51. *Capillary Activity in Aqueous Solution.*

By HERBERT MILLS.

AT the surface separating a solution from the vapour phase the concentration of the solute may be enriched at the expense of the bulk of the solution, and the excess solute so adsorbed is generally assumed to be determinable from Gibbs's equation $A = -c/RT.d\gamma/dc$. If all the excess is present as a unimolecular layer at the surface, the area per molecule of adsorbed solute can be calculated. The areas so determined are found to approach at saturation the values obtained by Adam (*Proc. Roy. Soc.*, 1921, *et seq.*) for the corresponding insoluble homologues, and upon this agreement the *a priori* assumption that the excess solute is present as an oriented unimolecular pure layer is presumed correct. This view presents a picture of adsorbed solute molecules separating at the surface of the solution at all concentrations from zero to bulk saturation. If such continuous separation occurs, then the graph for surface tension (γ) plotted against concentration (c) should be a smooth curve becoming parallel to the axis of concentration as shown in Fig. 1. This is the form of curve most frequently reported.

Materials soluble in water fall into two categories : those miscible in all proportions, *e.g.*, ethyl alcohol, and those which are only partially soluble and form conjugate solutions when excess is present, *e.g.*, amyl alcohol. In the former case it appears unnatural that even adsorption should cause separation of the pure solute from solutions, whilst in the latter case those forces which normally hold a limited amount of solute in solution should at least prevent separation of pure solute from the more dilute solutions. It is the purpose of the present work to offer the following picture of the process of adsorption in solutions containing solutes of limited solubility.

A solution containing an adsorbed active solute has at the surface an aqueous layer which contains the adsorbed excess and is therefore more concentrated than the bulk. The concentration of this aqueous layer changes in the same sense as the bulk of the solution, and so will reach saturation earlier. After the surface layer has reached maximum saturation, subsequent addition of the solute to the bulk of the solution will cause an additional excess of adsorbed solute which cannot be accommodated in the aqueous surface layer and will therefore separate in some other condition. The composition of this new layer may be that of pure solute, but is more probably a phase in which solute predominates, *i.e.*, of a composition corresponding to the conjugate layer appearing when considerable excess of solute is present. In passing from pure solvent to a saturated solution, a point is reached at which further adsorption causes the appearance of a fresh phase, a point which should be indicated by an inflexion in the γ–c graph as shown in Fig. 2.

FIG. 1.

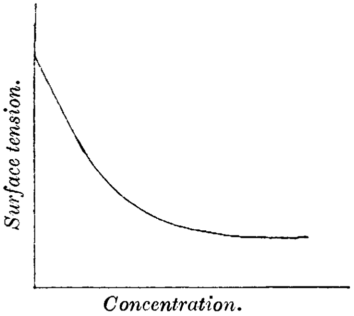
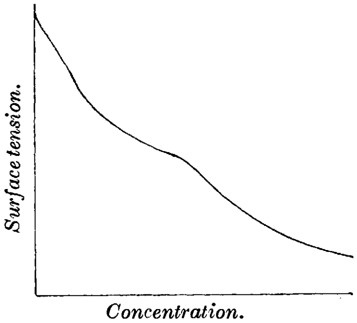


FIG. 2.



This gives a normal explanation of the effects of adsorption on the surface of a solution : it accounts also for the appearance of a complete layer of the conjugate solution at saturation in the body of the aqueous phase, since such conjugate layer has had its commencement some time before saturation is reached in the body and has increased from an attenuated film to a layer of normal density.

Marked inflexions in γ–c curves are not common, although if the above view of the surface conditions is correct they should appear in all cases where the solute is of limited solubility, since the commencement of a new phase considerably richer in active solute must produce a more rapid decrease of surface tension with concentration. Such inflexions have been reported, particularly with active solutes of slight solubility, *e.g.*, nonoic acid (Donnan and Barker, *Proc. Roy. Soc.*, 1911, **85**, 557) and *p*-toluidine (McBain and Dubois, *J. Amer. Chem. Soc.*, 1929, **51**, 3534). It will be seen from the present work that they are also observable in solutions of amyl alcohol, valeric acid, and *n*-hexoic acid. Furthermore, although no great significance has hitherto been attached to the observation, log γ–log c curves are generally known to be convex to the axes.

With amyl alcohol, valeric acid, and *n*-hexoic acid, the inflexions here obtained are not considerable, and this may account for their having remained unrecognised. Slight irregularities have been generally disregarded because the accurate determination of the surface tension of capillary-active solutions was difficult in the absence of any method whereby to ascertain when adsorption was complete and final equilibrium surface tension reached. Mills and Robinson (J., 1931, 1629), extending Sugden's modification of Jaeger's method to very fine jets, have shown that accurate comparative values may be obtained without the need of supplementary data and, moreover, that the progress of adsorption with time may be followed in the case of adsorbed solutes, so that the lowest stable surface tension is readily obtained at each concentration. This method has been used in the present research, and interesting adsorption data have been recorded for aqueous nonoic acid solutions.

In an attempt to determine the influence of chemical constitution upon capillary activity, Mills and Robinson (*loc. cit.*) obtained the following expression for aqueous solutions in which the depression (D) of the surface tension from that of water (in dynes/cm.) is directly proportional to the concentration of the solute, *viz.*, $D = 7{\cdot}9 \times 10^{-8} \times P^4 \times s$; P is the parachor of the solute and s is the surface concentration in g.-mols. per 1000 g. of water. The surface concentration s has a corresponding bulk concentration c, and the ratio s/c will be termed the coefficient of adsorption of the solute under the conditions of the experiment. If an inflexion is apparent in the graph, it must occur at a bulk concentration (c), having associated with it a surface layer of maximum concentration S and hence the ratio S/c must be related to the coefficient of adsorption. This ratio at the point of inflexion is only a particular example of comparing a bulk concentration with its associated surface concentration : it has been found to approximate closely to the coefficient of adsorption.

EXPERIMENTAL.

The data here presented were obtained with an apparatus similar to that described by Mills and Robinson (*loc. cit.*). The wider tube had a radius of approximately 1 mm., and the pressure difference for the two jets immersed in water at 16° equalled 59·7 cm. of water. Table I gives the change in surface tension with time for nonoic acid solutions of various concentrations, and these data are plotted in

FIG. 3.

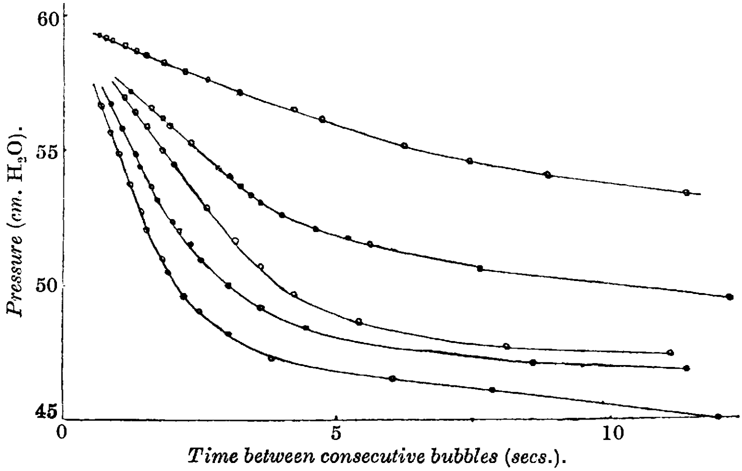


FIG. 4.

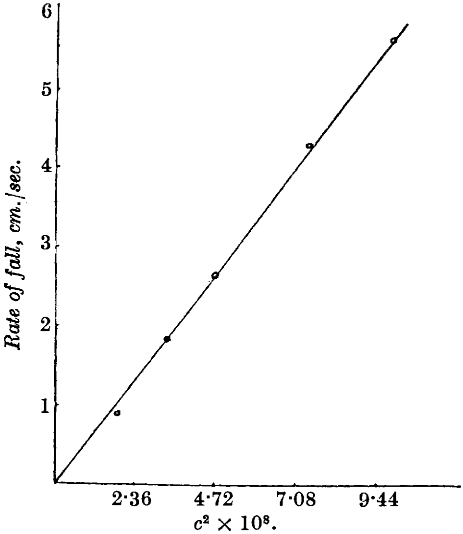


Fig. 3. There is an initial straight portion to each graph, and the constant rates of change during these periods have been determined from Table I and are plotted against the squares of the respective concentrations in Fig. 4. In Table I, for a given concentration c,

TABLE I.

$c \times 10^4$.	T.	P.	$P_1 - P_2$.	$T_1 - T_2$.	$\frac{P_1 - P_2}{T_1 - T_2}$.	Mean rate of fall, cm./sec.
1·38	0·65	59·3				
	0·75	59·2	0·1	0·1	1·0	
	0·9	59·1	0·1	0·15	0·67	
	1·1	58·9	0·2	0·2	1·0	
	1·3	58·7	0·2	0·2	1·0	
	1·5	58·5	0·2	0·2	1·0	
	1·8	58·3	0·2	0·3	0·67	
	2·2	58·0	0·3	0·4	0·75	
	2·6	57·6	0·4	0·4	1·0	0·89
1·84	1·2	57·2				
	1·6	56·6	0·6	0·4	1·5	
	1·8	56·2	0·4	0·2	2·0	
	1·9	55·9	0·3	0·1	3·0	
	2·3	55·3	0·6	0·4	1·5	
	2·8	54·4	0·9	0·5	1·8	
	3·0	54·1	0·3	0·2	1·5	
	3·2	53·7	0·4	0·2	2·0	
	3·4	53·4	0·3	0·2	1·5	1·85
2·20	1·1	57·0				
	1·3	56·4	0·6	0·2	3·0	
	1·5	55·9	0·5	0·2	2·5	
	1·8	55·0	0·9	0·3	3·0	
	2·0	54·5	0·5	0·2	2·5	
	2·6	52·9	1·6	0·6	2·67	
	3·1	51·7	1·2	0·5	2·4	2·68
2·75	0·85	56·7				
	1·05	55·8	0·9	0·2	4·5	
	1·3	54·9	0·9	0·25	3·6	
	1·4	54·4	0·5	0·1	5·0	
	1·6	53·7	0·7	0·2	3·5	
	1·7	53·2	0·5	0·1	5·0	4·32
3·15	0·65	56·7				
	0·8	55·7	1·0	0·15	6·7	
	1·0	54·9	0·8	0·2	4·0	
	1·2	53·8	1·1	0·2	5·5	
	1·4	52·8	1·0	0·2	5·0	
	1·5	52·1	0·7	0·1	7·0	5·64
	1·8	57·0	1·1	0·3	3·7	
	1·9	50·6	0·4	0·1	4·0	
	2·2	44·7	0·9	0·2	3·0	
	2·5	49·1	0·6	0·3	2·0	
	3·0	48·3	0·8	0·5	1·6	
	3·8	47·3	1·0	0·8	1·2	
	6·0	46·6	0·7	2·2	0·3	
	7·8	46·2	0·4	1·8	0·2	
	12·0	45·2	1·0	4·2	0·2	
	∞	43·5	1·7	∞		

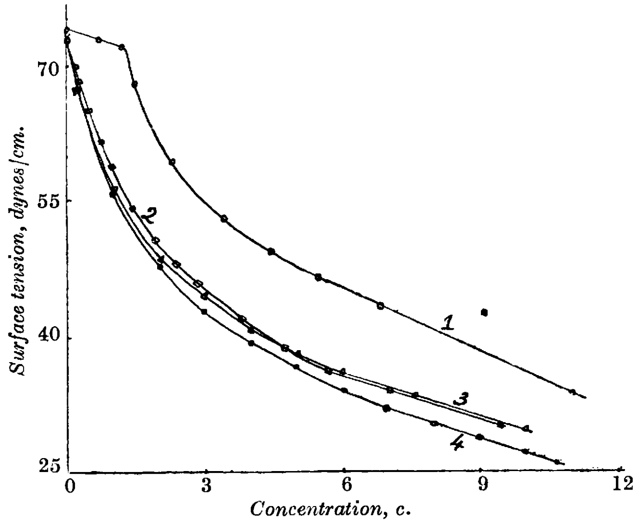
Summary.

$c \times 10^4$	1·38	1·84	2·20	2·75	3·15
$c^2 \times 10^8$	1·94	3·39	4·84	7·56	9·92
Mean rate of fall ...	0·89	1·85	2·68	4·32	5·64

the time in seconds between consecutive bubbles is denoted by T, and the surface tension of a surface of age T is given in its actually determined form, *i.e.*, as equivalent to so many cm. pressure of water, P. As an example, the data for the highest concentration are given in full, but for others they terminate at the point at which the graphs show deviation from the straight line.

For aqueous solutions of amyl alcohol, valeric acid, *n*-hexoic acid, and nonoic acid the γ–c data, from zero to the formation of the conjugate solution, are given in Table II. The maximum solubility of each substance in the aqueous layer was determined by diluting this saturated layer to half saturation, determining the surface tension, and referring this figure to the previously constructed γ–c graph. Fig. 5 gives the γ–c graphs for the various solutions, and Fig. 6 the corresponding log γ–log c graphs. In the table, s is determined from the formula on p. 421, and the other symbols have the significance already ascribed to them.

FIG. 5.



Concentration units.

Curve 1.	*Nonoic acid*	10 = 0·001	*mol. per* 1000 *g. water.*
,, 2.	n-*Hexoic acid*	10 = 0·09	,, ,, ,, ,,
,, 3.	*Valeric acid*	10 = 0·36	,, ,, ,, ,,
,, 4.	*Amyl alcohol*	10 = 0·39	,, ,, ,, ,,

Discussion of Results.

The adsorption data for nonoic acid presented by Mills and Robinson (*loc. cit.*) indicated an approximate proportionality between the square of the concentration and the initial constant rate of adsorption. By selecting more dilute solutions over a shorter range of concentration, this relationship has been shown to hold more closely. It is interposed here to illustrate how the bubble method indicates when stable equilibrium is reached, a point given by the lowest value of surface tension reached on continuous bubbling.

When a series of bubbles is formed at a fine jet under continuously diminishing pressure, each bubble removes the adsorbed layer and leaves exposed a fresh surface having a bulk concentration which, because of the diminution in pressure owing to the air removed, has a longer life before it in turn is removed as the next bubble. A very convenient instrument is thus available for the examination of the change in surface tension upon the ageing of surfaces subject to adsorption. The rate of adsorption is frequently extremely rapid and the phenomenon described would require for examination in those cases a more highly developed technique than that suggested by a stop-watch and water manometer. However, in the case of

FIG. 6.

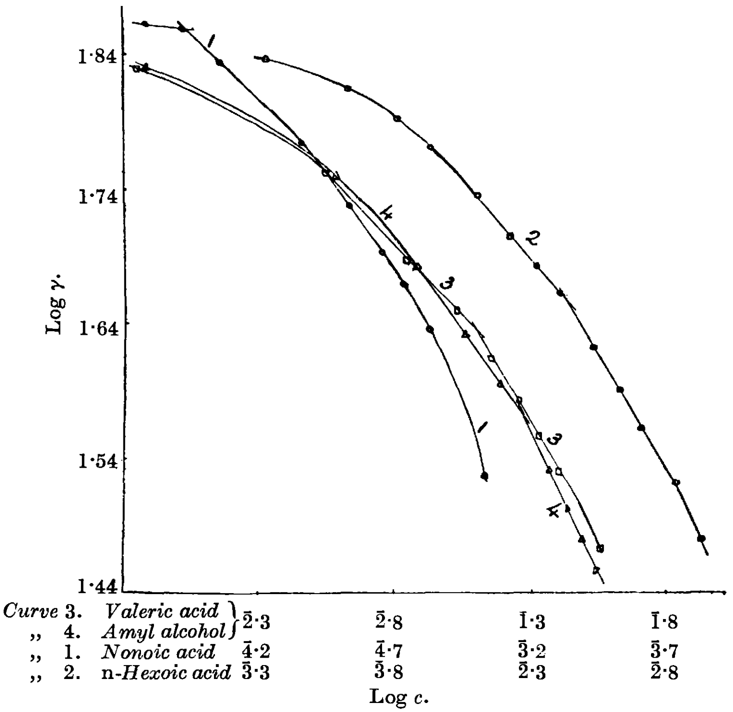


TABLE II.

Solute and temp.	γ.	s.	c.	s/c.	c at infltn.	S.	S/c.
Amyl alcohol at 16·5°	73·4		0·000				
	67·8	0·0181	0·0078	*2·32*			
	56·0		0·039				
	48·0		0·078				
	42·9		0·117				
	39·4		0·156				
	36·6		0·195		0·176	0·417	*2·31*
	34·0		0·234				
	31·9		0·273				
	30·3		0·312				
	28·7		0·351				
	27·1		0·390				
	26·0		0·417 (saturation)				
	24·3 (conjugate alcoholic layer)						
Valeric acid at 16°	73·5		0·000				
	67·6	0·0169	0·0072	*2·35*			
	56·4		0·036				
	48·8		0·072				
	44·6		0·108		0·132	0·361	*2·74*
	41·2		0·144				
	38·3		0·180				
	36·1		0·216				
	34·0		0·252				
	29·7		0·361 (saturation)				
	29·3 (conjugate acid layer)						
	γ.	$s \times 10^4$.	$c \times 10^4$.	s/c.	$c \times 10^4$ at infltn.	$S \times 10^4$.	S/c.
Nonoic acid at 10°	74·4		0				
	72·9		0·624				
	72·3	9·08	0·833	*10·9*			
	67·9		1·145		0·94	11	*11·7*
	59·3		2·290				
	53·4		3·435				
	49·5		4·580				
	46·7		5·500				
	43·3		6·870				
	33·7		11·000				
	29·5 (conjugate acid layer)						

The following data are due to Szyszkowski (*Z. physikal. Chem.*, 1908, **64**, 385):

n-Hexoic acid at 19°	73·1		0·000				
	68·4	0·0071	0·00212	*3·04*			
	65·1		0·00425				
	61·8		0·00641				
	58·9		0·00850				
	54·4		0·0128				
	50·7		0·0170				
	48·1		0·0212				
	45·9		0·0256		0·0282	0·09 (app.)	*3·2*
	42·0		0·0340				
	39·0		0·0425				
	36·5		0·0510				
	33·4		0·0680				
	30·2		0·0850				

(The saturation value for *n*-hexoic acid is not given here, but by analogy with valeric and nonoic acids it should be of the order of 0·09 g.-mol. per 1000 g. of water.)

nonoic acid a small solubility is associated with a large coefficient of adsorption, and when sufficiently dilute solutions are selected the rate becomes measurable.

The results obtained indicate that here the rate of adsorption is constant over a considerable range, frequently to a point beyond half saturation of the surface, and is then directly proportional to the square of the concentration.

In Fig. 5 the inflexion in the γ–c graph is very marked only in the case of nonoic acid, but in the other cases a change may be detected. The curves show no tendency to become asymptotic although the final surface tension in each case is but little removed from that of the associated conjugate layer. With the $\log \gamma$–$\log c$ graphs of Fig. 6, the positions at which the changes occur are more clearly marked, for the points on either side of the change appear to lie on two intersecting straight lines. Table II shows that the ratio of the concentration at the change point to the saturation concentration is approximately equal to the coefficient of adsorption. The agreement is sufficiently close to justify the conception that by adsorption the aqueous surface layer attains saturation before the bulk, and that the subsequent separation and growth of the associated conjugate layer occurs after this point. Furthermore, the agreement implies that the coefficient of adsorption is constant at least up to the change point. Hiss (Diss., Heidelberg, 1913) obtained a depression of 18·7 dynes/cm. for a $0{\cdot}284M$-solution of amyl alcohol at the moment of formation of the surface, and 38·8 dynes/cm. after complete adsorption. Proportionality being assumed between depression and surface concentration, these figures give a ratio $s/c = 2{\cdot}07$, which agrees with the value 2·31 determined for the adsorption coefficient, although the concentrations differ widely in the two cases. Adam (*loc. cit.*) found that, when insoluble materials were spread on water, the depression of surface tension rapidly became linear with the mass of material spread per unit surface. In Fig. 5, after the point of inflexion, the γ–c graphs rapidly become linear, showing that in these cases also a new phase is spreading upon the surface of the solution.

It is difficult completely to reconcile Gibbs's equation $A = -c/RT.d\gamma/dc$ with the foregoing. This equation does not differentiate between a surface layer of composition which changes as the solute accumulates in the surface solvent, and a surface layer of constant composition (that of the conjugate layer) but of changing density due to accumulation. The equation assumes the separation of a phase of constant composition, erroneously considered to be pure solute, and so should apply only to those conditions holding after the change point. In this region the adsorbed excess actually separated may be calculated, but to form a true estimate of the total adsorption there should be added to this that amount of material already adsorbed in the sub-adjacent saturated solvent layer. The magnitude of the correction thus applied depends upon the maximum solubility of the solute. With aqueous nonoic acid solutions, the surface excesses calculated from Gibbs's equation lie between 5 and 7×10^{-10} mol. per sq. cm., whilst the minimum amount adsorbed in the sub-adjacent layer is approximately 5×10^{-14} mol. per sq. cm. even if we assume this layer to be one molecule thick. In the case of amyl alcohol, the calculated excesses are slightly lower but of the same order as for nonoic acid, *viz.*, 3—6×10^{-10} mol. per sq. cm., but the minimum amount adsorbed in the sub-adjacent layer is 5×10^{-11} mol. per sq. cm. Thus in the verification of Gibbs's equation the experimentally determined excesses in the case of nonoic acid should show good agreement with the calculated values, whereas with amyl alcohol they should be appreciably higher. This is usually found to be so (see Donnan and Barker, *loc. cit.*, and McBain and Dubois, *loc. cit.*).

FIG. 7.

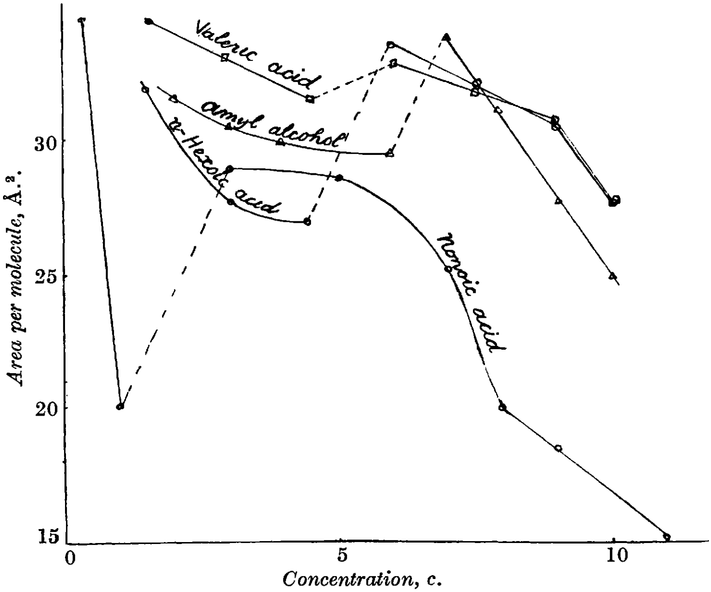


Fig. 7 represents graphically the application of Gibbs's equation to the γ–c graphs in Fig. 5. From the calculated surface excesses, the areas per molecule have been determined for the solute in the surface and these have been plotted against the bulk concentration.

All the graphs in Fig. 7 are similar in character, each showing a maximum and a minimum. The greatest difference in area between any two corresponding concentrations is 15 Å.^{2}, but for the greater part the variation is much less. This is to be expected from the form of the γ–c curves in Fig. 5. These are plotted so that the range of concentration from zero to saturation covers approximately the same length of abscissa in each case. The slopes of the graphs are very similar, from which it is obvious that the calculated excesses must be of the same order for solutions of the same degree of saturation. This must apply to the separation of the conjugate layer only, since it is hardly to be expected that solutes of such differing solubilities and adsorbabilities would have adsorbed excesses of the same order.

Although these graphs (Fig. 7) are difficult to interpret quantitatively, yet they follow qualitatively the changes occurring at the surface. As the bulk concentration increases from zero, there is a continuous increase in the amount adsorbed in the aqueous surface layer, shown by a decrease in the area per molecule. This adsorption proceeds to surface saturation and is followed by the commencement of actual separation of the conjugate layer. The new surface so originated contains only a very minute amount of separated solute, and so is shown by a sharp increase in the area per molecule. The growth of the attenuated film of constant composition is accompanied by a further progressive decrease in the area per molecule, after the occurrence of the sharp increase. In this way both maxima and minima are obtained, or rather, a discontinuity appears. The ultimate values for the areas per molecule of solute at saturation are much greater than those reached by the corresponding insoluble homologues (Adam, *loc. cit.*), so that there is no real evidence here in favour of the separated layer being pure solute. Nonoic acid appears to be an exception : here the c–A curves have an inflexion at a value of approximately 20 Å.^{2} and an ultimate value of 15. These data may be assumed to indicate an orientated layer of pure solute in a state of compression, but the probable explanation of this agreement lies in the relatively very low miscibility of nonoic acid and water, so that the conjugate layer separating is almost pure nonoic acid.

Summary.

1. In solutions containing active solutes of limited solubility, adsorption causes the growth of a layer of solvent more concentrated than the bulk of the solution. This layer reaches saturation before the bulk, and from this point onwards the associated conjugate layer accumulates, causing an inflexion in the γ–c curve.

2. The ratio of the maximum concentration to the bulk concen-

tration at the point of inflexion is equal to the ratio of any surface concentration, determinable from $D = 7{\cdot}9 \times 10^{-8} \times sP^4$, to its corresponding bulk concentration, and has been called the coefficient of adsorption for the solute concerned. It has the following mean values : Amyl alcohol 2·3, valeric acid 3·5, *n*-hexoic acid 3·1, nonoic acid 11·3.

3. An explanation has been offered for the fact that the actual amount of solute adsorbed at the surface of a solution determined experimentally is frequently much greater than that indicated by Gibbs's equation.

4. A method is indicated whereby rates of adsorption may be determined.

5. For nonoic acid the rate of adsorption has been found to be proportional to the square of the bulk concentration.

SOUTH WALES AND MONMOUTHSHIRE SCHOOL OF MINES,
TREFOREST, GLAMORGAN.
[*Received, November* 14*th*, 1931.]