XVII. *The Molecular Scattering of Light in Liquid Mixtures.*

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1. *Introduction.*

As is well known, there are many substances, *e. g.* phenol and water, which in the liquid state dissolve each other completely and form a single phase above a certain temperature, but below it are only partially soluble and divide into two coexistent phases. Such mixtures exhibit a marked opalescence or turbidity at temperatures slightly higher than that at which they separate into two layers. Smoluchowski[†] put forward a thermodynamic explanation of this phenomenon as due to the spontaneous local fluctuations of concentration which occur in the mixture and cause optical inhomogeneity. The problem was further handled by Einstein[‡], who made certain simplifying assumptions, namely, that the liquids are incompressible, that their specific volumes are negligibly small in comparison with those of the saturated vapours emitted by them, and that the latter can be treated as ideal gases, and on this basis derived a formula for the opalescence of the mixture in terms of experimentally determinable magnitudes, that is, the variation of its refractive index and of the partial vapour-pressures of its components with alteration of concentration. The simplifications referred to, however, considerably restrict the validity of the investigation which, in fact, can be regarded as strictly applicable only over a small range of temperature above that at which the mixture separates into two phases. For such a restricted range, the correctness of Einstein's formula has been experimentally established by the investigations of Fürth[§] and of Zernike[‖]. Actually, however, by using carefully purified liquids freed from dust by repeated distillation *in vacuo*, the opalescence in mixtures may be studied over any desired range of temperature and not merely in the immediate vicinity of the critical solution point, and very remarkable and interesting changes in the intensity of the scattered

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[*] Communicated by the Authors.
[†] *Annalen der Physik*, xxv. p. 219 (1908).
[‡] *Annalen der Physik*, xxxiii. p. 1295 (1910).
[§] *Wiener Sitzungsberichte*, p. 577, 1915.
[‖] Thèse, Amsterdam, 1915.

Phil. Mag. 45, 213-224, 1923.

light and the state of its polarization are observed.[*] These phenomena are also noticeable in mixtures of liquids which are completely soluble in each other at the ordinary temperature. It is found that Einstein's approximate investigation is not adequate to explain the observed facts in these cases and that a stricter investigation is called for. It is proposed in this paper to show how by a modification of the procedure adopted by Einstein, a *perfectly rigorous* expression for the light-scattering can be derived in terms of experimentally determinable quantities. A comparison is also made between the results of the modified theory and those observed in experiment. Specially noteworthy are the effects arising from *molecular anisotropy* which, of course, are not contemplated at all in Einstein's theory. These are discussed in detail in the course of the paper.

2. *Thermodynamical Theory: Application of Boltzmann's Principle.*

In order to deal with the problem under consideration, Einstein assumed that the refractive index of the mixture is a function of a single variable k which expresses the concentration of the mixture, that is the ratio of the mass of the second component present to that of the first component. This is not, however, correct. We have in reality to deal with *two* independent variables, namely, the densities of both components, and the local fluctuations of refractive index are determined by variations of both of these quantities. One way of determining the accidental deviations of density in a mixture is by applying the principles of statistical mechanics. This has been attempted by Ornstein[*]. In order, however, to express the results in terms of physically measurable quantities, it is simpler to use a purely thermodynamical treatment based upon Boltzmann's well-known relation between entropy and probability. In order to make use of this principle, we have to find the change of entropy resulting from small increases Δm_1 and Δm_2 in the masses, m_1 and m_2 of the components actually present in unit volume of the mixture. The probability of such deviations occurring spontaneously and their mean value may then be evaluated. In order to find the change of entropy involved we have to imagine the masses Δm_1 and Δm_2 introduced into unit volume of the mixture isothermally and by a reversible process. The following thermodynamical operation, which is a modification of that used by Einstein, enables this to be done.

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[*] Proc. Roy. Soc. Amsterdam, xv. p. 54 (1912).

Consider unit volume of the mixture enclosed in a cylinder fitted with a frictionless piston by which the hydrostatic pressure can be varied. The base of the cylinder has two openings, which may be either closed at will or fitted with membranes permeable respectively to the vapour of the first and second components only. A second and much larger reservoir similarly fitted with a piston and semi-permeable openings is assumed to be filled with the liquid mixture, this being maintained at the same temperature and at a hydrostatic pressure equal to the total vapour pressure ϕ of the mixture. The following isothermal operations may then be carried out.

Stage 1.

By means of auxiliary pumps applied to the semi-permeable openings, small masses (Δm_1) and (Δm_2) of the two components may be removed in the state of vapour from the reservoir, the volume of which is assumed to be so great that no appreciable alteration in the composition of its contents occurs in consequence of this removal.

If p_1 and p_2 be respectively the partial pressures of the vapours and v_1 and v_2 their specific volumes, the work done in the process is

$$-p_1v_1\Delta m_1-p_2v_2\Delta m_2+[s_1\Delta m_1+s_2\Delta m_2]\phi, \quad . \quad . \quad (1)$$

where s_1 and s_2 represent respectively the shrinkages of the volume of the mixture by removal of unit masses of the two components.

Stage 2.

Taking the masses (Δm_1) and (Δm_2) of the vapours thus separated, force simultaneously a mass (Δm_1) of the first component and a mass $(k\Delta m_1)$ of the second component into the cylinder the contents of which are maintained at a constant hydrostatic pressure ϕ, k being the fraction m_2/m_1. It is clear that in this operation the composition of the mixture, and therefore also its vapour-pressure, remain unaltered. The work done in this process is therefore

$$p_1v_1\Delta m_1+p_2v_2k\Delta m_1-[s_1\Delta m_1+s_2k\Delta m_1]\phi. \quad . \quad . \quad (2)$$

Stage 3.

Force the remaining portion $(\Delta m_2-k\Delta m_1)$ of the second component into the cylinder, the hydrostatic pressure in it being maintained at the equilibrium value of its total vapour-pressure at each instant. The work done in this process is

$$v_2(\Delta m_2 - k\Delta m_1)(p_2 + \tfrac{1}{2}\Delta p_2) - s_2(\Delta m_2 - k\Delta m_1)(\phi + \tfrac{1}{2}\Delta\phi), \quad . \quad (3)$$

where (Δp_2) and $(\Delta\phi)$ represent respectively the changes of the partial vapour-pressure and the total vapour-pressure resulting from the operation.

Stage 4.

The volume of the mixture in the smaller cylinder is now greater than at first by $(s_1\Delta m_1 + s_2\Delta m_2)$. The semi-permeable openings are now closed, and the piston enclosing the contents forced in by increasing the hydrostatic pressure till the original volume is restored. The work done in this process is

$$\tfrac{1}{2}\beta(\Delta p)^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

where β is the compressibility, of the mixture and (Δp) is the increase of hydrostatic pressure in the process.

Adding up (1), (2), (3), and (4) we find the total work done is

$$\tfrac{1}{2}(v_2\Delta p_2 - s_2\Delta\phi)(\Delta m_2 - k\Delta m_1) + \tfrac{1}{2}\beta(\Delta p)^2. \quad . \quad . \quad (5)$$

The quantity k is a measure of the concentration of the mixture. If it be altered to $k + \Delta k$ as the result of the operations set out above, it is easily seen that $m_1\Delta k = (\Delta m_2 - k\Delta m_1)$.

Hence (5) may be written in the form

$$\tfrac{1}{2}m_1\left(v_2\frac{\partial p_2}{\partial k} - s_2\frac{\partial\phi}{\partial k}\right)(\Delta k)^2 + \tfrac{1}{2}\beta(\Delta p)^2,$$

or, for brevity,

$$\tfrac{1}{2}\alpha(\Delta k)^2 + \tfrac{1}{2}\beta(\Delta p)^2. \quad . \quad . \quad . \quad . \quad . \quad (6)$$

The next step is to find the mean value of $(\Delta k)^2$ and $(\Delta p)^2$ in the deviations which occur spontaneously in a volume-element dv of the mixture. We may for this purpose use Boltzmann's principle in the form in which it has been expressed by Einstein,

$$dW = Ce^{-\frac{NE}{RT}} d\lambda_1 d\lambda_2 \ldots . d\lambda_n, \quad . \quad . \quad . \quad (7)$$

where $\lambda_1, \lambda_2 \ldots . \lambda_n$ are suitably chosen variables which determine the observable condition of the system and dW is the probability that the magnitudes λ_1, λ_2, etc., lie between λ_1 and $\lambda_1 + d\lambda_1$, λ_2 and $\lambda_2 + d\lambda_2$, etc., R, T, and N have the same significance as in kinetic theory. C is a constant and E is the work necessary to bring the system into the state under consideration from that of thermodynamical equilibrium. If $\lambda_1, \lambda_2 \ldots$ are assumed to be zero in the state of equilibrium and E can be expressed in the form

$$E=\tfrac{1}{2}a_1\lambda_1^2+\tfrac{1}{2}a_2\lambda_2^2+\ldots+\tfrac{1}{2}a_n\lambda_n^2, \quad . \quad . \quad . \quad (8)$$

then (7) assumes the familiar form of the Gaussian error-law and it may easily be shown by integration that

$$\left.\begin{aligned}\overline{\lambda_1}^2&=\mathrm{RT}/\mathrm{N}a_1,\ \overline{\lambda_2}^2=\mathrm{RT}/\mathrm{N}a_2,\ \text{etc.},\\ \overline{\lambda_1\lambda_2}&=\overline{\lambda_2\lambda_3}\ldots=0,\end{aligned}\right\}, \quad . \quad . \quad (9)$$

where the bars indicate the *mean value* of the quantities written under them.

Comparing (6) and (8), we find from (9) that for an elementary volume dv of the mixture

$$\left.\begin{aligned}\overline{(\Delta k)^2}&=\frac{\mathrm{RT}}{\mathrm{N}}\frac{1}{\alpha dv},\\ \overline{(\Delta p)^2}&=\frac{\mathrm{RT}}{\mathrm{N}}\frac{1}{\beta dv},\\ \text{and } \overline{\Delta k}\,\overline{\Delta p}&=0.\end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

Writing $\epsilon=\mu^2$ where μ is the refractive index of the mixture,

$$\Delta\epsilon=\frac{\partial\epsilon}{\partial k}\cdot\Delta k+\frac{\partial\epsilon}{\partial p}\Delta p,$$

and from (10), it follows at once that

$$\overline{(\Delta\epsilon)^2}=\frac{\mathrm{RT}}{\mathrm{N}dv}\left[\left(\frac{\partial\epsilon}{\partial k}\right)^2\Big/\alpha+\left(\frac{\partial\epsilon}{\partial p}\right)^2\Big/\beta\right]. \quad . \quad . \quad (11)$$

3. *Intensity of the Scattered Light: Comparison with Einstein's formula.*

From (11), the intensity of the opalescence radiation can be easily calculated. Using a relation given by the late Lord Rayleigh *, we find that in a direction at right angles to the incident beam (assumed to be unpolarized and of unit intensity), the intensity of the scattered light is

$$\mathrm{I}=\Sigma\frac{\pi^2(dv)^2\overline{(\Delta\epsilon)^2}}{2\lambda^4}\Big/r^2,$$

where λ is the wave-length and r is the distance of the volume-element from the point of observation. Substituting

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* Scientific Papers, vol. i. p. 526.

for $(\Delta\epsilon)^2$ from (11), and integrating over the whole volume of the fluid, say Ψ,

$$I=\frac{\Psi}{r^2}\cdot\frac{\pi^2RT}{2N\lambda^4}\left[\left(\frac{\partial\epsilon}{\partial k}\right)^2\bigg/ m_1\left(v_2\frac{\partial p_2}{\partial k}-s_2\frac{\partial\phi}{\partial k}\right)+\beta\rho^2\left(\frac{\partial\epsilon}{\partial\rho}\right)^2\right], \quad . \quad . \quad . \quad (12)$$

where ρ is the density of the mixture.

The principal difference between Einstein's expression for the light-scattering in liquid mixtures and that given here is that the former does not include the term proportional to the compressibility of the mixture which appears in (12). This term expresses the light-scattering due to the local thermal *fluctuations of density* in the mixture considered as a single substance. Using Lorentz's relation $(\epsilon-1)/(\epsilon+2)=\text{const.}\rho$, the second term in (12) may be developed and written in the form

$$\frac{\pi^2 RT\beta}{18\,N\lambda^4}(\mu^2-1)^2(\mu^2+2)^2\frac{\Psi}{r^2}. \quad . \quad . \quad . \quad . \quad (13)$$

The first term in (12) which represents the light-scattering due to the local *fluctuations of concentration* in the mixture may be simplified if we neglect $s_2\dfrac{\partial\phi}{\partial k}$ in comparison with $v_2\dfrac{\partial p_2}{\partial k}$ and assume, further, that the saturated vapour obeys the gas laws, in which case it may be written as

$$\frac{M_2}{2N\lambda^4}\cdot\frac{\frac{1}{m_1}(\partial\epsilon/\partial k)^2}{\partial\log p_2/\partial k}\cdot\frac{\Psi}{r^2}, \quad . \quad . \quad . \quad . \quad . \quad (14)$$

where M_2 is the molecular weight of the second component in the gaseous phase. (14) is Einstein's approximate result. The simplifications here made are only permissible when the vapour-pressure is not large.

The relative importance of the two effects, viz. the light-scattering due to fluctuations of density and concentration respectively, which contribute to its total observed intensity depends on the circumstances of the particular case. The first effect depends on the refractive index and compressibility of the mixture, and second on the variations of refractive index and of the partial vapour-pressures produced by a change in the composition of the mixture. In the immediate neighbourhood of the critical solution temperature, the partial vapour-pressures alter very little with the composition of the mixture, and the concentration-scattering becomes very great. On the other hand, at temperatures far removed from the critical solution point or in the cases in which the components are ordinarily completely miscible, the partial vapour-pressures change rapidly with concentration, the concentration scattering becomes less, and if the refractive indices of the components do not differ much, it may even become unimportant in comparison with the density scattering. The relative proportion of the two components in the mixture is also of importance. It is evident that when either of the components forms a vanishingly small proportion of the mixture, the concentration-scattering would disappear and the observed opalescence would be due entirely to the density-scattering in the remaining component. The composition of the liquid would also influence the density-scattering, since the refractive index and compressibility of the mixture are both functions of it.

4. *Effect of Molecular Anisotropy.*

The theory so far discussed rests on a purely thermodynamical basis and leads to the result that the light scattered in a direction transverse to the primary beam should be completely polarized. If we had proceeded on the basis of a molecular theory we should have obtained a precisely identical result, provided the molecules could be treated as isotropic or spherical scattering particles exerting forces on each other. Actually, however, this is far from being the case. Even in the case of gases, the transversely scattered light is known to be imperfectly polarized, and in liquids at ordinary temperatures this imperfectness of polarization of the scattered light is found to be much more strikingly evident. Taking this into account, we may, in considering the case of liquid mixtures, divide the total observed light-scattering in a direction transverse to the primary beam into three parts, which are assumed to be superposed on each other. A part Ω_1 arises from density fluctuations. A part Ω_2 arises from the concentration fluctuations. Both of these consist of polarized light, and their magnitudes are given by the thermodynamic theory already considered. Another part arises from the varying orientations of the anisotropic molecules, and this consists in great measure of unpolarized light. Denoting by r the ratio of intensity of the weak to the strong component of polarization in the transversely scattered light, we may write

$$r = \frac{2\Omega_4}{\Omega_1+\Omega_2+\Omega_3+2\Omega_4}, \quad . \quad . \quad . \quad . \quad . \qquad (15)$$

where $\Omega_3+4\Omega_4$ is the total intensity of the orientation-scattering of which a part Ω_3 consists of plane polarized light and the remaining portion, $4\Omega_4$, consists of unpolarized light, and is therefore equally divided between the two perpendicular directions of vibration. For all practical purposes Ω_3* is negligible, and it remains to determine the magnitude of Ω_4.

If we assume that the molecules in a liquid have their *orientations* entirely at random (though their *positions* are *not*), it is readily seen that the unpolarized part of the orientation-scattering would be simply proportional to the number of molecules n_1 and n_2 of each kind present in unit volume, and we may write

$$\Omega_4 = n_1\chi_1 + n_2\chi_2, \quad . \quad . \quad . \quad . \quad . \quad . \qquad (16)$$

where χ_1, χ_2 are constants characteristic of each kind of molecule. The magnitude of χ_1 and χ_2 may be determined from (15) and (16) when the values of r corresponding to the case in which the liquid contains only one component or the other are known, and the values of r and Ω_4 for any given composition of the mixture may then readily be calculated. The assumption that the orientation-scattering is simply proportional to the number of molecules per unit of volume is shown to be justified by the fact that in a number of cases it enables the value of r to be successfully predicted for a single substance in the state of liquid when the corresponding value of r for the same substance in the state of vapour is known.

It is evident from (15) that when Ω_1 or Ω_2 is very large, r will be very small. In other words, when either the density scattering or the concentration scattering is very large, the transversely scattered light is almost completely polarized. The latter condition arises when the observations are made in the immediate vicinity of the critical solution temperature. The former condition arises at the plait-point temperature of the mixture, *i. e.* at a temperature which

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* In the case of gases obeying Boyle's law, only 1/13 of the orientation-scattering consists of polarized light, as has been shown by Born. In the case of liquids under ordinary conditions, it is probably much smaller on account of the partial correlation of phase of the effects of contiguous molecules.

corresponds to the ordinary critical state for a simple fluid. In either of these cases, the orientation-scattering is a negligible part of the whole observed scattering.

5. *Comparison of Theory and Experiment.*

The theoretical results deduced above agree in their general features with experiment. The scattering of light by mixtures of phenol and water of varying concentrations has been studied in the authors' laboratory by Mr. V. S. Tamma for a range of 30° C. above its critical solution temperature (68° C.). The scattering is exceedingly large in the immediate neighbourhood of the critical solution point, and as the temperature is raised its intensity diminishes, but over the whole range the scattering remains much higher than that of the pure liquids taken together or separately. As is indicated by theory, the polarization of the light scattered in the mixture is far more complete than in pure phenol, which shows a large admixture of unpolarized light. Very near the critical solution temperature, the polarization is practically complete. But as the temperature is raised, it becomes less and less perfect.

Experiments have also been made on mixtures of ethyl alcohol and water. As the percentage of alcohol is increased, the scattering increases to a maximum, then comes down to a minimum and again increases. The extra scattering is largest for a mixture containing about 20 per cent. of alcohol. The case of this mixture is particularly complicated, inasmuch as both its compressibility and refractivity are anomalous. At 20° C., the compressibility is a minimum when the percentage by weight of alcohol is nearly 20. The refractivity of the mixture increases as the alcohol-content is increased, and reaches a maximum when there is about 80 per cent. by weight of alcohol, after which it again diminishes.

The following table gives the density-scattering calculated for different compositions in terms of that of water as a unit.

Percentage of alcohol by weight.	Compressibility at $20^\circ \times 10^6$.	Refractive index at 20° C.	Density scattering.
0	49	1·3375	1·00
10	42	1·3436	0·94
20	40	1·3500	0·94
40	47	1·3600	1·20
60	62·5	1·3670	1·68
80	81	1·3693	2·19
100	100	1·3674	2·72

To calculate the concentration-scattering, we require to know the partial vapour-pressures of the components, and curiously enough, the necessary data do not seem to exist for alcohol-water mixtures. Anyhow, the concentration-scattering would vanish at about 80 per cent. by weight of alcohol, since at that point there is no change of refractivity with concentration, and would be very small over the range 60 to 100 per cent. Since the refractivity of alcohol is not very different from that of water, the effect would not be large at any stage. This agrees with the observed facts.

Measurements of the intensity and polarization of the scattered light in binary mixtures of carbon disulphide and ether, and of benzene and normal hexane have been published by W. H. Martin *. By the use of relation (15), we can calculate the orientation-scattering. Partial vapour-pressure data for the first mixture are available †, and from (14) the concentration-scattering can be calculated. But owing to lack of compressibility data, we cannot calculate the density-scattering. Since, however, this forms only a small fraction of the total scattering in the present case, an error in its estimate would not be of much consequence.

In the attached graph are shown, A the concentration-scattering, B the unpolarized scattering, and C the sum of these two for different concentrations. The values of the total experimental scattering are also plotted in curve D. It will be seen that the curve of orientation-scattering is nearly a straight line, showing, in agreement with (16), that it is proportional to the number of the two kinds of molecules per unit volume. The concentration-scattering was calculated by using (14).

Now

$$\frac{\partial \log p_2}{\partial k} = \frac{1}{p_2}\frac{\partial p_2}{\partial k} = -\frac{x^2}{p_2}\frac{\partial p_2}{\partial x},$$

where x is the mass of the first component (in this case CS_2) in unit mass of the mixture. The values of $\frac{\partial p_2}{\partial x}$ were got from the partial vapour-pressure curve of ether. $\frac{\partial \epsilon}{\partial x}$ was calculated from the formula for the refractive index of mixtures

$$\frac{\epsilon-1}{(\epsilon+2)\rho} = \frac{\epsilon_1-1}{(\epsilon_1+2)\rho_1}x + \frac{\epsilon_2-1}{(\epsilon_2+2)\rho_2}(1-x),$$

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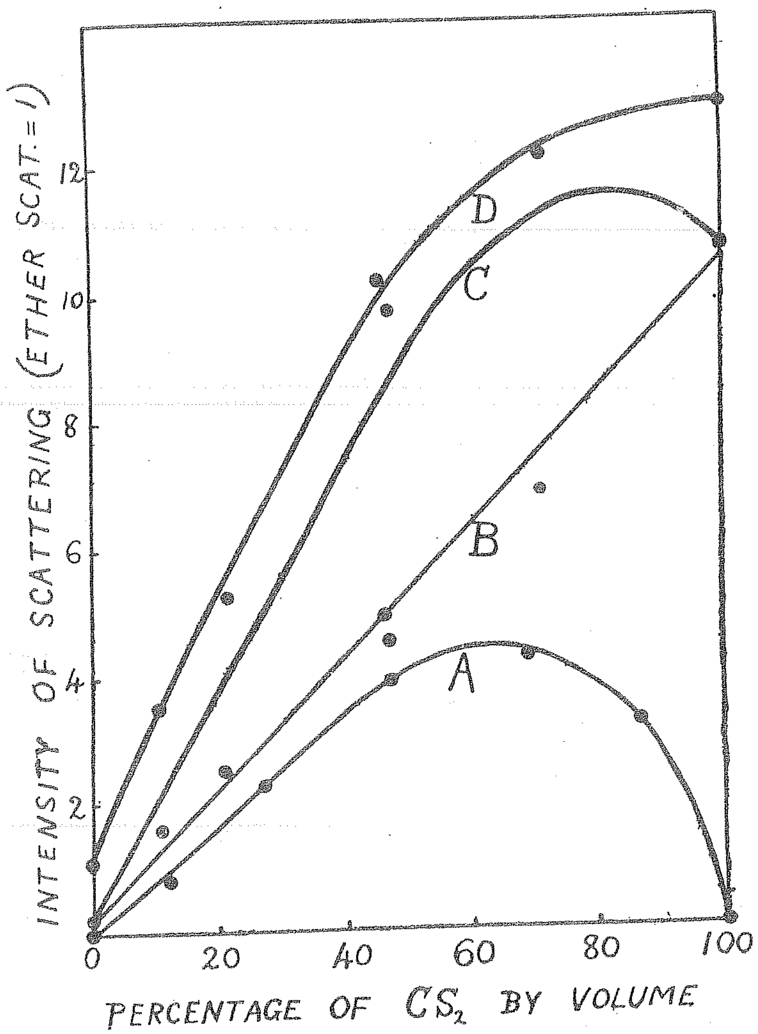
* Journal of Physical Chemistry, Jan. 1922.

† Guglielmo, *Acc. dei Lincei* (5) 1, i. pp. 242 & 294 (1892).

where ϵ_1, ρ_1, and ϵ_2, ρ_2 refer to the two components of the mixture.

It will be noticed that the curve C closely follows the experimental intensity-curve. The difference, no doubt, represents the density-scattering, which, however, cannot be calculated theoretically (except separately for the two pure liquids) as the compressibility of the mixture is not known.



For pure ether and pure CS_2 the density-scatterings are 0·85 and 2·80, so that if these are added to the orientation-scatterings, the total scattering fits into Martin's experimental curves. To make an adequate test of the theory, we require to know both the compressibilities and the partial vapour-pressures of pairs of liquids. Data regarding partial vapour-pressures are available for a number of pairs of liquids, and the measurement of compressibilities of mixtures is being undertaken in this laboratory in order to make a complete test of the theory of light-scattering in mixtures.

Summary and Conclusion.

In this paper, the approximate investigation of the scattering of light in liquid mixtures given by Einstein is revised and a perfectly rigorous formula is developed, in which account is taken of the compressibility of the mixture. It is shown that the thermodynamical investigation leads to the result that the light-scattering arises in two distinct ways: (1) due to spontaneous local fluctuations in the composition of the mixture, and (2) due to local fluctuations of its density. Einstein's approximate investigation ignores the second effect, which becomes very important when the observations are made at temperatures not close to the critical solution point or in the case of liquids which are completely miscible at ordinary temperatures.

(*a*) The scattering power is expressed in terms of the compressibility of the mixture, the variations of its refractive index, and the partial vapour-pressures of its constituents with the composition.

(*b*) A discussion is given of the effects of molecular anisotropy which gives rise to an additional "orientation-scattering." It is shown that the polarization of the transversely scattered light is imperfect as the result of molecular anisotropy, but it is considerably less so in the mixture than in the pure liquids, and, further, it becomes more and more perfect as the critical solution temperature is approached.

(*c*) A comparison of the results with the available experimental data shows a general agreement.

(*d*) Very similar methods may also be applied in the case of solutions of solids in liquids, and in the case of ternary mixtures.

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