102. *Combination of Fatty Acids with Nitrogen Bases. Part III. Molecular Weight, Surface Tensions, Viscosities, and Conductivities in Benzene of the System : Piperidine–Propionic Acid.*

By E. B. R. Prideaux and R. N. Coleman.

If the piperidine salts of the lower fatty acids are largely undissociated in the pure state, as suggested in Part II (this vol., p. 4), it might be expected that they would have this character also in the associating solvent benzene; and therefore the physical properties of various mixtures of acid and base in benzene would bear a general resemblance to those of corresponding mixtures without solvent. Solutions containing less than 25% of the salt are no better conductors than benzene itself (as is shown below), so the properties observed should be due to molecules alone, including polymers.

The experiments already carried out in the absence of solvent were repeated in benzene solution. For this purpose, the system, piperidine–propionic acid, was chosen as being typical of the series. The molecular complexity of piperidinium propionate in benzene was determined cryoscopically; the densities and surface tensions of solutions containing various proportions of piperidine and propionic acid were measured. The sum of the weights of acid and base in these experiments was always 25% of the whole.

The conductivities and viscosities of piperidinium propionate in benzene solution were observed over the range 0—100% of salt, and from these results the variation of the product $\Lambda\eta$ with concentration was deduced.

Molecular Complexity in Benzene.—Compounds dissolve in benzene either as single molecules or as polymers. Association is found even in simple non-polar, or very feebly polar, compounds, but is still more pronounced in substances of a polar character such as benzoic acid. Such behaviour was observed in a comprehensive investigation of the association of a large number of organic substances, representing many different types of compounds, in benzene and other solvents (Meisenheimer and Dorner, *Annalen*, 1930, **482**, 130); it was, further, concluded that as a general rule the degree of association increases linearly with the concentration of the solution. The relation of molecular association to electrolytic dissociation was studied by Turner (J., 1911, **99**, 880), who showed that the halogen salts of organic bases exhibited very pronounced association in chloroform, the degree of association in dilute solutions being much greater than that which other substances, *e.g.*, organic acids, show in concentrated solutions. It was concluded that substances which are associated are either electrolytes or conducting media, and that molecular association in non-ionising solvents is complementary to electrolytic dissociation in water; and it was pointed out that the rate of increase of association is generally linear for such substances, and that the degree of association is dependent on two factors, one for the acid and one for the base. It will be seen that these conclusions apply to the salt now under consideration.

The usual technique of the Beckmann cryoscopic method was followed, the liquid salt being introduced into weighed, dry benzene. It was necessary to employ a stirrer working through a mercury seal, for otherwise the salt absorbed moisture which, even in quite minute amounts, gave a turbid suspension, evidently due to the separation of an aqueous phase. The distribution ratio of the salt between water (with which it is completely miscible) and benzene is therefore very high. The solid benzene which separated was free from the salt.

The molecular weights were calculated in the usual way, the results being best summarised by the equation $\alpha = 0{\cdot}0112C + 1{\cdot}96$, in which α is the molecular complexity (M, obs./M, calc.), and C is the concentration (% by wt.) of the solution. Observations were carried out over the range $C = 5$—25. The salt exists in benzene, therefore, largely as double molecules, and α increases linearly with concentration. The molecular complexity is not, however, quite as great as is that of most of the halogen salts studied by Turner (*loc. cit.*); *e.g.*, for tetra- and for di-ethylammonium chloride, $\alpha = 3{\cdot}90$—$5{\cdot}90$ and $2{\cdot}51$—$3{\cdot}37$ respectively. The lower association of the piperidine salt in benzene would, according to the above theory, be connected with the relatively lower dissociation in the pure state.

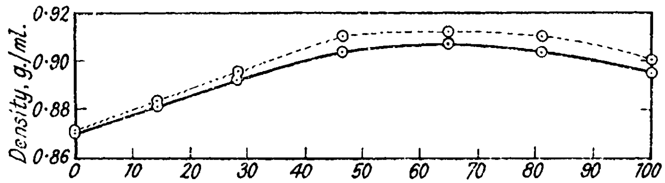
Densities and Surface Tensions.—These properties should be but little affected by the presence of benzene, and should therefore be calculable by the additive law. All mixtures contained 75% by weight of benzene, and a total of 25% of piperidine and propionic acid in various proportions as solute. Mixtures were prepared from stock solutions containing 25% of acid and base severally. Densities were determined by density bottle, and surface tensions by the double capillary-tube method, in a thermostat at 25·0° as already described (Part I, J., 1936, 1346). Precautions were taken against evaporation of benzene and absorption of moisture. Results are given in Table I, and represented graphically in Figs. 1 and 2.

TABLE I.

Acid in solute, wt. %.	$d_{4^\circ}^{25^\circ}$.	*d*, calc.	γ.	γ, calc.
0·0	0·8702	0·8716	28·48	28·46
14·5	0·8814	0·8837	28·56	28·65
28·4	0·8919	0·8953	28·79	29·12
46·5	0·9037	0·9102	29·00	30·14
64·9	0·9070	0·9119	28·72	29·26
81·1	0·9036	0·9099	28·24	28·41
100·0	0·8952	0·9005	27·14	27·51

Densities. The densities of the solutions first increase linearly with increasing proportion of acid, then pass through a rather flat maximum, and finally fall along a curve to the value for 25% of propionic acid in benzene. This behaviour is closely similar to that observed in the benzene-free system. In both cases the maximum density is not shown by the salt (which contains 46·5% of acid) but by a mixture of piperidine and propionic acid containing 65% of acid. If solutions of the acid–base mixtures in benzene obeyed the mixture law, a curve indicated by the broken line in Fig. 1 would be obtained, this being calculated as follows: Density of solution $= 0{\cdot}75d_B + 0{\cdot}25d_X$, where d_B is the density of benzene and d_X that of the benzene-free system interpolated from the previous results (Part I). This curve is seen to lie only slightly above that actually obtained, agreement being closer on the basic side of the curve, while on the acid side there is a small, fairly constant difference of 0·005—0·006. It may therefore be concluded that the mixture law is approximately obeyed between the densities of benzene and those of the system piperidine–propionic acid.

FIG. 1.



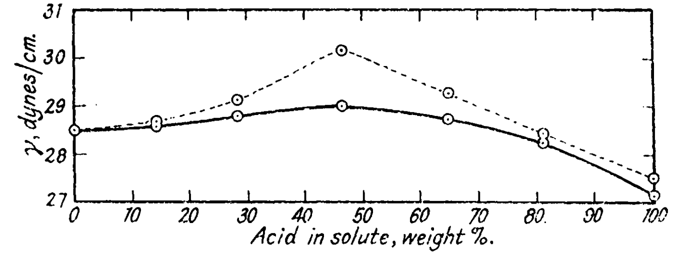


FIG. 2.

Surface tensions. It is evident that the general form of the surface tension curve due to different degrees of salt formation in the unsolvated system is broadly repeated in benzene solution. By assuming the mixture law, values of γ for the solutions, represented by the broken line on the graph, may be calculated by means of interpolations from the previous data of the benzene-free system, together with the surface tension of benzene itself. The values of γ so calculated are higher than those observed. Hence it is seen that the surface tensions of the pure system are lowered by the presence of benzene to a considerably greater extent than is accounted for by the additive effect due to the liquid of lower surface tension, *viz.*, benzene. The effect is, however, not uniform in different parts of the curve. Piperidine has a somewhat higher surface tension than benzene, and the surface tension of a 25% solution of the former is practically that required by the mixture law. As the acid content increases, the experimental curve departs further from the calculated, the difference reaching a maximum of 1·1 dynes/cm. at the salt concentration. Further addition of acid causes the curves to approach, and finally the pure acid in benzene has a value of γ a little below that required by the mixture law. Since propionic acid is capillary-active, it may be expected that this liquid will be concentrated in the surface, and will thus decrease γ. On the other hand, although piperidine may be capillary-active to most solvents, it has a higher surface tension than benzene itself, so there will be no tendency towards surface adsorption. The fact that the surface tension of the benzene solution of the salt itself is less than the calculated value cannot be accounted for by the concentration of the salt in the surface of the benzene, since the salt has a higher surface tension than benzene. Such an explanation would rather require negative adsorption, or a concentration of benzene molecules in the surface. In Part I, incomplete combination was suggested as an explanation of the low surface tensions of the piperidine salts of the fatty acids as compared with the values required for theoretical parachors. Similarly, it seems probable that, in benzene solution, enough free acid is produced by dissociation to permit surface adsorption, thus lowering the values of γ. This effect disappears in solutions containing sufficient excess of piperidine to suppress dissociation. The position of the maximum is the same as in the benzene-free system, *i.e.*, at 50 mols.%. The evolution of heat observed on mixing the constituents in benzene solution being taken into consideration, this maximum may be likewise attributed to the formation of a salt pair, or polymer, which is inactive, from capillary-active constituents.

The parachor of piperidinium propionate in benzene solution calculated from the mixture law according to the method of Hammick and Andrew (J., 1929, 754) is 376·6, while that of the salt free from solvent is 382·6. It has already been shown that the latter is below that calculated from the atomic values, and also below the sum of the parachors of free acid and base. Therefore the factors which cause this deviation are operative also in benzene solution. Evidence from the cryoscopic data indicates that a partial explanation is to be found in the association of the salt in solution.

Conductivities and Viscosities in Benzene.—Previous data for the conductivity of salts in benzene are limited, since, as a rule, salts are not sufficiently soluble to give conducting solutions. Piperidinium propionate, however, is miscible with benzene in all proportions. Cady and Baldwin (*J. Amer. Chem. Soc.*, **1921**, **43**, 646), studying reactions in benzene, found that copper melissate, lead stearate, and similar salts in this solvent showed some conductivity, which increased on passing in dry hydrogen chloride. Silver perchlorate is fairly soluble in benzene, but gives non-conducting solutions (Hill, *ibid.*, p. 254). The thiohydrate of aluminium bromide, $AlBr_3,H_2S$, is soluble in benzene, and the specific conductivity over the range 20—54% of salt has been shown by Jakubsohn (*Z. physikal. Chem.*, 1925, **118**, 31) to rise to $3{\cdot}54 \times 10^{-4}$ ohm^{-1} for the most concentrated solution.

Specific conductivities of piperidinium propionate in benzene were determined at 25·0° by the method already described. Finite values were obtained in solutions containing more than 30% of the salt. Densities in benzene (Table II) were found to give a nearly linear graph against the concentration. From these—by interpolation—molar conductivities were calculated, the results being included in Table III and shown in Fig. 3.

The maximum specific conductivity is observed at 72% of salt. The conductivities are of the same general order as those shown by the salt $AlBr_3,H_2S$ (see above) at corresponding concentrations. The maximum molar conductivity occurs at 66% of salt. It appears, therefore, that a mixture of the salt with a small quantity of benzene is a better conductor than the pure salt, in spite of the fact that benzene is a non-ionising solvent. Any increase of electrolytic dissociation would appear to be out of the question, since double molecules are already present in less concentrated solutions (see p. 462), and molecular complexity has been found to increase with increasing concentration. It is more probable that the relatively small proportion of free ions to which the conductivity of the pure salt is due is

TABLE II.

Salt, wt. %	100·0	87·1	69·2	58·3	48·6	34·0	0·0
d	1·0230	0·9998	0·9696	0·9535	0·9393	0·9187	0·8725
η	2·790	0·5697	0·1111	0·0549	0·0309	0·0164	0·0060

TABLE III.

Salt, wt. %.	$\kappa \times 10^4$.	Λ.	η.*	$\Lambda\eta$.	Salt, wt. %.	$\kappa \times 10^4$.	Λ.	η.*	$\Lambda\eta$.
100·0	5·47	0·0851	2·790	0·2374	48·2	4·21	0·1483	0·031	0·0045
85·2	9·00	0·1688	0·478	0·0807	34·5	0·52	0·0261	0·017	0·0004
71·3	9·66	0·2218	0·132	0·0293	20·6	0·00	0·0000	—	0·0000
60·6	8·02	0·2203	0·064	0·0141					

* Interpolated.

diminishing, although the mobility of the ions is increasing. The tendency towards a lower conductivity owing to the addition of a non-ionising solvent is at first more than counterbalanced by the increase due to greater mobility. The former factor soon begins to predominate, however, and the curve falls steeply through 50% of salt to a negligible conductivity at 25%. The general behaviour is similar to the conductivity variations of the salt in excess of acid and of base already observed.

FIG. 3.

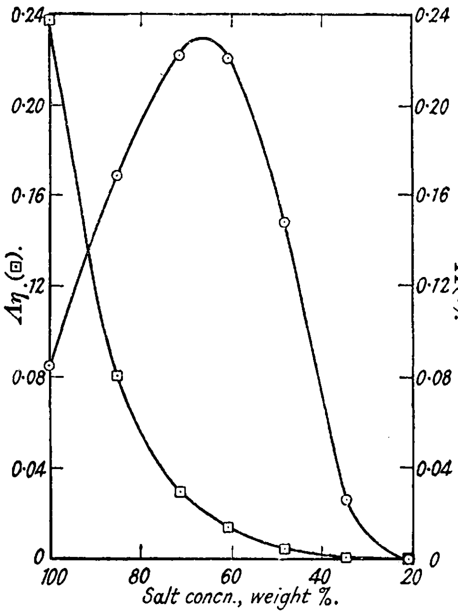
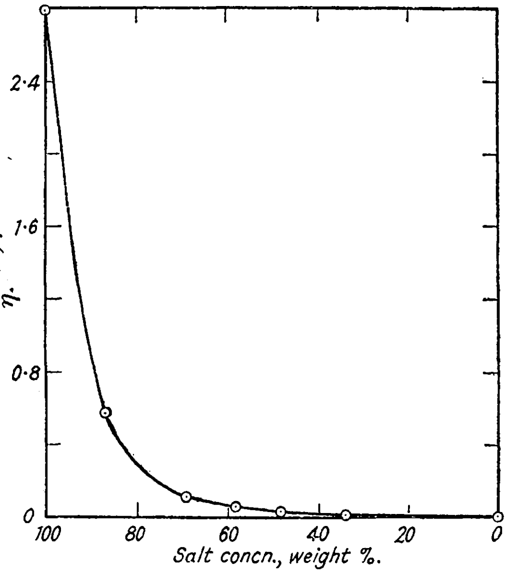


FIG. 4.



An examination of the variation of viscosity, η, with concentration shows that the increase in mobility may be largely, if not wholly, attributed to a rapid fall in viscosity on the addition of a relatively small quantity of benzene. Viscosity was determined as described in Part II, the usual precautions being taken. The results are included in Table II and shown by Fig. 4. The curve is seen to be approximately hyperbolic. Values were interpolated from this curve and included in Table III, whereby the product $\Lambda\eta$ was calculated. This is represented on Fig. 3, and is seen to fall steeply throughout with the addition of benzene. If this product is considered as representing the proportion of free ions, then the presence of the non-ionising solvent benzene has the effect of rapidly preventing the electrolytic dissociation of the salt.

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