CCXIX.—*Capillary Activity in Aqueous Solutions.*

By HERBERT MILLS and PERCY LUCOCK ROBINSON.

THIS investigation was undertaken primarily to discover whether any numerical relationship exists between the depression in surface tension brought about when certain substances are dissolved in water and the molecular properties of these solutes. A cursory examination of the existing data appeared to indicate that depressions in equimolecular solutions are related to the fourth power of the parachor (Sugden, J., 1924, **125**, 1185) of the solute. It is generally assumed that the surface tension–concentration curves for solutes lowering the surface tension of water, although differing considerably, have a portion at extreme dilution where $d\gamma/dc$ is constant, and for reasons given below, it was necessary to measure this constant in a number of cases. As the value of $d\gamma/dc$ is frequently small, a method of surface-tension measurement sensitive to small differences and yet capable of giving trustworthy relative results had to be found. To this end, an endeavour to increase to its utmost limits the sensitivity of the capillary-rise method by the use of extremely narrow capillaries only served to demonstrate its unsuitability by reason of the uncertainty of the results. Recourse was had to the method of maximum bubble pressure (compare Sugden, J., 1922, **121**, 808) which, after certain modifications, met all the requirements of precision and was, furthermore, extremely convenient in use. It appears to yield comparative values of a much higher order of accuracy than are obtainable by any other means.

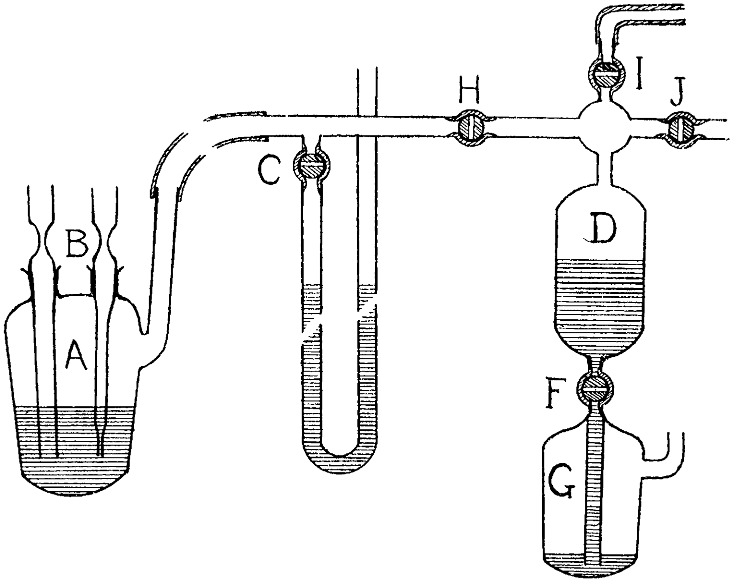
The examination of solutions of surface-active solutes by means of the apparatus devised indicated that these could be readily divided into two types, which seem to differ essentially in the relative values of *surface* and *bulk* concentrations of the dissolved materials. In those solutions in which the surface concentration is not greatly in excess of the bulk concentration, the relationship indicated above applies directly, whilst in those with a high surface concentration it would also appear to hold provided that the effect of the bulk concentration alone is considered. This second type displayed entirely novel phenomena which enabled the process of surface adsorption to be followed at least semi-quantitatively, demonstrated the relationship between concentration and maximum adsorption, and gave data for the preparation of the surface tension–concentration curve of a solution in which surface adsorption had been allowed to attain its maximum value.

EXPERIMENTAL.

Apparatus for Measurement of Surface Tension.

Relative Accuracy attainable.—Differences of surface tension of the order of 0·05 dyne per cm. might be expected to be susceptible of measurement by means of a capillary tube of 0·2 mm. radius and a cathetometer reading to 0·02 mm. Such a tube was tried, but the results were untrustworthy when solutions were substituted for pure liquids. It was then found that the objections raised by Sugden (*loc. cit.*) to the use in his method of jets of less than 0·05 mm. radius may be easily overcome, as may also those which he advanced against the use of water in the manometer (compare Hammick and Andrew, J., 1929, 754, who found water quite suitable). Jets with radii as small as 0·025 mm. have been successfully employed. These gave for surface tensions of the order of that of water a manometric head of that liquid of approximately 50 cm., measurable with an error of less than ± 0·02 mm. Results with a relative accuracy of ± 0·006 dyne per cm. were therefore to be anticipated, and were, in fact, actually realised.

FIG. 1.



Procedure.—The apparatus was in three parts : the vessel carrying the jets, the manometer, and the device for regulating the pressure of air over the liquid. The first consisted of a piece of glass of the shape shown in the diagram (Fig. 1), the body A of which was about 10 × 6 cm. and had in its upper surface two necks fitted with ground-in hollow stoppers carrying respectively the coarse and the fine jet. These necks were cupped to provide for a liquid seal, and were of different diameters so as to avoid misplacing the stoppers, the stems of which were of such a length that each jet was at the same level when the apparatus was in its normal working position. It was imperative that the air passing to the fine jet should be filtered, and to effect this a plug of cotton wool held in position by a constriction B was employed. A similar device in the case of the coarse jet served to keep the liquid under examination in a dust-free condition.

The coarse jets were cut directly from quill-tubing by a special steel cutting edge, and those which did not show a clean break were rejected. Fine jets were drawn from the same quill-tubing and were only attached to the apparatus after careful examination had shown them to be free from obvious fault. Preliminary experiments proved that jets having the walls very thick in relation to the orifice, and also those in which the capillary bore formed a long slow taper, were unsuitable. Jets in which the inner surface had become roughened through being drawn after the glass had cooled too far were also unsuitable. Final selection was made only after the jets had been tried under ordinary working conditions in an apparatus especially adapted for the purpose. The manometer, a **U**-tube of glass tubing of 8 mm. bore, was constructed so that the limbs were in contact over a length of about 65 cm., and was provided with a tap C.

The pressure-regulating device consisted of a cylindrical vessel D of 50 c.c. capacity containing mercury and attached at its upper end to an inverted **T**-piece carrying three taps. Mercury, under the control of tap F, ran into the lower vessel G. Tap H led to the manometer, I to the water pump and J to the atmosphere, an arrangement which allowed of the raising of mercury from G to D, the attaining of a suitable approximate pressure in the system, and its reduction by small amounts.

The general assembly of the apparatus, with the jet-vessel and the manometer almost submerged in the water of the thermostat, is sufficiently indicated by the diagram (Fig. 1), but some indication of the method of working is necessary. It was essential to ensure that the vessel carrying the jets and the jets themselves were clean and grease-free by steeping them in a chromic–nitric acid mixture, followed by copious washing with redistilled water and, finally, immediately before use, repeated rinsing with a portion of the solution to be investigated. The manometer was similarly cleaned, and frequent repetition of this cleaning was found to be a condition of satisfactory working with water as the gauge liquid.

In the actual determinations, the liquid under examination was placed in the jet vessel, and the pressure required for the wider jet was ascertained. With the large bubbles produced by such jets, an oscillating movement is induced in the manometer because the pressure increases up to a point after which the bubble bursts, but in practice the maximum pressure could readily be measured if the rate of bubble formation were one in 5—6 seconds. On the other hand, with fine jets the manometer difference decreases until the excess pressure used in starting the flow of bubbles is dissipated, whereupon, with pure liquids and solutions of solutes which are not appreciably adsorbed at surfaces, the formation of bubbles ceases. The final pressure reached is taken as a measure of the maximum bubble pressure. When, however, a solute which is adsorbed at the surface of the solvent is present, bubbles continue to be formed at ever-decreasing rates and pressures over a protracted period. Experience showed that, whatever the liquid, trustworthy results are more readily obtained immediately after the jet has been subjected to two or three bursts of rapid streams of bubbles.

Measurements of the height of liquid in the two limbs of the manometer were made by means of a cathetometer made by the Cambridge Instrument Company, and were of an accuracy of ± 0·02 mm.

The surface tension of the liquid (L) was given by

$$\gamma_{L} = \gamma_{\text{standard liquid}} \div \frac{\text{Jet pressure difference of standard liquid}}{\text{Jet pressure difference of L}}.$$

Relative Surface Tensions of Water, Benzene, and Ethyl Alcohol.

Before using these extremely fine jets for definitive experiments, it appeared desirable to examine their behaviour with several pure liquids. These were prepared in the manner detailed below, precaution being taken, by preliminary cleansing and subsequent repeated washing with the liquid in question, to ensure that the jet-vessel introduced no contamination.

Distilled water was redistilled from a trace of alkaline permanganate into a silica flask, with rejection of head and tail fractions. The middle fraction was twice distilled in the silica apparatus with further rejections, and the final middle fraction was distilled into the apparatus immediately before the measurements were made.

Commercial benzene, described as thiophen-free, was fractionated at a rate of one to two drops per second, and the middle fraction was washed successively with concentrated sulphuric acid, water, caustic potash solution, and water, and subsequently treated with mercury. The washing process was then repeated. The resulting liquid was fractionally crystallised hree times with the rejection of head and tail portions, and the main fraction was dried over phosphoric oxide for two days and again fractionally distilled. In the case of apparatus Nos. II and III the benzene used was distilled from phosphoric oxide through a small fractionating column directly into the bubbler and also into the capillary tube apparatus. The difference of these results from the accepted values indicated the presence of some impurity in the liquid, and as this was believed to be due to phosphoric oxide, the benzene used in apparatus Nos. I, IV, and V was refractionated and distilled a second time up a small column after leaving the phosphoric oxide.

"Absolute" alcohol was fractionated and refluxed for one day over freshly made quicklime, then for a similar period over metallic calcium, and fractionated. The main portion was further fractionated in the process of its transference to the apparatus.

TABLE I.

[The fundamental data were those of Mills and Robinson (J., 1927, 1823), *viz.*: Surface tension of water at 10° = 74·40 dynes/cm. Temperature coefficient = 0·15 dyne/cm. per degree.]

Liquid.	Temp.	Jet diffce., mm. water (H).	H_1/H_2 ($=\gamma_1/\gamma_2$).	γ.	
Apparatus I.					
1. Water	10·3°	434·90	1	74·36	(From data)
2. Water	13·7	431·34	1·0082	73·75	
3. Benzene	10·3	175·68	2·4753	30·04	
4. Benzene	13·7	177·78	2·5164	29·55	
Apparatus III.					
1. Benzene	25	199·02	1	27·97	(γ from App. II)
2. Alcohol	12·1	161·85	1·2279	22·77	

Liquid.	Temp.	Jet diffce., mm. water (H).	Mean H, mm. water.	Variations from mean, %.	H_1/H_2 ($=\gamma_1/\gamma_2$).	γ.	
Apparatus II.							
1. Water	25°	525·37	525·29	0·05	1	72·17	(From data)
2. Water	25	525·46					
3. Water	25	525·05					
4. Benzene	25	203·54	203·58	0·08	2·5802	27·97	
5. Benzene	25	203·74					
6. Benzene	25	203·46					
Apparatus IV.							
1. Water	10	475·32	475·25	0·05	1	74·40	(From data)
2. Water	10	475·30					
3. Water	10	475·12					
4. Benzene	10	*216·02	*215·97	0·02	2·4758	30·09	
5. Benzene	10	*215·98					
6. Benzene	10	*215·92					
Apparatus V.							
1. Benzene	12	264·23	264·25	0·01	—	—	
2. Benzene	12	264·27					
3. Benzene	12	264·26					

* Mm. of benzene, this liquid being used in the manometer.

For apparatus Nos. II and III the values obtained for benzene (27·97 at 25°) and alcohol (22·77 at 12·1°) should be compared with those obtained with capillary tubes in the same samples, *viz.*, 27·96 and 22·76 respectively.

If the datum value for water (74·40 ± 0·04 dynes/cm.) is accepted, then the above data may be used to fix absolute values for benzene and alcohol, *viz.*, 30·09 ± 0·01 and 22·96 ± 0·01, respectively, at 10°.

The value for alcohol is almost identical with the 22·95 obtained previously by the authors (*loc. cit.*); that for benzene may be compared with the following values at 10° : Sugden, 30·18; Jaeger, 30·10; Ramsay and Aston, 29·26; Richards and Carver, 30·18; Harkins and Brown, 30·10; mean, omitting Ramsay and Aston, 30·14 dynes/cm.

A consideration of the above results (Table I) indicates that fine jets with radii of the order 0·10—0·003 cm. may be used in this method. Results may be repeated with an error only slightly greater than that involved in the cathetometer readings, the effect of which on the surface-tension measurements depends both on the pressures involved and on the density of the liquid in the manometer : in practice it amounted to 0·02—0·03%.

The Surface Tension of Capillary-active Aqueous Solutions

(Solute only slightly adsorbed at the surface).

A fairly satisfactory empirical formula expressing the relationship between surface tension and concentration has been suggested by Szyszkowski (*Z. physikal. Chem.*, 1908, **64**, 385), *viz.*,

$$\Delta = (\gamma_M - \gamma_L)/\gamma_L = b \log (C/c + 1)$$

where γ_M and γ_L are the surface tensions of the solvent and the solution respectively, C is the molar concentration of the solute, and b and c are constants specific for each solute. The constant b varies very slightly, whereas c differs greatly from one substance to another, so much so, indeed, that the reciprocal $1/c$, *i.e.*, σ, is considered to be a measure of the capillary activity and is termed the specific capillary activity.

Table II shows the relationship between the specific capillary activities of a number of compounds calculated from Freundlich's data ("Colloid and Capillary Chemistry," pp. 65, 66) and (i) the molecular weight (M), (ii) molecular volume (MV), (iii) the parachor (P), and (iv) the fourth powers of each of the last three functions expressed in terms of the corresponding function of formic acid as unity. It is evident that of these ratios only σ/P^4 indicates any simple connexion between the terms involved. It appeared probable that more concordance might be achieved if some less general

TABLE II.

Compound.	M.	MV.	P.	$M^4/46^4$.	$(MV)^4/37{\cdot}1^4$.	$P^4/102{\cdot}2^4$.	$\sigma/0{\cdot}73$.
Formic acid	46	37·1	102·2	1·0	1·0	1·0	1·0
Acetic acid	60	56·6	141·2	2·9	5·4	3·6	3·9
Propionic acid	74	74·0	180·0	6·7	15·8	9·6	12·2
Butyric acid	88	90·7	219·2	13·4	35·7	21·1	26·9
*iso*Propyl alcohol ...	60	75·0	171·0	2·9	16·7	8·9	9·6
*iso*Butyl alcohol ...	74	91·3	210·0	6·7	36·7	20·3	27·8
Methyl acetate	74	77·9	180·2	6·7	19·4	9·6	10·2
Ethyl acetate	88	95·6	219·2	13·4	44·1	21·1	28·7
Propylamine	59	80·8	180·9	2·7	22·5	9·8	14·5
Allyl acetate	100	107·5	247·2	22·3	70·5	34·3	32·9

measure of capillary activity were substituted for σ, which refers to all concentrations. In very dilute solutions the mutual effect of the solute molecules must be at a minimum, a fact which probably accounts for the direct proportionality between depression of surface tension and concentration then generally assumed to obtain, and hence a measure of capillary activity under these conditions is free from the complications inherent in the specific capillary activity σ. To meet this, a new measure of capillary activity has been introduced; this is termed the " molar capillary activity " (D), and is the depression, obtained by extrapolation, at a concentration of 1 mol. per 1000 g. of solvent. Previously published experimental data were used in the preliminary survey of the effects of this change, which is given in Table III, whence it is apparent that whilst D/P^4 is not a constant, the results from such miscellaneous data are not unpromising.

TABLE III.

	Substance.	Conc. (g.-mols. per 1000 g.).	γ.	Depn., dynes/cm.	D.	$10^8 \times D/P^4$.
1a (T).*	Acetic acid	0·0625	72·73	1·67	26·72	6·72
3a (T).	Butyric acid	0·0076	72·83	1·55	204·0	8·84
4a (S).	Methyl alcohol	0·1294	73·22	1·18	9·12	12·1
5a (S).	Ethyl alcohol	0·0544	73·06	1·34	24·64	8·07
6a (S).	*iso*Propyl alcohol ...	0·0333	72·03	2·37	71·16	8·09
	n-Propyl alcohol ...	0·0312	71·60	2·80	89·74	10·2
7a (S).	*iso*Butyl alcohol ...	0·0279	69·05	5·35	191·8	9·83
13a (T).	Acetone	0·0312	72·55	1·85	59·29	9·01
14a (T).	Allylamine	0·125	69·2	5·2	41·60	5·00
15a (T).	Allyl alcohol	0·0625	71·70	2·70	43·20	6·56
16a (T).	Allyl acetate	0·0039	72·65	1·75	48·6	12·0
17 (T).	Propionic acid	0·0156	73·17	1·23	78·86	7·51
18 (T).	Methyl acetate	0·0312	71·81	2·59	83·00	7·95
19 (T).	Propylamine	0·0312	71·18	3·22	103·2	9·69
					Mean	8·7

* T = Data due to Traube; S = data due to Seith.

In order to obtain more accurate data, the method described above was used to determine the surface tension of solutions of the type under consideration, *i.e.*, capillary-active solutes giving solutions behaving in a manner similar to pure liquids in the bubbler. The commoner substances, taken from laboratory stock, were used after being subjected to the usual purifying processes, whilst others (B.D.H., A.R. materials) were used as received. At least three different low concentrations were employed and the results (Table IV) are believed to have an error of less than ± 0·1 dyne/cm.

TABLE IV.

Substance.	Conc. (g.-mols. per 1000 g.).	γ.	Depn., dynes/cm.	D.	D, mean.	$10^8 \times D/P^4$.
1. Acetic acid	0·05521	72·23	2·17	39·31	29·83	7·51
M = 60	0·08695	71·86	2·54	29·20		
P = 141·2	0·08695	72·30	2·10	24·14		
	0·13760	70·73	3·67	26·68		
2. Formic acid	0·0772	73·76	0·64	8·29	7·80	7·16
M = 46	0·1362	73·31	1·09	8·00		
P = 102·2	0·2725	72·46	1·94	7·12		
3. Butyric acid	0·00745	73·11	1·29	173·2	180·1	7·80
M = 88	0·02501	69·60	4·80	191·9		
P = 219·2	0·04479	66·36	8·04	179·5		
	0·05002	65·61	8·79	175·7		
	0·10030	61·23	13·17	131·3*		
4. Methyl alcohol	0·1040	73·76	0·64	6·154	6·575	8·71
M = 32	0·1229	73·81	0·59	4·802		
P = 93·2	0·1275	73·64	0·86	6·745		
	0·1542	73·23	1·17	7·589		
	0·2550	72·47	1·93	7·587		
5. Ethyl alcohol	0·0435	73·45	0·95	21·84	23·60	7·73
M = 46	0·0639	72·76	1·64	25·67		
P = 132·2	0·0680	72·63	1·77	26·03		
	0·0870	72·45	1·95	22·41		
	0·1075	72·00	2·40	23·32		
	0·1741	70·34	4·06	23·32		
6. *iso*Propyl alcohol	0·0413	71·39	3·01	72·86	72·25	8·45
M = 60	0·0660	69·59	4·81	72·49		
P = 171·2	0·1010	67·23	7·17	70·99		
	0·1320	65·76	8·64	65·45*		
	0·1675	66·10	8·30	49·56*		
7. *n*-Butyl alcohol	0·0224	70·15	4·25	189·7	187·4	9·61
M = 74	0·0372	67·55	6·85	184·2		
P = 210·2	0·0559	63·88	10·52	188·2		
	0·1118	57·11	17·29	154·6*		
	0·1229	55·66	18·74	152·5*		
8. Ethyl formate	0·03600	71·26	3·14	87·22	84·43	8·04
M = 74	0·04479	70·69	3·71	82·84		
P = 180·2	0·05407	69·90	4·50	83·22		
9. Ethyl acetate	0·02447	70·26	4·14	169·2	175·3	7·60
M = 86	0·03897	67·15	7·25	186·0		
P = 219·2	0·04894	66·00	8·40	171·7		
	0·09788	62·47	11·93	121·9*		
10. Butyl formate	0·00765	71·57	2·83	369·9	369·7	8·32
M = 102	0·01531	68·73	5·67	370·3		
P = 258·2	0·01949	67·21	7·19	368·9		

TABLE IV (*continued*).

Substance.	Conc. (g.-mols. per 1000 g.).	γ.	Depn., dynes/cm.	D.	D, mean.	$10^8 \times D/P^4$.
11. Ethyl malonate	0·00207	71·90	2·50	120·8	123·3	6·95
$M = 160$	0·00241	71·36	3·04	126·2		
$P = 365·1$	0·00385	69·54	4·86	126·2		
	0·00414	69·43	4·97	120·1		
	0·00928	63·71	10·69	115·2*		
12. Methyl benzoate	0·00310	72·00	2·40	774·1	769·9	7·92
$M = 136$	0·00311	72·00	2·40	771·5		
$P = 314·1$	0·00622	69·63	4·77	766·8		
	0·00901	67·38	7·02	779·1		
13. Acetone	0·05711	71·65	2·75	48·16	49·70	7·56
$M = 58$	0·08168	70·26	4·14	50·68		
$P = 160·2$	0·10030	69·36	5·04	50·26		
14. Allylamine	0·01477	73·32	1·08	73·12	70·22	8·44
$M = 57$	0·02215	72·84	1·56	70·42		
$P = 169·8$	0·02280	72·87	1·53	67·12		
	0·02790	72·80	1·60	57·34*		
15. Allyl alcohol	0·02607	73·21	1·19	46·64	46·02	7·03
$M = 58$	0·02824	73·09	1·31	46·40		
$P = 160·2$	0·03020	73·01	1·39	46·02		
	0·05215	72·38	2·02	38·74*		
16. Allyl acetate	0·00692	72·39	2·01	290·5	287·9	7·69
$M = 100$	0·01178	71·01	3·39	287·7		
$P = 247·2$	0·01384	70·45	3·95	285·5		
					Mean	7·91

Values of D marked * are excluded from means.

Graphs have been made and indicate that there is always a region of direct proportionality in the surface tension–concentration curve. This has been generally accepted, but does not appear to have had such an exhaustive experimental confirmation hitherto.

In the case of a number of substances, previous work has not been confirmed, and it is significant that the present values have all resulted in lessening the differences between individual results for D/P^4. Table IV shows that for some score of capillary-active substances, including acids, alcohols, esters, ketones, and amines, the " molar capillary activity " $D = KP^4$, where K is approximately $7·9 \times 10^{-8}$. Thus it would appear that this function is directly connected with constitution.

General rules already applying to such solutions (see Freundlich, *op. cit.*, pp. 65—77) are not invalidated by the above relationship. Thus, isomeric substances which have been shown to possess the same parachor, *i.e.*, to have identical bond values, are found to possess almost the same specific capillary activity. Again, the effect produced by a mixture of two capillary-active solutes on the surface tension of water may be calculated from the specific capillary activity of each provided that the values for b in Szyszkowski's equation are approximately equal. In dilute solution this may be neglected, and the effect calculated from $\Delta = K(D_1x_1 + D_2x_2)$ where Δ is the total depression, x_1 and x_2 the concentration of each solute in g.-mols. per 1000 g., and D_1 and D_2 the molar depressions.

Freundlich (*op. cit.*, p. 66), using Traube's experimental data for calculating *b* and *c*, has shown that the introduction of a double bond considerably diminishes the specific capillary activity. Such a large change in the molar capillary activity is hardly to be expected, since the double bond should cause a reduction of only 11 units in the parachor. This is well shown in Table V, where *D* has been calculated from the appropriate part of Freundlich's data, and it is obvious that the ratio D_1/D_2 is much nearer $P_1{}^4/P_2{}^4$ than is σ_1/σ_2.

TABLE V.

Substance.	*b*.	*c*.	σ.	σ_1/σ_2.	Conc.	Depn.	*D*.	$\frac{D_1}{D_2}$.	*P*.	$\frac{P_1{}^4}{P_2{}^4}$.
n-Propyl alcohol	0·1973	0·1515	6·60	4·07	0·0312	2·80	89·74	2·08	171·2	1·31
Allyl alcohol	0·3514	0·6180	1·62		0·0625	2·70	43·20		160·2	
Propyl acetate	0·1792	0·0157	63·7	2·65	0·0039	2·90	743·0	1·66	253·2	1·110
Allyl acetate	0·2197	0·0417	24·0		0·0039	1·75	448·6		247·2	
Propylamine	0·1459	0·0941	10·6	7·65	0·0312	3·22	103·2	2·48	180·8	1·28
Allylamine	0·4007	0·7420	1·35		0·1230	5·20	41·6		169·8	

Thus it would appear that the specific capillary activity, which comprises activities over a considerable concentration range, has less structural significance than the molar capillary activity, which is deduced from phenomena in dilute solutions.

The Effect on Apparent Capillary Activity of the Adsorption of the Solute at the Gas–Liquid Interface.

The parachor–activity relationship developed above is not incompatible with most of the features of capillary solutions, but is at variance with Traube's (*Annalen*, 1891, **265**, 27) view of a constant ratio between the concentrations necessary for the production of equal changes in surface tension in successive homologues. Thus, in the fatty acids each requires about one-third the concentration of its immediate predecessor for a similar depression, whereas the parachor rule would require the ratio between successive acids to be $[(P + 39)/P]^4$, which decreases with ascension of the series. The ratio between successive capillary activities, however, shows a fall closely adhering to that required by the parachor (Table VI;

data from Freundlich, *op. cit.*, p. 65), but from the third member of the series this similarity disappears. A comparison of the first and the last acid in the table shows the great difference between the ratios σ(nonoic)/σ(formic) = 9786 and P^4(nonoic)/P^4(formic) = 297.

TABLE VI.

Acid.	σ.	σ_{n+1}/σ_n.	P.	$(P_{n+1}/P_n)^4$.
Formic	0·73	—	102·2	—
Acetic	2·84	3·9	141·2	3·7
Propionic	8·93	3·1	180·2	2·7
n-Butyric	19·60	2·2	219·2	2·2
n-Valeric	68·50	3·5	258·2	1·9
n-Hexoic	233·00	3·4	297·2	1·8
n-Heptoic	555·00	2·4	336·2	1·7
n-Octoic	2222·00	4·0	373·2	1·6
n-Nonoic	7144·00	3·1	314·2	1·5

A saturated solution of nonoic acid, approximately 0·8 millimol. per litre, gives a depression about 33 times greater than would be anticipated from the parachor rule, which is undoubtedly due to the surface concentration considerably exceeding that in the bulk. Rayleigh showed that the surface tensions of soap and saponin solutions measured by the vibrating jet method were hardly distinguishable from that of water, but with a " static " method about one-third of that value. It may, therefore, be assumed that the former refer to surfaces containing only the bulk concentration of the solute. It is generally considered that the rate of adsorption is extremely rapid, although several investigators have obtained results which point to rates which are measurable. For instance, in the case of the drop-weight method, Forch (*Ann. Phys. Chem.*, 1899, **68**, 810), Rayleigh (*Proc. Roy. Soc.*, 1899, **48**, 321), Donnan and Barker (*ibid.*, 1911, **85**, 557), and Berczeller (*Imp. Z. phys. Chem. Biol.*, 1914, 379) have all shown that the apparent surface tension of a solution decreases as the time allowed for the formation of drops increases, but no attempt to compare rates of adsorption appears to have been made on these lines, although the data of Berczeller for 0·1% sodium oleate solution fall on a smooth curve and indicate that adsorption is far from complete even after four seconds:

Time (secs.) for formation of 1 drop	0	0·71	2·08	3·65
Reciprocal value of drop number ...	0·0228	0·0163	0·0139	0·0122

Considered as a curve giving the rate of surface adsorption, it may be used for estimating the tension of a surface of approximately the same concentration as the bulk of the liquid, *viz.*, at infinitely fast rates of formation.

Hiss (Diss., Heidelberg, 1913), from the time necessary for a spray of solution to assume a static meniscus, obtained data for an aqueous

0·284*M*-amyl alcohol solution at 14° which are represented graphically in Fig. 2 :

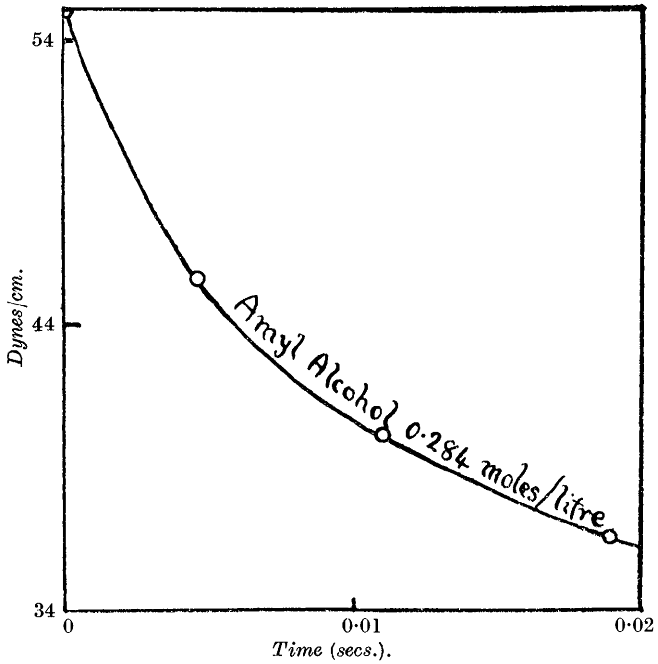
Time (secs.) for development of surface	0·0000	0·0047	0·0110	0·0189	∞
γ, dynes/cm.	54·9	45·7	40·2	36·6	34·8

Thus the depression in the surface tension due to a surface concentration of 0·284 mol. per l. of amyl alcohol is 18·7 dynes/cm., whilst with maximum surface adsorption it reaches 38·8 dynes per cm. It is not anticipated that the parachor rule would apply at a concentration of 0·284 mol. per l., but it is interesting to observe the change in D/P^4 when these findings are used to modify Seith's data for amyl alcohol (*Z. physikal. Chem.*, 1925, **117**, 257). Seith observed a depression of 1·42 dynes/cm. with a 0·00227*M*-solution of amyl alcohol at 10°, which gives $D/P^4 = 16{\cdot}2 \times 10^{-8}$. If it be assumed that the ratio of surface- to bulk-concentration is constant, then a bulk concentration of 0·00227 mol. is roughly equivalent to a totally adsorbed surface concentration of

$$0{\cdot}00227 \times (73{\cdot}6—34{\cdot}8)/(73{\cdot}6—54{\cdot}9),$$

i.e., 0·00471 mol. This being taken as the concentration to which

FIG. 2.



the depression of 1·42 dynes per cm. is attributable, a value of $7{\cdot}82 \times 10^{-8}$ for D/P^4 is obtained, which is near the value $7{\cdot}91 \times 10^{-8}$ previously obtained (p. 1637).

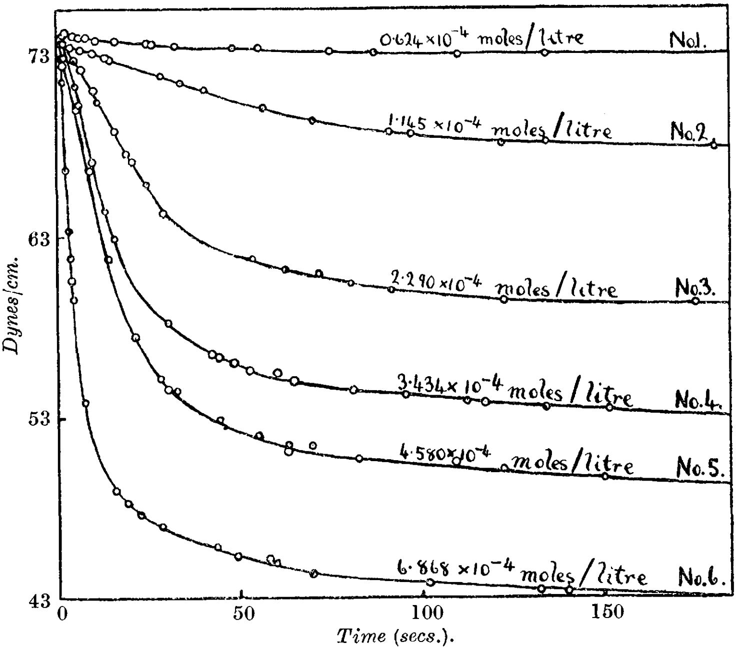
Similarly, Freundlich found a $0{\cdot}005M$-solution of heptoic acid gave surface tensions of 66 dynes per cm., as measured by the method of vibrating jets, and of 52·5 dynes per cm. when measured by capillary rise. These results give values for D/P^4 of approximately $11{\cdot}5 \times 10^{-8}$ and $34{\cdot}0 \times 10^{-8}$ respectively. Bohr (*Proc. Roy. Soc.*, 1909, **82**, 146) has shown, however, that in the dynamic methods the surfaces involved must be considered as persisting for a finite time; hence, $11{\cdot}5 \times 10^{-8}$ may hardly be taken as representing the depression of an absolutely fresh surface.

Apparently, therefore, if the parachor–molecular capillary activity relationship is to be critically examined for substances which are subject to considerable adsorption, it would be helpful if some method of obtaining the rate of adsorption were available; for hence the tension of surfaces at the instant of formation might be obtained by extrapolation. A phenomenon similar to that displayed by the drop-weight method evidently should occur in the bubble-pressure method, and was actually observable in appropriate solutions. Mention has been made (p. 1632) of the progress of a stream of bubbles and particularly of how such streams cease sharply with pure liquids and certain solutions, whilst with other solutions the intervals between consecutive bubbles gradually increase so that before the stream finally ceases they may be as great as three minutes. This effect is attributable only to adsorption at the air–liquid interface, and incidentally supplies data from which a rate of adsorption curve can be constructed. The phenomenon seems to occur in lower members of homologous series than has been apparent from other methods, having been observed with both butyric acid and butyl alcohol. Where the considerable decrease in bubble rate has not been observed, it is assumed that adsorption effects are negligible. Reduction of adsorption rate to one susceptible of observation is due, in all probability, to the low concentrations which may be used with the bubble method.

Hiss (*loc. cit.*) has shown for amyl-alcoholic solutions that the depression of the surface tension of water at maximum adsorption is about double the values found at minimum adsorption, or the increase of the concentration at the surface due to adsorption is equal to the concentration of the bulk.

By using Gibbs's equation $A = (C/RT) \, . \, d\gamma/dC$, it may be shown that in solutions of butyl or amyl alcohol having equal values of C, the surface excesses are in the approximate ratio 2/7, since this is the ratio of the values of the respective $d\gamma/dC$ deduced from Szyszkowski's σ values (Freundlich, *op. cit.*, p. 65, Table 22). Therefore, in the case of butyl alcohol the excess concentration in the surface must be approximately 2/7 of the bulk concentration, and hence only 7/9 of the depression observed by static methods is attributable to the bulk concentration. If this assumption be granted, allowance ought to be made in calculating the constant K. Although the change in bubble rate was observable with butyl-alcoholic solutions, it occurred over a very short space of time and hence the value of K in Table IV is high, but if it is corrected by the above factor, 7/9, it falls from $9{\cdot}61 \times 10^{-8}$ to $7{\cdot}49 \times 10^{-8}$ and is then much nearer the general mean $7{\cdot}91 \times 10^{-8}$.

FIG. 3.



The adsorption effect increases rapidly as a homologous series is ascended, and it may be anticipated that, for such solutions, the rate of adsorption will depend (i) upon the ratio of surface to bulk concentration at maximum adsorption, and (ii) upon the bulk concentration itself.

Nonoic acid was chosen for the investigation of the second of these points. The time between the detachment of two consecutive bubbles was measured with a stop-watch, the tap on the manometer being closed so that the pressure giving rise to the bubbles could be read at leisure. At the beginning of bubbling, when the rate was too fast for the time taken in the formation of one bubble to be estimated, the mean period for a series was measured, the tap leading to the manometer being closed after the passage of half the bubbles in order to ascertain the mean pressure. The pressures involved in the use of the wide jets were determined in the manner described above, and since these are small they are not sensibly affected by adsorption. Table VII gives specimen data for one concentration of nonoic acid solution, and the results for other concentrations in the same apparatus are presented graphically in Fig. 3. The jets employed gave a manometer difference of 477·48 mm. when used with water, and the surface tensions are calculated on this basis.

TABLE VII.

Aqueous solutions of nonoic acid.

Change in surface tension at various low concentrations against time.
(For water at 10° : Press. = 477·48 mm.; γ = 74·40 dynes/cm.)

No. 6. Concentration = 6·868 × 10^{-4} mol. per litre.

γ.	Time (secs.).	γ.	Time (secs.).	γ.	Time (secs.).	γ.	Time (secs.).
72·89	0·5	63·30	2·32	47·59	22·3	44·93	60·0
72·82	0·55	61·83	3·10	47·00	28·2	44·34	70·0
72·74	0·60	60·58	3·60	45·83	43·8	43·80	101·6
72·33	0·66	59·48	3·95	45·35	49·4	43·40	133·0
71·68	0·80	48·99	16·3	45·19	58·0	43·33	140·0
66·75	1·55	48·26	19·0				

The curves (Fig. 3) show a distinct decline in the rate of adsorption with dilution; *e.g.*, solution No. 6 almost reaches surface saturation after 30 secs., whilst in the same time the surfaces in solutions No. 2 and No. 3 are only about half saturated. It is difficult to estimate surface tensions at zero time with any precision from the graphs, because the method obviously requires a slight excess pressure to start the bubble stream, and in any case the difference from water is so small as to be almost unobservable even with fairly concentrated solutions. However, curves of the form shown in Fig. 4 are obtained by plotting $\log \gamma$ against $\log t$, and it is evident that for a brief interval after adsorption commences the curves approach the time axis asymptotically. Apparently, during this short period the effect of adsorption is very small, and the value of γ is substantially that of a fresh surface and as such has been used to determine D and K (Table VIII). The mean value of K is in fair agreement with that already found.

A comparison of the γ–C curve obtained from a plot of the surface tensions at maximum adsorption for the six concentrations (Fig. 3) with that given by Donnan and Barker (*Proc. Roy. Soc.*, 1911, **85**,

557) reveals points of interest. For this purpose the data of these workers, which relate to 16·3°, have been recalculated for 10° by

FIG. 4.

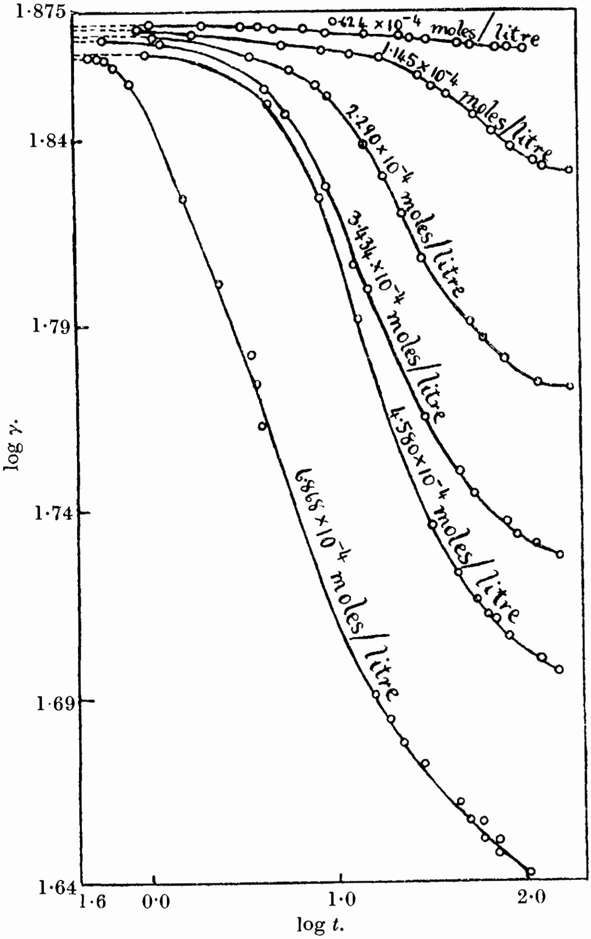


TABLE VIII.

Curve.	Mols. $\times 10^4$.	Log γ_0.	γ_0.	Depn., dynes/cm.	D.	$K \times 10^8$.
0	0	0·8716	74·40			
1	0·624	1·8708	74·27	0·13	2083	7·09
2	1·145	1·8703	74·18	0·22	1922	6·54
3	2·290	1·8678	73·76	0·64	2795	9·52
4	3·434	1·8670	73·62	0·78	2271	7·73
5	4·580	1·8631	72·97	1·43	3122	10·63
6	6·868	1·8626	72·88	1·52	2213	7·53
						Mean 8·17

assuming an alteration proportional to the change in the surface tension of water. The data for the two curves are given in Table IX and are plotted in Fig. 5, curve 1 being from Donnan and Barker's data (as recalculated) and curve 2 from ours.

FIG. 5.

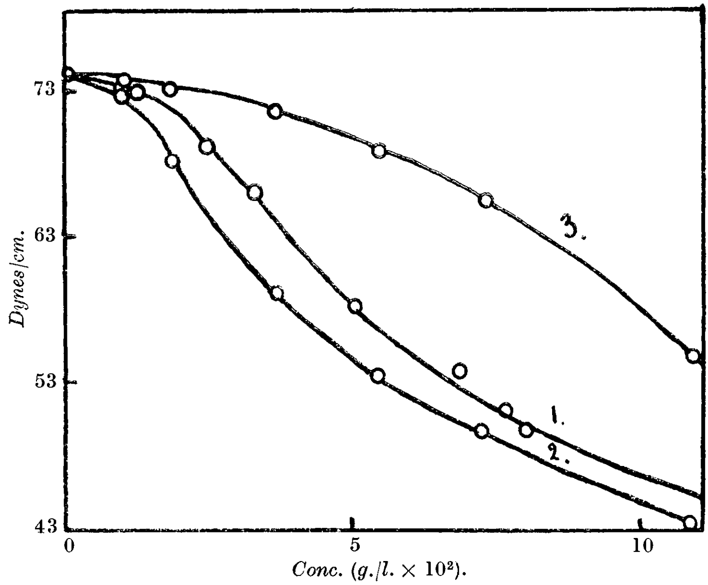


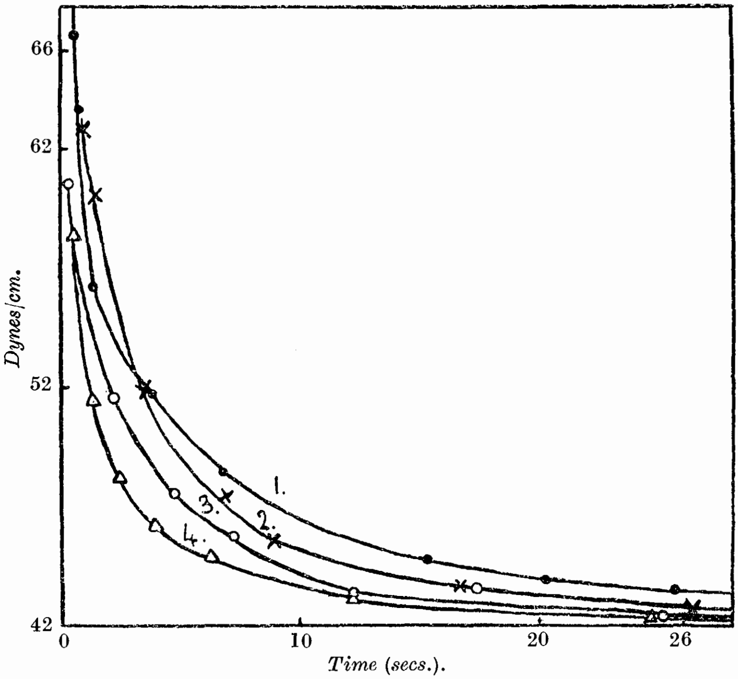
TABLE IX.

Donnan and Barker.		Present investigation.	
Conc., g./litre × 10^2.	γ.	Conc., g./litre × 10^2.	γ.
0	74·40	0	74·40
0·98	73·30	0·99	72·92
1·26	73·14	1·81	67·93
2·43	69·35	3·62	59·29
3·29	66·35	5·43	53·45
5·00	58·50	7·24	49·55
6·81	53·89	10·85	43·32
7·59	51·26		
8·06	50·10		

The difference between the two sets of values is no doubt due to Donnan and Barker's measurements having been made under conditions of incomplete adsorption. These authors set the time between drops at about 7 seconds, in the drop-weight method used, but it is obvious from curve 3 (a graph of our values at 7 secs.) that adsorption after this period is incomplete when the bubble method is used, and the difference is undoubtedly due to the extent to which adsorption has taken place at the surfaces under consideration. The speed at which adsorption proceeds is different in the two methods, but it is of interest that the present data give a curve identical with that of Donnan and Barker (Fig. 5, curve 1) if a particular degree of adsorption be arbitrarily chosen.

In order to observe the effect of jet size on the apparent rate of adsorption, four different sizes were used with a single solution of nonoic acid. The data so obtained are given in Table X and set out graphically in Fig. 6, from which it is evident that the apparent rate of adsorption increases with jet size, although the reason for this has not been discovered.

FIG. 6.



An interesting and possibly relevant observation is that, although with all liquids when wide jets are used, and with pure liquids and fine jets, the bubble develops and detaches itself without being projected into the liquid, yet with adsorbed solutes the bubble does not develop gradually but appears suddenly after a period and is ejected with such force that it actually travels downwards into the solution.

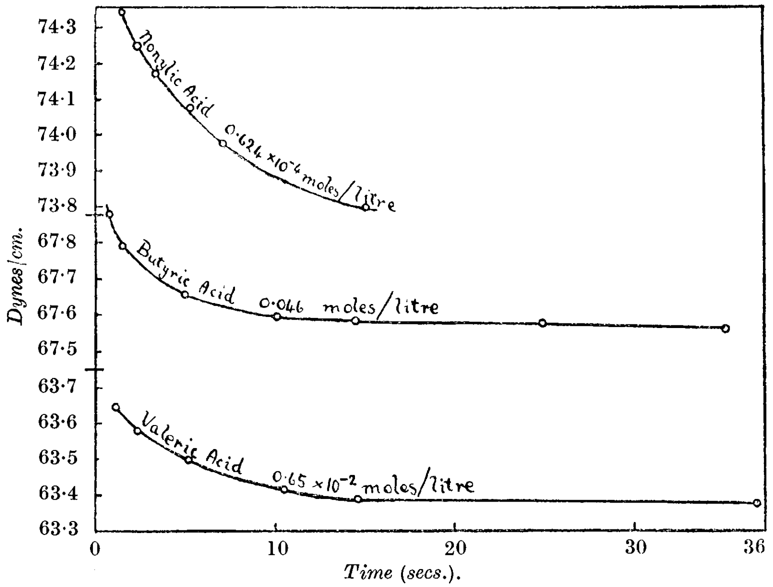
Inference (i) (p. 1642), *viz.*, that the rate of adsorption at a gas–liquid interface will increase as the ratio of concentration at maximum

TABLE X.

Adsorption and jet size (0·125 g. litre nonoic acid solution).

Jet 1. r = 0·0021 cm.		Jet 2. r = 0·0038 cm.		Jet 3. r = 0·0065 cm.		Jet 4. r = 0·0154 cm.	
γ.	t.	γ.	t.	γ.	t.	γ.	t.
66·50	0·6	63·60	0·9	60·50	0·6	58·38	0·7
62·70	1·0	60·00	1·6	51·42	2·2	56·32	0·8
56·00	1·4	51·72	3·7	47·67	4·8	51·30	1·4
51·82	3·9	47·12	7·0	45·70	7·2	48·14	2·4
48·13	6·8	45·73	8·9	43·40	17·4	46·00	4·0
45·41	11·8	43·40	16·7	42·20	25·0	44·78	6·2
44·56	15·4	42·36	26·2			43·20	12·2
43·68	20·3					42·30	24·8
43·15	25·6						

FIG. 7.



adsorption to the bulk concentration increases, was confirmed by constructing from data obtained with one piece of apparatus γ–C curves for solutions of n-butyric, n-valeric, and n-nonoic acids. The concentrations were chosen so that the changes of surface tension from no adsorption to total adsorption were approximately the same in the three cases, for this facilitates comparison of the curves obtained. The data are incorporated in Table XI and plotted in Fig. 7, where it will be seen that, although the concentrations used decrease rapidly from butyric acid to nonoic acid, the adsorption rate increases to a much greater extent, an effect which would be emphasised if equimolecular concentrations were employed.

TABLE XI.

Rates of adsorption with different solutes.

Butyric acid, 0·046 mol./litre.		Valeric acid, $0{\cdot}65 \times 10^{-2}$ mol./litre.		Nonoic acid, $0{\cdot}624 \times 10^{-4}$ mol./litre.	
γ.	t.	γ.	t.	γ.	t.
67·88	0·8	63·65	1·0	74·34	1·4
67·80	1·4	63·58	2·2	74·25	2·2
67·66	5·0	63·50	4·6	74·17	3·2
67·60	10·0	63·42	10·6	74·08	5·2
67·59	14·4	63·39	14·6	73·98	7·0
67·58	24·8	63·38	36·4	73·80	15·0
67·57	35·0				

The Experimental Verification of Gibbs's Adsorption Law.

The work of Donnan and Barker (*loc. cit.*) was undertaken specifically to afford an experimental verification of Gibbs's law (" Collected Papers," Vol. 1, p. 233). In Table XII, along with the original data, are given values for the surface excess derived from our γ–C curve, and it will be seen that these more nearly approach the observed surface excess than do the original calculated values.

TABLE XII.

			Gibbs's equation.			
		D. and B.	D. and B.		M. and R.	
	Conc., mols./c.c. $\times 10^7$.	A (obs.), mols./cm.^{2} $\times 10^{10}$.	$d\gamma/dC$ $\times 10^7$.	A (calc.), mols./cm.^{2} $\times 10^{10}$.	$d\gamma/dC$ $\times 10^7$.	A (calc.), mols./cm.^{2} $\times 10^{10}$.
A.	1·54	6·0	5·52	3·5	7·96	5·16
B.	3·16	9·6	5·54	7·2	4·84	6·43
C.	4·80	6·9	4·05	8·0	2·98	6·01
D.	5·09	5·8	—	—	2·62	5·61

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UNIVERSITY OF DURHAM, ARMSTRONG COLLEGE,
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