CRITICAL OPALESCENCE OF LIQUID MIXTURES.

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1. *Introduction.*

THE well-known formula of Smoluchowski-Einstein which gives Rayleigh's constant for the polarised coherent scattering due to density fluctuations in any medium, shows that the intensity of this scattering is proportional to the coefficient of isothermal compressibility β. If one approaches the critical point, the coefficient β increases rapidly and consequently one observes an abnormal increase in the intensity of scattering. This phenomenon is called the *critical opalescence*. It is a remarkable phenomenon easily observed but not so easy to interpret. For mixtures of certain pairs of liquids there exists a critical temperature of complete miscibility in the neighbourhood of which one finds a strong opalescence due uniquely to the fluctuations of concentration. The critical opalescence of binary liquid mixtures presents the same optical characteristics as those of pure liquids. The theory of Smoluchowski-Einstein shows that one gets an expression for the intensity of scattering in a liquid mixture by replacing in the expression for the intensity of scattering for a single liquid the coefficient β by a coefficient characteristic of the fluctuations in concentration which becomes infinite at the critical point of complete miscibility. By using carefully purified liquids freed from dust by repeated distillations *in vacuo*, the opalescence in mixtures could be studied over any desired range of temperature and not merely in the immediate neighbourhood of the critical point and very remarkable and interesting changes in the intensity of the scattered light and the state of polarisation are observed. There are certain features of the phenomenon, however, that do not find an explanation on the basis of the Smoluchowski-Einstein theory, one of which is that the depolarisation of the opalescent light remains finite instead of tending to zero as the critical solution temperature is reached. The above theory was afterwards modified by Ornstein, Zernike (1914, 1916, 1918, 1926), Placzek (1930) and Rocard (1933) but with very little success.

In a series of papers in these *Proceedings* (Krishnan, 1934–35) the author presented evidence for the first time that large molecular clusters exist in such liquid mixtures in the neighbourhood of the critical solution temperature. The essential idea involved in the author's experiments is the examination of the state of polarisation of the transversely scattered light when a beam of plane polarised light with its electric vector horizontal is passed through the medium. In such a case the scattering in the transverse horizontal directions would be completely unpolarised, *i.e.*, its depolarisation factor would be unity provided the scattering centres are of molecular dimensions. Any departure from the value of unity would therefore indicate that the scattering centres are no longer of molecular size but possess dimensions not small compared with the wave-length of light. The finite value of the depolarisation of the opalescent light arises from this fact.

Almost simultaneously with the author's discovery of molecular clustering in liquid mixtures, Rousset (1934) reported some quantitative data regarding the state of polarisation of the light scattered by binary liquid mixtures in the neighbourhood of the critical solution temperature. He finds that as one approaches the critical temperature, the depolarisation factor ρ_u diminishes at first and after attaining a minimum very near the critical solution temperature increases again rapidly. By assuming that the primary scattering is completely polarised he has attempted to explain the rapid increase of ρ_u in the immediate neighbourhood of the critical point by the existence of a secondary scattering partially depolarised, the intensity of which increases more rapidly than that of the primary scattering, if ΔT is sufficiently small. ΔT is the difference of temperature between any particular temperature and the critical solution temperature. The anomalous depolarisation observed in the neighbourhood of the critical point when the incident light is polarised with vibrations horizontal has been attributed by Rousset to secondary scattering, whereas the present author has attributed it to the presence of molecular clusters. A study of the dispersion of depolarisation of light-scattering in liquid mixtures very near T_c will be a decisive test. The recent investigations of the author (1937) on the dispersion of depolarisation of light-scattering in colloids have clearly shown that if there is any tendency for the formation of molecular clusters of size comparable with the wave-length of light, the depolarisation factors should exhibit an appreciable dispersion with wave-length. Hence it was thought desirable to go into this question in detail in order to decide once for all whether all the anomalies observed at the critical solution temperature of liquid mixtures could be explained on the basis of the formation of

molecular clusters or not. At first a brief resumé of the theory of secondary scattering as propounded by Rousset will be given and also the further consequences of this theory which has not been considered by him. These are tried out experimentally and the results are also given. Measurements of the intensity and the depolarisation factors ρ_u, ρ_v and ρ_h were made for three more binary mixtures and one ternary mixture over a range of temperature of about 30° above the critical solution temperature. A critical study of the theory of Gans (1936) has been made in relation to the experimental results obtained by the author from a detailed study of light-scattering. The bearing of these results on the anomalies of viscosity, magnetic birefringence, flow birefringence, etc., noticed in the vicinity of the critical solution temperature has also been discussed in detail in the present paper.

2. Theory of Secondary Scattering.

The principle underlying the calculations of Rousset is that when a beam of linearly polarised light is incident on a small volume of a mixture of two liquids, each individual volume element inside the mixture becomes a luminous source vibrating parallel to the incident electric vector and sends out radiations which he calls as the *primary scattering*. This in turn forms the source of exciting radiation. Each individual volume element under the influence of the primary scattering by all the other elements becomes a doublet and sends out radiations again. This he calls as the *secondary scattering*. Since the intensity of the primary scattering increases as the critical solution temperature is approached, the intensity of the secondary scattering also correspondingly increases and influences the observed depolarisation values.

CASE I. *Incident light and consequently the primary scattering vibrate parallel to OZ.*—

Let X_z and Z_z be the components parallel to OX and OZ respectively of the secondary scattering in the transverse horizontal direction OY. They are given by the following triple integrals,

$$X_z = \iiint_V \sin^3\theta. \cos^2\theta. \cos^2\phi. \, d\theta, \, d\phi. \, dr.$$

$$Z_z = \iiint_V \sin^5\theta. \, d\theta. \, d\phi. \, dr. \qquad\qquad (1)$$

where θ, ϕ and r are the spherical co-ordinates of the particular volume element under consideration.

CASE II. *The incident light and the primary scattering are polarised with vibrations parallel to OY.*

The components X_y and Z_y of the secondary scattering are given by

$$X_y = \iiint_v \sin^5\theta . \cos^2\phi . \sin^2\phi . \, d\theta . \, d\phi . \, dr.$$

$$Z_y = \iiint_v \sin^3\theta \cos^2\theta . \sin^2\phi , \, d\theta . \, d\phi . \, dr. \tag{2}$$

The integration should be extended throughout the volume of the mixture on which the light is incident.

If the scattering volume is in the form of a disc of radius R and height 2 H with its axis parallel to the Z-axis, the components of the secondary scattering for the two cases are given by

$$Z_y = X_z = \frac{\pi}{4}\left[R \text{ arc tan } \frac{H}{R} + R^2 H/(R^2 + H^2) \right]$$

$$X_y = \frac{Z_z}{8} = \frac{\pi}{4}\left[\tfrac{3}{4} R \tan^{-1} \frac{H}{R} - \tfrac{1}{4}\frac{R^2 H}{R^2 + H^2} + H . \log_e \frac{H^2 + R^2}{H^2} \right] \tag{3}$$

Since the primary scattering is supposed to be completely polarised, one does not observe it along the transverse direction OY when the incident beam is polarised with vibrations parallel to OY. But the two components X_y and Z_y of the secondary scattering which are observed, are not of the same intensity ; the depolarisation ρ_h of the secondary scattering is given by the ratio Z_y/X_y.

$$\rho_h^* = \frac{Z_y}{X_y} = \frac{1}{\tfrac{1}{4} + \log_e \frac{R}{H}} , \tag{4}$$

when H is small compared with R. For R = 10 H, $\rho_h = 0 \cdot 39$, *i.e.,* less than unity.

From further calculations he has shown that the components Z_y and X_z are not localised on the primary radiation but are of the same intensity throughout the whole volume of the fluid. The components Z_z and X_y have the maximum intensity at the centre of the primary track and the intensity diminishes as one goes farther away from the centre, the rate of diminution being governed by the ratio R/H. The whole result can be summarised schematically as shown in Fig. 1.

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* Rousset has taken ρ as equal to $\frac{X_y}{Z_y} = \tfrac{1}{4} + \log_e \frac{R}{H} = 2 \cdot 6$ when $\frac{R}{H} = 10$.
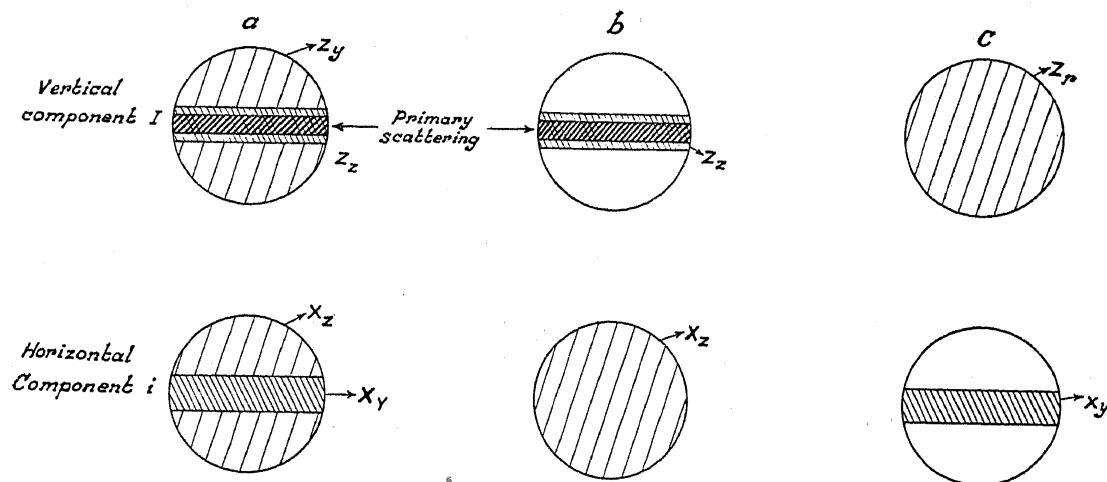
Fig. 1.

CASE 1. *Incident light is unpolarised.*—According to Rousset's calculations the vertical component I of the scattered light consists of a very intense pencil due to the primary scattering which is widened out owing to the superposition of the component Z_z of the secondary scattering and a background illumination due to the existence of the component Z_y of the secondary scattering (see Fig. 1 *a*). The horizontal component *i* consists of a diffuse track in the centre due to the component X_y and a background due to the component X_z. If one observes the scattered light through a Wollaston prism, one obtains a finite value for the depolarisation factor ρ_u.

CASE 2. *Incident light is polarised with vibrations parallel to OZ.*— The trace of the pencil disappears in the image *i* which reduces itself to a background illumination produced by the component X_z of the secondary scattering. One will find therefore that the factor of depolarisation ρ_v is zero (see Fig. 1 *b*).

CASE 3. *Incident light is polarised with vibrations parallel to OY.*— The trace of the incident beam disappears in the image I which is reduced to a background scattering provided by the component Z_y. In the image *i* there exists the component X_y with its edges more or less diffuse. For this case ρ_h is zero (see Fig. 1 *c*).

In an actual experiment the scattering vloume of the mixture is in the form of a rectangular parallelopiped of sides, $2a$, $2b$ and $2c$, $2b$ and $2c$ the width and height of the track respectively, being small compared with the length $2a$. For such a case the conclusions detailed above are valid. The value of ρ_h depends on the ratio c/a.

3. *Critical Remarks on the Theory of Secondary Scattering.*

1.   Although the intensity of scattering is comparatively greater near the critical solution temperature T_0, it is only a small fraction of the intensity of the incident light.   For $\Delta T = 4°C.$, ($\Delta T = T - T_0$), the intensity of scattering in water-isobutyric acid mixture is only 25 times that of pure benzene. (This value is taken from Rousset's measurements.)   The Rayleigh's constant for benzene is equal to 10^{-5}.   The Rayleigh's constant for the mixture is therefore equal to $2 \cdot 5 \times 10^{-4}$.   So the ratio of the intensity of the secondary scattering to that of the primary scattering at $\Delta T = 4°C.$ is equal to $2 \cdot 5 \times 10^{-4}$.   Since the primary scattering is completely polarised and the secondary scattering is depolarised to the extent of $\frac{1}{8}$, the value of ρ_u will be of the order of $0 \cdot 003$ per cent.   But the actual observed value of ρ_u, after making due allowance to convergence of the incident beam, is 1.5 per cent.   Supposing for a moment (as Rousset has remarked), that this $1 \cdot 5$ per cent. arises partly due to the depolarised orientation scattering and partly due to the depolarised secondary scattering, the orientation scattering should be 100 times more intense than the secondary scattering. Consequently at this temperature ρ_h should not be appreciably less than unity. But in all the mixtures investigated the value of ρ_h is unmistakably of the order of 0.2.   This low value of ρ_h can, therefore, be only ascribed to the existence of molecular clusters.

2.   It is well known that the orientation scattering does   not   vary appreciably with temperature provided the composition of the mixture is kept constant.   The intensity of the secondary scattering is proportional to the intensity of the primary scattering which increases as T_0 is approached. According to Rousset, $\rho_h = O/(O + S)$ where O is the component of the orientation scattering and S is the component of the secondary scattering. From a knowledge of the values of ρ_h at various temperatures the relative intensities of the secondary scattering at those temperatures could be evaluated.   The rate of increase of the secondary scattering with decrease of ΔT should be at least equal to that of the primary scattering, if not more. From a comparison of Tables I and II, one is led to believe that this is far from being the case.   The values of ρ_h and the intensity of scattering for phenol and water are taken from one of the author's earlier papers.

3.   According to Rousset's theory, the intensity distribution of the primary opalescent scattering is symmetrical about the direction perpendicular to the direction of the incident beam.   But it has been observed by various investigators including Rousset that the scattering in the forward direction is more intense than the scattering in the backward direction.

TABLE I.
Phenol and Water.

Temperature °C.	ρ_h observed %	Relative intensities of secondary scattering (calculated)	Relative intensities of primary scattering (observed)
95	75	1 (assumed)	1 (assumed)
90	66	1·5	1·2
87·5	61	1·91	1·3
83	51	2·9	2·1
80	47	3·4	2·9
77	39	4·69	3·8
74	31	6·7	7·8
69·5	16	15·8	45
69	12	22	53·0

TABLE II.
Phenol and Normal Hexane.

Temperature °C.	ρ_h observed %	Relative intensities of secondary scattering (calculated)	Relative intensities of primary scattering (observed)
74	100	..	1 (assumed)
64	80	1 (assumed)	1·14
59	75·5	1·03	1·33
57	72	1·56	1·66
50	63	2·4	3·1
45	55·8	3·24	5·45
42·9	44	5·48	14
41·2	25	12	30

This Mie effect is characteristic of the scattering by particles whose size is comparable with the wave-length of light.

4. If the opalescent scattering is really molecular in origin it should obey λ^{-4} law. Andant (1924), Rousset and others have found that very near the critical solution point the law of scattering is λ^{-n} where n is definitely less than 4. This fact of observation finds an easy explanation on the basis of *Schwarmbildung*.

5. According to Rousset's theory, when the incident beam is unpolarised or polarised with vibrations horizontal, the horizontal component of the light scattered in the transverse horizontal direction will be comparatively more diffuse, the intensity being maximum at the centre of the track and gradually falling off on either side. The track should also appear broader than the corresponding vertical component. This was tested out experimentally. Figs. 2(a) and 2(b) in Plate XIX represent the photographs of the light scattered by a mixture of phenol and hexane very near T_0 taken through a double-image prism, when the incident light is unpolarised and polarised with vibrations horizontal respectively. Figs. 3(a) and 3(b) represent the corresponding photographs taken through a double-image prism and a nicol, the nicol being so oriented as to equalise the two mutually perpendicular components. In all the cases the width of the track is the same for the two components. The distribution of intensity is also uniform throughout the cross-section of the tracks.

6. If $2a$ and $2c$ are the length and vertical depth of the track inside the medium, the values of ρ_u, ρ_v and ρ_h are functions of the ratio c/a according to the theory of Rousset. ρ_u and ρ_h should increase or decrease *pari passu* with c/a, whereas the variation of ρ_v should be in the opposite direction.

7. Since the secondary scattering depends only on the intensity of the primary scattering the observed values of the depolarisation factors should not exhibit any appreciable dispersion with wave-length. Table III gives the values of ρ_u, ρ_v and ρ_h measured for a mixture of phenol and normal hexane which was maintained a few degrees above the critical solution temperature, with different colour filters and for two different values of c/a.

The observed dispersion of depolarisation is not due to fluorescence for any trace of fluorescence will try to increase all the three quantities ρ_u, ρ_v and ρ_h and not only two of them. From a comparison of the observed dispersion of depolarisation with that observed in the case of inorganic sols which

TABLE III.

	$c/a = 0 \cdot 33$		$c/a = 0 \cdot 05$	
	Blue filter %	Orange filter %	Blue filter %	Orange filter %
ρ_u	1	0·54	1	0·48
ρ_v	0·21	0·1	0·23	0·09
ρ_h	22·0	24	21	25

do not possess any specific absorption (Krishnan, 1937) it can be inferred that the effect is really due to the finite size of the scattering particles and not due to secondary scattering.

8. According to the theory of Rousset, when the incident light is unpolarised the background scattering at points far away from the track should be completely unpolarised. If the plane of polarisation of the incident beam is horizontal the plane of polarisation of the background scattering will be vertical. If, on the other hand, the plane of polarisation of the incident beam is vertical, the background scattering should be completely polarised with vibrations horizontal. For different states of polarisation of the incident beam, the state of polarisation of the background scattering as seen in the transverse direction has been determined by means of a movable slit kept at points situated along a vertical at different distances from the centre of the track. The measurements were made with a phenol-hexane mixture very near the critical solution temperature and also with a casein solution the p$_H$ of which was adjusted so as to show an intense opalescence. The results are given in Table IV.

It is well known that in casein solution the protein molecules are very large in size. The similarity in the behaviour of the liquid mixture and the casein solution indicates that the scattering elements in the liquid mixture should also be molecular clusters of size comparable with the wave-length of light and not the individual molecules. In this connection the observations made on the nascent precipitate of sulphur formed when a little acid is added to a dilute and well filtered solution of hyposulphite will be of some interest. The light scattered transversely by the sulphur sol was observed through a double-image prism. In the early stages of the formation of the

TABLE IV.

The Width of the Track inside the Medium = 0·2 cm.

Medium	Position of the movable slit	ρ_u %	ρ_v %	ρ_h %
Phenol and hexane	Slit on track	0·7	0·31	36
	Slit just below track	6	2·8	49
	Slit 2 cm. below track	19·8	13·6	88·5
Casein solution measured with red light	Slit on track	1·73	0·7	42
	Slit just below track	22·7	10·5	95
	Slit 3 cm. below track	75	95	100

sol the double-image prism suitably rotated showed complete polarisation of the light scattered transversely. Somewhat later the minimum light seen transversely showed Tyndall's residual blue, indicating that for this colour the polarisation was no longer complete, while for the red colour it was more complete, the increase in wave-length compensating the growth of the particles. As the particles were allowed to grow, a stage was reached when the effects for blue and red light were well contrasted. A similar observation was made with one of the binary mixtures. The mixture was initially kept at about 25° C. above the critical solution temperature and was allowed to cool. A beam of light was focussed into the mixture and the scattered light was observed through a double-image prism and nicol. The nicol was used so as to equalise the intensity of the two components. As the temperature was slowly lowered the horizontal component was more bluish than the vertical component, the effect being most pronounced at the critical solution temperature.

From what has been said above it can be inferred that in the neighbourhood of the critical solution temperature of liquid mixtures, the molecules have got a tendency to group themselves together in the form of clusters and that the finite value of the depolarisation arises due to the fact that the size of the clusters becomes comparable with the wave-length of light.

4. *Experimental Results Obtained with a Few More Liquid Mixtures.*

The measurements of the depolarisation factors ρ_u, ρ_v and ρ_h were made for the following mixtures, phenol-normal hexane, phenol-normal heptane, aniline-normal heptane and benzene-acetic acid-water. The photo-electric method was employed for comparison of the intensities of scattering by these mixtures at various temperatures above the critical solution temperature. Very near T_0 the depolarisation factors were also measured with coloured filters also. The results are tabulated below. The intensity of scattering was measured using incident white light only. Necessary corrections are applied for the convergence of the incident beam.

The results obtained with the three binary mixtures confirm the author's conclusions regarding the formation of molecular clusters, which are discussed in detail in the earlier papers. The ternary mixture studied, also exhibits the same phenomenon. At the critical solution temperature the composition scattering which is completely polarised becomes large and the scattering due to the finite size also increases. The combined effect gives a finite value for the depolarisation ρ_u. As soon as the critical fog or the emulsion begins to appear a considerable increase in the size of the

TABLE V.

49% *Phenol and* 51% *Normal Hexane.*

Temperature	Colour of the filter used	ρ_u %	ρ_v %	ρ_h %	Relative intensity of scattering
71		1·4	0·62	100	1 (assumed)
62		1·0	0·45	84	1·25
55		0·6	0·25	78	2·75
50		0·49	0·19	59	6·25
47·5		0·43	0·14	42	11·4
46·5	orange	0·35	0·09	42	17·8
46·5	blue	0·65	0·12	24	
44·5	blue	0·55	0·09	12	43·8

TABLE VI.
54.2% *Phenol and* 45.8% *Heptane.*

Temperature	Colour of the filter used	ρ_u %	ρ_v %	ρ_h %	Relative intensity of scattering
74		2·5	1·25	100	1 (assumed)
64		1·8	0·8	80	1·14
59		1·6	0·7	75·5	1·33
57		1·4	0·6	72	1·66
50		1·0	0·27	63	3·1
45		0·54	0·16	55·8	5·45
42·9		0·49	0·12	44	14
42·6	orange	0·36	0·1	55	18
42·6	blue	0·58	0·16	40	
41·2	orange	0·43	0·1	30	30
41·2	blue	0·61	0·12	20	

TABLE VII.
56% *Aniline and* 44% *Normal Heptane.*

Temperature	Colour of the filter used	ρ_u %	ρ_v %	ρ_h %	Relative intensity of scattering
85		2·8	1·4	100	1 (assumed)
74		1·8	0·75	84	1·5
68		1·2	0·46	80	2·7
66		0·92	0·36	65	4·8
63		0·5	0·16	50	5·1
61·5	orange	0·44	0·08	32	8
60·8	orange	0·36	0·06	19	12

TABLE VIII.

Benzene, Acetic Acid and Water Mixture.

Temperature	Colour of the filters used	ρ_u %	ρ_v %	ρ_h %
54		4·1	2·0	100
48		3·1	1·3	93
45		1·7	0·7	81
40		0·9	0·31	70·5
38		0·67	0·22	65·5
37	blue	1·0	0·31	45
37	orange	0·6	0·22	55
37	red	0·4	0·15	
36	blue	0·74	0·12	37
36	orange	0·35	0·1	15

clusters formed takes place resulting in an increase in the value of ρ_u. In the case of the phenol-heptane mixture it was possible to detect the increase in the value of ρ_u even before the critical solution temperature was approached. This is because very near T_c the rate of increase of the depolarised size scattering with diminution of temperature is greater than the rate of increase of polarised composition scattering. This explains why Rousset observed an increase in the value of ρ_u very near T_c in some of the mixture studied by him. The fact that the dispersion of depolarisation is most pronounced at the critical solution temperature shows clearly that the size of the clusters formed is greatest at this temperature.

5. Theory of Gans.

Soon after the publication of the results on the molecular clustering in binary liquid mixtures by the author, Gans (1936) put forward a theoretical explanation of the observed anomalous depolarisation (*i.e.*, $\rho_h < 1$), on the basis of the swarm-formation in fluids. He has considered this problem from the standpoint of the theory of fluctuations under the simplifying

assumption that besides the density variations there are accidental variations of isotropy or orientation variations due to the formation of molecular groups, and that the linear dimension d is so small that $d^2 \ll \lambda^2$. Gans has derived a relation between the degree of depolarisation ρ_h and the form of the molecular aggregates. If the groups are spherical in shape ρ_h has its limiting value of unity. If on the other hand the groups are in the form of thin rods of length l,

$$\frac{1}{\rho_h} = 1 - \frac{4\pi^2}{42} \frac{l^2}{\lambda^2} \qquad (5)$$

For discs of radius r,

$$\frac{1}{\rho_h} = 1 + \frac{4\pi^2}{14} \frac{r^2}{\lambda^2} \qquad (6)$$

Katalinic and Vrkljan (1936) have extended Gans' theory. General conditions for the occurrence of the anomalous depolarisation for the case of three dimensional molecular swarms are derived by them without making too exact assumptions as to their form.

According to Gans' theory ρ_h should be greater as well as less than unity depending upon the shape of the swarms. But in all the mixtures studied so far, ρ_h is found to be less than unity and never greater than unity. It is also hard to believe that the clusters are of the same shape in all the mixtures. This is because of the limitations of Gans' theory. The theory is valid only for swarms whose linear dimension is such that $d^2 \ll \lambda^2$. For such small clusters only the first electric partial wave, *i.e.*, the dipole radiation, is usually taken into consideration. For large molecular clusters one has to take into consideration the higher electric partial waves as also the magnetic partial waves as indicated in Mie's theory.

6. Other Experimental Evidence.

Various other physical properties such as viscosity, flow birefringence, electric and magnetic birefringence, X-ray diffraction, etc., have been extensively studied by numerous investigators and the results obtained are intimately connected with the conclusions arrived at from light-scattering experiments. Reference to some of these properties has already been made in the author's earlier papers.

A systematic study of the viscosity of binary liquid mixtures at various temperatures and for various concentrations has been carried out by Zofia Szafranska (1935). It is found that when the solutions show no optical anomalies there is no trace of viscosity irregularity, whereas for mixtures which show optical anomalies he finds an abnormal increase in the viscosity

near the critical solution temperature. The increase is most pronounced for mixtures having the exact critical composition. The viscosity of the three component system, benzene-ethyl alcohol-water, has been measured in the neighbourhood of the critical point by Kimura (1936) and similar results have been obtained by him. These anomalies find an easy explanation on the basis of molecular clustering. The sudden increase of viscosity is caused by the existence of molecular aggregates, the increase being very much governed by the size of the aggregates which in turn is a function of the temperature of the mixture and also its composition.

The Kerr-effect in mixtures of nitrobenzene and heptane in the neighbourhood of T_c has been studied recently by Goldet (1936). The observed effect increases rapidly as the critical temperature is approached. The abnormal increase may be attributed to the formation of clusters.

7. Conclusion.

Critical composition mixtures near the critical point are usually regarded as colloidal emulsoids. It is well known that a substance will show the characteristics of a colloid if it contains particles graded down from those of microscopic to those of molecular dimensions. If on cooling a mixture a milky emulsion is obtained observation through a microscope will at once indicate that the medium contains particles whose diameters are of the order of the wave-length of light. On the other hand, the critical composition mixture very near the critical solution temperature, is more like a system which is intermediate between the two extreme cases, *i.e.*, the coarse disperse system and the molecular disperse system. The critical solution mixtures do not show any milky turbidity, but they show an opalescence which is characterised by double colour, *i.e.*, yellow by transmitted light and blue by scattered light. Optical investigations with an ordinary microscope do not reveal the existence of discrete particles. We find this type of opalescence in many typical colloidal systems, for example, in many protein solutions in which also no discontinuity can be traced with an ordinary microscope. At the critical point the vapour pressure is independent of concentration. The same phenomenon has been observed by Tammann in gelatin and gum arabic solutions. It may be remarked that the large increase in opalescence as well as the existence of pronounced minima in the values of ρ_u, ρ_v and ρ_h at the critical solution temperature of binary liquid mixtures bear a striking similarity to the observations of Subbaramaiah (1937) at the iso-electric point of protein solutions. But in spite of the similarity in optical behaviour, there are certain important characteristics of protein solutions which are not exhibited by mixtures.

The protein solutions progressively change with time. But it is a fact of observation that critical opalescence and such other phenomena exhibited by critical solution mixtures are invariant with time and depend only on the temperature of the mixture.

In conclusion the author takes this opportunity to express his grateful thanks to Professor Sir C. V. Raman, Kt., F.R.S., N.L., for his kind and helpful interest in the work.

8. Summary.

A critical review of the theory of secondary scattering proposed by Rousset in order to explain the finite value of the depolarisation of the opalescence of liquid mixtures is given. Further consequences of the theory of secondary scattering have been worked out and it is found that the experimental results obtained are not in accordance with the conclusions of the theory. From the results obtained it has been concluded that in the neighbourhood of the critical solution temperature of liquid mixtures the molecules have got a tendency to group themselves together in the form of clusters and that the finite value of the depolarisation of the opalescent light arises due to this fact. In the neighbourhood of T_c the secondary scattering has little or no effect on the depolarisation factor, although it may have an appreciable effect for $\Delta T < 0 \cdot 1° C$. where $\Delta T = T - T_c$. The measurements of the depolarisation factors ρ_u, ρ_v and ρ_h for three binary mixtures and one ternary mixture have been made over a range of temperature of 30° above T_c. The results obtained fully confirm the author's earlier report regarding the existence of clusters in liquid mixtures not only at the critical solution temperature but also at temperatures considerably removed from it. The theory proposed by Gans has been discussed in relation to the experimental results obtained by the author and the limitations of the theory have also been pointed out. The bearing of the results on the anomalies of viscosity, electric birefringence, etc., noticed by the earlier investigators in the vicinity of the critical solution temperature has been discussed in detail.

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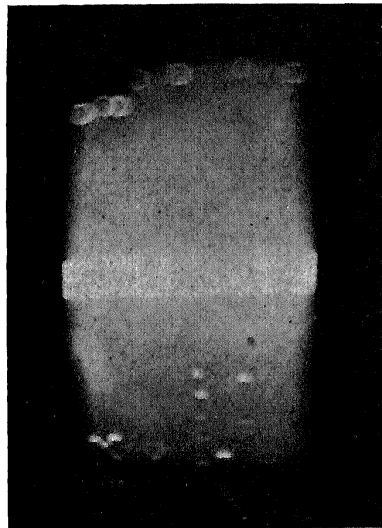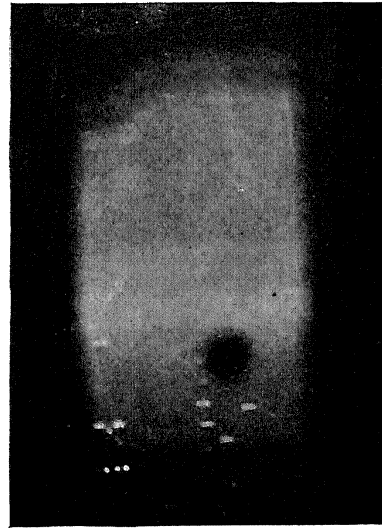Vertical ← Component

Horizontal ← Component
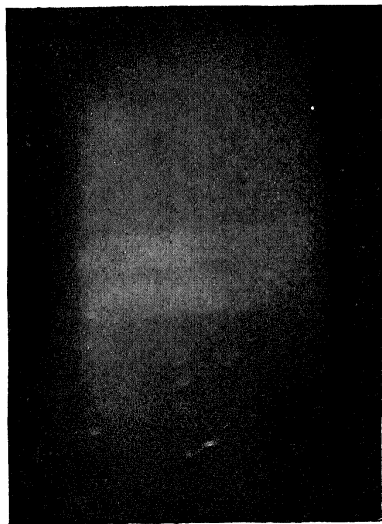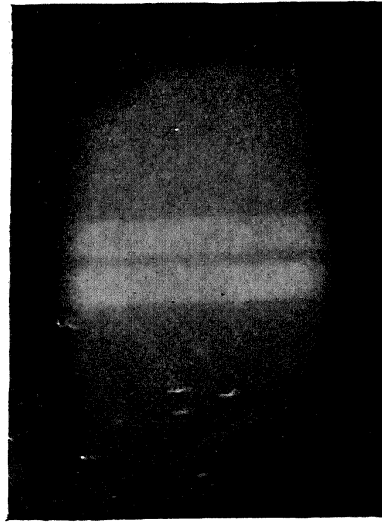
FIG. 2 (a).   FIG 2 (b).

FIG. 3 (a).   FIG. 3 (b).

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