from 1-chloro-2-propanol and sodium ethoxide, and from propylene glycol and diethyl sulfate.

5. The monoethyl ethers were differentiated by the selective cleavage of the secondary ether group with sulfuric acid and acetic anhydride.

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[14] Original manuscript received November 4, 1944.

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Isotropic and Anisotropic Liquid Phases in the System Hexanolamine Oleate–Water

BY EMANUEL GONICK AND JAMES W. MCBAIN

Hexanolamine oleate (4-methyl-4-amino-pentanol-2 oleate) is soluble in water in almost all proportions. The anhydrous soap is a yellowish waxy solid melting to an isotropic liquid at 58°.[1] At room temperature, as little as 3 or 4% of water is sufficient to convert it into an *isotropic* liquid. However, anisotropic liquid phases intervene between these concentrated solutions and the ordinary more dilute isotropic solutions.

Between 0 and 30% of soap in water, the solutions are isotropic, and are those of a typical colloidal electrolyte. However, it is remarkable that with increasing concentration these solutions become more and more jelly-like, reaching a maximum stiffness at approximately 12% soap, and upon further *concentration* become fluid again—all without change of phase. Between 30 and 85% soap at room temperature the solutions are birefringent, viscous liquids. Indeed a few of these anisotropic liquids are remarkable in being as free-flowing as an oil. This is a very unusual degree of fluidity for liquid crystals.

At sufficiently high temperatures, above 183°, all the systems of hexanolamine oleate and water are isotropic liquids, miscible in all proportions. It is again remarkable that even where the soap itself has so low a melting point, and while both concentrated and dilute solutions are isotropic solutions at room temperature, the intervening anisotropic solutions require such extreme elevations of temperature before they "melt" to become isotropic. In general, however, the transition temperatures between liquid crystals and isotropic phase are much lower than in the case of ordinary soaps. It had been hoped that there might be a maximum in the temperature boundary of one or other of the anisotropic phases at a temperature low enough to permit a direct study in ordinary apparatus open to the atmosphere. Then the change in conductivity and other properties accompanying the change from a single homogeneous isotropic phase to an anisotropic phase of the same composition and of almost the same temperature could be easily and directly measured. However, the two maxima lie at 156 and 183°, very much above the boiling point of the solutions.

The outlines of the phase diagram are here described, together with a number of physical properties of certain of the phases.

Experimental

The hexanolamine oleate was made by mixing equivalent amounts of Kahlbaum "purest" oleic acid and redistilled hexanolamine[2] (b. p. 60.2° at 6 mm. pressure, mol. wt. 117.3).

Phase Relations.—Solutions for phase studies were made by weighing the soap and conductivity water into Pyrex tubes, which were evacuated and sealed while the contents were frozen in a bath of Dry Ice and acetone. Compositions are expressed in true per cent. by weight. The tubes were then heated to the temperature of isotropy and tilted back and forth until the contents became homogeneous. The tubes were then observed between crossed polaroids while heated in a transparent furnace, made by wrapping nichrome wire around a piece of large-bore Pyrex tubing, stoppered at both ends and lagged with asbestos through which slits were cut on opposite sides to permit observation. Temperature was controlled by means of a rheostat. Thermometer readings were corrected for stem-exposure. Transition temperatures from isotropic phases were determined by the first appearance of birefringent specks upon slow cooling, these showing up as bright spots in the dark field of the crossed polaroids. Transitions were strictly reversible, the final disappearance of birefringent material on heating and its appearance on cooling occurring at the same temperature.

The results of these observations are tabulated in Table I and the phase diagram is graphed in Fig. 1.

TABLE I

VALUES OF T_i, THE TEMPERATURE AT WHICH ON SLOW COOLING THE FIRST DROP OF ANISOTROPIC LIQUID PHASE FORMS FROM THE HOMOGENEOUS ISOTROPIC LIQUID PHASE IN THE SYSTEM HEXANOLAMINE OLEATE–WATER

% Soap	T_i, °C.		% Soap	T_i, °C.
21.5	180		55.3	122
22.3	183		63.7	100
25.0	181		74.3	71
30.0	177	2 phases at room temp.	78.5	54
35.5	164		83.7	22
37.5	159		85.5	16.5
39.3	143		86.8	9
39.6	153		87.3	8
40.2	156		88.0	7
41.4	154		91.8	14
45.7	143		94.5	27
49.8	135		97.6	43

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(1) A sample of the oleate, recrystallized from acetone, turned from opaque solid crystals to anisotropic jelly at 54–58°, and finally to isotropic liquid at 68°. On cooling below 52°, this liquid froze to an opaque solid without passing through the anisotropic phase observed above. On reheating, the solidified soap melted directly to an isotropic liquid at 58°. The unrecrystallized soap also melted to isotropic liquid at 58°.

(2) Kindly supplied by the Shell Development Co., Emeryville, Calif.

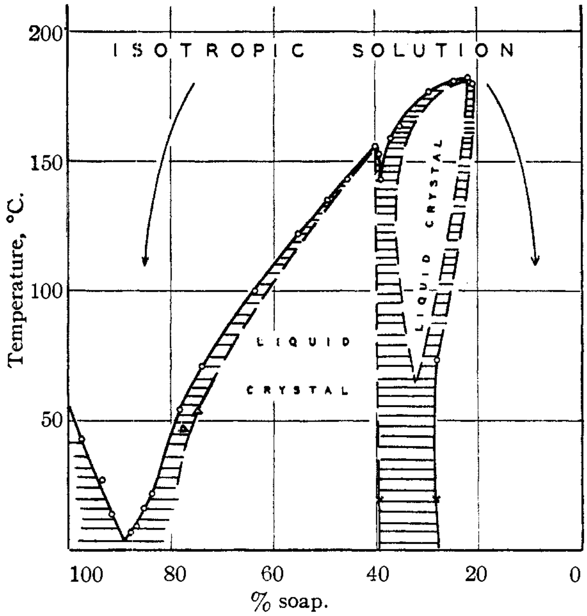

Fig. 1.—The phase diagram for the system hexanolamine oleate–water showing the extensive regions of mobile isotropic solutions (a 12% solution at room temperature is a jelly) and two regions of liquid crystalline solution stable to very high temperatures. Points determined by observation under crossed nickels are marked as circles, those from direct analysis by crosses, and those from conductivity by triangles, but systematic observations were made over the whole range of concentration and temperature.

In Fig. 1 experimental observations are represented by solid lines, while broken lines are used to represent assumed phase boundaries. No systematic attempt was made to ascertain the exact inner boundaries of the liquid crystalline phases. However, a temperature–conductivity curve for a 78.5% solution (*cf.* below) shows a sharp break at 47°, and for 75.7% at 53°, marking the inner boundary of the two-phase region at these concentrations. These points are represented by triangles in Fig. 1. Furthermore, observations made on the lower (isotropic) phase of the two-phase systems between 28 and 39.5% soap show that the 28% soap system, upon heating to 74° just begins to separate the characteristic blue and red anisotropic droplets of the right-hand inner liquid crystalline phase. This, therefore, marks the left-hand boundary of the isotropic region at this point, and the lower boundary of the inner liquid crystalline phase extends to somewhat below this temperature. The material for this observation was obtained by breaking open a tube which had been frozen in dry ice and paring off a section from the bottom of the isotropic phase.

When the hot tubes were cooled, the liquid crystalline phase as viewed between crossed polaroids made its appearance as amber luminous specks of irregular shape in most cases, but in the composition range from 30 to 40%, the birefringent phase was blue in color, changing gradually to mottled purple, green and finally amber as the temperature fell. This indicates uniform orientation throughout much of the phase, possibly along the glass surface. At room temperature the solutions in this range formed two layers of constant composition. The composition of these was: the upper layer, a birefringent phase, 39.5%; the lower, isotropic phase, 28%. These are indicated in Fig. 1 by crosses.

The colorless birefringent phase of the 30% system at room temperature, when viewed between crossed polaroids, appeared blue-green in one direction and amber when rotated 90° about the longitudinal axis of the tube, indicating one uniform orientation of the anisotropic liquid throughout. This phenomenon has not previously been observed.

An Anomalously Isotropic Solution.—During the course of the work a 53.35% solution of the soap was made up in a glass-stoppered flask. Contrary to expectations, it proved to be isotropic. As a check on the concentration, a solution of nearly the same concentration (53.25%) was made and proved, as usual, to be anisotropic. The indices of refraction were compared as measured in an Abbé refractometer. That of the anisotropic solution was 1.4172 at 25° as compared with 1.4171 for the anomalous isotropic solution, thus confirming the concentration. The anomalous solution was less viscous than the anisotropic solution. Occasionally, in other phase studies of soaps,[3a,b] an apparently isotropic sample has been reported in a usually birefringent region.

The phase diagram for the hexanolamine oleate system is rather similar to that for aqueous laurylsulfonic acid,[3a] which also exhibits two liquid crystalline regions extending up to high temperatures. It is interesting that the published diagram also includes a "region of pseudo isotropy" where liquid crystal usually appears. The chief contrast is in the much greater solubility of hexanolamine oleate and the wide range of existence of its more concentrated liquid crystalline solution. The well-known phase diagrams for alkali soaps contain the two anisotropic regions, middle soap and soap boiler's neat soap phase. Where the more concentrated liquid crystalline solution in the present instance would be identified with the soap boiler's neat soap phase, its lower limit of concentration would be only 38% soap instead of the 70% for ordinary soaps.

Indices of Refraction.—These were measured with an Abbé refractometer, using the boundary of the darkest field, which was bordered by a lighter fringe in the more concentrated solutions, and the results were corrected to 25° by multiplying by the ratio of the density of water at 25° to that at the temperature of the observation. A coefficient of expansion of the solution equal to that of water is thus assumed, but the error involved is negligible for the small temperature range (5–7°). The results, summarized in Table II, are linear with weight per cent. of soap, indicating a regular change in density with concentration without pronounced change in direction or trend.

TABLE II

INDICES OF REFRACTION OF HEXANOLAMINE OLEATE SOLUTIONS AT 25° AS MEASURED IN AN ABBE REFRACTOMETER

Wt. % soap	Index of refraction
3.410	1.3385
6.702	1.3441
10.40	1.3494
11.64	1.3521
16.10	1.3583
21.54	1.3669
48.21	1.4109
53.25	1.4172
62.29	1.4320

It has been shown[4] that formation of colloid from crystalloid has but a very minor influence upon refractive index.

Comparison of the Conductance of Anisotropic and Isotropic Liquid Solutions.—Electrical conductance is especially sensitive to changes in the state of aggregation of a conducting solute. The conductance of a 78.5% solution of hexanolamine oleate was measured at intervals from 25 to 90.5°, which includes the transition from liquid crystal to isotropic solution, T_i being 54°. A similar

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[3] (a) M. J. Vold, THIS JOURNAL, **63**, 1429 (1941); (b) J. W. McBain and M. C. Field, *J. Phys. Chem.*, **30**, 1549 (1926).

[4] J. Lipschitz and J. Brandt, *Kolloid Z.*, **22**, 141 (1918).

experiment was carried out for a 75.7% solution and the results are included in Fig. 1. In Fig. 2 the data for 78.5% have been plotted. The conductivity curve is seen to consist of three parts corresponding to the single-phase, liquid crystalline solution; the single-phase, isotropic solution; and the intervening two-phase region. The difference in the slopes of the two single-phase regions may be due in part to different coefficients of thermal expansion. By extrapolating the lower portion of the curve to 57°, one obtains the conductivity that the solution would have had, if superheating had been possible without transition to isotropic solution. This value is 3.25×10^{-4} mho as compared with 4.45×10^{-4} mho for the isotropic solution at the same temperature, or 73% of the latter.

The outstanding result is that the conductivity of the liquid crystalline phase is not very different from that of the isotropic solution of the colloidal electrolyte. This is in accordance with previous indications since those of the original experiments of McBain and Taylor,[5] although until now exact data have been lacking. It seems highly probable that the same colloidal micelles exist in the anisotropic solutions as in the isotropic solutions of the colloidal electrolyte, but that in the former these micelles are oriented and parallel with respect to each other over large tracts of the phase. This should have a distinct effect in reducing the effective mobility of the free cations or gegenions within the aqueous layers of the anionic micelles.

Although a large increase of viscosity occurs in passing from isotropic solution to liquid crystalline, the 37% decrease in conductance cannot be ascribed to this factor, since the change of viscosity is of an entirely higher order of magnitude, the isotropic phase being a freely flowing liquid, whereas the liquid-crystalline phase is somewhat pasty. In this respect the facts are similar to those established by Laing and McBain,[6] who were the first to show that a jelly has almost exactly the same conductivity as a sol of the same composition, in spite of the enormous difference in order of magnitude of the viscosity of the two. Probably the distinctly lower conductivity of the liquid crystal as compared with the isotropic solution should be ascribed to the larger proportion of ions having to move within the confines of the aqueous layers between parallel micelles.

A comparison of the equivalent conductances of the anomalous solution mentioned above with that of the normal solution of the same composition yields a similar result. The values are 3.538 and 2.373 mho-cm.^{2}/equiv., respectively 25°, an increase of 49% in passing from anisotropic to isotropic solution of the colloidal electrolyte. The physical chemical properties of a wide range of these solutions have been measured and will be discussed in another communication.

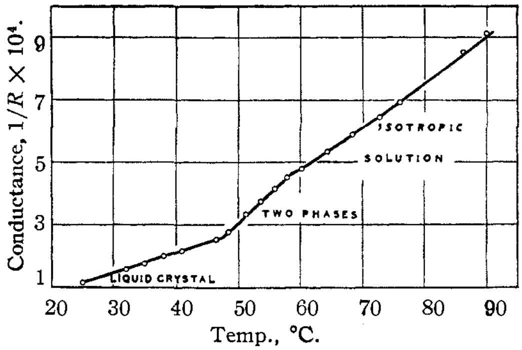

Fig. 2.—Observation of the conductance of 78.5% hexanolamine oleate system over the range from anisotropic liquid at room temperature to completely isotropic solution at elevated temperature, showing the phase boundaries and the lower conductance of the anisotropic liquid.

Summary

The phase diagram of aqueous systems of the exceptionally soluble colloidal electrolyte hexanolamine oleate has been mapped out with particular reference to the boundaries of the isotropic solutions. Although the isotropic solution extended to below room temperature both in dilute and extremely concentrated solution, two liquid crystalline solutions intervened which are stable up to 156 and 183°, respectively.

The conductances and indices of refraction of a number of these systems have been recorded.

It has been shown that the change in organization of an isotropic solution of colloidal electrolyte to anisotropic phase involves a minor decrease in electrical conductivity. It is concluded that the colloidal particles are micelles existing in both phases, but that in the anisotropic solutions the micelles are oriented and parallel over large tracts so that many of the gegenions are constrained to move within the aqueous atmospheres between the layers of micelles.

At room temperature aqueous hexanolamine oleate solution is a jelly at 12% soap, and liquefies reversibly as water is added or removed while the phase remains homogeneous and isotropic.

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(5) J. W. McBain and M. Taylor, *Z. physiol. Chem.*, **76**, 179 (1911).

(6) M. L. Laing and J. W. McBain, *J. Chem. Soc.*, **117**, 1506 (1920).