The sodium methylate solution is prepared by dissolving the required amount of metallic sodium in dry C. P. methanol. Although precautions should be taken to keep the solution dry, the presence of up to 1% of water introduces only a small error. The two alkalies should be compared frequently with standard 0.5 *N* acid. Anhydrides that are unreactive because of steric hindrance, may be heated with an excess of either alkali and back titrated cold with standard acid. In such cases, however, esters must be absent to avoid interference. Camphoric anhydride was the sole example of this class encountered.

Summary

1. A rapid and precise method for the determination of anhydrides of carboxylic acids based on sodium methylate titration has been developed. The method has been applied successfully to the following anhydrides: acetic, propionic, *n*-heptylic, succinic, glutaric, maleic, camphoric, benzoic, phthalic and furoic.

2. In connection with the above method, the hydrolytic cleavage of anhydrides was found to be accelerated by the use of pyridine.

3. The interference of lactones has been investigated. Phthalide and coumarin do not react. β-Methylumbelliferone reacts but does not interfere. Glucono-δ-lactone interferes with anhydride determinations.

WILMINGTON, DEL. RECEIVED OCTOBER 7, 1936

[CONTRIBUTION FROM THE KEDZIE CHEMICAL LABORATORY, MICHIGAN STATE COLLEGE]

The Surface Tensions, Densities, Free Surface Energies and Parachors of Some Derivatives of Benzylated Phenols[1]

BY D. T. EWING AND FRANCES W. LAMB

In this paper data are presented for the measurement of the surface tension and density at different temperatures of a series of new organic compounds, which are derivatives of benzylated phenols. From these values the molal free surface energy and parachors have been calculated. Although these physical factors have been evaluated for a number of organic compounds, reliable surface tension values of only four diphenyl and two triphenyl compounds have been reported previously.

The compounds used in these investigations were those prepared by R. C. Huston and associates in a series of investigations in this Laboratory. These substances were found to be of sufficient purity to warrant direct measurement without further purification. In each case the compounds had been carefully distilled many times.

Density measurements were made at different temperatures with a pycnometer which was essentially a bulb of glass blown on a capillary. A special pycnometer was made partly because in several cases the sample of liquid was limited to a few ml. and partly because the best density bulb is one which is spherical in form with only a fine capillary opening. In each case the pycnometer was carefully calibrated with water at the several temperatures. Density measurements were made at 25, 35 and 50°. For this purpose the substances were equilibrated in constant-temperature water-baths which did not vary in temperature more than 0.005°.

Surface tension measurements were made with a metal drop weight apparatus[2] supported on a heavy concrete pillar free from the floor of the laboratory to avoid any vibration. The radius of the tip was carefully determined with a Gaertner comparator and found to have a value of 0.26740 cm. The drop weight assembly with the liquid was lowered below the surface of the water in the thermostat and allowed to remain until the temperature of the liquid was a constant when the drop weight determinations were made. For each liquid, when the volume available permitted, 25 to 30 drops were formed very slowly into a weighing bottle and from this weight that of the drop was determined.

From the weight of the drop and the density of the liquid the surface tension γ was calculated by the equation

$$\gamma = \frac{mg}{2\pi r f(r/v^{1/3})}$$

where m = mass of drop in grams
g = 981 dynes
r = 0.26740 cm. the radius of the tip
v = volume of the drop

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(1) A portion of Part I of a thesis submitted to the Graduate Faculty of the Michigan State College by Miss Frances W. Lamb in partial fulfilment of the requirements for the Ph.D. degree, June, 1933.

(2) Harkins and Brown, THIS JOURNAL, **41**, 519 (1919)

TABLE I

	Compound	Temp., °C.	Wt. 1 drop, g.	Surface tension, dynes	d	$(m/d)^{2/3}$ ergs	P, obsd.	P, calcd.	ΔP
1	2-Chlorophenyl benzyl ether, b. p. 178–179°	25	0.042841	41.699	1.15494	1374.4	480.85		
		35	.041732	40.626	1.14607	1345.9	481.41	476.2	+ 5.21
		50	.040147	39.092	1.13338	1304.7	482.13		
2	2-Chlorobenzylphenol ether, b. p. 141–145°	25	.042974	41.836	1.18044	1359.0	470.84		
		35	.041742	40.644	1.17199	1326.6	470.82	476.2	− 5.38
		50	.040096	39.050	1.15764	1285.1	472.91		
3	2-Chloro-4-benzylphenol, b. p. 145–148°	25	.044938	43.722	1.18805	1414.1	473.01		
		35	.043869	42.700	1.17915	1388.0	473.79	476.2	− 2.41
		50	.042228	41.111	1.16653	1346.0	474.40		
4	2-*o*-Chlorobenzylphenol, b. p. 146–151°	25	.044416	43.236	1.21219	1379.8	463.20		
		35	.043782	42.623	1.20494	1365.7	463.42	476.2	−12.78
		50	.042444	41.328	1.19563	1331.1	463.43		
5	Benzoyl ester of 2-*o*-chlorobenzylphenol, b. p. 173–176°	25	.043708	42.551	1.20592	1766.5	683.17		
		35	.043137	41.998	1.19911	1750.0	684.81	693.9	− 9.09
		50	.042014	40.910	1.18696	1716.4	687.30		
6	2-Methyl-4,6-dibenzylphenol, b. p. 225–227°	25	.043630	42.393	1.09866	1737.0	669.21		
		35	.043008	41.796	1.09137	1720.2	671.31	689.9	−18.59
		50	.041870	40.709	1.80043	1686.8	673.86	...	...
7	3-Methyl-2,6-dibenzylphenol, b. p. 216–218°	25	.040410	39.336	1.09552	1614.9	658.72		
		35	.039938	38.878	1.09159	1599.8	659.56	689.9	−30.34
		50	.039112	38.077	1.08133	1576.8	661.93		
8	4-Methyl-2,6-dibenzylphenol, b. p. 236–238°	25	.041760	40.624	1.09651	1666.7	663.44		
		35	.041234	40.119	1.08998	1652.8	665.32	689.9	−24.58
		50	.040249	39.176	1.07990	1623.7	667.54		
9	6-Benzyl-2-phenylphenol, b. p. 193°	25	.044991	43.697	1.11662	1654.4	598.95		
		35	.044092	42.840	1.10926	1629.1	599.91	611.9	−11.99
		50	.042613	41.429	1.09693	1587.2	601.60		
10	4-Benzyl-2-phenylphenol, b. p. 200°	25	.045066	43.775	1.12321	1650.7	595.70		
		35	.044349	43.089	1.11590	1632.0	597.21	611.9	−14.69
		50	.043105	41.903	1.10424	1598.3	599.34		
11	6-Benzyl-4-bromo-2-phenylphenol, b. p. 215°	25	[a]		1.39834				
		35	.044878	43.732	1.39020	1707.1	627.15	662.8	−35.65
		50	.043724	42.615	1.37755	1673.6	628.83		
12	6-Bromo-4-benzyl 2-phenylphenol, b. p. 225°	25	[a]		1.34835				
		35	.044387	43.244	1.34109	1729.0	648.27	662.8	−14.53
		50	.043660	42.539	1.32842	1711.6	651.90	...	...
13	*o*-Hydroxyl-1-diphenylbutane, b. p. 144–146°	25	.038382	37.363	1.04937	1343.0	532.8		
		35	.037729	36.740	1.04072	1328.0	534.97	556.0	−21.03
		50	.036413	35.454	1.03055	1289.8	535.46		

[a] Reliable data not obtained because of high viscosity of compounds at 25°.

The f functions of $r/v^{1/3}$ were those determined by Harkins and Brown.[2]

The thirteen compounds investigated are as follows: 2-chlorophenylbenzyl ether and 2-chloro-4-benzylphenol, both prepared by G. W. Warren,[3] 2-chlorobenzylphenyl ether, 2-*o*-chlorobenzylphenol and the benzoyl ester of 2-*o*-chlorobenzylphenol, all prepared by P. S. Chen,[4] 2-*m*-methyl-4,6-dibenzylphenol prepared by Huston, Swartout and Wardwell,[5] 3-methyl-2,6-dibenzylphenol as prepared by Huston and Houk,[6] 4-methyl-2,6-dibenzylphenol prepared by Huston and Lewis,[7] 6-benzyl-2-phenylphenol, 4-benzyl-2-phenylphenol, 6-benzyl-4-bromo-2-phenylphenol and 6-bromo-4-benzyl-2-phenylphenol, all prepared by G. W. Warren,[8] and *o*-hydroxy-1,1-diphenylbutane by Strickler.[9]

The values obtained for the surface tension and density at the three temperatures are tabulated for each of the compounds. The molal free sur-

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[3] G. W. Warren, Master's thesis, 1931.

[4] P. S. Chen, Master's thesis, 1930.

[5] Huston, Swartout and Wardwell, THIS JOURNAL, **52**, 4484 (1930).

[6] Huston and Houk, *ibid.*, **54**, 1506 (1932).

[7] Huston and Lewis, *ibid.*, **53**, 2379 (1931).

[8] G. W. Warren, Senior report, 1930.

[9] Strickler, Master's thesis, 1927.

face energies $\gamma(m/d)^{2/3}$ and the parachors are evaluated from these experimental values and also tabulated. The parachor observed is calculated from Sugden's formula $P(\text{obsd.}) = m/d\gamma^{1/4}$ in which m is molecular weight, d the density and γ the surface tension.

In Table I it should be noted that compounds 1, 2, 3 and 4 are isomeric and have a molecular weight of 218.5. Compounds 6, 7 and 8 are isomeric, and have a molecular weight of 288.2. Compound 9 is isomeric with compound 10 (mol. wt. 260.1), and compound 11 is isomeric with compound 12 (mol. wt. 339.0).

A summary of the molal free surface energies and parachors (observed) at 35° together with the respective names of the liquids is given in the above table. The parachors (calculated) are given, column no. 8. These are obtained by adding the proper atomic and structural parachors for each compound.[10] In the last column the difference ΔP between the parachor (observed) at 35° and parachor (calculated) is tabulated.

In the table it is noted that in general as the molecular weights increase, the differences in the calculated and observed parachors increase. The values for ΔP are negative except in the first case and range from $+5$ to -35. Since the parachor values are proportional to molecular volume these negative values for ΔP would seem to indicate that these molecules are more closely packed together than is accounted for by the present structural parachors. In a calculation of parachor observed and parachor calculated for diphenylmethane[11] and diphenylethane,[1] Harkins and Ewing show negative values for ΔP of the same order as those found here. These results seem to indicate a need for the application of an additional structural parachor for compounds having two or more phenyl groups.

The parachor (calculated) is the same for compounds isomeric with one another; however, it is interesting to note the variation of the values for parachor (observed) for the different isomers. The observed parachor for compound 1, in which the chlorine and CH_2 groups are not on adjacent carbon atoms in the benzene ring, is 481.41 while in compound 2, in which they are on adjacent carbon atoms in the benzene ring, the value is 470.8, a difference of 10.59. Upon comparing compounds 3 and 4 in the same manner, it is noted that compound 4, where the chlorine and CH_2 group are on adjacent carbon atoms of the benzene ring, the value is 463.42, and for compound 3, in which these groups are not on adjacent carbon atoms, the value is 473.79. Here the difference is 10.37 and agrees with the above value of 10.59. Thus it would seem that with sufficient data some important relations could be evaluated for isomeric compounds in regard to their parachors.

The molal free surface energies range from 132.6 to 138.8 ergs for those compounds containing two phenyl groups, while the molal free surface energies for all compounds containing three phenyl groups range from 160 to 175 ergs.

Conclusion

1. Surface tensions and densities of 13 new derivatives of benzylated phenols have been determined, and their molal free surface energies and parachors have been evaluated.

East Lansing, Mich.

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(10) Sugden, *J. Chem. Soc.*, **125**, 1177 (1924).

(11) Harkins and Ewing, This Journal, **41**, 1977 (1919).