Sodium Dialkyl Phosphates: Surfactant Properties and Use in Heavy Duty Detergents

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Abstract

A study of the physical and surface active properties of the sodium salts of dialkyl phosphates has been made. These compounds have been evaluated for use as surfactants in built detergents and their performance has been compared with commercial surfactants.

The dialkyl hydrogen phosphates contained from 16–26 carbon atoms per molecule and were prepared from both straight chain alcohols and commercially available branched chain alcohols. In general, the surface active properties of the branched chain compounds are better than their corresponding straight chain compounds. Good detergency performance is obtained when the number of carbon atoms per molecule is between 17 and 23. Optimum performance is obtained with the symmetrical didecyl hydrogen phosphate salts made from commercial decyl alcohol produced by the oxo-process.

Introduction

ALTHOUGH a number of anionic organophosphorus surfactants have been marketed for some years, none of these products have been found suitable for use in heavy duty detergents. In addition, little information is available in the literature on either the surface active properties of dialkyl sodium phosphates or performance data on the use of these products in built detergents.

This paper describes the preparation of dialkyl sodium phosphates and their properties relative to their use in heavy duty detergents.

Experimental

Preparation of Dialkyl Hydrogen Phosphate. Didecyl hydrogen phosphate was prepared in the following manner.

Equipment: A three liter, three-necked flask was equipped with vacuum stirrer, reflux condenser (drying tube on top), dropping funnel and thermometer. The equipment was arranged so a cooling bath or heater could be used as required. A distillation unit was attached for stripping of alkyl chloride and later drying the final product.

Procedure: 4.5 mole (712.4 g) decyl alcohol was added to the flask and 1.5 mole (206.1 g) phosphorus trichloride was added dropwise while mixture was stirred at 300 rpm and temp maintained between 30–35C. The charge was stirred for one hr after addition of phosphorus trichloride, and the equipment arranged for vacuum distillation. Pressure was reduced to 1 mm after 1 hr vacuuming and liquid temp ranged from 13–25C (a small amount of heat was used). The charge was then heated and decyl chloride distilled off with liquid temp of 25–135C, vapor temp of 55–60C at 1 mm (absolute) pressure. Wt of the didecyl phosphonate was 542.3 g (99.7% of theory). Analysis was as follows: assay, 99.8%; total chlorine, 0.28% and phosphorus, 8.6%. The product was clear and colorless. The wt of the decyl chloride recovered was 250 g (95%); sp gr at 25C = 0.873 and $n_D^{25} = 1.4382$.

The didecyl phosphonate was chlorinated at 0–5C in 1.25 hr using 104.4 g (2.1% excess) chlorine. The charge was then stirred for 15 min at 1C. Vacuum was applied and pressure reduced to 10 mm in ca. 10 min. The vacuum was released and the cooling bath replaced with a heating mantle. 1200 ml water was added to the crude didecyl chlorophosphate and the charge stirred for two hr at reflux, 103C. After cooling, the charge was placed in a separatory funnel and, after removing the water layer, the wet product was transferred to a vacuum distillation unit for drying. The water was removed in one hr at liquid temp of 42–70C and pressures of 50 mm down to 1 mm. Yield of didecyl hydrogen phosphate was 497 g (91%) and had the following analysis: 93.7% diester, 1.6% monoester, sp gr 25C = 0.989, $n_D^{25} = 1.4479$, H_2O, 0.10% and total chlorine, 0.3%.

The didecyl hydrogen phosphate can be converted to the sodium salt by neutralization with caustic soda. One mole (378 g) didecyl hydrogen phosphate is added to 250 cc water containing 1 mole (40 g) sodium hydroxide. Good agitation is required to completely neutralize the dialkyl phosphate. The sodium didecyl phosphate can be used in slurry form (a slurry containing 60% solids will pour easily at room temp) or it can be dried to a waxy type solid.

TABLE I
Physical Properties of Dialkyl Hydrogen Phosphates

Compound carbon atoms per molecule	R	Yield %	Assay		n_D^{25}	Sp gr 25C	Appearance
			Di	Mono			
16	n-octyl	93	92.5	0.4	1.4408	0.963	Clear, colorless liquid
16	2 ethyl hexyl	96	94.2	0.7	1.4420	0.972	Clear, sl. yellow liquid
16	dimethyl hexyl*	92	93.7	1.9	1.4423	0.969	Clear, colorless liquid
18	trimethyl hexyl*	94	93.8	1.0	1.4487	0.965	Clear, colorless liquid
20	n-decyl	91	86.2	5.3	1.4452	0.946	Clear, colorless liquid
20	dimethyl octyl*	92	93.0	4.0	1.4460	0.945	Clear, colorless liquid
20	trimethyl heptyl*	94	93.7	1.6	1.4479	0.949	Clear, colorless liquid
22	undecyl**	93	90.2	7.3	1.4468	....	Clear, sl. off colored liquid
24	n-dodecyl	94	90.0	3.1	....	mp 60–61C	Fine white solid
24	trimethyl nonyl*	94	88.4	1.3	1.4490	.928	Clear, colorless liquid
26	tetramethyl nonyl*	91	96.0	3.0	1.4543	0.937	Clear, sl. yellow liquid

* Alcohols used were prepared by oxo-process, consisting mostly of isomers of the alcohols given in the table.
** Made from branched chain alcohol. The amount of various branched isomers is unknown.

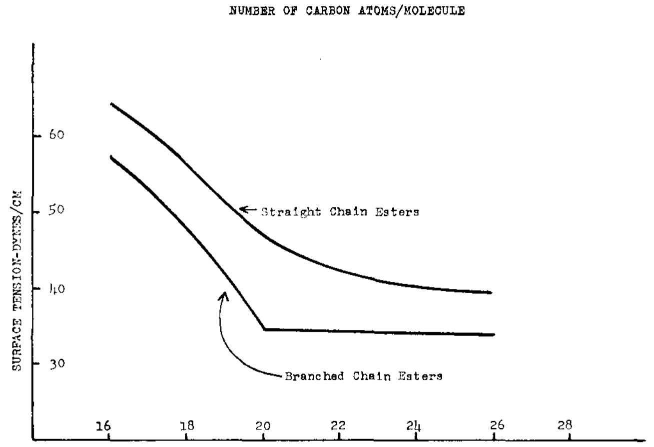


FIG. 1. Surface tension of sodium dialkyl phosphates as a function of the number of carbon atoms per molecule.
Temp = 25C.
Surfact concn = 25 ppm.

Other alkyl phosphates can be prepared in a similar manner; the physical properties of dialkyl hydrogen phosphates used in this work show in Table I.

Evaluation Procedures

1) Surface tension: A Du Nouy Interfacial Tensiometer was used to measure the surface tension of aqueous solutions.

2) Rate of wetting: The Draves and Clarkson Sinking Skein Test (AATCC Standard Test Method 17-1952, A.S.A., No. 14. 11-1956) was used to determine rate of wetting.

3) Critical micelle concentration (CMC): The CMC of anionic surfactants was measured by the marked color change which occurs in solutions containing both the surfactant and an appropriate dyestuff when the concn of the surfactant reaches the CMC level (1).

4) Detergency testing: The detergency studies were made using both a dry soiled cloth prepared in the laboratory from hotel vacuum cleaner dirt and a commercial carbon black, and oil soiled cloth.

Tests were run in a Terg-O-Tometer at 145 rpm with a wash cycle of 15 min, at a temp of 120F. The reflectance of washed cloths (120 sq in. of either dry soil or oily soiled cloth per washing receptacle) was read on a Hunter Multipurpose Reflectometer using a blue filter. The standard error in this method is 0.6 reflectance units. The performance index of surfactants was calculated by the following formula. Performance index = average units of soil removed from both types of soiled cloth used (x 10)/per cent surfactant in detergent.

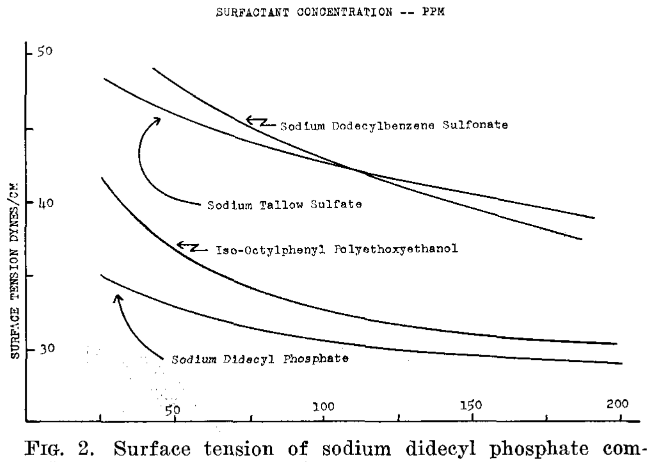
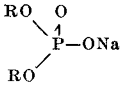


FIG. 2. Surface tension of sodium didecyl phosphate compared to some other commercial surfactants.

TABLE II
Sink Time and CMC of Symmetrical Sodium Dialkyl Phosphates as a Function of Chain Length and Chain Branching

		Sinking time (Draves and Clarkson) surfactant concn = 400 ppm	CMC
No. carbons/ molecule	R		
16	n-octyl	12 sec	2.00 x 10^{-3} M
16	2 ethyl hexyl	25 sec	10.5 x 10^{-3} M
16	dimethyl hexyl	12 sec	6.10 x 10^{-3} M
20	n-decyl	>5 min	....
20	dimethyl octyl	54 sec	1.68 x 10^{-3} M
20	trimethyl heptyl	37 sec	1.45 x 10^{-3}
24	n-dodecyl	>5 min	....
24	trimethyl nonyl	200 sec	1.56 x 10^{-3} M
26	tetramethyl nonyl	>5 min	....

Example: A detergent containing 8% sodium didecyl phosphate as surfactant removes 34 units of soil from one type of soiled cloth and 16 units from the other type. The average units of soil removed is 25. When this is multiplied by 10 and divided by the percent surfactant (8), we get (31.3) the Performance Index for sodium didecyl phosphate.

5) Biodegradability test: Surfactants being tested were added to Kankakee River water at a concn of 30 ppm. Solutions were stored at 74-76F, stirred daily and surface tensions measured periodically using a Du Nouy Interfacial Tensiometer.

Discussion

1) Surface Tension: The surface tensions of aqueous solutions of dialkyl phosphates show in Figure 1. These curves give the surface tension of the dialkyl esters at a concn of 25 ppm as a function of the number of carbon atoms in the molecule.

The upper curve gives the surface tension of the straight chain esters while the lower curve gives the values obtained for the most highly branched chain diesters studied.

Figure 2 shows the surface tension of aqueous solutions of the di(trimethyl heptyl) ester as compared to three other surfactants used or recommended for use in heavy duty detergents.

The surface tension of sodium didecyl phosphate solutions up to a concn of 200 ppm is far below that of either sodium dodecylbenzene sulfonate or sodium tallow sulfate and significantly below that of the nonionic surfactant, isooctylphenyl polyethoxyethanol, particularly at low concn.

2) Rates of wetting and CMC: The rates of wetting and CMC of several symmetrical sodium dialkyl phosphates are compared as a function of chain length and chain branching in Table II. They were measured at a concn of 400 ppm and the values obtained are

TABLE III
Sink Time and CMC of Sodium Didecyl Phosphate as Compared to Commercial Surfactants

Surfactant	Sinking time (Draves and Clarkson) surfactant concn = 400 ppm	CMC
Sodium didecyl phosphate........................	37 sec	1.45 x 10^{-3} M
Sodium tallow sulfate.............................	>5 min	....
Sodium lauryl sulfate..............................	47 sec	2.42 x 10^{-3} M
Sodium dodecyl benzene sulfonate..........	37 sec	3.46 x 10^{-3} M
Iso-octyl phenyl polyethoxyethanol..........	29 sec	9 x 10^{-4} M

TABLE IV

Formulation and Procedure for Evaluation of Surfactants in Heavy Duty Detergents

Detergent composition	Terg-O-Tometer procedure
50% Sodium tripolyphosphate	Detergent concn = 2.0 g/l
8% Sodium metasilicate	Water hardness = 175 ppm as $CaCO_3$ (synthetic mix 60–40 ratio of ca and mg)
0.5% Sodium carboxymethyl cellulose	Water temp = 120 F
X% Surfactant	pH = 10.0 ± 0.1
(41.5–X) % Sodium sulfate	Length of wash cycle = 15 min
	Agitator speed = 145 cycles/min

shown in the third column.

The octyl esters have a very rapid rate of wetting while, of the decyl esters, only the di(trimethyl heptyl) ester is moderately fast. As the mol wt increases, the rate of wetting drops off rapidly.

The CMC values given in the last column show that the CMC of the decyl esters are lower than those of the octyl esters, and the di(trimethyl heptyl) ester was found to have the lowest CMC of any of the phosphate surfactants for which this value was determined.

Table III shows the rates of wetting and CMC of the di(trimethyl heptyl) ester as compared to some commercial surfactants. It also shows that at a concn of 400 ppm, sodium tallow sulfate is much slower in rate of wetting than the other three surfactants.

There is a significant difference in the CMC values. Sodium didecyl phosphate has a significantly lower CMC than sodium tallow sulfate and is much superior to sodium dodecyl benzene sulfonate in this respect.

3) Detergency performance: The detergent composition and procedure used in comparing various surfactants show in Table IV. The first column gives the detergent composition; the second outlines the procedure used.

Our laundry tests were run at several levels of water hardness (50,100,175 and 300 ppm). Since the relative differences between the surfactants were quite similar at these various water hardness levels only the results obtained at 175 ppm are given.

The performance of several sodium dialkyl phosphates as a function of the total number of carbon atoms in the molecule shows in Figure 3.

The concn of the dialkyl phosphates was varied from 6–25% of the total formulation. The lowest concn of dialkyl phosphate which gave the max performance was used in determining the Performance Index.

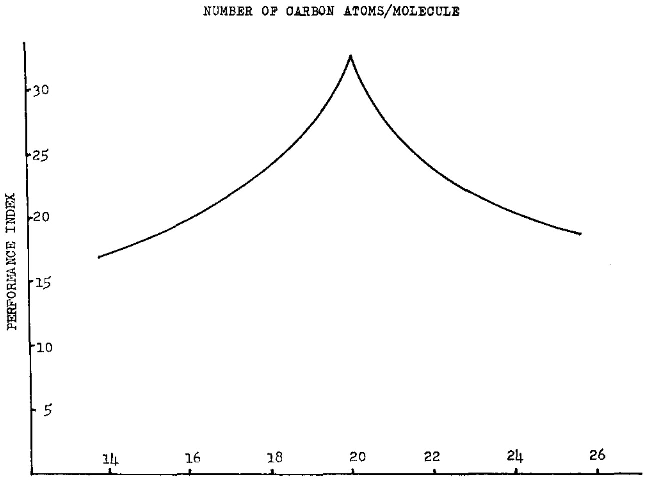


FIG. 3. Performance of sodium dialkyl phosphates in heavy duty detergents.

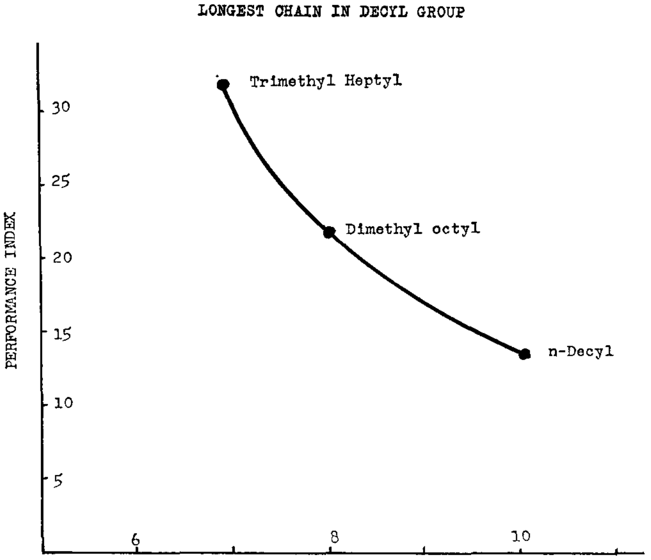


FIG. 4. Relative performance of sodium didecyl phosphates in heavy duty detergents.

Performance of the dioctyl ester (C_{16}) is very poor, but it begins to rise at the dinonyl ester (C_{18}) and rises sharply to a maximum with the didecyl ester (C_{20}). Performance then begins to recede at the diundecyl ester (C_{22}) and continues to drop through the ditridecyl ester (C_{26}).

Another significant factor influencing detergency is the chain branching of the dialkyl ester. Figure 4 shows that in the didecyl series the di(trimethyl heptyl) ester gives better performance than the di(dimethyl octyl) ester which in turn is better than the normal didecyl ester.

The detergency of the most highly branched didecyl ester di(trimethyl heptyl) ester as compared to compared to commercial surfactants in built detergents shows in Table V.

The surfactant concn in each built detergent is the lowest amount which gives max performance. Increasing the surfactant content above the level shown in Table V does not substantially improve the performance of the detergent.

This table shows that sodium didecyl phosphate gives max performance when used at 8% of the total detergent concn. It is slightly better than sodium tallow sulfate which required 10% to give the same performance. Approximately 25% sodium dodecyl benzene sulfonate is required to give comparable performance. The nonionic surfactant gives fair detergency at low concn and under the conditions of these tests it never gives performance equivalent to the anionic surfactant even at high concn.

4) Biodegradability: The loss of the surface active properties of sodium didecyl phosphate, sodium lauryl sulfate and sodium dodecyl benzene sulfonate

TABLE V

Performance of Sodium Didecyl Phosphate as Compared to Commercial Surfactants in Heavy Duty Detergents

Surfactant	Surfactant concn [a]	Performance (detergency units) [b]
Sodium didecyl phosphate	8%	25
Sodium tallow sulfate	10%	25
Sodium dodecyl benzene sulfonate	10%	18
	25%	25
Iso-octylphenyl polyethoxyethanol	10%	20
	25%	22

[a] Total detergent concn = 2.0 g/liter.

[b] Average of the sum of increase in whiteness from both types of soiled cloth used.

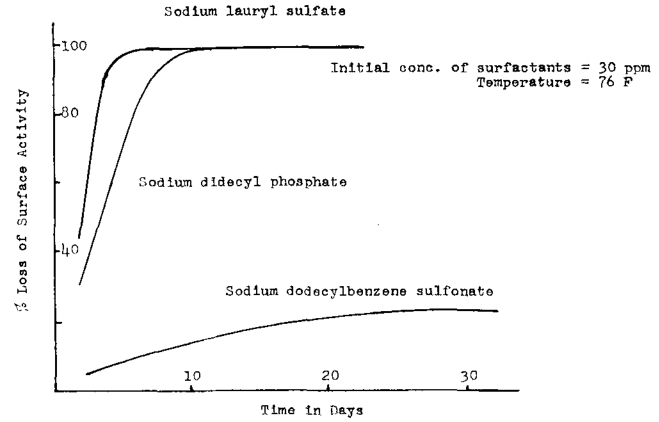


FIG. 5. Biodegradation of surfactants as determined by surface tension measurements.

when run in the so-called River Water Die-Away Test shows in Figure 5. Results indicate that at room temp sodium didecyl phosphates loses its surface active properties in approximately 10 days, sodium lauryl sulfate in 5 days and sodium dodecyl benzene sulfonate loses only 20% in 30 days.

Summary

A study of the salts of dialkyl hydrogen phosphates has shown that they possess some exceptional surface active properties particularly when the alkyl radicals are branched.

Laboratory evaluation of these surfactants for use in heavy duty detergents indicates that the branched chain didecyl ester performs exceptionally well. In fact, our laboratory evaluations show it to be considerably better than commercial surfactants being used in heavy duty detergents.

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The Endosperm Lipids of Three Canadian Wheats[1]

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Abstract

Flour samples were prepared from intact and degermed kernels of Hard Red Spring, Soft White Spring, and Amber Durum wheats. The "free" (hexane soluble) and "bound" (hexane resistant, water-saturated *n*-butanol extractable) lipids were extracted from the six flours and separated quantitatively by silicic acid column chromatography. Thin-layer chromatography (TLC) was used to monitor the column and to resolve the lipid classes into components. Gas-liquid chromatography (GLC) was used to obtain the fatty acid composition of the triglyceride, sterol ester, and phospholipid fractions, and also to determine the nature of the sterol components of the unesterified sterol and sterol ester classes.

Similar patterns of lipid classes were shown by all three varieties; the differences were in the degree of dominance. In fatty acid composition some varietal differences were found but the greatest difference was between lipid classes.

Introduction

Lipids comprise only a very small portion of the wheat endosperm; yet they have been of continuing interest to cereal chemists. Evidence suggests that lipids are involved in the ageing of flour, the quality of bread, and in the staling process. Extensive descriptive work on the role of lipids in flour properties has, however, resulted in a vast accumulation of apparently contradictory data (1,2).

Recently, studies of the composition of wheat lipids have received increasing attention (1). Separation of lipid classes has been accomplished by solvent fractionation (3) and by chromatography (4). The phospholipids have been further investigated by Coulson (5) and Houston (6), and Stevens (7) has studied the lipid contribution of germ oil to flour. Carter (8,9,10) has made an extensive study of glycolipids and it has been estimated that phytoglycolipid might amount to 4% of wheat lipid (11). Sitosterols (2), sitosteryl glucoside (10), as well as other plant sterols (2), have been reported in wheat lipids.

The present work is intended as a comparative study of the endosperm lipids in very different types of wheat. The objective is to separate the free and bound lipids of wheat endosperm into their component classes and to study the differences within and between classes in three representative varieties.

Materials and Methods

The wheat varieties Thatcher, Lemhi, and Mindum were chosen to represent Hard Red Spring, Soft White Spring, and Amber Durum wheats, respectively. The embryos were removed through the courtesy of F. B. Johnston, Food Research Institute. Seven pounds each of intact and degermed grain were milled in a micromill in the laboratory of A.G.O. Whiteside, Genetics and Plant Breeding Research Institute. The grain was tempered at 15.5% moisture and the milling produced a straight run flour of 65–70% extraction. The free lipids of the wheat endosperm used in this investigation were extracted from the flour with hexane and the bound lipids released by a further extraction with water-saturated *n*-butanol (12). A rotary evaporator was used to remove hexane under vacuum at 20C and butanol at 30C. Vacuum was always broken with nitrogen and the lipid stored under nitrogen in the dark at —15C.

Silicic Acid Column Chromatography. Separation of free and bound lipids into their classes was accomplished in the apparatus described by Sahasrabudhe and Chapman (13) using 90 g silicic acid in a column 25 mm diam. The dehydrating procedure and the gradient from pure hexane to 60% diethyl ether in hexane were essentially those described by Hirsch and

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[1] Contribution No. 5 of the Food Research Institute. Presented at the AOCS Meeting, Toronto, 1962.