12. *Intermolecular Forces in Liquid Systems. Part I. The Physical Properties of the Alkyl Carbonates.*

By Sydney T. Bowden and Emil T. Butler.

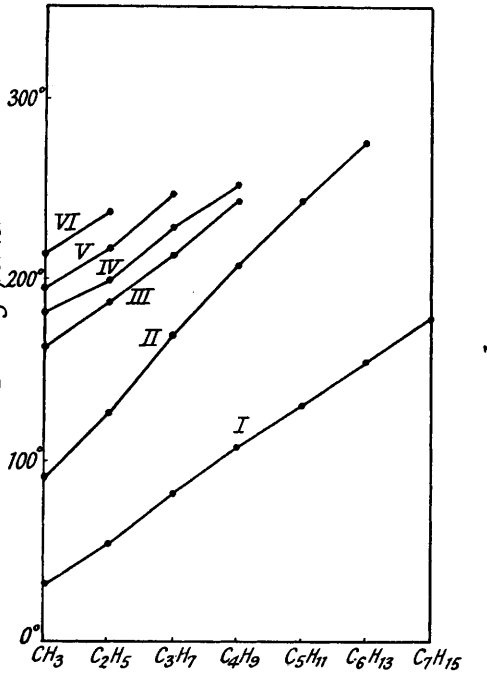
Although the organic carbonates are stable and easy to purify, the data relating to their physical properties are extremely meagre. We have now determined the ebullioscopic constant of methyl carbonate, and the density, refractive index, viscosity, surface tension, and parachor of the *n*- and the *iso*-derivatives of the series. It is shown that these liquid carbonates have the non-polar structure in which the central carbon atom has a normal octet. From the standpoint of homology the series offers interesting features with respect to the boiling point, viscosity, and parachor relationships.

The direct preparation of n-*hexyl carbonate* from sodium hexoxide and carbonyl chloride is described.

The anomaly in the b. p. of the first member of a homologous series is usually prominent when the substance contains two characteristic groups. This is exemplified in the b. p.'s of the glycols and the dicyano-derivatives of the paraffins. The esters of dibasic acids, however, show little evidence of such anomaly, and the b. p. rises progressively with the molecular weight as shown in Fig. 1. The carbonic esters, in particular, show a regular rise corresponding to the addition of each pair of methylene groups. From the practically linear relationship which obtains in this series, it may be shown that the absolute b. p. ($T°$) of an alkyl carbonate of molecular weight M is given by $T = 40{\cdot}41M^{0{\cdot}48}$.

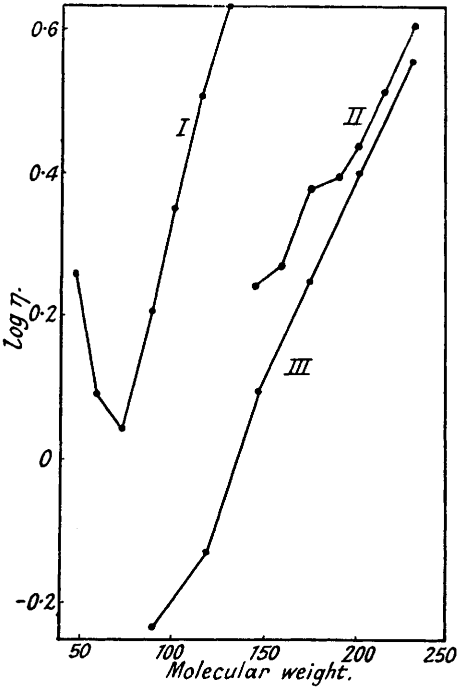
Young (*Phil. Mag.*, 1905, **9**, 6) showed that the b. p. increment corresponding to the addition of CH_2 in a homologous series is a function of the absolute b. p., and for many series (alkyl halides, *iso*paraffins, ethers, etc.) may be expressed by the formula $\Delta = 144{\cdot}86T^{0{\cdot}0148T}$. For esters, however, the calculated and the observed values are not in very good agreement, and for the alkyl carbonates the relation becomes $\Delta_2 = 250{\cdot}5T^{0{\cdot}0148T}$, where Δ_2 is the increment corresponding to two methylene groups. Recently, Burnop (J., 1938, 826) has shown that the empirical quantity $M \log_{10}T + 8{\cdot}0M$, denoted by (*b*), is additive, and this is evident from the agreement between the observed and the calculated values for the normal esters of the mono- and di-carboxylic acids given in Table I.

FIG. 1.



I, *Formates.* II, *Carbonates.* III, *Oxalates.* IV, *Malonates.* V, *Succinates.* VI, *Glutarates.*

FIG. 2.



I, *Monocarboxylic acids.* II, *Ethyl esters of dicarboxylic acids.* III, *Alkyl carbonates.*

TABLE I.

	Formate.		Carbonate.		Oxalate.	
	(*b*), obs.	(*b*), calc.	(*b*), obs.	(*b*), calc.	(*b*), obs.	(*b*), calc.
Methyl	211·1	208·1	306·3	304·1	398·7	394·4
Ethyl	255·2	253·1	394·2	394·1	485·7	484·4
n-Propyl	299·5	298·1	483·4	484·1	573·2	574·4
n-Butyl	344·1	343·1	572·3	574·1	662·5	664·1
n-Amyl	388·9	388·1	662·5	664·1		
n-Hexyl	433·4	433·1	751·8	754·1		

	Malonate.		Succinate.		Glutarate.	
	(*b*), obs.	(*b*), calc.	(*b*), obs.	(*b*), calc.	(*b*), obs.	(*b*), calc.
Methyl	443·1	439·4	486·8	484·4	531·4	529·4
Ethyl	529·3	529·4	573·6	574·4	619·2	619·4
n-Propyl	617·6	619·4	662·5	664·4		
n-Butyl	705·5	709·4				

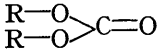
As in the case of other homologous series, the ratio of the absolute b. p.'s of any two alkyl carbonates is independent of the pressure. In Fig. 1, the influence of the CH_2 group in the ester part of the molecule is shown by the individual curves, and their successive vertical displacement indicates its influence in the non-ester part of the molecule. Since the curves for the esters of dibasic acids tend to converge, it appears that the b. p.'s of the higher carbonates will lie above those of the corresponding succinates, although the b. p. of methyl succinate is 129° higher than that of methyl carbonate.

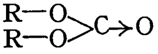
If the carbonyl group in the carbonates is given the value for the ketonic group, the value of $[R_L]_D$ corresponds fairly well with that calculated from the Eisenlohr constants.

The connexion between homology and viscosity has been studied by Dunstan and his collaborators (J., 1907, **91**, 90; *J. Physical Chem.*, 1909, **7**, 210), who found a fairly exact relationship between the molecular weights and the logarithms of viscosity in several homologous series. They pointed out that, owing to the operation of conjugation effects, the series of dibasic esters from the oxalate to the sebacate shows little regularity until the first three members are passed, as shown in Fig. 2. However, the curve approaches linearity from the glutaric ester, and the same phenomenon is evident in the fatty acid series (Gartenmeister, *Z. physikal. Chem.*, 1890, **6**, 524), but the linearity is much more striking in the case of the alkyl carbonates. For the higher carbonates, the viscosity is given by $\log \eta = 0{\cdot}005449M - 0{\cdot}7018$, where η is the viscosity and M the molecular weight.

The surface tension of methyl is higher than that of ethyl carbonate, but for the succeeding members there is a regular rise with increasing molecular weight. Of the alternative formulæ (I) and (II), the parachor values fully substantiate the non-polar formulation (I) in which carbon has its normal octet (Sugden, " The Parachor and Valency," Routledge, 1930, p. 117). There appears to be some doubt, however, as to the exact parachor contribution of the two oxygen atoms in the esters of monobasic acids. For instance, Sugden (*op. cit.*) points out that the observed contribution of O_2 (60·0) is appreciably lower than the calculated value for two oxygen atoms and a double bond (63·2). In Table II, P_A is the parachor calculated from the ordinary bond constants, P_B that obtained on the assumption that the constitutive effect is 3/2 times the value for esters of monobasic acids (since there are three oxygen atoms instead of two), and P_C the value calculated on the assumption that the constitutive effect is the same in both cases, *viz.*, — 3·2.

(I.)





(II.)

TABLE II.

Substance.	$P_{obs.}$.	P_A.	P_B.	P_C.	Substance.	$P_{obs.}$.	P_A.	P_B.	P_C.
Methyl carbonate ...	196·2	200·2	195·4	197·0	*n*-Amyl carbonate ...	508·2	512·2	507·4	509·0
Ethyl carbonate	274·5	278·2	273·4	275·0	*iso*Amyl carbonate ...	505·0	512·2	507·4	509·0
n-Propyl carbonate ...	352·3	356·2	357·4	353·0	*n*-Hexyl carbonate ...	587·8	590·3	585·5	587·1
n-Butyl carbonate ...	423·4	434·2	429·4	431·0	Ethyl oxalate	321·8	326·2	—	319·8
*iso*Butyl carbonate ...	428·1	434·2	429·4	431·0	Ethyl phthalate	492·0	499·1	—	492·7

With a view to elucidate further the nature of the " ester effect " we have determined the parachor of ethyl oxalate ($d_{4°}^{25°} = 1{\cdot}0751$; $\gamma^{25°} = 31{\cdot}42$ dynes/cm.) and have compared it with that of ethyl phthalate. In these cases also the observed parachor is appreciably lower than P_A, but is in close agreement with P_C, which is calculated by using the value $O_4 = 120{\cdot}0$. It may be concluded, therefore, that the most suitable value for the three oxygen atoms and the double bond in the organic carbonates is 80·0; *i.e.*, the parachor contribution of the two oxygen atoms of each esterified carboxyl group in both monobasic and dibasic derivatives is to be taken as 60·0, irrespective of whether the molecule contains other ethereal oxygen atoms or ring systems.

Recently, Lewis (J., 1938, 1062) has derived an equation connecting the parachor, viscosity and molecular weight of a liquid. At constant temperature, the equation takes the form $\log P^{\frac{2}{3}}\eta = A \log M - B$, where A and B are constants. The viscosities of the alkyl carbonates calculated from this equation with $A = 3{\cdot}1$ and $B = 4{\cdot}930$ are given in Table III. Apart from the discrepancy for the first member, the agreement is good for

TABLE III.

Carbonate.	M.	$\log P^{\frac{2}{3}}\eta$.	η, obs.	η, calc.	Carbonate.	M.	$\log P^{\frac{2}{3}}\eta$.	η, obs.	η, calc.
Methyl	90	1·2952	0·5845	0·3959	*n*-Butyl	174	1·9974	1·7634	1·844
Ethyl	118	1·4995	0·7476	0·7382	*n*-Amyl	202	2·2047	2·5158	2·576
n-Propyl	146	1·7923	1·2426	1·2100	*n*-Hexyl	230	2·3987	3·5691	3·522

the entire series, and the validity of the equation for non-polar liquids is completely substantiated.

EXPERIMENTAL.

Preparation of Materials.—The methyl and ethyl carbonates were carefully fractionated, kept for a few hours in contact with anhydrous calcium chloride, and then redistilled before use; b. p. 90·2° and 125·8°, respectively. *n*-Propyl carbonate was treated similarly and distilled at 67·5—67·8°/17 mm. The higher carbonates were fractionated under reduced pressure; b. p.'s: *n*-butyl, 96—98°/17 mm.; *iso*butyl, 85°/16 mm.; *n*-amyl, 126·7—127°/15 mm.; *iso*amyl, 125—125·2°/26 mm.

n-*Hexyl carbonate* was obtained in good yield by the following method. Pure *n*-hexyl alcohol (25 g.) was slowly treated with metallic sodium (5·8 g.) under reflux, and the reaction completed by raising the temperature to the m. p. of the metal. Sodium hexoxide was deposited at an early stage of the process, but the evolution of hydrogen ceased before the theoretical amount of sodium had reacted, and the unchanged metal was removed. To this hexoxide at 0° were added small portions of carbonyl chloride (15 g. in all), also at 0°, for the reaction is strongly exothermic; after standing for 4 hours, the mixture was heated on the steam-bath for an hour. Sufficient water was added to dissolve the colloidal sodium chloride, and the organic layer was separated and dried (anhydrous sodium sulphate). The benzene was removed by distillation, and the carbonate collected at 150—155°/20 mm. Further fractionation under reduced pressure gave the carbonate as a colourless liquid, b. p. 152—154°/20 mm. (Found: C, 67·4; H, 11·4. $C_{13}H_{26}O_3$ requires C, 67·8; H, 11·3%).

Physical Measurements.—The b. p.'s under ordinary pressure were determined by the simple distillation method, except that Siwoloboff's micro-method was employed for *n*-hexyl carbonate. In all cases the Anschütz thermometers had been calibrated at the National Physical Laboratory.

The determination of the ebullioscopic constant of methyl carbonate was undertaken with a view to ascertain the suitability of the liquid as solvent for molecular-weight determinations. Menzies's apparatus employing a differential water thermometer proved rather too sensitive at the b. p. of this ester. Accordingly, the measurements were carried out in the Swietoslawski type of apparatus, and repeatedly recrystallised benzil, thoroughly dried over activated silica gel, was employed as solute. The ebullioscopic constant over the concentration range 1·7—3·6% was 18·3°, a value intermediate between those of methyl formate (15·8°) and methyl acetate (20·6°).

The densities of the liquids were determined in 5-c.c. and 3-c.c. glass-capped pyknometers, the temperature being maintained at 25° ± 0·01° by means of an electrically-controlled thermostat. The weights were calibrated by Richards's method, and the necessary corrections applied for buoyancy.

The refractive indices for the Na_D line ($\lambda = 5893$) were determined by means of a Zeiss Pulfrich refractometer provided with a thermostatic control operating at 25°.

The viscosity and surface-tension measurements were carried out at 25° in the all-glass viscometer and surface tension apparatus described in the following paper.

The data obtained by the above methods are given below.

Carbonate.	B. p.	$d_{4°}^{25°}$.	$n_D^{25°}$.	$[R_L]_D$.	$\eta^{25°}$, cp.	$\gamma^{25°}$, dynes/cm.
Methyl	90·2°	1·06027	1·36696	19·068	0·5845	28·46
Ethyl	125·8	0·96926	1·38287	28·408	0·7476	25·70
n-Propyl	169·0	0·93988	1·39904	37·606	1·2426	26·36
n-Butyl	206·6	0·93884	1·41214	46·157	1·7634	27·07
*iso*Butyl	189·4	0·90858	1·40532	47·009	1·8317	24·89
n-Amyl	243·0	0·91001	1·41887	56·089	2·5158	27·39
*iso*Amyl	229·6	0·90222	1·41582	56·213	2·4653	25·80
n-Hexyl	275·0	0·90016	1·42617	65·551	3·5691	27·92

The liquids are not suitable for use as cryoscopic solvents, since they exhibit strong supercooling.

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