or rolling up, followed by emulsification. However, McBain and Hutchinson, and Harris have indicated that solubilization of fatty soil may also be an important factor in detergency (17,33). This has been confirmed in a recent investigation of detergency in solutions of nonionic detergents, in which the amount of solubilized triolein and tristearin fatty soil was determined by a radio-tracer technique (16). Triolein was solubilized by polyoxyethylene aliphatic alcohols and alkylphenols to the extent of 0.058%, whereas the amount of triolein solubilized by anionic detergents was negligible. Maximum solubilization occurred with nonionic detergents containing ten ethylene oxide units in the hydrophilic group and at temperatures slightly below the cloudpoint. Triolein was more prone to solubilization than tristearin, probably because of the steric factors involved. These findings are in line with micellar properties cited above, which are the determining factor in solubilization phenomena; in particular, that the c.m.c. values of nonionic detergents are much lower than those of ionic detergents with comparable hydrophobic groups, and the micellar sizes of nonionic detergents increase markedly with increasing temperature. No explanation can be given for the optimum chain length of ten units in the ethylene oxide adduct.

Let us now examine the concept of particulate soil removal in nonionic detergent solutions. It is generally accepted that the dispersion of particulate soil is a function of the amount of surfactant adsorbed at the liquid/solid interface. Therefore, Abe and Kuno have determined the adsorption isotherms of polyoxyethylene nonylphenols on dispersed carbon black from aqueous solutions as a function of ethylene oxide chain length (1). These adsorption isotherms are of the Langmuir type, and for a specific equilibrium concentration, the surface excess decreases with increasing hydrophilicity of the polyoxyethylene nonylphenols. Hence, the cross-sectional areas calculated from Langmuir's equation for monolayer adsorption increase with increasing ethylene oxide chain length, but are approximately five times larger than the corresponding areas at the air/water interface determined by others (19). According to Abe and Kuno, the polyoxyethylene nonylphenols are adsorbed via their hydrophobic groups, but no explanation is given for the discrepancy between the results at the two types of interfaces. Thus, the configuration of the nonionic detergents at the liquid/solid interface still remains an open question.

Likewise, the mode of adsorption of nonionic detergents at the liquid/solid interface has been investigated by Mathai and Ottewill using homogeneous materials (31). The effects of a homologous series of n-alkyl hexaoxyethylene glycol monoethers on the formation of positively or negatively charged silver iodide sols have been studied in the presence and absence of inorganic flocculating ions. The detergents did not appear to influence the nucleation of silver iodide, but had a retarding effect on the rate of growth of the sol particles. As the concentration of nonionic detergent was increased, the concentration of inorganic salt required to produce flocculation also increased. From the extent of adsorption at equimolar concentrations, which increased in the following order $C_8E_6 < C_{12}E_6 < C_{16}E_6$, it is concluded that the nonionic detergents are adsorbed via the alkyl chain and the solvation of the ethylene oxide chains enhances the stability of the sols. The adsorption approached a saturation value beyond the c.m.c. in analogy with results at the air/water interface. These initial investigations of solubilization and dispersion in aqueous and electrolyte solutions provide some background to explain the good detergency properties of nonionic detergents.

Foaming

Finally, the foaming properties of nonionic detergents are described. These have been studied for several homologous series as a function ethylene oxide chain length (46). In general, nonionic detergents form unstable foams; the most stable foams formed by nonionic detergents are comparable to that of sodium dodecylbenzenesulfonate in the absence of foam promoters. In each homologous series the foam formation and foam stability pass through a maximum at a critical hydrophilic-hydrophobic balance (CHHB). It has been shown that the CHHB corresponds to conditions of minimum foam drainage, as determined from foam fractionation experiments, and maximum resistance to film rupture. The resistance to film rupture is dependent on the magnitude of the cohesive forces existing in the adsorbed film. The cohesive forces are the summation of the van der Waals' forces between the hydrophobic groups and of inter- or intra-molecular hydrogen bonding forces operating between the ether oxygens of the hydrated ethylene oxide coils. Their magnitude may be deduced from the molecular configurations in the surface films (44). It has been shown that in each homologous series, the size of the ethylene oxide coils increases with increasing number of chain segments. From this, it follows that the spacing between neighboring hydrophobic groups in the air/water interface increases with increasing coil size, and consequently, the van der Waals' forces decrease. Thus, from consideration of the van der Waals' forces alone, a continuous decrease in cohesive forces with increasing length of the hydrophilic groups is expected. On the other hand, the reverse phenomenon is expected from consideration of the hydrogen bonding forces. However, since the effective range of hydrogen bridges is limited to a distance of 2.5Å, the inter- and intramolecular hydrogen bonding forces are expected to pass through a maximum with increasing coil size. It is evident from the summation of the two types of forces that the resultant cohesive forces pass through a maximum at an intermediate ethylene oxide chain length. Hence, the maximum resistance to film rupture at the CHHB or the corresponding maximum in foam formation and foam stability at the CHHB is explained.

Emulsions

One of the main applications of nonionic detergents is in emulsion technology, where these surfactants form now the largest and fastest growing group of emulsifying agents. A discussion of their function in emulsification would be beyond the scope of this paper on the physico-chemical properties of nonionic detergents in aqueous solutions, and, therefore, the reader is referred to Becher's comprehensive treatment of this subject (3).

REFERENCES

1. Abe, R., and H. Kuno, Kolloid-Z., *181*, 70 (1962).
2. Balmbra, R. R., S. J. Clunie, J. M. Corkill, and J. F. Goodman, Trans. Faraday Soc., *58*, 1661 (1962)
3. Becher, P., Emulsions: Theory and Practice, Reinhold Publishing Corp., New York, (1957).
4. Becher, P., J. Phys. Chem., *63*, 1675 (1959).
5. Becher, P., and N. K. Clifton, J. Colloid Sci., *14*, 519 (1959).
6. Becher, P., *Ibid.*, *16*, 49 (1961).
7. Becher, P., *Ibid.*, *17*, 325 (1962) and *18*, 196 (1963).
8. Becher, P., J. Phys. Chem., *66*, 374 (1962).
9. Corkill, J. M., J. F. Goodman, and R. H. Ottewill, Trans. Faraday Soc., *57*, 1627 (1961).
10. Debye, P., J. Phys. and Colloid Chem., *53*, 1 (1949).
11. Dwiggins, C. W., R. J. Bolen, and H. N. Dunning, J. Phys. Chem., *64*, 1175 (1960).
12. Dwiggins, C. W., and R. J. Bolen, *Ibid.*, *65*, 1787 (1961).
13. Dwiggins, C. W., and R. J. Bolen, *Ibid.*, *66*, 574 (1962).
14. Flory, P. J., J. Am. Chem. Soc., *62*, 1561 (1940).
15. Fine, R. D., JAOCS, *35*, 542 (1958).
16. Ginn, M. E., E. L. Brown, and J. C. Harris, *Ibid.*, *38*, 361 (1961).
17. Harris, J. C., *Ibid.*, *35*, 428 (1958).
18. Hoeve, C. A. J., and G. C. Benson, J. Phys. Chem., *61*, 1149 (1957).
19. Hsiao, L., H. N. Dunning, and P. B. Lorenz, *Ibid.*, *60*, 657 (1956).

20. Jelinek, C. F., and R. L. Mayhew, Ind. Eng. Chem., *46*, 1930 (1954).
21. Kelly, J., and H. L. Greenwald, J. Phys. Chem., *62*, 1096 (1958).
22. Kuriyama, K., Kolloid-Z., *180*, 55 (1962).
23. Kuriyama, K., *Ibid.*, *181*, 144 (1962).
24. Kuriyama, K., H. Inoue, and T. Nakagawa, *Ibid.*, *183*, 68 (1962).
25. Kushner, L. M., and W. D. Hubbard, J. Phys. Chem., *58*, 1163 (1954).
26. Kushner, L. M., W. D. Hubbard, and A. S. Doan, *Ibid.*, *61*, 371 (1957).
27. Lange, H., Proc. 3rd Intern. Congr. Surface Activity, Cologne, Section A, No. 46, (1960), vol. 1, p. 279.
28. Lange, H., Fette-Seifen-Anstrichmittel-Die Ernährungsindustrie, *64*, 457 (1962).
29. Mankowich, A., J. Phys. Chem., *58*, 1027 (1954).
30. Mankowich, A., Ind. Eng. Chem., *47*, 2175 (1955).
31. Mathai, K. G., and R. H. Ottewill, Kolloid-Z., *185*, 55 (1962).
32. Mayhew, R. L., and R. C. Hyatt, JAOCS, *29*, 357 (1952).
33. McBain, M. E. L., and E. Hutchinson, "Solubilization and Related Phenomena," Academic Press, Inc., New York (1955), p. 120, 215.
34. Mulley, B. A., J. Chem. Soc., *423*, 2065 (1958).
35. Mulley, B. A., Proc. 3rd Intern. Congr. Surface Activity, Cologne, Section A, No. 4 (1960) Vol. 1, p. 31.
36. Mulley, B. A., and A. D. Metcalf, J. Colloid Sci., *17*, 523 (1962).
37. Nakagawa, T., and K. Tori, Kolloid-Z., *168*, 132 (1960).
38. Nakagawa, T., K. Kuriyama, and H. Inoue, J. Colloid Sci., *15*, 268 (1960).
39. Ogg, C. L., W. L. Porter, and C. O. Willits, Ind. Eng. Chem., Anal. Ed., 17, 394 (1945).
40. Ooshika, Y., J. Colloid Sci., *9*, 254 (1954).
41. Reich, I., J. Phys. Chem., *60*, 257 (1956).
42. Ross, S., and J. P. Olivier, *Ibid.*, *63*, 1671 (1959).
43. Schick, M. J., S. M. Atlas, and F. R. Eirich, *Ibid.*, *66*, 1326 (1962).
44. Schick, M. J., J. Colloid Sci., *17*, 801 (1962).
45. Schick, M. J., *Ibid.*, *18*, 378 (1963).
46. Schick, M. J., and E. A. Beyer, JAOCS, *40*, 66 (1963).
47. Schick, M. J., Paper presented at the 143rd Nat. Meeting of the American Chemical Society in Los Angeles, March 31–April 5, 1963, J. Phys. Chem., in press.
48. Schönfeldt, N., "Oberflächenaktive Anlagerungsprodukte des "Äthylenoxyds." Wissenschaftliche Verlagsgesellschaft, Stuttgart (1959).
49. Siggia, S., A. C. Starke, J. J. Garis, and C. R. Stahl, Anal. Chem., *30*, 115 (1958).
50. Sirianni, A. F., and B. A. Gingras, Can. J. Chem., *39*, 331 (1961).
51. Stauff, J., and J. Rasper, Kolloid-Z., *151*, 148 (1957).
52. Tischbirek, G., Proc. 3rd Intern. Congr. Surface Activity, Cologne, Section A, No. 21 (1960) Vol. 1, p. 126.
53. Weil, J. K., R. G. Bistline, and A. J. Stirton, J. Phys. Chem., *62*, 1083 (1958).
54. "Physicochemical Studies in Aqueous Solutions of Nonionic Surface Active Agents," by T. Nakagawa and K. Shimoda, has been published after completion of this manuscript in "Colloidal Surfactants," by K. Shimoda, T. Nakagawa, B. Tamamuchi, and T. Isemura, Academic Press, New York, 1963.

Recent Advances in the Analysis of Surface-Active Agents by Non-Instrumental Methods

M. J. ROSEN, Department of Chemistry, Brooklyn College, City University of New York, Brooklyn, New York

THIS PAPER will deal with some of the recent advances in the non-instrumental analysis of surface-active agents. It will not presume to be an exhaustive compilation of all the recent advances in the field. The first portion of this paper will be devoted to applications of chromatography to the analysis of surface-active agents, the second portion will be devoted to the systematic detection of functional groups in surfactants by chemical means and the last portion to some recent chemical methods for the quantitative analysis of surface-active agents.

Chromatographic Methods

Recent applications of chromatography to the analysis of surface-active agents have developed along two major lines: 1) the use of ion-exchange resins to separate ionics from nonionics, and 2) the use of paper chromatography to separate and/or identify individual surfactants. There are a number of other applications for which chromatography has been used in this field, but the major efforts have been in the two directions mentioned. There are a number of sound reasons for this: The use of ion-exchange resins for the removal of ionic materials from nonionic is fundamentally a sounder approach than the use of nonionic adsorbents, such as silica gel, carbon, etc., which do not involve an ion exchange. The adsorption of an ionic surfactant by an ion exchange resin involves the exchange of an ion on the resin for a surfactant ion, and therefore the surfactant ion can be removed from the resin only by another, similarly-charged, ion. Washing with water or other solvents containing no ions cannot remove the surfactant ion from the resin. This is in contrast to adsorption on nonionic surfaces which do not involve ion exchange, where washing with a solvent may elute the adsorbed material. The numerous papers which have recently been published on the use of paper chromatography for the separation and/or identification of individual surfactants attest to the need that has existed for a convenient method for the separation and identification of homologs—that is, surfactants having the same functional group but with hydrophobic groups of different length or structure. Very little work has been done in the past on this problem. The approach via paper chromatography is convenient and has a multitude of precedents in other fields. It may be used for samples as small as 1 μg and requires only the simplest apparatus.

Ion Exchange

The principle involved in the use of ion exchange resins for the separation of nonionic and ionic surfactants can be illustrated, as follows:

$$\underset{\substack{\text{anion-exchange}\\ \text{resin}}}{\mathrm{Ra^+[X^-]}} + \underset{\substack{\text{anionic}\\ \text{surfactant}}}{\mathrm{M^+A^-}} \rightleftarrows \underset{\substack{\text{anion-exchange}\\ \text{resin + surfactant}\\ \text{anion}}}{\mathrm{Ra^+[A^-]}} + \mathrm{M^+X^-}$$

$$\underset{\substack{\text{cation}\\ \text{exchange}\\ \text{resin}}}{\mathrm{Rc^-[M^+]}} + \underset{\substack{\text{cationic}\\ \text{surfactant}}}{\mathrm{C^+X^-}} \rightleftarrows \underset{\substack{\text{cation-exchange}\\ \text{resin + surfactant}\\ \text{cation}}}{\mathrm{Rc^-[C^+]}} + \mathrm{M^+X^-}$$

The nonionic surfactant, having no ion to exchange with the resin, is not adsorbed by the resin and may be quantitatively recovered, unchanged, by washing the resin with an appropriate solvent.

There are a number of ways in which this principle can be applied. Voogt (45) separates nonionics from soaps, sulfonates and alkyl sulfates by passing the mixture first through a column of cation-exchange resin in the H^+ form to convert the carboxylates, sulfonates and sulfates to the corresponding free acids, then through an anion-exchange resin in the acetate form to adsorb the strongly acidic sulfonic and alkylsulfuric acids, and finally through an anion-exchange resin in the OH^- form to adsorb the carboxylic acids, leaving the nonionics in the filtrate.

$$\mathrm{Rc^-[H^+]} + \left\{\begin{array}{l}\mathrm{RCOO^-M^+}\\ \mathrm{RSO_3^-M^+}\\ \mathrm{ROSO_3^-M^+}\\ \text{Nonionic}\end{array}\right. \rightleftarrows \mathrm{Rc^-[M^+]} + \left\{\begin{array}{l}\mathrm{RCOOH}\\ \mathrm{RSO_3H}\\ \mathrm{ROSO_3H}\\ \text{Nonionic}\end{array}\right.$$

$$\mathrm{Ra^+[OAc^-]} + \left\{\begin{array}{l}\mathrm{RCOOH}\\ \mathrm{RSO_3H}\\ \mathrm{ROSO_3H}\\ \text{Nonionic}\end{array}\right. \rightleftarrows \mathrm{Ra^+}\left\{\begin{array}{l}\mathrm{[RSO_3^-]}\\ \mathrm{[ROSO_3^-]}\end{array}\right. + \left\{\begin{array}{l}\mathrm{RCOOH}\\ \mathrm{AcOH}\\ \text{Nonionic}\end{array}\right.$$