Table I (*Concluded*)

	Formula	Solubility	
		G./g.	Mole fr.
	Amines, Amides and Oximes		
Cyclohexylamine	$C_6H_{11}NH_2$	0.520	0.377
Diphenylamine	$(C_6H_5)_2NH$	Very low	...
Formamide	$HCONH_2$	0.062	.038
Methylformamide	$HCONHCH_3$	.365	.202
Dimethylformamide	$HCON(CH_3)_2$	.410	.261
Acetamide	CH_3CONH_2	Very low	...
N-Methylacetamide	$CH_3CONHCH_3$	0.427	.269
N,N-Dimethylacetamide	$CH_3CON(CH_3)_2$	.808	.452
N-Methyl-N-cyclohexyl-*n*-butanesulfonamide	$C_4H_9SO_2N(CH_3)C_6H_{11}$	.351	.490
N-Methyl-N-cyclohexylacetamide	$C_6H_{11}N(COCH_3)CH_3$	.600	.521
N-Ethyl-N-cyclohexylacetamide	$C_6H_{11}N(COCH_3)C_2H_5$	.565	.530
Ethyl methyl ketoxime	$C_2H_5(CH_3)C{=}NOH$	.315	.244
	Aldehydes and Ketones		
Benzaldehyde	C_6H_5CHO	0.430	0.349
Salicylaldehyde	*o*-$C_6H_4(OH)CHO$	.320	.315
Heptaldehyde	$CH_3(CH_2)_5CHO$	.473	.388
Paraldehyde	$C_6H_{12}O_3$	.385	.374
Cyclohexanone	$C_6H_{10}O$	.630	.421
Δ^2-Cyclohexenone	C_6H_8O	.473	.349
Acetylacetone	$CH_3COCH_2COCH_3$	.455	.394
Acetonylacetone	$CH_3COCH_2CH_2COCH_3$	.572	.434

ent types of solvents show that the same influence, *viz.*, complex formation by means of hydrogen bonding, is operative in the solutions of each compound.

Summary

The solubilities of methylene chloride have been determined over a range of pressure in several types of organic solvents.

The solubilities are high in esters, ethers, amines and N-disubstituted amides; roughly normal in acids, N-monosubstituted amides and oximes; extremely low in alcohols, and amides.

The remarkable similarity between methylene chloride and monofluorodichloromethane with respect to the way in which their solubilities vary in different types of solvents shows that hydrogen bonding is also present in solutions of methylene chloride in donor solvents.

Urbana and Bloomington, Illinois

Received September 9, 1938

[Contribution from the Chemistry Department of Emory University]

A Study of Organic Parachors. I. The Parachors of a Series of Isomeric Esters[1]

By Osborne R. Quayle, Katherine Owen and Reidus R. Estes[2]

Of the many attempts to relate physical properties and structure the parachor[3] has been one of the most successful. It has been of value in the determination of semi-polar bonds,[4] chelation,[5] singlet linkages[6] and degree of aromaticity and unsaturation.[7] From his first observations Sugden[3] concluded that the assigned constants held for all series, that the parachor was not influenced by temperature and that the parachors of isomers were identical. The differences between calculated and observed parachors and the differences between isomers were ascribed to experimental error. However, the parachors of branched heptanes[8] and octanes[9] were found to be

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[1] The authors wish to express their appreciation to Prof. E. Emmet Reid for his kindness in supplying the esters measured and for his valuable practical suggestions on the problem.

[2] Abstracted from a thesis by Reidus R. Estes presented to the Graduate Faculty of Emory University in partial fulfilment of the requirements for the degree of Master of Science, June, 1938.

[3] S. Sugden, *J. Chem. Soc.*, **125**, 1177 (1924).

[4] S. Sugden, J. B. Reed and H. J. Wilkins, *ibid.*, **127**, 1525 (1925).

[5] S. Sugden, *ibid.*, **318** (1929).

[6] S. Sugden, *ibid.*, 1173 (1927).

[7] S. Sugden, "The Parachor and Valency," Alfred A. Knopf, New York, N. Y., 1930, pp. 38–40.

[8] G. Edgar and G. Calingaert, This Journal, **51**, 1540 (1929).

[9] T. W. Richards, C. L. Speyers and E. K. Carver, *ibid.*, **46**, 1196 (1924).

TABLE I

SURFACE TENSIONS AND MOLECULAR VOLUMES

Ester	Symbol	Surface tension at				T'°	Mol. vol. M/D'
		26°	35°	50.5°	65°		
Methyl pentadecylate	1–15	29.41	28.38	27.35	26.11	54.4	305.4
Ethyl myristate	2–14	29.16	28.26	26.73	25.19	47.2	304.9
Propyl tridecylate	3–13	28.74	27.89	26.55	25.12	45.2	305.1
Butyl laurate	4–12	28.29	27.47	26.34	25.21	41.8	304.1
Amyl undecylate	5–11	28.22	27.25	26.07	24.94	39.6	303.4
Hexyl decylate	6–10	28.20	27.26	26.00	24.56	38.5	303.4
Heptyl pelargonate	7–9	28.07	27.10	26.25	24.61	27.8	303.1
		26°	35°	50°	65°		
Octyl caprylate	8–8	28.20	27.12	25.88	24.65	37.2	302.9
		25°	35°	50°	65°		
Nonyl heptoate	9–7	28.15	27.51	26.37	25.07	40.8	304.0
Decyl caproate	10–6	28.66	27.61	26.13	24.95	41.7	304.2
Undecyl valerate	11–5	28.39	27.71	26.38	25.26	43.0	304.3
Lauryl butyrate	12–4	28.80	28.18	26.74	25.41	47.2	305.4
Tridecyl propionate	13–3	29.40	28.68	27.35	26.13	55.8	307.4
Tetradecyl acetate	14–2	29.73	28.91	27.47	26.03	55.2	307.0
Pentadecyl formate	15–1	30.40	29.38	28.36	26.54	61.2	307.3

Surface tension = γ = 27 dynes/cm. at T'°; D' = density at T'°.

consistently lower than those of the normal isomers. The parachors of the lower members of the fatty acids series were found to be consistently higher than the calculated while the reverse was true of the higher members of the series.[10] Since many of these variations are greater than experimental error, it has been recognized that the parachor is constitutive as well as additive.[11]

The deviations from calculated parachors have thrown doubt upon the value of this physical constant. Certain regularities in these deviations from the hitherto accepted theoretical values have appeared. Further investigations of these deviations should be made. If the deviations are, in fact, generally or even frequently regular in nature, as a result of constitutive differences, the parachor will become of more rather than of less value once these regularities are determined.

This paper concerns the results of parachor measurements at four temperatures (25, 35, 50, 65°) of fifteen normal isomeric esters of the formula $C_{16}H_{32}O_2$.[12] Desreux[13] questioned the validity of comparing parachors calculated from unequal surface tensions because of the variation of C in Macleod's[14] relation, $\gamma = C(D-d)^4$. Since the comparison of parachors is tantamount to the comparison of molecular volumes at constant surface tension, it should be possible to overcome this objection by calculating molecular volumes from densities taken at temperatures where the surface tensions equal some convenient arbitrarily chosen

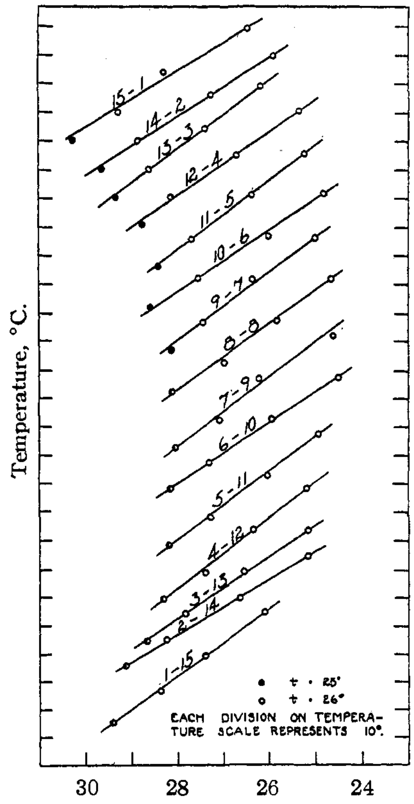

Fig. 1.—Variation of surface tension with temperature.

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(10) K. W. Hunten and G. L. Maas, THIS JOURNAL, **51**, 161 (1929).

(11) S. A. Mumford and J. W. C. Phillips, *J. Chem. Soc.*, 2112–2158 (1929); and others.

(12) The esters were prepared by J. R. Ruhoff and E. Emmet Reid, THIS JOURNAL, **55**, 3825–3828 (1933).

(13) V. Desreux, *Bull. soc. chim. Belg.*, **44**, 249–287 (1935).

(14) Macleod, *Trans. Faraday Soc.*, **19**, 38 (1923).

value (27 dynes/cm.). The surface tension-temperature relation was found to be linear within experimental error (±0.40%) over the 25–65° range studied (Fig. 1). Surface tensions used in calculating parachors were interpolated from graphs of experimental values (Fig. 1).

Densities of the esters were obtained by interpolation from the recorded values.[12] With one exception, the parachor was found to increase with the temperature (typical illustrative curves, Fig. 2), the maximum variation being 10.24 or 1.45%.

TABLE II

PARACHORS AT FOUR TEMPERATURES[15]

Ester	Parachors at 25°	35°	50°	65°
1-15	693.0	694.2	695.7	697.2
2-14	695.3	695.4	695.0	695.1
3-13	694.1	694.9	695.7	696.3
4-12	691.0	692.3	694.2	696.2
5-11	689.9	692.6	692.3	693.6
6-10	689.3	691.1	691.5	692.2
7-9	689.4	690.5	692.1	693.6
8-8	689.9	690.4	690.7	691.0
9-7	690.7	692.1	694.3	696.2
10-6	692.4	693.4	693.8	694.6
11-5	691.1	693.2	694.5	694.8
12-4	693.9	695.0	696.3	697.5
13-3	696.6	697.9	700.0	701.8
14-2	697.6	698.5	699.6	700.5
15-1	699.1	699.5	700.1	700.5

The parachor at all four temperatures measured and molecular volume when $\gamma = 27$ dynes/cm. showed a gradual decrease from either end of the series to a minimum for the central members (Figs. 3 and 4). The parachor values at 25° fall more nearly on a smooth curve than at higher temperatures. The general shape of the curve, however, at all the temperatures measured is unmistakably the same. The parachor variation in the series was found to be 9.67 or 1.38% at 25°, and 13.10 or 1.86% at 65° (Table II) while that for molecular volumes was found to be 4.51 or 1.46% (Table I) (estimated experimental error in parachor, ±0.20%).

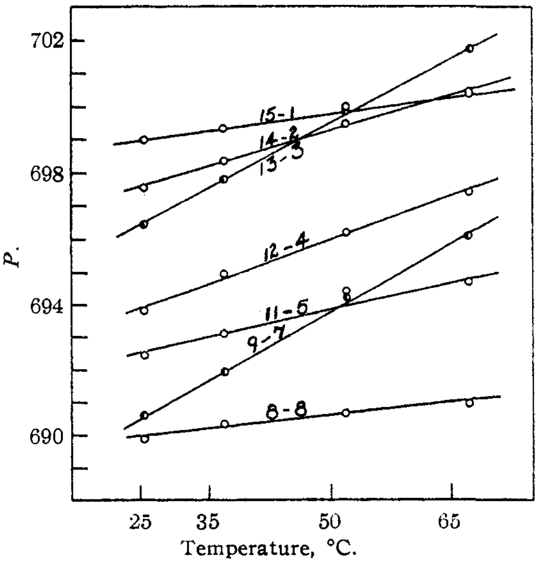

Fig. 2.—Variation of parachor with temperature.

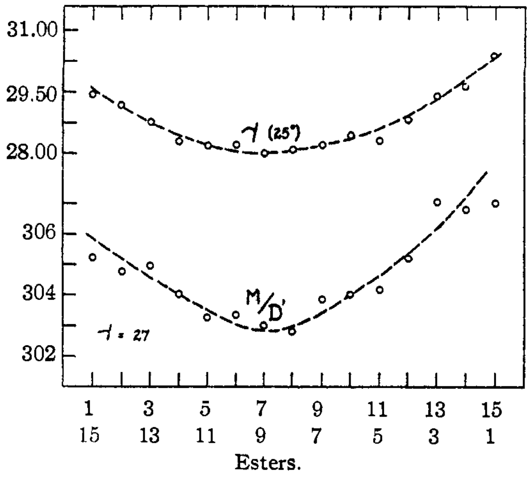

Fig. 3.—Variation of surface tension and molecular volume.

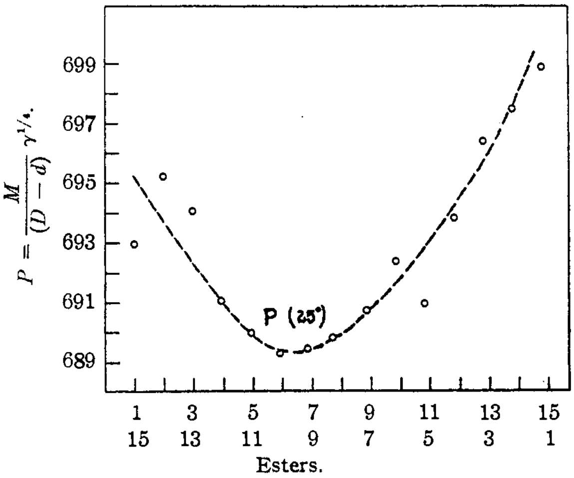

Fig. 4.—Variation of the parachor in the series.

Since unsaturation increases the parachor, it is indicated that the unsaturation of the ester group suffers least reduction by the combination of small and large groups present near the ends. Thus the parachor of methyl pentadecylate is 6.12 units less than that of pentadecyl formate

[15] The calculated value of the parachor for each of these esters, using the atomic constants of Mumford and Phillips,[11] is 699.0.

because of greater reduction of unsaturation by the methyl group in the former than by the hydrogen in the latter.

Similarly, large values for formates and small values for branched isomers have been observed in eight pairs of esters by Wender[16] in a study of parachors previously determined or calculated from previously recorded surface tensions.

Experimental.—Surface tensions were measured by Sugden's[3] modification of the method of maximum bubble pressure, using *m*-xylene[13] in the manometer and carefully purified benzene as a standard[17] for calibration of the apparatus. To ensure equal hydrostatic pressures, a maximum stable bubble was left on the large capillary while bubble pressures were being measured from the small capillary.[13] The manometer readings were taken with a cathetometer with an accuracy of 0.01 cm. Temperatures were controlled to ±0.08°. After calibration of the bubbler using accepted values of benzene (28.88 dynes/cm. at 20°),[18] readings were taken to check the calibration of CCl_4 and C_6H_5Cl. The observed values of 26.77 and 33.25 (20°) agree with accepted values (26.81 and 33.2).

Summary

1. The surface tensions of 15 normal isomeric esters ($C_{16}H_{32}O_2$) have been measured at 25, 35, 50, and 65° by the method of maximum bubble pressure.

2. The calculated parachors were found to decrease gradually from maxima of 695.3 and 699.1 at the ends of the series to a minimum of 689.3 near the center of the series.

3. Molecular volumes calculated from densities taken at constant surface tension (27 dynes/cm.) varied similarly to parachor.

4. The parachors were found to increase, in general, with the temperature.

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[16] Simon Wender, Emory University thesis, 1935, unpublished.

[17] S. Sugden, *J. Chem. Soc.*, **119**, 1483 (1921).

[18] Richards and Carver, THIS JOURNAL, **43**, 827 (1921).

EMORY UNIV., GA. RECEIVED AUGUST 29, 1938

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF OREGON STATE COLLEGE]

Pantothenic Acid. II. Its Concentration and Purification from Liver

BY ROGER J. WILLIAMS, JOHN H. TRUESDAIL, HARRY H. WEINSTOCK, JR., EWALD ROHRMANN, CARL M. LYMAN AND CHAS. H. MCBURNEY

In the first article of this series[1] was announced the discovery of a growth determinant of universal biological occurrence, which was named "pantothenic acid." At the time of this initial report no progress had been made toward the concentration or isolation of the substance and the evidence for the existence of a single effective substance in the various sources was based upon electrolytic, diffusion, hydrogenation, esterification and other experiments in which the behavior of the physiologically active principle was the crucial question.

The concentration of a substance offering the particular difficulties encountered in connection with pantothenic acid had never been accomplished previously and much exploration was required before effective methods could be devised. The difficulties mentioned are based upon the following facts. (1) It is predominantly an acid rather than a basic substance and hence the techniques and precipitants extensively useful with nitrogenous bases cannot be applied except indirectly. (2) The richest convenient source (liver) contains on the order of 40 parts per million, and hence 250 kg. of liver after an extended process yielded only about 3 g. of crude (approximately 40%) material from which the remaining impurities were removed with great difficulty. (3) The substance is highly hydrophilic and we have yet to find any salt or simple derivative which is not highly soluble in water. (4) Due, presumably, to the presence of several types of functional groups, even after purification the substance has failed to crystallize.[2] In this respect it appears to behave somewhat like β-hydroxyglutamic acid, which, according to Dakin,[3] makes up 10% of casein; yet is not available on the market at any price. (5) Pantothenic acid is itself

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[1] Williams, Lyman, Goodyear, Truesdail and Holaday, THIS JOURNAL, **55**, 2912 (1933).

[2] We are indebted to Professor Linus Pauling for X-ray examination of a sample which was suspected of possessing crystalline character. No diffraction pattern was observed and further study confirmed the non-crystalline character of the material.

[3] H. Dakin, *Biochem. J.*, **12**, 290–317 (1918).