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Citation: [The Journal of Chemical Physics](#) **2**, 147 (1934); doi: 10.1063/1.1749443

View online: <http://dx.doi.org/10.1063/1.1749443>

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# THE JOURNAL OF CHEMICAL PHYSICS

VOLUME 2

APRIL, 1934

NUMBER 4

## Concerning the Structure of N-Alcohol Solutions of Lithium Chloride

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(Received January 23, 1934)

Since in x-ray diffraction both experimental results and theoretical considerations are in agreement as to the presence of structure in liquids, an x-ray study is made of concentrated solutions of LiCl in the three normal alcohols, ethyl, propyl and butyl. A definite but tentative conclusion is that in these concentrated solutions of a strong electrolyte, both  $\text{Li}^+$  and  $\text{Cl}^-$  participate with the molecules of

the solvent in forming a common liquid cybotactic or quasi-crystalline structure. This is a new conception which may be made to include what have been described as "ionic clouds" and as "association." A conclusion of secondary importance is that the solutions are in fact solutions of the alcoholates of LiCl, although above the corresponding transition temperatures.

THE problem of the structure of concentrated electrolytic solutions is both interesting and difficult. Great advances have been made, but so far removed is a satisfactory understanding that additional evidence secured by every method of approach possible is highly desirable. The study of the structure of liquids by the diffraction of x-rays has shown beyond reasonable doubt that liquids generally have an orderliness in the arrangement of their molecules. One would expect that the x-ray method of investigation, though crude, could shed valuable light for, after all, it is a very direct approach to the nature of the structure of a liquid.

Since the x-ray results are only statistical time averages, the nature of the structure of a liquid cannot be obtained with the uniqueness possible in crystals. At the present time either one of two conceptions of the liquid structure seem to be plausible. One is that immediately about any point of observation, for a distance of from 10A to 20A, the arrangement of scattering centers approximates very closely to that of a crystal. If the liquid is near the freezing tempera-

ture, the crystal structure referred to is that of the solid. This approximately regular structure may change materially with temperature. An important feature of the picture is that the point of observation specified is any scattering center. The liquid is therefore assumed to be homogeneous. This conception could be only approximately correct, for this homogeneity would demand a repetition of like structure or a crystalline structure in fact, which obviously is not the case. It is in the approximation that allowance is made for temperature effects and the relative movement of the molecules. So the conception may be regarded as representing really a statistical mean rather than an instantaneous condition. The other plausible conception is not so clearly stated but is an instantaneous picture. It assumes that, at any instant, the liquid is spotted throughout with regions which are quite orderly, as assumed in the other view, fading away into regions with little orderliness. There is a constant shifting of position with the result that a given molecule does not continue to remain in a well-defined group. At any instant, then, part of

the molecules participate in one or the other of these regions. An orderly region may be called a "group," though of course without sharp boundaries. The name "cybotactic group" has been given to it for convenience. The liquid is not homogeneous in detail. The latter conception is probably nearer the truth though the x-ray observations do not distinguish between the two views. But the former one has the advantage of being easily applied to computation. This has been done and reasonable structures have been found<sup>1</sup> to give approximately the observed diffraction curves. It is fair to say that in view of the large number of consistent experimental results<sup>2</sup> and of the satisfactory comparison with theoretical considerations, liquids generally do have a structure and that these results, which give a clearer conception of solutions, may become of quantitative importance. To this structure the name "cybotaxis" has been given because it is neither fluid nor crystalline but yet a crude and unstable imitation of the latter. At times reference has been and will be herein made to cybotactic "groups," by using thereby the second conception given above of the liquid structure.

By interpreting the results now presented through the use of previous x-ray studies of liquids, the following tentative conclusion seems evident. In a concentrated solution of a strong electrolyte, LiCl, both the ions and the molecules of the solvent, n-alcohol, participate in the same liquid (cybotactic) structure and there is no significant change in the liquid structure as the unsaturated liquid passes through the solute's temperature of transition to an alcoholate. The importance of the conclusion, if true, is evident, for it gives a new relationship of ions with ions and ions with solvent.

<sup>1</sup> For water, Bernal and Fowler, *J. Chem. Phys.* **1**, 518 (1933); for para-azoxyanisole, Buchwald, *Ann. d. Physik* **10**, 558 (1931); for n-paraffins, Warren, *Phys. Rev.* **44**, 969 (1933); for ethyl ether near the critical point, Warren, *Phys. Rev.* **44**, 969 (1933). These computations follow the method of Zernike and Prins, *Zeits. f. Physik* **41**, 184 (1927) and Debye and Menke, *Phys. Zeits.* **31**, 797 (1930) and *Ergebnisse der Technischen Röntgenkunde*, Vol. II, p. 1, Akad. Verlagsgesell., Leipzig, 1931.

<sup>2</sup> For the lines of experimental evidence see Stewart, *Indian J. Physics* **7**, Pb. 6, 603 (1933).

#### PREVIOUS CONCLUSIONS

Prins<sup>3</sup> investigated water solutions of LiBr, LiI and KI. He applied the Debye-Hückel ionic cloud theory to ascertain the probability distribution of the anions and found certain qualitative agreement but also quantitative disagreement. Later he<sup>4</sup> investigated water solutions of KCl, NaBr, SrBr<sub>2</sub>, BaCl<sub>2</sub>, Ag NO<sub>3</sub> and Pb(C<sub>2</sub>H<sub>3</sub>O<sub>2</sub>)<sub>2</sub>. He concluded (1) that the ions are arranged in the solutions in a more orderly manner than would be expected according to the geometrical Spielraum, and (2) that the ionic cloud computations do not agree with experiment. Prins<sup>5</sup> also remarks that one may account for the absence of the typical gas diffraction picture by assuming that the ions have about them solid water shells which are independent of concentration and approximately monomolecular.

Meyer<sup>6</sup> has investigated the water solutions of NaCl and LiCl. The Cl<sup>-</sup> ions were sufficient in number to give a definite effect if arranged at corners of a cube 6 Å on a side or scattered at random throughout the liquid. The diffraction curve gave no evidence either of this structure or of gaseous scattering from Cl<sup>-</sup>.

Good<sup>7</sup> has used aqueous solutions of LiCl, NH<sub>4</sub> SO<sub>4</sub>, CaCl, KCl, KB, KI, and finds in the case of the sulphate a new inner ring which he suggests might be formed by complexes of water molecules and NH<sub>4</sub><sup>+</sup>.

#### EXPERIMENTAL METHOD

Mo K $\alpha$  radiation, Soller slits, methyl bromide ionization chamber and differential readings with SrCO<sub>3</sub> and ZrO<sub>2</sub> screens<sup>8</sup> 0.036 g/cm<sup>2</sup> and 0.0025 g/cm<sup>2</sup>,<sup>9</sup> respectively, were used. By this method the elimination of all but the Mo K $\alpha$  radiation was effected. This is shown by the diffraction curve of an aluminum rod 3 mm in diameter for

<sup>3</sup> Prins, *Zeits. f. Physik* **56**, 617 (1929).

<sup>4</sup> Prins, *Zeits. f. Physik* **71**, 445 (1931).

<sup>5</sup> Prins, *Naturwiss.* **21**, 435 (1931).

<sup>6</sup> Meyer, *Ann. d. Physik* **5**, 701 (1930).

<sup>7</sup> Good, *Physica Acta* **4**, 205 (1930).

<sup>8</sup> Ross, *Phys. Rev.* **28**, 425 (1926); *J.O.S.A.* **16**, 443 (1928).

<sup>9</sup> The number of g/cm<sup>2</sup> were chosen so that the transmission of wave-lengths other than the Mo K $\alpha$  would be equal for the two screens and yet the difference in transmission for the Mo K $\alpha$  would be an optimum.

which the readings with the filters were alike in all but the  $K\alpha$  region. The Soller slits were those previously described<sup>10</sup> and gave a peak width at half height of approximately 26 seconds with crystal diffraction.

The solutions were those of LiCl in n-ethyl, n-propyl and n-butyl alcohols. The percentage of saturation was obtained by dissolving the correct weight in the solvent. The saturated solution was secured by heating the base of a test tube containing the solvent and an excess of LiCl for two weeks, the temperatures of the base being maintained at 50°C. The solubility of LiCl in grams per 100 grams of the solvent was determined at 25°C and found to be 12 percent for n-butyl. This is in slight disagreement with other recorded values<sup>11</sup> for the same temperatures which are respectively 42.3 at 50°C and 10.6 at 25°C. The values of 24.7 percent for n-ethyl and 16.0 for n-propyl, quoted in Seidell, were verified and adopted. The solubility of the salt in n-butyl was redetermined after the solution had been standing in contact with excess LiCl for more than seven months, and the result obtained was 12.2 grams, an increase of less than two percent.

The solutions were placed in the path of the x-ray beam in a very thin-walled cylindrical glass container, having a diameter about 0.8 of the "optimum" thickness,<sup>12</sup> although the optimum thickness precaution is not so important with the differential filter readings as when using a zirconium filter only.

The temperature regulation of the solution in the path of the x-ray beam was obtained by the circulation of air in a heat insulated enclosure having very thin mica windows. For temperatures in the neighborhood of 0°C, the air was passed through a copper tube immersed in a bath of salt, ice, and water. For much lower temperatures, a current of cold air was obtained by evaporating liquid air from a special vessel containing an electric heater. The flow of the air and thus the temperature of the air bath was

controlled by the supply of heat through current regulation.

The following are possible corrections of the readings:

1. The effective difference in thickness of the fluid in the container at different angles of diffraction.
2. The variation in the absorption of the container and mica windows and in their scattering at different angles of diffraction.
3. The lack of parallelism of the x-rays and the penetration of the Soller slits.
4. The incoherent radiation.

For the small angles of diffraction used in this report, less than 15°, corrections 1 and 4 are not important, for as will be shown, no use is made of the exact position of diffraction peaks and great accuracy is not required. Corrections 2 and 3 were approximated as follows. The readings were taken throughout the range with the container empty. These were reduced because of absorption of Mo  $K\alpha$  when the liquid is in place, and then used as corrections for the actual observations. In taking readings the current in the ionization chamber was always read first with one filter in position and then the other. Then the spectrometer setting was altered to an equal angle on the other side of 0°.

## RESULTS

Figs. 1, 2 and 3 show the experimental curves for the x-ray ionization current with n-ethyl, n-propyl and n-butyl alcohols after correction is made for slit penetration, container and mica window scattering. Each point is the average of two, one on each side of  $\theta=0^\circ$ . The percentage of saturation is shown for each curve, all being taken at 24°C. Each curve has a different zero ordinate, as indicated on the left-hand margin, and all are altered to have the same maximum ordinate.

Fig. 4 shows the chief lithium chloride alcoholate crystal diffraction peaks obtained with samples secured by plunging a saturated solution of each into liquid air, the purpose being a very rapid formation of the crystals and thereby a lack of preferred orientation. Measurements were made on two solidifications in each instance and the readings were in sufficient agreement to assert that the chief diffraction peaks of each alcoholate have approximately the relative values

<sup>10</sup> Stewart, Phys. Rev. **30**, 232 (1927).

<sup>11</sup> Seidell's *Solubilities of Inorganic and Organic Compounds*, 2nd Ed., D. Van Nostrand, 1919.

<sup>12</sup> This optimum thickness was computed from the following value of  $\mu$ .

$$\mu/\rho = (1.36 \times 10^{-2} \lambda^3 \Sigma N^4 + 2.32 N) / \Sigma A$$

wherein  $N$  is the atomic number and  $A$  the atomic weight.

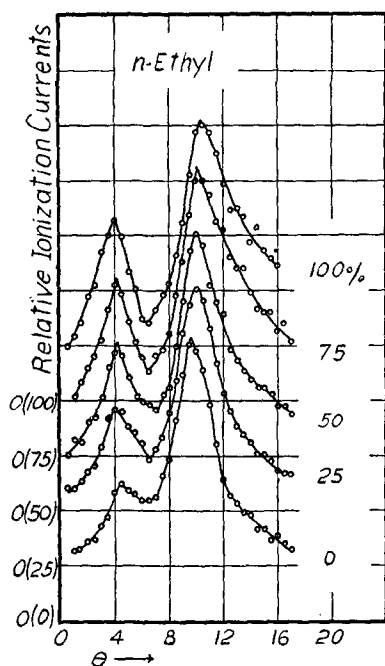


FIG. 1.

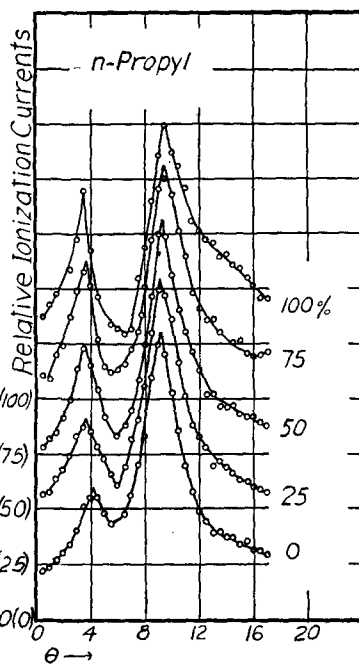


FIG. 2.

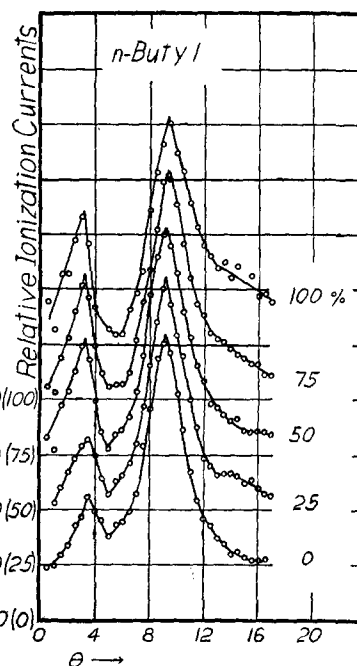


FIG. 3.

FIG. 1. Relative diffraction intensities, Mo  $K\alpha$  radiation, n-ethyl alcohol solutions of lithium chloride.

FIG. 2. Relative diffraction intensities, Mo  $K\alpha$  radiation, n-propyl alcohol solutions of lithium chloride.

FIG. 3. Relative diffraction intensities, Mo  $K\alpha$  radiation, n-butyl alcohol solutions of lithium chloride.

indicated. The complete curve in each case was not obtained because, as will be seen, the discussion involves only the chief intensity peaks. The temperature of observation for the alcoholates was kept at  $-15^{\circ}\text{C}$  which was well below the temperature for the solubility curve in each case. The temperature of the transition point or of the junction of the alcoholate and salt solubility curve is  $17.4^{\circ}\text{C}$  for the n-ethyl,<sup>13</sup>  $+3^{\circ}\text{C}$  for n-propyl and  $-3^{\circ}\text{C}$  for n-butyl as determined within  $1^{\circ}$  or  $2^{\circ}$  in these experiments.

In Fig. 5 a diffraction curve for each alcohol is taken several degrees below its transition temperature. Again zero ordinates are shifted for convenience and the maxima are reduced to the same scale. The solutions were 75 percent saturated at  $24^{\circ}\text{C}$ , and then cooled. The solid alcoholates would appear with these solutions at  $10^{\circ}\text{C}$  with the n-ethyl, at  $-9^{\circ}\text{C}$  to  $-10^{\circ}\text{C}$  with the n-propyl and at  $-20^{\circ}\text{C}$  to  $25^{\circ}\text{C}$  with the n-butyl alcohol. The temperatures of observation are respectively  $12^{\circ}\text{C}$ ,  $-7^{\circ}\text{C}$  and  $-10^{\circ}\text{C}$  and are

<sup>13</sup> Obtained by Turner and Bissett, J. Chem. Soc. **103**, 1904 (1913).

in each case below the transition temperature with the samples wholly liquid. Under this condition of temperature and concentration the solution is in each case that of the alcoholate.

## DISCUSSION

A reasonable deduction can be made directly by comparison of Fig. 5 with Figs. 1, 2 and 3, without the use of any assumptions. Each of the curves in Fig. 5 is closely like the curve for the same solution at  $24^{\circ}\text{C}$  as shown in the other figures. The ratio of major and minor peak intensities for a curve in Fig. 5 was computed and then compared with the like ratio in the corresponding curve in Figs. 1, 2 or 3. In the solutions with each alcohol the ratios are the same within 8 percent and the peak positions are alike within measurement error. There is a small difference in a noticeable lessening of the minor peak width at the lower temperature, which, other experiments show, may readily be only a direct temperature effect. But since the solutions at the lower temperatures in Fig. 5 are obviously alcoholate solutions, then because of the likeness of diffraction

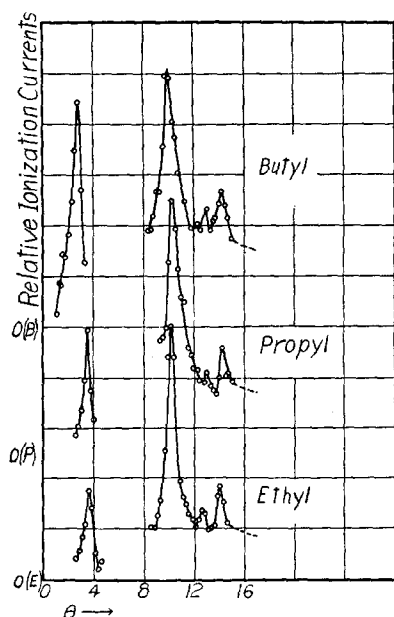


FIG. 4. Most prominent Mo  $K\alpha$  diffraction peaks with powdered lithium chloride alcoholate crystals.

tion, or the same arrangement of scattering centers, those in Figs. 1, 2 and 3, at the higher temperatures, would appear to be also the same alcoholate solutions.

A second conclusion can be obtained by reference to previous experiments with miscible solutions. It is that the ionic LiCl alcoholate forms a liquid structure with the solvent molecules and that the diffraction curves arise from this structure or grouping. This is fundamentally important, if true. For it is a conception of the rôle of the solvent molecules, of the ionic cloud and of association, all in one. It has been conclusively shown<sup>14</sup> that when two thoroughly miscible liquids are mixed, one does not get two corresponding sets of x-ray diffraction peaks for the solution, but only one, this corresponding to a cybotactic structure in which both constituents participate. Indeed, the evidence is that the case in liquids is analogous to that in solid solutions.<sup>15</sup> Thus one would expect that varied mixtures of a hypothetical liquid alcoholate and a n-alcohol

<sup>14</sup> Meyer, Phys. Rev. **38**, 1083 (1931).

<sup>15</sup> Of course the reference here is to the simple case of like crystals in the solid solutions. Experiments with liquids have not proceeded far enough to obtain analogies with all the cases found in solid solutions.

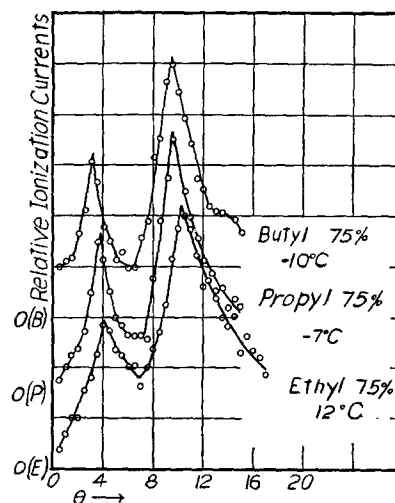


FIG. 5. Relative diffraction intensities, Mo  $K\alpha$  radiation, n-ethyl, -propyl, and -butyl solutions of lithium chloride at temperatures below the respective alcoholate transition points.

would give shifting peaks with the pattern altering from that of the n-alcohol to that of the alcoholate as the amount of alcoholate in the solution is varied. The position of the diffraction peaks for the hypothetical liquid alcoholate can be judged from the diffraction with the crystal form. For it is well known in liquid diffraction experiments that the liquid curve has its broad diffuse bands approximately in the regions of the greatest "density" of peak energies on the crystal diffraction curve. With increasing concentration of the alcoholate in the n-alcohols, the peaks shift as if the liquid solute alone would have peaks at the small angle of  $2^\circ$  or  $3^\circ$  and in the region greater than  $10^\circ$ . But this is just what the crystal alcoholate diffraction curves would suggest on the ground of the peak density rule already stated. Thus the change in diffraction curves with concentration is clearly consistent with the tentative conclusion that the ionic alcoholates of LiCl forms a liquid (cybotactic) structure with the solvent molecules. It would seem that the conclusion from miscible liquids is justified whether or not the alcoholate may exist as a separate liquid. It is upon the effect of the final mixture and the crystal itself that the argument is based.

One justification of the selection of the alcoholate as the solute in reaching the second conclusion has been expressed in the first conclusion above. Another is that the chief peaks for LiCl crystal for Mo  $K\alpha$  radiation would occur at  $13.9^\circ$  and  $16^\circ$ <sup>16</sup> and liquid peaks in this region could not, according to the above argument, give the observed effect of the concentration of LiCl. The solute must be the alcoholate. It thus seems that, from our present knowledge of x-ray diffraction in liquids, one is led to the definite but of course tentative conclusion that the liquid groupings in the solutions are those of the alcoholates in normal alcohol. The important feature is, however, that there is a liquid structure in which both  $\text{Li}^+$  and  $\text{Cl}^-$  participate with the alcohol molecules.

A confirmation of this view is that there is no evidence whatever for gaseous scattering due to  $\text{Cl}^-$  near  $0^\circ$ .<sup>17</sup> If there were random ions of  $\text{Cl}^-$  and if they were in sufficient number this gaseous scattering would be found. But in the case of the saturated solution of n-ethyl alcohol the number of chlorine ions is approximately one-fourth the number of alcohol molecules, and hence the number of scattering electrons in the former is about one-fifth of the latter. If the  $\text{Cl}^-$  ions give incoherent scattering as in a gas, there would be a noticeable relative increase in scattering near  $0^\circ$ . (The relative intensities in the various curves

have been reduced to the same value at the higher peaks.) In Figs. 1, 2 and 3, one finds no evidence whatever for gaseous scattering near the zero, for in Fig. 1 the curve for normal ethyl alcohol, if extended, would meet  $\theta=0^\circ$  at a point about 20 percent of the intensity of the chief maximum. For 20 percent saturation this is slightly increased but for 80, 75 and 100 percent saturation the corresponding value is actually decreased. In n-propyl and n-butyl alcohol the differences are negligible. Although these curves have not been corrected and presented so the diffraction with the same number of alcohol molecules is shown, yet the effect of the  $\text{Cl}^-$  ions, if at random, would clearly be in evidence.

Judging from these consistent evidences, one may then regard the conclusion as at least strongly indicated that the LiCl occurs in liquid cybotactic groups, in which both the alcoholate and alcohol participate. Presumably the LiCl is ionized and hence these temporary cybotactic structures may be regarded as analogous to ionic crystals. Indeed, it is already known that conduction in ionic crystals has definite similarities to conduction in electrolytes. Just how far this conception of the structure of concentrated electrolytic solutions will be found general one can only surmise. Experiments by the author in water solutions are at present in entire harmony with the view here expressed, but the details will be presented in a subsequent paper.

I wish to acknowledge with appreciation my indebtedness for the observational work recorded herein to Dr. R. M. Zabel, research assistant.

<sup>16</sup> According to the measurement of Davey, Phys. Rev. **21**, 143 (1923).

<sup>17</sup> Attention has already been called by Prins (reference 5) to this same absence of scattering in aqueous solutions.