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UNIVERSITY OF LOUISVILLE

THE FIRST APPROXIMATE CONDITIONS
//
FOR THE FORMATION OF
MESOMORPHOUS COACERVATES

A Thesis

Submitted to the Faculty
of the Graduate School
of the University of Louisville
in Partial Fulfillment
of the Requirements
for the Degree of

MASTER OF CHEMICAL ENGINEERING

Department of Chemical Engineering

Stanley H. Jury

September 1947

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THE FIRST APPROXIMATE CONDITIONS
FOR THE FORMATION OF
MESOMORPHOUS COACERVATES

Stanley H. Jury

Approved by the Examining Committee:

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Abstract

An analysis of the literature shows the close analogy between liquid crystalline phases in solution (fluids separating from main portion of solution and having some of the directional properties of crystals) and unipolar coacervates (solvated micelles of like charge separating as a distinct colloidal phase). A theory is here advanced that liquid crystalline phases in solution are the direct result of a maximum in osmotic pressure which is predictable from the first approximate equation of the Debye-Huckel theory in the same manner as unipolar coacervates were predicted by I. Langmuir. Application of the theory to aqueous soaps, investigated by Vold and associates, and to aqueous 10-bromo or 10-chlorophenanthrene-6-sulphonic acid has shown remarkably good agreement. As a further step toward testing the theory a study has been made of the osmotic behavior of aqueous Amaranth and Naphthol Yellow S solutions at 20°C, utilizing the indirect method of calculation based on measurement of the concentrations of isopiestic solutions. The supposition that these dyes have liquid crystalline phases in aqueous solution has been confirmed by plots of molar concentration versus osmotic pressure which show discontinuities (constant osmotic pressure over a range of concentration) indicating two liquid phases in equilibrium namely, the liquid crystalline phase and isotropic solution. In the

case of Naphthol Yellow S two discontinuities have been developed below the normal limit of solubility given by Holmes whereas Amaranth has only one. Thus a narrower concentration range for the liquid crystalline phase is indicated for the yellow. These facts have been interpreted utilizing proposed equilibrium diagrams. Application of the theory to the first (lowest concentration) discontinuity has shown good agreement for Amaranth and less satisfactory agreement for Naphthol Yellow S. In the latter case differences between fact and theory have been reconciled based on differences in molecular structure. Predicting higher order transitions is not considered to be within the scope of the present theory because fundamentally the Debye-Huckel first approximate equation is a dilute solution theory. Moreover, the equation would be expected to show agreement only when the mass is isotropic regardless of concentration. The fact that the equation takes no account of molecular constitution other than state of charge (ionic valence) is emphasized. It has been concluded that the present theory is highly satisfactory provided it is not applied indiscriminately.

INTRODUCTION

Industries interested in applying new materials to manufacturing processes are chiefly concerned with predicting the physical character of these materials. They are equally interested in completing their knowledge of the old materials if for no other reason than to establish a basis for comparison. This is true of industries manufacturing dyes, pigments, wetting agents, paper, plastics, paints, printing inks.

Materials which deviate from the established laws of physical chemistry are particularly troublesome. There are, for example, dyes and other compounds which dissolve in a solvent to produce apparently true solutions without any evidence of supersaturation. Yet these solutions possess some crystalline properties and for this reason have been associated with the names liquid crystal, crystalline liquid, mesophase, or anisotropic fluid.* They also exhibit anomalous viscosities and indistinct phase separation which are difficult if not impossible to predict.

There are, on the other hand, certain colloidal solutions whose separation into two liquid phases (coacervation) can be predicted based on a knowledge of osmotic character. These colloids possess micelles of like charge, consequently the separating phase has been named unipolar coacervate, which

*For meanings of specific words see glossary.

closely resembles liquid crystals in solution. Consequently one might believe that the same basic idea for predicting unipolar coacervating conditions might also be applied to liquid crystals in solution.

It is, in fact, the purpose of this investigation to (a) examine the osmotic character of two supposedly liquid crystalline solutions (aqueous Amaranth and Naphthol Yellow S dye solutions) and (b) show that the conditions under which liquid crystallinity in solution will occur are identical with those for unipolar coacervates.

HISTORICAL

Hitherto the distinction between liquid crystallinity and coacervation has been one of principle rather than degree; consequently the study of each has been quite independent of the other. These studies have been grouped as follows: (a) liquid crystalline melts, (b) coacervation of colloids, and (c) liquid crystalline solutions.

O. Lehman (1) in 1888 was perhaps the first to observe that certain crystals melted to give an opaque fluid which was anisotropic and which at some higher temperature cleared to give the normal isotropic melt. Subsequent investigations revealed that there were different types of anisotropic melts. G. Friedel (2) has assigned the name Nematic mesophase to those exhibiting thread like structure, and Smectic to those having soap like structure and exhibiting Grandjean terraces (an optical figure), focal conics (an optical figure), and the like. Cholesteryl was a name given to a third class which he later considered to be Nematic.

Many have examined the causes for the existence of anisotropic melts; and although there is still considerable disagreement, it is generally accepted that fundamentally they are due to particular electrical forces peculiar to the molecules involved. In the case of Nematic type melts the Swarm theory (3) of Bose is favored. The term "Swarm" is applied

because it is hypothesized that the optical peculiarities are due to aggregates of oriented molecules. It is interesting to note that the Nematic phase will orient on a brushed surface, and as Lawrence (4) points out, the electric moment of a Swarm is 10^5 that for single molecules and thus a high degree of association must be expected.

Vorlander (5) examined liquid crystalline melts in relation to their molecular structure. He discovered that linear type molecules favored liquid crystallinity and that substituent groups and their position determined the degree and type of liquid crystal formed. P-azoxyanisole is characteristic of the Nematic type while p-azoxy benzoic di-ethyl ester is typical of the Smectic form. Many hundreds of liquid crystalline compounds were synthesized varying in molecular weights and ranging as high as 1000. Vorlander also demonstrated that certain binary mixtures of isotropic melts gave anisotropic melts. He also prepared compounds which had as high as five clearing points, there being an anisotropic fluid between each successive pair of clearing points as well as between the melting point and the first (lowest temperature) clearing point.

Between the time of Vorlander's summary in 1925 and the Faraday Society Symposium (6) in 1933 the subject of Coacervation appears in the literature. Bungenberg de Jong and Krut (7) discovered a sort of "unmixing" in certain solutions

of colloids and later in supersaturated solutions of inorganic salts. In 1930 they proposed the name Coacervation for the process of separation and Coacervate for the denser solution which separated from the original. Two types of coacervates were recognized. The simple coacervate, which came from colloidal particles of like charge, was distinguished from the complex coacervate arising from bipolar lyophilic colloidal solution. A hydration theory was proposed to explain complex coacervation phenomena.

Dobry (8) demonstrated that cellulose acetate and chloroform can form a coacervated system, the stability being due to the nearly identical densities of coacervated and liquid phase. With cellulose acetate, ethyl alcohol and chloroform the compounds of high molecular weight are in the coacervated phase and the compounds of low molecular weight in the liquid phase. The osmotic pressure of the coacervate phase, found by plotting speed of filtration through denitrated collodion and extrapolating to zero speed, was found experimentally to be equal to the osmotic pressure of the solutions in equilibrium with it. The region of coacervation lies in the region of lower osmotic pressure; in this region the osmotic pressure of the liquid in equilibrium with the coacervated phase is small but is proportional to the concentration. The analogy between a coacervate system and a liquid vapor system is limited because small pressure applied to a coacervate phase

can cause tremendous decrease in volume of that phase; this, she points out, is contrary to the behavior of liquids. The liquid lost by the coacervate phase is not appreciably reabsorbed. Van der Waals equation is not considered applicable to coacervation.

Langmuir (9) considers complex coacervates as containing positive as well as negative micelles and therefore prefers the name bipolar coacervates. The hydration theory of Bungenberg de Jong is accepted as applicable to this type coacervate. Unipolar coacervates are those from colloids having charged particles which are coacervated by the addition of a salt containing polyvalent ions of opposite sign. The formation of tactoids from thixotropic sols, of schiller layers from iron oxide sols, the separation of tobacco virus solutions and bentonite sols into two liquid layers and the crystallization of proteins are regarded by Langmuir as examples of unipolar coacervation (micelles having like charges) which may involve attractive forces.

Langmuir has shown that the Coulomb attraction between the micelles and the oppositely charged ions in the solution gives an excess of attractive force which must be balanced by the dispersive action of thermal agitation (as a first approximation) and another repulsive force (which, although operative, is not specifically treated in the theory). Thus he contends that there is no need to assume long range van der Waals forces. He has criticized the past use of energy dia-

grams because it has ignored the effect of the thermal agitation and the attraction of the "gegenions" (counter ions) in solution. Instead of potential energy he proposed that osmotic pressure, P , be used which includes these previously neglected factors. A maximum in P as the colloid concentration increases is the condition for the separation into two phases (coacervation).

According to Langmuir the Debye-Huckel (10) theory (first approximate equation) for the osmotic pressure of electrolytes takes into account both these factors and permits a rough calculation of the conditions under which coacervation occurs. The second approximate equation, which considers particle size does not agree so well with experiment as the first approximation. The reasons for this lack of agreement are discussed.

Unfortunately the work of Langmuir was not concerned with the physical determinations of osmotic pressure as such. The mathematical theory was based almost entirely on optical observation. His remains a theory which still requires experimental proof. Speaking of developing a quantitative theory by substitution of a new radius for the Debye-Huckel radius parameter Langmuir concludes:

It hardly seems worth while to develop a theory along such lines until we have far better quantitative experimental data on unipolar coacervation with colloids having particles of known character.

Although the earlier investigations of liquid crystalline solutions were carried on concurrently with those of liquid crystalline melts, the former have been the less extensive of the two. The views were quite different from those for melts and in certain respects became much more complex. In general there appeared to be two classes of liquid crystals in solution; (a) those being or resembling certain fatty acid salts and (b) those forming in what are normally considered to be true solutions. Zocher et al (11) investigated the first class and reported that potassium and sodium oleate, cetyl xanthate, commercial lecithin, and sodium naphthenate gave Smectic liquid crystalline solutions.

Table I. Weight Concentration of Aqueous Soap Solutions Having Two Phases in Equilibrium

Sodium laurate		Sodium palmitate	
Per cent soap	Phases	Per cent soap	Phases
35.8-38	Isotropic solution and middle soap	29.1-31.1	Nigre and middle soap
52-55.4	Middle soap and neat soap	52.2-56.3	Middle soap and neat soap
75-77	Neat soap and waxy soap		
88-91.3	Waxy soap and curd fibre	79.3-86.9	Neat soap and curd phase

More recently Vold and associates have carried out a phase equilibrium study of the fatty compounds dodecylsulphonic acid salts (12), sodium laurate (13), sodium palmitate (14),

sodium stearate (15), sodium oleate (16), sodium myristate (17), hexanolamine oleate (18), and others. It has been shown, for example, that the vapor pressure concentration curves for aqueous sodium laurate and sodium palmitate at 90°C exhibit flats as shown in Table 1. The flats have been interpreted as indication of the coexistence of two phases in equilibrium also shown in Table 1.

The phase equilibria study also included solubility determinations and dilatometric measurements on the aqueous soap solutions. In the case of sodium myristate and dodecylsulphonic acid the data have been presented in the form of equilibrium diagrams reproduced in Figures 1 and 2. Figure 3 is a summary of Volds work. It can be seen that flats in the vapor pressure curve represent the intervals of concentration on the equilibrium diagram corresponding to the section of shaded areas which are cut by the 90°C ordinate. It will also be shown later that one of these intervals (probably that occurring at lowest concentration) is as would be expected from the Debye-Huckel theory.

The second class of liquid crystals in solution received the attention of some of the earlier investigators. The problem of accounting for the existence of this class was attacked by Zocher (19) from the standpoint of chemical constitution much the same as Vorlander did with melts. The technique was different in that Zocher dissolved available compounds in alcohol and applied them to rubbed surfaces to

detect the presence of liquid crystals. Since Methylene Blue gave positive results he tested many hundreds of other dyes and found that Neutral Red and very few others gave a more or less feeble test. The results forced the conclusion that the property was largely confined to dyes of the azine, oxazine and thiazine classes.

Gaubert retested Methylene Blue (20) and Neutral Red in aqueous solution in addition to many other dyes especially those with para substituents and added to the list the dyes Brilliant Crocein (21) and Tartrazine (22) and also p-amino-azotoluene (23) which gave liquid crystals in a variety of organic solvents. The disturbing factor was that molecular symmetry, molecular linearity and para substituents no longer determined liquid crystallinity as was the case for the melts prepared by Vorlander.

The recent work of Branner (24) with aqueous Potassium Methyl Orange shows that this compound also produces liquid crystalline solutions. The equilibrium diagram for the aqueous system is not unlike those for soaps which have been investigated by Vold. Liquid crystals separate from isotropic solution along the boundary 0.5 molar-80°C, .1 molar-55°C and 0.02 molar- below room temperature.

About 1915 Sandqvist prepared a series of phenanthrene compounds and found that the 10-bromo- and 10-chloro-phenanthrene-6-sulphonic acid (25) (26) (27) was liquid

Fig. 2.—The phase diagram of dodecyl sulfonic acid and water: ○, T_i ; □, T_o ; ▽, T_e ; eutectic temperatures determined dilatometrically; Δ, points defining the region of pseudo-isotropic appearance; A, LSO₃H with isotropic solution; B, LSO₃H·1H₂O with isotropic solution; C, LSO₃H·1H₂O with liquid crystal; D, LSO₃H with LSO₃H·1H₂O.

Fig. 1. The Phase Diagram of Dodecyl Sulphonic Acid and Water (12)

Fig. 1.—Phase diagram of the system sodium myristate-water: O, visual T_L ; $\odot$, microscopic T_L ; $\oplus$, T_h ; $\ominus$, T_c ; Δ , from vapor pressure measurements by W. W. Lee; $\square$, from dilatometric measurements; $\blacksquare$, transition temperatures of the anhydrous soap; $\bullet$, microscopic changes; $\odot$, microscopic changes whose temperatures are less certain.

Fig. 2. The Phase Diagram of Sodium Myristate and Water (17)

Fig. 3. Field Boundaries for Isotropic Aqueous Soap Solutions (17)

crystalline in water; whereas the 10-3- (28) varieties as well as the disulpho-compounds (29) were not. For a detailed description of his findings one may quote from the abstracts (30) (31)(32):

Solutions of 10-bromophenanthrene-6-sulphonic acid in water show a clouding at a temperature which is definite for any single concentration and is the same whether measured with rising or falling temperature. The molecular weight determined from freezing point is about 1300. No supersaturation is connected with the clouding of the solution, and no marked effect accompanies the separation of the phases. It was shown in the ultramicroscope that the solution was anisotropic. At a magnification of 300 the liquid showed the rounded drops and structure of an anisotropic liquid, and there was a color play when the analyzer was rotated. The optical properties and the existence of a critical point establishes the presence of liquid crystals in the solution. Measurement of the electrical conductivity and viscosity are in progress.

Investigation of the viscosity and optical properties of aqueous solutions of 10-bromophenanthrene-6-sulphonic acid has shown that the colloidal chemical nature of the solutions varies in a very extraordinary way with the concentration. In dilute solution the acid behaves like an ordinary electrolyte, but as the concentration increases the solution becomes more and more colloidal in character and ultimately a third stage is reached when the isotropic solution comes to resemble very closely a crystalline liquid. Fall of temperature has the same effect as increase of concentration and similar changes are brought about by the addition of certain foreign substances. The viscosity of the isotropic colloidal solutions increases very rapidly with the concentration of the acid and the temperature coefficient of the viscosity is much greater than that of solutions of crystalloids, but the electrical conductivity remains approximately normal even when the viscosity has become very large. Cryoscopic measurements indicate that the molecular weight of the acid is much greater in concentrated than in dilute solutions. Hydrochloric acid, nitric acid, and sulphuric acid produce much the same effect as

increase in concentration; weaker acids, as acetic and chloracetic have no appreciable influence, and sucrose is much less active than the mineral acids. These changes seem to be completely determined by the concentration, temperature and foreign substances in the solution and independent of the previous history of the solution. There is no change in viscosity marking the change from isotropic to anisotropic condition. The temperature at which the isotropic colloidal solutions are transformed into crystalline liquids are sharply defined and depend only on the concentration of the sulphonic acid and on the nature and quantity of the foreign substances present.

The 10- chloro and 10-bromophenthrene 6-sulphonic acids give anisotropic viscous liquids. Both the chloro and bromo compounds show at 18° and .04 N solution a viscosity of 1.03 ($H_2O=1$). To 6cc of such a solution was added 1cc 3N hydrochloric acid with a resulting viscosity for the bromo derivative of 6.1 while the chloro derivative shows 140. Dilute alkali solution also produces in the chloro compound a syrupy consistency but does not affect the bromo compound.

The formulae (33) for Sandqvist acids are

where R and R' are substituent radicals (for example $R = Cl$ and $R' = SO_3Na$).

The exact significance of Sandqvist's findings are far reaching. However, for the present work, the most significant point of all is that for those compounds giving liquid crystals in solution the determining conditions were (a) solute concentration, (b) temperature, and (c) foreign electrolyte concentration. Had Sandqvist used different solvents he un-

doubtedly would have added to these factors a fourth, (d) dielectric constant. Had he lived to witness publication of the Debye-Huckel first approximate equation for predicting osmotic pressure he would undoubtedly have shown its applicability here.

THEORETICAL

Clausius according to Ghosh (34) has devised an equation of state for the osmotic work which is free from any arbitrary assumption. The equation as modified by the work of Ghosh and Lewis and Randall (35) is

$$P = \frac{nRT}{V} - \frac{nRT^3(1-g)}{3V} \quad (1)$$

where

P = osmotic pressure (units consistent with R)

V = volume of solution (cc)

n = number of moles of solute

T = absolute temperature ($^{\circ}\text{K}$)

g = osmotic coefficient (dimensionless)

R = gas constant (usually cc. atmos./mole $^{\circ}\text{C}$)

Rewriting equation 1, converting moles/cc. to ions/cc. for the ionic species $n_1, n_2, \dots, n_i$, with valences $Z_1, Z_2, \dots, Z_i$ respectively, and substituting the Lewis-Randall ionic strength (36) for the ionic concentration insofar as it involves the osmotic coefficient

$$P = kT \sum n_i - \frac{kT^3(1-g) \sum (n_i Z_i^2)}{3 \times 2} \quad (2)$$

where k is the Boltzman constant.

Debye and Huckel (10) have derived the expression

$$(1-g) = \frac{e^2}{3DkT\lambda} \quad (3)$$

where

$$\lambda = \text{the Debye distance} = \frac{DkT\sum(n_i Z_i^2)}{4\pi e^2}$$

e = unit of electrostatic charge (esu)

D = dielectric constant of solvent

Substitution of equation 3 in equation 2 produces the first approximate equation:

$$P = kT\sum n_i - \frac{1}{3} \left[\frac{\pi e^6}{D^3 kT} \right]^{\frac{1}{2}} \left[\sum (n_i Z_i^2) \right]^{3/2} \quad (4)$$

Equation 4 can be reduced to more useful forms if attention is confined to two molecular species. The one is a color molecule with the color anion of concentration n_1 and valence Z_1 and cation of concentration n_2 and valence Z_2 . The other is a foreign electrolyte of anion concentration n_3 and valence Z_3 and cation concentration n_4 and valence Z_4 . The conditions for solution electrical neutrality are then fulfilled if

$$n_2 = \frac{n_1 Z_1}{Z_2} \quad (5)$$

and

$$n_4 = \frac{n_3 Z_3}{Z_4} \quad (6)$$

Expanding equation 4 and substituting the equivalents for n_2 and n_4 from equations 5 and 6 respectively

$$P = \left[n_1 + \frac{n_1 Z_1}{Z_2} + n_3 + \frac{n_3 Z_3}{Z_4} \right] kT - \frac{1}{3} \left[\frac{\pi e^6}{D^3 kT} \right]^{\frac{1}{2}} \left[n_1 Z_1^2 + n_1 Z_1 Z_2 + n_3 Z_3^2 + n_3 Z_3 Z_4 \right]^{3/2}$$

or

$$P = \left[n_1 \frac{Z_1 + Z_2}{Z_2} + n_3 \frac{Z_3 + Z_4}{Z_4} \right] kT - \frac{1}{3} \left[\frac{\pi e^6}{D^3 kT} \right]^{\frac{1}{2}} \left[n_1 Z_1 (Z_1 + Z_2) + n_3 Z_3 (Z_3 + Z_4) \right]^{3/2} \quad (7)$$

Determination of the maximum osmotic pressure requires that $\frac{\partial P}{\partial n_1} = 0$ for any solution with a fixed concentration of

foreign electrolyte. Equation 7 becomes

$$0 = \frac{\partial P}{\partial n_1} = \frac{kT}{Z_1 Z_2} - \frac{1}{2} \left[\frac{\pi e^6}{D^3 kT} \right]^{\frac{1}{2}} \left[n_1 Z_1 (Z_1 - Z_2) - n_3 Z_3 (Z_3 - Z_4) \right]^{\frac{1}{2}}$$

or

$$n_1 = \frac{\frac{4}{\pi} \left[\frac{D k T}{e^2} \right]^3}{Z_1^3 Z_2^2 (Z_1 + Z_2)} - \frac{n_3 Z_3 \left[\frac{Z_3 Z_4}{Z_1 (Z_1 + Z_2)} \right]}{Z_1 (Z_1 + Z_2)} \quad (8)$$

Substitution of this value for n_1 in equation 7 and rearranging

$$P_{\max} = \frac{\frac{4}{3\pi} \left[\frac{D}{e^2} \right]^3 [kT]^4}{Z_1^3 Z_2^3} + kT n_3 [Z_3 + Z_4] \left[\frac{1}{Z_4} - \frac{Z_3}{Z_1 Z_2} \right] \quad (9)$$

Substituting in equations 7, 8 and 9 the recent van Rysselberghe constants (37)

$$e = 4.8025 \cdot 10^{-10} \text{ esu}$$

$$k = 1.38047 \cdot 10^{-16} \text{ ergs / } ^\circ\text{C}$$

$$n_1 = \text{ions/cc} = 6.0228 \cdot 10^{20} C_1, \text{ where } C_1 = \text{molarity}$$

$$n_3 = \text{ " " " " } C_3, \text{ " } C_3 = \text{ " }$$

$$(N = 6.0228 \cdot 10^{23})$$

$$T = 293.16 \text{ } ^\circ\text{K}$$

$$(T_0 = 273.16 \text{ } ^\circ\text{K})$$

and (38)

$$D = 80 - .4(t - 20) \text{ for water at } 0 \leq t \leq 100^\circ\text{C}$$

$$= 80 \text{ at } 20^\circ\text{C}$$

$$\pi = 3.14159$$

$$\text{atmospheres} = 9.8692 \times 10^{-7} \times (\text{ergs/cc.})$$

$$\text{ergs/cc.} = \text{dynes/sq. cm.}$$

gives the final results:

$$P = 24.054 \left[C_1 \frac{Z_1 + Z_2}{Z_2} + C_3 \frac{Z_3 + Z_4}{Z_4} \right] - 6.6313 [C_1 Z_1 (Z_1 + Z_2) + C_3 Z_3 (Z_3 + Z_4)]^{3/2} \quad (10)$$

and at $P_{\max}$

$$G_1 = \frac{5.848}{Z_1^3 Z_2^2 (Z_1 + Z_2)} - \frac{C_3 Z_3 (Z_3 + Z_4)}{Z_1 (Z_1 + Z_2)} \quad (11)$$

$$P_{\max} = \frac{46.896}{Z_1^3 Z_2^3} + 24.054 C_3 (Z_3 + Z_4) \left[\frac{1}{Z_4} - \frac{Z_3}{Z_1 Z_2} \right] \quad (12)$$

The theory may be applied to the findings of Sandqvist and Vold et al. Consider first the increase in viscosity found by Sandqvist when 1 cc of 3 molar hydrochloric was added to 6 cc of .04 N (also .04 molar for reasons to be discussed) Sandqvist acid. Before the acid was added, the approximate concentration for liquid crystallinity is

$$G_1 = 0.243 \text{ molar (apparent)}$$

and thus .04 normal solutions being considerably below this limit would show low viscosity and no liquid crystals. After the acid was added, the contrary is true for the chloro compound as indicated by equation 11 which becomes

$$G_1 = 0.243 - 0.143 = 0.10 \text{ molar (apparent)}$$

This is reasonably within the range of .04 N considering that the constant in equation 11 was evaluated at 20°C; whereas the Sandqvist experiments were carried out at 18°C.

It will be noted in the computation of G_1 that the Sandqvist acid anion was considered 0.04 molar. Justification is based on the assumption that the bond between chlorine and phenanthrene is sufficiently polar to contribute to valence considerations but is at the same time sufficiently covalent

to resist titration (or reacts with dilute caustic so slowly as to escape attention). That the halogen bond is of questionable nature is shown by Sandqvist's report (39) that the chloro compound gives up hydrochloric acid as it melts. Similarly, O. Lehman's work (40) with the bromo acid has shown that it is easily soluble in alcohol but with subsequent decomposition and precipitation. It appears that the bromo compound is an exception to the assumption in that it is probably .02 molar, and the bromine bond is more polar than that for chlorine.

Treatment of the work of Vold et al requires that equation 11 be corrected for $T = 363.16$. The new constant is 3.053 and equation 11 becomes

$$C_1 = \frac{3.053}{Z_1^3 Z_2^2 (Z_1 + Z_2)} - \frac{C_3 Z_3 (Z_3 + Z_4)}{Z_1 (Z_1 + Z_2)} \quad (13)$$

in this case of pure solutions of uni-univalent soaps $C_1 = 1.527$ mols/l.(apparent). The approximate limits for the isotropic-middle soap equilibrium are listed in Table 2. The theory agrees reasonably well in the case of sodium palmitate and excellently in the case of sodium laurate. Thus, the theory appears to be acceptable.

The question of predicting the higher order transitions which developed from the work of Vold is not considered to be within the scope of the present theory since the first approximate equation is fundamentally a dilute solution theory.

Moreover the theory would be expected to show satisfactory agreement only when one of the equilibrium phases is isotropic regardless of concentration. Any attempt to account for the higher order transitions must take into consideration the additional forces or the new arrangement of forces characterizing anisotropic phases (structures in solution).

Table II Molarity of Aqueous Soap Solutions Containing Two Phases in Equilibrium

Sodium laurate	Sodium palmitate
1.56-1.67	0.987-1.055

Finding in the literature numerous examples with which to test the present theory is surprisingly difficult. Actually those cited above are the result of a several months search. Consequently additional research, particularly on the osmotic character of certain of the acid wool dyes, is considered useful. These dyes have become the subject of investigation based on experience which has shown that they exhibit anomalies in solution paralleling those for other materials described in the literature and meeting the exact description of liquid crystalline solutions.

EXPERIMENTAL

A. PURIFICATION OF DYES AND POTASSIUM CHLORIDE

The commercial dyes, Amaranth (Geigy Co.) and Naphthol Yellow S (National Aniline Co.), were selected as the subjects of investigation. At first the method of Neale (41) utilizing sodium acetate to repeatedly salt out the dyes followed by successive alcohol extractions appeared to be best. However, the solubility of the dyes in commercial alcohol (42) (43) prohibits the use of the procedure. It was necessary therefore to develop individual procedures.

A 50g sample of Naphthol Yellow S was slurried with 50 cc distilled water, set aside 24 hours to leach, and then vacuum filtered. This process was repeated once. The cake was then slurried with 150 cc 7% by weight ammonium carbonate (Merck ACS std.) in distilled water and leached 24 hours at which time 250 cc 10% ammonium carbonate were added to thin the suspension. After 48 more hours leaching the suspension was vacuum filtered and the cake reslurried with 300 cc 10% ammonium carbonate and set aside for 10 days. After filtering, the last step was repeated for 48 hours and filtered. The cake was dried 18 hours at 105°C and then 48 hours at 95°C and 26" Hg vacuum to remove any remaining water of crystallization as well as $(\text{NH}_4)_2\text{CO}_3$.

The purified dye was tested for solubility at 26°C which, according to Holmes (43), should be 8.96g anhydrous dye /100cc saturated solution. The dye dissolved to the extent of

about 50% of this value thus indicating that the dye was probably the mono ammonium sulphonate form, i.e., the hydroxyl did not form salt. The sodium content of the dye was nil as indicated by .0047 grams of ash obtained from 1.8548 grams purified dry sample. The pH of a saturated aqueous solution was 4.9 instead of the usual 8-8.5 for the raw form.

The purified Naphthol Yellow S was dissolved in distilled water, and NaOH (Merck) added in comparatively small quantity. The released ammonia (bound by the acid radicals) was removed by boiling till no further odor could be detected. This procedure was repeated several times until the pH of the saturated solution rose to 8.5. At this point a very small amount of NaOH increased the pH to 11. The resulting solution was concentrated sufficiently for crystallization. The precipitate was recrystallized from distilled water three more times and then made up in a standard distilled water solution. Drying a five cc sample in vacuo as before gave a concentration of .217 moles /L (mol. wt. ammonium salt = 358.20.).

A 50 gram sample of Amaranth was treated the same as the Yellow excepting for the caustic treatment. It too showed approximately half the solubility specified by Holmes (43) which is 7.20 g anhydrous dye /100cc saturated solution. From 1.0907 g purified Amaranth were obtained 0.2392 grams ash. The brown color of the ash indicated iron. Reashing with fuming nitric acid did not change the color nor the weight to

any significant extent. Solution of the ash in aqua regia gave a brown solution which after diluting and filtering with subsequent neutralization with ammonia gave the typical ferric hydroxide coagulum and water clear supernat liquid.

Large losses in purification necessitated starting with a new raw sample of 25 grams of Amaranth. This time it was slurried with 66cc water and 34cc concentrated HCL (Grasselli) and after 24 hours leaching it was vacuum filtered. The filtrate was deep brown (not bright red) indicating removal of iron which was confirmed by adding NH_4OH to give the same results as before.

The Amaranth precipitate was reslurried with 34cc concentrated HCL and 66cc water. The dye showed some solubility, and therefore 34cc more concentrated HCL were added. After being leached 8 hours the sample was filtered and washed on the filter with two 20cc portions of 6 molar acid. The precipitate was reslurried with 50cc 6 molar HCL and refiltered. The precipitate was washed on the filter with an additional 50cc 6 molar acid. By this time the dye showed remarkable solubility. The precipitate was dried by starting at 68°C and gradually raising it to 105°C during 24 hours.

Qualitative ashing as before showed only a faint trace of light tan color this time. The purified Amaranth sample was therefore dissolved in distilled water and neutralized with concentrated ammonia till a distinct odor of

ammonia persisted. The solution was boiled until all ammonia odor vanished. Boiling was continued until the solution became syrupy. The resulting solution was diluted and cooled to give a standard solution. Analysis as for Naphthol Yellows S gave a concentration of .133 molar (Amaranth molecular weight is 589.60).

Potassium chloride was selected as the standard for "isopiestic" comparison of vapor pressure to be described later. Purification consisted of dissolving 56g potassium chloride (Merck ACS grade) in 100cc distilled water, boiling to 50cc, and setting aside for 24 hours to permit recrystallization. A standard solution was made up which gave on analysis a concentration of 0.182 molar. (molecular weight of KCl is 74.55)

B. APPARATUS

Calculation of osmotic pressure (44) from measured vapor pressure and solution density was considered a most convenient method of carrying out this investigation. Preliminary measurements with a Bronsted-Richards (45) type differential vapor pressure comparator showed that our apparatus was not reliable without a complicated technique for continuously detecting leaks. Consequently the isopiestic apparatus devised by Robinson (48) and perfected by Seatchard (47) was decided upon.

The Seatchard apparatus consisted of a brass vacuum dessicator 3-7/8" in diameter 3-5/8" deep with a 3/16" wall into which could be inserted a brass pedestal with a 3-1/4" diameter top and 9/16" thickness and a 3/4" diameter 1/2" high centered support. The pedestal could be bolted in place. The pedestal has four 13/16" holes drilled 90° apart. The center of each hole is 7/8" from the center of the pedestal top. The size of the holes is such as to permit an easy fit of four gold plated brass cups which are 1" high and flared at the top allowing insertion of snug fitting brass covers for weighing purposes.

The brass dessicator was fitted through a lead gasket seal to a 1/2" thick 4" diameter removable brass top equipped with a centrally located white metal valve and detachable

screw nipple for attachment to a Cenco Hyvac oil vacuum pump. The desiccator top could be clamped in place by standing the assembly in a rectangular, vertical steel frame which had two thumb screws at the top to permit clamping action.

A steel shaft fitted with a pulley was welded to the top of the rectangular frame so that the complete assembly could be tilted at 45° and rotated in a brass bearing which was so located that the desiccator assembly would be completely immersed in a standard Sargent type thermoregulated water bath. The speed of rotation was 24 rpm.

The principle of operation is based on the isothermal distillation of water from regions of higher vapor pressure to those of lower vapor pressure until the vapor pressure of all regions (solutions) are equal. At equilibrium the solutions are said to be "isopiestic" (meaning equality of vapor pressure). Removal of air from the system eliminates errors due to gasses dissolved in solution and also removes foreign molecules from the distillation path between the gold plated cups containing the solutions.

The isothermal condition places a rather strenuous specification on a standard Sargent bath. It was found necessary to insert a low current relay into the normal circuit so as to obtain $20 \pm .09^\circ\text{C}$ regulation. This was considered adequate because the off-to-on time and vice versa normally amounted to one minute or less and thus the mass of metal involved could act as thermal buffer.

Fig. 4. Vacuum Desiccator,
Frames and Auxiliaries

Fig. 5. Vacuum Desiccator
Partially Assembled
Preparatory to
Loading.

Fig. 6. Vacuum Desiccator
Loaded and Clamped in Frame.

Fig. 7. Complete Desiccator
and Frame Assembly
Submerged in Thermo-
stat.

Fig. 8. Apparatus

In order that most effective thermal contact between pedestal and gold plated cups would be assured, about 20cc of KCL buffer solution was placed under the pedestal. Because of the 45° tilt, the buffer solution had easy access to the very small space (if any) between pedestal and cup. Thermal contact between solutions in the cups and the vapor phase was assured by partial immersion of a tiny nichrome wire helical in the solution of each cup. The helical has the added advantage that it increases stirring action through rotation, and increases the exposed surface of solution thus decreasing the time required to reach equilibrium.

The Scatchard isopiestic apparatus and auxiliaries are shown in Figs. 4-8.

All density determinations were made at 20°C using a 25 cc glass pycnometer equipped with ground glass capillary and ground glass thermometer. The weighings were made on a chainomatic type gravimetric balance equipped with a vernier making possible the reading of the fourth decimal place.

C. PROCEDURE

The density determinations were carried out in accordance with the procedure described in almost any elementary textbook of experimental physical chemistry and requires no further explanation than to mention that all solutions were made up volumetrically from the standard solutions and the tare of the dry assembled pycnometer was 18.4664 grams. It is also important to note that standardization of the pycnometer against pure water gave a density of 0.9991 grams/cc. at 20°C; whereas the accepted value, according to Lange's handbook, is 0.9982. Consequently all subsequent determinations were corrected by multiplying by the factor 0.9982/0.9991.

The technique employed in the determination of vapor pressures was that described by Scatchard. Before any runs were made the thermoregulated bath was standardized against a new Beckman type 0.01° mercury thermometer which in turn had been standardized using a 0-100°C thermometer (Sargent) calibrated to 0.1°C. During each run the bath was constantly checked using both thermometers.

Prior to starting a run the desiccator assembly, including three of the gold plated cups, nichrome helicals, and caps, was cleaned thoroughly and dried. Each cup, helical, and cap assembly were given a number; #1 was used exclusively for KCL solutions, #2 for Amaranth, and #3 for Naphthol Yellow S. After each assembly was tared, a measured volume of the

appropriate solution was placed in each cup, and then the assemblies were immediately reweighed. Each solution was previously prepared from its standard stock solution using a predetermined dilution ratio which was standard for all solutions made up for the particular run.

The desiccator was prepared by placing in it 17-20cc of a KCL buffer solution of approximately the same concentration as that in the KCL cup. The pedestal was inserted and bolted in place and all sealing surfaces liberally coated with vacuum sealing grease. At this point the cups were inserted, the caps removed, and the desiccator top clamped in place as rapidly as possible. The desiccator was evacuated for about ten minutes with gentle shaking to assist in boiling out the last traces of air. The vacuum valve was then closed and the detachable nipple replaced with a brass plug.

The complete assembly was rotated in the water bath; and after equilibrium had been reached, the procedure was repeated in reverse order. All three cups were capped as soon as the desiccator was opened, rinsed with distilled water, dried thoroughly, and immediately weighed. The buffer solution was remeasured to check for leaks, starting volume or less being the only basis on which a run was accepted for further consideration.

The time required for equilibrium was determined from a few preliminary runs. Less than one millilitre of solution in the cup always gave negligible change after three

days and up to 16 days even in the case of more dilute solutions. Three days was therefore adopted as standard.

D. RESULTS

A preliminary examination of the thermodynamic equation (44)

$$P = \frac{RT}{V_1} \ln \frac{p_0}{p_0 - (p_0 - p)} \quad (14)$$

where

$$V_1 = \frac{M_1}{1000 \left[\rho - C \frac{d\rho}{dC} \right]}$$

and

M_1 = gram molecular weight of the solvent

ρ = density of the electrolyte solution at the equilibrium concentration C , moles/l

$\frac{d\rho}{dC}$ = rate of change in solution density with change of concentration at equilibrium concentration C , moles/l

R = gas constant in liter-atmospheres

T = Kelvin temperature prevailing during the experiment

p_0 = vapor pressure of the pure solvent at the prevailing temperature (17.535 mm Hg at 20°C)

$p_0 - p$ = vapor pressure lowering at the equilibrium concentration of dissolved electrolyte

P = osmotic pressure of the solution in atmospheres

revealed that it would be most convenient to have the mathematical expressions for both $(p_0 - p)$ and P in terms of the concentration, C .

Graphical analysis of the density- determinations gave straight line relationships when ρ was plotted against C .

The equation of these straight lines were

$$\rho = .9982 + .2712C \quad (\text{Amaranth } 0 \leq C \leq .133) \quad (15)$$

and

$$\rho = .9982 + .2006C \quad (\text{Naphthol Yellow S } 0 \leq C \leq .298) \quad (16)$$

A similar plot of the data for KCl from Lange (48) handbook gave

$$\rho = .9982 + .0473C \quad (0 \leq C \leq .272) \quad (17)$$

A survey of the literature on vapor pressures of dilute aqueous KCl solutions at 20°C revealed that the data of Lovelace, Fraser and Sease (49) were most satisfactory. The equation

$$P_0 - P = \frac{.5950}{1 + .186C} \quad (18)$$

was derived by the method of simultaneous equations and gave a very satisfactory fit.

As a corollary of equations 15, 16 and 17

$$\% \text{ by wt. Amaranth} = \frac{217.4C}{3.681 + C} \quad (19)$$

$$\% \text{ by wt. Naphthol Yellow S} = \frac{178.6C}{4.976 + C} \quad (20)$$

$$\% \text{ by wt. KCl} = \frac{157.6C}{21.20 + C} \quad (21)$$

As a corollary of equations 15, 16, 17, 19, 20, and 21 and the fact that the concentration volume product is a constant for any one solution both before and after an isopiestic determination it is possible to derive the following simplified expressions (see appendix) for equilibrium concentrations:

$$C_e = \frac{3.681}{\frac{W_e}{W_s} \left[28.64 + 27.64 \frac{V_{H_2O}}{V_{Std. Soln.}} \right] - 1} \quad (\text{Amaranth}) (22)$$

$$C_e = \frac{4.976}{\frac{W_e}{W_s} \left[23.94 + 22.94 \frac{V_{H_2O}}{V_{Std. Soln.}} \right] - 1} \quad (\text{Naphthol Yellow S}) (23)$$

$$C_e = \frac{21.10}{\frac{W_e}{W_s} \left[115.6 + 114.6 \frac{V_{H_2O}}{V_{Std. Soln.}} \right] - 1} \quad (\text{KGL}) (24)$$

where

W_s = wt. of solution placed in the cup

W_e = wt. of solution at equilibrium

V_o = volume of the constituent used in making up the solution from which W_s was withdrawn.

Reexamination of equation 14 now shows that for solutions herein considered (50)

$$P = 3817.0 - 3068.6 \log (17.535 - (p_o - p)) \quad (25)$$

when the values of the constants are substituted because in every case $\rho = 0.9982 + \text{slope} \cdot C_e$ and $\frac{d\rho}{dC_e} = \text{slope}$ thus reducing $\rho - C_e \frac{d\rho}{dC_e}$ to the constant, 0.9982.

The exact procedure for computation of the results of any one isopiestic determination is reduced to three steps which are (a) the computation of equilibrium concentrations using equations 22, 23, and 24; and (b) the computation of $p_o - p$ using equation 18 combined with the value C_e computed from equation 24 and (c) the computation of the osmotic pressure using equation 25. The calculated values of C_e and $p_o - p$ for each run are presented in Table 3. They are also plotted

in Figs. 9 and 10.

The actual plots and calculated values of equation 25 are not included because any conclusion derived from them is also equally obvious from Figs. 9 and 10. Equation 25 would serve only to modify slightly the contour of curved portions of the figure but would leave horizontal flats unaffected. In either case it is the flats in which one is primarily interested. Hence all subsequent discussion pertaining to osmotic pressure refers to Figs. 9 and 10 with equation 25 being understood.

Table III Calculated Equilibrium Concentrations for Isopiestic Solutions

Run No.	Duration (days)	Concentration, G. (molarity)			Vapor pressure lowering (mm Hg)
		Potassium Chloride	Amaranth	Napthol Yellow S	
1	2	.017	.013	.020	.0104
2	3	.185	.162	.217	.1064
3	16	.092	.078	.086	.0542
4	3	.077	.063	.073	.0454
5	3	.142	.127	.155	.0825
6	3	.133	.122	.144	.0777
7	3	.087	.076	.084	.0514
8	3	.078	.065	.076	.0462
9	5	.078	.066	.076	.0460
10	4	.075	.065	.073	.0444
11	3	.167	.161	.190	.0969
12	3	.154	.145	.170	.0894
13	3	.135	.123	.142	.0785
14	2	.115	.101	.118	.0670
15	3	.165	.159	.185	.0950
16	3	.051	.038	.046	.0302
17	3	.048	.036	.041	.0285
18	3	.070	.056	.059	.0410
19	5	.068	.055	.059	.0401
20	3	.060	.048	.052	.0355
21	4	.053	.042	.046	.0315
22	3	.098	.087	.090	.0572

Note: Runs 11 and 12 were defective.

Fig. 9. Vapor Pressure Depression of Aqueous Amaranth Solutions at 20°C.

Fig. 10. Vapor Pressure Depression of Aqueous Napthol Yellow S Solutions at 20°C.

E. DISCUSSION

Inability to control a thermoregulated bath at 20°C during the summer months when tap water is considerably warmer, made it necessary either to add more equipment or to discontinue operations. The latter alternative was chosen considering that the available data were unusually consistent and gave a positive indication of the discontinuities which were of course expected. This procedure necessitated estimating the portions of the curves over the discontinuities. The estimates have been shown as flats since in two cases out of the three it is next to impossible to draw in any reasonable continuous estimate which would not have at least one point of zero slope. The ordinate of the flats were arbitrarily selected as the arithmetic average of the ordinates of adjacent data points.

The flat in the case of Amaranth might be questioned because there are only three points on the lower portion of the curve to support claim to the lower concentration boundary of the flat. This question appears unfounded, however, when it is considered that all data points around the flat are not only self consistent but are based on the same sample thus eliminating many possible sources of error which might be interpreted to account for the phenomenon.

Assuming the validity of the flats one resorts to

the phase rule for their interpretation. It is immediately obvious that they represent the coexistence of two phases which are in all probability isotropic solution and mesomorphous or liquid crystalline solution. Mesomorphism is a presupposition based on the microscopic character of these solutions.

According to the theory proposed the coexistence of the two phases is the direct result of a maximum in osmotic pressure having been obtained. That this is true is confirmed by Figs. 9 and 10, wherein the flats would represent the natural course of events. In order to test the ability of the theory to predict the occurrence of the lower concentration flats or split into two phases, one must again refer to equation 11.

For Amaranth whose formula is

Z_1 is 3 and Z_2 is 1 and thus for pure aqueous solutions at 20°C

$$C_1 = 0.054 \text{ molar (apparent)}$$

This agrees remarkably well with the range 0.038- 0.042 for the flat as read from Figs. 9 and 10.

Napthol Yellow S has the formula

where Z_1 is 2, Z_2 is 1 and

$$C_1 = 0.243 \text{ molar (apparent)}$$

From Figs. 9 and 10 the range of concentration is actually 0.062 to 0.070 which represents rather poor agreement. This fact might at first lead to a question of purity or some other factors, but experience shows that the findings are valid.

The results can be verified for both dyes by application of their aqueous solutions to glass and allowing them to become more concentrated through normal evaporation. The surface orienting effect of glass on the mesophase can be detected in polarized light. In the case of Amaranth the surface effect is always detectable. This is not true of the Yellow, however. Yellow solutions more concentrated than 0.1 molar do not show the effect. Solutions less concentrated than about 0.1 molar do show the effect only if evaporation is fairly rapid.

All the facts can be best explained by the schematic diagrams, Figs. 11 and 12. For both dyes the drying operation proceeds from left to right across the diagrams at approximately the 20°C level (lower quarter of diagram). As the common limit of solubility (line enclosing right hand shaded field) is crossed under normal drying conditions the Amaranth apparently gives a supersaturated mesophase, whereas the Yellow crystallizes out. In the case of rapid evaporation Amaranth acts the same as before, but the Yellow produces a supersaturated mesophase only when the starting solution is

sufficiently dilute to cross the mesophase region.

The lack of good agreement between theory and experiment in the case of the yellow is also not too disturbing when cognizance is taken of the fact that the theory recognizes no differences in molecular constitution. That this factor is operative is evidenced by the following quotation from Vold (12):

For such mesomorphic forms to exist the molecule must contain groups of contrasting intermolecular forces so that a temperature range exists within which the violence of thermal agitation is large enough to overcome some but not all of the mutual attractions and repulsions which at a lower temperature lead to the arrangement of the molecules in a regular crystal lattice. Further, these groups must be so located that such a partial melting permits a random distribution in some directions without disturbing the regular periodic spacing in other directions.

Even though Amaranth and Naphthol Yellows S are both sulpho salts and the yellow would be expected on this basis to show the same good agreement as Amaranth, the fact that the yellow differs in that it is a nitro compound can not go without recognition. It appears, therefore, that the theory is highly satisfactory provided it is not applied indiscriminately.

Fig. 11 Proposed Phase Diagram for the
System Amaranth and Water

Fig. 12 Proposed Phase Diagram for the
System Naphthol Yellow S and Water

SUMMARY AND CONCLUSIONS

A study of the osmotic behavior of aqueous Amaranth and Naphthol Yellow S solutions at 20°C has been carried out using the indirect method of measuring the concentrations of isopiestic solutions. These results in conjunction with others from the literature have been used in testing the theory proposed that liquid crystalline mesophases are the direct result of a maximum in osmotic pressure which can be predicted from the Debye-Huckel theory first approximate equation exactly the same as unipolar coacervates were predicted by Langmuir.

It has been found that both dyes do exhibit phase separation, but the Naphthol Yellow S exhibits the phenomenon over a narrower range of concentration than does the Amaranth.

All cases including those from the literature agree remarkably well with the theory proposed with the exception of the case of Naphthol Yellow S. In the latter case the difference between fact and theory has been reconciled based on differences in molecular constitution.

It has been concluded that the theory is highly satisfactory provided it is not used indiscriminately.

LITERATURE CITED

Periodicals

- (3) Ornstein, L. S. and Kast, W., Trans Faraday Soc., 29, 931-44 (1933)
- (4) Lawrence, A. S. C., Roy. Microscop. Soc., 58, 30 (1938)
- (6) Symposium, Trans. Faraday Soc., 29, 899-1086 (1933)
- (7) Bungenberg de Jong, H. G. and Kruyt, H. R., Kolloid Z., 50, 39-48 (1930)
- (8) Debry, Mae. A., J. Chim. Phys., 36, 102-10 (1939)
- (9) Langmuir, I., J. Chem. Phys., 6, 873-96 (1938)
- (10) Debye, P. and Huckel, E., Physik. Z., 25, 97 (1924)
- (11) Zocher, H. and Birstein, V., Z. physik. Chem., Abt. A, 142, 177-85 (1929)
- (12) Vold, M. J., J. Am. Chem. Soc., 63, 1427-32 (1941)
- (13) Vold, R. D. and Vold, M. J., J. Am. Chem. Soc., 61, 37-44 (1939)
- (14) Vold, R. D. and Ferguson, R. H., J. Am. Chem. Soc., 60, 2066-76 (1938)
- (15) McBain, J. W., Vold, R. D. and Frick, M., J. Phys. Chem., 44, 1013-24 (1940)
- (16) Vold, R. D., J. Phys. Chem., 43, 1213-31 (1939)
- (17) Vold, R. D., Reivere, R. and McBain, J. W., J. Am. Chem. Soc., 63, 1293-6 (1941)
- (18) Gonick, E. and McBain, J. W., J. Am. Chem. Soc., 68, 683-5 (1946)
- (19) Zocher, H. and Coper, K., Z. Physik. Chem., 132, 295 (1928)
- (20) Gaubert, P., Compt. rend., 200, 679-80 (1935)
- (21) Ibid, 198, 951-3 (1934)
- (22) Ibid, 197, 1436-8 (1933)
- (23) Ibid, 163, 392-4 (1916)

- (24) Branner, Fr., Nord. Kemikermode, Forh. 5, 207-9 (1939)
- (25) Sandqvist, H., Kolloid Z., 19, 113-21 (1916); J. Chem. Soc., II, 110, 586
- (26) Sandqvist, H., Ber. 48, 2054-5 (1915)
- (27) Sandqvist, H., Arkiv. Kemi. Min. Geol., 7, #2 (1917)
- (28) Sandqvist, H., Arkiv. Kemi. Min. Geol., 6, #13 (1917)
- (29) Sandqvist, H., Ber. 50, 774-7 (1917) through J. Chem. Soc. I, 112, 552
- (30) Sandqvist, H., Chem. Absts., 10, 715 (1915)
- (31) Ibid, 11, 1350 (1916)
- (32) Ibid, 12, 807 (1917)
- (33) Sandqvist, H., Ber. 53, 168-71 (1920)
- (34) Ghosh, J. C., J. Chem. Soc., 113, 707-15 (1918)
- (37) Van Rysselberghe, P., J. Am. Chem. Soc., 65, 1249 (1943)
- (39) Sandqvist, H. and Hagelin, A., Ber. 51, 1515-26 (1918)
- (40) Lehmann, O., Ann. Physik., 55, 81-102 (1918)
- (41) Neale, S. M., Am. Dyestuff Reprtr., 23, 109-11 (1934)
- (42) Holmes, W. C., Stain Tech., 2, 68-70 (1927)
- (43) Ibid, 3, 12-13 (1928)
- (45) Bronstead and Richards, J. Am. Chem. Soc., 50, 3028-36 (1928)
- (46) Robinson, J. Am. Chem. Soc., 56, 1830-36 (1934)
- (47) Seatchard, G., Hamer, W. J. and Wood, S. E., J. Am. Chem. Soc., 60, 3061-70 (1938)
- (49) Lovelace, B. F., and Sease, V. B. and Fraser, J. C. W., J. Am. Chem. Soc., 43, 102-10 (1921)
- (52) Lawrence, A. S. G., Trans. Faraday. Soc., 29, 1008-15 (1933)

- (53) Rinnie, F., Trans. Faraday. Soc., 29, 1016-32 (1933)
- (54) Mlodzieyevskii, A., Kryst. Min., 52, 1-10 (1913)
- (55) Vold, M. J., J. Am. Chem. Soc., 65, 465-9 (1943)
- (56) Scheibe, G. and Kandler, L., Naturwissenschaften., 26, 412-13 (1938)
- (57) Sheppard, S. E., Science, 93, 42-3 (1941)
- (58) Scheibe, G., Kandler, L. and Ecker, H., Naturwissenschaften, 25, 75 (1937)
- (59) Jelley, E. E., Nature, 139, 631-2 (1937)
- (60) Scheibe, G., Marais, A. and Ecker, H., Naturwissenschaften, 25, 474-5 (1937)
- (61) Hoppe, W., Kolloid Z., 101, 300-5 (1942)
- (62) Zoehrer, H., Z. physik. Chem., 98, 293-337 (1921)
- (63) Szegvari, A., physik. Chem., 112, 295-316 (1924)
- (64) Zoehrer, H., Z. anorg. allgem. Chem., 147, 91-110 (1925)
- (65) Ostwald, Wo. and Walter, R., Kolloid Z., 76, 291-313 (1936)
- (66) Papkova, T. P., - Kwitzel, Kolloid., 69, 57-65 (1934)
- (67) Ibid, 71, 165-8 (1935)
- (68) Hatschek, E. and Jane, R. S., Kolloid Z., 39, 300-13 (1926)
- (69) Freundlich, H., Schuster, C. and Zoehrer, H., Z physio. Chem., 105, 119-44 (1923)
- (70) Krause, G. A., Brit. pat. 483, 221 April 7, 1938
- (71) Kondo, T., Z. wiss. Phot. 31, 153-67, 185-99 (1932)
- (72) Kuhn, W. and Erdos, G., Kolloid Z., 70, 241-61 (1935)
- (73) Zoehrer, H., and Jacoby, F. G., Kolloidchem. Beihefte, 24, 365-417 (1927)

Books

- (1) Lehman, O., "Molekular Physik.", Leipzig (1888)
- (2) Friedel, G., Chapt. III of Alexander, J., "Colloid Chemistry", Vol. I. NY, The Chemical Catalogue Co., Inc., (1926)
- (5) Vorlander, D., "Chemische Kristallographie der Flussigkeiten", University Hall a.d.s. (1924)
- (35) Getman, F. H. and Daniels, F., "Outlines of Theoretical Chemistry", 5th. edition, p. 479. NY, John Wiley and Sons, (1931)
- (36) Lewis and Randall, "The Thermodynamics and the Free Energy of Chemical Substances", p 373, NY, McGraw Hill Book Company (1923)
- (38) "International Critical Tables", Vol VI, pg. 78 NY, McGraw Hill Book Company, Inc. (1929)
- (44) Glasstone, S., "Textbook of Physical Chemistry", 2nd. edition, pp. 669-70 NY, D. Van Nostrand Company, (1946)
- (48) Lange, N. A., "Handbook of Chemistry", 6th. edition, p. 1291 Sandusky, Ohio, Handbook Publishers, Inc., (1946)
- (50) Lange, N. A., "Handbook of Chemistry", 6th. edition, p. 1444 Sandusky, Ohio, Handbook Publishers, Inc., (1946)
- (51) Freundlich, H., "New Conceptions in Colloidal Chemistry", Pg. 108 NY, Dutton and Company, (1926)

APPENDIX

List of Symbols

cc	Cubic centimeters
C_i	Molar concentration at the i^{th} stage or for the i^{th} mole specie
D	Dielectric constant of solvent
e	Unit of electrostatic charge (esu)
g	Grams
g	Osmotic coefficient (dimensionless)
k	Boltzman constant, R/N , where N is the Avogadro number
l	Liter
M_1	Gram mole weight of solvent
M_2	Gram mole weight of solute
mm	Millimeters
n	Gram moles
N	Normality expressed as gram equivalents per liter Avogadro's number
n_i	Number of gram ions of i^{th} specie in a cubic centimeter
P	Osmotic pressure in consistent units
p	Vapor pressure (consistent units). Subscript zero indicates pure solvent
R	Gas constant (consistent units)
T	Absolute temperature (K°)
V_1	Partial molar volume of solvent referred to solvent in vapor state
V	Volume (cubic centimeters)
W_i	Gram weight as i^{th} stage
λ	The Debye distance (consistent units)

ρ Density (grams/cc)

o,s,e, Subscripts referring to the specific stages of a run, namely, preparatory, starting and at equilibrium respectively.

Glossary

Anisotropic	Having directional properties
Anomalous	Abnormal
Bipolar	Possessing both positive and negative charged particles
Coacervate	Solvated micelles which have collected into a liquid aggregate
Coacervation	The process of dividing into a coacervate phase and supernant liquid phase
Common limit of solubility	The normal solubility as determined by standard methods
Complex coacervate	Containing positive and negative solvated micelles (bipolar coacervate)
Crystalline liquid	See liquid crystalline
Gegenions	The German equivalent for counter ions or ions of opposite charge
Homopolar	Having one type of charge
Indistinct phase separation	Two phases, the one being finely dispersed in the other
Isopiestic	Equal vapor pressures
Isotropic	Without directional properties
Liquid crystalline	Liquid possessing some properties of crystal
Lyophilic	Having affinity for solvent
Mesomorphous	Being intermediate between crystal and liquid (liquid crystalline)
Mesophase	An intermediate phase, in this case the liquid crystalline or anisotropic liquid phase
Metastable	Temporarily existent (unstable)

Molar(apparent)	Mols/l concentration calculated from formulae involving ionic strength
Nematic	A type of liquid crystal with thread like structure
Simple coacervate	Containing solvated micelles of like charge (unipolar coacervate)
Smectic	A type of liquid crystal with soap like structure
Streaming double refraction	Refracting power which due to flow differs in two directions at right angles to each other
Swarm	An ordered arrangement of particles (probably molecules) in a liquid mass
Tactoid	Coacervate which spontaneously assumes a common orientation resembling a swarm
Thixotropic	Fluids whos viscosity is sensitive to touching or stirring
Unipolar coacervate	Solvated micelles of like charge which have collected into a liquid aggregate

Table IV Density of Aqueous Amaranth Solutions at 20°C.

Concentration (molarity)	Net weight of solution in pycnometer (g)	Density (g/cc.)
.000	24.9789	.9982
.005	25.0148	.9997
.011	*24.9990	.9990
.015	25.0838	1.0024
.022	*25.0838	1.0024
.033	*25.1684	1.0058
.035	25.2176	1.0078
.044	*25.2490	1.0090
.053	25.3374	1.0126
.055	*25.3253	1.0121
.057	25.3664	1.0137
.066	25.4242	1.0160
.070	25.4527	1.0172
.075	25.4882	1.0186
.077	*25.4257	1.0161
.088	25.5703	1.0219
.091	25.5876	1.0226
.099	*25.6669	1.0233
.100	25.6563	1.0253
.109	25.7242	1.0280
.111	25.7384	1.0286
.119	25.7878	1.0306
.122	*25.7827	1.0304
.132	*25.8658	1.0337
.138	25.8822	1.0343

Note (*) values rejected due to air bubbles.

Table V Density of Aqueous Naphthol Yellow S Solutions at 20°C.

Concentration (molarity)	Net weight of solution in pycnometer (g)	Density (g/cc.)
.018	25.0706	1.0019
.036	25.1640	1.0056
.054	25.2555	1.0093
.072	25.3470	1.0129
.090	25.4369	1.0165
.108	25.5358	1.0205
.126	25.6224	1.0239
.145	25.7113	1.0275
.163	25.8006	1.0311
.181	25.8901	1.0347
.199	25.9811	1.0383
.208	26.0249	1.0400
.217	26.0676	1.0418
.225	26.1056	1.0433
.243	26.1783	1.0462
.253	26.2438	1.0488
.269	26.3201	1.0519
.286	26.3966	1.0549
.298	26.4521	1.0571
.380	26.8233	1.0720

Table VI Starting and Equilibrium Weights of Solutions

Run No.	Starting weight (g)			Equilibrium weight (g)		
	Potassium Chloride	Amaranth	Napthol Yellow S	Potassium Chloride	Amaranth	Napthol Yellow S
1	1.0014	.9967	.9906	.9571	.9258	.9510
2	1.0314	1.0266	1.0462	1.0258	.8496	1.0414
3	.5100	.5208	.5170	.5066	.4458	.6432
4	.5066	.4458	.6432	.6067	.5481	.7597
5	.5134	.5122	.5095	.5314	.4303	.5673
6	.5314	.4303	.5673	.5646	.4460	.6102
7	.5646	.4460	.6102	.8588	.7100	1.0269
8	.8588	.7100	1.0269	.9568	.8181	1.1342
9	.9568	.8181	1.1342	.9602	.8120	1.1400
10	.9602	.8120	1.1400	.9950	.8215	1.1795
13	.5125	.5127	.5445	.5615	.4253	.6185
14	.5615	.4253	.6185	.6097	.4701	.6859
15	.6097	.4701	.6859	.6963	.5538	.8182
16	.6963	.5538	.8182	.8172	.6671	.9761
17	.8172	.6671	.9761	.5727	.4320	.6360
18	.5068	.4996	.5199	.6067	.5832	.8153
19	.6067	.5832	.8153	.6426	.6102	.9034
20	.6426	.6102	.9034	.4462	.3947	.6348
21	.4462	.3947	.6348	.4556	.4048	.6326
22	.4556	.4048	.6326	.5159	.4640	.7153
23	.5159	.4640	.7153	.5816	.5268	.8154
24	.5816	.5268	.8154	.3181	.2582	.4184

Table VI Con't.

Note: Composition of solutions placed in cups for Run 1 was 0.5 volumes standard solution to 5 volumes water. Run 2 was standard solutions. Run 3 was half and half by volume, and it was not changed for Run 4. Run 5 was 2 volumes standard solution to 0.5 volumes water and was not changed for Runs 6-11. Runs 11 and 12 were rejected for defects and leaks. Run 13 was standard solutions which were not changed for Runs 14-17. Run 18 was 1 standard solution to 2 water and was used through Run 24.

Table VII The Lowering of the Vapor Pressure of Water
at 20°C Produced by Dissolved Potassium Chloride (49)

Concentration (moles per 1000 g. water)	Concentration (molarity calculated)	Vapor pressure lowering (mm Hg)
.0498	.0496	.0293
.0704	.0698	.0408
.0997	.0987	.0573
.2013	.1980	.1136

Note: Vapor pressure of pure water at 20°C is 17.535 mm Hg

Table VIII Density of Aqueous Potassium
Chloride Solutions at 20°C (48)

Concentration (g/l.)	Specific Gravity (g/cc.)
10.05	1.0046
20.22	1.0110
40.96	1.0239

Sample Calculations

Illustration 1. Computing the density of a 0.133 molar Amaranth aqueous solution from data given in Table 5 of the appendix.

Net weight of solution is 25.8822 grams

Pycnometer correction is 0.9982/0.9991

$$\rho = \frac{\text{Net weight of solution} \times \text{Pycnometer correction}}{\text{Apparent volume of solution}}$$

$$= \frac{25.8822 \times 0.9982}{(25 \times 0.9991)} = 1.0343 \text{ grams/cc.}$$

Illustration 2. Computing the equilibrium concentration of the Amaranth solution in Run 1 from data given in Table 7 of appendix.

$$V_o \text{ water} = 5 \text{ cc.}$$

$$V_o \text{ std. soln.} = .5 \text{ cc.}$$

$$W_o = .9258$$

$$W_s = .9967$$

$$C_o = \frac{C_s \times \text{Volume of solution in cup at start}}{\text{Volume of solution in cup at equilibrium}}$$

$$\text{Volume of solution in cup at equilibrium} = \frac{W_o}{\rho_o}$$

$$C_s \times \text{Volume of solution in cup at start} = 1000 \times \text{moles of dye in cup}$$

$$\text{Hence; } C_o = \frac{1000 \times \text{moles of dye in cup} \times \rho_o}{W_o}$$

$$\text{where; Moles of dye in cup} = \frac{W_s \times \text{Weight \% dye at start}}{100 \times M_2}$$

$$\text{and; } \frac{\text{Weight \% dye at start}}{100} =$$

$$\frac{(V_o \times \rho_o \times \text{Wt. fraction dye}) \text{std. soln.}}{(V_o \times \rho_o) \text{std. soln.} + (V_o \times \rho_o) \text{water}}$$

$$\text{Therefore; } C_o = \frac{1000 \times \rho_o \times W_s \times (V_o \times \rho_o \times \text{Wt. fract. dye}) \text{std. soln.}}{W_o \times M_2 \times [(V_o \times \rho_o) \text{std. soln.} + (V_o \times \rho_o) \text{water}]}$$

Illustration 2. Con't.

Substituting; $\rho_o = 0.9982 + 0.2712 C_o$

$$M_2 = 589.604$$

$$\rho_{\text{std. soln.}} = 0.9982 + 0.2712 \times 0.133$$

Weight fraction dye in standard solution = 0.0759

$$\rho_{\text{water}} = 0.9982 \text{ at } 20^\circ\text{C}$$

and rearranging;

$$C_o = \frac{3.681}{(W_o/W_s)(28.64 + 27.64xV_o \text{ water}/V_o \text{ std. soln.}) - 1}$$

Applied to the specific problem;

$$C_o = \frac{3.681}{(0.9258/0.9967)(28.64 + 27.64x5/0.5) - 1} = 0.013 \text{ mols/l.}$$

Illustration 3. Computing the vapor pressure lowering of solutions in Run 1 using data given in Table 3 of text also equation 18 text

$$C_o \text{ KCl} = 0.017 \text{ molar}$$

$$p_o - p = 0.595x C_o / (1 + 0.186x C_o) = 0.595x 0.017 / (1 + 0.186x 0.017) \\ = 0.0104 \text{ mm Hg}$$

Illustration 4. Computing the osmotic pressure of solutions in Run 1 using equation 25 of text and data given in Table 3 of text

$$p_o - p = 0.0104 \text{ mm Hg}$$

$$P = 3817.0 - 3068.6 \log(17.535 - (p_o - p))$$

$$= 3817.0 - 3068.6 \log(17.535 - 0.0104) = 0.9 \text{ atmospheres}$$

Compounds Possessing Liquid Crystalline Phases in Solution

Compound	Formula	Type phase and solvent	Reported by:
Tartrazine		Nematic and Smectic in water	(21)(22)
Methylene Blue		Nematic in water	(20)(19)
Neutral Red		"	(20)(19)
Brilliant Crocein		Water	(21)
Anisal-p-aminoazo-toluene		Et ₂ O, C ₆ H ₆ , PhMe, CHCl ₃ , and CS ₂	(23)
10-bromophen-anthrene-6-sulphonic acid		Nematic more hydrated than Smectic	(51)(53) (25)(26)
10-chlorophen-anthrene-6-sulphonic acid		Water	(27)
Potassium Methyl Orange		"	(24)
Salvarsan		"	(51)

Compound	Formula	Type phase and solvent	Reported by:
Anisal- α -benzal-azo- α -naphthyl-amine		Water. Also clearing pt. at 110°C pure	(53)
Sodium benzoate		Water	(53)
Sodium m-bromo-benzoate		"	(53)
Methylene Green		Alcohol	(19)
Cyanine		"	(19)
Gallo-cyanine		"	(19)
Seto-cyanine		"	(19)
Celestin Blue		"	(19)
Fast Blue	$C_{20}H_{15}(SO_3Na)(C_6H_5)_3N_3$ (Sulphonated Aniline Blue)	"	(19)

Compound	Formula	Type phase and solvent	Reported by:
New Methylene Blue	$(\text{CH}_3)_2\text{N}$ $\text{N}(\text{CH}_3)_2\text{Cl}$	Alcohol	(19)
	<p>or</p> $(\text{C}_2\text{H}_5)_3\text{N}$ $\text{NH}(\text{C}_2\text{H}_5)_3\text{Cl}$		
Lithium Tartrate	$\begin{array}{c} \text{CHOHC}=\text{O} \\ \quad \quad \quad \text{OLi} \\ \\ \text{CHOHC}=\text{O} \\ \quad \quad \quad \text{OLi} \end{array}$	Water	(52)
Commercial Lecithin	$\begin{array}{c} \text{CH}_2\text{OC}=\text{O} \\ \quad \quad \quad \text{R}_1 \\ \\ \text{CHOC}=\text{O} \\ \quad \quad \quad \text{R}_2 \\ \\ \text{CH}_2\text{O}-\text{P}(\text{OH})-\text{OCH}_2\text{CH}_2\text{N}(\text{CH}_3)_3\text{OH} \end{array}$ <p>(R_1CO and R_2CO represent acyl groups of the higher fatty acids)</p>	Smectic in water	(11)
Potassium Oleate	$\text{CH}_3(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_7\text{C}(=\text{O})\text{OK}$	Smectic in water	(11)
Sodium naphthenate		"	(11)
Cetyl Xanthate	$\text{CH}_3(\text{CH}_2)_{14}\text{CH}_2\text{C}(=\text{S})\text{SNa}$	"	(11)
Sodium Palmitate	$\text{CH}_3(\text{CH}_2)_{14}\text{C}(=\text{O})\text{ONa}$	"	(14)
Sodium Laurate	$\text{CH}_3(\text{CH}_2)_{10}\text{C}(=\text{O})\text{ONa}$	"	(13)
Sodium Oleate	$\text{CH}_3(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_7\text{C}(=\text{O})\text{ONa}$	"	(16)(11)

Compound	Formula	Type Phase and solvent	Reported by:
Dodecyl sulphonic acid	$\text{CH}_3(\text{CH}_2)_{11}\text{SO}_3\text{H}$	Smectic in water	(12)
Sodium Stearate	$\text{CH}_3(\text{CH}_2)_{16}\overset{\text{O}}{\underset{\text{ONa}}{\text{C}}}$	"	(15)
Sodium Myristate	$\text{CH}_3(\text{CH}_2)_{12}\overset{\text{O}}{\underset{\text{ONa}}{\text{C}}}$	"	(17)
Lithium Palmitate	$\text{CH}_3(\text{CH}_2)_{14}\overset{\text{O}}{\underset{\text{OLi}}{\text{C}}}$	"	(55)
Hexanolamine Oleate	$\text{CH}_3(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_7\overset{\text{O}}{\underset{\text{HO}(\text{CH}_2)_6\text{NH}_2}{\text{C}}}$	"	(18)
Ammonium Oleate	$\text{CH}_3(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_7\overset{\text{O}}{\underset{\text{ONH}_4}{\text{C}}}$	EtOH plus water	(54)
N,N'-diethyl pseudoisocyanine chloride or Diethyl-ψ-cyanine chloride		Water	(56)(57)(58) (59)(60)(61)
Pinacyanol		Water	(60)

**Compounds Yielding Sols which Resemble
Liquid Crystalline Phases (*)**

Compound	Formula	Dispersing medium	Reported by:
Bentonite clay	Hydrated Sodium Aluminum Silicate	Water	(9)(62)
Vanadium pentoxide	V_2O_5	"	(9)(62)(63)(64)
Tobacco mosaic	Indefinite	"	(9)
Protein crystals	Indefinite	"	(9)
Iron Oxide	$Fe(OH)_3$	"	(9)(64)
Silver cyanate	$AgCNO$	"	(9)(64)
Benzopur-purin 4B		"	(62)(63)(64)(65)(66)(67)(68)(69)
Benzobrown	Probably:	"	(62)

Compound	Formula	Dispersing medium	Reported by:
Primuline		Water	(62)
Alizarine		"	(62)
Sodium alizarine sulphonate		"	(62)
Anthracene		"	(62)
Cerasin Orange	Not available	"	(62)
Chrysophenine B		Water	(63)(64) (66)(67)
Cotton Yellow GX		Water	(63)(69) (72)
Aniline Blue 2BL		Dissolved in EtOH; then poured into water	(62)(70)
Sudan Blue	Not available	"	(70)
Metanil Yellow		Water	(71)
A group of 160 dyes		Investigated using flow technique	(71)

Compound	Formula	Dispersing medium	Reported by:
A group of 450 dyes		Investigated (71) using photo-anisotropic technique	

Note: (*) These compounds in most cases yield transparent coherent sol phases which are claimed to resemble liquid crystalline phases in solution because they exhibit streaming double refraction and are composed of colloidal micelles consisting of rod shaped particles with parallel orientation which at higher concentrations spontaneously collect into oriented groups (tactoids) the physical nature of which closely resembles that of the swarm in liquid crystalline solution. The sol phase is different in its reaction to externally applied forces such as those existing on an anisotropic surface. This test may even be completely negative. The sols are also distinguished by the low true solubility of the solute and method of preparation. The liquid crystalline phase in solution is developed as the result of simple solution of a compound in a solvent, whereas the sol formation requires dispersion technique with particular attention given to dispersive temperature and time and solute concentration as well as utilization of intermediate solvents.

It is apparent that the sol phase is metastable because it changes with time perhaps through the unsatisfied forces of crystallization. The equilibrium diagram for the majority of systems probably resembles Figure 12 except that

the regions of coexistent phases and mesophase are non-existent, and the common limit of solubility shifts to a much lower range of concentration being about 0.35% by weight in the case of aqueous Benzopurpurin 4B at room temperature. The phases existing in the remaining shaded area of the diagram then become "liquid crystalline like sol phase (metastable)" or "solid (stable)" and "isotropic solution".

There is an alternative explanation for the equilibrium diagram for some of the subject materials if one considers their solution as being supersaturated rather than colloidal. In this case the common limit of solubility in Figure 12 would shift as before but the regions of coexisting phases and mesophase would remain. The regions bounded by the common limit of solubility and the outer boundary of the coexistent phases region would represent "supersaturated solution" (metastable). The coexistent phases region would represent "supersaturated solution" (metastable) and "mesophase" (metastable). These regions and the metastable "mesophase" region would change with time eventually being transformed to the stable solid and stable isotropic saturated solution.

The present theory probably applies to both the supersaturated solution type and the sol type system. However, in the latter case, it would be necessary to first determine the electrical character of the rod shaped particles.

Bibliography

Periodicals

Coacervation

- Bungenberg de Jong, H. G., "Oriented Coacervates and Their Bearing Upon the Formation of Colloid Crystals," *Proc. Acad. Sci. Amsterdam*, 38, 426-34 (1935)
- Bungenberg de Jong, H. G. and Bank, O., "Behavior of Microscopic Bodies Consisting of Biocolloid Systems Suspended in Aqueous Medium," *Proc. Acad. Sci., Amsterdam*, 42, 83-8 (1939)
- Bungenberg de Jong, H. G. and Linde, P. V. D., "Coacervate Sols and Their Relation to the Theory of Lyophilic Colloidal Stability," *Proc. Acad. Sci. Amsterdam*, 38, 419-26 (1935)
- Bungenberg de Jong, H. G., Saubert, G. G. P. and Booy, H.L., "Influence of Organic Nonelectrolytes on Oleate and Phosphatide Coacervates," *Protoplasma*, 29, 481-97 (1938)
- Bungenberg de Jong, H. G., Saubert, G. G. P., and Booy, H.L., "Influence of Organic Nonelectrolytes on Oleate and Phosphatide Coacervates," *Protoplasma*, 30, 1-38 (1938)
- Bungenberg de Jong, H. G. and Winkler, K. G., "Disintegration in Crystalloidal Neutral Salt Solution Analogous to Complex Coacervation of Biocolloidal Solutions," *Z. anorg. allgem. chem.*, 232, 119-32 (1937)
- Dobry, Mme. A., "Coacervation," *J. Chim. Phys.*, 35, 387-94 (1938)
- Dobry, Mme. A., "Coacervation," *Rev. can. biol.*, 1, 353-65 (1942)
- Kruyt, H. R., "The Stability of Colloidal Solutions," *Bull. Soc. Chim.*, (5), 4, 1925-41 (1937)
- Kruyt, H. R. and Bungenberg de Jong, H. G., "Extension of the Theory of Complex Coacervation to Ionic Disperse Systems," *Proc. Acad. Sci., Amsterdam*, 38, 714-21 (1935)

- Pirene, H., "Liquid Precipitations. Application of Coacervation Theory to Electrolytes", Rev. universelle mines, 13, 227-8 (1937)
- Schoofs, J., "Complex Coacervations", Rev. universelle mines, 13, 219-27 (1937)
- Tjaden, R. S., Modderman and Holleman, L. W. J., "Coacervation" Nature, 129, 654 (1932)

Liquid Crystalline Melts

- Bogojawlenski, A. and Winogradow, N., "On the Relation of Melting Point and Clarification Point Curves of Liquid Crystals and Mixtures of the Same", Chem. Lab. Univ. Dovpat. Z. physik. Chem., 60, 432
- Bose, E., "For and against the Emulsion Theory of Crystalline Liquids", Tech. Hochschule, Danzig Langfuhr. Physik. Z. 8, 513-18
- Bose, E., "Theory of Anisotropic Liquids II", Danzig., Physik. Z. 10, 230-44 (1909)
- Bose, E., "On the Physical Properties of Emulsions, in Particular Concerning Their Relations to Crystalline Fluids", Physik. Zeitschr., 8, 347 (1907)
- Bradfield, A. E. and Jones, B., "Two Apparent Cases of Liquid Crystal Formation", J. Chem. Soc. 1929, 2660-1
- Chatelain, P., "The Orientation of Liquid Crystals by Stroked Surfaces", Compt. rend. 214, 32-4 (1942)
- Conrat, F., "Change of Density of Anisaldazine at the Clearing Temperature", Physik. Z., 10, 202-6
- Ebert, L. and Hartel, H. V., "The Dipole Momentum and the Anisotropy of Liquids", Physik. Z. 28, 786-90 (1927)
- Feex, G., "Crystallization of Mesomorphic Substances in the Magnetic Field Obtaining a Solid with Orientated Molecules", Compt. rend. 187, 822-3 (1928)
- Friedel, G., "The Mesomorphic States of Matter", Ann. physik., 18, 273-474 (1922)
- Gaubert, P., "The Liquid Crystals of Anisal-p-amino acetoluenes" Compt. rend., 176, 907-9 (1923)

- Gaubert, P., "The Planes of Grandjean", Compt. rend. 177, 698-700 (1923)
- Grandjean, P., "Application of the Theory of Magnetism to Anisotropic Liquids", Compt. rend 164, 280-3 (1917)
- Kast, W., "Conditions for Appearance of an Anisotropic Liquid Phase", Naturwissenschaften, 25, 234-5 (1937)
- Lehman, O., "Extension of the Sphere of Existence of Fluid Crystals by Admixture", Ann. Physik., 4 21, 181-92 Karlsruhe
- Lyons, C. G. and Rideal, E. K., "Phase Diagrams for Unimolecular Films", Proc. Cambridge Phil. Soc. 26, 419-20 (1930)
- Ornstein, L. S., Kast, W. and Bouma, P. J., "The Liquid Crystal Character of Dipole Fluids at the Melting Point", Proc. Acad. Sci. Amsterdam, 35, 1209-12 (1932)
- Oseen, C. W., "Contribution to the Theory of Anisotropic Liquids", Arkiv. Mat. Astron-Fysik 18, #8, 23pp (1923)
- Robberecht, J., "Piezometric Research V. Anisotropic Liquids Under Pressure", Bull. soc. Chim.-Belg. 47, 597-638 (1938)
- Voigt, W., "Liquid Crystals and Anisotropic Liquids (Supplement)", Gottingen. Physik. Z. 17, 305-7 (1916)
- Vorlander, D., "Colloidal Solutions of Dyes and of Colophony in Liquid Crystals", Z. physik, Chem., 85, 701-5
- Vorlander, D., "Investigation of the Molecular Form by Means of Crystalline Liquids", Z. physik. Chem. 105, 211-54 (1923)
- Vorlander, D., "New Crystalline Fluids", Z. physik. Chem., 57, 356-64 (1907)
- Vorlander, D., "Optical Voids, Crystalline Liquids and Various Kinds of Crystalline Liquids", Physik. Z., 31, 428-35 (1930)
- Vorlander, D., "Polymorphism of Crystalline Liquids", Ber., 70, 1202-12 (1937)
- Vorlander, D., "Polymorphism of Liquids", Chem. Inst. Univ. Halle a. S. Ber., 40, 4527-37

- Vorlander, D., and Fischer, J., "The Uniaxial Direction of Crystalline Liquids", Ber., 63, 2506-10 (1930)
- Vorlander, D. and Gahren, A., "Formation of Crystalline Liquids by Mixing Substances", Chem. Inst. Univ. Halle a. S. Ber., 40, 1966-69
- Weygand, G. and Gabler, R., "The Effect of Molecular Structure on the Appearance of Liquid Crystals," Naturwissenschaften, 27, 28-9 (1939)
- Weygand, G. and Gabler, R., "New Group of Crystalline-liquid Substances, the Homologous p, p-diphenylpyridazine", J. prakt. Chem. 115, 221-6 (1938)
- Weygand, G. and Gabler, R., "Occurance of more than Two Polymorphic, Crystalline-liquid Phases in Azomethine Compounds", J. prakt. Chem. 151, 215-20 (1938)
- Weygand, G. and Gabler, R., "Retardation of Arrangement Between Ordinary and Crystalline Liquids as well as the Types Among Themselves", Z. physik. Chem. B44, 69-74 (1939)
- Weygand, G. and Gabler, R., "The Thermal Persistence of Crystalline Liquid Phases", Ber., 71, 2399-2405 (1938)
- Willers, F. A., "Viscosity Anomalies of Emulsion in the Condition of Turbulent Flow", Danzig Physik. Z., 10, 244-8
- Wyk, A. van., "The Orienting Influences of a Magnetic Field, of Walls and of Mutual Interactions", Ann. Physik 5, 3, 879-933 (1929)
- Zocher, H., "The Action of Magnetic Electric and Mechanical Forces upon Mesophases", Physik. Z. 28, 790-6 (1927)

Liquid Crystalline Solutions

- Cornish, E. C. V., "Density Measurements of Soap Solutions", Z. physik. Chem. 76, 210-11
- Goniek, E. and McBain, J. W., "Cryoscopic Evidence for Micelle Association in Aqueous Solutions of Nonionic Detergents", J. Am. Chem. Soc. 69, 334-336 (1947)
- Lehmann, O., "Ionic Migration in Liquid Crystals of Hydrated Ammonium Oleate", Ann. Physik. 57, 244-56 (1918)

- Sandqvist, H., "Tabular Review of the Literature on Phenanthrene Derivatives for the years 1902-1912 inclusive", Arb. Utgifna Med. Understod of Wilhem Ekman's Universitetsfond, Uppsala No. 14, 106pp
- Sandqvist, H. and Hagelin, A., "Mono and Dichloro Phenanthrene", Ber. 51, 1515-26 (1918)
- Somerfeldt, E., "The Investigation of Liquid Crystals in Converging Polarized Light", Physik. Z. 9, 234
- Vold, M. J., "Liquid Crystalline, Waxy and Crystalline Phases in Binary Mixtures of Pure Anhydrous Soaps", J. Am. Chem. Soc. 63, 160-8 (1944)
- Vold, M. J., Macomber, M. and Vold, R. D., "Stable Phases Occuring Between True Crystalline and True Liquid for Single Pure Anhydrous Soaps", J. Am. Chem. Soc., 63, 168-75 (1941)
- Vold, R. D., "Anhydrous Sodium Soaps, Heats of Transition and Classification of the Phases", J. Am. Chem. Soc. 63, 2915-24 (1941)
- Vold, R. D., "Soap Phases", Soap, 16, #6, 31-4; 71, 73-4 (1940)
- Vold, R. D., Liggett, C. W. and McBain, J. W., "Systems of Sodium Palmitate in Organic Liquids," J. Physic. Chem. 44, 1058-71 (1940)
- Vold, R. D. and Vold, M. J., "Thermal Transition of the Alkali Palmitates", J. Phys. Chem. 49, 32-42 (1945)
- Wallerant, F., "On the Fluid Crystals of Ammonium Oleate", rend. 143, 694-95 (1907)

Nature of Dye Solutions

- Bayliss, "The Properties of Colloidal Systems. The Osmotic Pressure of Electrolytical Dissociated Colloids", Proc. Roy. Soc. (London), B84, 229-54 (1911)
- Bergmann, E. and Weizmann, A., "Dipole Moments and Molecular Structure XVII. The Dipole Moments of Azo Dyes and some Similar Substances", Trans. Faraday. Soc., 32, 1318-26 (1936)
- Biltz, W., "Osmotic Pressure of Colloids. III Further Contributions to the Dialysis and Osmosis of Solutions of Dyes", Z. physik. Chem., 77, 91-116 (1911)

- Biltz, W. and Vegesack, A., "Osmotic Pressure of Colloids. II Osmotic Pressure of Some Dye Solutions", Z. physik. Chem., 73, 481-512 (1910)
- Bird, C. L., "Modern Theory and Practice of Wool Dying III The Nature of Solutions", Textile Recorder #707, 34, 36, 39 (1942)
- Breyer, B., "The Effect of Substituents on the Chemical Physico-Chemical and Biological Behavior of Chemical Compounds. A theory of the Relation between Chemical Constitution and Biological Action, Biochem. Z., 301, 65-93 (1939)
- Brintzmeier, H. and Sehall, A., "Determination of the Weight of Organic Dye Ions by Dialysis", Z. anorg. allgem. Chem., 225, 213-16 (1935)
- Brodie, W. and Adams, R., "Optically Active Dyes II Absorption", J. Am. Chem. Soc., 46, 2032-43 (1924)
- Donnan, F. G. and Harris, A. B., "Osmotic Pressure and Conductivity of Aqueous Solutions of Congo Red and Reversible Equilibria", J. Chem. Soc. (London), 99, 1554-77 (1911)
- Durfee, W. C., "The Numerical Solubility of Dyes", Proc. Am. Assoc. Textile Chem. Colorist, (1931) 103-4; Am. Dyestuff Reporter, 20, 185-6 (1931)
- Garner, W., "Capillary Phenomena Exhibited by Dye Solutions and Sols", J. Soc. Dyers and Colourists, 49, 346-55 (1933)
- Ghosh, J. C. and Dutt, S. C., "Variation of the Surface Tension of Aqueous Solutions of Certain Dyestuffs with Time", J. Indian Chem. Soc., 6, 903-10 (1929)
- Ghosh, J. C. and Nath, M. C., "Variation of the Surface Tension of Aqueous Solutions of Certain Complex Organic Substances with Time", J. Phys. Chem. 36, 1916-27 (1932)
- Gotze, J., "Peculiar Dyes Obtained Instead of Pseudocyanines," Angew. Chem., 49, 563-4 (1936)
- Hamer, F. M., "Pseudocyanine Condensation", J. Chem. Soc., 1928, 206-15

- Hammarston, E., and Hammarston, H., "The Osmotic Pressure of Several Electrolytes of Higher Molecular Weight", *Arkiv. Kemi. Mineral Geol.*, (27), 8, 16pp. (1923)
- Hartley, and Robinson, C., "The Diffusion of Colloidal Electrolytes and other Charged Colloids", *Proc. Roy. Soc. (London)*, A 134, 20-35 (1931)
- Heyl, G., "Colloidal Properties of Dyes", *Color Trade. J.*, 13, 190-3 (1923); 14, 47-9, 149-51; 15, 4-6 (1924)
- Hellborn, K., "Saturated Solutions of Dyestuffs", *Pharm. Ztg.*, 72, 497 (1927)
- Holmes, W. C., "Colloidal Phenomena in Dye Solutions", *J. Am. Chem. Soc.*, 49, 790-1 (1927)
- Holmes, W. C., "Stain Solubilities I Data in Literature", *Stain Tech.*, 2, 44-9 (1927)
- Holmes, W. C. and Peterson, A. R., "Transmission Spectra of Dyes in Solid State", *J. Phys. Chem.*, 36, 1248-54 (1932)
- Jablonski, C. F., "Report on (the determination of) Coloring Matters in Food; (Quantitative Separation of Amaranth and Tartrazine)", *J. Assoc. Official Agr. Chem.*, 11, 434-8 (1928)
- Jablonski, C. F., "Report on (the analysis of) Coloring Matters (used) in Foods", *J. Assoc. Official Agr. Chem.*, 13, 412-6 (1930)
- Jablonski, C. F., "Report on (the determination of) Coloring Matters in Food", *J. Assoc. Official Agr. Chem.*, 15, 362-9 (1932)
- Jelley, E. E., "Spectral Absorption and Fluorescence of Dyes in the Molecular State", *Nature*, 138, 1009-10 (1936)
- Jerpes, E. and Hellgren, E. G., "The Osmotic Pressure of some Electrolytes of High Molecular Weight", *Biochem. Z.* 145, 57-62 (1924)
- Knecht, E. and Bately, J. P., "Condition of Some Dyestuffs in Aqueous Solution", 7th Int. Cong. Appl. Chem., London 1910, *J. Chem. Ind.*, 28, 697
- Lauer, W. and Miller, S., "The Structure of Hydroxyazo Compounds", *J. Am. Chem. Soc.*, 57, 520-25 (1935)

- Lehner, S. and Smith, J. E., "Dyeing of Cotton: Particle Size and Substantivity I", J. Am. Chem. Soc., 57, 497-504 (1935)
- Lehner, S. and Smith, J. E., "Dyeing Cotton. Substantative Dyes and Salt Sensitivity", Ind. Eng. Chem. 27, 20-5 (1935)
- May, C. E. and Hunt, H., "Some Azo Dyes Soluble in Non Aqueous Solvents", Ind. and Engg. Chem., 20, 384-88 (1928)
- McBain, J. W. and Liu, T. H., "Diffusion of Electrolytes, Non Electrolytes and Colloidal Electrolytes", J. Am. Chem. Soc., 53, 59-74 (1931)
- Morgan, G. T. and King, H. J. S., "Residual Affinity and Coordination. IX Cobaltammine Salts of the Nitro Dyes" J. Chem. Soc., 121, 1723-9 (1922)
- Morton, T. H., "Dyeing of Cellulose with direct Dyestuffs. Importance of the Colloidal Constituents of the Dye Solution and of the Fine Structure of the Fibre", Trans. Faraday. Soc., 31, 262-84 (1935)
- Rabinowitch, E. and Epstein, L. P., "Polymerization of Dyestuffs in Solution. Thionine and Methylene Blue", J. Am. Chem. Soc., 63, 69 (1941)
- Robinson, G., "Diffusion Coefficients of Dye Solutions and Their Interpenetration", Proc. Roy. Soc. (London) A148, 681-95 (1935)
- Robinson, G., "Dyestuffs as Colloids", J. Soc. Dyers and Colourists, 50, 161-5 (1934)
- Robinson, G., "Nature of the Aqueous Solutions of Dyestuffs", Trans. Faraday Soc., 31, 245-61 (1935)
- Scheibe, G., "Mechanism of Sensitization of Photochemical Reactions Especially the Assimilation Reaction by Dyes", Naturwissenschaften, 25, 795 (1937)
- Sheinker, N. S., "Study of the Degree of Dispersion of Dyes by the Diffusion Method", J. Phys. Chem. (USSR), 4, 860-4, 865-70 (1933)
- Sheppard, S. E. and Geddes, A. L., "Effect of Solvents Upon the Absorption Spectra of Dyes. IV Water as Solvent: A Common Pattern", J. Am. Chem. Soc., 66, 1995-2010 (1944)

- Standing, H. A., "Dyeing of Cellulose with Direct Dyes", Trans. Faraday Soc., 41, 410-34 (1945)
- Tanaka, R., "Colloid Chemical Studies on Dyestuff Sols I Sol Formation of the Congo Acid by Washing Peplization", Kolloid. Z., 53, 200-5 (1930)
- Valke, E. I., "Measurements of the Diffusion of Dyestuffs", Trans. Faraday. Soc., 31, 230-245 (1935)
- Valke, E. I., "Particle Size in the Vat Dyeing of Cellulose", J. Am. Chem. Soc., 63, 1433-1437 (1941)
- Vickerstaff, T. V. and Lemin, D. R., "Aggregation of Dyes in Aqueous Solutions", Nature 157, 373 (1946)
- Weltzien, W. and Gotze, K., "Substantative Dyes (salt colors) and their Behavior Toward Viscose and Cuprammonium Rayon II Dyeing of Rayon", Seide, 32, 401-13 (1927); Chem. Zentr. 1928 I, 975-6
- Zsigmondy, R., "State of Division of Dyes of High Molecular Weight in Aqueous Solution", Z. physik. Chem., 111, 211-33 (1924)

Optical Activity in Colloidal Solutions

- Chatlain, P., "The Scattering of Light by Liquid Crystals", Compt. rend., 218, 652-4 (1944)
- Fruendlich, H., "Colloidal Structures in Biology", J. Phys. Chem. 41, 1151-61 (1937)
- Fruendlich, H., "Double refraction of Vanadium Pentoxide Sols", Z. Elektro, Chem. 22, 27-33 (1916)
- Fruendlich, H. and Diesselhorst, H., "Double Refraction of Vanadium Pentoxide Sols", Physik. Z. 16, 419-25 (1915)
- Oster, G., Doty, P. M. and Zimm, B. H., "Light Scattering Studies of Tobacco Virus", J. Am. Chem. Soc. 69, 1193-97 (1947)

Theory of Color

- Bury, C. R., "Auxochromes and Resonance", J. Am. Chem. Soc. 57, 2115-2118 (1935)

- Grossley, M. and Resenvelt, P., "Color and Constitution I Effect of Isomerism on the Color of Certain Azo Dyes", *Ind. Eng. Chem.* 16, 271-3 (1924)
- Raman, C. V. and Bhagavantam, S., "The Relation Between Color and Molecular Structure in Organic Compounds", *Indian J. Physics*, 4, Pt. 1, 57-78 (1929)
- Reynolds, W. B., "A Simplified Discussion of Color and Constitution of Azo Dyes", *Am. Dyestuff Reporter*, 32, 455-6, 465-7 (1943)

Theory of Ionized Solutes and Nature of Solutions

- Arnold, O. and Williams, J. W., "The Resistance and Capacity Behaviors of Strong Electrolytes in Dilute Aqueous Solutions. I Method for the Simultaneous Observation of Conductance and Dielectric Constant at High Radio Frequencies", *J. Am. Chem. Soc.*, 58, 2613-24 (1936)
- Baborevsky, J. and Valisek, J., "The Absolute Hydration of H, Li, Na, K, Cl, and Br Ions in Their Normal Solutions", *Chem. Listy.*, 21, 227-31 (1927)
- Birline, T. and Fajans, K., "Nature of the Covalent Binding", *J. Chem. Phys.*, 10, 691-2 (1942)
- Bjerrum, N., "Thermodynamics of Activity Coefficients and Osmotic Coefficients", *Z. physik. Chem.*, 104, 406-32 (1923)
- Bonino, G. B., "A Theory of Concentrated Solutions of Strong Electrolytes I Theoretical Considerations", *Mem. accad. Italia*, 4, 415-44 (1933)
- Bonino, G. B. and Gentola, G., "A Theory of Concentrated Solutions of Strong Electrolytes. Possibility of its Application to the Calculation of Osmotic Coefficients", *Atti. accad. Lincei.*, 18, 145-9 (1933)
- Bonino, G. B. and Rolla, M., "III Calculation of the Lowering of the Vapor Pressure of the Solvent", *Ibid*, 465-79
- Bonino, G. B. and Valglio, V., "Ionic Radius and Osmotic Activity", *Gazz. Chim. ital.* 59, 49-56 (1929)
- Born, M., "Volumes and Heats of Hydration of Ions", *Z. Physik* I, 45-8 (1920)

- Born, M. and Heisenberg, W., "Influence of Deformability of Ions on Optical and Chemical Constants", Z. Physik., 23, 388-410 (1924)
- Böttcher, G. J. F., "Computation of the Radius and the Polarizability of a Number of Ions", (Rotterdam) Rec. trav. chim., 65, 19-38 (1946) in English
- Böttcher, G. J. F., "A Differential Method for the Calculation of the Mean Radius of Particles", (Rotterdam) Rec. trav. Chim., 65, 14-18 (1946) in English
- Böttcher, G. J. F., "The Molecular Refraction of Aqueous Solutions of Electrolytes", Rotterdam Rec. trav. chim., 65, 39-49 in English
- Bronstead and La Mer, "The Activity Coefficients of Ions in Very Dilute Solutions", J. Am. Chem. Soc., 46, 555-74 (1924)
- Cavallaro, L., "Cryoscopic Investigations IV Calculation of the Cryoscopic Lowering of Aqueous Solutions of Alkaline Chlorates and Alkaline Earth Chlorates", Gazz. Chem. Ital., 71, 269-88 (1941)
- Debye, P. and Pauling, "Interionic Attraction Theory of Ionized Solutes IV The Influence of Variation of Dielectric Constant on Limiting Law for Small Concentrations", J. Am. Chem. Soc., 47, 2129-34
- Dunning, W. J. and Schutt, W. J., "The Dielectric Properties of Aqueous Solutions of Salts", Trans. Faraday Soc., 34, 467-79 (1938)
- Earl of Berkley, and Hartley, E. G. J., "Further Determinations of Direct Osmotic Pressures", Proc. Roy. Soc. London (A) 92, 477-92 (1916) of Trans Roy Soc. (London), 206, 481-507 (1906)
- Earl of Berkley, Hartley, E. G. J., and Burton, G. V., "Osmotic Pressure of Aqueous Solutions of Calcium Ferrocyanide I Concentrated Solutions", Trans., Roy. Soc. (London) (A) 209, 177-204
- Earl of Berkley, Hartley, E. G. J. and Stephenson, J., "Osmotic Pressure of Aqueous Solutions of Calcium Ferrocyanide II Weak Solutions", Trans. Roy. Soc. Faraday (A) 209, 319-36

- Eyring, "The Energy of Activation for Bimolecular Reactions Involving Hydrogen and the Halogens, According to the Quantum Mechanics", J. Am. Chem. Soc., 53, 2537-49 (1931)
- Fajans, K., "Deformation of Ions and Molecules Based Upon Refractometric Data", Z Elektrochem., 34, 502-20(1928)
- Fajans, K., "Electronic Structure of Molecules III Quantization of Molecules", J. Chem. Phys., 10, 759-60 (1942); "V Stabilization and Bonding of Quantized Radicals", 761; "IV Difficulties in the Valence Bond Theory", 764-1
- Fajans, K., "Incomplete Dissociation in Solutions of Strong Electrolytes", J. Chem. Phys., 9, 283 (1941)
- Fajans, K., "Molar Volume, Refraction and Interionic Forces", J. Chem. Phys., 9, 282 (1941)
- Fajan, K., "Polarization of Ions and Lattice Distances", J. Chem. Phys., 9, 281-2 (1941)
- Fajans, K., "Thermal Expansion Compressibility and Electronic Polarizability of Ionic Crystals", Phys. Rev., 61, 543
- Fajans, K. and Baner, M., "Electronic Structure and Stability of Hydrogen Halides and of Complex Ions, XO_4 ", J. Chem. Phys. 10, 410-15 (1942)
- Fajans, K. and Berlin, T., "Electronic Structure of Molecules VI Quantization of Molecules Inter and Intra Molecular Forces", Phys. Rev. 63, 309-12 (1943)
- Fajans, K. and Johnson, O., "Apparent Volumes of Individual Ions in Aqueous Solutions," J. Am. Chem. Soc. 64, 668-78 (1942)
- Fajans, K. and Johnson, O., "Ion-Solvent Interaction and Individual Properties of Electrolytes," Trans. Electrochem. Soc., 82, 15pp (1942) preprint
- Fouard, E., "Osmometry of Salt Solutions and the Arrhenius Theory of Ions", Compt. rend 153, 769-72; J. physigne, 5 I, 627-43
- Fuoss, R. M., "Influence of Dipole Fields Between Solute Molecules", J. Am. Chem. Soc., 56, 1027-1030 (1934)

- Ghosh, J.C., "A General Theory of Electrolyte Solutions", *Z. Physik. Chem.* 98, 211-38 (1921)
- Gillett, G., "Aqueous Solutions. Origin of Osmotic Effects", *Compt. rend.*, 177, 257-8 (1923)
- Gillett, G., "Aqueous Solutions and Osmotic Pressure," *Bull. Soc. Chim. belg.*, 26, 415-8 (1913)
- Gillett, G., "Aqueous Solutions", *Verviers. Bull. Soc., belg. Chem.*, 23, 119-29 (1909)
- Glesteen, L. F. and Kraus, C. A., "Properties of Electrolytic Solutions. XXIII Conductance of Several Quaternary Onium Salts in Ethylene Chloride at 25°C.," *J. Am. Chem. Soc.*, 69, 451-54 (1947)
- Gopal, R., "A Statistical Study of the Variation of Specific Conductivity with Concentration of Electrolytes in Aqueous Solutions", *J. Indian Chem. Soc.*, 20, 62-8 (1943)
- Grinell, Jones, Karol, Mysels, and Juda, W., "The Measurement of the Conductance of Electrolytes. IX The Use of the Cathode Ray Oscillograph as a Detector," *J. Am. Chem. Soc.*, 62, 2919-22 (1940)
- Gucker, F. T., "The Apparent Molal Expansibility of Electrolytes and the Coefficient of Expansibility (Thermal Expansion) as a Function of Concentration," *J. Am. Chem. Soc.*, 56, 1017-21 (1934)
- Hartley, G. S., "Application of the Debye-Huckel Theory to Colloidal Electrolytes", *Trans. Faraday Soc.*, 31, 31-50 (1935)
- Johnson, I. and LaMer, V. K., "The Determination of the Particle Size of Monodisperse Systems by the Scattering of Light", *J. Am. Chem. Soc.*, 69, 1184-92 (1947)
- Jones, J. H., Spuhlen, F.J. and Felsing, W. A., "The Determination of the Activity Coefficients of the Methylamine Hydrochlorides from Freezing Point Data," *J. A. Chem. Soc.* 64, 965-968 (1942)
- Keevil, N. B., "Vapor Pressure of Solutions at High Temperature," *J. Am. Chem. Soc.*, 64, 841-850 (1942)

- Lee, F. H. "Molar Polarization and Radius-ratio of Ions",
Nature, 155, 698-9 (1945)
- London, F., "Properties and Applications of Molecular Forces",
Z. physik. Chem., Abt. B11, 222-51 (1930)
- London, F., "Theory and Systematics of Molecular Forces," Z.
Physik., 63, 245-79 (1930)
- Maibaum, B. K., "Dielectric Constants of Concentrated Solutions of Strong Electrolytes at Ultra High Frequencies", J. Exptl. Theoret. Phys. (USSR), 12, 231-45 (1942)
- Malov, J. N., "Anomaly of the Electric Conductivity of Concentrated NaCl Solution in Region of Decimeter Waves", J. Tech. Phys. (USSR), 9, 2004-11 (1939)
- Malov, J. N., "Variation of the Electric Conductivity of Electrolytes with Frequency," J. Exptl. Theoret. Phys. (USSR), 14, 221-3 (1934)
- Manchet, W., Jahrstorfer, M., and Zepfer, H., "Gas Solubility and Hydration," Z. anorg. allgem. Chem., 141, 45-81 (1924)
- Mayer, J. E. and Mayer, M. G., "The Polarizabilities of Ions from Spectra," Phys. Rev., 43, 605-11 (1933)
- Nanty, T. and Valet, M., "Specific Inductive Capacity of Colloidal Solutions", Compt. rend., 194, 883-4 (1932)
- Noyes, A. A., "The Interionic Attraction Theory of Ionized Solutes. I Critical Presentation of Theory," J. Am. Chem. Soc., 46, 1080-98 (1924)
- Noyes, A. A., "The Interionic Attraction Theory of Ionized Solutes II Testing of Theory with Experimental Data," J. Am. Chem. Soc., 46, 1098-1116 (1924)
- Noyes, A. A., and Baxter, W. P., "Interionic Attraction Theory of Ionized Solutes. III Testing of the Theory in Alcoholic Solvents," J. Am. Chem. Soc., 47, 2122-9 (1925)
- Ostwald, Wo. and Mandler, K., "The Osmosis and Swelling of Disperse Systems," Kolloid Z., 24, 7-27 (1919)

- Pearce, J. N. and Pumpkin, G. G., "The Apparent and Partial Molar Volumes of NH_4Cl and of Cu SO in Aqueous Solutions at 25° ," J. Am. Chem. Soc., 59, 1221-1222 (1937)
- Philippon, M., "A New Form of Electric Resistance of Electrolytes," Bull. Acad. roy. Belgice, Classe des sci., 8, 76-80 and 384-7 (1923); Chem. Zentr., III, 5 (1923); of Bull. Acad. roy. Belgice, (5) 7, 387
- Ray, S., "Electrolytes Resistance with A. G., "Z. Electrochem. 36, 545-50 (1930)
- Robinson, R.A. and Sandar, D.A., "The Activity Coefficients of the Alkali Chlorides and of Lithium Iodide in Aqueous Solutions from Vapor Pressure Measurements," J. Am. Chem. Soc., 56, 1830-35 (1934)
- Sand, H.J.S., "The Anomaly of Strong Electrolytes Especially with Reference to the Theories of J. C. Ghosh," Phil. Mag., 45, 129-44 and 281-92 (1923)
- Sate, N. V., Phalnikar, N. L. and Bhide, B. V., "Dielectric Constants of Inorganic Salts," J. Indian Chem. Soc. 22, 29-36 (1945)
- Seatchard, G., "The Application of the Debye-Huckel Theory of Electrolytes to Concentrated Solutions," Physik. Z., 33, 22-32 (1932)
- Seatchard, "The Hydration of Sucrose in Water Solution as Calculated from Vapor Pressure Measurements," J. Am. Chem. Soc., 43, 2406-(1921)
- Scott, A. F., "Studies in the Solubilities of the Soluble Electrolytes. V An Estimation of the Radii of Ions in Saturated Solutions," J. Phys. Chem., 35, 1410-7 (1935)
- Shedlovsky, T. and Brown, A. S., "The Electrolyte Conductivity of Alkaline Earth Chlorides in Water at 25°C ," J. Am. Chem. Soc., 56, 1066-107 (1934)
- Shedlovsky, T. and MacInnis, D. A., "The Determination of Activity Coefficients from the Potentials of Concentration Cells with Transference. III KCl . IV CaCl_2 ," J. Am. Chem. Soc., 59, 503-6 (1937)
- Smith, H. W., "The Nature of Secondary Valence," J. Phys. Chem., 25, 160-0 (1921)

- Smith, H. W., "Nature of Secondary Valence. II Partition Coefficients," J. Phys. Chem., 25, 204-63 (1921)
- Smith, H. W., "The Nature of Secondary Valence. III Partition Coefficients in the System Water-Ether (supplementary notes)" J. Phys. Chem., 25, 605-15; 616-27 (1921)
- Smith, H. W., "The Nature of Secondary Valence, IV Partition Coefficients in the System Glycerol-Acetone," J. Phys. Chem., 25, 721-34 (1921)
- Smith, H. W., "The Nature of Secondary Valence. V Partition Coefficients in Systems Containing Water as One Component with Special Reference to Absolute Values of Series Constants," J. Phys. Chem., 26, 256-71; 349-57 (1922)
- Smith, H. W. and White, T. A., "The Distribution Ratios of Some Organic Acids Between Water and Organic Liquids" J. Phys. Chem., 33, 1953-74 (1929)
- Symposium, "Osmotic Pressure", Trans. Faraday Soc., (1917)
- Symposium, "The Ionization Theory," Trans. Faraday Soc., 15, 1-178 (1919)
- Symposium, "The Ionization Theory", Trans. Faraday Soc., 23, 334 (1927)
- Tlicher, L. M. and Kraus, G. A., "Properties of Electrolytic Solutions. XXIV Conductance of Some Substituted Ammonium Salts in Ethylene Chloride," J. Am. Chem. Soc., 69, 454-56 (1947)
- Wyman, J., "The Dielectric Constant of Mixtures of Ethyl Alcohol and Water from 5-40°C," J. Am. Chem. Soc., 53, 3292-3301 (1931)

Vapor Pressure Measuring Devices

- Edgar, G. and Ryan, W. O., "The Factors Determining the Hygroscopic Properties of Soluble Substances. I The Vapor Pressures of Saturated Solutions," J. Am. Chem. Soc., 44, 570-77 (1922)
- Gibson, R. E. and Adams, L. H., "Changes of Chemical Potential in Concentrated Solutions of Certain Salts," J. Am. Chem. Soc., 55, 2679-95 (1933)

- Lovelace, B. F., Bahlke, W. H. and Frazer, J. G. W., "A Study of the Vapor Pressure of Aqueous Solutions of Mannite," J. Am. Chem. Soc., 42, 1793-1808 (1920)
- Lovelace, B. F., Bahlke, W. H. and Frazer, J. G. W., "Vapor Pressures of Lithium Chloride Solutions at 20°C," J. Am. Chem. Soc., 45, 2930 (1923)
- Menzies, A. W. C., "A Surface Condensation Error in Certain Measurements of Vapor Pressure by the Gas Current Saturation Method," J. Am. Chem. Soc., 42, 978-85 (1920)
- Newton, R. F. and Tippetts, E. A., "The Activity of Water in Solution of Barium Chloride," J. Am. Chem. Soc., 58, 280 (1936)
- Pearce, J. N. and Nelson, A. F., "The Vapor Pressures of Aqueous Solutions of Lithium Nitrate and the Activity Coefficients of some Alkali Salts in Solutions of High Concentration at 25°C," J. Am. Chem. Soc., 54, 3544 (1932)
- Scatchard, G., Jones, P. T. and Prentiss, S. S., "The Freezing Points of Aqueous Solutions. I A Freezing Point Apparatus," J. Am. Chem. Soc., 54, 2676-90 (1932); "II Potassium, Sodium, Lithium Nitrate," 2690-96; "III Ammonium Chloride, Bromide, Iodide, Nitrate, Sulphate," 2696-2708
- Stokes, R. H., "The Measurement of Vapor Pressure of Aqueous Solutions by Bithermal Equilibration Through the Vapor Phase," J. Am. Chem. Soc., 69, 1291-6 (1947)
- Tartar, H. V., Newschwander, W. W. and Ness, A. T., "A Thermodynamic Study of the System Zinc Sulphate-Sulphuric Acid-Water at 25°C," J. Am. Chem. Soc., 63, 28-36 (1941)

Books

- Davis, W. A. and Sadtler, S. S., "Allens Commercial Organic Analysis" 4th edition, Philadelphia, Penn., P. Blakiston's Sons and Company, 1925
- Debye, P., "Polar Molecules" NY, Chemical Catalogue Co. 1929
- Fajans, K., "Chemical Forces and Optical Properties of Substances" NY, McGraw Hill Book Company, 1931

- Falkenhagen, H., "Electrolytes" revised 1934, NY, Oxford University Press, 1934
- Findley, A, "Osmotic Pressure" NY, Longmans Green and Co. 1919
- Hewitt, J. T., "Synthetic Colouring Matters. Dyestuffs Derived from Pyridine, Quinoline, Acridine and Xanthene," NY Longmans, Green and Company 1922
- Hildebrand, J.H., "Solubility" 2nd edition NY, Reinhold Publishing Corporation, 1936
- Jacobs, M. B., "The Chemistry and Technology of Food and Food Products," Vol. I, pp. 303, NY, Interscience Publishers, Inc., 1944
- Jones, H.C., "Nature of Solutions" NY, D. Van Nostrand Co. 1917
- Latimer, W. M., "Oxidation Potentials" 1st edition, NY, Prentiss-Hall Incorporated, 1938
- Mott, N. F. and Gurney, R. W., "Electronic Processes in Ionic Crystals" NY, Oxford University Press, 1940
- Pauling, L., "The Nature of the Chemical Bond" 2nd edition, Ithaca, NY, Cornell University Press, 1945
- Rice, O.K., "Electronic Structure and Chemical Binding" 1st edition, NY, McGraw Hill Book Company, 1940
- Smyth, "Dielectric Constant and Molecular Structure" NY, Chemical Catalogue Company, 1931
- Tammann, G., "States of Aggregation" NY, D. Van Nostrand Co. 1925
- Valko, E.E., "Physical Chemistry of Textile Processes" NY, Interscience Publishers, 1947
- Van Vleck, J.H., "The Theory of Electric and Magnetic Susceptibilities" NY, Oxford University Press, 1932 1st edition
- Von Busaghi, A., "Colloid Systems" 1st edition, (Especially pp. 120-39), NY, Oxford University Press, 1925

VITA

Stanley Henry Martin Jury was born of Lewis Edwin and Gertrude Bastjan Jury on March 3, 1916, at Appleton, Wisconsin. He received his primary education at the First Ward School and the Roosevelt Junior High School, his secondary training at Appleton Senior High School, and his college training at the University of Cincinnati, receiving his Chemical Engineering Degree in April, 1942. He entered the Graduate School in September, 1946, and received his Masters Degree in Chemical Engineering from the University of Louisville in September, 1947.

At the University of Cincinnati, Mr. Jury was enrolled in the cooperative plan. As student engineer he was employed by the Janesville Cotton Mills at Janesville, Wisconsin, the Sanitone Division of Emery Industries, Inc., at Cincinnati, Ohio, and Formica Insulation Company also at Cincinnati. He was also a member of the Reserve Officers Training Corp.

After completion of his undergraduate work, Mr. Jury was commissioned and entered upon active duty as Ordnance Officer with the United States Army Ordnance Department. He spent four years in Britain and Europe returning to the United States in November, 1945.

Upon relief from active duty, Mr. Jury assisted a business associate in organizing the Polacoat Corporation at Springfield, Ohio, which was incorporated for the purpose of doing research and contract engineering. He resigned in September, 1946, to become an inactive member preparatory to his being placed on graduate status at the University of Louisville.

Mr. Jury is a member of the National Honor Society and Sigma Xi.