215. *Combination of Fatty Acids with Nitrogen Bases. Part IV. Diethylamine and Propionic Acid: Densities, Surface Tensions, Conductivities, and Viscosities of the Liquid Anhydrous System.*

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

The variation of certain physical properties of the systems, piperidine–lower fatty acids, has been studied in Parts I, II, and III (J., 1936, 1346; this vol., pp. 4, 462). This work has now been extended to another organic base in order to ascertain whether the results obtained with piperidine are typical of the system, moderately strong base–weak acid, or whether they are peculiar to this heterocyclic base. The base required was an aliphatic amine, which should be liquid at 25° and have a dissociation constant of not less than 10^{-4}. The only one fulfilling these conditions, besides being readily obtainable and not too volatile, is diethylamine, which has b. p. 55·5° and K_b $1{\cdot}26 \times 10^{-3}$ at 25°. The volatility is, however, rather greater than desirable, and special precautions have to be taken on this account.

Since it was not considered necessary to carry out experiments with all the acids previously studied, propionic acid was selected as being typical of the series. The surface tensions, densities, conductivities, and viscosities of the acid–base system were measured, and also the temperature coefficient of the salt in the case of the last three properties. Molar volumes, parachors, and conductivity–viscosity products were deduced from these data.

Experimental.

The diethylamine was of the best quality obtainable, practically the whole of the sample distilling at the correct b. p. The purity was checked by titration, and the liquid was then used without further purification. Specimens of the diethylamine salts of the acids, propionic to octoic, were prepared by weighing out a suitable quantity of the acid, and adding slightly less than the required volume of diethylamine from a graduated pipette. The exact amount was reached by adding the base drop by drop. These salts were colourless, deliquescent, viscous liquids, miscible in all proportions with alcohol, ether, and benzene. The propionate and butyrate mixed in all proportions with water to give clear solutions. On diluting a concentrated solution of the salts of the higher acids, at a certain point cloudiness was observed, which persisted as more water was added. Since these acids are only partly miscible with water, it seems probable that this cloudiness is due to hydrolysis of the salt, rather than to the partial miscibility of the salts themselves in water. This behaviour is also observed with the piperidine salts. The propionate and butyrate solidified to colourless needles having well-defined m. p.'s of 13° and 23° respectively. The *iso*valerate gave a less sharp m. p. of *ca.* 6°; the higher members of the series failed to crystallise. A large molecular volume thus appears to be associated with a strong tendency to supercool.

On account of the volatile nature of diethylamine, each individual mixture was prepared by first weighing out a suitable quantity of propionic acid and then adding the required volume of diethylamine, with cooling in ice. The bottle was stoppered and weighed, and the contents thoroughly mixed by vigorous shaking.

The viscosity and conductivity were first measured in a thermostat at 25° by the methods described in Part II. Drying tubes on both limbs of the viscometer contained anhydrous sodium sulphate and soda-lime. The liquid was transferred by pipette to the twin capillary-tube apparatus (Part I), and the capillary rise determined. A pyknometer was then filled, and the density of the mixture measured. Every precaution was taken throughout to ensure that the liquid was in contact with the atmosphere for a minimum of time, on account both of the volatility of the base and of the somewhat deliquescent nature of the mixtures.

The temperature coefficients of density, conductivity, and viscosity of the salt were determined exactly as before. Conductivities were steady and reproducible, and were not changed even after the sealed conductivity cell had been kept for 6 hours at 100°. Efforts to obtain the variation of surface tension with temperature failed, as it was found that, especially at higher temperatures, the difference in height of the liquid in the two capillary tubes increased with time, and that, on creating a new meniscus, a somewhat lower value was again obtained. This was probably due to evaporation of diethylamine, produced by an appreciable molecular dissociation of the salt, which would give a surface in the meniscus richer in acid, and hence with a higher surface tension. This effect was also observed to a lesser extent with mixtures containing the base in excess. At 25°, however, the change was only 0·002 cm. in 20 minutes, so that a true value at this temperature was obtained by first allowing the liquid in the vessel to attain the temperature of the thermostat, and then immersing the capillaries and taking the reading within 15 minutes.

Properties of the system diethylamine–propionic acid.

Acid, mols. %.	*d*.	σ.	$\kappa \times 10^3$.	η.	*n*.	*V*.	Λ.	$\Lambda\eta \times 10^4$.
0·0	0·7045	19·28	0·000	0·0035	0·000	103·8	0·000	0
11·8	0·7520 *	—	0·012	0·010 *	—	—	0·010	1
18·6	0·7800 *	—	0·304	0·015 *	—	—	0·153	23
23·8	0·8021	21·57	0·701	0·021 *	0·312	119·9	0·270	57
32·3	0·8410	23·95	1·165	0·044	0·477	129·0	0·315	138
41·9	0·8890	29·20	1·31	0·153	0·721	142·4	0·259	396
46·8	0·9133	30·97	1·25	0·306	0·879	151·5	0·215	659
50·0	0·9260	31·45	1·21	0·461	1·000	159·0	0·192	887
52·7	0·9348	31·56	1·19	0·550	0·898	149·6	0·198	1090
55·6	0·9422 *	—	—	0·562	—	—	—	—
57·7	0·9473	31·63	1·36	0·539	0·733	134·9	0·250	1348
64·7	0·9623	31·32	1·75	0·379	0·545	118·5	0·380	1441
75·9	0·9820	30·21	2·93	0·168	0·318	99·1	0·914	1535
80·6	0·9872 *	—	3·29	0·112 *	—	—	1·270	1422
84·2	0·9902 *	—	3·10	0·080 *	—	—	1·471	1177
87·6	0·9913	28·13	2·52	0·056 *	0·142	85·1	1·512	847
92·4	0·9906 *	—	0·829	0·031 *	—	—	0·816	253
97·0	0·9880 *	—	0·009	0·017 *	—	—	0·022	4
100·0	0·9844	26·06	0·000	0·0102	0·000	75·2	0·000	0

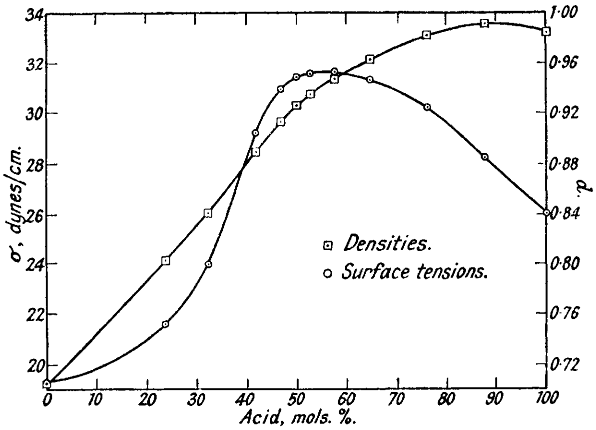
* Interpolated.

Properties of diethylammonium propionate.

Temp.	*d*.	$\kappa \times 10^3$.	η.	Λ.	$\Lambda\eta \times 10^4$.	Temp.	*d*.	$\kappa \times 10^3$.	η.	Λ.	$\Lambda\eta \times 10^4$.
20·2°	0·9296	1·02	0·587	0·161	948	44·4°	0·9118	2·16	0·196	0·349	684
25·0	0·9260	1·21	0·461	0·192	887	49·4	0·9080	2·52	0·161	0·408	658
30·0	0·9221	1·42	0·364	0·227	825	54·8	0·9042	2·83	0·133	0·461	613
34·6	0·9189	1·67	0·295	0·267	789	59·8	0·9003	3·24	0·111	0·530	588
39·4	0·9154	1·90	0·240	0·306	733						

In the tables, *d* is the density, σ the surface tension, κ the specific conductivity, η the viscosity, *n* the molar fraction of salt, *V* the molar volume, and Λ the molar conductivity.

FIG. 1.



DISCUSSION.

Densities.—On the basic side of the curve (Fig. 1) an almost linear graph is obtained, closely resembling that for the systems containing piperidine. The maximum is considerably displaced to the side of excess acid, *i.e.*, at 88 mols. % of acid. Piperidine–propionic acid showed this effect to a less extent, the maximum being at about 60 mols. %. There is thus contraction when the acid and the base combine to form the salt, but the volume of a mixture of the salt with acid is considerably less than that of a mixture containing an equal excess of base, even allowing for the smaller specific volume of the acid as compared with the base. This may be perhaps explained by changes in the ionisations of the salt in the two media (see p. 1026). The variation of density of the salt with temperature is linear, and may be expressed by the equation $d = 0{\cdot}9445 - 7{\cdot}35 \times 10^{-4}t$.

Surface Tensions.—Fig. 1 indicates that the general character is similar to that of the systems piperidine–lower fatty acids : the maximum is displaced from the salt concentration towards the side of that component having the higher surface tension : in the present case it occurs with excess of acid, but in the piperidine systems, with acids of higher molecular weight than butyric, it is found on the basic side, the acids having the lower surface tension. The same three factors discussed in Part I (*loc. cit.*, p. 1350) are again operative. The predominant effect is the high surface tension of the salt, and the rounded summit is explained by its molecular dissociation, which is diminished by excess of either constituent. The small amounts of the highly capillary-active diethylamine, thus produced, lower the surface tension of the salt to a value below that shown by a mixture containing a small excess of acid. With the addition of excess of base the surface tension falls more rapidly than the mixture law allows, on account of surface adsorption of the base, until, the surface layers becoming saturated, the rate of change of surface tension is diminished, and a concave curve results.

Molecular Volumes.—The molecular volumes of mixtures of the salt with excess of acid and of base were calculated as before, and when plotted against the molar fractions of salt in the mixtures give a graph similar in all respects to those of the piperidine systems (Part I). The points lie slightly below the values required by the mixture law, the deviation being more marked on the acid side. The difference between the sum of the molecular volumes of acid and base and that of the salt is 20·0, *i.e.*, there is a contraction of 11·2% on combination. The corresponding figure for piperidinium propionate is 10·2%. This contraction, presumably due to the formation of ions, is thus of the same order in both salts.

Parachors.—The experimental value of the parachor of diethylamine is 217·5, the value calculated from Sugden's constants being 219·8. The observed parachor of the salt is 376·4, being 22·0 units below the calculated value of 398·4, a deviation of 5·5%. This is of the same order, although not quite as great, as the deviation of 26·7 (6·5%) in the case of piperidinium propionate. This parachor deviation thus seems to be characteristic of the formation of ions by the transference of the proton from the acid to the base, and to this it may be therefore largely ascribed—together with the possibility of association, and the effects of surface adsorption. It may be noted that the parachor of diethylammonium propionate, on the basis of Mumford and Phillips's constants (J., 1929, 2112), is 377, *i.e.*, practically the same as the observed value. An error was made in recording the parachors of the salts of piperidine calculated by this system (Part I, *loc. cit.*, p. 1353). The values are all 5 units low, and should read :

Salt.	P of salt.	P, obs.	Salt.	P of salt.	P, obs.
Propionate	386	382·6	Hexoate	506	491·7
Butyrate	426	418·5	Heptoate	546	527·9
*iso*Valerate	466	453·6	Octoate	586	568·2

This does not affect the conclusions drawn therefrom. The characteristics of the basic side of the surface-tension curve make it apparent that the parachors of mixtures of salt and excess base will be too greatly influenced by the effects of surface adsorption to have any real significance. Moreover, Hammick and Andrew (J., 1929, 754) do not consider that the mixture law for parachors will hold when the surface tensions of the two liquids differ by more than 7 dynes/cm.

Conductivities.—The specific and molar conductivities of diethylammonium propionate are of much the same order as those of the piperidine salt. The values are rather greater, but, as will be shown, this is probably due to the lower viscosity. The temperature coefficients, $(d\kappa/dt)/\kappa$, are 0·034 at 25° and 0·026 at 60°. These are similar to the corresponding values for piperidinium heptoate, *viz.*, 0·049 and 0·028, so the same conclusions may be drawn, that the diethylamine salt belongs to the class of weak electrolytes. The molar conductivity varies with temperature according to the equation $\Lambda = 9{\cdot}37 \times 10^{-5}t^2 + 1{\cdot}95 \times 10^{-3}t + 0{\cdot}084$.

Fig. 2 shows the variation of specific and molar conductivities of the system diethylamine–propionic acid. Molar conductivities are calculated by assuming that the salt alone conducts the current, and are therefore obtained on the basis of g.-mols. of salt present per litre of the mixture. As before, two maxima are observed, with a minimum close to 50 mols.%; that on the acid side is much more pronounced than that on the basic side. The conductivity of the salt is thus considerably greater when dissolved in propionic acid than when in diethylamine.

FIG. 2.

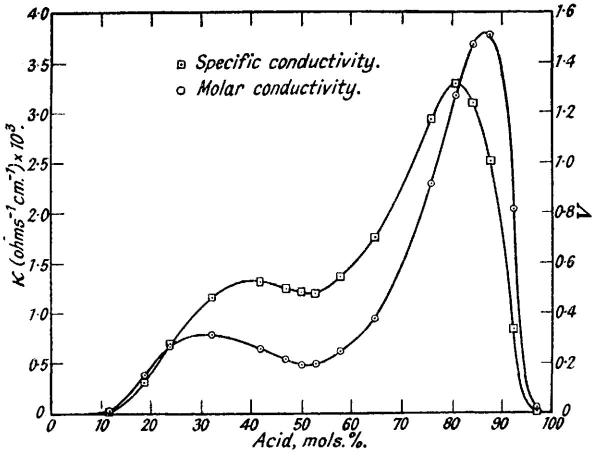


FIG. 3.

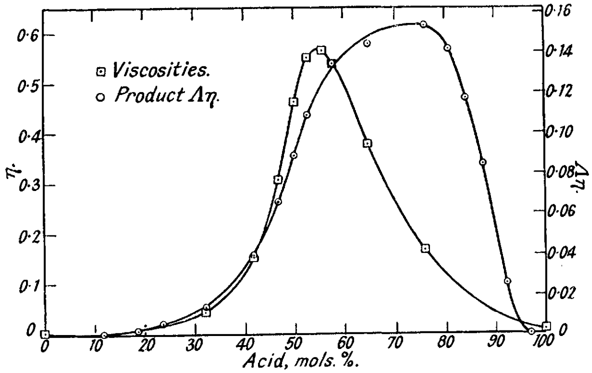
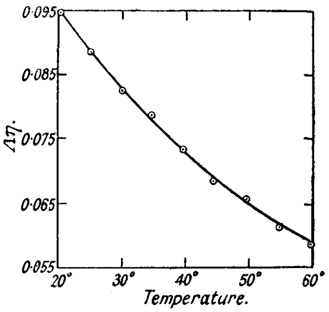


FIG. 4.



Viscosities.—Variation of viscosity of the system is shown by Fig. 3. The maximum is again displaced towards the component having the higher viscosity, but the displacement is slightly greater than for the system piperidine–hexoic acid, *viz.*, 5 mols.% instead of 3 mols.%. The curve is also not symmetrical but falls more steeply on the basic side. The variation of viscosity with temperature is expressed by the equation $\log \eta = 787{\cdot}4/(T - 104{\cdot}1) - 4{\cdot}397$, where T is the absolute temperature, in accordance with Andrade's general formula for associated liquids (*Nature*, 1930, **125**, 309).

Conductivity–Viscosity Products.—Experimental viscosity values, together with values interpolated from the curve, were used to calculate the product $\Lambda\eta$, the variation of which with concentration is shown by Fig. 3. An indication of the proportion of free ions contained by the salt in the various mixtures is thus obtained. There is some departure of the experimental points from a smooth curve near the maximum, but here both the Λ and the η values are rapidly changing in opposite senses, and small experimental errors will be increased in the product. The two maxima of the Λ curve are reduced to a single maximum, as was the case with the piperidine system, but whereas in that system there was a shift of this maximum only 5 mols. % away from the equivalent point to the acid side, it is now removed 25 mols. % in the same direction. The proportion of ions in the salt seems, therefore, to be definitely increased by the addition of excess of acid. This would appear to be contrary to the general non-ionising character of propionic acid as a solvent, so the effect is perhaps due to the formation of an acid salt which gives more dissociated ions than the normal salt. This explanation has already been advanced to explain the less marked displacement in the piperidine system. The presence of a relatively greater proportion of ions in excess acid than in excess base is also suggested by the form of the density curve, since low volumes (high densities) are to be associated with ionisation.

The variation of $\Lambda\eta$ of the salt with temperature (Fig. 4) shows the same characteristics as that of piperidinium heptoate; $\Lambda\eta$ is far from constant and falls rapidly with rising temperature, the rate of fall, however, decreasing at higher temperatures. The values of the molar conductivity and of $\Lambda\eta$ are here compared with those of the salts discussed in the previous papers:

	Λ.	$\Lambda\eta$.		Λ.	$\Lambda\eta$.
Piperidinium propionate...	0·0851	0·2374	Piperidinium heptoate	0·0627	0·0860
Piperidinium hexoate	0·0657	0·1042	Diethylammonium propionate	0·192	0·0887

Hence, although diethylammonium propionate has a higher molar conductivity than any of the other salts, yet it has a $\Lambda\eta$ value of the same order as that of the heptoate, so that, according to this, the degree of ionisation of the propionate of diethylamine is the same as that of the higher members of the series of the piperidine salts of the lower fatty acids.

University College, Nottingham.

[*Received, May 7th,* 1937.]