[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF EMORY UNIVERSITY]

A Study of Organic Parachors. VIII. A Supplementary Series of Tertiary Chlorides[1]

BY KATHERINE O. SMART AND OSBORNE R. QUAYLE

The parachor values for a series of tertiary chlorides[2] have been previously reported from this Laboratory and values for the CH_2 group in various positions have been suggested by which the parachors of other tertiary chlorides may be calculated. Nine additional supplementary tertiary chlorides have been prepared and their refractive indices, densities, surface tensions, and parachors have been determined. The chlorides were prepared from highly purified tertiary alcohols[3] according to the method suggested by Whitmore and Williams.[4] Purification by distillation is prevented by decomposition. Refractive indices[5] were determined at 20, 25 and 35°. Densities and surface tensions were determined at 25, 45 and 55° and parachors were calculated for the same temperatures. $P = M\gamma^{1/4}(D - d)$. The data obtained are given in Table I and the variation of refractive indices, densities, surface tensions, and parachors with temperature are shown in Figs. 1, 2, 3 and 4, respectively. Surface tensions were determined by the maximum bubble pressure method using a bubbler previously described.[6]

TABLE I

PHYSICAL PROPERTIES DETERMINED FOR NINE TERTIARY CHLORIDES

Chloromethane	T	n^{20}_D	T	D	γ	P exp.
Methylethyl-butyl	20	1.4317	25	0.8722	23.38	382.6
	25	1.4293	45	.8552	23.49	382.8
	35	1.4249	55	.8466	22.50	382.5
Methylpropyl-butyl	20	1.4360	25	.8719	26.00	421.3
	25	1.4338	45	.8550	24.02	421.3
	35	1.4296	55	.8467	23.04	421.3
Methylbutyl-butyl	20	1.4383	25	.8678	26.26	461.0
	25	1.4363	45	.8519	24.40	461.1
	35	1.4321	55	.8440	23.49	461.0
Methylmethyl-amyl	20	1.4263	25	.8552	24.54	386.8
	25	1.4240	45	.8379	22.55	386.8
	35	1.4193	55	.8293	21.69	386.8
Methylethyl-amyl	20	1.4351	25	.8702	26.03	422.3
	25	1.4330	45	.8534	24.14	422.6
	35	1.4286	55	.8452	23.15	422.2
Methylpropyl-amyl	20	1.4389	25	.8698	26.54	461.2
	25	1.4369	45	.8537	24.66	461.3
	35	1.4327	55	.8457	23.70	461.1
Ethylbutyl-amyl	20	1.4464	25	.8721	27.19	537.2
	25	1.4442	45	.8568	25.48	537.0
	35	1.4400	55	.8491	24.56	537.0
Propylbutyl-amyl[a]	20	1.4450	25	.8583	27.02	580.9
	25	1.4428	45	.8432	25.16	581.1
	35	1.4387	55	.8356	24.26	581.1
Butylbutyl-amyl	20	1.4490	25	.8675	27.48	613.7
	25	1.4468	45	.8525	25.50	613.6
	35	1.4428	55	.8450	24.58	613.4

[a] Sample discolored after long standing; less pure than other chlorides.

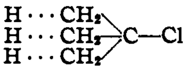
In Table II the experimental parachor values are compared with the values predicted by the position table previously reported[2] and with the values calculated using the earlier constants of Mumford and Phillips.[7] Mumford and Phillips[7] first introduced a strain constant for tertiary branching but did not consider this to vary with the length of the chains involved. The per cent. deviation of the predicted value from the observed reaches 0.5 and 0.6 for the most complex chlorides measured; the average deviation is 0.2. The minimum deviation using the older values is 0.9% and the average is 1.9%.

TABLE II

COMPARISON OF EXPERIMENTAL AND CALCULATED PARACHOR AT 25°

Chloro-methane	Exp.	Predicted	% Dev.	M. & P.	% Dev.
MEB	382.6	381.8	−0.2	390.4	+ 2.0
MPB	421.3	420.8	− .1	430.4	2.1
MBB	461.0	461.1	+ .02	470.4	2.0
MMA	385.8	386.0	− .2	390.4	0.9
MEA	422.3	422.5	+ .02	430.4	1.9
MPA	461.2	461.5	+ .07	470.4	1.9
EBA	537.2	537.5	+ .03	550.4	2.5
PBA	580.9	577.4	− .6	590.4	1.6
BBA	613.7	617.4	+ .5	630.4	2.6
		Algebraic sum	−0.5		+17.5
		Average	.2		1.9

From the newly reported parachors, excluding the value for propylbutylamylchloromethane, several additional position values for the CH_2 increment in tertiary chlorides may be calculated. These together with those previously reported[2] make possible the construction of a chart, Table III, from which the parachor for any tertiary chloride may be calculated by addition; assuming that the structure



$$\begin{matrix} H\cdots CH_2 \\ H\cdots CH_2 \\ H\cdots CH_2 \end{matrix}\!\!>\!C\text{—}Cl$$

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[1] The authors wish to express their appreciation to Professor E. Emmet Reid, research consultant to the department, for his continued interest and suggestions in connection with this investigation.

[2] O. R. Quayle, K. Owen and E. M. Beavers, THIS JOURNAL, 61, 3107 (1939).

[3] Prepared by Harry M. Stubbs of this Laboratory.

[4] Whitmore and Williams, THIS JOURNAL, 55, 406 (1933).

[5] Refractive indices by Harry M. Stubbs, this Laboratory.

[6] O. R. Quayle and K. O. Smart, THIS JOURNAL, 66, 937 (1944).

[7] S. A. Mumford and J. W. C. Phillips, *J. Chem. Soc.*, 2112 (1929).

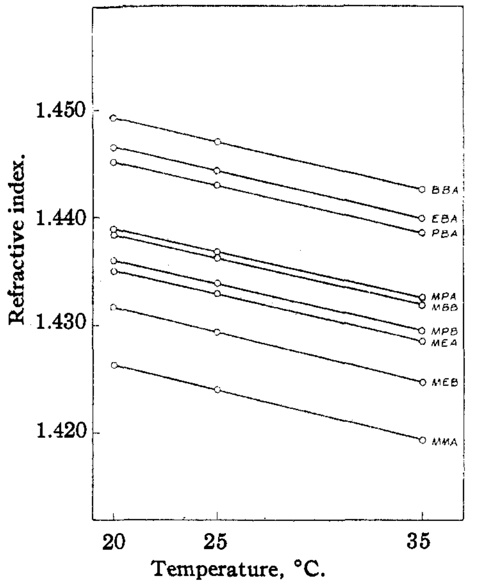


Fig. 1.—Refractive indices of tertiary chlorides.

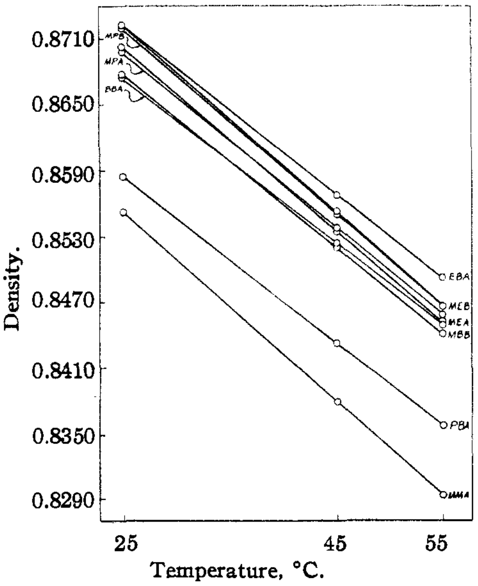
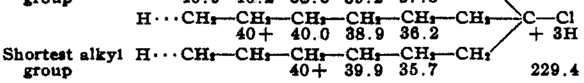


Fig. 2.—Densities of tertiary chlorides.

in the chloride calculated has the parachor value 229.4, the experimental value for *t*-butyl chloride.

TABLE III

POSITION VALUES OF CH_2 IN PARACHORS OF TERTIARY CHLORIDES



CH_2 groups further removed from the chlorine than shown may be considered as 40.

For example, the parachor of methylethylamylchloromethane would be calculated as follows

t-butyl chloride	229.4
amyl group	
1st CH_2 included in *t*-butyl linkage	——
2nd CH_2	37.5
3rd CH_2	39.2
4th CH_2	38.6
5th CH_2	40.2
ethyl group,	
1st CH_2 included in *t*-butyl linkage	——
2nd CH_2	36.2
methyl group, included in *t*-butyl linkage	——
Calculated parachor	421.1

Similar position values for tertiary alcohols have been reported.[8] When the CH_2 position values

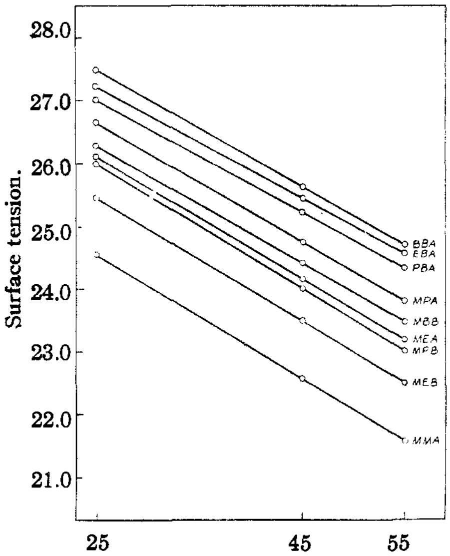


Fig. 3.—Surface tensions of tertiary chlorides.

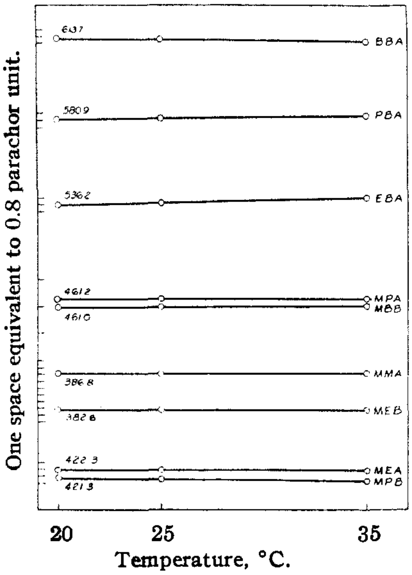


Fig. 4.—Parachors of tertiary chlorides.

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[8] O. R. Quayle and K. O. Smart, THIS JOURNAL, 66, 935 (1944)

for the alcohols are used to calculate the chlorides deviations of 0.5% or less are obtained with one exception, propylbutylamylchloromethane. A few values for branched chain hydrocarbons have been reported.[9] Using the same position values deviations of the same magnitude are indicated. It is suggested that further measurements may permit the construction of a CH_2 position table for tertiary structures not limited to any one type of compounds.

Summary

1. The refractive indices, densities, surface tensions and parachors for nine supplementary tertiary chlorides have been reported, at three temperatures.

2. The predicted and experimental values of the parachors have been shown to be in close agreement.

3. A table has been constructed for use in calculating the parachor of any tertiary chloride having normal alkyl groups.

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RECEIVED SEPTEMBER 22, 1944

(9) O. R. Quayle, R. A. Day and George Brown, THIS JOURNAL, 66, 938 (1944).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

The Acidity of Buffered and Unbuffered Sulfuric Acid Solutions in Nitromethane[1]

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Studies of the behavior of electrolytes in nitromethane solution thus far have been largely restricted to conductivity measurements. Because of its relatively high dielectric constant (37), it is to be expected that nitromethane should favor the dissociation of dissolved salts. The recent conductivity studies of Wright, Murray-Rust and Hartley[3] and of Walden and Birr[4] demonstrate that this is not the case, and do in fact indicate that many salts are associated in this solvent even at very great dilutions.

According to the calculations of Walden and Birr, nitromethane shows relatively little tendency to solvate ions, particularly cations, and only the larger ions studied in the above investigations were found to approach ideal electrolytes in their behavior. Wright, Murray-Rust and Hartley found that the addition of 0.1% of water resulted in a very great increase in the conductivity of those electrolytes which deviated most greatly, while tetraethylammonium salts, which were normal in their behavior, were relatively unaffected by added water. This indicates that the effect of the water was to solvate the ions, thus decreasing the degree of association.

Nitromethane is a very weak base, as is shown by the work of Hantzsch[5] and of Wright, Murray-Rust and Hartley.[3] Hantzsch found by cryoscopic measurements that nitromethane was soluble but not ionized in absolute sulfuric acid. The conductivity measurements of Wright, Murray-Rust and Hartley showed that 0.02–0.05 molar solutions of sulfuric, thiocyanic, benzenesulfonic and nitric acids have an equivalent conductivity of 1–5 units, while hydrochloric acid had no effect at all on the conductivity of nitromethane. Perchloric acid, on the other hand, was found to have an equivalent conductivity of about 70 units, indicating that this is a relatively strong acid in nitromethane.

Because of its low basicity, nitromethane seemed well suited for making acidity measurements on strong acids, and the present work was undertaken for that purpose. The measurements were made colorimetrically, using the indicators of Hammett and Deyrup.[6]

The distribution of some of the indicators between nitromethane and water and benzene and water was also measured, and the results are given.

Apparatus

A Klett-Beaver[7] colorimeter was used. The scales, readable to 0.1 mm., were calibrated and found to have no error exceeding 0.2 mm. One of the conventional sets of cups and plungers was removed and replaced with a closed cup, which was used for the test solutions. This cup consisted of a glass cylinder closed at one end with an optically plane glass surface, and fitted at the other end with a standard taper ground glass joint. The inner member of this joint formed the plunger, and this also was closed by an optically plane surface. The distance between the two surfaces was measured both directly against the colorimeter scale, and by placing a dye solution in both the open and closed cups and comparing in the colorimeter. The distance was found by both methods to be 50 mm. well within the limits of experimental error.

The standard solutions were placed in the open cup. Although nitromethane evaporates quite rapidly, no drift was observed in the readings, indicating that the rate of evaporation of solvent from the open cup was not large enough to affect the results. . Beer's law was shown to hold for the indicators in nitromethane solution at the concentrations used.

Weights and volumetric ware were calibrated wherever necessary. All volumetric ware used was cleaned and dried out overnight at 110° and allowed to cool while being flushed out with a stream of dry air. After cooling to room temperature, flasks were stoppered until used.

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(1) Dissertation submitted by Louis Charles Smith in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Faculty of Pure Science, Columbia University.

(2) Present address: 4800 Forbes St., Pittsburgh, Pa.

(3) Wright, Murray-Rust and Hartley, *J. Chem. Soc.*, 199 (1931).

(4) Walden and Birr, *Z. physik. Chem.*, **A163**, 263, 321 (1932).

(5) Hantzsch, *ibid.*, **65**, 41 (1908).

(6) Hammett and Deyrup, THIS JOURNAL, **54**, 2721 (1932).

(7) The Klett Manufacturing Co., New York; J. J. Beaver, *J. Optical Soc. Am.*, **18**, 41 (1929).