L. Cohen, Algeciras/Spain, A. Moreno and J. L. Berna, San Roque/Spain*

LAS magnesium salts – a contribution to mildness and performance

A number of properties of linear alkylbenzene sulfonate magnesium salts (LAS_2Mg) in aqueous solutions as compared to sodium salts have been measured, such as: surface tension, critical micelle concentration, specific conductivity, viscosity, solubility, biodegradability, toxicity and water hardness stability.
Other tests such as the zein, wetting, laundry detergency performance and dishwashing tests have been conducted as well.
Some specific properties of magnesium salts have been confirmed or established and potential new applications identified in the detergents and cosmetics sectors.

Eine Reihe von Eigenschaften linearer Alkylbenzolsulfonsäure Magnesium- und Natriumsalze wurden in wäßrigen Lösungen vergleichend gemessen: Oberflächenspannungen, kritische Micellbildungskonzentrationen, Viskositäten, Löslichkeiten, biologische Abbaubarkeiten, Toxizitäten und Wasserhärtestabilitäten.
Es wurden ferner bestimmt: die Hautverträglichkeiten mittels des Zein-Tests, das Netzvermögen, die Waschkraft, das Geschirrspülvermögen.
Bekannte Eigenschaften der Magnesiumsalze wurden dabei bestätigt und bisher unbekannte festgestellt, wodurch den Produkten neue Anwendungsmöglichkeiten auf dem Gebiet der Reinigung oder der Kosmetik erschlossen werden.

1 Introduction

In recent years the barrier between effective surfactants (primary applications) and mild surfactants (cosmetics) has been overcome by magnesium surfactants.

The literature is full of statements such as:
- The irritation potential of anionics can be moderated by changing the counterion [1].
- Magnesium alkylbenzene sulfonate (LAS_2Mg) is effective in applications involving maximum penetration or soil softening [2].
- Magnesium surfactants can be described as basic and mild, basic in terms of their foaming and cleansing properties, and mild as proven in several in vivo and in vitro tests [3].

Fatty alcohol sulfates, alkyl ether sulfates and olefin sulfonates are the three strong anionics used in cosmetics and toiletry formulations. Besides their use in cosmetics, mild surfactants are also needed for hand dishwashing applications.

According to [3], there is an appropriate way to meet all cleansing, foaming and mildness requirements; changing the counterion of anionics from sodium to magnesium.

As all the published works refer to sulfomethylesters (SME) [4] or alcohol sulfates AS [1, 3], an overall comparison of magnesium versus sodium alkylbenzene sulfonate (LAS Na) has been conducted.

The linear alkylbenzene used in this study was a commercial sample from the DETAL process [10] with the following composition: phenyl C10, 17 % w/w; phenyl C11, 47.8 % w/w; phenyl C12, 35.2 % w/w; 2-phenyl alkane, 29.5 % w/w; molecular weight, 234.7.

2 Physicochemical properties

As all solid and liquid interfaces in an alkaline medium are negatively charged, a mutual repulsion takes place between the interfaces and the negatively charged hydrophilic groups of anionic surfactants. However, close approach is possible when the hydrophobic interactions between the hydrophobic parts of the molecules and the interfaces are stronger than the sum of the forces of repulsion and attraction vis a vis the solvent. The compression of the electric double layer by magnesium ions is stronger than by sodium ions and hence repulsion of similarly charged particles is reduced. As a result adsorption of the surfactant is enhanced, surface activity is increased and critical micelle concentration is reduced [5].

2.1 Surface tension

Surface tension as a function of concentration has been measured for both magnesium and sodium alkylbenzene sulfonate on LAUDA MGW equipment at 35 °C using the ring method.

Figure 1 shows that surface tension is lower for magnesium than for sodium counterion regardless the concentration used.

Efficiency was defined by *Rosen* [6] as the surfactant concentration required to lower solvent surface tension 20 mN/m. The concentrations found are 37 ppm for sodium and 12 ppm for magnesium LAS, thus indicating that magnesium sulfonate is more efficient than the sodium salt.

Effectiveness, is defined as the reduction of solvent surface tension attained at a surfactant concentration close to

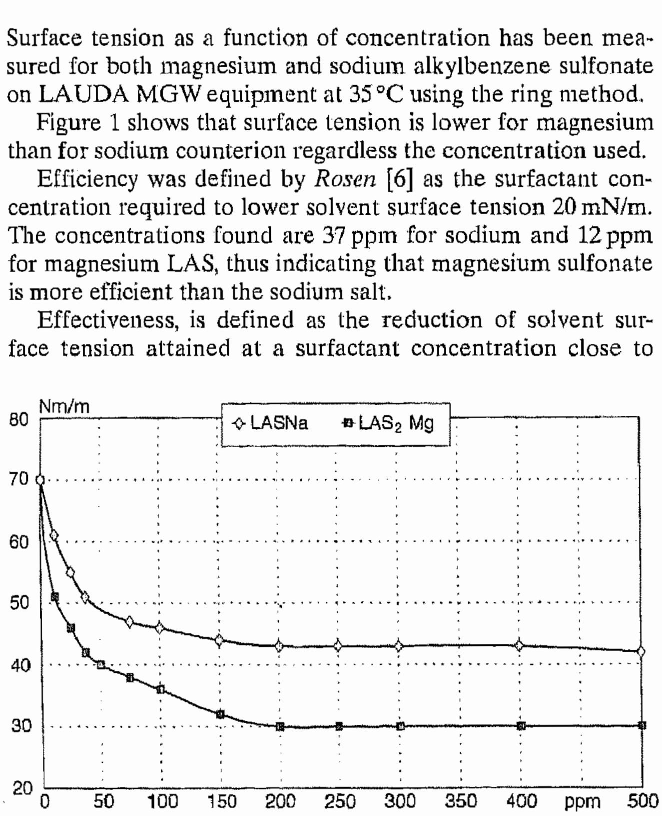

Fig. 1. Surface tension

* Avenida Ramón Puyol s/n 11202, Algeciras – Spain

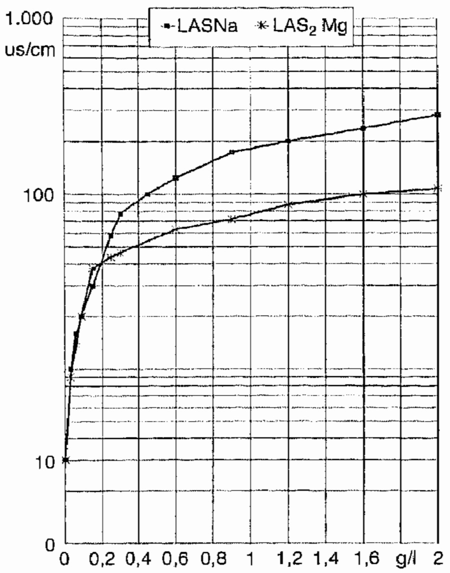

Fig. 2. Specific conductivity

the critical micelle concentration (c. m. c.). The results obtained are 30 mN/m for magnesium and 43 for sodium, thus indicating magnesium sulfonate to be more effective than sodium LAS.

Efficiency as well as effectiveness of a surfactant in reducing surface tension should reflect the concentration of the surfactant at the interface relative to that in the bulk liquid phase.

According to *Rosen* [6], the replacement of sodium counterion by one more tightly bound such as magnesium increases both efficiency and effectiveness.

2.2 Critical micelle concentration

The results plotted in Figure 2 have been obtained by measuring the specific electrolytic conductivity at different LAS concentrations on a CRISSON-522 equipment.

The c. m. c. values corresponding to the break in the curves were 0.3 g/l (0.9 mmol/l) for sodium sulfonate and 0.15 g/l (0.24 mmol/l) for magnesium sulfonate.

These results can be explained in terms of the fact that c. m. c. reflects the counterion micelle degree of binding and therefore, in aqueous systems, increased binding of the counterion causes a decrease in the c. m. c. of the surfactant [7]. The extent of binding of the counterion increases with increase in its polarizability and valence [6].

2.3 LAS – Calcium precipitation boundary diagram

This diagram (Fig. 3) is a log-log plot of the surfactant and calcium ion concentrations. It shows the water hardness stability of the surfactant in a more precise form than does the more widely used stability test (DIN 53905). The diagram was obtained by visual observation of the turbidity of LAS-calcium solutions prepared in 1-L glass bottles. The diagram is a graphical representation of points at which the onset of precipitation is observed.

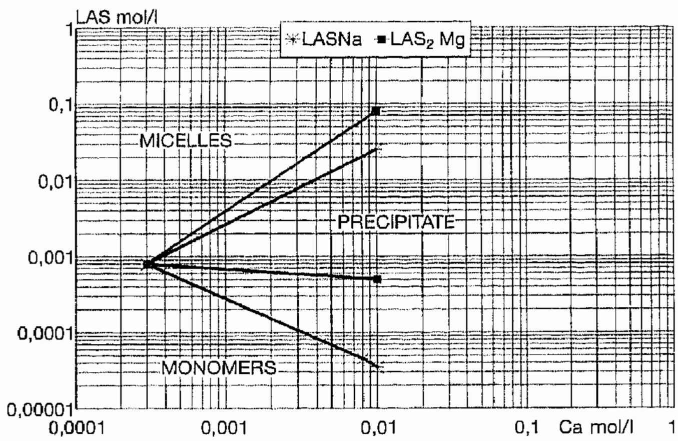

Fig. 3. LAS-Ca Precipitation Diagram

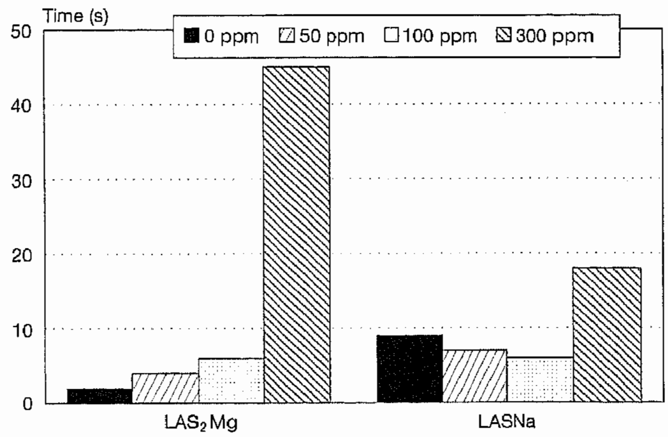

Fig. 4. Wetting 1,2 g/l

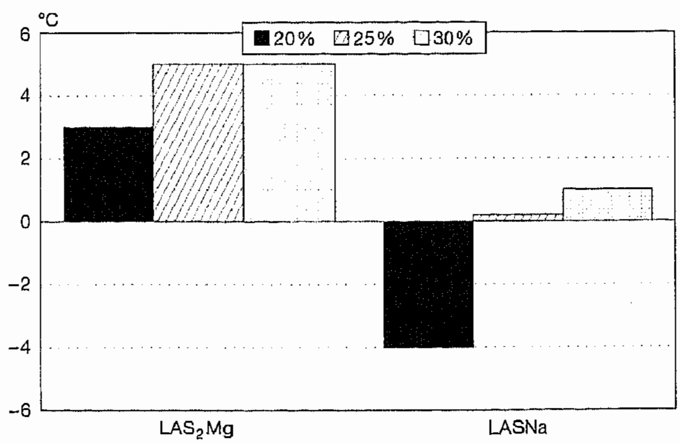

Fig. 5. Cloud point

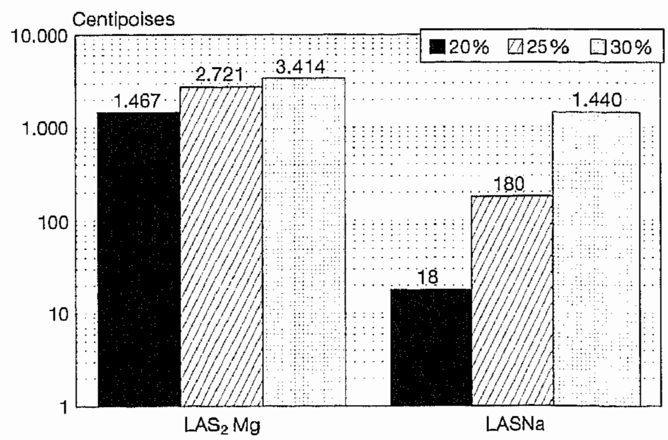

Fig. 6. Viscocity at 20°C

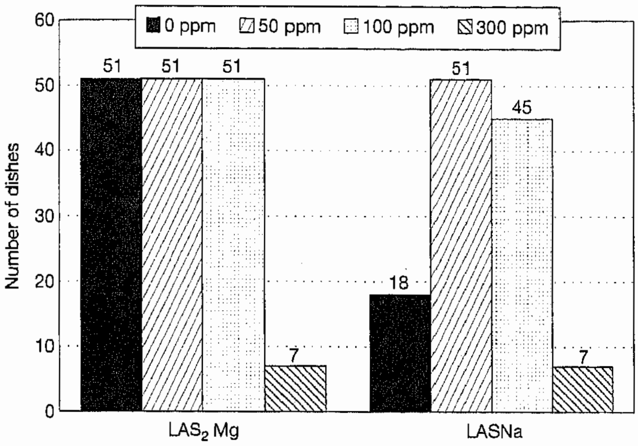

Fig. 7 Dishwashing, fat /olive oil, 0.33 g/l, 49 °C

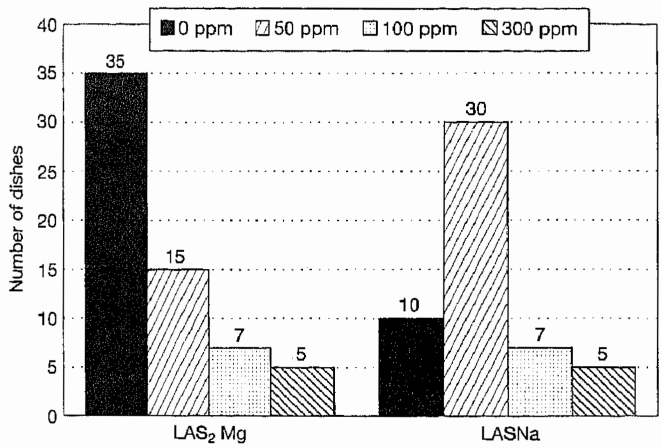

Fig. 8. Dishwashing, Crisco, 0.33 g/l, 49 °C

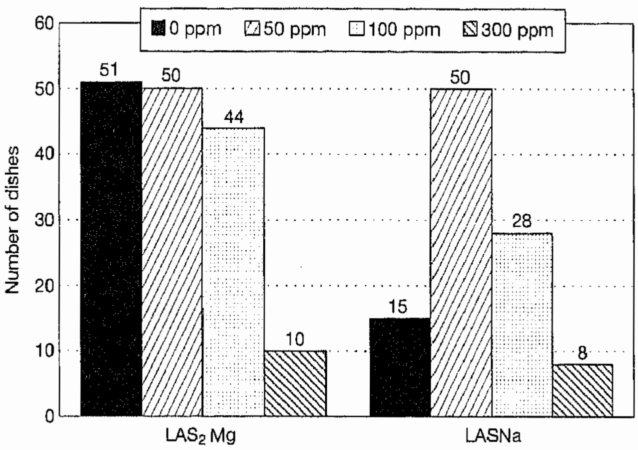

Fig. 9. Dishwashing, tomato sauce, 0.33 g/l, 49 °C

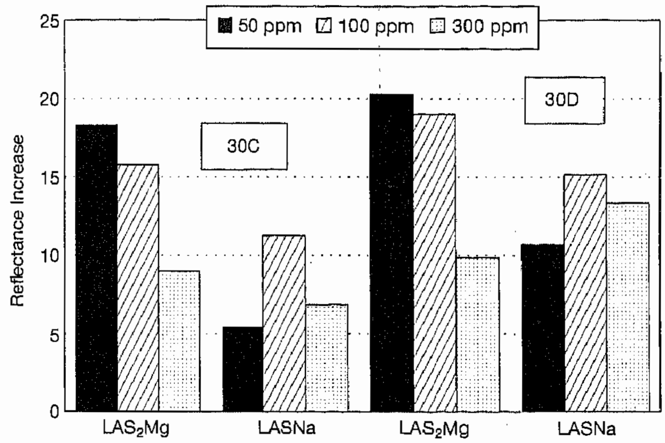

Fig. 10. Detergency, Krefeld 1.2 g/l, 30 °c

As can be observed, there are three distinct diagram regions. In the monomer state, up to 0.0005 mol/l of surfactant, no precipitation of LAS_2Mg takes place, while LASNa starts to be precipitated at 0.000035 mol/l and 0.01 mol/l of calcium. In the second region belonging to the micelle state, where both magnesium and sodium sulfonate behave similarly. It is worthwhile to point out that in the precipitation zone there were significant differences in the appearance of precipitates where LASNa/Ca mixtures produced a more agglomerated and structured precipitate than LAS_2Mg/Ca blends.

It is concluded that below 0.001 mol/l of surfactant, LAS_2Mg is more stable to calcium water hardness than LASNa.

2.4 Wetting ability

According to *Rosen* [6], as the surfactant becomes more soluble it has a lesser tendency to migrate to the interface and its wetting ability is reduced.

This property has been measured by the Draves test. The results are plotted in Fig. 4.

Up to 100 ppm LAS_2Mg has a higher wetting power than LASNa. At 300 ppm, surprisingly, the phenomenon is reversed.

2.5 Solubility

Cloud points, the temperatures at which transparent sulfonate solutions become cloudy on cooling, are plotted in Fig. 5. LAS_2Mg has a slightly lower solubility than LASNa.

2.6 Viscosity

Magnesium ions have a well known build-up effect on viscosity. This explains why magnesium sulfonates are more viscous than sodium whatever the concentration use as shown in Fig. 6.

2.7 Conclusions

As compared to the sodium salt, the magnesium salt of linear alkylbenzenesulfonate in aqueous solution LAS

- is more surface-active
- has a much lower critical micelle concentration
- is more stable to calcium water hardness at low concentrations
- has a higher wetting power at low and medium water hardness
- has a lower water solubility
- has a higher viscosity

3 Performance

3.1 Dishwashing test

According to *Cox* [2], soil removal from a hard surface is a two-step process which involves penetration of surfactant into the soil and soil softening; after that, emulsification, wetting and agitation are also needed. Penetration is accomplished by minimizing the water solubility of the surfactant. As water solubility is reduced, penetration increases, because

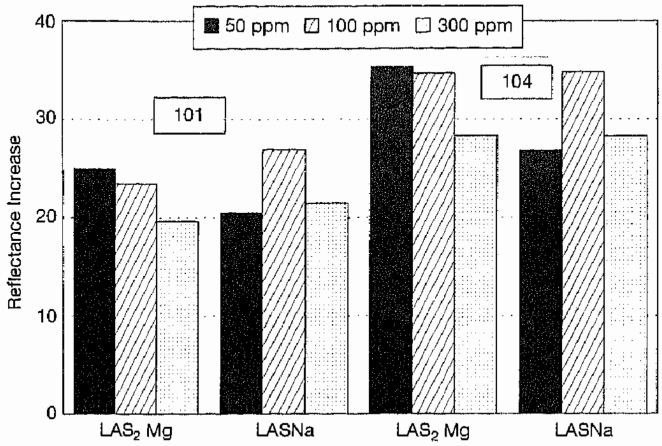

Fig. 11. Detergency, EMPA, 1.2 g/l, 30°C

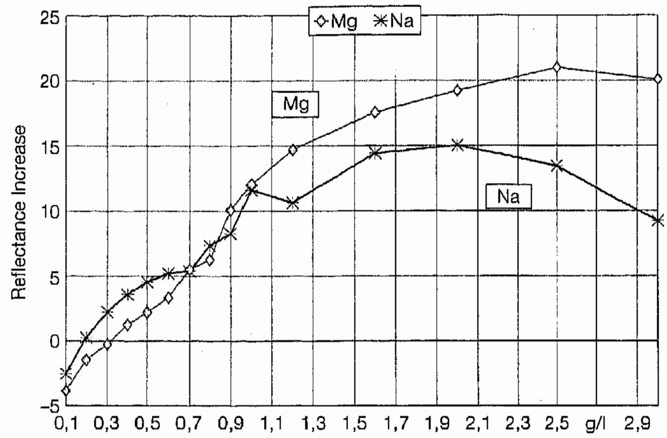

Fig. 12. Detergency, Krefeld, 30°C, 150 ppm, 30°C

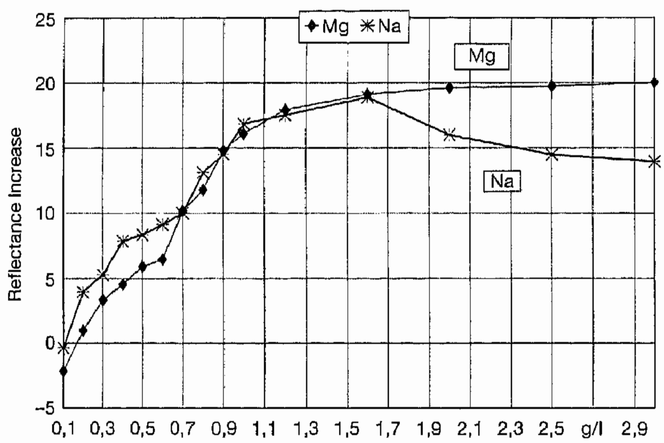

Fig. 13. Detergency, Krefeld 30D, 150 ppm, 30°C

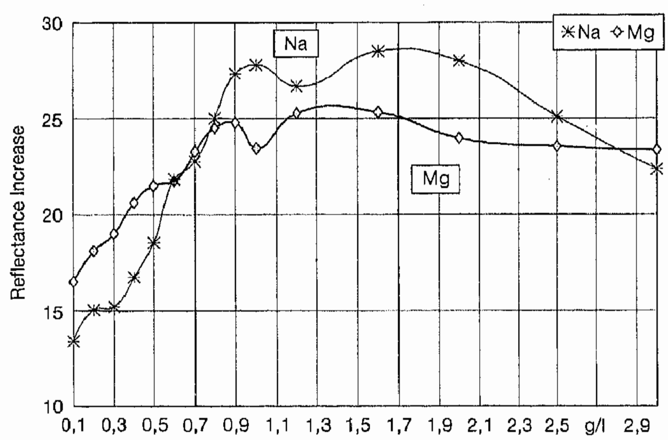

Fig. 14. Detergency, EMPA-101,150 ppm, 30°C

the surfactant concentrates more strongly at the soil/water interface. In this sense LAS-Mg combinations would be very effective [2]. Besides this, magnesium surfactants have larger micelle size than sodium [4] and can theoretically solubilize larger amounts of grease or soil.

To confirm this, many tests have been carried out using different types of soil and varying water hardness. Depending on the latter, different conclusions can be drawn, as shown in Figs. 7, 8 and 9.

The dishwashing method is described in detail in reference 9. It studies particularly the foam stability of different solutions of surfactant to various amounts of soil:

Fat/olive oil: LAS_2Mg performs better than LASNa.

Crisco: Up to 50 ppm LASNa gives better results than LAS_2Mg; beyond 50 ppm, both surfactants behave similarly.

Napolitan sauce: The performance of LAS_2Mg is significantly higher than that of LASNa.

3.2 Detergency

Washing was carried out in the Terg-O-Tometer according to ASTM-D-3050/75.

Detergency vs. water hardness

Different standard artificially soiled clothes were tested as shown in Figs. 10 and 11.

The LAS concentration used of 1.2 g/l, corresponds to a detergent formulation with 20 % active ingredient and a 6 g/l dosage.

Krefeld 30C and 30D: LAS_2Mg performs better than LASNa over the whole water hardness range tested.

EMPA 101 and 104: At low water hardness, LAS_2Mg is more efficient than LASNa.

Detergency vs. surfactant concentration

The test has been carried out at a fixed water hardness, 150 ppm covering a wide surfactant concentration interval, ranging from 0 to 3 g/l.

The results are plotted in Figs. 12, 13, 14 and 15.

Krefeld 30C and 30D

Up to 0.8 g/l, LASNa performs better than LAS_2Mg.

From 0.8 to 3g/l, LAS_2Mg performs as well as or better than LASNa.

EMPA-101 and 104: There are three distinct zones:

From 0 to 0.8 g/l, where LAS_2Mg is superior to LASNa.

From 0.8 to 2.5 g/l, where LASNa is superior to LAS_2Mg.

Beyond 2.5 g/l, where LAS_2Mg is superior to LASNa.

3.3 Foaming power

The results based on the Ross-Miles test plotted on Fig.16, indicate no significant differences between both LAS_2Mg and LASNa surfactants.

4 Biodegradability and toxicity

4.1 Biodegradability

The biodegradability determination was carried out using the OECD 303 A confirmatory test. The elimination in percent

DOC was 85 % for the magnesium salt versus 89 % for the sodium salt, thus indicating that the counterion has no influence on biodegradability.

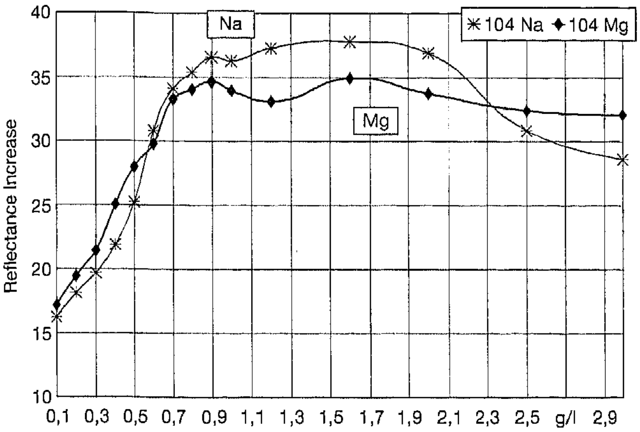

Fig. 15. Detergency, EMPA-104, 150 ppm, 30 °C

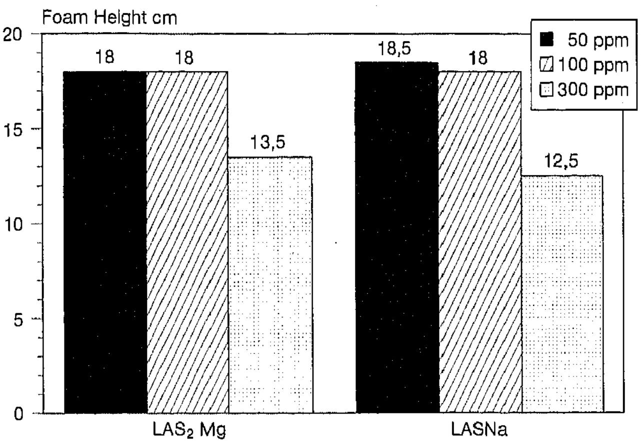

Fig. 16. Ross-Miles test, 0.5 g/l, 49 °C

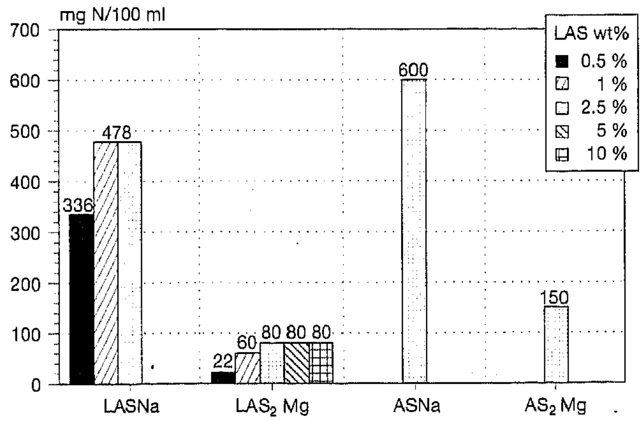

Fig. 17. Zein-Test

Table 1. Toxicity according to the OECD 202 test

	LC50 24 h (ppm)	LC50 48 h (ppm)
LASNa	21,5	8,4
LAS_2Mg	18,2	8,2

4.2 Toxicity with Daphnia Magna

The OECD 202 test method was used. The results which are summarized in Table 1 indicate that the LAS counterion has no significant effect on toxicity.

5 Skin compatibility

The Zein test, a widespread in vitro screening test for evaluating the skin irritancy of surfactants, has been used. The test is based on solubilization of the water-insoluble zein protein by surfactants. Solubilization of zein is measured by determining the nitrogen content of the solubilized protein giving the so called zein number. According to *Kästner* [8] the ability of a surfactant to dissolve the water-insoluble zein protein correlates very well with in vivo test data.

Irritation of human skin is due to the formation of a complex between protein present in the skin and the surfactant. According to *Seibert* [1] the extent to which a combination of anionic surfactant and a protein takes place depends on many factors. Only surfactant monomers or submicellar species penetrate membranes whereas micelles would presumably be too large to penetrate. A reduction of c. m. c. results in lower levels of free monomers and therefore surfactants with high c. m. c. penetrate faster. A review of the literature dealing with the effect of the counterion of anionic surfactants on irritation potential shows that a significant reduction in the latter occurs when magnesium is used as compared to sodium.

The results plotted in Fig. 17 include data for fatty alcohol sulfates (AS) from *Seibert* [1]. These results confirm the above-mentioned theory and demonstrate that magnesium salts are significantly less irritant than sodium salts regardless the surfactant concentration used.

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The authors of this paper

Dr. *Leon Cohen* got his PhD in chemistry at Sevilla University. In 1994 he got the EURCHEM designation. He has been working for Petresa from 1970 to 1996. Since 1989 he has been a professor of chemistry at the university of Cadiz, EUPA, Avda Ramon Puyol s/n. Algeciras/Spain.

Mr. *A. Moreno* graduated in chemistry at Granada University in 1965. In 1969 he joined Petresa where he is currently Head of the Chemical Department.

Mr. *J. L. Berna* graduated in chemistry at the University of Zaragoza (Spain) in 1967 and in Petroleum Technology at Madrid University in 1969. In 1971 he joined Petresa as a Research chemist and he is at present the Research and Development Director of this company.

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