

2. *Combination of Fatty Acids with Nitrogen Bases. Part II. Piperidine and Lower Fatty Acids: Conductivities and Viscosities of Liquid Anhydrous Salts.*

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IN Part I (J., 1936, 1346) the existence of a definite conductivity was adduced as evidence that the piperidine salts of the lower fatty acids contain a certain proportion of free ions. This work will now be described in more detail.

Conductivities of the Salts.—The Kohlrausch method is not well suited for the determination of the conductivity of oily liquids on account of uncertainties in the nature of products of polarisation at platinised electrodes and the practical difficulty of obtaining a good telephone minimum in liquids of such low conductivity. We therefore used Gram and Cullen's method (*J. Biol. Chem.*, 1923, 57, 477), in which the fall of potential across a known resistance (60,000 ohms) is compared with the fall across the same resistance with the cell in series; the direct current of the mains was used. If E_1 and E_2 are the respective falls of potential observed across the resistance, the resistance, R , of the cell is given by $R = 60,000(E_1 - E_2)/E_2$. The method has been used by one of us in measuring the conductivities of protein solutions (*Trans. Faraday Soc.*, 1935, 31, 349), and has been checked by the Kohlrausch measurements. The salts were prepared by mixing weighed stoichiometrical quantities of the constituents, special precautions being taken to prevent access of moisture. They were transferred to the conductivity cell by a special device, which likewise avoided contact with air. (The cell was stoppered, sealed with collodion, and placed in a ther-

mostat at 25°, regulated to within 0.02°.) These precautions were necessary, since some earlier results with specimens dried by anhydrous sodium sulphate were found to be in error on account of the extremely hygroscopic nature of the salts, which gave values for conductivities higher than those finally observed. We consider, however, that values obtained with these precautions are a close approximation to the true conductivities (κ) of the salts. From the molar volumes previously determined, the molar conductivities (Λ) were calculated. The results are summarised in Table I. It was possible to read the voltmeter to within 0.2 volt (the p.d. being of the order of 200 volts); so that a value for the conductivities could be obtained correct to three significant figures.

TABLE I.

Salt.	$\kappa \times 10^4$.	Λ .	Salt.	$\kappa \times 10^4$.	Λ .
Propionate	5.47	0.0851	Hexoate	3.17	0.0657
Butyrate	4.54	0.0784	Heptoate	2.80	0.0627
isoValerate	2.03	0.0388	Octoate	2.15	0.0520

With the exception of the salt of the branched-chain acid, the *isovalerate*, these salts thus show a progressive diminution of conductivity with increase of molecular weight.

Variation of the Conductivity with Temperature.—The heptoate was chosen for this experiment. The ends of a small U-tube were joined by sealing on a Y-piece. Through the open end the apparatus was successively washed with water, ether, and dry ether, and dried by a current of warm dry air. The salt was introduced with a minimum access of air, and the vessel was then partly evacuated through drying tubes and sealed. The sealed-in platinum electrodes were protected by external tubes bent upwards, and were connected by mercury, with copper-wire leads passing down these tubes. The conductivity cell could thus be completely immersed in water. Conductivities were taken at intervals of about 5° from 15° to 60°, by adjusting the thermoregulator of the thermostat, and were quite steady and reproducible. They are given in Table II, together with molar conductivities, calculated from previous determinations of the variation of density with temperature.

TABLE II.

Temp. ...	15.4°	20.8°	25.0°	30.1°	35.2°	39.7°	44.8°	50.0°	54.6°	59.9°
$\kappa \times 10^4$...	1.63	2.20	2.80	3.50	4.49	5.32	6.52	7.77	9.08	10.54
Λ	0.036	0.049	0.063	0.079	0.101 ₅	0.120 ₅	0.148	0.177 ₅	0.208	0.240
$\Lambda\eta$	—	0.0930	0.0881	0.0816	0.0766	0.0700	0.0654	0.0614	0.0578	0.0513

The variation of specific conductivity with temperature follows a smooth curve of the usual form. The temperature coefficients, α , calculated by the formula $\alpha = (d\kappa/dt)/\kappa$, are 0.049 at 25°, and 0.028 at 60°. The variation of molar conductivity with temperature, t , agrees with the equation $\Lambda = 5.375 \times 10^{-5}t^2 + 5.25 \times 10^{-4}t + 0.0152$.

Comparison with Fused Salts.—Conductivities of typical ionised salts are as a rule much higher than those of the present type; *e. g.*, for KCl (776°), $\kappa = 2.240$; for NaNO₃ (310°), $\kappa = 0.977$; for NaCl (850°), $\kappa = 3.50$. A closer comparison can be made with the alkylammonium picrates studied by Walden, Ulich, and Birr (*Z. physikal. Chem.*, 1928, **131**, 1), since these have lower m. p.'s (*ca.* 150°); as a result of the determination of the conductivities in the fused state and in non-dissociating solvents, such as chloroform and dichloromethane, it was concluded that the tetra-substituted compounds were almost completely dissociated in the fused state, whereas the less highly substituted compounds were largely undissociated. Typical values are:

Salt	(C ₃ H ₇)NH ₃ Pic	(C ₃ H ₇) ₄ NPic	C ₅ H ₁₁ N.C ₂ H ₅ .CO ₂ H
$\kappa \times 10^4$	61.06	139.8	5.47
Λ	1.311	5.188	0.0851

It appears that piperidinium propionate at 25° has a rather lower conductivity than the lower-substituted alkylammonium picrates at 150°, but if the difference of temperatures and consequent difference of ionic mobilities are taken into account, it may well be that the conductivities are of the same order. If, therefore, the theory that conductivities of the

order shown by the lower-substituted picrates indicate a partial dissociation be extended to the salts under consideration, it will be concluded that they, too, are largely undissociated in the liquid state. The term "undissociated" is here taken in the sense of Bjerrum's more recent definition. Thus, in the equation $C_5H_{11}N, C_3H_7 \cdot CO_2H \rightleftharpoons C_5H_{11}NH^+ + C_3H_7 \cdot CO_2^-$, the symbol on the left denotes, not undissociated molecules, but ions associated in pairs. According to Bjerrum, it is characteristic of strong electrolytes that their ions do not undergo any significant changes of properties when they are combined: the ions can approach closely without appreciable deformation. On the other hand, we may assume that the present compounds appear to be weak electrolytes, the undissociated molecules consisting of pairs of ions, linked by a polar binding, having undergone at the same time strong deformation. The actual existence of a covalent link between the acid and piperidine, which is required by truly undissociated compounds, would appear to be impossible, since nitrogen can hardly exceed its octet of electrons, for, according to Sidgwick's theory of valency, this can only take place with elements of the second short period and onward.

In support of the present views as to the constitution of these salts there is also the fact that ions of large volume are more deformable than those of small volume. The connection between molecular volumes and the structure of fused salts has been studied by Klemm (*Z. anorg. Chem.*, 1926, **152**, 295), who showed that molten molecules have a relatively high, and ions a low, molar volume. Walden showed that the picrates of the tetrasubstituted ammonium bases had low molar volumes. In Part I (*loc. cit.*) it was shown that those of the piperidine salts of the fatty acids are only slightly less (approximately 15 units) than the sums of the values of the constituents; and the molar volumes are therefore large compared with those of ordinary salts. According to Klemm's hypothesis, the salts will be largely molecular, *i.e.*, the ions will be much deformed. This is also supported by the fact that the conductivities of the higher members become progressively lower, indicating that the salts are becoming more molecular in character; at the same time, the deviation of the observed molar volume from the additive relation becomes less, indicating a relatively larger molar volume.

The temperature coefficients of conductivity also throw light upon the constitution. According to Biltz (*Z. anorg. Chem.*, 1924, **133**, 306), the temperature coefficients of strong electrolytes are lower than those of weak electrolytes. For sodium chloride, α (see above) is 0.0009; for aluminium chloride, a weak fused electrolyte, α is 0.02; and for piperidinium heptoate, it is about 0.04 (mean value). In this respect also, the piperidinium salt belongs to the class of weak electrolytes.

Variation of Conductivity with Composition.—The electrical conductivities of the binary liquid system, acid-base, have been investigated by several workers. Aniline-acetic acid and pyridine-acetic acid were studied by Trifonow and Tscherbow (*Ann. Inst. Anal. Physico-Chim.*, 1926, **3**, 459), and aniline-phenol by Howell and Robinson (J., 1933, 1032). If the results were plotted as mols. % against specific conductivities, curves were obtained convex to the concentration axis, and falling to the zero conductivities of the pure components at each end. Aniline-acetic acid mixtures show a maximum at 17 mols. % of aniline, and pyridine-acetic acid a maximum at 80 mols. % of the acid. It was concluded that maxima correspond to the formation of dissociated compounds, but that they are always displaced to the side of the component with the lower molecular weight and viscosity. These conductivities however, changed with time and were not absolute values. In the system phenol-aniline, studied by Howell and Robinson, conductivity begins to rise sharply at about 1 phenol : 2 aniline, attributed to the formation of a compound of this composition. The maximum occurs at 83 mols. % of phenol, *i.e.*, aniline phenoxide in excess of phenol. The conductivity-composition curves of allylthiocarbimide with piperidine, *o*-toluidine, and aniline show two maxima with a sharp minimum at 50 mols. % (Trifonow *et al.*, *Bull. Inst. rec. biol. Perm.*, 1931, **7**, 343).

Conductivities of piperidine and hexoic acid in various proportions were determined by the technique already described. The results are included in Table III and shown graphically in Fig. 1. The curve shows two maxima, one on the piperidine and one on the acid side, at 35 and 74 mols. % of acid respectively. These are rather more marked when molar, instead of specific, conductivities are plotted, and occur then at 33 and 78 mols. % of acid

respectively. Molar conductivities are calculated on the basis of g.-mols. of salt present per litre of the mixture.

TABLE III.

Acid, mols. %.	$\kappa \times 10^4$.	Λ .	$\Lambda\eta$.	Acid, mols. %.	$\kappa \times 10^4$.	Λ .	$\Lambda\eta$.
13.4	0.16	0.0118	0.0007	62.0	3.39	0.0964	0.1133
22.5	1.33	0.0589	0.0054	68.7	3.66	0.1296	0.0855
31.8	4.40	0.1391	0.0267	76.2	3.75	0.1796	0.0575
42.3	4.13	0.0994	0.0698	78.8	3.45	0.1869	0.0464
50.0	3.17	0.0657	0.1042	83.7	1.63	0.1170	0.0205
57.2	3.17	0.0788	0.1294				

The present case would appear to be a good example of Trifonow and Tscherbow's rule, the existence of two maxima (not found in mixtures of the acid-base type previously reported) confirming the chemical individuality of the salt, the maximum conductivity due to which is shifted to the side of each component of lower molecular weight and viscosity, *i.e.*, the free base and the acid. It was suspected that the intermediate minimum at the salt composition was due chiefly, if not wholly, to viscosity effects. It was therefore decided to determine viscosities, η , in order to supply data for the product $\Lambda\eta$, and also to extend the comparison of these systems to yet another physical property.

FIG. 1.

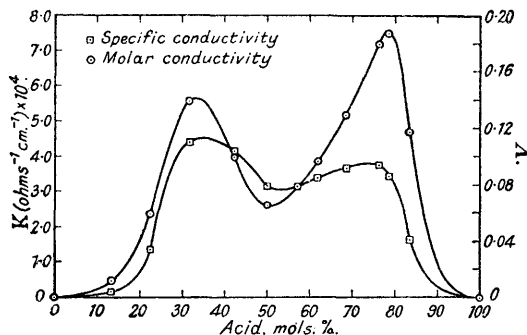
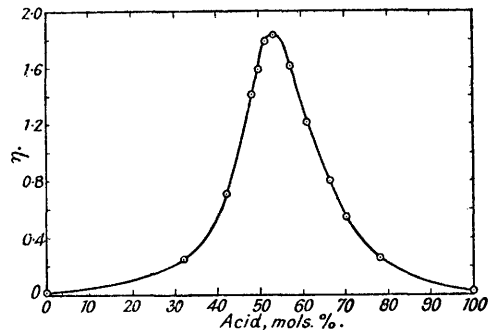


FIG. 2.



Variation of Viscosity with Composition.—It is obvious that the viscosities of the salts are much higher than those of either constituent, following a general law that, in the same system of acid-base, maximum values of η are connected with maxima of electrolytic dissociation. It is generally agreed that a better comparison of mobilities is obtained when the Λ values are corrected for viscosity by using the product $\Lambda\eta$.

The Ostwald-Poiseuille viscometer was calibrated with a 60% sucrose solution, having a time of outflow of 302 seconds at 25°. This solution has η 0.4402 ("International Critical Tables"), and d 1.2847. Every precaution was taken to exclude moisture both in preparing the various mixtures and during the actual experiment, as it was found that a small trace of moisture had a large effect in lowering the viscosity. In mixtures on the acid side of the curve, the limbs of the apparatus were connected with tubes containing loosely packed calcium chloride; for those on the piperidine side this was replaced by anhydrous sodium sulphate. Density values were interpolated from previous results. The variation of η with mols. % of acid is given below, and represented graphically by Fig. 2.

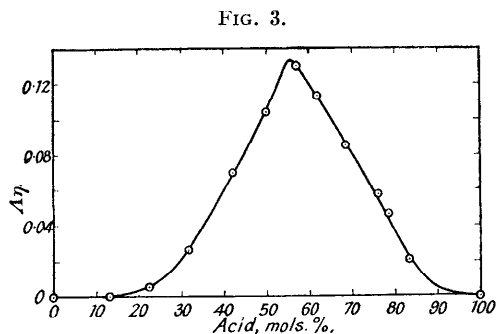
Acid, mols. %	0.0	32.3	42.5	48.6	50.0	51.7	53.7
η	0.022	0.204	0.711	1.414	1.586	1.785	1.833
Acid, mols. %	57.6	61.4	66.7	70.5	78.3	100.0	
η	1.618	1.221	0.808	0.551	0.262	0.028	

The values for the pure acid and base are taken from Landolt-Börnstein's "Physico-Chemical Tables."

The pronounced maximum in the viscosity curve is evidently connected with salt form-

ation, although it does not occur exactly at the equivalence point. It is displaced about 3 mols. % to the acid side, which is also the side of higher viscosity. This behaviour recalls the displacement of the maximum surface tension from the point of equivalence in the case of the salts from isovaleric to octoic acid. Hence, similar results are observed in the net effects upon σ and η of all the factors which are supposed to operate in the system, *i.e.*, formation of salts, molecular aggregates, dissociation, and the independent influence of each component according to some "mixture law."

Only viscosities being now considered, it is desirable to give a brief account of the work on and interpretation of viscosity maxima in binary mixtures. The simple view taken by Graham (*Phil. Trans.*, 1861, **151**, 373), that a maximum in the viscosity-composition curve definitely indicated the existence of a compound and established its composition, is now considered to be far too explicit, although it may be true in particular cases. The position was reviewed by Thole, Mussell, and Dunstan (J., 1913, **103**, 1108), who showed that associated liquids in general, and hydroxylated liquids in particular, have relatively high viscosities, and that maxima in the curves imply association, proceeding in the direction of complex formation. With regard to the system base-weak acid, there is much evidence that maxima occur usually on the acid side of the salt composition. This is true of aniline and acetic acid (*idem*, *ibid.*), and in the analogous case of *o*-toluidine-acetic acid the maximum lies at 72 mols. % of acid (Trifonow *et al.*, *loc. cit.*). In the systems aniline-*m*-cresol and toluidine-*m*-cresol, it lies at 65 mols. % of cresol; for pyridine with acetic and butyric acids at 77.9



and 74.4 mols. % respectively, *i.e.*, approximately 4 mols. of acid to 1 of pyridine (Tsakalotos, *Bull. Soc. chim.*, 1908, **3**, 234). Indeed, it was pointed out by Faust (*Z. physikal. Chem.*, 1912, **79**, 97) that there is always a maximum when the constituent liquids are acid and base, but that the composition of a compound cannot be deduced from this, since it frequently alters with the temperature and depends on the relative viscosities of the components. This effect was stressed by Tammann and Pillsbury (*Z. anorg. Chem.*, 1928, **172**, 143), who divided viscosity isotherms into four main groups.

In the case of a weak acid with a weak base, maxima are found, but are displaced towards the composition of the component having the higher viscosity; *e.g.*, aniline-*o*-chlorophenol has a maximum at 54 mols. % of aniline, and phenol-aniline at 62 mols. % of phenol. Since these compounds are strongly dissociated in the liquid state, these displacements are to be expected. The same is true of salts of guaiacol with aniline, pyridine, etc. (Puschin and Pinter, *Z. physikal. Chem.*, 1929, *A*, **142**, 211). It thus appears to be the exception rather than the rule for the maximum to fall exactly at the salt composition, and the fact that it lies closer than usual in the present case indicates a higher degree of combination, both molecular and electrolytic, than in the cases previously investigated.

Variation of $\Delta\eta$ with Composition.—Values of η were interpolated from the viscosity curve, and used to calculate the product $\Delta\eta$ given in col. 4 of Table III: the curve for the latter function differs considerably from that for Λ , as is shown by Fig. 3. The two maxima in the Λ curve are evidently due to the fact that, up to these points on each side of the salt composition, increase in the mobilities of the ions more than compensates for diminution in their concentration. There is a new single maximum, which represents the maximum of concentration \times mobility. It will be observed that this is slightly on the acid side, *i.e.*, 55 mols. % of acid. If the maximum of ionisation and also the maximum of viscosity were exactly at the equivalence point, the $\Delta\eta$ curve would fall on either side. Actually, however, Δ is increasing, and also η is increasing for a short distance in the acid side. This can only mean that concentration as well as the mobility of the ions is increased by an excess of acid. This is also shown by the fact that, in the Λ curve, the acid maximum is much higher than the base maximum, in spite of the fact that the viscosity of a mixture containing

excess of base, *e.g.*, 40 mols. % of acid, is much lower than that of a corresponding mixture with excess of acid (60 mols. % acid). This seems to point to a greatly increased electrolytic dissociation due to either (a) increased ionising power of the acid considered as a medium, (b) repression of molecular dissociation of the salt, which is principally due to the weakness of the acid, or (c) formation of an acid salt which gives more dissociated ions than the stoichiometrical salt. With regard to (b), it may be noted that, although the molecular dissociation of an anhydrous fused salt may appear to be symmetrical: $\text{BH}^+\text{A}^- \rightleftharpoons \text{B} + \text{HA}$, yet it is the proton affinities of the acid anion and the anhydro-base which determine the dissociation. If both have high proton affinities (weak acid), molecular dissociation will be extensive; on the other hand, if the proton affinity of the anion is low (strong acid), and that of the anhydro-base is high, molecular dissociation will be slight and electrolytic dissociation extensive: $\text{BH}^+\text{A}^- \rightleftharpoons \text{BH}^+ + \text{A}^-$. Condition (c) shows the dissociation of an acid salt derived by addition of the acid to an ampholyte type which is itself ionised but not dissociated, thus: $\text{BH}^+\text{A}^- + \text{HA} \rightleftharpoons \text{BH}_2\text{A}^+ + \text{A}^-$.

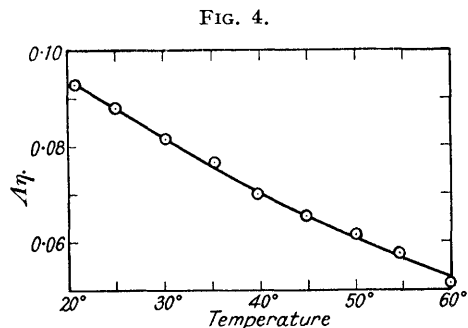
Variation of $\Delta\eta$ with Temperature.—The constancy or otherwise of the product $\Delta\eta$ with variation of temperature affords another basis of comparison between these salts and other fused salts. Materials for such comparison have been collected by Walden, Ulich, and Birr (*loc. cit.*). According to the Stokes–Einstein law, the mobilities of ions are proportional to the expression $1/\eta r$ in which r is the radius of the ion. This is not exactly obeyed by aqueous electrolytes, although the agreement is better at higher temperatures. It cannot be expected to hold strictly for fused electrolytes, since (1) mutual effects of the ions on one another alter with temperature, and (2) the degree of dissociation of many salts may alter with temperature. Since the dissociation of the picrates of the tetrasubstituted bases is considered to be complete at all temperatures, variation (2) should be negligible, and picrates of quaternary bases should show more constant values of $\Delta\eta$. Actually, this product was found to be fairly constant in salts such as tetra-amylammonium picrate, although an even better constancy is found with one or two partially substituted compounds such as diethylammonium picrate.

Piperidinium heptoate, whose variation of conductivity with temperature had been determined, was employed in this experiment. The thermostat was regulated by hand to $\pm 0.02^\circ$. Densities were interpolated from previous results. Observed values are shown below:

Temp.	17.6°	25.0°	30.1°	34.9°	39.9°	44.8°	49.7°	54.8°	59.7°
η	2.392	1.404	1.036	0.772	0.577	0.441	0.352	0.274	0.217

The variation of viscosity with temperature can be accurately expressed by the equation $\log \eta = 676.0/(T - 144.6) - 4.252$, where T is the absolute temperature. This is therefore in accordance with Andrade's general formula for associated liquids (*Nature*, 1930, **125**, 309), *viz.*, $\log \eta = \beta/(T - \theta) + \alpha$. The simple formula $\log \eta = \beta/T + \alpha$, proposed for unassociated liquids, was shown by Prasad (*Phil. Mag.*, 1933, **16**, 263) to hold for the fused salts sodium and potassium nitrates and lead bromide, whereas for lead chloride the introduction of the constant θ was necessary. This was attributed to incomplete association at lower temperatures, so that piperidinium heptoate in this respect belongs to the class of only partly dissociated salts represented by lead chloride.

Values of η were interpolated from the curve and used to calculate the product $\Delta\eta$, included in line 4 of Table II and shown in Fig. 4: $\Delta\eta$ is far from constant, but falls considerably with rise of temperature. It resembles in form rather the $\Delta\eta$ curve of many fused salts, *e.g.*, sodium and potassium chlorides, but lies at a lower level, and has an even smaller value than most of the fused picrates already referred to. Owing to the nature of the curves



of these salts, it was possible to extrapolate to a limiting value of about 0.36—0.42. Such extrapolation is not possible in the present case. It was noted that in general the salts of quaternary bases had the highest values; then followed the primary, the secondary, and finally the tertiary. There is therefore a superficial similarity in this respect between the piperidine salts and the tertiary ammonium picrates. Likewise, when comparison is made between the molar conductivities of the picrates and the heptoate under such conditions of temperature that all salts have the same viscosity, then the salt of the tertiary base, piperidine, shows a value resembling most closely those of the tertiary ammonium bases. It has been noted already that Walden considers the low Λ values of the salts of these bases to be due to less complete dissociation, and substitution of a weaker fatty acid for picric acid may still further reduce the dissociation. The values for the picrates are approximate only, obtained by the interpolation of Walden's results :

Salt.	η .	t .	Λ .
Piperidinium heptoate	0.214	60°	0.0627
Triamylammonium picrate	0.2165	120	0.197
Propylammonium picrate	0.21	127	1.45
Diethyldipropylammonium picrate	0.21	117	2.62

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[Received, November 7th, 1936.]