Hydrotropic and Surfactant Properties of Novel Diisopropyl Naphthalene Sulfonates[1]

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ABSTRACT: A novel surfactant and hydrotrope, sodium diisopropylnaphthalene sulfonate (SDIPNS) has been developed. It contains about 92% diisopropylnaphthalene sulfonate, compared to other materials which are less than 50% diisopropylnaphthalene sulfonate. Aqueous solutions of 34-36% active SDIPNS have dual functionality. They have excellent surface properties and are compatible with conventional anionic, nonionic, and amphoteric surfactants. They demonstrate good laundering detergency in combination with sodium lauryl ethoxy sulfate, with or without builder. They maintain surface activity in 150 ppm hard water (Ca^{2+}/Mg^{2+} = 2:1), 5% NaCl, pH 2, and pH 12. They are effective hydrotropes. They enhance surfactant solubility, raise the cloud point of nonionic surfactants, and modify the viscosity of surfactant formulations. They are light in color and are low-foaming.

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KEY WORDS: CMC, Draves wetting, hydrotrope, laundry, organic solvents, sodium diisopropylnaphthalene sulfonate, surface tension, surfactant, viscosity modification.

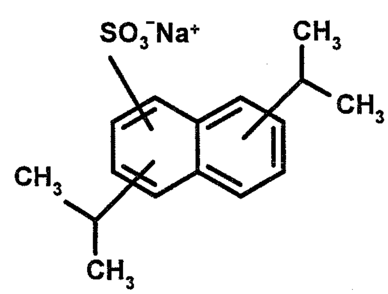
A unique sodium diisopropylnaphthalene sulfonate (SDIPNS) that contains about 92% diisopropylnaphthalene sulfonate has both hydrotropic and surfactant properties. There are several definitions of hydrotropy and hydrotropes in the literature. "Hydrotropy is the solubilizing effect in water caused by materials that need not be surface active and that do not need to form micelles to effect their action" (1). Hydrotropes are "shortchain organic compounds with a polar group that could serve as agents to dissolve poorly water soluble substances into water, if added in high concentrations" (2). Surfactants display surface activity.

Alkylbenzenesulfonates and alkylnaphthalenesulfonates act as hydrotropes to modify solubilities, viscosities, and other properties of surfactants and surfactant formulations. Sodium toluenesulfonate and sodium xylenesulfonate are the best-known hydrotropes, but alkylnaphthalenesulfonates also possess hydrotropic properties. A paper was presented at the 1997 AOCS Annual Meeting, and subsequently published, describing the hydrotropic properties of some short-chain alkylbenzene- and alkylnaphthalene sulfonates (3). Another paper was presented at the 1998 AOCS Annual Meeting describing some of the hydrotropic properties of a novel alkylnaphthalene sulfonate, SDIPNS. It was published as well (4). This paper describes both hydrotropic and surfactant properties of that material.

A 35% active aqueous solution of SDIPNS is a multifunctional ingredient, acting both as an effective hydrotrope and as a surfactant.

EXPERIMENTAL PROCEDURES

Materials. SDIPNS is available as high-salt (SDIPNS–HS) and low-salt (SDIPNS–LS) versions. The only difference between them is the sodium sulfate content. The LS version contains less than 1% sodium sulfate, while the HS version can contain up to 7% sodium sulfate. A total of five brands of diisopropylnaphthalene sulfonate is on the market in the United States. About 92% of the naphthalene sulfonate in the materials discussed in this paper is diisopropylnaphthalene sulfonate, as described in a previous paper (4), with the remainder being mono- and triisopropylnaphthalene sulfonates. The material is a mixture of isomers where the isopropyl moieties can appear at any carbon in the naphthalene system. SDIPNS–HS and SDIPNS–LS were obtained from RÜTGERS Organics Corporation (State College, PA). The structure is shown in Scheme 1.



SCHEME 1

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Ethoxylated alcohol surfactants were supplied by Shell Chemical Company (Houston, TX). The solvent *d*-limonene was supplied by Florida Chemical Company (Winter Haven, FL). Sodium hexyldiphenyloxide disulfonate and sodium dodecyldiphenyloxide disulfonate were supplied by The Dow Chemical Company (Midland, MI). Other chemicals were acquired from laboratory supply houses. Unless otherwise specified, deionized water was used to prepare surfactant dilutions. Hard water, as referred to in this paper, was prepared as 100 ppm Ca^{2+} and 50 ppm Mg^{2+} by using $MgCl_2 \cdot 6H_2O$ and $CaCl_2 \cdot 2H_2O$ to approximate typical hard water as found in U.S. tap water. For testing in HS conditions, a solution of 5% NaCl was used.

Diisopropylnaphthalene sulfonates, 35% active, are denoted by the letters “A,” ”S,” and ”M.”

Methods. Clarity and turbidity were visual observations. Viscosities were measured on a Brookfield LVDV-II+ viscometer (Stoughton, MA). Cloud points were determined using the ASTM method (5). Ross-Miles foam tests were done using the ASTM method (6). Surface tension was measured using a DuNoüy ring tensiometer supplied by CSC Scientific Company (Fairfax, VA) and a Krüss K 10 ST Digital Tensiometer supplied by Krüss USA (Charlotte, NC). The critical micelle concentration (CMC) was determined by plotting surface tension on the y-axis against the logarithm of concentration on the x-axis and observing the concentration at which the slope becomes zero. Solubilities were measured by determining the maximum concentration of solute which would result in a clear, stable solution. Terg-O-Tometer® testing was done by Scientific Services S / D, Inc. (Sparrow Bush, NY). Structures were prepared on Isis Draw (MDL Information Systems, San Leandro, CA); graphs were drawn using Statistica (Statsoft Inc., Tulsa, OK).

RESULTS AND DISCUSSION

A working definition of a hydrotrope is that it is a short-chain, organic compound with a polar group which maintains single phase, optically clear, thermodynamically stable concentrated mixtures of surfactant that would otherwise phase separate in the absence of the hydrotrope. It prevents phase separation from aqueous solution by modifying the association structures of the more hydrophobic surfactants. Conventional hydrotropes are amphiphilic but with less hydrophobic character than common surfactants. In general, they do not form micelles and are, at most, weakly surface-active. SDIPNS performs a dual function in formulations by providing both surfactant properties and hydrotrope properties.

Surface activity. Unlike conventional hydrotropes such as sodium xylene sulfonate (SXS), SDIPNS–HS reduces the surface tension and forms micelles in aqueous solution. Thus, the molecule performs a dual function by providing surfactant properties as well as hydrotrope properties to formulations. The CMC is slightly higher than 1% active, as indicated in Figure 1. SDIPNS–HS also can be used in applications requiring high electrolyte concentrations. It retains its surfactant properties in 5% aqueous NaCl, in 150 ppm hard water (Ca^{2+} / Mg^{2+}), and at high and low pH, as Figure 2 shows.

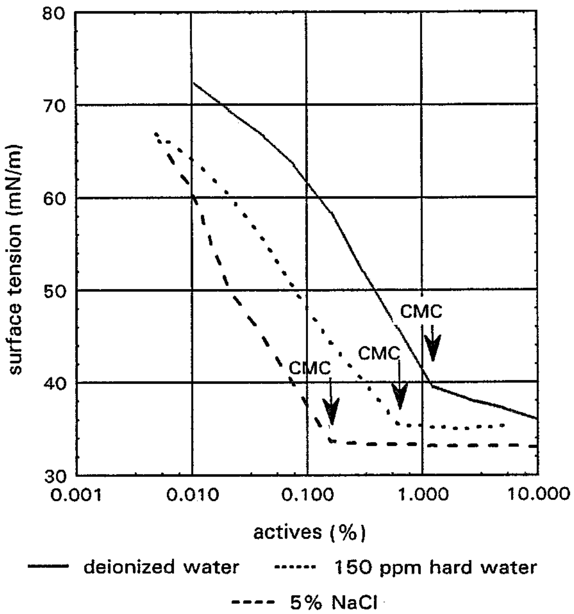

FIG. 1. Surface tension of sodium diisopropylnaphthalene sulfonate-high salt (SDIPNS–HS) at 20°C. CMC, critical micelle concentration.

SDIPNS–HS is completely compatible with conventional anionic, nonionic, and amphoteric surfactants, such as alkyl benzene sulfonate, alkyl sulfate, alkyl ethoxy sulfate, or alcohol ethoxylate. Figure 3 summarizes CMC and surface tension information for combinations of other surfactants with SDIPNS–HS and when tested in additional conditions. The surface properties of combinations of SDIPNS–HS with conventional surfactants are generally dominated by the conventional surfactant.

Laundering tests. In Terg-O-Tometer tests, the combination of SDIPNS–HS and sodium lauryl ethoxy sulfate (SLES-3EO) showed good performance. SDIPNS–HS in a zeolite-built powder and an unbuilt liquid were compared to a sodium dodecylbenzene sulfonate (SDDBS) / SLES-3EO blend and to two commercial laundry detergents. Good performance was observed when SDIPNS–HS replaced SDDBS in a SDDBS / SLES-3EO combination. The comparisons are shown graphically in Figure 4. The total score shown is the total reflectance increase for the soiled swatches after washing minus the redeposition score. With its low-foaming nature, SDIPNS–HS is amenable for use in laundering conditions without excessive foam, e.g., horizontal-axis washing machines.

Draves wetting. SDIPNS–HS and SDIPNS–LS demonstrate intermediate wetting times compared to other materials, as shown in Figure 5. Compatibility with conventional surfactants is shown in Figure 6 for Draves wetting times with combinations of 1:3 SDIPNS and conventional surfactants.

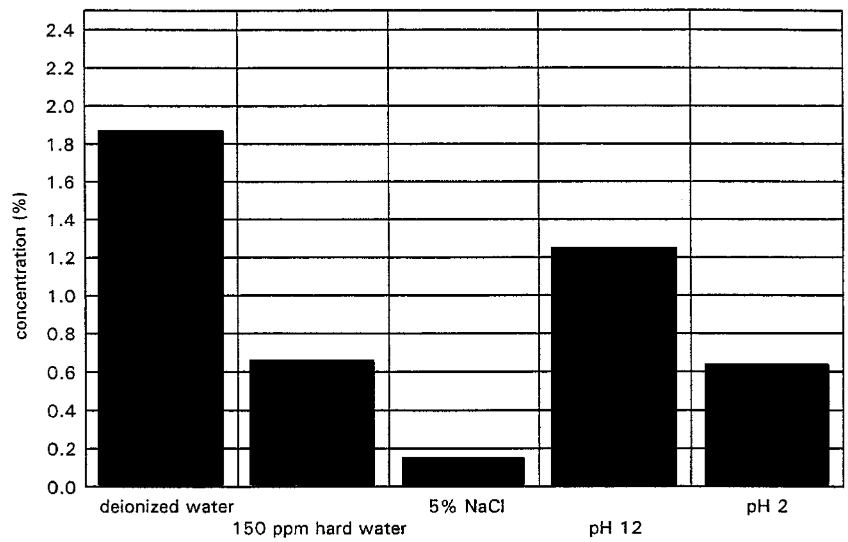

FIG. 2. CMC of SDIPNS–HS under various conditions at 20°C. See Figure 1 for abbreviations.

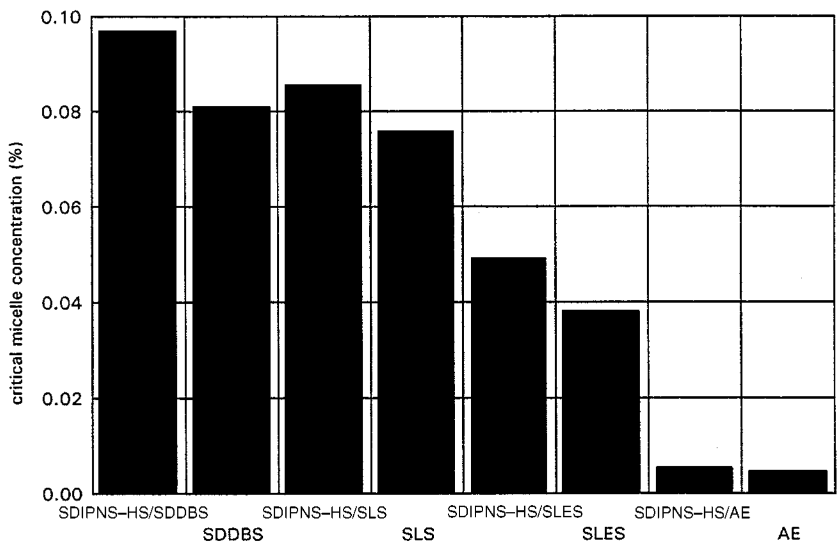

FIG. 3. CMC of 1:3 SDIPNS–HS/conventional surfactant at 20°C. SDDBS, sodium dodecylbenzene sulfonate; SLS, sodium lauryl sulfate; SLES, sodium lauryl ethoxy-3EO sulfate; AE, alcohol ethoxylate denoted as C_nEO_x where n = hydrocarbon chain length and x = degree of ethoxlation. Unless otherwise indicated material used was $C_{12-15}EO_9$. See Figure 1 for other abbreviations.

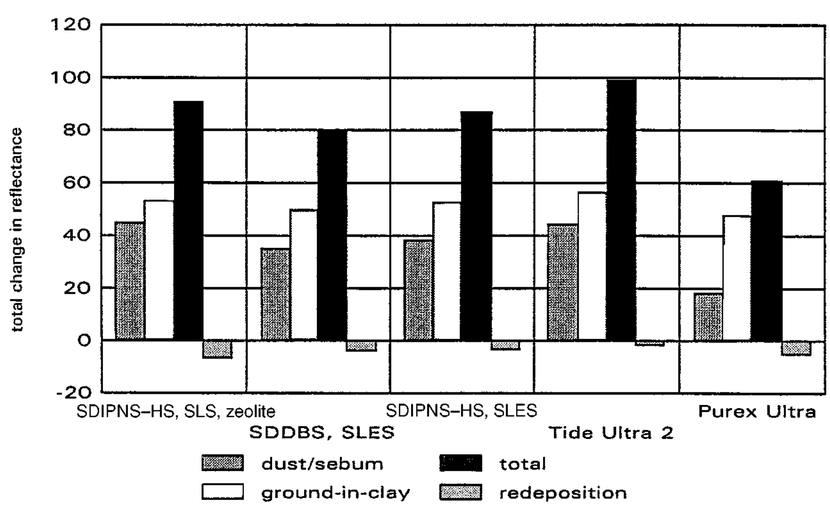

FIG. 4. Terg-O-Tometer comparisons: 41°C, 10 min wash, 5 min rinse. See Figures 1 and 3 for abbreviations.

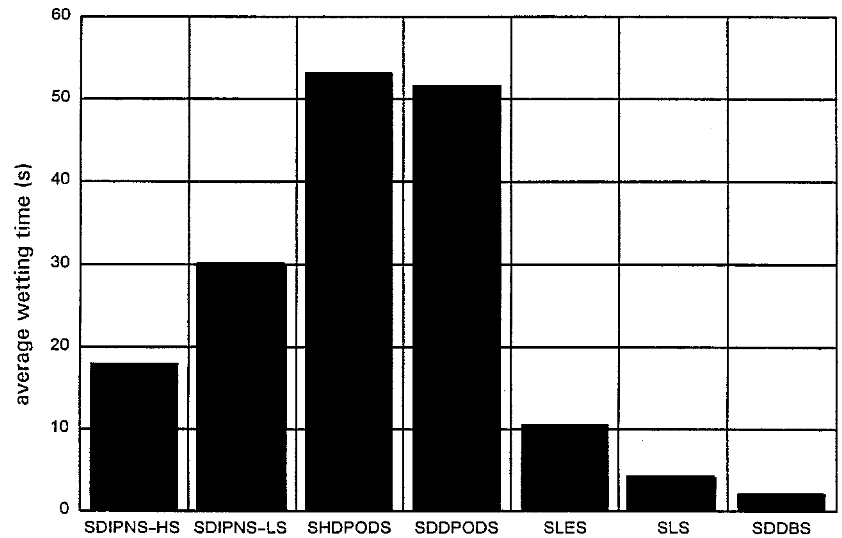

FIG. 5. Draves wetting times, 0.5% active, 21°C, 5 g cotton skein. LS, low salt; SHDPODS, sodium hexyldiphenyloxide disulfonate; SDDPODS, sodium dodecyldiphenyloxide disulfonate. See Figures 1 and 3 for other abbreviations.

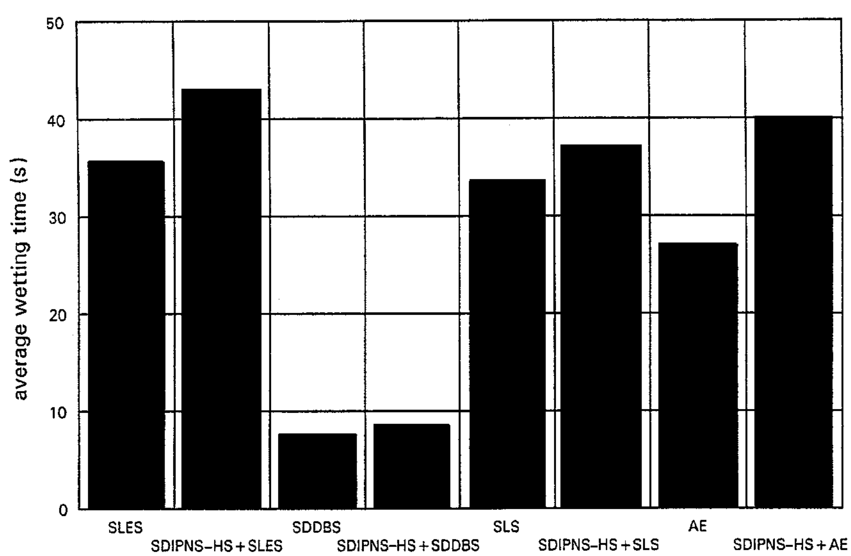

FIG. 6. Draves wetting times, 0.1% actives, 21°C, 5 g cotton skein. Combinations are 1:3 SDIPNS/conventional surfactant. See Figures 1 and 3 for abbreviations.

Solubility of organic solvents. SDIPNS–HS has exceptional power to solubilize organic solvents, especially chlorinated solvents. Percentages of organic solvents that are solubilized with SDIPNS–HS are as follows: 1,1,1-trichloroethane, 40.1; tetralin, 35.7; *m*-dichlorobenzene, 31.7; methyl acetate, 30.0; benzene, 22.9; hexanol, 21.9; toluene, 20.5; tetrachloroethylene, 19.6; *d*-limonene, 18.4; cumene, 15.2; 1-hexene, 9.4; cyclohexane, 9.4; nonene, 6.8; octane, 5.1; and kerosene, 4.3. With chloroform, SDIPNS–HS forms a clear, inverse micelle phase in all proportions. The organic solvent *d*-limonene has high solubility in SDIPNS. It is soluble up to 18% in 35% active SDIPNS–HS and 8% in 35% active SDIPNS-LS. The graph in Figure 7 compares *d*-limonene solubility in SDIPNS to other diisopropylnaphthalene sulfonates, and the graph in Figure 8 compares it to conventional hydrotropes, e.g. sodium cumene sulfonate, SXS, and sodium toluene sulfonate. Spray-dried SDIPNS–LS is soluble in both pine oil, up to an equal weight ratio, and *d*-limonene, forming nonaqueous solutions. The solubility of toluene is about 25% in 35% active SDIPNS–HS and about 15% in 35% SDIPNS–LS. The high toluene solubility in SDIPNS is shown in Figures 9 and 10,

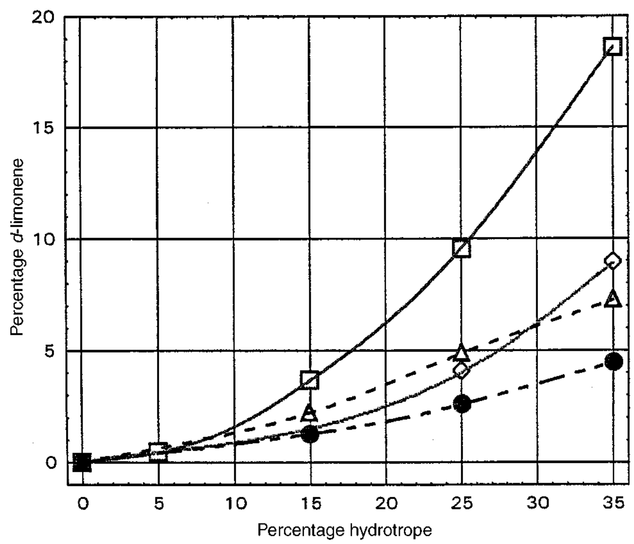

FIG. 7. Solubility of *d*-limonene in SDIPNS and other diisopropylnaphthalene sulfonates. □, SDIPNS–HS; ◇, SDIPNS–LS; △, "M"; ●, "S." "M" and "S," coded comparable products; see Figures 1 and 5 for abbreviations.

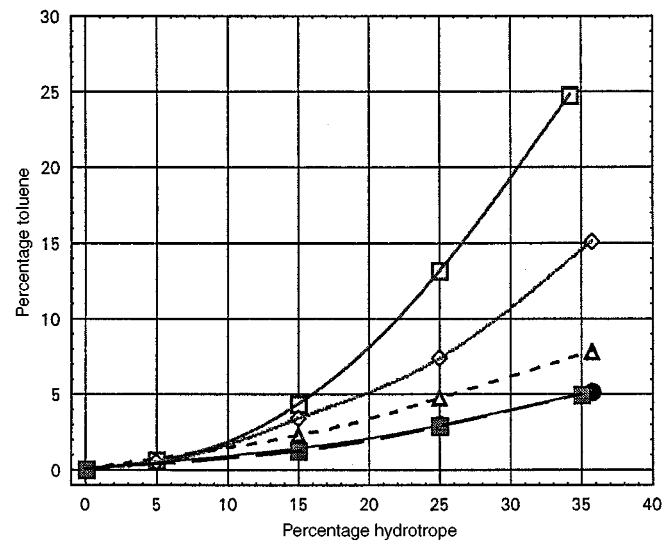

FIG. 9. Solubility of toluene in SDIPNS and other diisopropylnaphthalene sulfonates. □, SDIPNS–HS; ◇, SDIPNS–LS; △, "M"; ●, "A"; ■, "S." See Figures 1 and 5 for abbreviations.

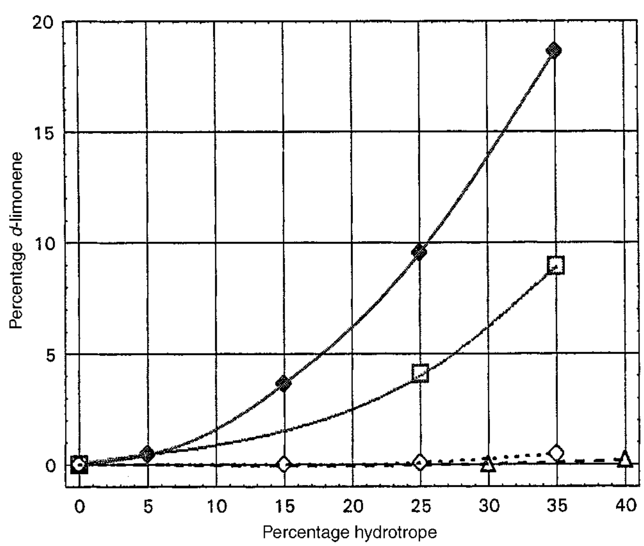

FIG. 8. Solubility of *d*-limonene in SDIPNS and conventional hydrotropes. ◆, SDIPNS–HS; □, SDIPNS–LS; △, SXS; ◇, SCS. SXS, sodium xylene sulfonate; SCS, sodium cumene sulfonate. See Figures 1 and 5 for other abbreviations.

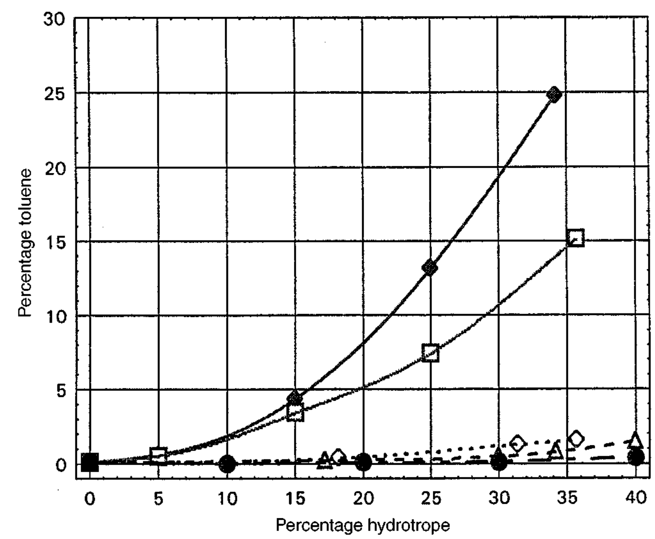

FIG. 10. Solubility of toluene in SDIPNS and conventional hydrotropes. ◆, SDIPNS–HS; □, SDIPNS–LS; ◇, SCS; △, SXS; ●, STS. STS, sodium toluene sulfonate. See Figures 1, 5, and 8 for other abbreviations.

in comparison to other diisopropylnaphthalene sulfonates in Figure 9 and in comparison with conventional hydrotropes in Figure 10.

Cloud-point elevation for nonionic surfactants. Hydrotropes raise the cloud point of nonionic surfactants. SDIPNS is a very efficient hydrotrope for cloud-point elevation. The HS and LS versions have a similar effect. This is illustrated in the graph in Figure 11 where the cloud-point elevation of a 1% solution of a 9-mole ethoxylated C12–15 alcohol by SDIPNS is compared to several other materials.

Viscosity modification. Hydrotropes modify the viscosity of surfactant formulations; SDIPNS is an efficient hydrotrope for viscosity control. LS and HS versions have a similar effect. The graph in Figure 12 shows the effect on the following typical heavy-duty liquid formulation: dodecyl benzene sulfonic acid, 29.10%; diethanolamine, 5.30%; 9-mole ethoxylated alcohol, C_{12}–C_{15}, 5.00%; hydrotrope, as indicated; NaOH, 2.30%; and deionized water, remainder.

Foam properties. SDIPNS–HS alone is a low-foaming surfactant and can be used as the sole surfactant where

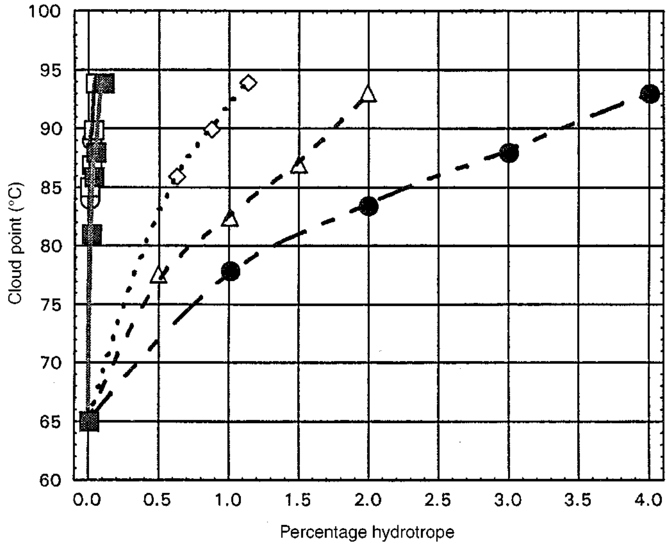

FIG. 11. Effect of hydrotrope on cloud point of 1% C_{12-15} alcohol, 9-mole ethoxylate. ○, SDIPNS–HS; □, SDIPNS–LS; ◇, SCS; △, SXS; ●, STS; ■, SHDPODS. See Figures 1, 5, 8, and 10 for abbreviations.

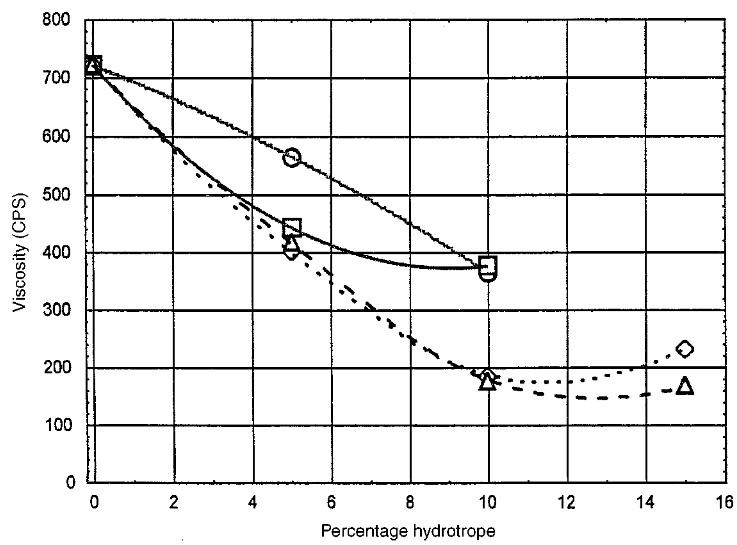

FIG. 12. Viscosity of a heavy-duty liquid formulation at 25°C. ○, SCS; □, SDIPNS–HS; ◇, SXS; △, STS. See Figures 1, 8, and 10 for abbreviations.

low foam is a requirement. It can be combined with other surfactants to yield high-foaming formulations. Figure 13 shows Ross-Miles foam heights for combinations of SDIPNS–HS with sodium lauryl sulfate, SLES, SDDBS, and alcohol ethoxylate at a ratio of SDIPNS–HS/surfactant of 1:3.

Color. SDIPNS–HS and SDIPNS–LS have Gardner color values of 3 to 4. This corresponds to a light yellow color that is comparable to conventional surfactants. This light color is achieved with no postprocessing color removal, so there is no bleach residue in the material. Figure 14 shows the color of SDIPNS, several conventional surfactants, and another diisopropylnaphthalene sulfonate.

Compatibility. SDIPNS–HS is completely compatible with anionic, nonionic, and amphoteric surfactants. For example, it is compatible with alkyl benzene sulfonate, alkyl sulfate, alkyl ethoxy sulfate, and alcohol ethoxylate. The surface properties of combinations of SDIPNS–HS with conventional surfactants are influenced most strongly by the conventional surfactant. The phase diagrams in Figures 15–17 demonstrate the range of single-phase behavior.

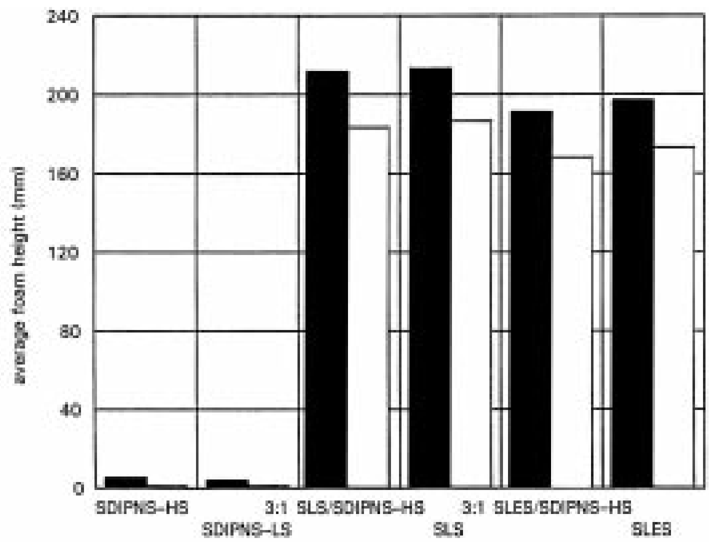

FIG. 13. Ross-Miles foam heights, 0.1% total actives, 21°C. ■, Initial; □, 5 min. See Figures 1, 3, and 5 for abbreviations.

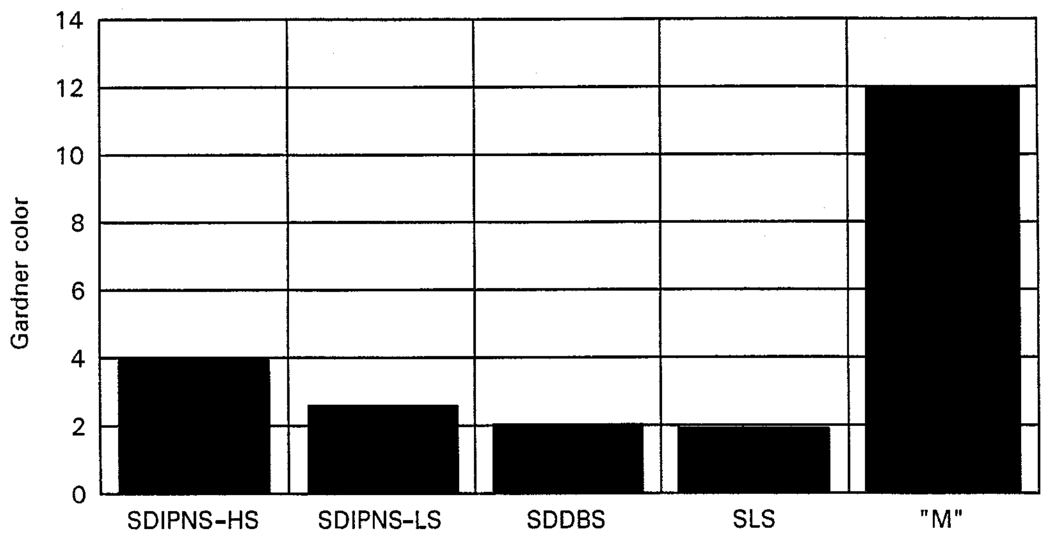

FIG. 14. Gardner color, 35% aqueous solutions. See Figures 1, 3, and 5 for abbreviations.

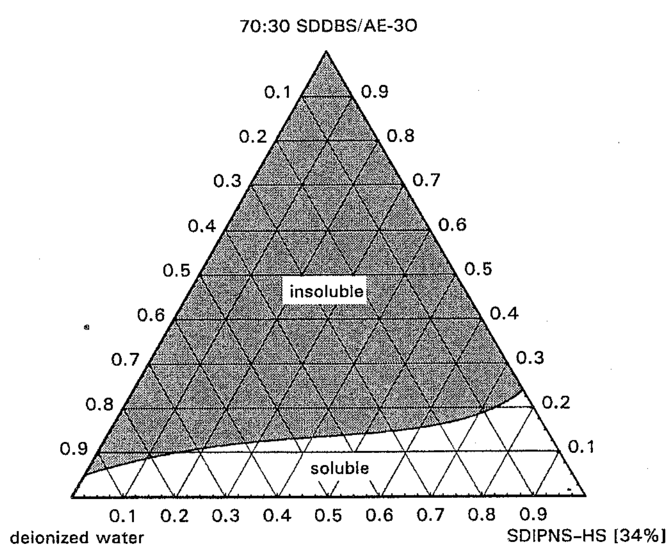

FIG. 15. SDIPNS/70:30 SDDBS/AE-3EO/DI water. See Figures 1 and 3 for abbreviations.

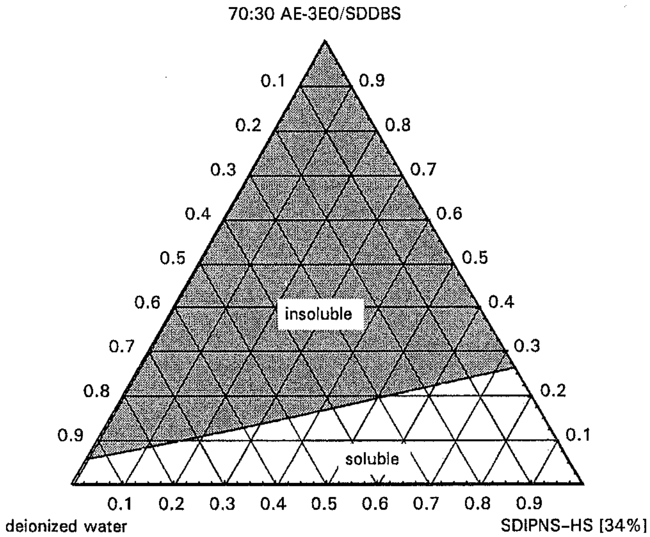

FIG. 16. SDDBS/70:30 AE-3EO/SDDBS/deionized water. See Figures 1 and 3 for abbreviations.

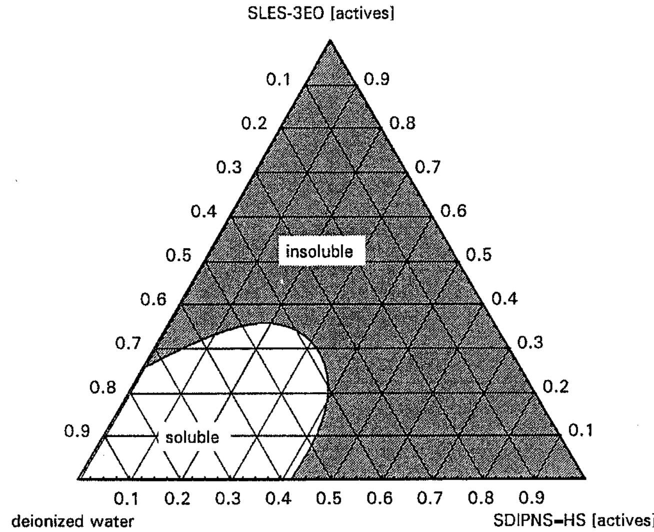

FIG. 17. SDIPNS/SLES-3EO/deionized water. See Figures 1 and 3 for abbreviations.

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