291. *Combination of Fatty Acids with Nitrogen Bases. Part I. Piperidine and Lower Fatty Acids: Surface Tensions, Molecular Volumes, and Parachors.*

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

The combinations of organic bases with organic acids in absence of water have received much less attention than those in aqueous solution. The salts formed may be associated, dissociated as molecules, and as ions, and they may exhibit transitions between the behaviour of true salts and that of binary mixtures of substances which do not combine chemically.

Piperidinium acetate was described by Zoppellari (*Gazzettà*, 1896, **26**, 257) as forming deliquescent crystals, m. p. 103°, but little is known about the piperidine salts of other fatty acids. On mixing equivalent proportions of anhydrous piperidine and fatty acids, heat is generated, but there is no separation of solid salts at room temperature. In the system acid–base–salt, all the components are liquid, and it is therefore possible to observe what effect the formation of a compound has on the variation of physical properties with chemical constitution. The properties chosen are the surface tensions, leading to parachors and requiring the densities and molecular volumes.

The densities of pairs of liquids having a similar and non-polar constitution are closely additive; those of polar, especially hydroxyl-containing, pairs show positive deviations, *i.e.*, contraction takes place on mixing. It is to be expected that these deviations will become greater when chemical combination occurs. Pairs investigated by Bramley (J., 1916, **109**, 10), between some of which chemical combination should have occurred, are: phenol and acetone, phenol and aniline, dimethylaniline and pyridine. These, however, only showed slight positive deviations from the mixture law. The only pair which gave a maximum of density was phenol and quinoline at 47 mols. % of phenol. The surface tensions of many binary mixtures were examined by Morgan and Scarlett (*J. Amer. Chem. Soc.*, 1917, **39**, 2275), who concluded that small deviations having a maximum value at 50% by weight of each constituent were due to the physical effect of one liquid upon the other; large deviations with a maximum at points other than 50% by weight were ascribed to the formation of chemical compounds. The systems examined were chiefly of a type in which chemical combination can only be indefinite, *e.g.*, acetic acid and benzene. The present data should show clearly the effect of chemical combination. Additional information will be gained by the electrical properties, which have been determined in part and will be the subject of a further communication.

EXPERIMENTAL.

Preparation and Properties of the Salts.—The piperidine and the fatty acids from propionic to octoic were all of the highest quality. Piperidine, after partial dehydration over anhydrous sodium sulphate, was redistilled over caustic potash, and then over barium oxide. The purity was further checked by titration of weighed quantities with standard acid. The fatty acids were redistilled, and their molecular weights checked by titration with standard alkali.

When the constituents are mixed, they evolve considerable heat, giving colourless deliquescent liquids, which obviously have much higher viscosities than the constituents. They are miscible in all proportions with alcohol and ether, and also, when quite dry, with benzene, light petroleum, and hexane. The m. p.'s are difficult to determine on account of the slowness of the change, and the high viscosities. With the exception of the propionate, they have all been frozen by strong cooling in ice and salt, or solid carbon dioxide and ether. There is a strong tendency to supercool, and the propionate in particular only gave a glass after 18 hours' immersion in solid carbon dioxide and ether. The crystals were colourless needles in every case. For these reasons the following values are only approximate.

Acid.	M. p. of acid.	M. p. of piperidine salt.	Acid.	M. p. of acid.	M. p. of piperidine salt.
Acetic	+17°	103° *	Hexoic	− 1·5°	+17°
Propionic	−23	—	Heptoic	−10	+22
Butyric	− 2	+10	Octoic	+16	+32
*iso*Valeric	−51	+20			

* Zoppellari (*loc. cit.*).

Except for the salt of the branched-chain acid, the m. p.'s of the salts increase steadily with rise of molecular weight; there is no alternation in the odd and even members, as with the free acids. Although *iso*valeric acid has an exceptionally low m. p., that of its salt is relatively high.

Combination curves of the fatty acids with piperidine resemble closely those of the corresponding titrations with alkali, as was proved by potentiometric titrations. The salts in aqueous solution appear to be highly dissociated, and only slightly hydrolysed.

Densities and Surface Tensions of the Anhydrous Systems.—All measurements were made at 25·0° in a thermostat heated by gas and regulated to ± 0·02°. Densities were determined in the usual way in a density bottle or pyknometer, holding 3·5 c.c., which was washed with alcohol and ether and dried between each experiment; the accuracy was about 0·0002 g./ml. Surface tensions were determined from the rise in two capillary tubes. These were set in a rubber stopper, in contact along their length and dipped into the liquid contained in a specimen tube. They were depressed in the liquid, then raised, and carefully set vertical. Atmospheric moisture and carbon dioxide were excluded by a soda-lime tube. The differences in capillary heights, h_1 and h_2, were observed by a Wilson cathetometer in the usual way. If r_1 and r_2 are the radii of the tubes, d the density of the liquid, and σ the surface tension, then for each tube h_1 or $h_2 = 2\sigma/rgd$. Therefore if $h_1 - h_2 = h$, $\sigma = hdgr_1r_2/2(r_2 - r_1)$, and since $r_1 = 0{\cdot}0205$ and $r_2 = 0{\cdot}0449$ cm., $gr_1r_2/2(r_2 - r_1) = 18{\cdot}49$. This absolute value of the apparatus constant was checked by comparison with benzene and water, the values found for σ being 28·0 and 71·80 respectively, whereas standard values are 27·4 to 28·3 and 71·8 to 71·9 directly from Tables or by interpolation. In view of the satisfactory agreement the apparatus constant was used without correction.

The density and capillary rise of pure piperidine were first determined. A small quantity of acid was then added slowly, with cooling in order to prevent darkening of the liquid; density and capillary rise were redetermined in the same order, and the liquid was weighed. More acid was then added, and so on, up to an equivalent. Another series of observations was then made similarly, piperidine being added to the pure acid. The results are shown graphically in Figs. 1 and 2.

Fig. 1.

Relation between density (g./ml.) and composition of mixtures of piperidine with acids $C_2H_5{\cdot}CO_2H$ *to* $C_7H_{15}{\cdot}CO_2H$.

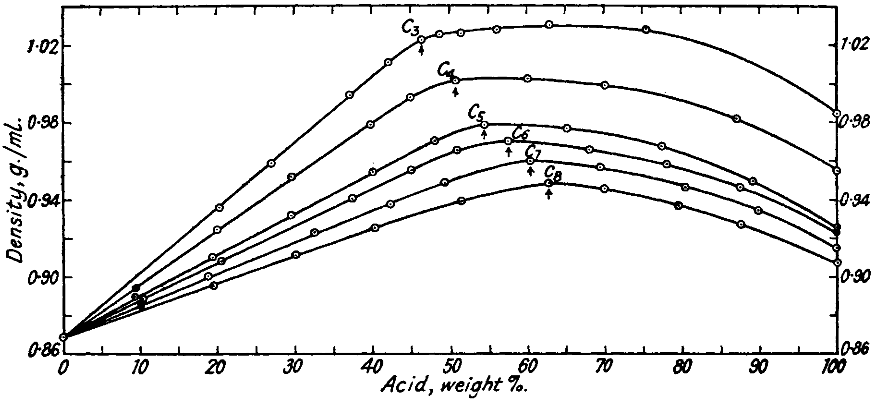
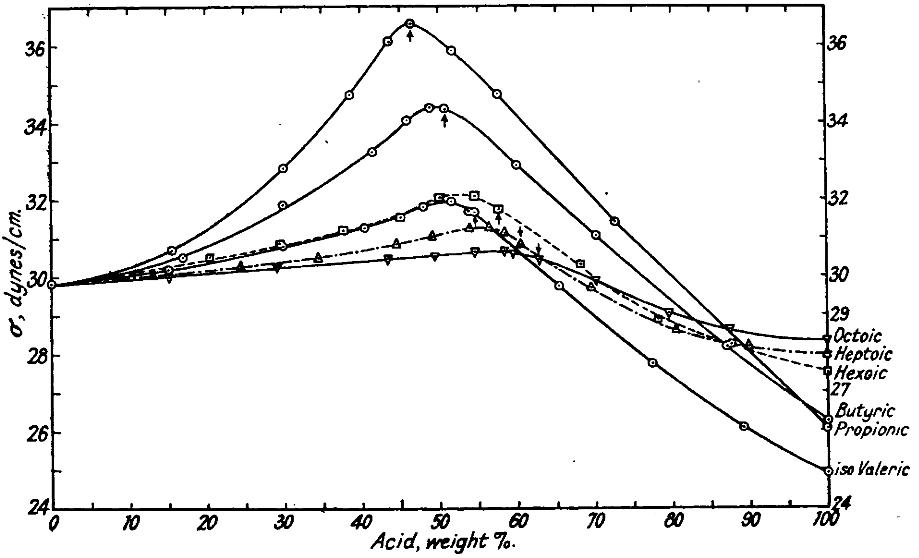


Fig. 2.

Relation between surface tension and composition of mixtures of piperidine with fatty acids.



Densities.—In every case progressive salt formation is accompanied by an increase in density, which is nearly linear up to within about 10% of the stoicheiometric proportion of piperidine. The numerical results are summarised in the following formulæ, in which x represents the % by weight of acid :

Propionic	$D = 0{\cdot}8690 + 0{\cdot}00335x$	(up to 40% acid)
Butyric	$D = 0{\cdot}8690 + 0{\cdot}00277x$	(up to 40% acid)
*iso*Valeric	$D = 0{\cdot}8690 + 0{\cdot}00213x$	(up to 45% acid)
Hexoic	$D = 0{\cdot}8690 + 0{\cdot}00189x$	(up to 45% acid)
Heptoic	$D = 0{\cdot}8690 + 0{\cdot}00163x$	(up to 50% acid)
Octoic	$D = 0{\cdot}8690 + 0{\cdot}00140x$	(up to 50% acid)

For excess of acid, the graphs are distinctly curved, and the densities are expressed to a fair degree of accuracy by equations of the second or third order, thus (x being % of piperidine) :

Propionic $D = 0{\cdot}9844 + 0{\cdot}00335x - 779 \times 10^{-7}x^2 + 5{\cdot}5 \times 10^{-7}x^3$
Butyric $D = 0{\cdot}9549 + 0{\cdot}00252x - 332x^2$
*iso*Valeric $D = 0{\cdot}9258 + 0{\cdot}00246x - 282x^2$
Hexoic $D = 0{\cdot}9230 + 0{\cdot}00214x - 247x^2$
Heptoic $D = 0{\cdot}9145 + 0{\cdot}00211x - 244x^2$
Octoic $D = 0{\cdot}9058 + 0{\cdot}00203x - 240x^2$

Densities of mixtures in equivalent proportions, *i.e.*, salts, are shown by the mark ↑ on the figures. These are maximum densities except for the propionate, for which this point lies about 20% on the piperidine side of the maximum. The maxima are flat, denoting dissociation, and are little changed by a considerable excess of acid. The densities of the salts decrease with rise of molecular weight; *i.e.*, they follow the order of the densities of the free acids. The increase of density on combination also diminishes rapidly with increase in molecular weight, being 0·101 g./ml. for the propionate and 0·056 g./ml. for the octoate. This is probably connected with the more intense interionic forces of the smaller anions. Contraction on combination is more clearly expressed in terms of specific volumes; *e.g.*, in the above examples, 100 g. of piperidinium propionate occupy 97·8 ml., the calculated value for the mixture being 100/0·922 = 108·5 ml., and the corresponding figures for the octoate are 105·5 and 112·2 ml.

The specific volumes characteristic of the salts may be compared with those in admixture with excess of acid and of base. The volume of a mixture of salt and excess acid is less than that for an equal excess of piperidine, allowance being made for the fact that the acids have a smaller specific volume than piperidine. If the density of acid and of piperidine are constant in the presence of the salt, it appears that the salt occupies a greater volume when in piperidine than when in acid solution: this is possibly connected with its ionisation in these two liquids as solvents. In particular, it is noteworthy that the specific volume of the mixture decreases on the addition of a slight excess of propionic acid to the propionate, although the former has a higher specific volume than the latter.

Surface Tensions.—The relation between surface tension and composition of mixtures cannot be expressed by equations of simple type. The values are given in Table I and shown in Fig. 2.

TABLE I.

Surface tension of mixtures of piperidine with fatty acids.

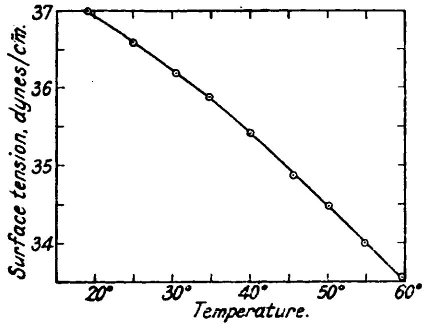
Propionic acid, wt. % ...	0·0	15·7	30·1	38·6	43·7	46·5	51·7	57·3	72·7	100·0			
σ	29·83	30·69	32·82	34·70	36·11	36·58	35·83	34·75	31·40	26·06			
Butyric acid, wt. % ...	16·9	30·0	41·5	46·0	48·9	50·8	60·0	70·2	87·1	100·0			
σ	30·50	31·86	33·27	34·06	34·39	34·39	32·90	31·04	28·17	26·21			
*iso*Valeric acid, wt % ...	15·1	30·0	40·3	48·1	51·6	53·9	54·5	65·3	77·4	89·2	100·0		
σ	30·19	30·80	31·25	31·82	31·94	31·68	31·67	29·75	27·76	26·08	24·90		
Hexoic acid, wt. %	20·5	29·6	37·6	45·1	50·1	54·7	57·7	68·2	78·1	87·7	100·0		
σ	30·50	30·83	31·21	31·55	32·06	32·10	31·75	30·30	28·91	28·21	27·49		
Heptoic acid, wt. % ...	13·1	24·5	34·5	44·5	49·1	54·0	56·5	58·4	60·4	69·5	80·7	89·8	100·0
σ	30·05	30·26	30·50	30·84	31·03	31·23	31·29	31·12	30·82	29·70	28·60	28·19	27·97
Octoic acid, wt. %	15·0	29·1	43·3	49·3	54·5	58·2	59·4	62·9	70·1	79·7	87·6	100·0	
σ	30·01	30·30	30·49	30·54	30·63	30·68	30·60	30·46	29·89	29·02	28·61	28·34	

Surface tensions of the *n*-acids rise with molecular weight, and that of *iso*valeric acid lies considerably below those of its normal homologues. The order of surface tensions of the free acids is reversed in the case of the salts, the propionate having the highest. Consequently, the rate of change of σ in passing from acid to salt diminishes as molecular weight increases. The same is also true on the piperidine side, since, as the molecular weight rises, σ for the salt approaches that of piperidine. The maximum σ, which is exactly at the salt concentration for the propionate and butyrate, moves over to the piperidine side as the molecular weight increases. Surface tension–composition curves of mixtures which have been previously investigated, *e.g.*, chlorobenzene and acetone, chlorobenzene and ethyl propionate, benzene and acetic acid, benzene and phenol, showed negative deviations (up to nearly 3 dynes/cm.) from the mixture law. Maximum deviation is usually shown at the 50% mixtures by weight, and this was considered to indicate a mutual effect of the surface tensions of each liquid on the other (Morgan and Griggs, *J. Amer. Chem. Soc.*, 1917, **39**, 2261; Morgan and Scarlett, *loc. cit.*). Mixtures of water and acetone showed a much larger deviation, which was ascribed to the formation of a compound. On the whole, the evidence seems very strong that the observed maxima, at or near the 50% molar compositions, are characteristic of salt formation. This connects these low-melting salts with the fused, highly ionised, inorganic salts which are known to have high surface tensions and low molecular volumes (Jaeger, *Z. anorg. Chem.*, 1917, **101**, 1).

The curves obtained may be regarded as resultants of three factors : (1) The mixture law : if each component retained its own surface tension and was present on the surface in the same proportion as in the interior, then graphs would be rectilinear on either side of the salt. (2) Molecular dissociation, which would decrease the real proportion of salt in any apparent mixture and would be repressed by an excess of base or acid : this would account for the rounded summits, the actual amounts of salt on each side of the maximum diminishing less rapidly than the amounts calculated from the proportions of constituents; at the salt point, the amount of salt, and also its degree of molecular dissociation, is at a maximum. (3) Surface adsorption of a capillary-active constituent, *i.e.*, the free acid, and to a lesser extent, the piperidine; in accordance with Gibbs's law, this depresses the surface tension and accounts for the concavity of the curves.

These effects operating simultaneously will account for the observed form of the curves. The predominant effect is the high surface tensions of the salts, and this becomes less important as the molar weights of the acids rise. The next is the factor (1), and this also enters as a small factor as the surface tensions of the free acids approach that of piperidine. Last is the factor (3), which will always operate, according to Harkins, Clark, and Roberts (*J. Amer. Chem. Soc.*, 1920, **42**, 700), in such a way as to present the least active part of the molecule, usually the non-polar hydrocarbon radical, to the air–vapour phase. This effect is, as already shown, common to our mixtures and the non-reacting pairs already quoted.

FIG. 3.



The operation of all three effects may now be illustrated. In the case of the propionate the ionisation is at a maximum, as we have proved by conductivities of the anhydrous systems. The surface tension of the salt is therefore very high as compared with those of the constituents, and since the molecular dissociation is low, there is little of these present, and the maximum therefore coincides with the salt composition. Moreover, both piperidine and propionic acid are equally capillary active, at least in aqueous solution. Now, in the case of the hexoate, factors (2) and (3) become more important. The salt is molecularly dissociated, giving some capillary-active fatty acid which lowers σ. Addition of a slight excess of piperidine at first represses this dissociation, allowing σ to rise to its maximum value, but further additions lower it again on account of factor (1). On the acid side, σ continues to fall rather more rapidly than according to the mixture law, on account of surface adsorption, until its bulk concentration becomes so great that surface adsorption can no longer alter its concentration in the surface.

Variation of Surface Tension with Temperature.—The effect of temperature upon surface tension of the propionate was investigated with a view to obtain information as to the molecular complexity of such salts. All experimental methods were the same as before. The thermostat was regulated by hand to within ± 0·02°. The results are given in Table II and Fig. 3. The decrease in density with rising temperature is linear and may be expressed by the equation $d = 1{\cdot}043 - 0{\cdot}00083t$. The decrease of σ, however, is only linear between 40° and 60°. Below 40° the rate of decrease is smaller. The Eötvos–Ramsay–Shields temperature coefficient from 40° to 60° is 2·30; from 20° to 30°, however, it is only 1·40. If the normal coefficient is 2·12, this would indicate a change in the degree of association from 0·88 (*i.e.*, dissociation) to 1·86. However, the values of this " constant " for a number of salts with organic cations show a wide range, extending from 0·47 for ethylammonium nitrate to 2·88 for tetrapropylammonium picrate (Sugden and Wilkins, J., 1929, 1291).

TABLE II.

Temp.	19·18°	25·00°	30·44°	34·84°	40·20°	45·40°	50·10°	54·80°	59·84°
d (g./ml.)	1·028	1·023	1·018	1·015	1·010	1·006	1·002	0·9986	0·9945
σ	37·00	36·58	36·19	35·89	35·42	34·87	34·48	33·99	33·56
$\sigma\ (M/d)^{2/3}$	1067	1058	1051	1043	1034	1021	1011	999	989

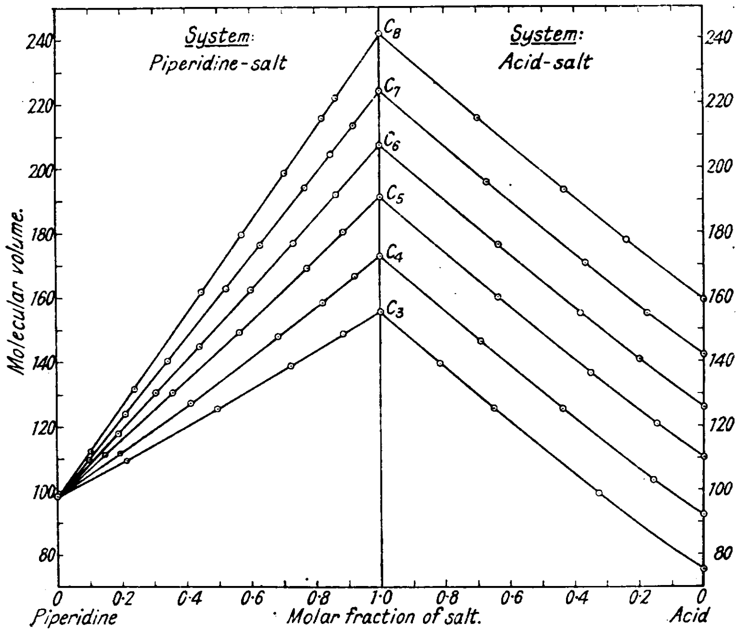
Molecular Volumes.—From the density results it will be evident that the molecular volumes lie below those calculated by the law of mixtures. On the assumption that the salt with a molecular weight $M_A + M_B$ is mixed in various proportions, x, with the molecules M_A or M_B, the mean molecular weight $= x(M_A + M_B) + (1 - x)M_A$, etc. For a mixture of 15·7% of propionic acid (M 74·05) with 84·3% of piperidine (M 85·12), *i.e.*, 0·212 mol. of acid and 0·996 mol. of base, the amount of salt is 0·212 mol. and that of free base is 0·784 mol. The mean molecular weight is therefore $(0{\cdot}212 \times 159{\cdot}2) + (0{\cdot}784 \times 85{\cdot}12) = 100{\cdot}5$, and this divided by d, 0·9200, gives the molecular volume 109·2. The molecular volumes of the salts, observed and calculated on the foregoing assumptions, are given below (the molecular volume of piperidine at 25·0° is 98·0):

Molecular Volumes of Piperidine Salts at 25·0°.

Acid.	V_M of acid.	V_M of acid $+ V_M$ of $C_5H_{11}N$.	V_M of salt, obs.	Diff.	Acid.	V_M of acid.	V_M of acid $+ V_M$ of $C_5H_{11}N$.	V_M of salt, obs.	Diff.
Propionic......	75·2	173·2	155·6	17·6	Hexoic	125·8	228·8	207·1	16·7
Butyric.........	92·2	190·2	172·8	17·4	Heptoic	142·2	240·2	224·1	16·1
*iso*Valeric......	110·3	208·3	191·2	17·1	Octoic.........	159·2	257·2	241·8	15·4

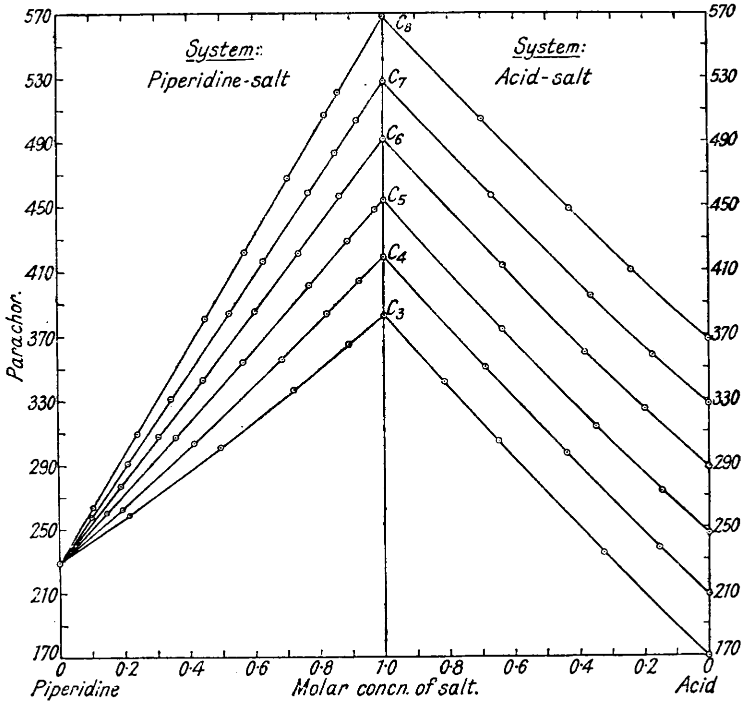
The molecular volume of each salt has been reduced by combination to nearly the value which would be shown by the salt of an acid having one carbon atom less; *e.g.*, the observed molecular volume of piperidinium *iso*valerate is nearly equal to that calculated for the butyrate. This change is much greater than that which would be caused by the annulment of the atomic volume of a hydrogen atom, which enters the piperidine molecule as a proton. The contraction is probably due to ionisation, the interionic forces acting as in water, although less strongly on account of the much lower dielectric constants of the anhydrous systems. The results of electrolytic conductivity determinations suggest that cation and anion are only free to a small extent, the rest being present as ion pairs of the type suggested by Bjerrum, which are also, however, contracted and distorted on account of their relatively large volumes and high compressibilities as compared with inorganic salts.

Fig. 4.



Parachors.—The molecular volumes of acid, base, and salt at the same temperature are under more closely corresponding conditions than usually prevail in salt formation. Nevertheless, parachors should indicate still more definitely any departures from the additive law due to ionisation. The parachors of base, acid, and salt are calculated as usual from the experimental values of σ and d, the molecular weights of mixtures being calculated from mean molecular weights derived as above. In Fig. 5 they are plotted against molar fractions of the salt. The curves resemble in general those for molecular volumes; they are nearly straight, conforming to the mixture law. It has been shown by Hammick and Andrew (J., 1929, 754) that the law of mixtures is fairly well obeyed by a mixture of two liquids, whose surface tensions do not differ by more than 7 dynes/cm. Actually there is a slight negative deviation from the mixture law, the parachors being given by the interpolation formulæ :

FIG. 5.



	Mixtures of x mol. fractions of salt with	
	(1) piperidine.	(2) acid.
Propionic	$P = 229{\cdot}0 + 135{\cdot}3x + 18{\cdot}3x^2$	$P = 170{\cdot}0 + 195{\cdot}4x + 17{\cdot}2x^2$
Butyric	$P = 229{\cdot}0 + 169{\cdot}5x + 20{\cdot}0x^2$	$P = 208{\cdot}6 + 192{\cdot}5x + 17{\cdot}4x^2$
*iso*Valeric	$P = 229{\cdot}0 + 215{\cdot}7x + 8{\cdot}9x^2$	$P = 246{\cdot}3 + 184{\cdot}3x + 23{\cdot}0x^2$
Hexoic	$P = 229{\cdot}0 + 250{\cdot}7x + 12{\cdot}0x^2$	$P = 288{\cdot}0 + 176{\cdot}3x + 27{\cdot}4x^2$
Heptoic	$P = 229{\cdot}0 + 292{\cdot}4x + 6{\cdot}5x^2$	$P = 327{\cdot}2 + 175{\cdot}7x + 25{\cdot}0x^2$
Octoic	$P = 229{\cdot}0 + 333{\cdot}0x + 6{\cdot}2x^2$	$P = 367{\cdot}4 + 176{\cdot}8x + 24{\cdot}0x^2$

The curves approximate more closely to a straight line on the piperidine side; on the acid side the deviations from the mixture law are somewhat greater. The experimental value for piperidine itself agrees closely with that calculated from Sugden's constants (J., 1924, **125**, 1177). Parachors of the fatty acids themselves are about 10 units too low, this deviation decreasing as the homologous series ascends. *iso*Valeric acid shows a greater deviation, branched-chain compounds having smaller parachors than straight-chain compounds. It is generally accepted that the fatty acids are associated (they show low values of the Ramsay–Shields coefficient), and on these grounds the low values of the parachors are usually explained. However, Mumford and Phillips (J., 1929, 2112) assign a lower value to the parachor of hydrogen when combined with oxygen on account of the high electron affinity of the latter element. With this assumption, the parachors of the fatty acids again become normal.

The observed parachors of the piperidine salts of the fatty acids fall considerably below those calculated from the atomic constants, bonds, and structural units; and also below the sums of experimental parachors of acid and base (see Table III). Calculated values of the parachors ΣP contain the value — 1·6 of the semipolar bond, which has also been assigned to the combination

TABLE III.

	P, obs.	ΣP, calc.	$\Sigma P - P$.
Piperidine ...	229·0	230·7	1·7
Acids.			
Propionic ...	170·0	180·2	10·2
Butyric	208·6	219·2	10·6
*iso*Valeric ...	246·3	258·2	11·9
Hexoic	288·0	297·2	9·2
Heptoic	327·2	336·2	9·0
Octoic.........	367·4	375·2	7·9

	P, obs.	ΣP, calc.	$\Sigma P'$, calc. from $P_A + P_B$.	$\Sigma P - P$.	$\Sigma P' - P$.
Salts.					
Propionate	382·6	409·3	399·0	26·7	16·4
Butyrate ...	418·5	448·3	437·6	29·8	19·1
*iso*Valerate	453·6	487·3	475·3	33·7	21·7
Hexoate ...	491·7	526·3	517·0	34·6	25·3
Heptoate ...	527·9	565·3	556·2	37·4	28·3
Octoate......	568·2	604·3	596·4	36·1	28·2

of two ions by Sugden (J., 1929, 1291). Ionisation is known to have a great effect on the parachor. In the case of fused salts, *e.g.*, stannous and lead chlorides, $P > \Sigma P$, but the reverse holds for silver chloride (Sugden, " The Parachor and Valency," 1930, p. 178). A few metallic salts of organic acids may show $P < \Sigma P$, but salts of organic bases, *e.g.*, tetralkylammonium bases, may be nearly normal, $P \sim \Sigma P$ or $P > \Sigma P$. Few salts of organic bases with organic acids have been investigated from this point of view. Tetrapropylammonium picrate, in which ionisation should be complete, gives $P \sim \Sigma P$. Mumford and Phillips (*loc. cit.*), on theoretical grounds, assign quite different values to the parachors of ions. In particular, they calculate a value for the ion $:NH_2^{\cdot}$ of 25. For these salts, there is also the question of the anion $C_nH_{2n+1}\cdot CO_2$. If the parachor of the hydrogen atom attached to oxygen is subtracted from that of the acid as calculated by Mumford and Phillips, we obtain the following results :

$C_5H_{10}NH_2$, $P = 225·8$.

Salt.	ΣP of salt.	P, obs.	Salt.	ΣP of salt.	P, obs.
Propionate.................	381·0	382·6	Hexoate	501·0	491·7
Butyrate	421·0	418·5	Heptoate	541·0	527·9
*iso*Valerate.................	461·0	453·6	Octoate.................	581·0	568·2

The agreement is better than before, but a deviation remains which increases with increasing molecular weight. Other possible explanations for these deviations are the association of the salts and the effect of surface adsorption, which, however, is relatively slight, and hardly affects $\sigma^{\frac{1}{4}}$.

It may be noted also that if the parachors of the propionate are calculated from the surface tension and density results between 20° and 60°, the values are not strictly constant, changing from 381·9 (at 19·2°) to 385·2 (at 59·8°). The rate of change falls off considerably at higher temperatures, so that at 60° it appears to be approaching a constant value. The change is too small to bring the parachor appreciably nearer to the theoretical value, but, nevertheless, has significance. It is usually found that for associated liquids, *e.g.*, the lower fatty acids, the parachor is not independent of temperature, but increases as the temperature rises (Sugden, *op. cit.*, p. 166). It would thus seem from the evidence of the parachor, that the propionate is associated at 20°, the degree of association falling off at higher temperatures. This also agrees with the results indicated by the Ramsay–Shields coefficient, *k*, which changes so markedly over this range. Evidence has been obtained of an abnormal value of *k* for the hexoate, which accordingly also must be regarded as associated at lower temperatures. Nevertheless, such variations of parachor are of a minor order compared with the considerable diminution due to salt formation. We consider that this is, in the main, to be explained by the exceptionally low molecular volumes resulting from rather intense changes acting on highly compressible ions.

UNIVERSITY COLLEGE, NOTTINGHAM.

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