218. *Conductivity in the Three-component System Oleic Acid–Potassium Oleate–Water.*

By James W. McBain and Alexander Stewart.

The physicochemical properties of aqueous acid soap systems have received hardly any study. Soap solutions themselves have been shown by numerous investigations to be only slightly hydrolysed, the main product of hydrolysis being acid soap. Crystalline acid soaps of definite composition have been shown to exist in the anhydrous two-component systems soap–fatty acid (for references, see McBain and Stewart, this vol., p. 924). These exhibit such formulæ as potassium hydrogen dioleate, KOl,HOl, and in a few cases there is a second compound such as disodium hydrogen tripalmitate, 2NaP,HP. All such acid soaps exhibit a transition temperature, above which they decompose at once to form a liquid of composition intermediate between fatty acid and soap and a solid which is either the next higher acid soap or pure soap itself.

In aqueous systems, as noted by Chevreul in 1823, acid soaps are manifested as sediments. In the case of aqueous sodium palmitate to which palmitic acid is added, the solid acid soap formed was sufficiently insoluble to permit McBain, Taylor, and Laing (J., 1922, **121**, 621) to find that the conductivity of the soap solution at 90° was largely destroyed when sufficient palmitic acid had been added to form the composition 2NaP,HP. This was above the transition temperature limiting the possible existence of NaP,HP.

Finally, the phase-rule equilibria of the three-component system lauric acid–potassium laurate–water has been explored between 100° and 360° (McBain and Field, *J. Amer. Chem. Soc.*, 1933, communicated). When the present study was begun at the University of Bristol in 1925, it was not realised how soluble in each other these three components are, even at room temperature, and a systematic phase-rule study of this three-component system will be required for final interpretation. We have as guide a knowledge of the three corresponding two-component systems (potassium oleate–oleic acid, McBain and Stewart, *loc. cit.*; potassium oleate–water, McBain and Elford, J., 1926, 421; oleic acid and water are immiscible liquids), and analogies with the three-component laurate system in which the types of equilibria at high temperatures must in general resemble those in the present system at much lower temperatures.

Experimental.

A carefully screened and calibrated conductivity set with Cambridge Scientific Instrument Co. thermionic valve oscillator and tuned telephone was used. The temperature was 25·000° ± 0·002° (corr.). Two conductivity cells were used as described in previous communications by Dr. Laing. The cell constants were 0·3589 and 8·1932, respectively, as found with *N*/10- and *N*/100-potassium chloride prepared according to Kraus and Parker, with conductivity water of 0·6—1·0 × 10^{-6} mho.

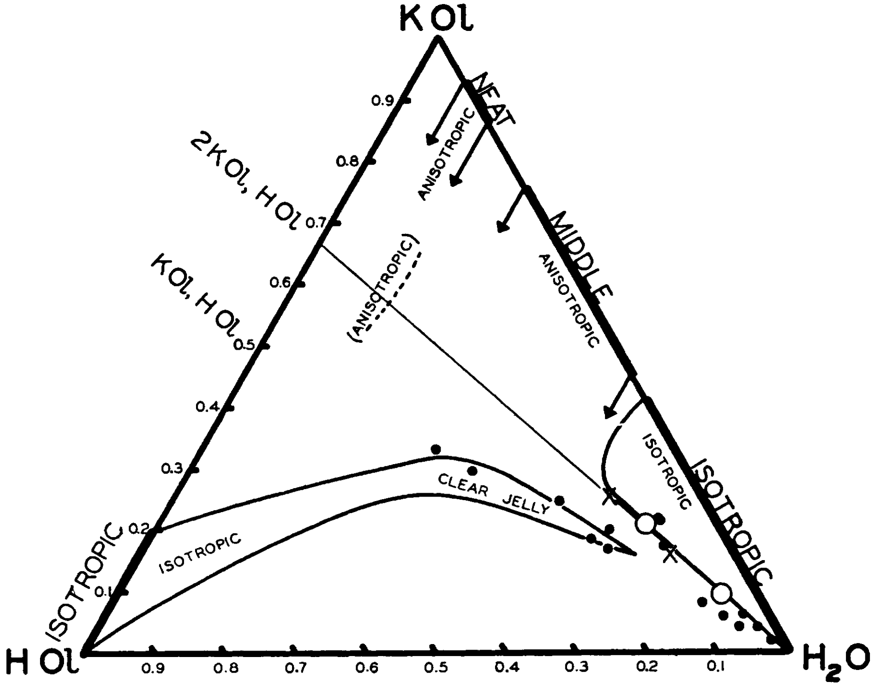
Three series of typical solutions were measured, containing 1, 2, and 3 equivs. of potassium oleate to one of oleic acid, and from these the values given in the tables were obtained. Analyses were carried out by the method described by Laing (*J. Physical Chem.*, 1924, **28**, 681). The saponification values of the acid soaps were in good agreement with the results of this method.

The earlier more dilute solutions were made from a fresh sample of oleic acid (" Kahlbaum ") and metallic potassium by the method of Bunbury and Martin (J., 1914, **105**, 417). Stirring was effected without producing frothing by slow rotation on a horizontal shaft for 10—14 days. It would be impossible to prepare some of the plastic concentrated systems by this method; hence, the alternative method was finally employed of using, in place of oleic acid, pure potassium hydrogen dioleate, prepared as previously described [the four specimens had *M*, 601·7, 604·7, 600·2, and 602·3 (calc., 602·6); mean iodine value 85·5 (calc., 84·3)]. Such solutions had the advantage of being colourless.

Description of the Three-component Systems.—There are no solids in the portions of the three-component system under observation at room temperature; nor can any of the solutions be resolved in the ultramicroscope.

FIG. 1.

Provisional sketch of the phase-rule diagram at 25° for the system potassium oleate–oleic acid–water.



There are present only isotropic liquids (one aqueous and one largely oleic acid) and an anisotropic liquid (liquid crystal). The latter may be derived from middle soap or from neat soap; it is not known which. In the lower middle of the diagram exist clear isotropic jellies, probably formed as a long projecting tongue from the anhydrous solution of potassium oleate in liquid oleic acid. All other systems studied were heterogeneous mixtures of the above.

A sketch of a phase-rule diagram for the three-component system at 25° is given in Fig. 1. The right-hand corner is determined with some probability. The units are fractional proportions, *i.e.*, fractions of the number of mols. of potassium oleate and oleic acid associated with such fraction of a kg. of water that the total composition at any point adds up to unity.

The isotropic soap solutions consisting of aqueous potassium oleate in concentrations from 0 up to about $0{\cdot}8N_w$ are extended into the three-component system by the addition of oleic acid. The chief result of the present study is to show that they can dissolve only 1 mol. of oleic acid for 2 mols. of potassium oleate, and that therefore this isotropic field is bounded on the left by the straight line which points from the H_2O corner towards the composition 2KOl,HOl. The tie lines from the lower part of this boundary will run approximately parallel to the base of the diagram. It is remarkable that the solubility of oleic acid in these soap solutions does not appear to be appreciably greater even at 180°, in contrast to the behaviour of the three-component laurate system.

The position of the isotropic tongue, which represents a clear jelly towards the middle of the diagram, rather resembles that in the laurate system.

The position of the boundary of the anisotropic liquid is not known except that it must cut the line corresponding to the proportions 2KOl,HOl. It might equally well come from the boundary of middle or of neat soap. Both of the latter exist in the two-component aqueous system even below room temperature, but middle soap is unknown in anhydrous soap systems, whereas the neat soap phase comes down to 107° where it reaches the composition KOl,HOl in the anhydrous two-component system.

The 19 points within the diagram were systems of known composition whose description corresponded with their relation to the boundaries drawn. Some were photographed between crossed Nicols. The anisotropic plastic nature of the liquid in equilibrium with the more concentrated aqueous solutions was confirmed by examination of the residue after pressure filtration through a porous pot.

Crystals of potassium hydrogen dioleate placed in water quickly swell, becoming surrounded by a sheath of gel-like material. Solutions more dilute than $0{\cdot}07N_w$ are milky emulsions, with droplets (probably oleic acid in the most dilute solutions) showing a black cross under the polarising microscope. Slightly more concentrated solutions show the striking phenomenon of elasticity; after being rotated, the solution comes to rest and then spontaneously rotates in the reverse direction.* This structural elasticity is confirmed by the tendency for lumps of clear jelly to separate on standing. $0{\cdot}1N_w$-Solution is a thin gel, and above this concentration the opacity decreases with increasing concentration. Thus, a $0{\cdot}3N_w$-solution is a clear jelly (single phase) when hot, becoming slightly cloudy on cooling, whereas a $0{\cdot}75N_w$-solution is a clear jelly at room temperature. A $1{\cdot}0N_w$-solution is slightly cloudy at room temperature and becomes a solid white curd at 5°. It is therefore evident that at room temperature this series of solutions has traversed two heterogeneous and one homogeneous region of the phase-rule diagram. Hence, dilution of a clear jelly instantly produces a milky liquid. These phenomena may be paralleled by the action of carbon dioxide (even from the air) on potassium oleate solutions, and they are not due to oxidation, for they occur equally well with air-free solutions in an atmosphere of nitrogen. Addition of sufficient potassium hydroxide immediately produces a clear soap solution.

Two systems of gross composition $0{\cdot}2089N_w$-2KOl,HOl and $0{\cdot}0788N_w$-2KOl,HOl, respectively, creamed, forming a clear lower layer and an upper layer of emulsion, both phases containing almost but not quite the same proportion of KOl to HOl, giving the direction of the tie line and the position of the phase boundary at the lower end. Their composition in " fractional proportions " was as follows :

Original solution.		Upper layer.		Clear lower layer.	
KOl.	HOl.	KOl.	HOl.	KOl.	HOl.
0·257	0·128	0·377	0·195	0·210	0·097
0·128	0·064	0·163	0·084	0·098	0·048

Addition of potassium chloride to aqueous solutions of potassium hydrogen dioleate salts out all the oleate as crystals of KOl,HOl, even from extremely dilute solutions. Sucrose and glycerol have no visible effect except perhaps slightly to diminish cloudiness. Alcohol causes separation of an aqueous solution containing two equivalents of oleic acid to one of potassium oleate into two layers, whereas alcoholic solutions of potassium hydrogen dioleate are clear.

In Table I is given the hydrolysis alkalinity (concentration of free hydroxyl ion) of typical solutions as measured by Miss K. Hay by the indicator method (McBain and Hay, J., 1929, 589).

The freezing-point lowering of a solution of $0{\cdot}0983N_w$-KOl,HOl by the Beckmann method was 0·021°, corresponding to a concentration of crystalloid of $0{\cdot}0113N_w$, one-ninth of the gross concentration. This shows that the acid soap (2KOl,HOl) exists chiefly as such, in colloidal form, in the dilute aqueous solution, and that it is likewise but little dissociated. The system measured is heterogeneous, the aqueous phase containing only 1HOl to 2KOl.

Results of Conductivity Measurements.—The results of the conductivity measurements are

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* Compare the similar observation of Hatschek and Jane with $N/20$-ammonia solution to which a few drops of oleic acid have been added (*Kolloid-Z.*, 1926, **38**, 33); see also the similar behaviour of white of egg (Almquist and Lorenz, *U.S. Egg and Poultry Magazine*, April, 1932, p. 20).

TABLE I.

Effect of Excess of Oleic Acid on the Alkalinity of Potassium Oleate at 90° and at 20°.

K(N_w).	Ol(N_w).	Excess HOl, %.	$[OH']_{90°}$.	$[OH']_{20°}$.
0·04	0·04	0·00	0·00154	0·0008
0·0406	0·07267	78·98	0·00036	0·0008
0·025	0·025	0·00	0·00134	0·00074
0·02558	0·03837	50·00	0·00037	0·00022
0·0185	0·0185	0·00	0·0012	0·0007
0·01761 (cloudy)	0·02639	49·85	0·0008	0·00035
0·014	0·014	0·00	0·0010	0·00045
0·0139 (very cloudy)	0·0288	107·2	0·00033	0·000115

given in Tables II and III. The conductivity of heterogeneous systems is, of course, uncertain whenever there is a tendency towards separation of the unequally conducting phases. Furthermore, the equilibria, especially in the highly viscous systems, are slow of attainment; but, to hasten this, the solutions were prepared as before described and brought to approximate equilibrium by shaking and heating. Experiments were carried out at least in duplicate. The values here recorded represent well-mixed systems soon after preparation. Probably on account of slow oxidation, which may be accelerated by platinum electrodes and by shaking, there is a slow, nearly linear increase of conductivity over long periods of time which lies between 0·3 and 1% per day.

The values in the first two horizontal lines of Table III were obtained directly, the remainder by interpolation.

TABLE II.

Specific Conductivity and Specific Volume of Aqueous Systems containing (i) *added* KOl,HOl; (ii) *added* KOl *and* HOl *in the proportion* 2KOl,HOl; (iii) *added* KOl *and* HOl *in the Proportion* 3KOl,HOl.

	N_w.*	v.	$\kappa \times 10^4$.	N_w.*	v.	$\kappa \times 10^4$.	N_w.*	v.	$\kappa \times 10^4$.
(i)	0·000982	1·0040	0·624	0·01016	1·0042	1·221	0·1948	1·0081	8·182
	0·00194	1·0040	0·842	0·0724	1·0056	3·734	0·2588	1·0092	8·60
	0·00497	1·0041	1·028	0·0983	1·0061	4·307	0·974	1·0165	31·69
	0·00992	1·0042	1·384	0·1502	1·0072	5·167			
(ii)	0·238	1·0054	7·84	0·0477	1·0043	3·58	0·0157	1·0041	2·40
	0·00542	1·0040	1·51						
(iii)	0·236	1·0035	21·90	0·0169	1·0039	4·09	0·00566	1·0040	2·12
	0·0358	1·0039	5·54	0·00997	1·0040	2·91	0·00177	1·0040	1·05

* N_w is the number of equivs. of K per 1000 g. of water.

TABLE III.

Equivalent and Specific Conductivities of Systems containing Definite Amounts of Potassium Oleate (N_w) *to which varying Amounts of Oleic Acid are added.*

Excess HOl, equivs. %.	Specific conductivity × 10^4.			Equivalent conductivity.		
	0·2N_w.	0·1409N_w.	0·02106N_w.	0·2N_w.	0·1409N_w.	0·02106N_w.
0·00	76·2	—	—	40·6	—	—
24·24	—	24·3	5·16	—	18·3	24·9
33·33	18·6	14·1	4·6	10·2	10·6	21·6
50	7·5	6	2·6	4	4—5	13
100	7	5	2	4	4	9

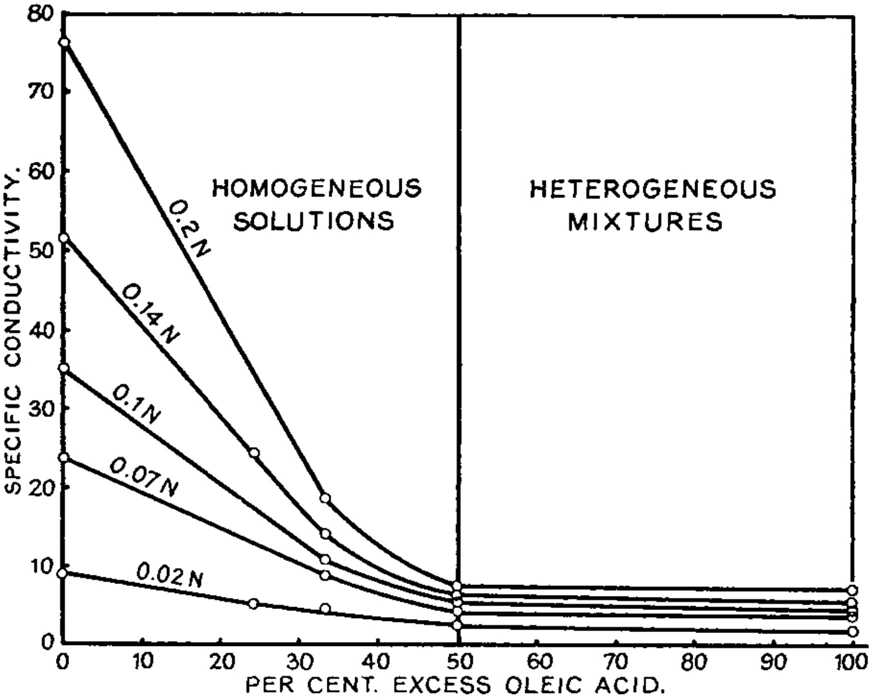
DISCUSSION.

The conductivity results are examined in Fig. 2, obtained by interpolation. It will be seen at once that Fig. 2 agrees with the predictions of Fig. 1 in that the specific conductivity of any potassium oleate solution falls rapidly and almost linearly upon progressive addition of oleic acid until the composition 2KOl,HOl is attained (50% excess of acid) and thereafter falls very slowly with further addition of oleic acid. This is because the aqueous soap solutions dissolve the oleic acid and remain homogeneous until, at 50% excess, saturation is reached and a new, poorly conducting phase begins to appear in increasing amount.* The behaviour of the equivalent conductivity (referred to potassium) is similar.

When the proportions of potassium oleate and oleic acid are kept constant and only the total concentration is varied, the equivalent conductivity corresponds to about two-thirds dissociation in very dilute solutions (0·001—0·002). With increasing concentration the degree of dissociation falls very rapidly until at 0·1 it has become constant at only a few units %.

FIG. 2.

Effect on the specific conductivity of solutions of potassium oleate caused by progressive addition of oleic acid up to and beyond saturation, which occurs at a composition corresponding to 50% *equivalents excess* (2KOl,HOl).



SUMMARY.

1. Potassium oleate solutions dissolve oleic acid until saturation is reached when one-half of an equivalent of oleic acid has been added for each equivalent of soap. The equivalent conductivity thereby falls to about one-tenth of its value except in very dilute solution.
2. Conductivity, freezing point, and hydrolytic alkalinity agree in showing that the acid soap in solution is mostly undissociated and mostly colloid.
3. The phase in equilibrium with the stronger saturated solutions is anisotropic (liquid crystal) and contains almost the same proportions of potassium oleate and oleic acid (2KOl,HOl) but with less water. The phase in equilibrium with lower concentrations is isotropic, consisting primarily of oleic acid in which potassium oleate and then water dissolve.

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* Compare Carrière's statement (*Chem. Weekblad*, 1923, **20**, 206) that, on addition of oleic acid, a hot solution of sodium oleate splits into two phases, and foaming immediately ceases.