GAS–LIQUID CHROMATOGRAPHY
OF LINEAR DETERGENT ALKYLATES

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Although a multitude of anionic surfactant types have been synthesized and tested during the past two decades, one of the types to have achieved major commercial importance is the alkyl-aryl sulphonate type.

In considering these compounds it is evident that it is the hydrophobic part of the molecule which governs the efficiency of the surfactant. Information about this hydrophobic, or hydrocarbon, part of the molecule is then of major importance, and owing to the difficulty of examination by conventional chemical techniques this study was undertaken.

Alkylates supplied commercially can be divided into two main groups, those formed by alkylation of benzene with tetrapropylene, and those formed by alkylation of benzene with a straight chain olefin. Owing to the extremely complex nature of the tetrapropylene benzene types, satisfactory separations have not so far been obtained. Alkylates prepared from *n*-olefins (linear alkylates), however, represent much more simple systems. This is evident from the fact that linear types have a very restricted number of isomeric variations for each possible aliphatic chain length. Table I readily illustrates this limitation.

TABLE I

NUMBER OF POSITIONAL ISOMERS
OF MONOPHENYL-*n*-ALKANES

Aliphatic chain	Number of carbon atoms	Number of possible phenyl positions
Hexane	6	3
Heptane	7	4
Octane	8	4
Nonane	9	5
Decane	10	5
Dodecane	12	6

As can be seen from this table, the number of possible isomeric phenyl positions can be calculated as being (Number of C-atoms/2) where fractional values are rounded upward to the nearest whole number. Current commercial linear alkylates, Shell's Dob 83 and Dobane JN being examples, generally contain significant amounts of aliphatic chain lengths other than dodecyl.

This paper confirms this and gives a characterisation of chain lengths together with the spread of phenyl attachment on these chains.

<center>EXPERIMENTAL</center>

Apparatus

A Pye argon chromatograph* with argon as carrier gas.

Columns

All columns were of glass 4 ft. long and ¼ in. I.D. The stationary phase which effected best separation was Apiezon L grease. This was dissolved in a volatile solvent, 40–60° light petroleum, slurried with Celite (Embacel by May and Baker, 60–100 mesh), oven dried, and packed by vibration.

Operating conditions

Separations were carried out at 130°, using a detector voltage of 1750 V, a sensitivity of " × 10" and a flow rate of 40 ml per min of Argon (measured by a soap bubble manometer). Inlet pressure was 10 lb./sq.in. and sample size was 0.05 μl. Under these conditions the column efficiency was approximately 650 theoretical plates per foot.

<center>DISCUSSION</center>

Figs. 1 and 2 show the chromatograms obtained under standard conditions for Dob 83 and Dobane JN. The problem of identifying these peaks was overcome in several stages. It was observed that the peaks occurred in definite groups and it seemed
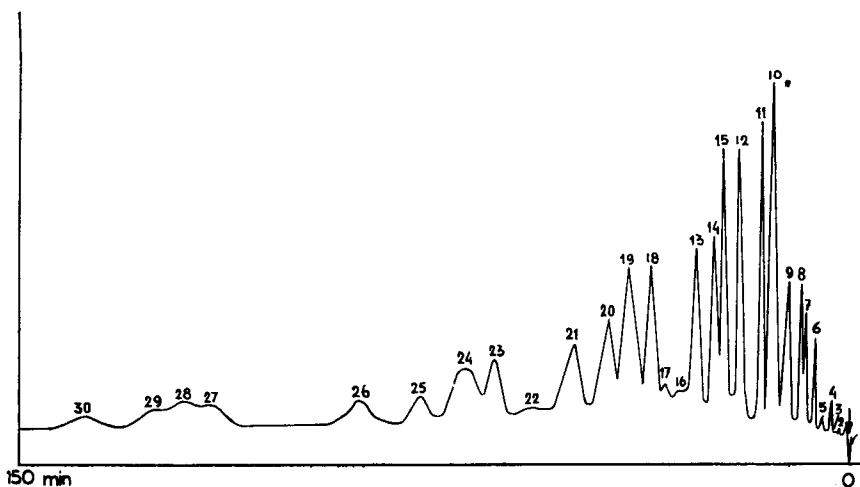

Fig. 1. Chromatogram of Dob 83. Sample size: 0.05 μl; column: 5 % w/w Apiezon L/(60–100 mesh) Celite (4 ft. long); temp.: 130°; flow rate: 40 ml argon/min; inlet pressure: 10 lb./sq. in.; outlet pressure: atmospheric; detector voltage: 1750 V; sensitivity: × 10; chart speed: 6 in./h. For key to peak numbers see Table II.

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* W. G. Pye and Co. Ltd., Granta Works, Cambridge.

likely that, in general, these would be of similar molecular weight, at a first approximation. Calculation of retention volumes showed that some of the sets of peaks were common to both materials but, particularly in Dob 83, there were extra sets at lower molecular weights.

A personal communication from DENZLER[1] had indicated that there was no sign, from mass spectrometric evidence, of primary alkylbenzenes, thus reducing the number
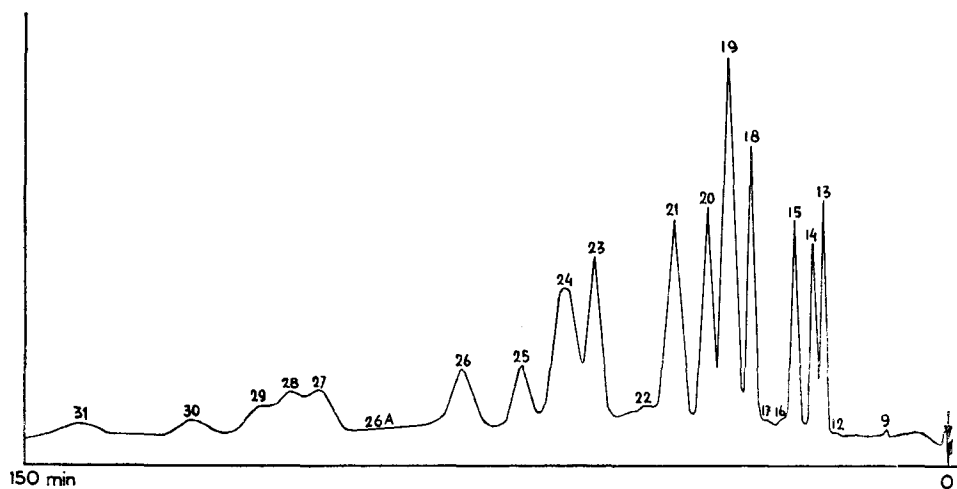

Fig. 2. Chromatogram of Dobane JN. For conditions see legend to Fig. 1.

of possible isomers, given in Table I of the introduction, by one in each case. It then seemed logical that isomerisation had occurred during alkylation. At first sight therefore, looking at Fig. 1, it was seen that peaks 17 to 21 and 22 to 26 might be regarded as the phenyl-undecanes and phenyl-dodecanes. It was then necessary to ascertain in which order these peaks were within the given molecular weight. Marker compounds 1-, 2- and 3-phenyl-dodecanes were then synthesised and a sample of a mixture of 2-, 3-, 4-, 5- and 6-phenyl-dodecanes was received. These immediately showed that peaks 23 and 18 were out of context and that twinning of the 5- and 6-phenylundecanes, and 5- and 6-phenyl-dodecanes had occurred. Calculating $\log_{10}$ retention volume and plotting these values against selected peak numbers[2] identified the homologous series of the substituents (Figs. 3 and 4).

The percentage weight of each isomer was then obtained by the method of weighing each peak. These weights, together with the relative retention data for each isomer are shown in Table II.

From this information the mass distribution and the phenyl distribution for each alkylate was obtained (Tables III and IV). The apparent molecular weight of each alkylate calculated from these data compared favourably with the molecular weight obtained by ebulliometry.

In addition to the peaks which were positively identified there were four remaining unidentified peaks. These peaks, 16, 17, 22 and 26A account for 6.52 % of the total

TABLE II

EXAMINATION OF SHELL ALKYLATES DOB 83 AND DOBANE JN

(Retention volumes relative to n-hexadecane = 1.00)

Peak No.	Isomer	Dob 83		Dobane JN	
		Relative retention volume	Area of each peak, % of total area	Relative retention volume	Area of each peak, % of total area
1	3-Phenylpentane	0.04	0.03		
2	2-Phenylpentane	0.05	0.14		
3	3-Phenylhexane	0.07	0.06		
4	2-Phenylhexane	0.09	0.25		
5	4- and 3-Phenylheptane	0.14	0.25		
6	2-Phenylheptane	0.17	0.86		
7	4-Phenyloctane	0.21	1.19		
8	3-Phenyloctane	0.22	1.63		
9	2-Phenyloctane	0.28	2.90	0.28	0.05
10	5- and 4-Phenylnonane	0.35	6.49		
11	3-Phenylnonane	0.40	5.33		
12	2-Phenylnonane	0.52	6.08	0.52	0.18
13	5-Phenyldecane	0.58	5.97	0.58	3.73
14	4-Phenyldecane	0.63	4.94	0.63	3.47
15	3-Phenyldecane	0.71	6.10	0.71	4.76
18	2-Phenyldecane	0.92	5.75	0.92	7.27
19	6- and 5-Phenylundecane	1.03	8.15	1.03	13.33
20	4-Phenylundecane	1.11	5.41	1.11	7.07
21	3-Phenylundecane	1.27	6.30	1.27	9.06
23	2-Phenylundecane	1.66	4.28	1.66	8.72
24	6- and 5-Phenyldodecane	1.80	5.94	1.80	11.02
25	4-Phenyldodecane	2.00	2.54	2.00	4.76
26	3-Phenyldodecane	2.28	3.37	2.28	6.73
27	2-Phenyldodecane	2.96	2.27	2.96	4.04
28	7-Phenyltridecane	3.08	2.04	3.08	3.60
29	6- and 5-Phenyltridecane	3.25	1.80	3.25	2.87
30	4-Phenyltridecane	3.54	1.19	3.54	1.29
31	3-Phenyltridecane	4.05	1.24	4.05	2.64
32	2-Phenyltridecane	5.31	1.10	5.31	1.04

TABLE III

MASS DISTRIBUTION OF SHELL ALKYLATES DOB 83 AND DOBANE JN

Mass distribution	Shell Dob 83 (% wt.)	Shell Dobane JN (% wt.)
148 (C_5 side chain)	0.17	—
162 (C_6 side chain)	0.31	—
176 (C_7 side chain)	1.01	—
190 (C_8 side chain)	5.72	0.05
204 (C_9 side chain)	17.90	0.18
218 (C_{10} side chain)	22.76	19.23
232 (C_{11} side chain)	24.14	38.18
246 (C_{12} side chain)	14.12	26.55
260 (C_{13} side chain)	7.37	11.44
Assorted branched side chain alkylates	6.52	4.38
Average mol. weight*	225.0	238.2
M.W. by ebulliometry	226.0	238.0

* Assuming average molecular weight for assorted branched side chain alkylates.

TABLE IV

WEIGHT DISTRIBUTION BY PHENYL POSITION
OF SHELL ALKYLATES DOB 83 AND DOBANE JN

Phenyl position	Shell Dob 83 (% wt.)	Shell Dobane JN (% wt.)
1-Phenyl	0.0	0.0
2-Phenyl	23.63	21.25
3-Phenyl	24.19	23.19
4-Phenyl	18.90	16.59
5-Phenyl	17.17	17.34
6-Phenyl	7.95	13.61
7-Phenyl	2.04	3.60
Branched side chain	6.52	4.38

weight in Dob 83, and 4.38 % of the total weight in Dobane JN. These unidentified peaks are probably due to branched side chain alkylates.

Small amounts of C_{14} alkyl chains are also known to be present in both alkylates but the peaks were too small and diffuse to be examined.

No peaks were found for the 1-phenyl-n-alkanes thus confirming the mass spectrometric evidence.
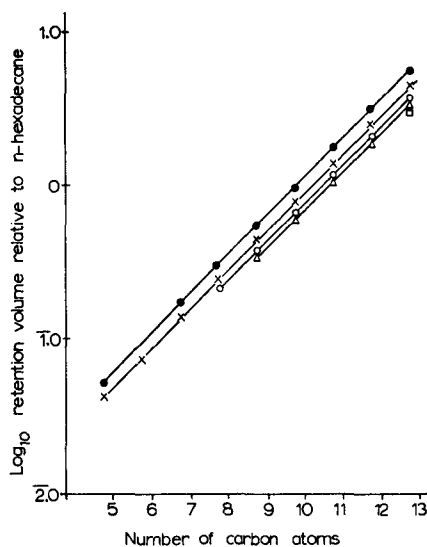

Fig. 3. Relationship between log_{10} retention volume and number of carbon atoms for Dob 83. ● = 2-phenyl isomers; × = 3-phenyl isomers; O = 4-phenyl isomers; △ = 5-phenyl and 5- and 6-phenyl isomers; □ = 7-phenyl isomers.
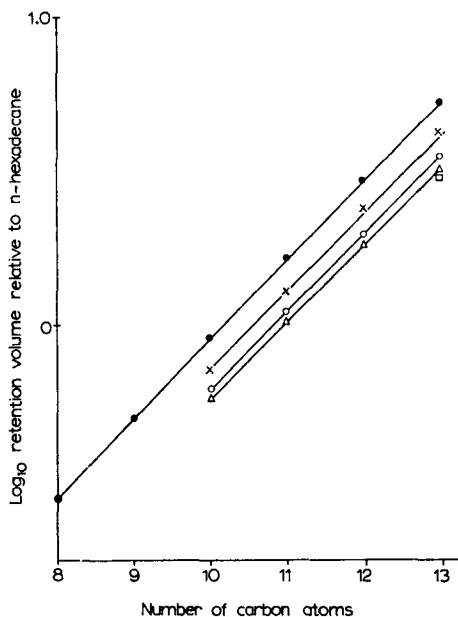
Fig. 4. Relationship between log_{10} retention volume and number of carbon atoms for Dobane JN. ● = 2-phenyl isomers; × = 3-phenyl isomers; O = 4-phenyl isomers; △ = 5- and 6-phenyl isomers; □ = 7-phenyl isomers.

SUMMARY

Apiezon L grease was found to be a selective liquid substrate for separating linear detergent alkylates by gas–liquid chromatography. The most important point which arises from this work is that substantially complete identification has been achieved of the components of a commercial alkylbenzene. Retention volumes, relative to n-hexadecane, are given for all the compounds appearing in two commercial samples of linear detergent alkylate, namely Shell's Dob 83, and Dobane JN.

REFERENCES

[1] R. E. DENZLER, Colgate-Palmolive, New Jersey, personal communication.
[2] A. T. JAMES AND A. J. P. MARTIN, *Biochem. J.*, 50 (1952) 679.