13. *Intermolecular Forces in Liquid Systems. Part II. Viscosity, Surface Tension, and Parachor Relationships in Binary Systems.*

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The properties of systems containing methyl or ethyl carbonate and non-polar and dipolar liquids have been studied with a view to ascertain the nature of the intermolecular forces. Errera's rules connecting the type of viscosity–concentration curve with the dipole moments of the components are found to apply to all the systems investigated except those containing nitrobenzene.

The surface tension–composition curves for the mixtures are negative, and show a minimum corresponding to identity of the surface and the bulk phase in the cases of methyl carbonate–benzene, ethyl carbonate–chloroform, and ethyl carbonate–carbon tetrachloride. No obvious relationship exists between the surface adsorption and the dipole moments of the components.

The parachor of the alkyl carbonate preserves a constant value in all the systems except those containing nitrobenzene, where the solute parachor increases with the concentration. It is shown that liquid mixtures may be classified into three types according as the parachor–concentration curve is (*a*) a horizontal line, (*b*) a straight line rising with the solute concentration, and (*c*) a curve showing a non-linear relationship between parachor and concentration. Under suitable conditions, the parachor of the solute in non-polar and dipolar systems can be found by extrapolation with an accuracy of 1%.

ATTEMPTS have recently been made to correlate the viscosity–composition curves of binary mixtures with the polarity of the components. Errera (*Z. physikal. Chem.*, 1929, **140**, 273) suggests that dipole association and non-polar association arising from van der Waals forces are responsible for the form of the viscosity–composition curve, and that the occurrence of either type of association leads to enhanced viscosity. If dipole association is strongly operative, the formation of an addition compound is possible, and in this case the curve may exhibit a maximum. On this basis Errera proposes the following rules: (1) When both components have zero dipole moment, or when one component is non-polar and the other dipolar, the viscosity–composition curve is negative. (2) The curve is positive when both components are dipolar.

Mixtures of methyl and ethyl carbonates with the non-polar liquids benzene and carbon tetrachloride exhibit negative η–c curves as shown in Fig. 1. The curve for methyl carbonate–benzene shows a minimum corresponding to 53% of carbonate, and the mixtures of chloroform with methyl carbonate and with ethyl carbonate show maxima corresponding to the concentrations 44% and 62% respectively. The deviation of the viscosity ($\Delta\eta$) from the linear value is brought into prominence in Fig. 2, where the viscosity deviation is plotted against the concentration of the solution.

We are indebted to Dr. George Thomson for carrying out dipole-moment measurements with a view to test the applicability of Errera's rules to systems containing the alkyl carbonates. The esters have moments of the order of 1D., and their mixtures with other liquids, except nitrobenzene, conform to the above rules. For nitrobenzene mixtures, the rule demands that the curve should be positive, but actually it is negative. This behaviour, however, is not unique, for a similar type of curve is found for the dipolar system ethyl alcohol–nitrobenzene. Hence, it is evident that a binary system of two dipolar liquids may give either a positive or a negative η–c curve. The apparently anomalous behaviour of systems containing nitrobenzene is to be referred to the special characteristics of the nitro-group, and it is clear that factors other than polarity determine the viscosity of the system.

The positive curves with maxima obtained for methyl carbonate–chloroform and ethyl carbonate–chloroform recall the behaviour of the system acetone–chloroform (Schultze, *Z. physikal. Chem.*, 1919, **93**, 37; McLeod, *Trans. Faraday Soc.*, 1934, **39**, 482), where complex formation has been postulated to account for the maximum on the curve. Glasstone (*ibid.*, 1937, **33**, 204) has discussed the possibility of the donation of an electron pair from the oxygen atom to the hydrogen of chloroform, $\mathrm{Me_2CO} \longrightarrow \mathrm{H{\cdot}CCl_3}$. This refers, however, to a molecule containing a true ketonic group, and the formation of complexes, such as $\mathrm{(RO)_2CO} \longrightarrow \mathrm{H{\cdot}CCl_3}$, in the case of the carbonic esters appears to be much less likely.

Fig. 1.

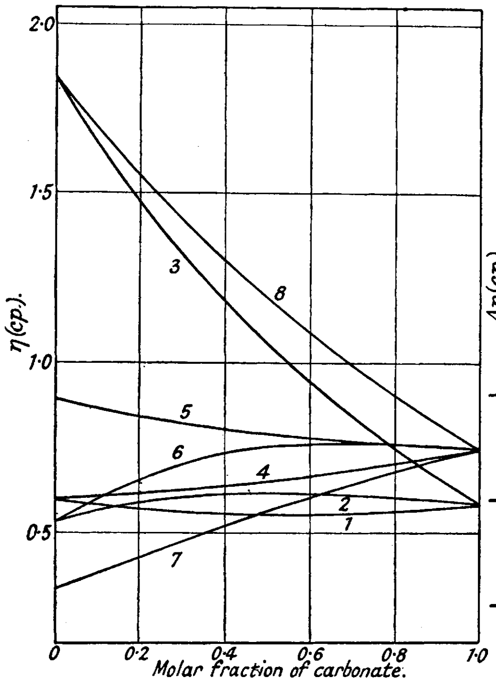
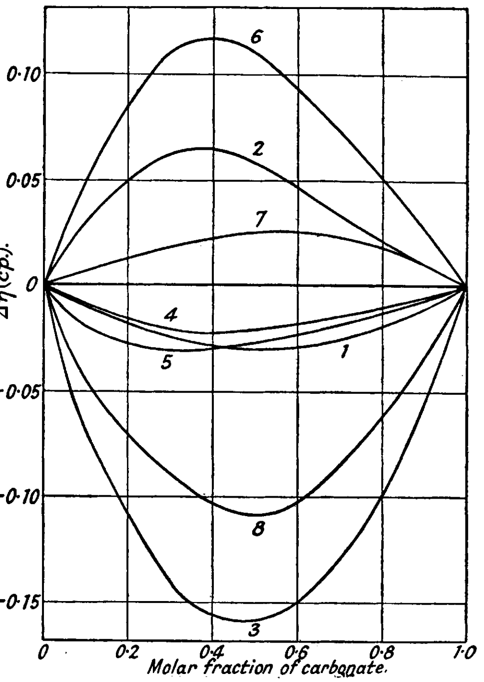


Fig. 2.



(1) *Methyl carbonate–benzene.* (2) *Methyl carbonate–chloroform.* (3) *Methyl carbonate–nitrobenzene.* (4) *Ethyl carbonate–benzene.* (5) *Ethyl carbonate–carbon tetrachloride.* (6) *Ethyl carbonate–chloroform.* (7) *Ethyl carbonate–acetonitrile.* (8) *Ethyl carbonate–nitrobenzene.*

Although the viscosity of solutions has been the subject of extensive study, the surface tension of liquid mixtures has received little attention apart from studies relating to adsorption in dilute solution. On the assumption that the two liquids are unassociated and under corresponding states, Stachovsky (*Z. Elektrochem.*, 1928, **34**, 111) deduced that $\gamma = \gamma_1\gamma_2/(\gamma_1N_2 + \gamma_2N_1)$, where γ, γ_1, and γ_2 are the surface tensions of the mixture and of the pure components, and N_1 and N_2 are the respective molar fractions in the mixture. There is fairly good agreement between the observed and the calculated values of the surface tension of mixtures of ethyl acetate with benzene and with carbon tetrachloride, where the critical temperatures do not differ greatly. In some cases, such as nitrobenzene–benzene and nitrobenzene–ethyl acetate, the agreement is also good, although the difference in the critical temperatures of the components is large.

As shown in Table I, there is fairly satisfactory agreement between the observed and the calculated values for mixtures of ethyl carbonate with benzene and with acetonitrile, but the discrepancy is more pronounced for ethyl carbonate–nitrobenzene. In all cases

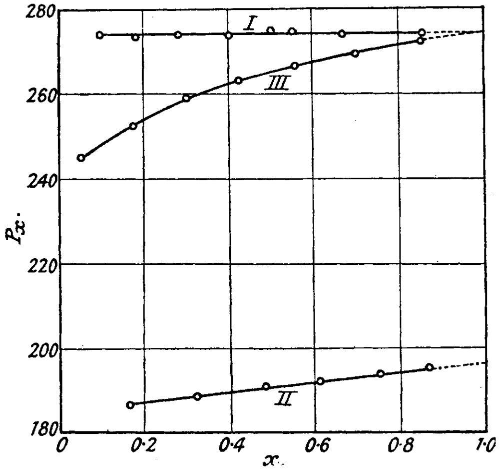
Table I.

Ethyl carbonate–benzene.			Ethyl carbonate–acetonitrile.			Ethyl carbonate–nitrobenzene.		
N_1.	γ, obs.	γ, calc.	N_1.	γ, obs.	γ, calc.	N_1.	γ, obs.	γ, calc.
0·0497	27·99	28·08	0·1601	27·84	28·03	0·0519	41·05	41·62
0·1506	27·59	27·80	0·2225	27·52	27·84	0·1727	37·34	38·56
0·2690	27·22	27·49	0·3017	27·22	27·60	0·3010	34·55	35·79
0·3377	26·85	27·17	0·4001	27·07	27·33	0·4226	32·40	33·50
0·5186	26·54	26·85	0·5035	26·74	27·03	0·5535	30·47	31·35
0·6685	26·10	26·49	0·6554	26·36	26·60	0·6938	28·76	29·32
0·8588	25·82	26·03	0·7927	26·06	26·24	0·8519	27·16	27·47

the calculated values are consistently higher than the observed values. This equation fails completely for methyl carbonate–benzene and ethyl carbonate–chloroform, since the γ–c curves for these systems pass through a minimum. Consideration of Gibbs's adsorption formula shows that, if the addition of component A to component B lowers the surface tension, the concentration of A in the surface phase will be greater than in the bulk phase. If, moreover, the addition of B to A likewise reduces the surface tension, the concentration of B in the surface phase will be greater for similar reasons. It follows, therefore, that there will be a certain mixture of minimum surface tension in which the composition of the surface layer will be the same as that of the liquid in bulk. The minimum surface tension is realised in a 0·35M-solution of methyl carbonate in benzene and in a 0·80M-solution of ethyl carbonate in chloroform. In so far as the surface layer may be considered a distinct phase, the case is analogous to that of an azeotropic system where the pressure–composition curve passes through a minimum corresponding to the attainment of identity in the compositions of the liquid and the vapour phase, as embodied in the Gibbs–Konovalov rule.

Calculations of the parachor of the solute reveal that the solutions may be classified into three types: (i) the solute parachor P_x is independent of the dilution and the P_x–c curve is a horizontal straight line as shown in Fig. 3; (ii) the solute parachor is dependent on the concentration and the P_x–c curve is a straight line rising with the molar fraction of the solute; (iii) the solute parachor depends on the concentration but the P_x–c curve is not a straight line. In agreement with the observations of Hammick and Andrew (J., 1929, 754), it is found that the systems belong to Type (i) when the surface tensions of the pure components do not differ by more than 5 dynes/cm. When, however, the surface tensions differ by more than 14 dynes/cm., as in methyl carbonate–nitrobenzene, the system belongs to Type (ii), while the system ethyl carbonate–nitrobenzene with surface tensions differing by over 17 dynes/cm. belongs to Type (iii). Although Semerano and Fabbrini (*Atti Accad. Venito-Trentino-Istriana*, 1932, **23**, 17) have maintained that the linear relation connecting the contribution of solvent and solute to the parachor of a solution is strictly valid only when the components have the same surface tension, it is clear from the present results and those of previous workers (Hammick and Andrew, *loc. cit.*; Ray, *J. Indian Chem. Soc.*, 1935, **12**, 248) that the parachor of the solute in non-ionising solvents can be found to an accuracy of 1% by extrapolation. On the other hand, anomalous results are obtained with aqueous solutions (*idem, ibid.*, 1938, **15**, 43; Lakhani and Daroga, *ibid.*, p. 37), and it appears that a distinction must be made between atomic and ionic parachors.

FIG. 3.



I. *Ethyl carbonate–chloroform.*
II. *Methyl carbonate–nitrobenzene.*
III. *Ethyl carbonate–nitrobenzene.*

EXPERIMENTAL.

Purification of Materials.—The methyl and ethyl carbonates were purified as described in the preceding paper.

" AnalaR " Benzene, extra pure for molecular-weight determinations, was distilled from sodium wire before use; b. p. 80·1°, $d_{4^\circ}^{25^\circ}$ 0·87287, n_D 1·49774. The value for $d_{4^\circ}^{25^\circ}$ differs by 0·0005 from that given in the International Critical Tables, but is practically identical with that obtained by Martin (J., 1932, 2662).

" AnalaR " Carbon tetrachloride, dried over freshly dehydrated calcium chloride, was fractionated through an eight-pear column; b. p. 76·8°, $d_{4^\circ}^{25^\circ}$ 1·58447. " AnalaR " Chloroform was washed with water, dried over calcium chloride, and fractionated; b. p. 61·0°, $d_{4^\circ}^{25^\circ}$ 1·47972. Acetonitrile was carefully fractionated and finally distilled from phosphoric oxide; b. p. 81·6°, $d_{4^\circ}^{25^\circ}$ 0·77680; n_D 1·34161. Nitrobenzene, extra pure for molecular-weight determinations, was dried over calcium chloride and distilled; b. p. 210·0°; $d_{4^\circ}^{25^\circ}$ 1·19805.

Viscosity Measurements.—The measurements were made in an Ostwald type of viscometer, constructed entirely of glass and provided with a hollow, ground stopper by means of which it was possible to circulate water and dry air through the apparatus and to carry out the actual viscosity measurements in a closed system. The instrument conformed to Specification No. 188 (Determination of Viscosity in Absolute Units, 1929) of the British Engineering Standards Association, and the design incorporated Barr's recommendations (" Monograph of Viscometry," Oxford University Press, 1931). The capillary, 12 cm. long and of 0·2 mm. radius, was specially selected with due regard to uniformity of bore, and the upper bulb was blown to a pear shape in order to facilitate the draining of the liquid. The instrument was set vertically to a plumb-line in an electrically-controlled thermostat at 25° ± 0·01°, and the times of flow were noted by means of a stop-watch which had been tested against a standard chronometer.

Since the simple Ostwald equation is not strictly valid if the times of flow of the two liquids are very different, a kinetic-energy correction was applied by means of the equation $\eta = d(At - B/t)$, where d is the density and A and B are constants, which may be evaluated by

TABLE II.

Methyl carbonate and benzene.

x.	$d_{4^\circ}^{25^\circ}$.	η.
0·00000	0·87287	0·5996
0·17170	0·90256	0·5803
0·34401	0·93281	0·5679
0·51315	0·96382	0·5618
0·67640	0·99503	0·5622
0·83748	1·02711	0·5700
1·00000	1·06027	0·5845

Methyl carbonate and chloroform.

x.	$d_{4^\circ}^{25^\circ}$.	η.
0·00000	1·4797	0·5348
0·14270	1·4161	0·5833
0·28121	1·3552	0·6106
0·42254	1·2930	0·6193
0·56361	1·2341	0·6135
0·71110	1·1741	0·6023
0·85503	1·1166	0·5908
1·00000	1·0603	0·5845

Methyl carbonate and nitrobenzene.

x.	$d_{4^\circ}^{25^\circ}$.	η.
0·00000	1·1981	1·8472
0·16259	1·1804	1·5449
0·31931	1·1620	1·3010
0·47837	1·1419	1·0884
0·61267	1·1231	0·9314
0·75557	1·1017	0·7875
0·87341	1·0826	0·6838
1·00000	1·0603	0·5845

Ethyl carbonate and benzene.

0·00000	0·8729	0·5996
0·04966	0·8793	0·6016
0·15061	0·8915	0·6096
0·26897	0·9048	0·6229
0·44400	0·9193	0·6407
0·51860	0·9296	0·6571
0·66854	0·9430	0·6825
0·85880	0·9585	0·7185
1·00000	0·9693	0·7476

Ethyl carbonate and carbon tetrachloride.

0·00000	1·5847	0·8973
0·07871	1·5241	0·8655
0·23879	1·4095	0·8362
0·39362	1·3071	0·8082
0·53205	1·2218	0·7937
0·66938	1·1425	0·7790
0·77652	1·0854	0·7701
0·89475	1·0216	0·7586
1·00000	0·9693	0·7476

Ethyl carbonate and chloroform.

0·00000	1·4797	0·5348
0·10610	1·4026	0·6091
0·18017	1·3532	0·6539
0·28350	1·2892	0·7024
0·40278	1·2222	0·7387
0·55015	1·1482	0·7571
0·66426	1·0969	0·7586
0·85469	1·0206	0·7547
1·00000	0·9693	0·7476

Ethyl carbonate and acetonitrile.

x.	$d_{4^\circ}^{25^\circ}$.	η.
0·00000	0·7768	0·3391
0·09602	0·8162	0·3842
0·22248	0·8558	0·4439
0·30165	0·8756	0·4808
0·40007	0·8964	0·5263
0·50347	0·9144	0·5710
0·65539	0·9358	0·6511
0·79265	0·9512	0·6812
1·00000	0·9693	0·7476

Ethyl carbonate and nitrobenzene.

x.	$d_{4^\circ}^{25^\circ}$.	η.
0·00000	1·1981	1·8472
0·05189	1·1853	1·7641
0·17273	1·1560	1·5989
0·30103	1·1256	1·4220
0·42262	1·0971	1·2768
0·55354	1·0671	1·1336
0·69379	1·0356	0·9964
0·85192	1·0009	0·8597
1·00000	0·9693	0·7476

measuring the times of flow of two liquids of very different kinematic viscosity. The standard liquids employed for this purpose were water and ethyl ether, and the viscosity values used in the calculations were those given in the International Critical Tables. The values of the constants for the present instrument were $A = 0{\cdot}0024965$ and $B = 1{\cdot}496$.

The densities of the pure liquids and the solutions were determined pyknometrically in the same thermostat. The results are given in Table II where d is the density and η is the viscosity in centipoises.

Surface-tension Measurements.—The surface tension of the liquids was measured in a modification of the Jaeger–Sugden apparatus (J., **1924**, **125**, 27), immersed in a thermostat at 25° ± 0·01°. The bubbling tubes were carefully selected with regard to uniformity of bore, and the radii were 0·1383 cm. and 0·007 cm. respectively. The pressure gauge and aspirating unit were also immersed in baths to avoid accidental temperature fluctuations. With these precautions, there was no difficulty in obtaining successive readings consistent to within 0·3%. The apparatus was calibrated by using pure benzene ($\gamma = 28{\cdot}21$ dynes/cm.).

The results are given in Table III, where d is the density of the solution and γ the surface tension in dynes/cm. The parachor of the solute P_x is obtained from the parachor of the solution P_m and that of the solvent P by means of the following relations : $P_m = P(1 - x) + P_x x$; $P_m = M_m\gamma^{\frac{1}{4}}/(d - d')$; $M_m = M_s(1 - x) + M_x x$, where x is the molar fraction of the solute, M_x its molecular weight, M_s the molecular weight of the solvent, γ the surface tension of the solution, d the density of the solution and d' the density of the vapour, which is negligible at 25°.

TABLE III.

Methyl carbonate and benzene.

x.	$d_{4^\circ}^{25^\circ}$.	γ.	P_m.	P_x.
0·00000	0·87287	28·21	206·1	—
0·17170	0·90256	28·11	204·4	196·2
0·34401	0·93281	28·10	202·8	196·0
0·51315	0·96382	28·07	201·2	196·5
0·67640	0·99503	28·21	199·6	195·8
0·83748	1·02711	28·34	198·0	196·6
1·00000	1·06027	28·46	—	196·2
			Mean	196·2*

Methyl carbonate and chloroform.

x.	$d_{4^\circ}^{25^\circ}$.	γ.	P_m.	P_x.
0·00000	1·4797	26·21	182·6	—
0·14270	1·4161	26·45	184·5	195·1
0·28121	1·3552	26·50	186·4	195·8
0·42254	1·2939	26·77	183·3	195·6
0·56361	1·2341	26·88	190·6	196·7
0·71110	1·1741	27·13	192·2	196·0
0·85503	1·1166	27·94	194·2	196·9
1·00000	1·0603	28·46	—	196·2
			Mean	196·0

Methyl carbonate and nitrobenzene.

0·00000	1·1981	43·08	263·1	—
0·16259	1·1804	39·92	250·6	186·4
0·31931	1·1620	37·27	239·2	188·3
0·47837	1·1419	34·99	228·5	190·8
0·61267	1·1231	33·06	219·5	192·0
0·75557	1·1017	31·45	210·9	194·0
0·87341	1·0826	30·12	203·9	195·3
1·00000	1·0603	28·46	—	196·2

Ethyl carbonate and benzene.

0·00000	0·87287	28·21	206·1	—
0·04966	0·87925	27·99	209·4	272·7
0·15061	0·89152	27·59	216·1	273·0
0·26897	0·90482	27·22	224·2	273·6
0·38771	0·91702	26·85	232·3	273·7
0·51860	0·92958	26·54	241·3	274·0
0·66854	0·94298	26·10	251·2	273·6
0·85880	0·95846	25·82	264·4	274·0
1·00000	0·96926	25·70	—	274·5
			Mean	273·5

Ethyl carbonate and nitrobenzene.

0·00000	1·1981	43·08	263·1	—
0·05198	1·1853	41·05	262·2	245·1
0·17273	1·1560	37·34	261·3	252·4
0·30103	1·1256	34·55	261·8	258·6
0·42262	1·0971	32·40	263·0	262·9
0·55354	1·0671	30·47	264·9	266·3
0·69379	1·0356	28·76	267·4	269·3
0·85192	1·0009	27·16	271·0	272·4
1·00000	0·9693	25·70	—	274·5

* The mean value refers to the mixtures only.

Although the dipole moments of the substances are widely different, it is evident from Fig. 3 that the extrapolation method is entirely reliable in the case of non-ionising media.

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