19. *The Physical Properties of Some Aliphatic Compounds.*

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Measurements are reported of the densities, refractive indices, surface tensions, and viscosities, at 20° and 25° whenever practicable, of a number of aliphatic compounds of different types.

The results are briefly discussed from the standpoint of the parachor thesis previously advanced (*J.*, 1929, 2112).

In the decade following publication of a paper on the evaluation and interpretation of parachors (*J.*, 1929, 2112) the authors undertook, as opportunity arose, the determination of the surface tension and other physical properties of a number of aliphatic compounds, with the object of obtaining further evidence in support of the thesis then advanced, namely that the CH_2 parachor increment of 39 units originally adopted by Sugden (*J.*, 1924, **125**, 1177) was too small and should be replaced by one of 40 units, and that constitutive deviations from parachor additivity could be accounted for by the systematic introduction of " strain constants." The investigation was interrupted by the war, and as circumstances have since arisen which make it impossible to resume the collaboration, it has been thought desirable to place on record the results obtained up to 1939.

The original aim of the investigation was twofold : (i) to obtain a representative value for the CH_2 increment by examining the average parachor increase over a considerable CH_2 interval in a number of different aliphatic series; and (ii) to obtain more detailed information on the magnitude of the parachor defect associated with accumulation of negative groups in a molecule, particularly on one carbon atom. With the first object in view, a series of *n*-hexadecyl compounds was prepared, and their parachors, determined at uniform temperature as far as practicable, were compared with those of the corresponding *n*-butyl derivatives. Later, examination was made of a number of intermediate members in some of the series, to check the atomic or group constants concerned. The second aim of the investigation involved measurement of the parachors of a number of polyhalogenated hydrocarbons, ethers, and sulphides, and of a series of alkyl mono-, di-, and tri-chloroacetates, and αω-dihalogeno- and -di-carbethoxy-alkanes.

EXPERIMENTAL.

Many of the compounds were purified from commercially available materials (generally from Messrs. British Drug Houses or Schering-Kahlbaum). As regards the others, the methods of preparation employed were those in general use. Thus, the *n*-alkyl halides were prepared from the corresponding purified alcohols by treatment with the requisite phosphorus halide. (In the case of the *n*-amyl compounds, the alcohol was synthesised from purified *n*-butyl bromide, which was also the starting point for the preparation of synthetic *n*-valeric acid.) The chlorinated esters were obtained by esterification of the appropriate acid with the requisite purified alcohol, and the alkyl 2-chloroethyl ethers by the action of methyl or ethyl sulphate on ethylene chlorohydrin. 2 : 2′-Dichlorodiethyl ether was prepared in a manner analogous to that used by Kamm and Waldo (*J. Amer. Chem. Soc.*, 1921, **43**, 2223), and pentachlorodiethyl ether by treating the condensation product of chloral and ethylene chlorohydrin with phosphorus pentachloride (Henry, *Ber.*, 1874, **7**, 763). Tetra- and penta-methylene dichloride were prepared from adipamide and piperidine, respectively, by the method of von Braun (*Ber.*, 1905, **38**, 2340; 1906, **39**, 4119). The *n*-alkyl sulphides were obtained by the action of sodium sulphide on the appropriate alkyl bromide, and 2-chlorodiethyl sulphide by the action of thionyl chloride on the condensation product of sodium thioethoxide and ethylene chlorohydrin (Mayer, *Annalen*, 1877, **240**, 310). All the products were purified to constant properties by repeated fractionation through a Young column. The preparation of the *n*-hexadecyl compounds and of the polychlorinated sulphides has already been reported (*J.*, 1931, 1732; 1929, 535). See also *Rec. Trav. chim.*, 1933, **52**, 175, 181, and *J.*, 1934, 1657 for the preparation of the higher ethyl esters, alcohols, and acetates.

Refractive indices were measured, at 20° whenever possible, with a calibrated Abbé refractometer. The other physical properties were determined at two temperatures (20° and 25° where practicable), the values quoted being the means of at least two determinations, made with different apparatus, at each temperature. The densities were determined with water-calibrated specific-gravity bottles, all weighings being reduced to a vacuum; the surface tensions were measured by Sugden's modification of the maximum bubble-pressure method (*J.*, 1922, **121**, 860), using bubblers calibrated with pure benzene (f.p. 5·5°, b. p. 80·2°, d_4^{20} 0·8790, n_D^{20} 1·5012), taking γ_{20} = 28·88 dynes/cm.; the viscosities were determined in small Ostwald-type viscometers conforming in general characteristics to the standards laid down in British Standard Specification No. 188—1929, and calibrated with water and/or standard sugar solutions.

RESULTS.

Compound.	F. p.	B. p. (760 mm. except where stated).	t.	d_4^t.	n_D^t.	$[R]_D$.	Surface tension (dynes/cm.).	Parachor.	Viscosity (centipoises).
2 : 5-Dimethylhexane	—	109·2°	20°	0·6994	1·3933	38·98	19·9	344·7	0·485
			25	0·6959	—	—	19·4	344·2	0·456
n-Decane	—	173·3	20	0·7307	1·4116	48·37	24·0	430·8	0·920
			25	0·7270	—	—	23·5	430·6	0·855
n-Hexadecane	17·6°	285·8	20	0·7746	1·4350	76·22	27·8	670·7	3·53
			25	0·7712	—	—	27·35	670·9	3·10
n-Hexadec-1-ene	—	159·5	20	0·7825	1·4428	75·95	27·9	658·7	3·09
		(21 mm.)	25	0·7792	—	—	27·45	658·8	2·76
n-Propyl chloride	—	46·5	20	0·8890	1·3900	20·94	22·15	191·6	0·355
			25	0·8830	—	—	21·5	191·5	0·337
n-Butyl chloride	—	78·4	20	0·8866	1·4021	25·42	23·75	230·4	0·450
			25	0·8811	—	—	23·1	230·2	0·427
*iso*Butyl chloride	—	68·4	20	0·8780	1·3978	25·42	21·95	228·1	0·457
			25	0·8725	—	—	21·4	228·1	0·431

RESULTS (*continued*).

Compound.	F. p.	B. p. (760 mm. except where stated).	*t*.	d^t_4.	n^t_D.	$[R]_D$.	Surface tension (dynes/cm.).	Parachor.	Viscosity (centipoises).
n-Amyl chloride	—	107·9°	20°	0·8840	1·4125	30·02	25·15	269·9	0·580
			25	0·8795	—	—	24·55	269·7	0·547
tert.-Amyl chloride	—	85·6	20	0·8659	1·4050	30·16	22·3	267·4	0·599
			25	0·8612	—	—	21·8	267·3	0·560
n-Hexyl chloride	—	134·3	20	0·8790	1·4195	34·67	26·15	310·2	0·743
			25	0·8745	—	—	25·55	310·0	0·696
n-Heptyl chloride	—	160·0	20	0·8759	1·4255	39·33	26·9	349·9	0·956
			25	0·8715	—	—	26·35	349·9	0·890
n-Octyl chloride	—	183·8	20	0·8735	1·4298	43·93	27·65	390·1	1·23
			25	0·8695	—	—	27·15	390·1	1·135
sec.-Octyl chloride	—	171·9	20	0·8660	1·4283	44·17	26·4	388·9	1·055
			25	0·8616	—	—	25·9	389·1	0·973
n-Hexadecyl chloride	α 7·4°	195	20	0·8649	1·4495	80·93	31·1	711·8	6·34
	β 12·1	(22·5 mm.)	25	0·8616	—	—	30·6	711·7	5·51
Allyl chloride	—	45·0	20	0·9349	1·4165	20·56	23·7	180·5	0·347
			25	0·9290	—	—	23·1	180·5	0·331
Chlorobenzene	—	131·3	20	1·1065	1·5246	31·14	33·25	244·1	0·801
			25	1·1013	—	—	32·65	244·1	0·756
Benzyl chloride	—	67	20	1·0993	1·5391	36·06	37·65	285·1	1·40
		(14 mm.)	25	1·0945	—	—	36·95	285·0	1·29
Ethyl bromide	—	38·2	20	1·4612	1·4242	19·04	24·1	165·2	0·397
			25	1·4515	—	—	23·45	165·2	0·379
*iso*Propyl bromide	—	59·4	20	1·3096	1·4251	24·02	23·1	205·9	0·487
			25	1·3017	—	—	22·5	205·9	0·463
n-Butyl bromide	—	101·5	20	1·2758	1·4397	28·28	26·6	243·9	0·633
			25	1·2687	—	—	26·0	243·8	0·597
*iso*Butyl bromide	—	91·1	20	1·2641	1·4362	28·34	24·75	241·5	0·637
			25	1·2568	—	—	24·1	241·7	0·601
n-Amyl bromide	—	129·4	20	1·2190	1·4443	32·93	27·35	283·3	0·803
			25	1·2132	—	—	26·8	283·2	0·753
n-Hexyl bromide	—	154·6	20	1·1746	1·4475	37·57	28·2	323·7	1·013
			25	1·1691	—	—	27·65	323·7	0·941
n-Heptyl bromide	—	69·5	20	1·1406	1·4498	42·16	28·6	363·0	1·29
		(17 mm.)	25	1·1352	—	—	28·1	363·1	1·19
n-Octyl bromide	—	202·2	20	1·1126	1·4526	46·86	29·1	403·0	1·64
			25	1·1077	—	—	28·6	403·0	1·50
n-Hexadecyl bromide	16·3	190	20	0·9992	1·4614	83·87	31·8	725·3	7·81
		(11 mm.)	25	0·9952	—	—	31·4	725·3	6·75
Ethyl iodide	—	72·3	20	1·9364	1·5130	24·21	28·85	186·7	0·584
			25	1·9253	—	—	28·2	186·7	0·557
n-Propyl iodide	—	102·5	20	1·7478	1·5051	28·85	29·2	226·1	0·735
			25	1·7385	—	—	28·6	226·1	0·695
n-Butyl iodide	—	130·2	20	1·6150	1·4999	33·50	29·25	264·9	0·877
			25	1·6070	—	—	28·7	265·0	0·826
n-Hexyl iodide	—	76·5	20	1·4391	1·4926	42·79	30·25	345·5	1·39
		(23 mm.)	25	1·4326	—	—	29·75	345·7	1·285
n-Hexadecyl iodide	22·5	184	25	1·1220	1·4795	89·07	32·4	748·9	8·43
		(4 mm.)	30	1·1180	—	—	32·0	749·2	7·27
Methylene chloride	—	39·8	20	1·3283	1·4233	16·29	28·0	147·1	0·437
			25	1·3191	—	—	27·15	147·0	0·416
Chloroform	—	61·2	20	1·4892	1·4458	21·36	27·2	183·1	0·566
			25	1·4798	—	—	26·55	183·2	0·538
Carbon tetrachloride	—	76·75	20	1·5942	1·4603	26·47	26·75	219·5	0·968
			25	1·5846	—	—	26·15	219·6	0·902
1 : 2-Dichloroethane	—	83·6	20	1·2527	1·4448	21·02	32·45	188·5	0·829
			25	1·2454	—	—	31·75	188·6	0·775

Results (*continued*).

Compound.	F. p.	B. p. (760 mm. except where stated).	*t*.	d^t_4.	n_D.	$[R]_D$.	Surface tension (dynes/cm.).	Parachor.	Viscosity (centipoises).
1 : 3-Dichloropropane	—	120·8°	20°	1·1859	1·4483	25·52	33·8	229·7	1·034
			25	1·1800	—	—	33·05	229·6	0·963
1 : 4-Dichlorobutane	—	155·0	20	1·1408	1·4549	30·20	34·8	270·4	1·43
			25	1·1353	—	—	34·05	270·2	1·315
1 : 5-Dichloropentane	—	182·0	20	1·1006	1·4566	34·87	35·3	312·3	1·815
			25	1·0956	—	—	34·6	312·1	1·655
Ethylidene dichloride	—	57·3	20	1·1757	1·4167	21·15	24·75	187·7	0·490
			25	1·1680	—	—	24·1	187·7	0·465
1 : 1 : 2-Trichloroethane	—	114·1	20	1·4424	1·4715	25·87	33·75	222·9	1·19
			25	1·4355	—	—	33·0	222·7	1·10
1 : 1 : 2 : 2-Tetrachloro-	—	146·1	20	1·5953	1·4940	30·62	35·6	256·9	1·765
ethane			25	1·5876	—	—	34·9	256·9	1·615
1 : 1 : 1 : 2 : 2-Penta-	—	160·5	20	1·6813	1·5030	35·57	34·55	291·7	2·58
chloroethane			25	1·6740	—	—	33·85	291·5	2·23
1 : 2 : 3-Trichloropropane	—	156·0	20	1·3880	1·4834	30·35	37·8	263·3	2·505
			25	1·3818	—	—	37·05	263·2	2·23
1 : 2-Dichloroethylene,	—	48·4	20	1·2583	—	—	26·4	174·6	0·423
cis			25	1·2502	—	—	25·8	174·7	0·400
1 : 2-Dichloroethylene,	—	60·1	20	1·2841	—	—	28·3	174·1	0·474
trans			25	1·2771	—	—	27·65	174·0	0·451
Trichloroethylene	—	86·9	20	1·4642	1·4775	25·38	29·5	209·1	0·566
			25	1·4559	—	—	28·8	209·1	0·532
Perchloroethylene	—	121·2	20	1·6230	1·5055	30·33	32·1	243·2	0·891
			25	1·6145	—	—	31·4	243·2	0·842
1 : 2-Dibromoethane	—	131·1	20	2·1802	1·5385	26·98	38·85	215·1	1·73
			25	2·1700	—	—	38·2	215·2	1·60
1 : 3-Dibromopropane	—	166·2	20	1·9812	1·5230	31·13	40·1	256·4	2·07
			25	1·9727	—	—	39·4	256·4	1·90
Ethyl *n*-butyl ether	—	92·0	20	0·7495	1·3820	31·71	20·75	290·8	0·421
			25	0·7448	—	—	20·25	290·8	0·397
Ethyl *n*-hexadecyl ether	19·9°	195	20	0·8182	1·4394	86·96	29·4	769·3	6·12
		(21 mm.)	25	0·8150	—	—	28·95	769·3	5·25
Methyl 2-chloroethyl	—	90·3	20	1·0522	1·4108	22·30	29·25	208·9	0·633
ether			25	1·0461	—	—	28·5	208·7	0·591
2-Chlorodiethyl ether	—	108·4	20	0·9954	1·4118	27·12	27·45	249·6	0·730
			25	0·9894	—	—	26·9	249·8	0·677
1 : 2-Dichlorodiethyl	—	51	20	1·1670	1·4418	32·40	29·8	286·2	1·285
ether		(27 mm.)	25	1·1610	—	—	29·1	286·0	1·165
2 : 2′-Dichlorodiethyl	—	177·9	20	1·2192	1·4573	31·95	37·6	290·4	2·41
ether			25	1·2130	—	—	37·0	290·7	2·14
1 : 2 : 2-Trichloro-	—	62	20	1·3227	1·4648	37·07	32·8	321·0	2·46
diethyl ether		(13 mm.)	25	1·3155	—	—	32·2	321·3	2·18
1 : 2 : 2 : 2 : 2′-Penta-	—	112·5	20	1·5733	1·5025	46·25	38·9	391·1	9·36
chlorodiethyl ether		(12·5 mm.)	25	1·5669	—	—	38·3	391·0	7·83
Ethyl formate	—	54·3	20	0·9237	1·3599	17·69	23·8	177·1	0·402
			25	0·9173	—	—	23·15	177·1	0·382
Ethyl acetate	—	77·15	20	0·9007	1·3728	22·26	23·95	216·3	0·452
			25	0·8946	—	—	23·3	216·3	0·425
Ethyl butyrate	—	121·4	20	0·8794	1·3922	31·45	24·6	294·1	0·672
			25	0·8742	—	—	24·0	294·0	0·627
Ethyl valerate	—	145·1	20	0·8750	1·4005	36·09	25·4	333·8	0·821
			25	0·8703	—	—	24·85	333·8	0·763
Ethyl hexoate	—	167·0	20	0·8717	1·4072	40·72	26·0	373·4	1·024
			25	0·8672	—	—	25·45	373·3	0·948
Ethyl octoate	—	207·0	20	0·8676	1·4180	50·01	27·2	453·2	1·58
			25	0·8635	—	—	26·75	453·4	1·44

RESULTS (*continued*).

Compound.	F. p.	B. p. (760 mm. except where stated).	*t.*	d_4^t.	n_D^t.	$[R]_D$.	Surface tension (dynes/cm.).	Parachor.	Viscosity (centipoises).
Ethyl nonoate	—	119°	20°	0·8661	1·4219	54·61	27·8	493·6	1·95
		(23 mm.)	25	0·8621	—	—	27·35	493·8	1·77
Ethyl laurate	−3·4°	275	20	0·8628	1·4310	68·47	29·05	614·1	3·36
			25	0·8591	—	—	28·6	614·3	2·99
Ethyl myristate	10·85	308·8	20	0·8616	1·4363	77·80	29·9	695·5	4·97
			25	0·8581	—	—	29·45	695·7	4·36
Ethyl palmitate	α 19·2	198·5	25	0·8568	1·4380	87·10	29·95	776·2	5·78
	β 23·2	(13·5 mm.)	30	0·8535	—	—	29·5	776·2	5·08
Ethyl margarate	α 25·2	200	30	0·8517	1·4380	91·94	29·65	817·3	5·815
	Tr↓ 11·5	(10 mm.)	35	0·8484	—	—	29·2	817·3	5·095
Methyl acetate	—	56·9	20	0·9342	1·3614	17·56	24·8	176·9	0·385
			25	0·9279	—	—	24·1	176·8	0·364
n-Propyl acetate	—	101·6	20	0·8874	1·3844	26·92	24·6	256·2	0·585
			25	0·8822	—	—	24·0	256·2	0·551
n-Butyl acetate	—	125·6	20	0·8796	1·3942	31·58	25·2	295·7	0·734
			25	0·8746	—	—	24·6	295·7	0·688
*iso*Butyl acetate	—	117·1	20	0·8745	1·3898	31·45	23·7	292·9	0·697
			25	0·8695	—	—	23·15	292·9	0·651
n-Amyl acetate	—	149·2	20	0·8753	1·4028	36·26	25·8	335·1	0·924
			25	0·8707	—	—	25·25	335·1	0·862
n-Hexyl acetate	—	170·5	20	0·8726	1·4096	40·89	26·55	374·9	1·17
			25	0·8681	—	—	26·0	374·9	1·075
n-Octyl acetate	—	211·5	20	0·8681	1·4193	50·11	27·8	455·5	1·85
			25	0·8638	—	—	27·3	455·7	1·68
n-Hexadecyl acetate	α 18·5	204	20	0·8611	1·4408	87·14	30·95	778·7	8·05
	β 22·1	(18 mm.)	25	0·8577	—	—	30·5	778·9	6·75
Ethyl malonate	—	199·3	20	1·0547	1·4139	37·93	31·9	360·8	2·15
			25	1·0494	—	—	31·3	360·8	1·94
Ethyl succinate	—	216·6	20	1·0402	1·4200	42·33	31·9	397·8	2·81
			25	1·0353	—	—	31·3	397·8	2·48
Ethyl adipate	−22	251	20	1·0076	1·4272	51·53	32·5	479·0	3·50
			25	1·0034	—	—	32·0	479·0	3·08
Ethyl suberate	—	283	20	0·9827	1·4325	60·81	32·75	560·3	4·74
			25	0·9783	—	—	32·2	560·5	4·17
Ethyl azelate	−19·8	172	20	0·9732	1·4344	65·40	32·85	600·7	5·32
		(18 mm.)	25	0·9692	—	—	32·35	600·9	4·65
Ethyl sebacate	+1·65	184	20	0·9631	1·4364	70·15	33·0	642·6	5·96
		(18 mm.)	25	0·9591	—	—	32·45	642·5	5·18
Ethyl ethylmalonate	—	208·2	20	1·0082	1·4164	46·86	29·8	436·0	2·41
			25	1·0037	—	—	29·1	435·4	2·15
Ethyl *n*-butylmalonate	—	239·0	20	0·9749	1·4226	56·42	29·1	515·0	3·47
			25	0·9703	—	—	28·55	515·0	3·02
Ethyl *n*-hexadecylmalonate	α 12·7	241	20	0·9118	1·4443	112·04	31·45	998·3	18·2
	β 25·1	(9·5 mm.)	25	0·9080	—	—	30·95	998·4	14·9
Ethyl benzoate	—	212·2	20	1·0468	1·5051	41·56	35·4	349·7	2·22
			25	1·0421	—	—	34·75	349·7	1·99
Ethyl chloroformate	—	92·6	20	1·1392	1·3952	22·84	26·1	215·3	0·557
			25	1·1325	—	—	25·45	215·2	0·528
Methyl chloroacetate	—	129·6	20	1·2345	1·4214	22·31	35·2	214·1	1·143
			25	1·2281	—	—	34·5	214·1	1·048
Ethyl chloroacetate	—	143·1	20	1·1510	1·4212	27·00	32·0	253·2	1·194
			25	1·1446	—	—	31·35	253·3	1·096
n-Propyl chloroacetate	—	162·9	20	1·1038	1·4253	31·65	30·95	291·7	1·50
			25	1·0977	—	—	30·35	291·9	1·365
n-Butyl chloroacetate	—	181·7	20	1·0707	1·4291	36·26	30·4	330·2	1·71
			25	1·0652	—	—	29·8	330·2	1·55

RESULTS (*continued*).

Compound.	F. p.	B. p. (760 mm. except where stated).	t.	d_4^t.	n_D^t.	$[R]_D$.	Surface tension (dynes/cm.).	Parachor.	Viscosity (centipoises).
Methyl dichloroacetate	—	143·9°	20°	1·3786	1·4424	27·46	34·0	250·4	1·546
			25	1·3712	—	—	33·25	250·4	1·414
Ethyl dichloroacetate	—	157·3	20	1·2804	1·4375	32·15	31·35	290·1	1·60
			25	1·2734	—	—	30·75	290·3	1·46
n-Propyl dichloroacetate		175·7	20	1·2234	1·4402	36·85	30·65	328·9	1·91
			25	1·2171	—	—	30·1	329·1	1·74
n-Butyl dichloroacetate	—	194·8	20	1·1841	1·4420	41·34	30·1	366·0	2·20
			25	1·1783	—	—	29·5	365·9	1·98
Methyl trichloroacetate	—	153·4	20	1·4870	1·4565	32·46	33·0	286·0	1·85
			25	1·4800	—	—	32·3	285·8	1·69
Ethyl trichloroacetate	—	167·3	20	1·3841	1·4501	37·17	30·8	325·8	1·72
			25	1·3773	—	—	30·2	325·8	1·57
n-Propyl trichloroacetate	—	185·5	20	1·3187	1·4507	41·93	30·6	366·4	2·04
			25	1·3123	—	—	30·05	366·5	1·86
n-Butyl trichloroacetate	—	206·0	20	1·2736	1·4514	46·43	30·55	405·1	2·38
			25	1·2674	—	—	30·0	405·2	2·14
2-Chloroethyl acetate	—	145·1	20	1·1556	1·4230	27·02	33·6	255·3	1·61
			25	1·1492	—	—	32·9	255·5	1·46
2-Chloroethyl chloroacetate	—	202·7	20	1·3584	1·4624	31·79	41·5	293·3	4·27
			25	1·3520	—	—	40·8	293·4	3·73
2-Chloroethyl dichloroacetate	—	213·0	20	1·4570	1·4738	36·91	39·8	330·0	5·09
			25	1·4504	—	—	39·1	330·0	4·41
2-Chloroethyl trichloroacetate	—	217·5	20	1·5329	1·4805	41·90	37·3	364·1	5·43
			25	1·5262	—	—	36·6	364·0	4·70
Ethyl β-chloropropionate	—	162·4	20	1·1044	1·4253	31·63	31·65	293·2	1·625
			25	1·0994	—	—	31·1	293·3	1·48
Diethyl sulphide	—	92·1	20	0·8367	1·4425	28·47	25·3	241·6	0·446
			25	0·8316	—	—	24·7	241·6	0·422
Di-*n*-butyl sulphide	—	188·1	20	0·8388	1·4525	47·07	27·35	398·6	1·072
			25	0·8348	—	—	26·8	398·5	0·995
Di*iso*butyl sulphide	—	170·0	20	0·8285	1·4471	47·16	25·1	395·0	0·944
			25	0·8244	—	—	24·6	395·0	0·880
Di*iso*amyl sulphide	—	215·3	20	0·8341	1·4531	56·48	26·3	473·0	1·525
			25	0·8303	—	—	25·85	473·2	1·395
2-Chlorodiethyl sulphide	—	59 (20 mm.)	20	1·0758	1·4898	33·47	33·1	277·8	—
2 : 2′-Dichlorodiethyl sulphide	14·4°	107 (15 mm.)	20	1·2746	1·5270	38·36	42·7	319·0	4·3
2-Chloroethyl 1 : 2-dichlorovinyl sulphide	—	107 (15 mm.)	20	1·4315	1·5562	43·01	40·9	338·3	2·8
2-Chloroethyl 1 : 2 : 2-trichlorovinyl sulphide	—	123 (15 mm.)	20	1·5425	1·5700	48·06	41·7	372·3	3·9
1 : 1 : 2-Trichloroethyl 2-chlorovinyl sulphide	—	122·5 (15 mm.)	20	1·5404	1·5661	47·85	41·7	372·8	5·7
1 : 2 : 2-Trichloroethyl 1 : 2-dichlorovinyl sulphide	—	134·5 (15 mm.)	20	1·6293	1·5778	53·02	41·8	406·2	6·5
1 : 1 : 2 : 2 : 2 : 2′-Hexachlorodiethyl sulphide	—	158·5 (15 mm.)	20	1·6849	1·5683	57·66	43·45	452·6	25·4
1 : 1 : 1′ : 2 : 2′ : 2′-Hexachlorodiethyl sulphide	—	159·5 (15 mm.)	20	1·6841	1·5681	57·68	43·35	452·5	29·4
1 : 1 : 1′ : 2 : 2 : 2′ : 2′-Heptachlorodiethyl sulphide	—	171 (15 mm.)	20	1·7473	1·5741	62·58	43·2	486·1	42·7
n-Butyl cyanide	—	141	20	0·7993	1·3975	25·06	27·6	238·3	0·753
			25	0·7952	—	—	27·1	238·4	0·705
n-Hexadecyl cyanide	31·7	195 (8 mm.)	30	0·8284	1·4431	80·44	31·35	717·8	7·65
			35	0·8254	—	—	30·85	717·5	6·55

RESULTS (*continued*).

Compound.	F. p.	B. p. (760 mm. except where stated).	t.	d^t_4.	n^t_D.	$[R]_D$.	Surface tension (dynes/cm.).	Parachor.	Viscosity (centipoises).
n-Amylamine	—	105·3°	20°	0·7561	1·4115	28·65	25·15	258·1	0·720
			25	0·7519	—	—	24·65	258·3	0·658
n-Propyl alcohol	—	97·2	20	0·8053	1·3862	17·53	23·9	165·0	2·29
			25	0·8016	—	—	23·5	165·0	2·015
n-Butyl alcohol	—	117·9	20	0·8102	1·3992	22·13	24·8	204·1	2·98
			25	0·8066	—	—	24·35	204·1	2·60
*iso*Butyl alcohol	—	108·0	20	0·8030	1·3953	22·13	23·0	202·0	3·82
			25	0·7994	—	—	22·55	201·9	3·24
n-Amyl alcohol	—	137·5	20	0·8146	1·4103	26·81	25·6	243·3	3·68
			25	0·8110	—	—	25·15	243·3	3·19
n-Hexyl alcohol	—	156·6	20	0·8198	1·4174	31·35	26·55	282·8	5·32
			25	0·8164	—	—	26·05	282·7	4·52
n-Heptyl alcohol	—	175·9	20	0·8236	1·4238	35·96	27·25	322·2	7·00
			25	0·8202	—	—	26·75	322·0	5·87
n-Octyl alcohol	—	194·6	20	0·8265	1·4287	40·57	27·9	361·7	9·13
			25	0·8232	—	—	27·4	361·9	7·55
n-Butyric acid	—	163·4	20	0·9585	1·3981	22·18	26·8	209·0	1·72
			25	0·9537	—	—	26·2	208·9	1·57
n-Valeric acid	—	185·6	20	0·9386	1·4085	26·86	27·4	248·8	2·25
			25	0·9342	—	—	26·85	248·7	2·03
n-Hexoic acid	—	205·3	20	0·9271	1·4162	31·44	28·05	288·2	3·22
			25	0·9230	—	—	27·55	288·2	2·87
n-Octoic acid	15·9°	237·7	20	0·9110	1·4279	40·70	29·2	367·8	6·09
			25	0·9070	—	—	28·7	367·8	5·29
n-Nonoic acid	12·0	254·0	20	0·9052	1·4322	45·33	29·7	407·9	8·30
			25	0·9013	—	—	29·2	407·9	7·15

DISCUSSION.

The results obtained, given in the accompanying table, agree in general with those of other workers, and in particular with the recent data of Timmermans and his collaborators (*J. Chim. physique*, 1926, **23**, 747; 1928, **25**, 411; 1930, **27**, 401; 1932, **29**, 529; 1934, **31**, 85; 1935, **32**, 501, 589; 1937, **34**, 693; cf. Roland and Lek, *Bull. Soc. chim. Belg.*, 1931, **40**, 177) and of Vogel (*J.*, 1934, 333; 1943, 16, 637; 1946, 133; 1948, 607 *et seq.*, 1804 *et seq.*).

The only marked discrepancies occur with the surface tensions of the C_6—C_8 alcohols, and one or two other liquids of high viscosity, where the capillary rise method used by these workers appears to give low and erratic results. The discontinuity in surface tension at C_7 in the alcohol series noted by Smith and Sorg (*J. Physical Chem.*, 1941, **45**, 671) has not been confirmed.

In view of the incompleteness of the investigation, and of the recent extensive work of Vogel in the same field, little useful purpose would be served by detailed analysis of the results now reported. A few points, however, merit brief discussion.

First, as regards the CH_2 parachor increment: The present measurements of parachor increase from C_4 to C_{16} in nine different aliphatic series support a mean increment of 40 units originally advocated in our earlier paper and now accepted by Vogel on the basis of his own data. It must, however, be appreciated that this is a representative average value, and that owing to slight variation of the exponent in the Kleeman–MacLeod relation, $\gamma = C(D - d)^4$, from compound to compound, the observed increment in any given case depends both on the temperature range of measurement, and on the particular series being examined and the number of terms considered. The parachor is, in fact, not strictly a constant, and only approximately homologously additive.

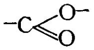
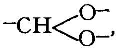
The atomic and group constants previously evaluated on the basis of this increment reproduce satisfactorily the parachor data now reported, and would not therefore appear to require significant modification. Such constants are, not unnaturally, much the same as those recently put forward by Vogel on the same basis, as will be seen from the subjoined tabular summary of the more important values.

Atom or Group.	*P* value. M. & P.	*P* value. V.	Atom or Group.	*P* value. M. & P.	*P* value. V.
CH_2	40	40·0	Cl	55	55·2
H in CH_2	15·4	15·7	Br	69	68·8
C in CH_2	9·2	8·6	I	90	90·3
CH_3	55·4	55·4	CN	64·7	64·6
C_2H_5	95·4	95·4	O in ethers	20	19·8
Allyl	123·6	124·3	S in sulphides	50	48·6
Phenyl	190	188·3	CO_2– in esters	65·2	63·4
Double bond	19	19·9	OH in alcohols	30	30·2
6-Ring	0·8	1·4	CO_2H	75·2	73·7

M. & P. = Mumford and Phillips *J.*, 1929, 2112 (Table I).
V. = Vogel, *J.*, 1948, 1833 (Table XXII).

In the case of many atoms and groups (*e.g.*, halogen, ethereal oxygen, cyanogen, etc.) the two sets of constants are indeed virtually identical, though with certain of the more complex groupings (*e.g.*, phenyl, CO·O in esters) they differ by one or more units. Vogel's values are based on much more extensive data, but any resulting gain in accuracy would appear to be largely offset by the circumstance that each group value has been independently evaluated, and cannot be quantitatively computed by summation of its component atomic and structural constants. This applies, rather illogically, to the lower alkyl groups themselves in Vogel's system, in which the successive CH_2 differences from methyl to octyl are given as 40, 39·9, 39·8, 39·7, 40, 40·7, and 40, respectively, one curious result of this being that the calculated parachor of, say, *n*-hexane, varies according to whether it is considered as *n*-hexyl + H (270·7), *n*-amyl + methyl (270·4), *n*-butyl + ethyl (270·7), di-*n*-propyl (271·0), $4CH_2$ + 2 methyl (270·8), or $6CH_2$ + 2H (271·4).

The decrement of 3 units previously noted as applying to branched-chain groups of the type $-CHR_2$ receives support from the parachors of the few *iso*-compounds now reported, and it is interesting to note in this connection that according to Vogel the parachor values of *iso*- and *sec.*-alkyl groups range from 1·5 (*iso*butyl) to 4·1 (*sec.*-butyl) units lower than those of the corresponding *n*-groups.

The well-defined parachor defect associated with accumulation of negative atoms and groups (X) around a central carbon atom would appear to depend to a rather greater extent than was originally surmised on the size and polarity of the atoms and groups concerned, but the parachors now reported, and other recently recorded data, confirm in general the earlier conclusion that for X = Cl, OEt, CO_2Et, and for similar groups the decrement (" strain constant ") associated with $-CHX_2$ groups may be taken as 3 units, with $-CX_3$ groups 6 units, and with compounds of the type CX_4 9 units, within the limits of experimental error; and further, that for such atoms and groups the more complex effect of accumulation on adjacent carbon atoms can be adequately estimated in the manner previously outlined. The depressive effect of negative accumulation on the parachor has been recognised by Vogel in his latest paper (*loc. cit.*), but qualitatively only, and apparently without full appreciation of its applicability, for example, to esters  $-C\begin{smallmatrix}\diagup O- \\ \diagdown\!\!\!= O\end{smallmatrix}$ as in acetals  $-CH\begin{smallmatrix}\diagup O- \\ \diagdown O-\end{smallmatrix}$, and of its occurrence to a varying extent in the chlorides and oxychlorides of phosphorus and sulphur, and in many of the esters of the inorganic acids (cf. Table VIII in our original paper).

The general validity of parachors calculated in accordance with the scheme outlined in that table has received additional support from the measurements of Pearson and Robinson (*J.*, 1933, 1427) on sulphur hexafluoride, and of Denbigh and Whytlaw-Grey (*J.*, 1934, 1346) on disulphur decafluoride. In both cases, allowing a " strain constant," due to accumulation, of −15 units per S^{vi} atom, and assuming that the valencies of the latter comprise two co-valent bonds and four " singlet " linkages, the values obtained for the latter linkage (−11·2 and −11·1, respectively) agree closely with similar values derived from other compounds, *e.g.*, tellurium tetrachloride (−11·4; Simons, *J. Amer. Chem. Soc.*, 1930, **52**, 3488; with Te = 79) and phosphorus pentachloride (−10·5; Sugden, *J.*, 1927, 1173). The " strain constant " would here appear to connote the screening effect of the surrounding halogens on the central atom, and to be distinct from the defect attributed, following Sugden, to " singlet " linkages, which is presumably connected with the formation of bonds involving inner electron orbits.

The need for assuming the presence of such linkages in compounds of this type, and of semipolar double (" dative ") bonds in the corresponding oxyhalides and esters, can to some extent be avoided by assigning different parachor values to the central atom in its different valency states (cf. previous paper, p. 2125; also Sippel, *Ber.*, 1930, **63**, *B*, 2185; Buehler, *J. Tennessee Acad. Sci.*, 1931, **6**, 27; Hunter and Samuel, *Rec. Trav. chim.*, 1935, **54**, 114). This procedure, however, does not eliminate the depressive effect of accumulation, and moreover leads to inconsistent and improbable atomic values for the elements concerned in their higher valencies. Thus, according to Samuel (*J. Chem. Physics*, 1944, **12**, 167) the atomic parachor of P^{v} is 18·3 in $POCl_3$, though only 11·0 in PCl_5, whilst that for S^{vi}, given as +13·9 in SO_2Cl_2, is, on the same basis (using Sugden's value of 25 for F), −6·7 in SF_6. So far as concerns the " dative " bond, Vogel's conclusion that parachor data provide no evidence for the presence of co-valent double bonds in the esters and oxyhalides of sulphur and phosphorus, as maintained by G. M. Phillips, Hunter, and Sutton (*J.*, 1945, 146), would appear to be well-founded (cf. Wells, *J.*, 1949, 55).

The view previously advanced, that the effective parachor value of the hydrogen atom depends inversely on the electron affinity of the atom to which it is attached, has been discussed in some detail by Pearson and Robinson (*J.*, 1934, 736) and supported and extended by their measurements of the parachors of the non-metallic hydrides (*J.*, 1932, 972; 1934, 730, 880). Confirmation of the lower parachor value of H in OH groups has also been afforded by Vogel for alcohols and acids (*J.*, 1948, 1814), though attributed by him to variation in the parachor of the oxygen atom.

In the light of modern views on structure, a number of the interpretations of deviations from parachor additivity suggested in our previous paper require some modification, and the atomic and structural constants then put forward could doubtless be more precisely evaluated with the aid of the very considerable additional data now available. Taking the system as originally advanced twenty years ago, however, it may be noted that, of the 690 parachor values recorded by Vogel since Part I of his present series (*J.*, 1934, 333), the difference between calculated (Mumford and Phillips) and observed parachors exceeds 2% in only 23 instances (*i.e.*, 3% of the total), whilst for over 80% of the compounds the agreement is within 1%.

Direct comparison with Vogel's system is not possible for the whole of this series, as his method of computation is not at present applicable to many of the complex esters, etc., considered in his earlier papers. Of more than six hundred compounds listed since Part VII of the series (*J.*, 1943, 16), however, only 63 are not computable by the atomic and group constants given by Vogel in his latest paper, these including, *inter alia*, *tert.*-butyl and amyl compounds, naphthalene derivatives, acetylenedicarboxylic esters, aromatic *tert.*-amines, and a variety of polyhalogenated compounds. Exclusion of these, and the few compounds for which surface tension data are not given, leaves 527 compounds of a wide variety of types, whose parachors can be evaluated by both systems; when this is done, the following comparative analysis of results is obtained.

	Percentage of compounds for which the difference between calc. and obs. parachors is		
System of evaluation.	Within 0·5%.	Within 1%.	Above 2%.
Vogel's data (527 compounds).			
Vogel	67·8	88·7	2·1
Mumford and Phillips	52·9	85·5	1·7

It will be seen that the overall agreement is not very different in the two cases, although Vogel's system gives somewhat closer reproducibility with a greater number of compounds. This is not surprising in view of the circumstance that his constants were derived exclusively from the data to which they are now applied. In the following table a similar comparison is made with parachor data from the measurements of Timmermans and his collaborators (*loc. cit.*) and from the determinations reported in this paper, excluding in both instances such multi-branched and polyhalogenated compounds as cannot at present be evaluated by Vogel's system.

	Percentage of compounds for which the difference between calc. and obs. parachors is		
System of evaluation.	Within 0·5%.	Within 1%.	Above 2%.
Timmerman's data (126 compounds).			
Vogel	54·8	79·4	5·5
Mumford and Phillips	54·0	86·5	3·2
Data from present paper (102 compounds).			
Vogel	63·7	89·2	3·0
Mumford and Phillips	63·7	96·0	1·0

The position is here somewhat different, the values calculated according to Vogel showing the smaller overall agreement. It would seem, therefore, that the employment of a multiplicity of independently evaluated and unrelated group constants is a refinement which over-estimates the precision of the parachor, and that there is much to be said for adhering to the scheme advocated in our original paper.

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