

STUDIES ON THE APPLICATION OF SULPHONIC ACIDS HAVING LIPOPHILIC GROUPS

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1. Introduction

Sulphonic acids having lipophilic groups are used as fat-splitting agents, and their salts as wetting agents and detergents. The author studied the application of these sulphonic acids and their salts not only as the above-mentioned agents but also as flotation agents and antiseptics.

In the first place, these sulphonic acids were used for trial in the place of soap in the soap flotation process, and their property as a froth-collecting agent for aluminium ore was investigated. Subsequently, the detergency properties of alkyl phenol sulphonates having dodecyl- or cetyl-radical were investigated. Further, the fat-splitting powers of dodecyl phenol sulphonic acid and its halogen derivatives were examined, since these compounds had not yet been used as fat-splitting agents. It seems that the electronegativity of the phenol nucleus is increased by the introduction of halogen into the nucleus, which in turn strengthens the property of dodecyl phenol sulphonic acid as an acid. As a result, the fat-splitting power of its halogen derivatives may increase. This is the very reason why the author examined the halogen derivatives. Antiseptics having capillary activity are known, but sulphonate having a lipophilic group had never before been used as an antiseptic. Since some kinds of sulphonate are known to be useful as germicides, some of them which have little toxic character may be used as antiseptics. Not only dodecyl phenol sulphonate and its halogen derivatives but also dodecyl benzene sulphonate was tested as an antiseptic, for the purpose of determining whether the antiseptic power is ascribed to the action of a special radical or solely to the capillary activity. α -Chlorodibutyl naphthalene sulphonic acid was synthesized and used for trial as a fat-splitting agent for the same reason that the halogen derivatives of dodecyl phenol sulphonic acid as fat-splitting agents were used. While sulphonic acids having one or two alkyl radicals introduced into aromatic hydrocarbon are known, only a few sulphonic acids having three alkyl radicals and possibly no one having four alkyl radicals had been previously known. In the present study, tetrabutyl naphthalene sulphonic acid and similar compounds, and their salts were used as fat-splitting agents and detergents, respectively, for the purpose of investigating how the property of alkyl aryl sulphonic acid varies with increasing the lipophilic property by introducing an increased number of alkyl radicals into aromatic hydrocarbon. Also the properties of surface active agents and fat-splitting agents prepared for trial from naphthalene, β , β -dinaphthyl, *n*-butyl alcohol, sulphuric acid, etc. were studied, for the purpose of investigating how

TABLE 1

Ore	Flotation agent (g/t)	Pulp conc. (%)	Pulp temp. (°C)	pH value of pulp Before flotation	After flotation	Flotation time			Amount of floated ore			Amount of residual ore	
						10 min. g	%	" 20 min. g	%	" 30 min. g	%	g	%
Quartzite	Kontakt 500.....	20	17	5.6	6.6	0.1	0.2	0.4	0.8	1.6	3.2	48.2	96.8
"	" , water glass 100.....	"	18	"	"	0.7	1.4	1.2	2.4	1.8	3.6	47.9	96.4
"	" , anhydrous sodium carbonate 500.....	"	17	"	7.5	10.3	20.7	12.3	24.7	15.3	30.7	34.5	69.3
"	" , sulphuric acid 500.....	"	"	"	2.2	5.3	10.7	6.5	13.1	7.5	15.1	42.2	84.9
"	Divulson D 500.....	10	15	5.9	5.4	0.3	1.2	1.1	4.4	3.3	13.3	21.6	86.7
"	" , water glass 100.....	"	16	"	6.2	0.5	2.0	0.9	3.6	2.2	8.9	22.6	91.1
"	" , anhydrous sodium carbonate 500.....	"	13	"	6.7	9.5	38.2	13.1	52.6	15.8	63.5	9.1	36.5
"	" , sulphuric acid 500.....	"	14	"	2.6	8.3	33.5	11.9	48.0	12.8	51.6	12.0	48.4
"	S.....	20	10	6.0	7.2	1.0	2.0	1.4	2.8	1.8	3.6	47.8	96.4
"	S'.....	10	7	5.9	7.7	Trace	Trace	0.1	0.4	0.3	1.2	24.6	98.8
Bauxite	Kontakt 500.....	20	16	5.6	6.6	38.0	76.3	39.3	78.9	40.4	81.1	9.4	18.9
"	Divulson D 500.....	10	"	5.9	6.5	19.0	76.6	20.6	83.1	21.4	86.3	3.4	13.7
"	" , water glass 100.....	"	24	"	"	19.5	73.3	21.4	85.9	22.9	92.0	2.0	8.0
"	S.....	20	9	"	"	37.0	74.3	42.7	85.7	42.8	85.9	7.0	14.1
"	S'.....	10	11	"	7.2	19.0	76.3	22.0	88.4	23.0	92.4	1.9	7.6

S: Anhydrous sodium carbonate 500, water glass 100, camphor white oil 100, and oleic acid 500.

S': Double the amount of the above-mentioned reagents.

the property of alkyl aryl sulphonic acid varies with increasing the lipophilic property by using the bimolecular condensation product of aromatic hydrocarbon as the aryl radical. In this case, a mixture of naphthalene and β, β -dinaphthyl was used, because β, β -dinaphthyl alone hardly reacts with *n*-butyl alcohol and sulphuric acid. These studies are briefly described below.

2. Kontakt and Divulson D as Flotation Agents

As is well known, there are nonsulphide ores that are unfloatable with xanthates but are floatable by the soap flotation process in which fatty acids or their salts are used. In the flotation of these nonsulphide ores, several series of sulphonic acids or their salts besides fatty acids or their salts have been proposed as froth-collecting agents. Espumin¹⁾ is a flotation agent for aluminium ores. The author used Kontakt and Divulson D, well known German splitting agents, in these experiments as a flotation agent for aluminous shale.²⁾

A flotation machine for 50 g resembling the Denver Equipment Machine was constructed. The flotation test was performed in the usual way. The results obtained by investigating the floatability of quartzite and bauxite with Kontakt or Divulson D are indicated in Table 1. The results of the flotation experiment with aluminous shale, with Kontakt or Divulson D, and with oleic acid, camphor white oil, water glass, and anhydrous sodium carbonate, are shown in Table 2.

TABLE 2. (Flotation Time, 10 Minutes)

Flotation agent (g/t)	Pulp conc. (%)	Pulp temp. (°C)	pH value of pulp			Weight (%)	Assays (%)		Recovery (%)	
			Before flotation	After flotation			Al ₂ O ₃	SiO ₂	Al ₂ O ₃	SiO ₂
Kontakt 500	20	17	6.0	4.7	Concentrate	76.6	62.25	10.21	85.4	39.3
					Tailing	23.4	34.80	51.65	14.6	60.7
Divulson D 500	10	19	6.0	4.3	Concentrate	77.5	61.91	12.23	85.9	47.6
					Tailing	22.5	34.89	46.36	14.1	52.4
Anhydrous sodium carbonate 500 Water glass 100 Camphor white oil 100 Oleic acid 500	20	22	6.0	4.9	Concentrate	76.3	61.76	12.74	84.4	48.8
					Tailing Ore	23.7	36.73 55.83	42.98 19.91	15.6	51.2

The results obtained by using sulphonic acids having lipophilic groups such as Kontakt and Divulson D now in current use as fat-splitting agents as flotation agents are a little better than those obtained by using oleic acid, camphor white oil, water glass, and anhydrous sodium carbonate. The flotation test on aluminous shale with Kontakt or Divulson D was performed advantageously under the following conditions: particle size -200 mesh; regulating agent is not added; flotation is done at room temperature; pH value 4~5; flotation time 10 minutes; (1) pulp concentration 20%, Kontakt 500 g/t or (2) pulp concentration 10%, Divulson D 500 g/t.

3. Properties of Dodecyl and Cetyl Phenol Sulphonates as Detergents

There are reports by Krafft³⁾ and Johnson⁴⁾ on the synthesis of higher alkyl phenol, but their processes are complicated. According to several patented methods in France,⁵⁾ England,⁶⁾ and America,⁷⁾⁸⁾ the said phenol, though the combination of alkyl

radical with phenol nucleus differs from the above-mentioned case, was prepared by simpler methods than the above-mentioned methods, and it was then sulphonated to obtain higher alkyl phenol sulphonate. In this study, dodecyl and cetyl phenols were synthesized essentially following the English patent. The prevailing literature describes higher alkyl phenol sulphonates as being valuable detergents, but their properties are scarcely described. Therefore, an investigation was made of their properties. The relative surface tension and the relative interfacial tension against kerosene of aqueous solutions of dodecyl and cetyl phenol sulphonates were determined, because these capillary activities are primary factors for the estimation of detergency properties. The stabilities of these aqueous solutions against lime and acid were also investigated, and then their relative superiority as a detergent was discussed in this study.⁹⁾ Dodecyl phenol sulphonate was synthesized as follows: Equal amounts of phenol, dodecyl alcohol, and anhydrous zinc chloride were placed in a three-necked flask provided with an efficient mechanical stirrer, and the mixture was heated for sixteen hours at 190~200° C. Dodecyl phenol was separated from the reaction product by vacuum distillation. Dodecyl phenol sulphonic acid was obtained by sulphonating dodecyl phenol with 11% fuming sulphuric acid at 55~60° C while stirring. After removal of the unsulphonated matter with ether, the sodium salt of the said sulphonic acid was added with *ca.* 10 N sulphuric acid in the presence of ether. Pure dodecyl phenol sulphonic acid was obtained on removal of ether from the ether solution.

The Traube stalagmometer was used for the determination of the relative surface tension of dodecyl and cetyl phenol sulphonates. Their relative interfacial tension against kerosene (b.p. 200~250° C) was determined with the Hillyer pipette.¹⁰⁾ Both surface tension and interfacial tension at 25° C were expressed in relative values referred to those of distilled water at 25° C as 1. The results are shown in Tables 3, 4, 6, and 7. In Table 5, the influence of temperature on the surface tension is shown by comparing the surface tensions of 0.25% samples at 50° C with those at 25° C, the latter being taken as 1. Stabilities of dodecyl and cetyl phenol sulphonates against lime and acid are shown in Table 8. Stabilities of the samples

TABLE 3. Relative Surface Tension of Dodecyl Phenol Sulphonates at 25° C

Concentration (%)	Sodium salt	Potassium salt	Aniline salt	Pyridine salt	Triethanolamine salt
0.01	0.745	0.865	0.598	0.661	0.741
0.05	0.623	0.574	0.428	0.481	0.586
0.1	0.540	0.492	0.417	0.459	0.540
0.25	0.485	0.458	0.415	0.434	0.484
0.5	0.483	0.444	0.415	0.432	0.482
0.75	0.482	0.443	0.414	0.425	0.475
1	0.474	0.430	0.408	0.425	0.465

TABLE 4. Relative Surface Tension of Cetyl Phenol Sulphonates at 25° C

Concentration (%)	Sodium salt	Potassium salt	Aniline salt	Pyridine salt	Triethanolamine salt
0.01	0.837	0.798	0.852	0.765	0.767
0.05	0.624	0.610	0.555	0.583	0.607
0.1	0.583	0.568	0.518	0.533	0.556
0.25	0.527	0.527	0.492	0.498	0.520
0.5	0.501	0.504	0.481	0.485	0.499
0.75	0.492	0.502	0.478	0.481	0.491
1	0.490	0.490	0.470	0.478	0.489

TABLE 5. Variation of Surface Tension with Temperature

	Sodium salt	Potassium salt	Aniline salt	Pyridine salt	Triethanolamine salt
Dodecyl phenol sulphonate	1	1	1	1	1
25° C	0.929	0.934	0.948	0.933	0.905
50° C	0.071	0.066	0.052	0.062	0.095
Difference					
Cetyl phenol sulphonate	1	1	1	1	1
25° C	0.914	0.888	0.853	0.867	0.896
50° C	0.086	0.112	0.147	0.133	0.104
Difference					

TABLE 6. Relative Interfacial Tension of Dodecyl Phenol Sulphonate against Kerosene at 25° C

Conc. (%)	Sodium salt	Potassium salt	Aniline salt	Pyridine salt	Triethanolamine salt
0.01	0.370	0.513	0.243	0.278	0.329
0.05	0.221	0.250	0.041	0.081	0.203
0.1	0.141	0.147	0.018	0.064	0.153
0.25	0.133	0.100	0.004	0.049	0.142
0.5	0.129	0.092	—	0.039	0.138
0.75	0.123	0.083	—	0.030	0.132
1	0.114	0.077	—	0.021	0.126

TABLE 7. Relative Interfacial Tension of Cetyl Phenol Sulphonate against Kerosene at 25° C

Conc. (%)	Sodium salt	Potassium salt	Aniline salt	Pyridine salt	Triethanolamine salt
0.01	0.297	0.435	0.450	0.276	0.321
0.05	0.161	0.255	0.243	0.189	0.262
0.1	0.138	0.200	0.191	0.167	0.176
0.25	0.131	0.191	0.110	0.141	0.149
0.5	0.112	0.133	0.093	0.116	0.132
0.75	0.111	0.124	0.085	0.102	0.123
1	0.109	0.117	0.083	0.100	0.114

TABLE 8. Stabilities against Lime (I) and Acid (II) at Room Temperature

		Sodium salt	Potassium salt	Aniline salt	Pyridine salt	Triethanolamine salt
I	Dodecyl phenol	0.3	0.4	0.7	0.8	0.6
	Emulsive point	0.8	0.8	1.5	1.5	1.0
	Turbid point					
	Cetyl phenol	0.5	0.5	0.2	0.9	1.0
II	Emulsive point	1.1	4.0	0.8	2.0	2.8
	Turbid point					
[Contrast: Sodium oleate: Emulsive point 0.05, turbid point 0.2.]						
The emulsive and turbid points of each sample were ∞.						
[Contrast: Sodium oleate: Emulsive point 0.1, turbid point 0.4.]						

against lime and acid are indicated by cc of N/5 CaCl₂ or N/10 HCl which was dropped into 10 cc of 0.2% aqueous solution of the samples at room temperature until the solution reached the emulsive and turbid points.

The capillary activity of dodecyl phenol sulphonates is generally superior to that of cetyl phenol sulphonates, and the variation of the surface activity according to temperature is smaller for the former than for the latter. The capillary activity of

their aniline and pyridine salts is more excellent than that of their sodium salt. As for the stability against lime, cetyl phenol sulphonate is superior to dodecyl phenol sulphonate. The stability against acid is far superior for both sulphonates. The capillary activity of the aniline and pyridine salts of dodecyl phenol sulphonic acid is especially excellent. The stability of these two salts against lime is not particularly excellent, but the stability against acid is far superior. Therefore the said salts can be regarded as excellent detergents.

4. Dodecyl Phenol Sulphonic Acid and Its Halogen Derivatives as Fat-Splitting Agents

As described in Sect. 3, dodecyl phenol sulphonate is valuable as a detergent. But the said sulphonic acid had, so far as is known, not been used as a fat-splitting agent. Dodecyl phenol sulphonic acid and its halogen derivatives, such as chloro- and iodo-derivatives, were synthesized in this experiment, and the fat-splitting power of these products was compared with that of dodecyl benzene sulphonic acid and Kontaktpalter.¹¹⁾ The bromo-derivative was not examined for a reason mentioned later.

For the synthesis of chlorododecyl phenol sulphonic acid, sodium dodecyl phenol sulphonate prepared by the method described in Sect. 3 was chlorinated with potassium chlorate and hydrochloric acid, and crude chlorododecyl phenol sulphonic acid obtained by extraction with ether was purified in the following way. An aqueous solution of the crude product was neutralized with caustic soda until the pH value became 1~2. The solution was evaporated to dryness, the residue washed with ether to remove the unsulphonated matter, and then ether was added to the insoluble residue. Free sulphonic acid was then obtained by treating the sulphonate in ether with *ca.* 10 N sulphuric acid and distilling off the ether. The chlorine content of its sodium salt determined by the Stepanow¹²⁾-Bacon¹³⁾ method was 9.02%. Iodododecyl phenol sulphonic acid was synthesized by the action of iodine on dodecyl phenol sulphonic acid in a carbon tetrachloride solution, using pyridine as a carrier. The purification was done in the same way as above-mentioned. Dodecyl benzene sulphonic acid was prepared by sulphonating dodecyl benzene obtained by the Fittig reaction, and it was purified by recrystallization of its sodium salt from warm water. In an attempt to prepare bromododecyl phenol sulphonic acid by reacting bromine with dodecyl phenol sulphonic acid in a carbon tetrachloride solution, using pyridine as a carrier, there were indications that a portion of the sulfo-group was replaced by bromine. For this reason, it was excluded from the present research. The purified Kontaktpalter was prepared by washing an ether solution of Kontaktpalter with *ca.* 3 N hydrochloric acid and then removing the ether by distillation.

The fat-splitting experiment was performed as follows. To 5 cc of rape oil refined with sulphuric acid were added 5 cc of 1 N sulphuric acid and a fat-splitting agent in a proportion of one part to 100 parts of oil when the agent was sulphonic acid or 0.0001 mole of the fat-splitting agent per 5 cc of the oil when it was barium salt. The mixture was set in reaction at 100° C for five hours with *ca.* 500 r.p.m. stirring. The increase of acid value caused by splitting was calculated from the acid values before and after the experiment and corrected for the changes in weight caused by splitting. The fat-splitting power was expressed as 100 times the corrected increase of acid value divided by the ester value before the experiment. In Table 9, the

TABLE 9

	I	II
$C_{12}H_{25}\cdot C_6H_5OH\cdot SO_3H$	82.9	84.2
$Cl\cdot C_{12}H_{25}\cdot C_6H_5OH\cdot SO_3H$	84.2	87.1
$I\cdot C_{12}H_{25}\cdot C_6H_5OH\cdot SO_3H$	88.4	86.1
$C_{12}H_{25}\cdot C_6H_4\cdot SO_3H$	75.1	81.1
Kontaktspalter on the market		75.2
Kontaktspalter purified		79.5

results obtained by using 0.0001 mole of barium salt are shown in (I), and the results obtained by using one part of sulphonic acid per 100 parts of oil are shown in (II).

Dodecyl, chlorododecyl, and iodododecyl phenol sulphonic acids had not previously been used as fat-splitting agents. But it is now ascertained that the fat-splitting power of each of the said sulphonic acids is superior to that of dodecyl benzene sulphonic acid and Kontaktspalter. It is also demonstrated clearly that the fat-splitting power of dodecyl benzene sulphonic acid is increased by introducing the hydroxyl radical into the benzene nucleus, and further by introducing chlorine or iodine.

5. Dodecyl Phenol Sulphonate and Its Halogen Derivatives as Antiseptics

Phenols are of course used as germicides, but lower alkyl phenols are toxic. The chemical property of higher alkyl phenol resembles that of higher alcohol,⁴ the toxic strength decreases, and the germicidal action generally increases by introducing halogen or an aliphatic radical into the phenol nucleus. Alkyl phenol sulphonate is

TABLE 10

		Days elapsed→													
Amount of antiseptics ↓		3	4	5	6	7	8	9	10	11	12	13	14	15	30
0		+	+	+	+	+	+	+	+	+	+	+	+	+	+
1 100,000	Sample 1	-	+	+	+	+	+	+	+	+	+	+	+	+	+
	" 2	-	+	+	+	+	+	+	+	+	+	+	+	+	+
	" 3	-	+	+	+	+	+	+	+	+	+	+	+	+	+
	" 4	-	+	+	+	+	+	+	+	+	+	+	+	+	+
	" 5	+	+	+	+	+	+	+	+	+	+	+	+	+	+
1 20,000	Sample 1	-	-	-	-	-	-	-	+	+	+	+	+	+	+
	" 2	-	-	-	-	-	-	-	-	+	+	+	+	+	+
	" 3	-	-	-	-	-	-	-	-	-	+	+	+	+	+
	" 4	-	-	-	-	-	-	-	-	-	-	-	-	+	+
	" 5	+	+	+	+	+	+	+	+	+	+	+	+	+	+
1 10,000	Sample 1	-	-	-	-	-	-	-	-	-	-	-	-	-	-
	" 2	-	-	-	-	-	-	-	-	-	-	-	-	-	-
	" 3	-	-	-	-	-	-	-	-	-	-	-	-	-	-
	" 4	-	-	-	-	-	-	-	-	-	-	-	-	-	-
	" 5	+	+	+	+	+	+	+	+	+	+	+	+	+	+

+ shows that the surface of soy has been covered with mould.

Sample 1. Addition of butyl *p*-hydroxybenzoate.

" 2. " sodium dodecyl phenol sulphonate.

" 3. " sodium chlorododecyl phenol sulphonate.

" 4. " sodium iodododecyl phenol sulphonate.

" 5. " sodium dodecyl benzene sulphonate.

also useful as a germicide.⁷⁾ In consideration of the above-mentioned facts, sodium dodecyl phenol sulphonate and its halogen derivatives, such as chloro- and iodo-derivatives, were studied as antiseptics.¹⁵⁾ The bromo-derivative was excluded from the study for the reason mentioned in Sect. 4. Sodium dodecyl benzene sulphonate, however, was included.

Sodium dodecyl phenol sulphonate and its chloro- and iodo-derivatives, and sodium dodecyl benzene sulphonate, were obtained by neutralizing an aqueous solution of each sulphonic acid, prepared by the method mentioned in Sect. 4, with caustic soda. For the estimation of the effect of antiseptics, a sample of 15° Bé soy was added to the sodium sulphonate to be tested and putrid soy was allowed to stand at 29° C until the surface of soy was covered with mould. By way of comparison a similar experiment was performed with butyl *p*-hydroxybenzoate. The results are indicated in Table 10.

As an antiseptic for soy, sodium dodecyl phenol sulphonate has at least the same effect as butyl *p*-hydroxybenzoate. The antiseptic power is increased slightly by introducing chlorine or iodine to the phenol nucleus of sodium dodecyl phenol sulphonate. On the contrary, sodium dodecyl benzene sulphonate, having no hydroxyl radical, shows scarcely any effect as an antiseptic for soy.

6. α -Chlorodibutyl Naphthalene Sulphonic Acid as a Fat-Splitting Agent

α -Chlorodibutyl naphthalene sulphonic acid was synthesized by treatment of α -chloronaphthalene and *n*-butyl alcohol with conc. sulphuric acid, and its fat-splitting power was determined. This sulphonic acid had not previously been as a fat-splitting agent. For the sake of comparison, the fat-splitting power of dibutyl naphthalene sulphonic acid was also determined.¹⁶⁾

There are several reports^{17) 18) 19)} on the synthesis of α -chloronaphthalene. The author adopted a process which consisted of adding 1% of ferric chloride to naphthalene, and then passing dried chlorine gas through the mixture at *ca.* 100° C. The α -chloronaphthalene thus obtained (boiling at 260~265° C) and *n*-butyl alcohol were placed in a three-necked flask equipped with a mechanical stirrer. The flask was heated at *ca.* 100° C, and conc. sulphuric acid was added dropwise. The temperature of the reaction substance rose temporarily above 100° C owing to exothermic reaction. The heating was continued for 5 hours with stirring. Thus crude α -chlorodibutyl naphthalene sulphonic acid was obtained. It was converted to sodium salt to which an adequate amount of water was added, unsulphonated matter was removed with ether, and then pure α -chlorodibutyl naphthalene sulphonic acid was obtained by treating the sodium salt with *ca.* 10 N sulphuric acid followed by extraction with ether. Dibutyl naphthalene sulphonic acid was prepared as follows. To naphthalene and *n*-butyl alcohol (mole ratio 1 : 2), conc. sulphuric acid was added dropwise at 70~80° C with active stirring, and then the temperature was raised slowly. The temperature of the reaction substance, however, rose to 120~130° C temporarily. Heating and stirring were continued for 2 hours at *ca.* 100° C. Thus crude dibutyl naphthalene sulphonic acid was obtained. Its purification was carried out as mentioned above. The fat-splitting experiment was performed in the same way as described in Sect. 4, using one part of the fat-splitting agent to 100 parts of oil. The results are shown in Table 11.

TABLE 11

Fat-splitting agent→ Conc. of sulphuric acid (N) ↓	Rape oil		Coconut oil	
	$\text{Cl}\cdot\text{C}_8\text{H}_{18}\cdot\text{C}_{10}\text{H}_4\cdot\text{SO}_3\text{H}$	$\text{C}_8\text{H}_{18}\cdot\text{C}_{10}\text{H}_5\cdot\text{SO}_3\text{H}$	$\text{Cl}\cdot\text{C}_8\text{H}_{18}\cdot\text{C}_{10}\text{H}_4\cdot\text{SO}_3\text{H}$	$\text{C}_8\text{H}_{18}\cdot\text{C}_{10}\text{H}_5\cdot\text{SO}_3\text{H}$
0	62.2	35.1	62.7	53.0
0.5	85.7	79.8	84.1	80.4
1	88.5	84.2	84.9	84.5

α -Chlorodibutyl naphthalene sulphonic acid had not yet previously been used as a fat-splitting agent. The fat-splitting power of this sulphonic acid tested with rape and coconut oils is superior to that of dibutyl naphthalene sulphonic acid which is known as an excellent fat-splitting agent.

A comparison of fat-splitting powers of fat-splitting agents on a given fat, based on the results of a fat-splitting experiment carried out in the shortest possible time and under the same conditions as far as possible, is generally applicable when the relative strength not containing absolute value is concerned, regardless of the career of the fat refined with sulphuric acid before fat-splitting. But it is significant that a comparison of fat-splitting powers of the same fat-splitting agent on different fats is not always valuable, even for the estimation of the relative strength, because the degree of variation of fat-splitting power due to the career of fats refined with sulphuric acid before fat-splitting, is not alike for each sample of fats.

7. Tri- and Tetra-butyl Naphthalene Sulphonic Acids as Fat-Splitting Agents

Tri- and tetra-butyl naphthalene sulphonic acids were prepared from naphthalene, *n*-butyl alcohol, and conc. sulphuric acid. The fat-splitting power of the said sulphonic acids had not previously been determined; therefore it was investigated and compared with that of dibutyl naphthalene sulphonic acid.²⁰⁾

Tetra-butyl naphthalene sulphonic acid was prepared as follows. In a three-necked flask fitted with a mechanical stirrer were placed naphthalene and *n*-butyl alcohol (mole ratio 1 : 4). To this was added conc. sulphuric acid dropwise at 70~80° C with active stirring. And then the temperature was raised very slowly. The operation was carried out cautiously, for the evolution of heat in this case was great. Stirring at *ca.* 100° C was continued for about 2 hours, by which time crude tetra-butyl naphthalene sulphonic acid was obtained. Its purification was performed in the same manner as that of dibutyl naphthalene sulphonic acid. Tributyl naphthalene sulphonic acid was prepared as follows. It was prepared from naphthalene and *n*-butyl alcohol (mole ratio 1 : 3) treated with conc. sulphuric acid by almost the same method used in preparing tetra-butyl naphthalene sulphonic acid, but the amount of sulphuric

TABLE 12

Fat-splitting agent→ Conc. of sulphuric acid (N) ↓	Soy-bean oil			Coconut oil		
	$\text{C}_{16}\text{H}_{36}\cdot\text{C}_{10}\text{H}_3\cdot\text{SO}_3\text{H}$	$\text{C}_{12}\text{H}_{27}\cdot\text{C}_{10}\text{H}_4\cdot\text{SO}_3\text{H}$	$\text{C}_8\text{H}_{18}\cdot\text{C}_{10}\text{H}_5\cdot\text{SO}_3\text{H}$	$\text{C}_{16}\text{H}_{36}\cdot\text{C}_{10}\text{H}_3\cdot\text{SO}_3\text{H}$	$\text{C}_{12}\text{H}_{27}\cdot\text{C}_{10}\text{H}_4\cdot\text{SO}_3\text{H}$	$\text{C}_8\text{H}_{18}\cdot\text{C}_{10}\text{H}_5\cdot\text{SO}_3\text{H}$
0	65.2	60.7	50.4	83.3	81.8	77.8
0.5	91.7	91.0	82.0	89.7	89.6	86.5
1	94.6	92.8	89.3	90.2	90.0	89.9

acid used was smaller. Also the evolution of heat was smaller. The fat-splitting experiment was carried out by the same process as in Sect. 4. The results are indicated in Table 12.

The fat-splitting power of tri- and tetra-butyl naphthalene sulphonic acids on soybean and coconut oils is superior to that of dibutyl naphthalene sulphonic acid, the well-known powerful fat-splitting agent. It has now been ascertained that the fat-splitting power of tetrabutyl naphthalene sulphonic acid is a little superior to that of tributyl naphthalene sulphonic acid.

8. Properties of Tetrabutyl Naphthalene Sulphonate as a Detergent

No literature exists on tetrabutyl naphthalene sulphonate. This compound was prepared and its properties as a detergent were investigated in the experiment described in this paper. For the sake of comparison, the properties of dibutyl naphthalene sulphonate, principal ingredient of Nekal, were also investigated.²¹⁾

Sodium tetrabutyl naphthalene sulphonate was obtained from the refined tetrabutyl naphthalene sulphonic acid described in Sect. 7.²⁰⁾ The determination of the relative surface and interfacial tensions of sodium tetra- and di-butyl naphthalene sulphonates, and mixtures containing an equal quantity of the said sulphonates and sodium sulphate or sodium pyrophosphate, was carried out by the method described in Sect. 3.⁹⁾ The results are shown in Tables 13 and 14. Table 15 shows the influence of temperature on the surface tension and the stabilities against lime and acid.

Sodium tetrabutyl naphthalene sulphonate is superior to sodium dibutyl naphthalene sulphonate in the capillary activity and the changes of surface activity with temperature. There is scarcely any difference between both sulphonates in the sta-

TABLE 13. Relative Surface Tension at 25° C

Added matter→ Conc. (%) ↓	Sodium tetrabutyl naphthalene sulphonate			Sodium dibutyl naphthalene sulphonate		
	—	Sodium sulphate	Sodium pyrophosphate	—	Sodium sulphate	Sodium pyrophosphate
0.01	0.948	0.896	0.901	0.978	0.952	0.973
0.05	0.725	0.594	0.619	0.750	0.741	0.743
0.1	0.615	0.518	0.537	0.640	0.629	0.633
0.25	0.527	0.456	0.466	0.535	0.503	0.528
0.5	0.495	0.447	0.455	0.495	0.475	0.477
0.75	0.492	0.445	0.447	0.492	0.472	0.474
1	0.485	0.443	0.446	0.492	0.468	0.471

TABLE 14. Relative Interfacial Tension against Kerosene at 25° C

Added matter→ Conc. (%) ↓	Sodium tetrabutyl naphthalene sulphonate			Sodium dibutyl naphthalene sulphonate		
	—	Sodium sulphate	Sodium pyrophosphate	—	Sodium sulphate	Sodium pyrophosphate
0.01	0.475	0.439	0.443	0.512	0.448	0.471
0.05	0.309	0.218	0.227	0.369	0.276	0.311
0.1	0.197	0.091	0.101	0.276	0.219	0.220
0.25	0.064	0.017	0.022	0.097	0.065	0.067
0.5	0.015	—	—	0.045	0.018	0.021
0.75	—	—	—	0.045	0.015	0.018
1	—	—	—	0.044	—	0.015

TABLE 15. Variation of Surface Tension with Temperature (I), and the Stabilities against Lime (II) and Acid (III) at Room Temperature

	Added matter	Sodium tetrabutyl naphthalene sulphonate			Sodium dibutyl naphthalene sulphonate		
		—	Sodium sulphate	Sodium pyrophosphate	—	Sodium sulphate	Sodium pyrophosphate
I	25° C	1	1	1	1	1	1
	50° C	0.947	0.971	0.974	0.979	0.968	0.97
	Difference	0.053	0.029	0.026	0.021	0.032	0.03
II	Emulsive point	0.2	0.4	1.1	0.1	0.7	1.0
	Turbid point	0.4	0.7	1.7	0.4	1.0	1.9
[Contrast : Sodium oleate : Emulsive point 0.05, turbid point 0.2.]							
III	The emulsive and turbid points of each sample were ∞.						
	[Contrast : Sodium oleate : Emulsive point 0.1, turbid point 0.4.]						

bility against lime. Both have a far superior stability against acid. Sodium tetrabutyl naphthalene sulphonate, in itself, is a more excellent detergent than sodium dibutyl naphthalene sulphonate. By adding sodium sulphate or sodium pyrophosphate as a builder, the difference in the surface active properties of both sulphonates becomes more marked.

9. Surface Active Agent Prepared from Naphthalene, β , β -Dinaphthyl, *n*-Butyl Alcohol, Sulphuric Acid, etc.

The surface active properties of sodium sulphonate prepared from naphthalene, β , β -dinaphthyl, *n*-butyl alcohol, sulphuric acid, etc., were investigated. The relative surface tension, the relative interfacial tension against kerosene, and the stabilities against lime and acid were determined.²²⁾ These properties were compared with those of sodium dibutyl naphthalene sulphonate.

The surface active agent was prepared from naphthalene, β , β -dinaphthyl, *n*-butyl alcohol, sulphuric acid, etc. as follows. There are already valuable reports on the reaction of preparing β , β -dinaphthyl dy treatment of naphthalene with $AlCl_3$ ²³⁾ or Japanese acid clay.²⁴⁾ In this study, β , β -dinaphthyl (m.p. 180~181° C), prepared from naphthalene by using activated clay in the place of Japanese acid clay, was used. In a three-necked flask were placed naphthalene and β , β -dinaphthyl (4 : 1) together with *n*-butyl alcohol, and conc. sulphuric acid was added dropwise at *ca.* 70° C with active stirring. The temperature was then raised slowly. The temperature of reaction product rose to 120~130° C temporarily. Stirring was continued for two hours at *ca.* 100° C. The crude sulphonic acid thus obtained was neutralized with caustic soda, and unsulphonated matter was removed with ether. Pure sulphonic acid was obtained by the action of *ca.* 10 N sulphuric acid on the sulphonate in the presence of ether. Neutralization of the sulphonic acid with caustic soda gave pure sulphonate. Thus, a surface active agent, consisting of sodium sulphonate prepared from naphthalene, β , β -dinaphthyl, *n*-butyl alcohol, sulphuric acid, etc., was obtained. The determination of the relative surface and interfacial tensions of this surface active agent and the mixture containing an equal quantity of the agent and sodium sulphate or sodium pyrophosphate, was performed by the method mentioned in Sect. 3.⁹⁾ The results are shown in Tables 16 and 17. Table 18 shows the stabilities against

lime and acid and the influence of temperature on the surface tension.

In the capillary activity and the variation of surface activity with temperature, this surface active agent, sodium sulphonate prepared from naphthalene, β , β -dinaphthyl, *n*-butyl alcohol, sulphuric acid, etc. (A), is superior to sodium dibutyl naphthalene sulphonate (B). In the stability against lime, there is scarcely any difference between the two. Both are excellent in their stability against acid. The increase of capillary activity caused by the addition of sodium sulphate or sodium pyrophosphate is greater for A than for B. Therefore, A can be regarded as a more excellent surface active agent than B.

TABLE 16. Relative Surface Tension at 25° C

Added matter→ Conc. (%) ↓	—	Sodium sulphate	Sodium pyrophosphate
0.01	0.950	0.921	0.922
0.05	0.742	0.645	0.671
0.1	0.638	0.553	0.569
0.25	0.535	0.482	0.491
0.5	0.503	0.469	0.476
0.75	0.495	0.467	0.472
1	0.495	0.465	0.470

TABLE 17. Relative Interfacial Tension against Kerosene at 25° C

Added matter→ Conc. (%) ↓	—	Sodium sulphate	Sodium pyrophosphate
0.01	0.601	0.409	0.413
0.05	0.339	0.184	0.190
0.1	0.228	0.058	0.065
0.25	0.077	0.012	0.020
0.5	0.028	—	—
0.75	0.020	—	—
1	0.018	—	—

TABLE 18. Variation of Surface Tension with Temperature (I), and the Stabilities Against Lime (II) and Acid (III) at Room Temperature

	Added matter	—	Sodium sulphate	Sodium pyrophosphate
I	25° C	1	1	1
	50° C	0.955	0.953	0.967
	Difference	0.045	0.047	0.033
II	Emulsive point	0.1	0.3	0.9
	Turbid point	0.4	0.7	1.9
[Contrast: Sodium oleate: Emulsive point 0.05, turbid point 0.2.]				
III	The emulsive and turbid points of each sample were ∞ . [Contrast: Sodium oleate: Emulsive point 0.1, turbid point 0.4.]			

10. Fat-Splitting Agent Prepared from Naphthalene, β , β -Dinaphthyl, *n*-Butyl Alcohol, Sulphuric Acid, etc.

The fat-splitting power of the sulphonic acid prepared from naphthalene, β , β -dinaphthyl, *n*-butyl alcohol, sulphuric acid etc., was determined and compared with

those of dibutyl naphthalene sulphonic acid and Kontaktpalter.²⁵⁾

As a fat-splitting agent, the pure sulphonic acid mentioned in Sect. 9²²⁾ was used. The fat-splitting experiment was performed by the process described in Sect. 4.¹¹⁾ The results are indicated in Table 19. Table 20 shows the fat-splitting power of dibutyl naphthalene sulphonic acid as compared with that of Kontaktpalter.²⁰⁾

TABLE 19

Fat-splitting agent→ Conc. of sulphuric acid (N) ↓	Soy-bean oil		Coconut oil	
	Sample I	Sample II	Sample I	Sample II
0	74.9	67.3	80.1	75.6
0.5	89.9	87.3	93.0	91.2
1	90.5	89.6	93.1	92.1

Sample I: Fat-splitting agent prepared for trial from naphthalene, β , β -dinaphthyl, *n*-butyl alcohol, sulphuric acid, etc.

Sample II: Dibutyl naphthalene sulphonic acid.

TABLE 20. Fat-Splitting Experiment against Coconut Oil

Conc. of sulphuric acid (N)→ Fat-splitting agent ↓	0	0.5	1
C ₈ H ₁₈ ·C ₁₀ H ₅ ·SO ₃ H	77.8	86.5	89.9
Kontaktpalter on the market	49.4	80.9	81.7

It has become clear that the fat-splitting power of the sulphonic acid prepared from naphthalene, β , β -dinaphthyl, *n*-butyl alcohol, sulphuric acid, etc. on soy-bean and coconut oils is a little superior to that of dibutyl naphthalene sulphonic acid. The fat-splitting power of dibutyl naphthalene sulphonic acid on coconut oil is more excellent than that of Kontaktpalter.

The figures for the fat-splitting power recorded in each table in the preceding experiments have generally a good reproducibility. As noted briefly in Sect. 6,¹⁶⁾ it must be borne in mind, however, that the fat-splitting power of a fat-splitting agent is not always alike for each sample of fats of the same sort. It differs according to the history of each sample prior to the fat-splitting experiment, as is seen from Tables 19 and 20 in the case of the fat-splitting power of dibutyl naphthalene sulphonic acid on coconut oil.

11. Summary

The following results were obtained by using sulphonic acids having lipophilic groups as fat-splitting and flotation agents, and by using their salts as detergents and antiseptics. It has been ascertained that certain fat-splitting agents, such as Kontakt and Divulson D, are a little superior to oleic acid, etc. as flotation agents.

It has become clear that the capillary activity of dodecyl phenol sulphonate is generally superior to that of cetyl phenol sulphonate; especially the pyridine and aniline salts of dodecyl phenol sulphonate are excellent detergents.

Dodecyl phenol sulphonate and its halogen derivatives are equal or a little superior to butyl *p*-hydroxybenzoate as antiseptics for soy.

The fat-splitting powers of dodecyl phenol sulphonic acid, of its halogen derivatives, of α -chlorodibutyl naphthalene sulphonic acid, of tri- and tetra-butyl naphtha-

lene sulphonic acids, and of a fat-splitting agent prepared from naphthalene, β , β -dinaphthyl, *n*-butyl alcohol, sulphuric acid, etc. are greater than the fat-splitting power of Kontaktsplter.

Tetrabutyl naphthalene sulphonate and a surface active agent prepared from naphthalene, β , β -dinaphthyl, *n*-butyl alcohol, sulphuric acid, etc. have more excellent surface active properties than dibutyl naphthalene sulphonate, which is the principal ingredient of Nekal.

It has been ascertained that sulphonic acids having halogen in lipophilic group, such as chloro- and iodo-dodecyl phenol sulphonic acids and α -chlorodibutyl naphthalene sulphonic acid, are more excellent in fat-splitting power than sulphonic acids having no halogen. For polybutyl naphthalene sulphonic acid or its salt, within the limits of the research, the fat-splitting power and the capillary activity become greater with increasing butyl radicals introduced into the naphthalene nucleus. The fat-splitting power and the capillary activity become more excellent, when the lipophilic property of butyl aryl sulphonic acid or its salt is increased by using the bimolecular condensation product of aromatic hydrocarbon, such as β , β -dinaphthyl, together with naphthalene.

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