177. *The Surface Tensions and Partial Vapour Pressures of Aqueous Aniline Solutions.*

By JAMES C. SPEAKMAN.

CALCULATIONS, based on an application of the Gibbs adsorption equation to the existing surface-tension data, of the minimum area occupied by an aniline molecule in the surface of its aqueous solution have led to an unexpectedly high result, *viz.*, 28·5 sq. Å. (*cf.* Rehbinder and Taubmann, *Z. physikal. Chem.*, 1930, **147**, 201; Kosakewitsch and Uschakowa, *ibid.*, 1931, **157**, 188). In general, this value is higher than can be reconciled with the known dimensions of the aniline molecule, if it is assumed that a complete, unimolecular layer of orientated molecules is built up in the surface as the bulk concentration increases; and in particular, it is higher than the corresponding areas given by similar molecules according to the data collected by the last two authors (*e.g.*, *p*-toluidine 25·5, phenol 24 sq. Å.). It seemed possible that this anomaly might be due either to errors in the surface-tension data, or to failure of the implicit assumption that the concentrations and activities of aniline were identical. Several cases are known in which anomalies have arisen in the latter way. For instance, the minimum area calculated for a phenol molecule was also unaccountably high (36·5 sq. Å.) before the activity measurements were introduced by Goard and Rideal (J., 1925, **127**, 1668). Again, with acetic acid solutions, when mole-fractions were used in the Gibbs equation, the minimum area occupied by each molecule in the surface was evaluated as about 43 sq. Å.; wholly suitable activity data do not seem to be available, but a rough application of those given by Lewis and Randall (" Thermodynamics," p. 290) reduces the calculated minimum area to approximately 30 sq. Å., which is more nearly in agreement with the areas given by the higher fatty acids.

For solutions of aniline, surface-tension measurements have been made by Worley (J., 1914, **105**, 263) and by Seith (*Z. physikal. Chem.*, 1925, **117**, 265), but, as the results of these workers do not agree, and as those of Seith do not cover the entire concentration range, these data have now been redetermined. Partial vapour pressures of aniline, which are assumed to be proportional to the activities, have also been measured.

EXPERIMENTAL.

Purification of Aniline.—The aniline was purified by shaking with dilute acid, washing with water, drying over solid potassium hydroxide, and two distillations under reduced pressure at about 80°. The product, which retained a slightly yellow tint, gave $D_{4^\circ}^{20^\circ}$ 1·0216 and $n_D^{20^\circ}$ 1·5860. Solutions were made in distilled water that had been boiled and cooled in a stream of nitrogen. They became somewhat coloured after several days, and over a period of some weeks their surface tensions appeared to diminish slightly (though this may have been due to the production of some substance which tended to contaminate the capillary tubes). For these reasons all measurements were made with freshly prepared solutions.

Surface Tensions.—Surface tensions were measured by a method previously described (J., 1933, 1449). Two sets of capillary tubes were used and gave concordant results within the limits of error (± 0·2). All measurements were made at 20·0°, and the results are in Table I.

In calculating the surface tensions, an exact knowledge of the densities of the solutions was not needed, but they were determined in order that concentrations could, if desired, be converted into molalities or mole-fractions; the densities differed little from that of water, ranging from 0·9982 for the pure solvent to 1·0001 for the saturated solution. Owing to the difficulties which may arise in working with a saturated solution, its surface tension was not directly measured; by a short extrapolation this quantity was estimated to be 47·3 ± 0·2 dynes/cm.

The results obtained in this research differ widely from those of Worley, but agree approximately with those of Seith, who, however, worked at a rather lower temperature.

Partial Vapour Pressures.—Partial vapour pressures were determined by the modification of the gas saturation method, which depends on comparison of the unknown vapour pressure with that of pure water (cf., *e.g.*, Washburn and Heuse, *J. Amer. Chem. Soc.*, 1915, **37**, 309; Dobson and Masson, J., 1924, **125**, 668). The gas used was nitrogen, stored in an aspirator over water, and passed thence through (1) a saturator containing water, (2) a first absorber

TABLE I.

Surface tensions of aniline solutions.

Concn. (mols./l.).	γ (dynes/cm.).	Concn. (mols./l.).	γ (dynes/cm.).	Concn. (mols./l.).	γ (dynes/cm.).	Concn. (mols./l.).	γ (dynes/cm.).
0·000	72·75	0·080	67·0	0·168	58·2	0·290	51·0
0·042	70·3	0·109	63·2	0·190	56·7	0·347	48·7
0·045	70·5	0·111	62·7	0·216	55·2	0·356	48·3
0·066	68·4	0·138	60·6	0·272	52·2		

containing 98% sulphuric acid, (3) a pre-saturator and (4) a saturator, both containing the solution under investigation, (5) a second absorber, and (6) a guard-tube containing phosphoric oxide; (1), (3), and (4) were immersed in a thermostat at 20·0°. 3—4 Litres of gas were passed in each experiment at a rate of about 1 l./hr. The increase in weight of the first absorber represented the amount of water vapour carried over from the pure solvent, that of the second absorber the combined amounts of water and aniline vapours from the solution. The weight of the aniline alone (0·006—0·001 g. in these experiments) was found by diluting the sulphuric acid, running in excess of *N*/100-bromate–bromide solution, and estimating the excess iodometrically. From these data, the vapour pressure of pure water being taken as 17·53 mm., the partial vapour pressure of the aniline was calculated with the aid of the assumption that the vapour obeyed the simple gas equation; allowance was made for the fall of pressure through the apparatus as shown by appropriately placed manometers. The results, which could be reproduced to within 2%, are in Table II.

TABLE II.

Partial vapour pressures of aniline.

Concn. (mols./l.).	Partial v.p. (mm.).	Concn. (mols./l.).	Partial v.p. (mm.).	Concn. (mols./l.)	Partial v.p. (mm.).
0·066	0·071 0·076	0·165	0·164 0·167	0·312	0·295
0·080	0·085	0·190	0·195	0·356	0·338 0·344
0·128	0·136 0·139	0·221	0·220	0·385 (satd.; in presence of excess aniline)	0·354 0·356 0·367
		0·256	0·256		

The experimental data were theoretically sufficient for calculating the partial vapour pressure of the water also, but this quantity differs so little from that of pure water that its variation lies below the limits of experimental error. However, it may be deduced thermodynamically that, for the range of concentrations over which the partial pressure of aniline obeys Henry's law (*i.e.*, up to about 0·2*M*), the partial pressure of water must obey Raoult's law; for more concentrated solutions, the change in the vapour pressure of the water can be obtained by a graphical integration of the Duhem–Margules equation, and it is concluded that the value for the saturated solution is 17·42 mm.

Solubility of Aniline in Water.—The concentration of the saturated solution at 20·0° was found to be 0·385*M*.

DISCUSSION.

When Henry's law ceases to apply to the partial vapour pressures of aniline, it is no longer permissible to use concentrations instead of activities, and the adsorptions formerly calculated are incorrect. Values of the surface tension interpolated from a smooth curve were plotted against logarithms of corresponding similarly interpolated vapour pressures of aniline, and the adsorptions calculated in the usual way from the slope $-d\gamma/d\log p_a$ (cf. Table III). The slope increased with concentration, approaching a maximum value

TABLE III.

Surface tensions, partial vapour pressures of aniline, and surface adsorptions of aniline (interpolated at round concentrations).

Concn. (mols./l.)	0·000	0·050	0·100	0·150	0·200	0·250	0·300	0·350	0·385 (satd.)
γ (dynes/cm.)	72·75	69·9	64·1	59·6	56·2	$53{\cdot}2_5$	50·6	48·5	47·3
Partial v.p. of aniline (mm.)	0·000	0·053	0·105	0·157	0·205	0·250	0·295	0·335	0·359
Adsorption (molecules/cm.^{2} $\times 10^{-14}$)	—	1·0	2·8	3·0	3·4	3·85	4·05	4·19	4·27

at saturation, which corresponded to a maximum adsorption of 4·27 ($\pm$ 0·05) $\times 10^{14}$ molecules per sq. cm. and to an area per molecule of 23·4 ($\pm$ 0·3) sq. Å.; this area agrees reasonably well with those found for similar molecules, and is consistent with the formation of a film composed entirely of aniline molecules at the surface. It is to be noted that this type of behaviour occurs with other partially soluble, surface-active solutes (*e.g.*, phenol) and is likely to be general; a film of solute molecules is completed on the surface simultaneously with the bulk phase becoming saturated; as the proportion of solute is further increased, a second phase is laid down upon the foundation of this surface film, which then becomes an interfacial film.*

It has been customary to compare the minimum areas obtained in this way with those found by Adam for condensed films of the insoluble long-chain derivatives after extrapolation to zero compression. His value for aniline derivatives is 24 sq. Å. (" Physics and Chemistry of Surfaces," p. 50). It may, however, be doubted whether this comparison can be justified further than as an approximation. In the first place, the minimum areas obtained as in this paper do not correspond to zero compression; if the views of various authors (*e.g.*, Schofield and Rideal, *Proc. Roy. Soc.*, 1925, *A*, **109**, 57) are accepted, the film must be regarded as under a compression of $\gamma_0 - \gamma$ dynes per cm., in the present instance equal to about 25 units. If the comparison were valid, therefore, it ought rather to be made with the area found by Adam for a like compression; actually this leads to a rather better agreement (*op. cit.*, p. 49), but the fact is not regarded as important. In the second place, it is generally held that the films given by soluble substances such as aniline are in a condition analogous to that of a gas above its critical point; if this is true, a comparison with the *condensed* film of an insoluble substance cannot be wholly satisfactory.

Corresponding values of F and FA/kT (cf. Schofield and Rideal, *loc. cit.*) were calculated from the present data. When plotted graphically, for values of F greater than 5, the points lay rather roughly on a straight line. The irregularity being disregarded (since the magnitude of FA/kT is very sensitive to slight errors in the data), the line may be represented by the equation $FA/kT = F\,.\,17/kT + 0{\cdot}4$, but the values of the constants are subject to considerable uncertainties.

THE UNIVERSITY, SHEFFIELD. [*Received, April 17th,* 1935.]