[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF EMORY UNIVERSITY]

A Study of Organic Parachors. V. Constitutive Variations of the Parachors of a Series of Normal Ketones[1]

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It has been shown in the present series of papers and by others that the parachor is of a highly constitutive nature and varies with the degree of unsaturation of the compounds considered. Definite values may be assigned to specific groups, such as the tertiary alcohol, >C—OH, and tertiary chloride, >C—Cl, linkages, which vary with the alkyl groups attached.[3,4] The present paper is concerned with the determination of the parachor values of the fifteen normal chained ketones of eleven or less carbon atoms and with the evaluation of the constitutive variations in the value of the carbonyl group as different alkyl groups are attached.

Eight of the ketones studied were prepared by standard methods in this Laboratory and seven were of the highest grade commercially available (Eastman Kodak Co.). All were refractionated. The boiling ranges are given in Table I. The density and surface tension of acetone were determined at 24.80° only. Methyl ethyl ketone was measured at 34.85, 45.10 and 50.15° and values for 24.80° were determined by extrapolation. The densities and surface tensions of the other ketones were determined at 24.80, 34.85 and 50.15° (Table I). The maximum bubble pressure method was used for the determination of surface tension. Readings were checked by independent observers with a maximum deviation of 0.2%.

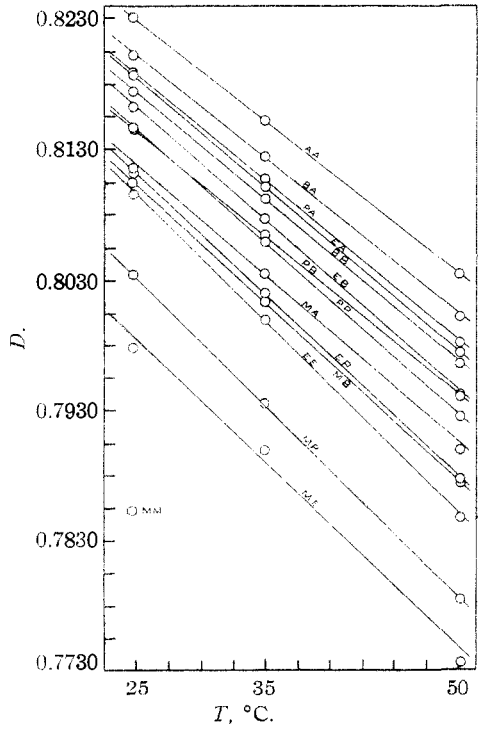

Fig. 1.—Variation of density with temperature.

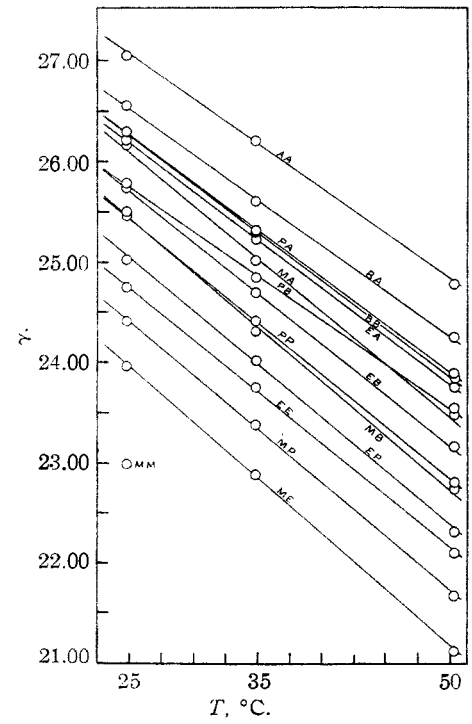

Fig. 2.—Variation of surface tension with temperature.

The parachor values (Table I) were calculated using the equation $P = M\gamma^{1}/_{4}/(D - d)$, where γ is the surface tension, M the molecular weight, D the density of the liquid, and d the density of the vapor at the same temperature. The density of the vapor is relatively small and is included in the calculations only with those ketones where its

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(2) Abstracted from material presented by William Josiah Clegg to the Graduate faculty of Emory University in partial fulfillment of the requirements for the degree of Master of Science, June, 1940. Present address, University of Texas, Austin, Texas.

(3) K. Owen, O. R. Quayle and E. M. Beavers, THIS JOURNAL, **61**, 900 (1939).

(4) O. R. Quayle, K. Owen and E. M. Beavers, *ibid.*, **61**, 3107 (1939).

TABLE I

BOILING POINTS, DENSITIES, SURFACE TENSIONS AND THE PARACHORS OF FIFTEEN NORMAL KETONES

Ketone	Boiling range, °C.	Pressure, mm.	T	D	d	γ	P^a	P^b
MM	55.2–55.5	741.8	24.80	0.7854	0.0007	22.99	162.1	161.6
ME	78.3–78.5	736.3	24.80	.7979	.0004	23.97	199.8	199.5
			34.85	.7899	.0006	22.88	199.9	
			50.15	.7736	.0010	21.13	200.2	
MP	100.9–101.0	741.8	24.80	.8034	.0003	22.41	238.4	238.0
			34.85	.7936	.0004	23.38	238.8	
			50.15	.7785	.0006	21.68	238.9	
MB	127.1–127.3	748.2	24.80	.8105	.0002	25.50	277.8	277.5
			34.85	.8014	.0002	24.32	277.6	
			50.15	.7874	.0003	22.72	277.8	
MA	148.0–148.2	741.1	24.80	.8118		26.17	318.1	319.5
			34.85	.8035	.0001	25.02	317.9	
			50.15	.7901	.0002	23.48	318.2	
EE	100.0–100.2	749.7	24.80	.8097	.0002	24.73	237.3	237.4
			34.85	.8000	.0004	23.74	237.8	
			50.15	.7848	.0006	22.11	238.2	
EP	120.9–121.1	747.9	24.80	.8113	.0002	25.03	276.2	277.3
			34.85	.8021	.0003	24.01	276.5	
			50.15	.7877	.0004	22.32	276.5	
EB	143.9–144.1	742.7	24.80	.8163	.0001	25.72	315.0	
			34.85	.8077	.0002	24.69	315.2	
			50.15	.7941	.0002	23.17	315.2	
EA	167.0–167.1	746.2	24.80	.8188		26.21	354.3	
			34.85	.8103		25.22	354.6	
			50.15	.7974		23.75	355.0	
PP	141.8–142.0	748.6	24.80	.8147		25.47	314.9	315.1
			34.85	.8060	.0002	24.40	314.9	
			50.15	.7925	.0003	22.81	315.0	
PB	161.9–162.1	748.5	24.80	.8146		25.77	354.6	
			34.85	.8065		24.85	354.9	
			50.15	.7939		23.55	355.8	
PA	88.8– 89.2	25.5	24.80	.8190		26.30	393.3	
			34.85	.8108		25.31	393.5	
			50.15	.7982		23.89	393.9	
BB	102.3–102.7	44.3	24.80	.8174		26.30	394.0	
			34.85	.8093		25.29	394.1	
			50.15	.7966		23.85	394.6	
BA	205.0–205.1	743.0	24.80	.8203		26.56	432.5	
			34.85	.8125		25.60	432.6	
			50.15	.8003		25.24	433.2	
AA	120.9–121.0	25.3	24.80	.8231		27.05	471.8	
			34.85	.8153		26.20	472.6	
			50.15	.8035		24.78	472.9	

[a] Values determined by authors. [b] Mean values of Cowan, Jeffery and Vogel.

value is appreciable, as indicated in Table I. The variations of densities, surface tensions and the parachors with temperature are shown respectively in Figs. 1, 2 and 3.

The parachor values of eight of the ketones in Table I are in striking confirmation of the mean values reported by Cowan, Jeffery and Vogel[5] upon these ketones at comparable temperatures. Although the surface tensions were measured by a different method (capillary rise), the maximum deviation in the values is 0.3%. Cowan, Jeffery and Vogel noted a large divergence of their values from the calculated values, based upon the constants of Mumford and Phillips,[6] but did not have available as complete series.

The parachor value for the carbonyl group in

(5) Cowan, Jeffery and Vogel, *J. Chem. Soc.*, 171 (1940).

(6) Mumford and Phillips, *ibid.*, 2112 (1929).

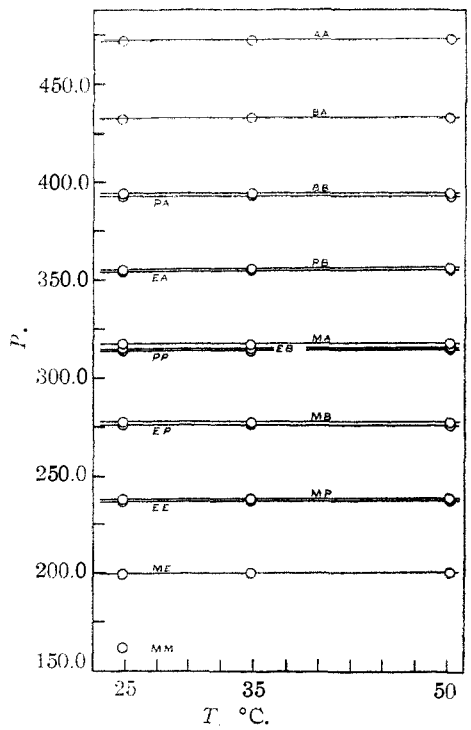

Fig. 3.—Variation of the parachor with temperature.

each ketone was calculated by subtracting the values for the alkyl groups (Mumford and Phillips)[6] from the observed parachor of the compound. The deviation of the values calculated from direct observation and the theoretical values varies from +3.1 units in the case of acetone to −6.6 units in the case of diamyl ketone. The maximum value, 51.3, for the carbonyl is 23% greater than the minimum for this group, 41.6. This difference is attributed to the constitutive effect of the alkyl groups upon the carbonyl.

The values for the carbonyl group arranged in series are shown in Table II. It will be noted that in each series, both horizontal and vertical, there is in general a decrease in the value of the carbonyl as the size of the attached alkyl groups are increased. This decrease is greatest with the first lengthening of the chain, the carbonyl approaching a constant value for the longer chains.

TABLE II

EXPERIMENTAL VALUES FOR THE CARBONYL GROUP IN NORMAL KETONES AT 25°

MM	ME	MP	MB	MA
51.3	49.0	47.9	46.9	47.3
	EE	EP	EB	EA
	47.0	45.6	44.4	43.8
		PP	PB	PA
		44.1	44.3	42.7
			BB	BA
			43.4	42.0
				AA
				41.6

The decrease in the carbonyl values is in accord with the theory that the parachor affords a measure of the relative unsaturation of a series of compounds and that the effective volume of the carbonyl group is decreased by a greater absorption of its residual or partial valence by the larger attached groups. In other words, there is a greater intramolecular attraction, or interaction, between the external field created by the carbonyl group and the larger aliphatic groups. This leads to a partial neutralization of the effective field of force of the carbonyl group.

Summary

1. The surface tensions, densities and parachors of the fifteen normal ketones of eleven or less carbons have been determined.

2. The parachor value for the carbonyl group has been found to be definitely constitutive and to decrease with the size of the attached alkyl groups.

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