# Surfactant-Mediated Phase Transfer as an Alternative to Propanesultone Alkylation. Formation of a New Class of Zwitterionic Surfactants†

Kirk D. Schmitt*

*Central Research Laboratory, Mobil Research and Development Corporation, P.O. Box 1025, Princeton, New Jersey 08543*

*Received December 5, 1994*®

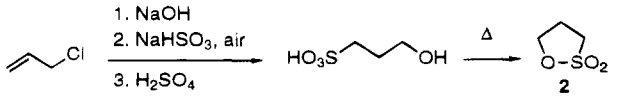
A synthesis of propanesulfonate surfactants **5** is presented which avoids carcinogenic propanesultone **2** as an alkylating agent. A small amount of the final desired surfactant or an easily destroyed sulfate surfactant is added to a starting alcohol **3** as a phase transfer agent, the alcohol is converted to its corresponding allyl ether **4** with 50% NaOH and allyl chloride, and the allyl ether is converted to propane sulfonate **5** by air-catalyzed addition of bisulfite. Diallyl ether produced as a solvolysis byproduct is cyclized to furan sulfonate **9**. Cyclization of diallylamine with bisulfite produces pyrrolidinium sulfonate **13** and diallylmethylalkylammonium salts **14** yield a new class of zwitterionic surfactants **11** which are substantially more soluble in both water and hydrocarbons than the corresponding ammonium propanesulfonates, **12**. The stereochemistry of the cyclic products is consistent with a radical chain mechanism for the addition of bisulfite.

## Introduction

Enhanced recovery of oil from subterranean reservoirs by miscible water flooding requires surfactants which produce very low interfacial tension between crude oil and connate water, which are thermally stable, and which, above all, are cheap. The water in reservoirs can often be described more appropriately as brine, with salt concentrations ranging from 1 to 30% and concentrations of calcium or magnesium not in the 100 ppm range usually associated with hard water, but as high as 1000–10 000 ppm. Surfactants must be stable from 30 to 110 °C for periods as long as 1 or 2 years. The economics of recovery is dominated by the cost of the surfactant.[1] In this report we describe a synthesis which dramatically lowers the cost of production of a class of highly brine tolerant surfactants. Mechanistic considerations of this synthesis led to the design of a new class of zwitterionic surfactants which have utility in both aqueous and nonaqueous systems.

For oil recovery from shallow reservoirs where salt concentrations are <2%, petroleum sulfonate surfactants suffice. They are both cheap and stable. As salt concentrations increase it is necessary to make the surfactant increasingly hydrophilic. This can be accomplished relatively inexpensively by ethoxylation of alcohols or phenols. To increase the optimum temperature[2] and to further increase hydrophilicity,[3] sulfate or sulfonate end groups are generally used in addition to ethoxylation, **1a-1d** ($R(OCH_2CH_2)_nO(CH_2)_mSO_3Na$, $n$ = 2–10, **a-d** $m$ = 0–3). Commercially available sulfates **1a** have excellent tolerance for brine[4] but the sulfate group is easily hydrolyzed[5,6] under reservoir conditions. Methane- and ethanesulfonates **1b** and **1c** are more stable than **1a**, but the first truly stable homologues are the propanesulfonates **1d**.

Propanesulfonates of amines, alcohols, and phenols are conveniently prepared in the laboratory using propanesultone, **2**. Propanesultone reacts directly with amines




**2**

to form zwitterionic ammonium propanesulfonates[7,8] and has been reported to react directly with methanol,[9] but its direct reaction with fatty alcohols and phenols is complicated by side reactions and a small equilibrium constant. Consequently, alcohols and phenols are invariably converted to their alkoxide salts with sodium or sodium methoxide and then reacted with propanesultone to form the sodium propanesulfonate **1d**.[10,11]

Propanesultone is manufactured by a multistep sequence where the most critical step involves a distillative cyclization which apparently must be carried out on a relatively small scale using a thin film if yields are to be high.[12] In addition to being an expensive component in a propanesulfonate synthesis, propanesultone is also a potent carcinogen[13,14] as measured by topical and internal

* To whom correspondence should be addressed. Phone: 609-737-4227. Fax: 609-737-4722. E-mail: kdschmitt@crl.mobil.com.

† Dedicated to Professor Glen A. Russell on the occasion of his 70th birthday and in memory of Dr. Robert F. Bridger.

® Abstract published in *Advance ACS Abstracts,* July 1, 1995.

(1) Bansal, V. K.; Shah, D. O. In *Micellization, Solubilization, and Microemulsions*; Mittal, K. L., Ed.; Plenum Press: New York, 1987; pp 87–115.
(2) Herrmann, C. U.; Klar, G.; Kahlweit, M. In *Microemulsions*; Robb, I. D., Ed.; Plenum Press: New York, 1982; pp 1–17.
(3) Boyle, M. H.; McDonald, M. P.; Rossi, P.; Wood, R. M. In *Microemulsions*; Robb, I. D., Ed.; Plenum Press: New York, 1982; pp 103–114.
(4) Austad, T.; Bjørkum, P. A.; Rolfsvåg, T. A. *J. Pet. Sci. Eng.* **1991**, *6*, 125.
(5) Kurz, J. L. *J. Phys. Chem.* **1962**, *66*, 2239–2246.
(6) Austad, T.; Fjelde, I. *Coll. Surf. A: Phys. Eng. Aspects* **1993**, *81*, 263-267.
(7) Linfield, W. M.; Abend, P. G.; Davis, G. A. *J. Am. Oil. Chem. Soc.* **1963**, *40*, 238.
(8) Parris, N.; Weil, J. K.; Linfield, W. M. *J. Am. Oil. Chem. Soc.* **1976**, *53*, 60–63.
(9) Helberger, J. H.; Heyden, R. W.; Winter, H. M. *Liebigs Ann. Chem.* **1954**, *588*, 71.
(10) Gartner, V. R. U. S. Patent 2 799 702, 1957.
(11) Helberger, J. H. et al. German Patent 743 570, 1954.
(12) Helberger, J. H. *Liebigs Ann. Chem.* **1954**, *588*, 71.
(13) Ashby, J.; Paton, D. *Mutat. Res.* **1993**, *286*, 3–74
(14) Paxman, D. G.; Robinson, J. C. *Regul. Toxicol. Pharmacol.* **1990**, *12*, 296–308.

0022-3263/95/1960-5474$09.00/0 

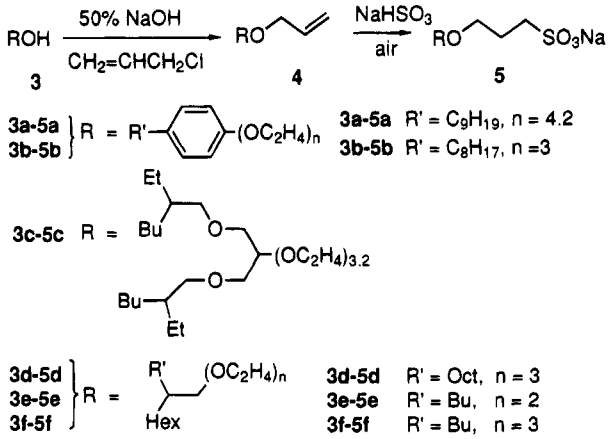
**Table 1. Reaction of Allyl Chloride, 50% NaOH, and 3a at 100 °C**

| time at reflux (h) | uncatalyzed reactn (% completion) | reactn catalyzed by **5a** (% completion) |
|---|---|---|
| 1 | 70 | 84 |
| 3 | 77 | 86 |
| 6 | 79 | 97 |
| 22 | 83 | 99 |

application to mice[15,16] and by back-mutation in microorganisms.[16,17]

## One-Pot Synthesis of Propanesulfonate Surfactants

Our sulfonate synthesis is adapted from the synthesis of propanesultone. An ethoxylated alcohol or phenol (**3**) is alkylated with allyl chloride and the resulting ether (**4**) converted to the propanesulfonate (**5**) by addition of bisulfite. To reduce costs and minimize the formation of hazardous wastes an all-aqueous route was developed.




Gibson[18] studied the reaction $RX + HO(CH_2CH_2O)_nH \rightarrow R(CH_2CH_2O)_nH$ and found that glycols act as phase transfer catalysts, but mono- and diethers do not. With 50% NaOH as base, no organic solvent, and only a 2- to 4-fold excess of glycol, he was able to obtain high selectivity to the monoether by virtue of the fact that, as the reaction proceeds, the glycol phase transfer agent is consumed. This reaction has been exploited by others.[19-21] With an excess of the more reactive allyl chloride and using 50% NaOH we find that polyether alcohols can also function as phase transfer catalysts. The reaction of ethoxylate **3a** was rapid at first but, as the concentration of **3a** fell, it slowed and stopped at around 80% conversion to ether **4a**. This was true even if a large excess of base and allyl chloride was used, indicating it is the polyether alcohol which is promoting the reaction.

If ≤20 mol % of sulfonate **5a** is added to the reaction mixture to maintain phase transfer efficiency, the conversion of ethoxylate **3a** was quantitative (Table 1). After distillation of the excess allyl chloride, air was bubbled through and aqueous bisulfite added. Ether **4a** was converted quantitatively to a 96:4 mixture of sulfonate **5a** and the corresponding sulfite **6a** for an overall yield of 95%. Sulfite addition does not take place at all without an added surfactant. Sufficient surfactant must be added to produce a nearly or completely homogeneous appearing mixture. An alcohol cosolvent is extremely important in determining the relative formation of sulfite **6a** versus sulfonate **5a**. Table 2 shows that a wide range of alcohol cosolvents produce high conversion of ether **4a** but that MeOH (or no cosolvent) produces predominately sulfite and that higher alcohols produce mainly sulfonate **5a**. In general, for **5a-5f**, EtOH is the optimum cosolvent.

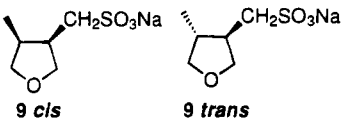
**Table 2. Effect of Substituting Alcohol Cosolvents on Product Mix (4: alcohol:$H_2O$ ≈ 250 mmol:40 mL:50 mL)**

| cosolvent | conversion (**4** → **5** + **6**) | sulfonate:sulfite (**5**:**6**) |
|---|---|---|
| none | 96 | 3:97 |
| MeOH | 95 | 15:85 |
| EtOH | 99 | 96:4 |
| *n*-PrOH | 94 | 90:10 |
| *i*-PrOH | 99 | 85:15 |
| *t*-BuOH | 99 | 86:14 |

Addition of some of the final product to catalyze the reaction has a certain chicken-or-egg character, but it is not necessary to use the actual desired product. Conversion is 50–85% in the uncatalyzed alkylations, and commercially available sulfates such as Neodol sulfate, $C_{12}H_{25}(OCH_2CH_2)_nOSO_3Na$, can be used to promote the sulfitation. Sulfates can be removed by hydrolysis in acid or base followed by extraction or liquid chromatography. Ethoxylates **3b-f** were converted to sulfonates **5b-5f** in 87-96% overall yield after a first cycle bootstrapped by Neodol sulfate.

## Mechanistic Considerations

HPLC analysis of the sulfitation reaction showed the same two minor sulfonates in each reaction. On the basis of retention times, these could have been **7**, $HOCH_2CH_2CH_2SO_3Na$, and **8**, $O(CH_2CH_2CH_2SO_3Na)_2$, from sulfitation of allyl alcohol and allyl ether (both of which were detected by GC). Addition of bisulfite to allyl alcohol confirmed that the peak assigned to **7** was the monosulfonate, but when 2 mol of bisulfite was added to 1 mol of diallyl ether, only the first half of the addition was exothermic and the products that resulted were the cyclic sulfonates, **9**. The retention time of sulfonates **9** matched the unknown.

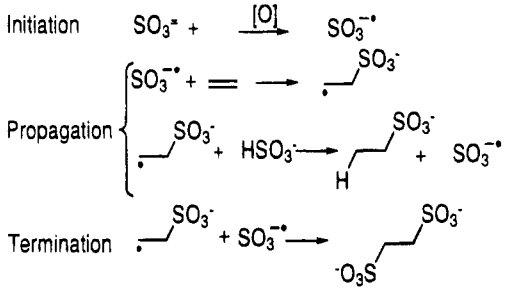



The major isomer (**9-*cis*:9-*trans*** = 3:1) was assigned the *cis* structure because of the relative upfield shifts of its $CH_2SO_3$ and $CH_3$ carbons.[22-24]

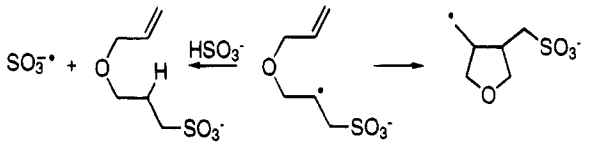
Formation of the *cis* five-membered ring is consistent with the mechanism of addition of bisulfite to olefins.[25,26] The reaction probably proceeds via a radical chain. That

(15) Ulland, B.; Finkelstein, M.; Weisburger, E. K.; Rice, J. M.; Weisburger, J. H. *Nature (London)* **1971**, *230*, 460–1.
(16) Slaga, T. J. et al. *Cancer Res.* **1973**, *33*, 769–776.
(17) Mohn, G. *Arch. Toxikok.* **1971**, *28*, 93–104.
(18) Gibson, T. *J. Org. Chem.* **1980**, *45*, 1095-1098.
(19) Palegrosdemange, C.; Simon, E. S.; Prime, K. L.; Whitesides, G. M. *J. Am. Chem. Soc.* **1991**, *113*, 12–20.
(20) Strzelbicki, J.; Charewicz, W.; Beger, J.; Hinz, L. *Can. J. Chem.* **1988**, *66*, 1695-1700.
(21) Sukata, K. J. *Synth. Org. Chem. Jpn.* **1981**, *39*, 443–444.
(22) Friedel, R. A.; Retcotsky, H. L. *J. Am. Chem. Soc.* **1963**, *85*, 1300–1306.
(23) Dalling, D. K.; Grant, D. M. *J. Am. Chem. Soc.* **1967**, *89*, 6612–6622.
(24) Christl, M.; Reich, H. J.; Roberts, J. D. *J. Am. Chem. Soc.* **1971**, *93*, 3463–3468.
(25) Norton, C. J.; Seppi, N. F.; Reuter, M. J. *J. Org. Chem.* **1968**, *33*, 4158–4165.
(26) Mayo, F. B.; Walling, C. *Chem. Rev* **1940**, *27*, 351–412.

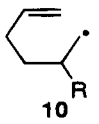
the mechanism is a radical mechanism may be deduced from the fact that the addition does not proceed at all if air is not bubbled through. That it is a chain may be deduced from the fact that at least 250 mol of olefin are converted for every mole of $O_2$ passed through the reactor.




In the specific case of allyl ether the first formed alkyl radical has the option of either cyclizing or abstracting a hydrogen from bisulfite.



Two factors probably control the complete formation of cyclic product. First, the rates of radical cyclization in hexenyl systems such as **10** tend to be high with

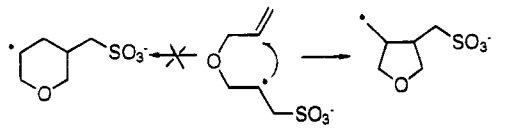


**10**

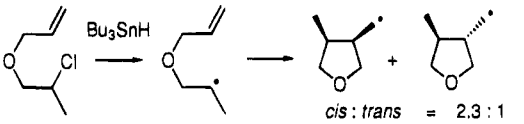
typical unimolecular rate constants[27] of about $10^5-10^6$ $s^{-1}$. Second, we added the bisulfite to the olefin solution at a rate such that the concentration of bisulfite was quite low, probably never higher than $10^{-3}$ mol/L. If $[NaHSO_3] \leq 10^{-3}$ mol/L, the chain transfer rate constant would have to be within a factor of 10–100 of diffusion controlled to compete with cyclization.

$$k_{\text{chain transfer}} > \frac{10^5-10^6\ \text{s}^{-1}}{10^{-3}\ \text{mol/L}} = 10^8-10^9\ \text{L/mol s}$$

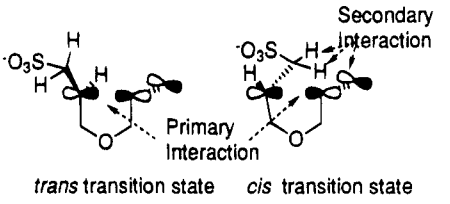
Formation of the less stable primary tetrahydrofuranyl radical instead of the more stable secondary tetrahydropyranyl radical is consistent with the kinetic control of hexenyl radical cyclization generally seen when the olefinic part of the molecule is unsubstituted.[28]



Formation of mainly **9-*cis*** is consistent with the experimental observations of Beckwith.[29,30] Beckwith noted that the hexenyl radical formed by tri-*n*-butyltin hydride abstraction of chlorine from 2-chloropropyl allyl ether also cyclizes to a predominantly *cis*-tetrahydrofuranyl methyl radical in about the same *cis/trans* ratio we observe.




The stereoselectivity of this and similar cyclizations was anticipated in calculations by Hoffman and Moss.[31] They predicted a stabilization of the transition state leading to the *cis* product as long as the transition state occurs early on the reaction coordinate, that is, before steric repulsion can become dominant. Since the rate is very rapid, an early transition state is indicated. The stabilization is thought to arise via a hyperconjugative delocalization of the C–H $\sigma$ and $\sigma^*$ orbitals with the olefin p orbital. The transition state leading to the *cis* product has this type of favorable secondary interaction; the *trans* does not.



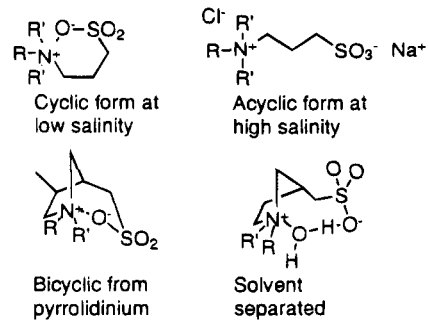

Addition of sulfite to olefins in our system is controlled by the solvent composition. In surfactant in water, C–O bond formation predominates, but in surfactant, alcohol, and water C–S bond formation is favored, Table 2. Mainly C–S addition of $SO_3^-$ to olefins has been explained by Ozawa and Kwan[32] to be because 62% of the spin density for $SO_3^-$ is on sulfur. They contrasted this with addition of $SO_4^-$ where 100% of the bond formation is C–O and 100% of the spin densitiy is on oxygen. These same authors reported[33] ESR data for $SO_3^-$ in water and that the ESR of $SO_3^-$ in ethanol/water could be observed, but did not report whether the spin density distribution of the radical was different between the two solvents. Presumably, a difference in spin distribution between the solvents could account for the selectivity.

## Cyclization of Diallylammonium Compounds to Surfactants

The possibility that other diallylic structures might be cyclized led us to consider pyrrolidinium zwitterions **11** as possible substitutes for trialkylammonium propanesulfonates **12**, $RR'N^+(CH_2)_3SO_3^-$. Sulfonates **12** are known to be hard water resistant surfactants,[7,8] and their potential as brine resistant surfactants has been recognized.[34] With R = $C_{16-20}$, R′ = $CH_3$, sulfonates **12** are quite insoluble in water and low brine but are increasingly soluble as the salt concentration increases. This may be explained as representing a transition from an internal cyclic ion pair to a pair of external acyclic ion pairs. Presumably the tighter internal ion pair is more

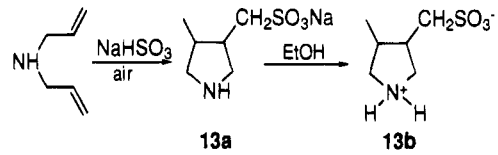
(27) Julia, M. *Acc. Chem. Res* **1971**, *4*, 386–392.
(28) Beckwith, A. L. J.; Easton, C. J.; Serelis, A. K. *J. Chem. Soc., Chem. Commun.* **1980**, 482–483.
(29) Beckwith, A. L. J.; Blair, I.; Phillipou, G. *J. Am. Chem. Soc.* **1974**, *96*, 1613–1614.
(30) Beckwith, A. L. J.; Lawrence, T.; Serelis, A. K. *J. Chem. Soc., Chem. Commun*, **1980**, 484–485.
(31) Hoffman, R; Levin, C. C.; Moss, R. A. *J. Am. Chem. Soc.* **1973**, *95*, 629–631.
(32) Ozawa, T.; Kwan, T. *Polyhedron* **1983**, *2*, 1019–1023.
(33) Ozawa, T.; Setaka, M.; Kwan, T. *Bull. Chem. Soc. Jpn.* **1971**, *44*, 3473–3474.
(34) Stournas, S. U. S. Patent 4 216 097, 1980.

poorly hydrated, and only as the $Na^+$ (or $Ca^{2+}$) concentration increases does the more highly hydrated acyclic form appear.

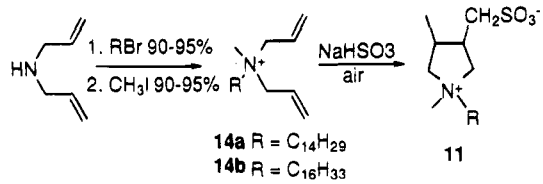



The pyrrolidinium sulfonates **11**, on the other hand, could adopt the cyclic internal ion pair only by forming the highly strained bicyclo [3.2.1] system or the solvent-separated bicyclo[5.2.1] system because of the geometric constraints of the pyrrolidine ring. They should probably exist as the acyclic zwitterion and consequently should exhibit greater solubility than the propanesulfonates at both low and high salinities.

The bisulfite cyclization of diallyl compounds is general. Diallylamine was converted to the pyrrolidinesulfonates **13a-*cis*** and **13a-*trans*** (4.9:1) in 98% yield in less than 1 h at 0 °C. The zwitterion **13b** was isolated by alcohol extraction and preparative reversed phase chromatography of the dried reaction mixture.




The diallylammonium compounds **14a** and **14b** were prepared using conventional reactions, recrystallized, and converted to the pyrrolidinium sulfonates **11a** and **11b** in 90–95% yield as determined by $^{13}C$ and $^{14}N$ NMR, but it was necessary to add 5 equiv of bisulfite. The ammonium salts were synthesized with methyl iodide, and it is known that iodide catalyzes the electrochemical oxidation of sulfite to sulfate.[35] The chloride salts of **14a** and **b** could be converted in 90–95% yield with slightly more than 1 equiv of bisulfite.




The prediction of increased solubility for pyrrolidinium sulfonates at both low and high salt concentrations was fulfilled. The pyrrolidinium sulfonate head group increases the solubility of surfactants in both water and oil dramatically compared to the propanesulfonate. Whereas propanesulfonates **12** are essentially insoluble in water and only soluble to about 2% in a limited range of brines, pyrrolidinium sulfonates **11** are soluble to 10% over a wide range of brine concentrations (Table 3). Surprisingly, **11**, unlike **12**, is also soluble is nonpolar solvents (a 5% solution of **11b** in toluene is stable at least 1 year), giving these materials utility as detergents in fuels and lubricants as well as water. Despite the substantial changes in water and oil solubility imparted by the pyrrolidinium sulfonate, water–oil interfacial behavior does not change significantly with respect to propanesulfonates. Thus, at 2% surfactant concentration in 12% brine the interfacial tension measured by the spinning drop method[36] against a typical Texas crude oil for **12** and **11b** are both unspectacular, but on addition of an alcohol cosurfactant both produce very low oil–water interfacial tension (Table 4).

**Table 3. Solubility of Surfactants in Brines at Room Temperature ($NaCl:CaCl_2:MgCl_2$ = 13.2:2.6:0.8 (by Weight))**

| surfactant | brine concn (wt %) | solubility limit (wt %) |
|---|---|---|
| **12**, R = $C_{14}H_{29}$, R′ = $CH_3$ | 9–21 | 3 |
| **12**, R = $C_{16}H_{33}$, R′ = $CH_3$ | 12–19 | 2 |
| **11a**, R = $C_{14}H_{29}$ | 20–28 | ≥3 |
| **11a**, R = $C_{14}H_{29}$ | 0–20 | 14 |
| **11b**, R = $C_{16}H_{33}$ | 20–28 | ≥2 |
| **11b**, R = $C_{16}H_{33}$ | 0–20 | 10 |

**Table 4. Interfacial Tension of Brine against Crude Oil at Room Temperature (Brine with $NaCl:CaCl_2:MgCl_2$ = 13.2:2.6:0.8 (by Weight))**

| surfactant composn (2% surfactant) | % brine | interfacial tension (mdyn/cm) |
|---|---|---|
| **12**, R = $C_{16}H_{33}$, R′ = $CH_3$ | 12 | 700 |
| **11b**, R = $C_{16}H_{33}$ | 12 | 250 |
| **12**, R = $C_{16}H_{33}$, R′ = $CH_3$ + 0.57% hexanol | 12 | 40 |
| **11b**, R = $C_{16}H_{33}$ + 0.57% hexanol | 12 | 33 |
| **11b**, R = $C_{16}H_{33}$ + 0.57% hexanol | 16.6 | 6 |
| **11a**, R = $C_{14}H_{29}$ + 0.57% hexanol | 22 | 13 |

## Conclusion

The surfactant-mediated synthesis of propanesulfonate surfactants is an easily scalable, clean, and economic method which avoids the safety hazards and cost of working with propanesultone. It is less convenient on a laboratory scale for new surfactants because of the need to bootstrap the first cycle, but is still a viable route. Pyrrolidinum sulfonate surfactants produced with bisulfite from diallylammonium compounds have substantial solubility advantages over tetraalkylammonium propanesulfonate surfactants but comparable interfacial properties.

## Experimental Section

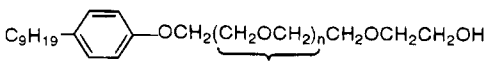
**General.** Ethoxylated phenols **3a,b** were obtained from GAF Corp. Neodol sulfate was from Shell. Ethoxylated alcohols **3c** and **3e** were gifts from D. H. Hoskin of this laboratory. 2-Butyl-1-octanol was from Wiley Organics and 2-hexyl-1-decanol from Henkel. All other chemicals were obtained from Aldrich Chemical Co. and were used as received. HPLC analysis was obtained on either a Whatman ODS C-18 column eluting at 2 mL/min with a solvent which changed linearly from 70% MeOH/30% $H_2O$ to 100% MeOH over 15 min or a Waters $\mu$-Bondapack C18 column eluting with 0.05 M $Bu_4N^+H_2PO_4^-$ in 86% MeOH/14% $H_2O$. Detection was either by UV at 277 nm or by refractive index. Preparative reversed phase chromatography was performed on a Water's Associates Prep 500 chromatograph using Water's C18 reversed phase

(35) Yen, S. C.; Chapman, T. W. *J. Electrochem. Soc.* **1985**, *132*, 2149–56.

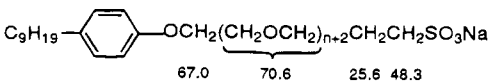
(36) Cayias, J. L.; Schechter, R. S.; Wade, W. H. *Adsorption at Interfaces, ACS Symposium Series #8*; Mittal, K. L., Ed.; American Chemical Society: Washington, 1975; pp 234–47.

radial compression columns, MeOH/$H_2O$ solvent mixtures, and refractive index detection. $^{13}C$ and $^{14}N$ NMR was obtained on a JEOL FX-200 in $D_2O$ (unless otherwise noted) with shifts referenced to $Me_3Si(CH_2)_3SO_3Na$ and $NH_4NO_3$, respectively. $^{13}C$ NMR proton multiplicities were assigned using the INEPT technique.[37]

**5a from 3a via Propanesultone.** A solution of 100 g (250 mmol) of **3a** in 220 mL of $PhCH_3$ was purged with $N_2$ via three cycles of a Firestone valve, water was removed azeotropically, 5.59 g (243 mmol) of clean Na was added, the mixture was refluxed with mechanical stirring overnight, and then 29.0 g (238 mmol) of freshly distilled propanesultone in 25 mL of $PhCH_3$ was added all at once. The temperature rose to 47 °C. After 2 h HPLC indicated complete reaction. The solution was evaporated in vacuum, dissolved in 800 mL of methanol, filtered through a 0.45 μm Millipore filter, and purified by preparative HPLC using 6% $H_2O$ in MeOH as eluant to give 102 g (75%) of a waxy white solid whose HPLC indicated 0.2–0.3% alcohol **3a** remained. Alcohol **3a** is a commercial mixture with an isomeric alkyl group and a distribution of ethoxy groups averaging 4.2 per molecule. Anal. Calcd for $C_{26.4}H_{45.8}NaO_{7.2}S$: C, 59.44; H, 8.65; Na, 4.31; S, 6.01. Found: C, 59.73; H, 8.47; Na, 4.20; S, 5.70. $^{13}C$ NMR of **3a-5a** show the following distinctive peaks:




**3a**




**5a**

**One Pot Conversion 3a to 5a.** A solution of 19.3 g of allyl chloride (252 mmol), 10 g of 50% NaOH (128 mmol), 20.3 g of **3a** (50 mmol), and 5.05 g of **5a** (9.5 mmol) was heated at reflux and stirred mechanically under argon. After 22 h, HPLC indicated the alcohol (99%) converted to a 96:4 mixture of **5a** and **6a**, the excess allyl chloride was distilled off, the reaction was cooled, air was flowed through the flask at about 15 mL/min, and 40 mL of 95% ethanol was added. After the mixture was stirred briefly to assure air saturation a solution of 15.7 g of $NaHSO_3$ and 3.6 g of $Na_2SO_3$ in 42 mL of $H_2O$ was added dropwise over 15 min. An exotherm took the temperature to 34 °C and HPLC analysis after 3 h indicated less than 1% allyl ether **4a** remained. The flask was cooled to 15 °C, inorganics were filtered off, and the ethanol and water were removed under vacuum to give 33.5 g of pale yellow wax. In addition to the peaks expected for sulfonate **5a** two additional peaks due to one carbon each were seen at 62.9 ppm and 25.1 ppm. These are assigned to the $NaO_2SOCH_2CH_2$ carbons of sulfite **6a**. This material was shown to be the sulfite by heating the reaction product at 60 °C at 0.05 Torr for 4 h and collecting the evolved gas in a dry ice trap. Infrared analysis showed this gas to be sulfur dioxide. $^{13}C$ NMR of the remaining material in moist $CDCl_3$ showed the peak at 62.9 ppm to be gone and a new peak at 57.4 ppm to have appeared consistent with the replacement of $NaO_2SOCH_2CH_2CH_2OCH_2-$ with $HOCH_2CH_2CH_2OCH_2-$. HPLC analysis of this material no longer showed **6a**.

**15-Hexyl-4,7,10,13-tetraoxatricosane-1-sulfonic Acid, Sodium Salt (5d). 5d** was prepared from **3d** in one pot in 87% yield using a procedure analagous to that for **5a**. An analytical sample was obtained by recrystallization from acetone. $^{13}C$ NMR (2:1 $(CD_3)_2SO$:$CDCl_3$): 73.79, 69.99, 69.75, 69.56, 69.12, 48.32, 37.70, 31.42, 30.98, 29.57, 29.23, 29.08, 28.79, 26.30, 25.62, 22.21, 13.88. Anal. Calcd for $C_{25}H_{51}NaO_7S$: C, 57.89; H, 9.91; Na, 4.43; S, 6.18. Found: C, 58.04; H, 9.97; Na, 4.29; S, 6.26.

**12-Butyl-4,7,10-trioxaoctadecane-1-sulfonic Acid, Sodium Salt (5e). 5e** was prepared from **3e** in one pot in 92% yield using a procedure analagous to that for **5a**. An analytical sample was obtained by recrystallization from acetone after preparative HPLC. $^{13}C$ NMR (2:1 $(CD_3)_2SO$:$CDCl_3$): 73.76, 70.02, 69.77, 69.60, 48.39, 37.75, 31.44, 31.03, 30.74, 29.31, 28.68, 26.39, 25.61, 22.69, 22.27, 13.99. Anal. Calcd for $C_{19}H_{39}NaO_6S$: C, 54.52; H, 9.39; Na, 5.49; S, 7.66. Found: C, 54.56; H, 9.46; Na, 5.83; S, 8.02.

**15-Butyl-4,7,10,13-tetraoxaheneicosane-1-sulfonic Acid, Sodium Salt (5f). 5f** was prepared from **3f** in one pot in 96% yield using a procedure analagous to that for **5a**. An analytical sample was prepared by preparative HPLC. $^{13}C$ NMR (2:1 $(CD_3)_2SO$:$CDCl_3$): 73.74, 69.99, 69.75, 69.56, 48.37, 37.70, 31.42, 31.03, 30.69, 29.27, 28.64, 26.35, 25.62, 22.65, 22.21, 13.93. Anal. Calcd for $C_{21}H_{43}NaO_7S$: C, 54.52; H, 9.37; Na, 4.96; S, 6.93. Found: C, 54.65; H, 9.42; Na, 4.96; S, 7.32.

**Furansulfonate 9.** A solution of 31.9 g (307 mmol) of $NaHSO_3$ in 170 mL of $H_2O$ was added dropwise over 15 min to a room temperature solution containing 15 g (153 mmol) of diallyl ether, 150 mL of $H_2O$, and 150 mL of ethanol while air was bubbled through at about 15 mL/min. The temperature rose to 40 °C. The mixture was evaporated to dryness and extracted with ethanol in a Soxhlet extractor and the ethanol-soluble material recrystallized from methanol to give 21.7 g (72%) of white crystals. $^{13}C$ NMR **9-*cis***: 74.2, 70.3, 49.2 (3t), 37.6, 35.1 (2d), 12.3 (q). $^{13}C$ NMR **9-*trans***: 73.6, 72.4, 52.7 (3t), 42.1, 38.6 (2d), 14.8 (q). Anal. Calcd for $C_6H_{11}NaO_4S$: C, 35.63; H, 5.48; Na, 11.37; S, 15.86. Found: C, 35.51; H, 5.41; Na, 11.47; S, 15.89.

**Pyrrolidinesulfonates 13.** A mixture of 15 g (154 mmol) of diallylamine, 150 mL water and 150 mL of *tert*-butyl alcohol at 4 °C was treated with 16.1 g (155 mmol) of $NaHSO_3$ and 1 g (7.9 mmol) of $Na_2SO_3$ while air was bubbled through at ~15 mL/min. After 30 min, the inorganic salts were filtered off and the reaction mixture evaporated in vacuum to give 30.5 g (98%) of a white solid, **13a**. This solid was purified by reversed phase chromatography to give 25.1 g (91%) of **13b** after vacuum drying at 25 °C. $^{13}C$ NMR **13b-*cis***: 52.2, 50.3, 48.2 (3t), 38.0, 35.3 (2d), 13.0 (q). $^{13}C$ NMR **13b-*trans***: 53.3, 51.7, 50.8 (3t), 41.9, 38.3 (2d), 14.9 (q). Anal. Calcd for $C_6H_{13}NO_3S$: C, 40.21; H, 7.31; N, 7.82; S, 17.89. Found: C, 40.56; H, 7.11; N, 7.45; S, 17.60.

**Diallylhexadecylmethylammonium Iodide and Chloride 14b. General Procedure for Forming 14.** A solution of 50 g (164 mmol) of 1-bromohexadecane and 150 mL (1200 mmol) of diallylamine was refluxed overnight and cooled, and 350 mL of petroleum ether was added followed by 150 mL of 7% $NaHCO_3$. The layers were separated, extracted once with 150 mL of 7% $NaHCO_3$ and once with 100 mL of saturated NaCl, filtered through 4 Å sieves, evaporated in vacuum, and Kugelrohr distilled at 140–160 °C/0.05 Torr to give 48.6 g (93%) of pale tan oil. $^{13}C$ NMR (in $CDCl_3$): 136.0 (d), 116.9, 56.9, 53.5, 32.0, 29.8, 27.6, 27.2, 22.8 (8t), 14.1 (q). This crude amine was diluted with 200 mL of EtOH and heated at 55 °C while 33.2 g (234 mmol) of MeI was added (exotherm) dropwise over 10 min. After 30 min, the EtOH was removed in vacuum and the product recrystallized from acetone/$Et_2O$ to give 59.8 g (87%) of yellow crystals. $^{14}N$ NMR **14b**: −313. $^{13}C$ NMR **14b**: 129.8 (d), 124.3, 63.8, 61.4 (3t), 48.2 (q), 32.4 (large, broad), 31.9, 26.4, 22.7 (4t), 14.1 (q). Anal. Calcd for $C_{23}H_{46}NI$: C, 59.60; H, 10.00; N, 3.02; I, 27.38. Found: C, 59.77; H, 9.94; N, 3.09; I, 26.88. The chloride salt was prepared by passing an aqueous solution of the iodide through a 100% molar excess of $OH^-$ exchange resin Amberlite IRA-100 (1.4 mequiv/mL), titrating to pH 7 with HCl, and removing the $H_2O$ in vacuum.

**Surfactant 11b. General Procedure for Forming 11.** A room temperature solution of 225 mL of $H_2O$, 225 mL of *tert*-butyl alcohol, 43.2 g (93.1 mmol) of **14b** was stirred while air was bubbled through at 2 mL/min, and a mixture of 34.2 g (329 mmol) of $NaHSO_3$ and 9.8 g (77.8 mmol) of $Na_2SO_3$ in 150 mL of $H_2O$ was added over 2 h. After 2 h $^{14}NMR$ indicated 90% conversion. After purification by chromatography there was obtained 20.6 g of white wax (53%). $^{14}N$ NMR **14b**: −305. Anal. Calcd for $C_{23}H_{47}NSO_3$: C, 66.13; H, 11.34; N, 3.35; S,

(37) Doddrell, D. M.; Pegg, D. T. *J. Am. Chem. Soc.* **1980**, *102*, 6388–6390.

7.68. Found: C, 66.00; H, 10.53; N, 3.33; S, 7.34. When the chloride salt was substituted for the iodide $^{14}N$ NMR indicated 94% conversion after 2 h when only 80.8 mmol of $NaHSO_3$ and 19.1 mmol of $Na_2SO_3$ were used in the reaction.

**General Procedure for Ethoxylated Alcohols. 2-[2-[2-[(1-Butyloctyl)oxy]ethoxy]ethoxy]ethanol (3f).** 2-Butyl-1-octanol (40 g, 215 mmol) and 250 mL of xylene were degassed with Ar via three Firestone valve cylcles, dried azeotropically, and cooled in ice, 135 mL of 1.6 M (216 mmol) BuLi in hexane was added, and the hexane was distilled off. 2-[2-[2-(2-chloroethoxy)ethoxy]ethoxy]tetrahydro-2*H*-pyran[38] (52.4 g, 207 mmol) was added, the mixture was refluxed for 1 week, cooled, dissolved in 1 L of $Et_2O$, extracted three times with 100 mL of $H_2O$ and once with saturated NaCl, and filtered through 4 Å sieves, the solvents were removed in vacuum, the residue was dissolved in 1 L of EtOH, 15 g of pyridinium *p*-toluenesulfonate was added, and the resulting mixture was refluxed overnight. After cooling the mixture was neutralized with 4.5 g of KOH and partitioned between 600 mL of $Et_2O$ and 100 mL of $H_2O$, the $Et_2O$ was washed twice with 100 mL of $H_2O$ and once with 100 mL of $H_2O$ and filtered through 4 Å sieves, the solvents were removed in vacuum, and the residue was distilled at 110–120 °C/0.1 Torr to give 41.5 g (63%) of **3f**. $^{13}C$ NMR **3f** ($CDCl_3$): 74.87, 72.72, 70.77, 70.68, 70.53, 61.76 (6t), 38.19 (d), 31.95, 31.47, 31.17, 29.81, 29.13, 26.89, 23.19, 22.75, (8t), 14.13 (q). Anal. Calcd for $C_{18}H_{38}O_4$: C, 67.88; H, 12.03. Found: C, 67.69; H, 12.37.

**2-[2-[2-[(1-Hexyldecyl)oxy]ethoxy]ethoxy]ethanol, 3d. 3d** was prepared similarly in 44% yield after Kugelrohr distillation at 160–190 °C/0.03 Torr from 2-[2-[2-(2-chloroethoxy)ethoxy]ethoxy]tetrahydro-2*H*-pyran[38] and 2-hexyl-1-decanol.

$^{13}C$ NMR **3d** ($CDCl_3$): 74.82, 72.82, 70.82, 70.68, 70.53, 61.67 (6t), 38.28 (d), 32.00, 31.51, 30.20, 29.86, 29.71, 29.47, 26.94, 22.75, (8t), 14.13 (q). Anal. Calcd for $C_{22}H_{46}O_4$: C, 70.54; H, 12.38. Found: C, 70.98; H, 12.43.

**Acknowledgment.** I wish to thank Professor G. A. Russell and Dr. R. F. Bridger for discussions of this work, Dr. D. H. Hoskin for the ethoxylated alcohols, and S. S. Barreiro for the interfacial tension measurements. This work was supported by the Mobil Research and Development Corp.

JO942052A

(38) Bartsch, R. A.; Cason, C. V.; Czech, B. P. *J. Org. Chem.* **1989**, *54*, 857–60.