ORIGINAL ARTICLE

Synergism and Performance Optimization in Liquid Detergents Containing Binary Mixtures of Anionic–Nonionic, and Anionic–Cationic Surfactants

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Abstract In this paper evaluation of surface active and application properties in liquid detergent formulations containing binary mixtures of anionic–nonionic, and anionic–cationic surfactants is discussed. Surfactants used include: linear alkylbenzene sulfonate (LAS), alcohol ether sulfate (AES-2EO), alcohol ethoxylate (AE-7EO), lauryl dimethyl amine oxide, and alkyl hydroxyethyl dimethyl ammonium chloride (AHDAC). Surface active parameters relating to the effectiveness and efficiency of surface tension reduction were determined from the surface tension data. Non-ideal solution theory was used to determine the degree of interactions between the two surfactants, and the conditions under which a mixture of two surfactants show synergism in surface active properties. Our data indicated that synergism in mixed surfactants increases with the degree of charge difference between the surfactants. In both mixed micelle and mixed monolayer formation, the degree of interactions between the two surfactants in the mixture increased in the following order: LAS/AE < AES-2EO/amine oxide < AES-2EO/AHDAC. This synergistic behavior as presented in this paper leads to unique application properties and improved performance in terms of foam volume, and soil removal which has applications in formulation of dishwashing liquids, and laundry detergents.

Introduction

Significant changes have occurred in the liquid detergent market in recent years. Many new products have been introduced on to the North American and European markets in dishwashing and laundry liquid categories. There has been many changes in the formulation of these products as a result of changes in consumer habits and practices and advances in surfactant technologies. New formulations have been developed which posses improved performance, low irritation potential, and are more compatible with the environment. Surfactants normally incorporated in these formulations include: anionic and nonionic, as well as soap, amphoteric and cationic surfactants. Selecting an optimum mixture of surfactants for liquid detergents which adequately meets a wide variety of end-use specifications needs a careful balance of performance, formulation ease and flexibility, cost, and environmental requirements [1, 2].

In the formulation of such products, usually mixtures of surfactants, rather than individual surfactants, are used to improve the application properties of the final product. Mixtures of anionic and nonionic surfactants are used in laundry detergents to improve oily soil removal and performance in hard water conditions. Another example is the use of mixtures of anionic–nonionic surfactants, or anionic-amphoteric surfactants to improve foam performance and mildness in dishwashing liquids. In most cases when a mixed surfactant system is used the objective is synergism, when the properties of the mixture is better than those

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achievable with the individual surfactants [3, 4]. Although the synergistic behavior between surfactants has been known for many years, the investigation of synergism in quantitative terms is a recent development. Based on ideal solution theory it is possible to determine the degree of interactions between the two surfactants, and to identify the conditions under which a mixture of two surfactants shows synergism in the fundamental surface properties [5–9, 12].

In this paper evaluation of surface active and application properties in liquid detergent formulations containing binary mixtures of anionic–nonionic, and anionic–cationic surfactants is discussed. Surface active parameters relating to the effectiveness and efficiency of surface tension reduction, and interaction parameters were determined from the surface tension data. In addition, foam performance, and detergency of surfactant mixtures were evaluated, and the conditions under which a mixture of two surfactants show synergism in the application properties were identified.

Experimental

Materials

Surfactants used in this study are shown below. These were all commercial samples and were not specially purified.

Anionic Surfactants

Sodium linear alkylbenzene sulfonate C10-C13 (LAS). In this study we used Na-LAS prepared by sulfonation and neutralization of commercial linear alkylbenzene (LAB) obtained from the UOP-HF (hydrofluoric acid) process with average molecular weight of 244 g/mol and the following carbon chain distribution: Phenyl-C10 = 8 %, Phenyl-C11 = 26 %, Phenyl-C12 = 35 %, Phenyl-C13 = 29 %, Phenyl-C14 = 2 %. Other LAB parameters were: 2-Phenyl content: 16 %, 3-Phenyl content: 15 %, and total 4, 5, 6, 7 Phenyl content: 69 %.

Sodium alkyl ether sulfate: C12-C14, 2EO (AES-2EO), average molecular weight of 395 g/mol, and 27 % active substance*.

Nonionic Surfactants

Linear alcohol ethoxylate: C12-C14, 7EO (AE-7EO), average molecular weight of 487 g/mol.

Lauryldimethylamine oxide, R = C12-C14, average molecular weight of 229, 31 % active substance*.

Cationic surfactant: *Alkyl hydroxyethyl dimethyl ammonium chloride* (AHDAC), R = C12-C14, average molecular weight of 307 g/mol, 40 % active substance*.

*Received from Functional Chemical Division, Clariant International Ltd., Muttenz, Switzerland.

Surface Chemical Measurements

All surface tension profiles were measured at 25 °C using the Du Nouy ring method with a Krüss Model K10ST tensiometer equipped with a constant temperature circulating water system. The measured surface tensions (γ) were plotted versus logarithmic surfactant concentration. Linear least squares fit to the profile generated the CMC value and the slope. The surface excess concentration (Γ) was calculated according to the equation derived from the Gibb's adsorption isotherm [3]

$$\Gamma = \frac{\partial \gamma / \partial \log C}{2.303 \, nRT}$$

where $n = 1$ for dilute nonionic surfactants or 1:1 ionic surfactants in the presence of an excess amount of a common non-surfactant ion, and $n = 2$ for 1:1 ionic surfactant in the absence of other solutes. $R = 8.31 \times 10^7$ ergs/mol. K, C is concentration in mol/L, γ is in mN/m, and $\partial \gamma / \partial \log C$ is the slope of the steepest part of the curve before critical micelle concentration (CMC) is reached. T is absolute temperature, and γ is in mol/cm^2.

The area per surfactant head group (A) at air–water interface was calculated using the following equation, where N is Avogadro's number (6.026×10^{23})

$$A = \frac{10^{16}}{\Gamma \times N}$$

Efficiency and effectiveness of surface tension reduction were calculated according to Rosen [3]. The actual micellar participation (in mole fraction) of each surfactant was determined using the following equation [3, 6]

$$\frac{\left(X_1^M\right)^2 \ln \frac{C_{12}\alpha}{C_1 X_1^M}}{\left(1 - X_1^M\right)^2 \ln \frac{C_{12}(1-\alpha)}{C_2\left(1-X_1^M\right)}} = 1$$

where X_1: mole fraction of surfactant 1 in micelle, C_1: CMC of surfactant 1, C_2: CMC of surfactant 2, C_{12}: CMC of mixed micelle system of surfactant 1 and 2, and α: mole fraction of surfactant 1 in solution.

The magnitude of the interactions between the two surfactants can be quantified by determination of a β factor according to Rosen [3, 6] and Rubingh [7]

$$\beta^M = \frac{\ln\left(\alpha C_{12}^M / X_1^M C_1^M\right)}{\left(1 - X_1^M\right)^2}$$

We shall note that the above equations were developed for mixtures of pure surfactants. In the case of commercial surfactants used in our work, the above equations should be used with caution as such surfactants are mixtures of

surface active materials, due to the non-homogeneous materials used in manufacturing and the presence of unreacted raw materials and by-products.

Detergency Test

Detergency tests were performed using a Terg-o-tometer apparatus equipped with a controlled temperature bath system. Standard artificially soiled fabrics supplied by EMPA Testmaterials (St. Gallen, Switzerland) were used in our experiments. The following fabric/soil combinations were used:

EMPA-106 Cotton fabric, soiled with carbon black/ mineral oil
EMPA-142 Polyester/Cotton: 65/35 fabric, soiled with lipstick

Soil removal on the washed fabrics were determined by reflectance measurement (Data Color Instruments). Washing tests were carried out at: 4 g/L surfactant concentration, 40 °C temperature, in distilled water, 1 L wash volume, 15 min wash, and 5 min rinse cycle.

Foam Volume Test

Foam volume was measured according to the ASTM D1173-53 method using the Ross-Miles apparatus at 25 °C temperature [11].

Results and Discussions

Surface Chemical Studies

Figure 1 shows the surface tension versus logarithmic surfactant concentration for different mixtures of LAS and AE-7EO nonionic surfactants. Surface active parameters as determined from this data are shown in Table 1. As shown here addition of nonionic surfactant has a major effect in lowering of CMC value of LAS and significant improvement in efficiency of surface tension reduction. Further analysis of the surface tension data as shown in Table 2
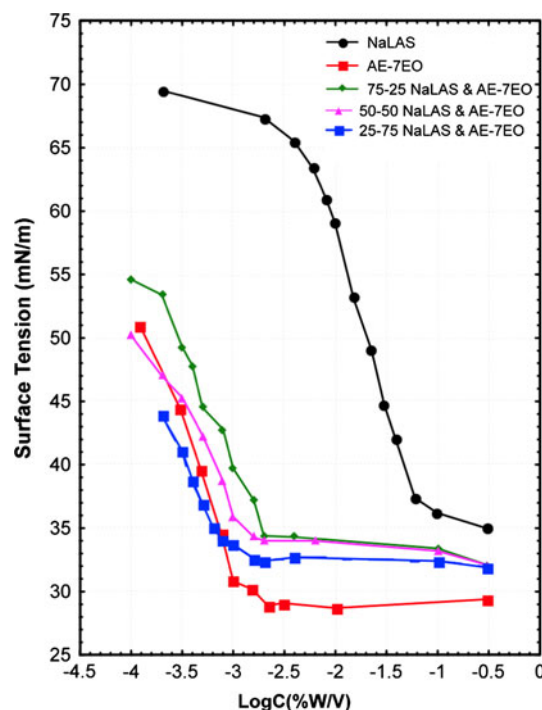

Fig. 1 Tensiograms for mixtures of LAS/AE-7EO system

indicates that the mole fraction of LAS in solution (0.82) is significantly higher than the mole fraction of LAS in the micelles (0.26). Therefore, the mixed micelle system contains predominately nonionic surfactants. A β value of −3.9 as determined in the case of LAS/AE-7EO: 75/25 indicates relatively strong interactions between anionic and nonionic surfactants. This β value of −3.9 compares with the value of −5.8 for mixture of pure surfactants: C12 LAS and C12 AE-8EO as referenced by Rosen [3].
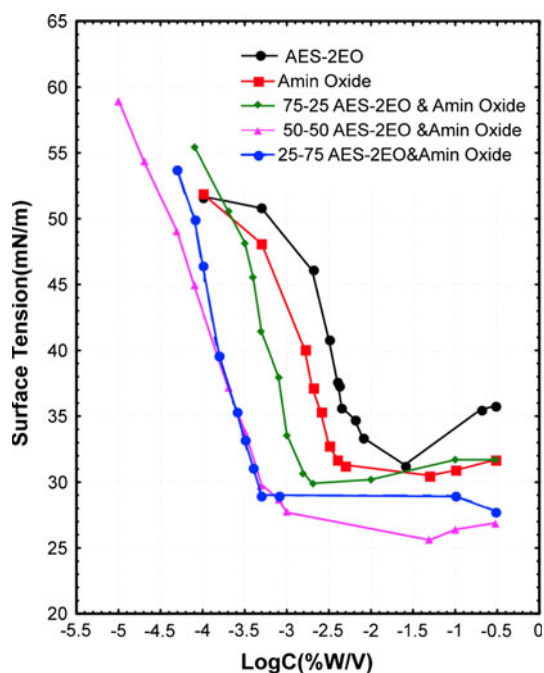
Figure 2 shows the surface tension versus logarithmic surfactant concentration for different mixtures of AES-2EO and amine oxide surfactants. The pH of the solutions was 7.5 at which the amine oxide is nonionic. Surface active parameters as determined from this data are shown in Table 3. All mixed systems exhibit significantly lower surface tension and CMC values compared to individual surfactants. As shown here addition of amine oxide surfactant has a major effect in lowering of CMC value of

Table 1 Surface active properties for mixtures of LAS/AE-7EO system

% LAS	% AE-7EO	CMC %(W/V)	CMC (Molar)	γ_{min} (mN/m)	A (Å)	Efficiency $P(C_{20})$ % × 1000	Effectiveness (mN/m)
100	0	0.0714	2.075×10^{-3}	35.05	35	186	37
75	25	2.4×10^{-3}	6.98×10^{-5}	34.3	61	0.3	38
50	50	1.33×10^{-3}	3.87×10^{-5}	34.1	52	0.1	38
25	75	9.59×10^{-4}	2.79×10^{-5}	32.5	59	0.05	40
0	100	1.2×10^{-3}	2.3×10^{-5}	29.02	36	0.1	43

Table 2 Mole fraction of LAS in solution and in micelle for different mixtures of LAS/AE-7EO

LAS/AE-7EO	Mole fraction anionic		β
	Solution	Micelle	
100/0			
75/25	0.82	0.26	−3.9
50/50	0.6	0.2	
25/75	0.33	0.13	
0/100			

Fig. 2 Tensiograms for mixtures of AES-2EO/amine oxide system

AES-2EO and significant improvement in efficiency of surface tension reduction. Further analysis of the surface tension data results in a β value of −7.5 as determined in the case of AES-2EO/amine oxide: 75/25, indicating a strong interactions between anionic and amine oxide surfactants, and synergy in surface active properties. The
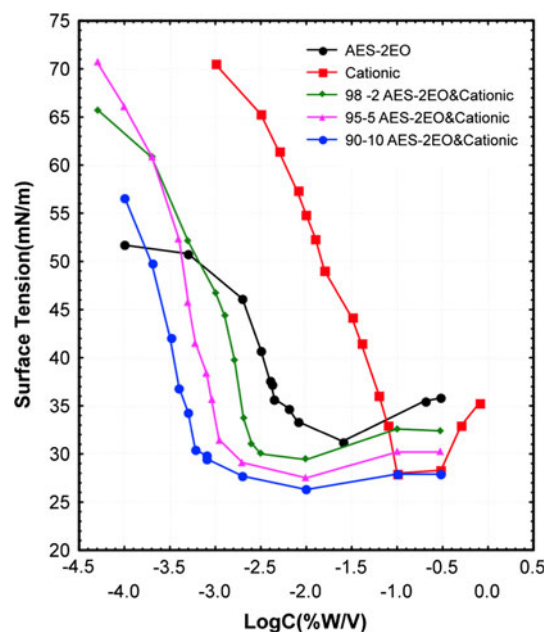
Fig. 3 Tensiograms for mixtures of AES-2EO/AHDAC system

magnitude of this interaction is larger than the one observed in the case of LAS/AE-7EO system.

Figure 3 shows the surface tension versus logarithmic surfactant concentration for different mixtures of AES-2EO and Alkyl hydroxyethyl dimethyl ammonium chloride (AHDAC) surfactants with high ratio of anionic to cationic surfactant. Surface active parameters as determined from this data are shown in Table 4. All mixed systems exhibit significantly lower surface tension and CMC values compared to individual surfactants. As shown here addition of the cationic surfactant has a major effect in lowering of CMC value of AES-2EO and significant improvement in efficiency of surface tension reduction. Further analysis of the surface tension data results in a β value of −12 as determined in the case of AES-2EO/AHDAC: 95/5, indicating a strong interactions between anionic and cationic surfactants, and synergy in surface active properties. This β value of −12 compares with value of −13.2 for the mixture of pure surfactants: sodium decyl sulfate and C14 alkyl trimethyl ammonium bromide as referenced by Rosen [3].

Table 3 Surface active properties for mixtures of AES-2EO/amine oxide system

% AES-2EO	% Amine oxide	CMC %(W/V)	CMC (molar)	γ_{min} (mN/m)	A (Å)	Efficiency $P(C_{20})$ % × 1000	Effectiveness (mN/m)
100	0	6.09×10^{-3}	1.56×10^{-4}	31.3	28	0.5	41
75	25	1.2×10^{-3}	3.08×10^{-5}	31.7	35	0.2	40
50	50	7.46×10^{-4}	1.9×10^{-5}	26.6	50	0.05	45
25	75	5.05×10^{-4}	1.29×10^{-5}	28.9	45	0.07	43
0	100	3.60×10^{-3}	1.6×10^{-4}	31.4	39	0.1	41

Table 4 Surface active properties for mixtures of AES-2EO/AHDAC system

% AES-2EO	% AHDAC	CMC %(W/V)	CMC (molar)	γ_{min} (mN/m)	A (Å)	Efficiency $P(C_{20})$ % × 1000	Effectiveness (mN/m)
100	0	6.09×10^{-3}	1.56×10^{-4}	31.3	28	0.5	41
98	2	2.49×10^{-3}	6.38×10^{-5}	29.7	19	0.5	42
95	5	1.68×10^{-3}	4.3×10^{-5}	27.5	29	0.4	45
90	10	7.7×10^{-4}	1.97×10^{-5}	26.3	24	0.2	46
0	100	0.119	3.9×10^{-3}	28.1	34	14	44

Table 5 Foam volume of LAS/AE-7EO mixtures in distilled water and 300 ppm water hardness

Sample	% Surfactant in mixture		Foam height (cm) distilled/300 ppm water hardness
	LAS	AE-7EO	
1	100	0	20/14.5
2	75	25	16/18.5
3	50	50	15/18.5
4	25	75	14.5/18
5	0	100	16/13

Table 8 Detergency of LAS/AE-7EO mixtures, EMPA 142 test fabric

Sample	% Surfactant in mixture		Soil removal (%)
	LAS	AE-7EO	
1	100	0	35
2	75	25	39
3	50	50	37
4	25	75	36
5	0	100	36

Table 6 Foam volume of AES-2EO/amine oxide mixtures in distilled water and 300 ppm water hardness

Sample	% Surfactant in mixture		Foam height (cm) distilled/300 ppm water hardness
	AES-2EO	Amine oxide	
1	100	0	20/19.5
2	75	25	23/21.5
3	50	50	22/21.5
4	25	75	22/21
5	0	100	18/17.5

Table 9 Detergency of AES-2EO/amine oxide mixtures, EMPA 142 test fabric

Sample	% Surfactant in mixture		Soil removal (%)
	AES-2EO	Amine oxide	
1	100	0	35
2	75	25	38
3	50	50	37
4	25	75	45
5	0	100	43

Table 7 Foam volume of AES-2EO/AHDAC mixtures in distilled water and 300 ppm water hardness

Sample	% Surfactant in mixture		Foam height (cm) distilled/300 ppm water hardness
	AES-2EO	AHDAC	
1	100	0	20/19.5
2	98	2	21/21.5
3	95	5	18.5/22
4	90	10	19/22.5
5	0	100	16/16

Table 10 Detergency of AES-2EO/AHDAC surfactant mixtures, EMPA 142 test fabric

Sample	% Surfactant in mixture		Soil removal (%)
	AES-2EO	AHDAC	
1	100	0	35
2	98	2	34
3	95	5	38
4	90	10	55
5	0	100	42

The magnitude of the interactions observed here is significantly larger than the one observed in the case of AES-2EO/amine oxide, and LAS/AE-7EO systems.

Foam Volume Measurements

Table 5 show the results of foam volume tests in distilled water and under 300 ppm water hardness conditions for different mixtures of LAS/AE-7EO system. Significant

improvement in foam volume is observed for mixed surfactant systems under hard water condition. Although there is a significant drop in foam performance of LAS in hard water, addition of nonionic surfactant improves foam performance, and water hardness tolerance of anionic.

Table 6 show the results of foam volume tests in distilled water and under 300 ppm water hardness conditions for different mixtures of the AES-2EO/amine oxide system. Results indicate significant improvement in foam volume for mixed surfactant systems under both soft water and hard water conditions, which makes this system particularly useful for dishwashing formulations.

Table 7 shows the results of foam volume tests in distilled water and under 300 ppm water hardness conditions for different mixtures of AES-2EO/Cationic surfactant system. For such mixtures where there is a high ratio of anionic to cationic in composition, foam volume data indicate significant improvement in foam volume for the mixed surfactant systems particularly under hard water conditions.

Detergency Tests

Results of detergency tests are shown in Tables 8, 9 and 10 for EMPA-142 test fabric: Polyester/Cotton: 65/35 fabric, soiled with lipstick, which was particularly sensitive to the surfactant composition. For the LAS/AE-7EO some improvement in soil removal is observed for surfactant mixtures, especially for the LAS/AE-7EO: 75/25 mixture. For AES-2EO/Amine oxide combination, significant improvement in soil removal was observed at high ratio of amine oxide to AES-2EO mixture. For AES-2EO/Cationic surfactant mixtures, significant increase in soil removal was observed for AES-2EO/Cationic: 90/10 mixture which makes such systems particularly useful in laundry detergent applications.

Conclusions

In this paper evaluation of surface active and application properties in liquid detergent formulations containing binary mixtures of anionic–nonionic, and anionic–cationic surfactants is discussed. Surfactants used include: linear alkylbenzene sulfonate, alcohol ether sulfate, ethoxylated alcohol, lauryl dimethyl amine oxide, and alkyl hydroxyethyl dimethyl ammonium chloride. Surface active parameters relating to the effectiveness and efficiency of surface tension reduction, and interaction parameters were determined from the surface tension data. Non-ideal solution theory was used to determine the degree of interactions between the two surfactants. Conditions under which a mixture of two surfactants show synergism in the fundamental surface properties, and application properties were identified.

Our data indicated that synergism in mixed surfactants increases with the degree of charge difference of surfactants. In both mixed micelle and mixed monolayer formation, degree of interaction between the two surfactants in mixture increases in the following order:

NaLAS/AE-7EO < AES-2EO/amine oxide < AES-2EO/cationic surfactant.

This synergy, as presented in this paper, and also shown by other investigators [8, 10] leads to unique application properties and improved performance in terms of foam volume, and soil removal in the formulation of liquid detergents. For the binary mixture of AES-2EO/amine oxide significant improvement in foam performance is observed, especially in high water hardness conditions which makes this combination particularly useful for manual dishwashing formulations. For AES-2EO/Cationic surfactant mixture, improved oily soil removal was observed at high ratio of anionic/cationic surfactant which has applications in formulations of laundry detergents.

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