Mayer's Theory of Condensing Systems

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Structure of Liquid Aliphatic Amines

The Table I below gives the results of x-ray diffraction study in five liquid di-acyl amines and in n-amyl and tri-n-amyl amines. The usual technique of production of x-rays and of obtaining diffraction haloes in liquids was employed. The second column gives the Bragg spacing d, calculated from the diameter of the diffraction halo. The third column gives the constant k, in Raman[1] and Ramnathan's theory, i.e., the ratio of d to $(m/p)^{\frac{1}{3}}$, which for spherical molecules should have a value between 0.8 and unity.

It is seen that the value of Bragg spacing has the constant value 4.46A for all the normal di-acyl amines examined. This value is close to 4.60A, which is the diameter of a carbon-atom-chain in aliphatic liquid molecules found by previous workers.[2] This constant value for the spacing cannot represent the distance between two carbon-chains in the same molecule of an acyl amine, since the diffraction haloes are far from sharp. The possible explanation of this value of the spacing is, therefore, that it represents the distance between two carbon-chains belonging to two adjacent molecules of the amine.

We may assume that the flat pyramidal shape of the NH_3 molecule is maintained in the acyl amine molecule, in which one, two or three carbon-chains replace the hydrogen atoms. Taking into account the tendency of long chains to arrange themselves parallel to one another and adopting Stewart's[3] idea of "Cybotactic state" in liquid, the required condition for diffraction is obtained if we suppose that in the liquid, the molecules are piled up one above the other, the vertices of the adjacent pyramids fitting into each other and the corresponding edges lying close and parallel. Here, the Bragg spacing will be the mean distance between two carbon-chains lying along corresponding edges of adjacent pyramids and this will be nearly equal to the thickness of the chain, since the packing can be as close as possible. The whole arrangement of the molecules will, therefore, somewhat resemble a row of rather flat tripods, placed one above the other, the three legs of one lying close and alongside those of its neighbor. It is found that in the haloes of the tri-acyl amines, there is considerable intensity within the diffraction halo but the outer edge is sharply defined. This is readily explained on the above picture, as the outer limit corresponds to the closest approach of one edge of a pyramid towards the corresponding one of its neighbor. Any disarrangement of the row of pyramids will increase the mean distance between corresponding carbon-chains and give the inner scattering of the halo.

It will be also seen from the table that the spacing for an

TABLE I.

Liquid	$d = \dfrac{\lambda}{2 \sin \theta/2}$	k
Di-n-propyl amine	4.46A	0.730
Di-iso-propyl amine	5.48A	.890
Di-n-butyl amine	4.46A	.685
Di-n-amyl amine	4.46A	—
Di-iso-amyl amine	4.84A	.693
n-amyl amine	4.34A	.624
Di-n-amyl amine	4.46A	—
Tri-n-amyl amine	4.70A	.603

iso-amine is larger than that for the normal one—an effect of the side linkage in the chain. Also, the value of the constant k in the last column is, in all cases but one, below 0.7, showing that the molecules are not spherical in shape. Only in the case of di-iso-propyl amine, it is more than .8. This must be due to the fact that this molecule is more nearly spherical in shape, since there is a side linkage attached to a short carbon-chain.

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[1] Raman and Ramnathan, Proc. Ind. Ass. Cult. Sci. p. 127 (1923).
[2] Stewart and Morrow, Phys. Rev. 30, 232 (1927).
[3] Stewart, Rev. Mod. Phys. 2, 116 (1930).

Mayer's Theory of Condensing Systems

Mayer's general results[1] can be derived almost immediately from the theory of dissociating assemblies, thus avoiding much of his preliminary argument. Fowler's general method[2] for gaseous assemblies with any number of components and reactions is at once applicable to a gas of one component and any number of reactions—clustering processes or collisions. The dissociating molecule of type S is now a collision or cluster of S atoms. Fowler's equations (479) and (484), giving the law of mass action and the external pressure on the gas, are then, with classical partition functions, almost obviously identical with Mayer's equations (43) and (37) when recast into the notation there used. The present more general argument is applicable to any type of partition function, proving very directly the generality of Mayer's results.

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[1] Joseph E. Mayer, J. Chem. Phys. 5, 67 (1937).
[2] R. H. Fowler, *Statistical Mechanics*, 2nd Edition, §5·3.

On the Symmetries of the Fields About Ions in Solution. Equilibrium between Forms of Different Symmetry

The absorption spectra of solutions of trivalent europium are so sharp that it is possible to resolve the multiplets induced by the electrical fields about the europium ions. It was found[1] that the multiplets consisted of different numbers of components depending upon the nature of the solutions. Such differences were sought as a parallel to the different structures which arise in the spectra of crystals when a rare earth is subject to crystal fields of various symmetries.

In this note we shall describe new features in the spectra of aqueous solutions of europium nitrate and of europium chloride, especially in the blue region which contains lines rather easy to follow. This group consists of four lines in the chloride and three lines in the nitrate of different spacing, sharpness and relative intensities.[2] These
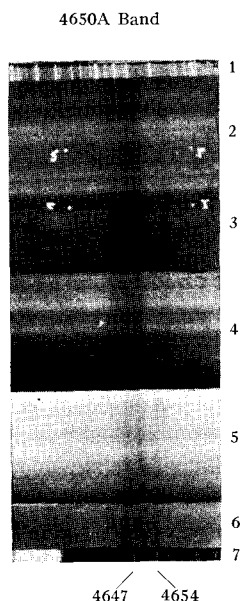
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4647   4654

FIG. 1. 1-Fe arc. 2-EuCl₃ .0025 M. 3-EuCl₃ .95 M. 4-Eu(NO₃)₃ .0025 M. 5-Eu(NO₃)₃ .009 M. 6-Eu(NO₃)₃ .95 M. 7-Fe arc.

separate patterns remain unchanged from about 1.5 M to about 0.01 M as observed with a 21-ft. grating. On diluting to 0.0007 M, we could discover no change in the pattern of the chloride but when the nitrate was diluted to 0.0007 M, its group which had consisted of three lines now had changed over to four, indistinguishable in character from those of the chloride. At concentrations between 0.01 M and 0.0007 M, the nitrate showed both spectra and with increased dilution the chloride pattern gained intensity at the expense of the nitrate pattern. (See Fig. 1.)

Europium nitrate in aqueous solution has then distributed itself between two discrete configurations in equilibrium corresponding to different symmetries of the fields about the europium ions. There is some resemblance here to the situation in which two allotropic modifications of a crystal are present together, with this difference, that the equilibrium in the solution of the nitrate takes place within one phase.

In a forthcoming note it will be shown that europium nitrate and europium chloride are strong electrolytes similar to and of the same order of strength as lanthanum nitrate and lanthanum chloride which have served as standard salts in thermodynamic studies of trivalent ions. Because of the close resemblance of europium to other rare earths, we regard the existence of discrete forms of different symmetry as no rare phenomenon—among trivalent ions, at any rate.

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[1] S. Freed and S. I. Weissman, J. Chem. Phys. 6, 297 (1938).
[2] Since the publication of the previous note, we have discovered that G. Urbain (J. Chem. Phys. 4, 243 (1906)) had observed differences between the spectrum of europium nitrate and of europium chloride in aqueous solution.

Symmetries of the Fields About Ions in Solution and Electrolytic Dissociation

Recent experiments[1] have shown that the fields about the ions of trivalent europium in aqueous solution are sharply defined in their intensities and orientations and that these differ with the nature of the solution. However, with a solution of a given salt, the structures in the spectra which respond to changes in the fields are not affected when the solution is diluted. The wave-lengths of the lines, their sharpness, relative intensities, the spacings within the multiplet, all remain unchanged, from concentrated to dilute solutions. Europium chloride has four lines in a particular group in the blue region. No change could be observed in the character of the lines when the concentration was varied from about 1.5 M to 0.0007 M. Corresponding to this group of lines, europium nitrate has three lines, altogether different in quality from the four of the chloride. These lines experience no change when the solution is diluted, even though a new additional form makes its appearance[2] at about 0.01 M. The spectrum of the new form is indistinguishable from that of the chloride. As dilution proceeds the "chloride-structure" of the nitrate becomes more intense relative to the original "nitrate-structure." Nevertheless, even though the total intensity of each structure varies, the relative intensities within the structure, the sharpness, and the intervals remain invariable throughout dilution.

The theory of Bethe[3] prescribes into how many components a particular energy level will be decomposed by an electrical field of given symmetry. The magnitude of the intervals between the components is a measure of the strength of the fields. We have found that the spectrum of a crystal of hydrated europium nitrate contains three lines in its blue group, having roughly the same intervals as originate from a solution of the nitrate. We are then to conclude that the fields about the europium ions in the crystal are roughly of the same intensity as the fields about the ions in solution. Furthermore this intensity does not change with dilution.

A natural assumption to make at this point is that the salts of europium are revealing bonds which are permanently oriented. If that description is to be correct, it must not exclude the electrolytic dissociation of the salts since, as we shall show, salts of europium are strong electrolytes in about the same measure as the salts of lanthanum. The latter have repeatedly served to illustrate and test the inter-ionic attraction theory.

There is such a mass of different data on the close resemblance among the ions of the rare earths[4] that there can be little doubt concerning the resemblance with respect to ionization also. As a final check on these inferences, which, to be sure, involve little interpolation, Mr. I. M. Klotz of this laboratory measured the electrical conductivities of solutions of europium nitrate and of europium chloride and found them to be nearly of the same magnitude as those of the corresponding lanthanum salts. Mr. Klotz will publish his data shortly. As to thermodynamic behavior—the freezing point lowering of lanthanum nitrate at 0.01 M is 3.35 times[5] that of the same concentration of mannose and at 0.001 M it is 3.75 times.