245. *Dipole Moments and Molecular Structure of Methyl and Ethyl Carbonates.*

By George Thomson.

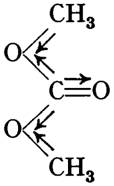
The dipole moments of methyl and ethyl carbonates have been measured in benzene solution at 25°, and calculation made, with allowance for induction effects, of the moments of possible planar models for these molecules. The value calculated for the configuration of minimum moment for methyl carbonate agrees with the experimental value. Consideration of ethyl carbonate is complicated by the presence in the molecule of four possible axes of free rotation, but it is thought that this, if it is at all possible, is limited to rotation of the terminal methyl groups about the nearer C–O linkage. A possible source of anomaly in Kubo's measurements in the vapour state on methyl carbonate and dimethoxymethane is indicated.

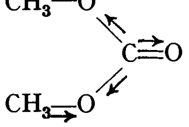
It is demonstrated by calculation of the induction effects in ethyl ether that these are sufficient to account for the difference in moment between methyl and ethyl ethers without postulating any change in the oxygen valency angle.

The dipole moments of the carbonic esters are of interest since the molecules contain two or more putative axes of free rotation. Kubo and his collaborators (*Sci. Papers Inst. Phys. Chem. Res. Tokyo*, 1936, **30**, 169; 1937, **32**, 129) found that the moment of methyl carbonate vapour increased steadily from 0·86 at 55° to 1·00 at 206·2° (all moments are given in Debye units); the moment of ethyl carbonate, on the other hand, was constant at 1·06 over the range 79·5—203·9°. From consideration of these results and of the Raman spectra, they concluded that oscillatory intramolecular motion was possible in methyl carbonate but that ethyl carbonate had a fixed structure.* In calculating maximum and minimum moments no account was taken of induction effects. In the present investigation the moments of methyl and ethyl carbonates have been measured in benzene solution at 25°, and an attempt has been made to calculate minimum and maximum values of moment for each compound, induction effects being allowed for by using Groves and Sugden's method (J., 1937, 1992). The experimental values are 1·06 for the methyl and 0·90 for the ethyl compound. It is noteworthy that whereas Kubo found that in the vapour state at comparable temperatures the moment of methyl carbonate was always less than that of ethyl carbonate, the reverse holds in these measurements in solution. The latter is the order one expects if, as seems probable, electrostatic repulsion holds the alkyl groups as far apart as possible, *i.e.*, the C–O–C–O–C chain forming an extended "zig-zag," the configuration of minimum dipole moment. The value 0·90 for the moment of ethyl carbonate in benzene solution is in agreement with Kubo's value of 1·06 in the gaseous state since, if the solvent effect is normal, the values found in benzene solution are very nearly 0·9 times the gaseous value.

Methyl Carbonate.—The central carbon atom must be coplanar with the three oxygen atoms. The configurations of minimum and maximum moment will be those in which the carbon atoms of both methyl groups are also in this plane, *viz.*, (A) and (B) respectively.

(A.)





(B.)

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* Kubo found the graph of polarisation of methyl carbonate against $1/T$ to be a straight line: an increasing moment requires a curve. Extrapolation of the straight line to $1/T = 0$ gave an intercept of 30·9 c.c., leading to the improbable value of 12·4 c.c. for the atomic polarisation. This does not seem an adequate reason for assuming a temperature coefficient of the moment, since small errors in the absolute value of the dielectric constant and/or the density (which is calculated indirectly and subject to greater error than the measurement of dielectric constant) have been shown to suffice in many cases to explain apparently abnormal values of P_A.

(The directions of the primary moments are indicated.) The second is extremely improbable, since in it the nuclei of the methyl carbon atoms are separated by only 1·65 A. and electrostatic repulsion must be strong. There will also be an attractive force between the dipole situated at the C=O bond and those situated at the CH_3–O bonds, so the plane zig-zag configuration (A), or one not differing greatly from it, seems probable.

In the calculation of moment Groves and Sugden's notation is used throughout. The values of α used are: C, 0·96; CH_2, 1·82; CH_3, 2·25; the interatomic distances are taken to be C=O, 1·28 A; C–O, 1·43 A., and atomic radii C, 0·77 A. and O, 0·66 A. The valency angles are assumed to be $-\mathrm{C}-\widehat{\mathrm{O}}-\mathrm{CH_3} = 111°$ as in methyl ether (Sutton and Brockway, *J. Amer. Chem. Soc.*, 1935, **57**, 473; Groves and Sugden, *loc. cit.*) and $\mathrm{O}-\widehat{\mathrm{C}}=\mathrm{O} = 125°$ (Groves and Sugden, *loc. cit.*). It is assumed that the primary C–O dipoles are situated at the points of contact of the carbon and oxygen atoms, the primary C=O dipole midway between the carbon and oxygen nuclei. The values of bond moments used are those calculated from the moments of vapours by Groves and Sugden (*loc. cit.*), *viz.*, C=O, 2·28; CH_3–O, 2·30. For the C–O bond the value 1·9 has been adopted, derived from the value for CH_3–O by deducting 0·4 as the resultant of the three hydrogen atoms acting tetrahedrally in the methyl group. There is, of necessity, an uncertainty about this value, but it probably represents the lower limit for the C–O dipole. A higher value for this dipole will give higher values for the calculated minimum moments of the carbonates. The induced moments taken into account are those induced in the methyl groups by the C=O dipole and by the C–O dipole in the same half of the molecule and those induced in the central carbon atom by the CH_3–O dipoles. Groves and Sugden (*loc. cit.*) have calculated that in dimethyl ether the moment induced in each methyl group by the more remote C–O dipole is represented by a moment 0·398 $\mu_{\mathrm{C-O}}$ inclined at an angle of 12·6° to the adjacent C–O bond. Since the same valency angle has been assumed for oxygen in the present calculations, this value has been accepted for the moment induced in each methyl group by the more remote C–O dipole in the same half of the molecule. The moment induced in the central carbon atom by each CH_3–O dipole will be $(0{\cdot}398 \times 0{\cdot}96/2{\cdot}25)\,\mu_{\mathrm{CH_3O}}$, *i.e.*, 0·170 $\mu_{\mathrm{CH_3O}}$, α_{C} being substituted for $\alpha_{\mathrm{CH_3}}$. It remains to calculate for configurations (A) and (B) the moments induced in the methyl groups by the C=O dipole. Obviously, only the components induced parallel to the primary C=O moments need be evaluated, since the components at right angles vanish by symmetry. From the appropriate diagrams, $\Sigma A_x = -0{\cdot}2290$ in (A) and $+\ 0{\cdot}09682$ in (B), whence the components of induced moment parallel to the C=O dipole are calculated to be $-0{\cdot}0785\,\mu_{\mathrm{C=O}}$ for (A) and $0{\cdot}0946\,\mu_{\mathrm{C=O}}$ for (B). The minimum and maximum values of moment are found by compounding and resolving in the direction of the C=O dipole the moments shown in Fig. 1A and Fig. 1B respectively.

From Fig. 1A the resultant is

$$2{\cdot}28 - 2(1{\cdot}90 \cos 55°) - 2(2{\cdot}30 \cos 56°) + 2(0{\cdot}398 \times 1{\cdot}90 \cos 43{\cdot}4°) + 2(0{\cdot}170 \times 2{\cdot}30 \cos 42{\cdot}4°) - 2(0{\cdot}0785 \times 2{\cdot}28)$$

which gives 1·154.

From Fig. 1B the resultant is

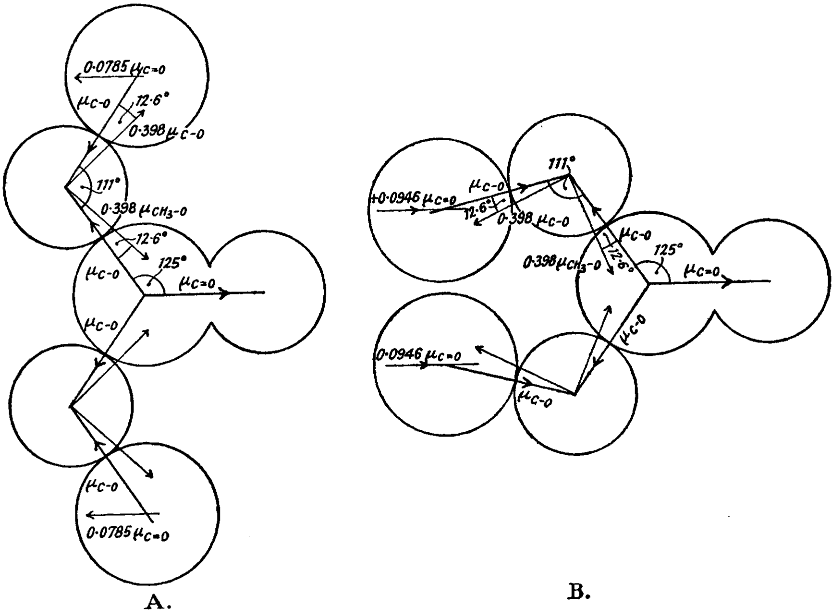
$$2{\cdot}28 - 2(1{\cdot}90 \cos 55°) + 2(2{\cdot}30 \cos 14°) - 2(0{\cdot}398 \times 1{\cdot}90 \cos 43{\cdot}4°) + 2(0{\cdot}170 \times 2{\cdot}30 \cos 67{\cdot}6°) + 2(0{\cdot}0946 \times 2{\cdot}28)$$

which gives 3·94.

These values are for methyl carbonate in the gaseous state: in benzene solution, if $\mu_{\mathrm{soln.}} = 0{\cdot}9\,\mu_{\mathrm{gas}}$, they would be about 1·04 and 3·33 respectively. The experimental value is 1·06. It would appear, therefore, that in benzene solution methyl carbonate has a configuration approximately represented by Fig. 1A. Kubo's values (*Sci. Papers Inst. Phys. Chem. Res. Tokyo*, 1937, **32**, 129) for the moment of methyl carbonate in the gaseous state are all considerably lower than the value here calculated as the minimum value of the moment. The same author had previously (*ibid.*, 1936, **29**, 179) recorded a similar variation of moment with temperature in the case of dimethoxymethane, whereas the moment of diethoxymethane was almost constant over a similar range of temperature. Löbering and Fleischmann (*Ber.*, 1937, **70**, 1680) have shown that the methods previously described for preparing dimethoxymethane (methylal) are unsatisfactory since it forms an azeotropic mixture with methyl alcohol. It appears that the true b. p. is about 35° instead of 42·3°. Bowden (private communication) refers to difficulty in purifying methyl carbonate and stresses the necessity for *short* preliminary treatment with freshly heated calcium chloride to break down any azeotrope with the alcohol. Kubo's separation from alcohol by crystallisation followed by fractional distillation will not achieve this. He records no physical properties other than the b. p., so comparisons are difficult, but it seems certain that instead of dimethoxymethane he used the azeotropic mixture with methyl alcohol, and probable that his methyl carbonate was also contaminated with methyl alcohol. This probably accounts for the anomalous behaviour of these compounds. Further measurements seem to be desirable.

Constancy of Oxygen Valency Angle.—The possibility of a different value of oxygen valency angle in ethyl carbonate must be considered. From the variation in moment as one passes up the series of normal aliphatic ethers it has been argued that the oxygen valency angle must increase with increasing size of the alkyl angle. Stuart ("Molekülstruktur," 1934) has expressed the view that the angle is probably constant and that induction effects are sufficient to explain the change in moment from one member to another of this homologous series. Calculation shows that this is the case. The same values are assumed for the bond moments and valency angles as in the case of methyl ether (discussed by Groves and Sugden, *loc. cit.*), and the carbon valency angle is taken as 109·5°. There is the possibility of free rotation of the methyl groups about the CH_2–O bonds, so two symmetrical plane configurations (Figs. 2A and 2B) are possible, of which B is highly improbable on account of the close approach of the carbon atoms. The induced moments calculated for A are :

FIG. 1.



(*a*) That induced in each methyl group by the nearer C–O dipole. This was estimated from Groves and Sugden's calculation (*loc. cit.*) of the induced moment in the β carbon atom of ethyl halides. It is 0·034 μ_{C-O} parallel to the C–O dipole and 0·237 μ_{C-O} at right angles.

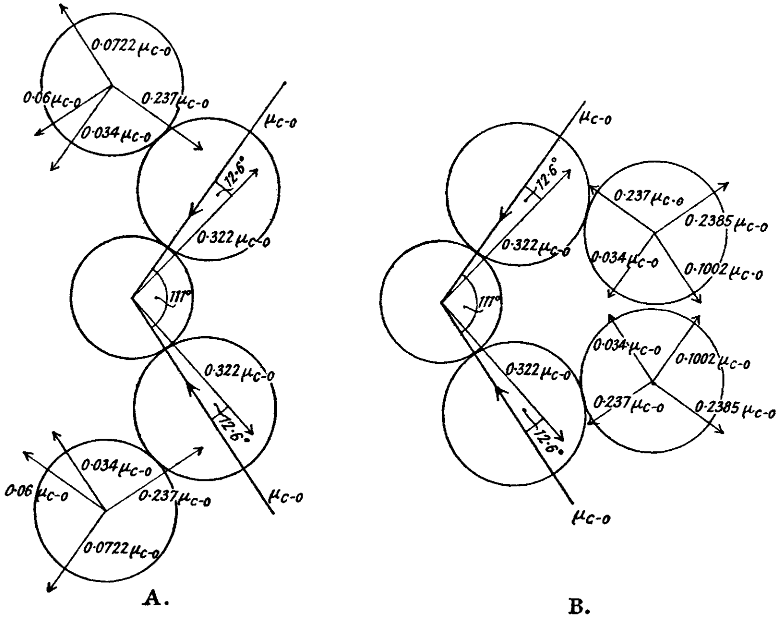
(*b*) The moment induced in each methyl group by the more remote C–O dipole. From the appropriate diagrams $\Sigma A_x = 0{\cdot}1165$ and $\Sigma A_y = 0{\cdot}2032$, whence the moment induced is 0·0722 μ_{C-O} parallel to the remote C–O dipole and 0·0600 μ_{C-O} at right angles.

(*c*) The moment induced in each methylene group by the more remote C–O dipole. This can be derived from the values of the induced moments in the methyl groups of methyl ether by substituting $\alpha_{CH_2} = 1·82$ for $\alpha_{CH_3} = 2·25$. The induced moment is then $(0·398 \times 1·82/2·25)\ \mu_{C-O}$, *i.e.*, $0·322\ \mu_{C-O}$ at an angle of 12·6° to the nearer C–O dipole. The resultant moment of the molecule is obtained by resolving the induced moments in the same direction as the resultant of the primary C–O moments. It is

$$2 \times 2·30(\cos 55·5° + 0·34 \cos 55·5° + 0·0722 \cos 55·5° - 0·322 \cos 42·9° - 0·237 \cos 34·5° + 0·0600 \cos 34·5°)$$

which gives 1·126, in excellent agreement with Sanger's gas value 1·146 (*Physikal. Z.*, 1930, **31**, 306). Stuart (*op. cit.*), from consideration of the intramolecular potentials, concluded that the methyl groups probably had an oscillatory motion with an amplitude of 70° about the position here denoted by (A).

FIG. 2.



A. B.

For the alternative (and improbable) plane configuration (B) the only difference in magnitude will be in the moment induced in each methyl group by the more remote C–O dipoles. From the appropriate diagrams $\Sigma A_x = -0·2939$ and $\Sigma A_y = 0·0484$, whence the induced moment is $-0·1002\ \mu_{C-O}$ parallel to the more remote C–O dipole and $0·2385\ \mu_{C-O}$ at right angles. As before the resultant is given by

$$2 \times 2·30(\cos 55·5° - 0·322 \cos 42·9° + 0·034 \cos 55·5° + 0·237 \cos 34·5° - 0·1002 \cos 55·5° - 0·2385 \cos 34·5°),$$

which gives 1·344. Accordingly the oxygen valency angle has been assumed to be 111° in ethyl carbonate.

Ethyl Carbonate.—Corresponding to the plane configuration (A) of methyl carbonate there are two symmetrical plane configurations (Fig. 3, A_1 and A_2) for ethyl carbonate, produced by rotation of the terminal methyl groups about the C–C axis. From the plane configuration (B) of methyl carbonate only one symmetrical plane configuration for ethyl carbonate can be derived (Fig. 3, B) and the same objections apply to this as to configuration (B) for methyl carbonate. The induced moments for A_1 are calculated as follows :

(*a*) The moment induced in each methylene group by the C=O dipole is estimated from the calculations for methyl carbonate to be — (0·0785 × 1·82/2·25) $\mu_{C=O}$, *i.e.*, — 0·145, parallel to the C=O dipole.

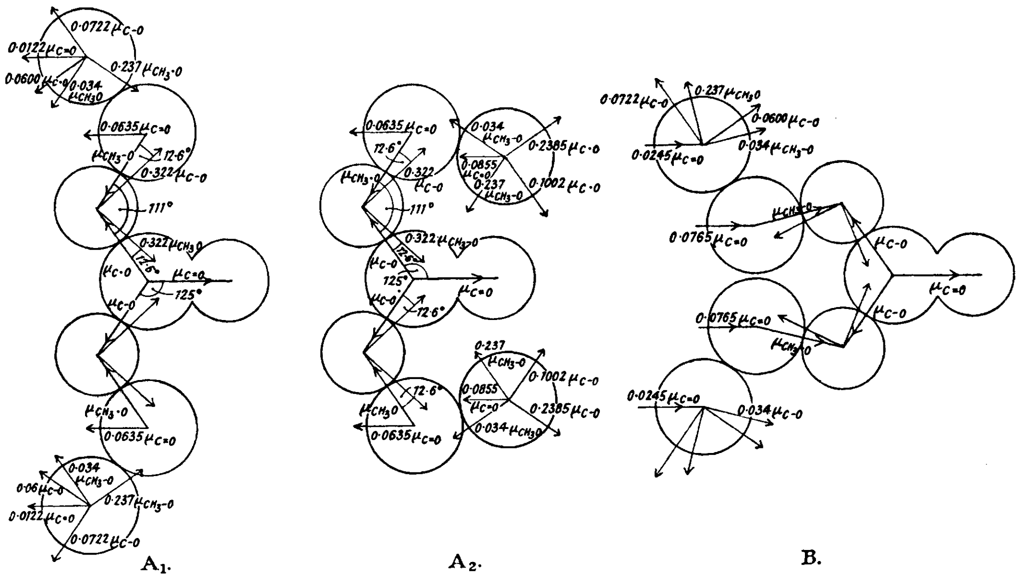
(*b*) That induced in each methyl group by the C=O dipole is found from the appropriate diagram to be — 0·0122 $\mu_{C=O}$, *i.e.*, — 0·0278, parallel to the C=O dipole. [In both (*a*) and (*b*) the components at right angles to the primary dipole vanish by symmetry.]

(*c*) That induced in each methylene group by the more remote C–O dipole in the same half of the molecule is estimated (cf. ethyl ether) to be 0·322 μ_{C-O} at an angle of 12·6° to the nearer C–O dipole, *i.e.*, 43·4° to the direction of the C=O dipole.

(*d*) The moment induced in the central carbon atom by the more remote C–O dipoles will be, as in methyl carbonate, for each C–O dipole 0·170 μ_{CH_3-O} at an angle of 42·4° to the C=O axis.

(*e*) The induction in each methyl group due to the remote C–O dipole in the same half of the molecule has the components 0·0722 μ_{C-O} parallel to the C–O dipole and 0·0600 μ_{C-O} at right angles (cf. " zig-zag " configuration of ethyl ether).

FIG. 3.



(*f*) The induction in each methyl group due to the nearer CH_3–O dipole in the same half of the molecule has the components 0·034 μ_{CH_3-O} parallel to the C–O dipole and 0·237 μ_{CH_3-O} at right angles (cf. ethyl halides; Groves and Sugden, *loc. cit.*).

The resultant moment is given by

2·28 — 2(2·3 cos 56°) — 2(1·9 cos 55°) — 2(0·145) — 2(0·0278) + 2(0·322 × 1·90 cos 43·4°) + 2(0·170 × 2·30 cos 42·4°) — 2(0·0722 × 1·90 cos 55°) + 2(0·0600 × 1·90 cos 35°) — 2(0·034 × 2·30 cos 56°) + 2(0·237 × 2·30 cos 34°),

which gives — 0·880.

For the alternative plane configuration A_2 the only induced moments which differ in magnitude from those estimated for A_1 are (*b*) and (*e*). From the appropriate diagram (*b*) is found to be — 0·0855 $\mu_{C=O}$, *i.e.*, — 0·195; (*e*), the moment induced in each methyl group by the more remote C–O dipole in the same half of the molecule, is estimated (cf. " ring " configuration of ethyl ether) to have the components — 0·1002 μ_{C-O} parallel to the C–O dipole and 0·2385 μ_{C-O} at right angles. With the appropriate alterations in three terms in the above calculation, this gives the value — 1·617.

For the configuration in Fig. 3B the only induced moments for which data have not so far been obtained are those induced in the methyl groups by the C=O dipole. From the appropriate diagram $\Sigma A_x = +0\cdot06086$, whence $\mu_{1x} = 0\cdot0245\,\mu_{C=O}$, *i.e.*, 0·056. The moment induced in each methylene group by the C=O dipole can be calculated from the value found for the methyl group in configuration (B) of methyl carbonate: it will be $-(0\cdot0946 \times 1\cdot82/2\cdot25)\,\mu_{C=O}$, *i.e.*, 0·1744. The resultant moment of the whole molecule will be

$$2\cdot28 - 2(1\cdot90\ \cos\ 55^\circ) + 2(2\cdot30\ \cos\ 14^\circ) + 2(0\cdot1744) + 2(0\cdot056) - 2(0\cdot322 \times 1\cdot90\ \cos\ 26\cdot6^\circ) + 2(0\cdot170 \times 2\cdot30 \cos 67\cdot6^\circ) + 2(0\cdot034 \times 2\cdot30 \cos 14^\circ) - 2(0\cdot237 \times 2\cdot30 \cos 76^\circ) - 2(0\cdot0722 \times 1\cdot90 \cos 55^\circ) + 2(0\cdot060 \times 1\cdot90 \cos 35^\circ)$$

which reduces to 4·145.

The improbability of this structure is borne out by comparison of this calculated value with the experimental values of 1·06 in the gaseous state (Kubo) and the present value 0·90 in benzene solution. It seems likely that the attractive forces between the C=O dipole and the more remote C–O dipoles are sufficient to lock the methylene groups in the position shown in Fig. 3, A_1 and A_2. The magnitude of the moment and its constancy over a wide range of temperature may be due either to a locking of the terminal methyl groups in some position intermediate between those shown in A_1 and A_2 or to completely free rotation of these groups. The mean resultant moment for free rotation of the methyl groups, with allowance for variation in induction effects, is not readily calculable.

EXPERIMENTAL.

Apparatus.—Dielectric constants were measured by a resonance method using a dynatron oscillator and a quartz resonator in the measuring circuit to detect the resonance point. The frequency was 932·5 kc./sec. In the measuring circuit, the condenser system consisted of a specially constructed variable condenser of 17 μμF. range (with a scale and vernier enabling settings to be made to 0·001 μμF.) and a set of six fixed condensers (approximate capacities 12, 24, 48, 96, 192 and 384 μμF. respectively) which could be connected in parallel with the variable condenser by means of mercury cups. The condensers were individually shielded, and inter-calibrated in terms of scale divisions of the variable condenser. The experimental cell used was modified slightly from the Sayce and Briscoe type (J., 1925, **127**, 315). The thermostat in which the cell was immersed was a large glass accumulator jar filled with liquid paraffin (about 10 l.), electrically heated and maintained at 25° ± 0·05° by a benzene-filled thermoregulator. The cell was filled and emptied, washed and dried in position in the thermostat.

Materials.—The benzene used as solvent was prepared from B.D.H. " extra pure " liquid as already described (J., 1937, 1051). The specimens of methyl and ethyl carbonates were very kindly supplied by Dr. S. T. Bowden, University College, Cardiff.

In the following tables the symbols have their usual significance.

Methyl Carbonate in Benzene.

f_2.	$d_{4^\circ}^{25^\circ}$.	ϵ_{25°.	P_2.	f_2.	$d_{4^\circ}^{25^\circ}$.	ϵ_{25°.	P_2.
0·0000	0·87368	2·2725	—	0·02352	0·87743	2·3003	42·4
0·0089878	0·87510	2·2828	42·6	0·029542	0·87839	2·3074	42·45
0·020037	0·87688	2·2965	42·4	0·037882	0·87970	2·3170	42·45

$_\infty P_2 = 42\cdot4$; $n_D^{25^\circ} = 1\cdot36696$, $d_{4^\circ}^{25^\circ} = 1\cdot06027$; whence $P_E = 19\cdot05$, $P_{O+A} = 23\cdot35$ c.c., and $\mu = 1\cdot06$.

Ethyl Carbonate in Benzene.

0·0000	0·87368	2·2725	—	0·016641	0·87588	2·2834	45·2
0·01002	0·87474	2·2793	45·4	0·019705	0·87598	2·2853	45·4
0·013516	0·87524	2·2817	45·45				

$_\infty P_2 = 45\cdot4$; $n_D^{25^\circ} = 1\cdot38297$, $d_{4^\circ}^{25^\circ} = 0\cdot96926$; whence $P_E = 28\cdot39$, $P_{O+A} = 17$ c.c., and $\mu = 0\cdot90$.

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