MOLECULAR CLUSTERING IN BINARY LIQUID MIXTURES.

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Received May 20, 1935.
(Communicated by Sir C. V. Raman, KT., F.R.S., N.L.)

1. *Introduction.*

IT is well known that certain binary liquid mixtures, *e.g.*, those of phenol and water, carbon disulphide and methyl alcohol, etc., exhibit a marked opalescence or turbidity at a temperature known as the critical solution temperature, slightly higher than that at which they separate into two layers. This phenomenon of opalescence in liquid mixtures has been experimentally studied by many investigators. The theoretical explanation of critical opalescence put forward by Smoluchowski and later more completely formulated by Einstein, stimulated quantitative studies of the phenomenon by several physicists. The spectral character of the opalescent light was studied by Fürth[1] for a mixture of phenol and water, while Zernike[2] quantitatively studied the intensity of opalescence in methyl iodide-pentamethylene mixtures. But the observations of these investigators were restricted only to a small range of temperature above the critical solution temperature. Later, however, V. S. Tamma working at Calcutta made a study of the scattering of light by phenol-water mixtures over a range of some thirty degrees Centigrade above the critical solution temperature, while Kamesvara Rav[3] studied in detail the intensity and state of polarisation of the light scattered by mixtures of carbon disulphide and methyl alcohol over a wide range of temperatures above and below the critical solution temperature. Very recently, Rousset[4] has 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.

The investigators mentioned above studied the scattering by liquid mixtures using incident unpolarised light alone. The importance in such investigations of making comparative studies with the incident light in

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[1] B. Fürth, *Wiener Berichte*, 1915, 124, 577.

[2] F. Zernike, *Thesis Amsterdam*, 1915.

[3] C. Kamesvara Rav, *Proc. Ind. Assoc. Culti. of Sci.*, 1925, **9**, 19.

[4] A. Rousset, *Compt. Rend.*, 1934, **198**, 2152; **199**, 716.

different states of polarisation has been stressed by the author in recent papers in these Proceedings. Using incident unpolarised light, as also light polarised with the electric vector respectively vertical and horizontal, different measures of the state of polarisation of the transversely scattered light are obtained, namely ρ_u, ρ_v and ρ_h corresponding to these three cases. So long as the optical heterogeneity of the scattering medium can be identified as due to the individual molecules (as in the case of an ordinary gas or liquid), it is not necessary to measure all these three quantities separately, for

$$\rho_h = 1, \text{ and } \rho_u = 2\,\rho_v / \,(1 + \rho_v) \qquad \ldots \qquad \ldots \qquad \ldots \quad (1)$$

When, however, the above condition is not satisfied, *i.e.*, when the optical heterogeneity of the scattering medium cannot be identified as due to the individual molecules (as in the case of emulsions and colloids), ρ_h does not have its limiting value unity, but will be definitely less than 1 and the relation between ρ_u and ρ_v quoted above is not satisfied. It is then insufficient to measure ρ_u alone and a determination of ρ_v and preferably also of ρ_h should be made in order to give us a correct idea of the state of dispersion of the particles in the medium. The measurement of ρ_h would be the most sensitive indicator of the state of dispersion (*e.g.*, cluster formation, etc.), as any departure of its value from unity would indicate an appreciable size of the scattering particles. The present author[5] has shown that there is a very general relation connecting ρ_u, ρ_v and ρ_h namely

$$\rho_u = (1 + {}^1/\rho_h) \,/ (1 + {}^1/\rho_v) \quad \ldots \qquad \ldots \qquad \ldots \qquad \ldots \quad (2)$$

of which equation (1) is a special case and which follows theoretically as a consequence of the dynamical principle of reciprocity. It is useful, however, to measure all the three quantities ρ_u, ρ_v and ρ_h as the accuracy with which the data satisfy the theoretical relation (2) serves as a check on the reliability of the experimental measurements.

In a recent paper the author[6] has reported preliminary observations with mixtures of carbon disulphide and methyl alcohol which showed clearly that the depolarisation ρ_h of the transversely scattered light falls to values considerably less than unity as the critical solution temperature is approached. These observations furnished for the first time positive evidence for the existence of large clusters in liquid mixtures not only at the critical solution temperature but also at temperatures considerably above that temperature. In the present investigation a more detailed study has been made of the opalescence of a series of binary liquid mixtures, and the results confirm the preliminary report and also prove the validity for such mixtures of the reciprocity formula quoted above. The experimental results have obviously

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[5] R. S. Krishnan, *Proc. Ind. Acad. of Sci.*, (A), 1935, **1**, 782.

[6] R. S. Krishnan, *Ibid.*, 1934, **1**, 211.

an important bearing on the theories of critical opalescence, including those which have been put forward subsequent to the work of Smoluchowski and Einstein.

2. *Details of the Experiment.*

The chief difficulty in the work is to prepare perfectly dust-free mixtures having the correct critical composition. This is necessary as the phenomenon of critical opalescence is most pronounced for a mixture having exactly a certain composition. The mixtures were prepared in the following way. The component liquids were taken from freshly opened bottles and after being purified by distillation, were mixed in the exact critical proportion. About 75 cubic centimetres of the mixture was then transferred into a clean dry double bulb, one bulb of which was smaller than the other. The capacity of the smaller bulb was about 100 c.c. and its walls were comparatively thick; before being attached to the second bulb, this was properly annealed to relieve any strain present. The bulb containing the mixture was cooled by immersing it in freezing mixture, and the double bulb was evacuated and sealed off. Dust-free mixture was then obtained in the smaller bulb by repeated slow distillation and washing back; for the final distillation, the mixture was almost completely distilled into the smaller bulb, the process being carried out very slowly. The bulb containing the dust-free mixture was then sealed off from the other, and was painted black outside leaving three windows for entry and egress of the light.

The experimental arrangement employed in the present investigation was similar to the one described in the previous paper. But the following alterations were made in order to get a very intense beam and to avoid experimental errors as far as possible. The carbon arc was replaced by a 20-ampere projection lantern. The light from this lantern was first condensed on a square aperture (2 mm. square). The light emerging out of this aperture was passed through a long focus lens of small aperture (4 cms. diameter). The image of the slit was brought to focus at a distance of about 50 centimetres from the lens. This portion of the track passed through the bulb containing the mixture to be examined. The bulb was kept immersed in dust-free distilled water contained in a rectangular brass vessel provided with three glass windows, one for the entrance of light, the second for its exit and the third for the observation of the transversely scattered light. The vessel was heated electrically when required. A square-ended Nicol (aperture 2·5 cms. square) was used for polarising the incident beam. The method of Cornu was adopted for the measurement of depolarisation of the transversely scattered light.

The particular mixture to be studied was kept immersed in the bath the temperature of which was maintained slightly above the critical solution temperature. The incident beam being polarised with vibrations horizontal or vertical as desired, the transversely scattered light was viewed through a double-image prism. It was found that in the immediate neighbourhood of the critical solution temperature, when the incident beam was polarised with its electric vector horizontal, the horizontal component in the scattered light was distinctly greater than the vertical component, *i.e.*, ρ_h was less than 1. The temperature of the mixture was then slowly raised up to the point at which the horizontal component and the vertical component of the scattered light when the mixture was illumined with light polarised with vibrations horizontal, were equal in intensity, *i.e.*, ρ_h was equal to 1. At this temperature the depolarisations ρ_u, ρ_v and ρ_h were measured using respectively incident unpolarised light and incident light polarised with vibrations vertical and horizontal. The mixture was then slowly cooled down, and the measurements of ρ_u, ρ_v and ρ_h were made for a series of temperatures up to the critical solution temperature. The mixture was thoroughly shaken before each measurement.

As has long been recognised, the main source of error in the study of "Rayleigh scattering" is fluorescence. This is caused to a large extent by the presence of impurities, but in a smaller degree it is attributed to photochemical action of light on the medium. The former type of fluorescence was avoided by using freshly distilled liquid mixtures. The latter type of fluorescence may be avoided by not exposing the mixtures unduly to light. In the mixtures employed, whether flourescence existed or not was tested out by using complementary filters, and it was found that none of the mixtures employed was sensibly fluorescent.

Another possible source of error in the measurement of low depolarisations is the convergence of the incident beam. Strictly speaking, the depolarisation of the transversely scattered light should be measured with an incident parallel beam of light. Since, however, the molecular scattering of light is a comparatively feeble phenomenon, it is necessary to have a very intense source of illumination, and this necessitates recourse to a lens which gives a convergent beam. In the present experiment the angle of convergence was about 4° which was further reduced to 3° inside the medium by the liquid in the rectangular cell. According to Gans[7] the convergence correction for ρ_u is $\frac{\omega^2}{8}$, where ω is the angle of convergence, and for a convergence angle of 3°, the correction would be 0·0003. It should be remarked, however, that Gans derived his correction on the assumption that the rays reaching the focus are incoherent with each other. We know, however, that this is

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[7] R. Gans, *Phys. Zeits.*, 1927, **28**, 661.

not the case and that the individual rays are more or less completely coherent at the focus. Nevertheless, the error that would be introduced due to convergence is the same as that given by Gans's formula. For ρ_v the correction is one-half of the correction for ρ_u as has been shown in detail by Mr. R. Anantakrishnan. In view of the theoretical position, measurements of ρ_u, ρ_v and ρ_h were made for a mixture very near the critical solution temperature using an iris diaphragm to vary the aperture of the lens. It was found that when the aperture of the lens was reduced from 4 cms. to less than 1 cm. there was practically no change in the values obtained for ρ_u, ρ_v and ρ_h. Thus at least in the present case, the neglect of the convergence correction appears to be justified.

Another important source of error in depolarisation measurements is the background illumination which becomes appreciable in the neighbourhood of the critical solution temperature. This type of error was avoided in the present investigation by viewing the two components against the same background.

3. Results.

The values of ρ_u, ρ_v and ρ_h for various mixtures at various temperatures are tabulated below. In every case, the measurements were made from the

Critical Composition and Critical Solution Temperature of the Mixtures used.

TABLE I.

Mixture	Weight % of the first component	Critical solution temperature
1. Carbon disulphide-methyl alcohol ..	85	40°C. (upper consolute point.)
2. Methyl alcohol-normal hexane ..	30	29°C. " "
3. Water-isobutyric acid ..	50	25°·5 C. " "
4. Aniline-cyclohexane ..	46	30°C. " "
5. Nitro benzene-normal hexane ..	50	14°C. " "
6. Aniline-normal hexane ..	52	56°·5 C. " "
7. Phenol-water ..	34	69°C. " "
8. Water-triethyl amine ..	70	19°C. (lower consolute point.)

(*a*) *Carbon disulphide-Methyl alcohol Mixture.*

TABLE II.

Temperature of the mixture	ρ_h	ρ_v	ρ_u (observed)	ρ_u (calculated)
62°·2 C.	100 %	4·1 %	8·2 %	7·9 %
57°·5 C.	93 %	2·8 %	5·8 %	5·7 %
55° C.	90 %	2·1 %	4·5 %	4·3 %
52°·5 C.	83 %	1·7 %	3·95 %	3·7 %
50° C.	73 %	1·3 %	2·8 %	3·0 %
47°·5 C.	68 %	1·1 %	2·8 %	2·7 %
45° C.	59 %	0·93 %	2·4 %	2·5 %
42°·5 C.	45·5 %	0·62 %	2·0 %	2·0 %
40°·5 C.	27 %	0·34 %	1·5 %	1·6 %
40° C.	25 %	0·27 %	1·5 %	1·4 %

(*b*) *Methyl alcohol-Normal hexane Mixture.*

TABLE III.

Temperature of the mixture	ρ_h	ρ_v	ρ_u (observed)	ρ_u (calculated)
50° C.	100 %	1·4 %	3·1 %	2·8 %
47°·5 C.	87 %	1.1 %	2·7 %	2·3 %
45° C.	81 %	1·0 %	2·4 %	2·2 %
42°·5 C.	68 %	0·84 %	2·1 %	2·0 %
40° C.	63 %	0·76 %	2·0 %	1·95 %
37°·5 C.	61 %	0·76 %	1·9 %	2·0 %
32°·5 C.	53 %	0·62 %	1·7 %	1·8 %
29°·5 C.	33·3 %	0·37 %	1·5 %	1·5 %
29° C.	27 %	0·37 %	1·5 %	1·7 %

(c) *Water-Isobutyric acid Mixture.*

TABLE IV.

Temperature of the mixture	ρ_h	ρ_v	ρ_u (observed)	ρ_u (calculated)
40° C.	100 %	1·8 %	3·4 %	3·6 %
37°·5 C.	90 %	1·5 %	3·1 %	3·1 %
35° C.	81 %	1·3 %	2·7 %	2·9 %
32°·5 C.	70 %	1·1 %	2·4 %	2·6 %
30° C.	59 %	0·7 %	2·0 %	1·9 %
28° C.	53 %	0·6 %	1·8 %	1·7 %
26° C.	39 %	0·5 %	1·5 %	1·8 %
25°·5 C.	27 %	0·34 %	1·5 %	1·6 %

(d) *Aniline-Cyclohexane Mixture.*

TABLE V.

Temperature of the mixture	ρ_h	ρ_v	ρ_u (observed)	ρ_u (calculated)
55° C.	100 %	2·5 %	4·7 %	4·9 %
50° C.	93 %	2·0 %	3·6 %	4·0 %
47°·5 C.	90 %	1·5 %	3·1 %	3·2 %
45° C.	87 %	1·4 %	2·5 %	2·6 %
42°·5 C.	81 %	1·2 %	2·4 %	2·7 %
40° C.	75·5 %	0·93 %	2·1 %	2·2 %
37°·5 C.	70 %	0·69 %	1·5 %	1·6 %
35° C.	68 %	0·43 %	1·1 %	1·1 %
32° C.	57 %	0·37 %	1·0 %	1·0 %
30°·8 C.	40·5 %	0·27 %	0·93 %	0·93 %
30°·2 C.	22 %	0·15 %	0·84 %	0·84 %
30° C.	17 %	0·12 %	0·84 %	0·82 %

(e) *Nitrobenzene-Normal hexane Mixture.*

TABLE VI.

Temperature of the mixture	ρ_h	ρ_v	ρ_u (observed)	ρ_u (calculated)
45° C.	100 %	4·1 %	7·7 %	7·8 %
40° C.	87 %	3·0 %	6·7 %	6·3 %
35° C.	81 %	2·3 %	5·4 %	5·0 %
30° C.	75 %	2·0 %	4·4 %	4·6 %
25° C.	66 %	1·3 %	3·0 %	3·2 %
22° C.	61 %	0·93 %	2·2 %	2·4 %
18°·5 C.	42 %	0·5 %	1·7 %	1·7 %
16°·5 C.	34 %	0·37 %	1·3 %	1·5 %
14°·5 C.	25 %	0·27 %	1·1 %	1·3 %
14° C.	16 %	0·12 %	0·93 %	0·87 %

(f) *Aniline-Normal hexane Mixture.*

TABLE VII.

Temperature of the mixture	ρ_h	ρ_v	ρ_u (observed)	ρ_u (calculated)
83° C.	100 %	1·4 %	2·5 %	2·75 %
77°·5 C.	90 %	1·1 %	2·2 %	2·3 %
75° C.	84 %	1·0 %	2·1 %	2·2 %
72° C.	78 %	0·93 %	2·0 %	2·1 %
69° C.	70 %	0·62 %	1·5 %	1·5 %
66° C.	59 %	0·49 %	1·3 %	1·3 %
62°·5 C.	49 %	0·43 %	1·1 %	1·3 %
59° C.	45·5 %	0·32 %	1·1 %	1·0 %
57°·5 C.	37·5 %	0·32 %	1·0 %	1·2 %
56°·5 C.	21 %	0·19 %	1·0 %	1·1 %

(*g*) *Phenol-Water Mixture.*

TABLE VIII.

Temperature of the mixture	ρ_h	ρ_v	ρ_u (observed)	ρ_u (calculated)
95° C.	75 %	1·00 %	2·2 %	2·3 %
90° C.	66 %	0·7 %	1·5 %	1·7 %
87°·5 C.	61 %	0·6 %	1·4 %	1·6 %
83° C.	51 %	0·43 %	1·1 %	1·3 %
80° C.	47 %	0·34 %	0·93 %	1·0 %
77° C.	39 %	0·27 %	0·77 %	0·96 %
74° C.	31 %	0·23 %	0·75 %	1·0 %
71° C.	26 %	0·19 %	0·7 %	0·93 %
69°·5 C.	16 %	0·12 %	0·62 %	0·87 %
69° C.	12 %	0·07 %	0·62 %	0·65 %

(*h*) *Water-Triethyl amine.*

TABLE IX.

Temperature of the mixture	ρ_h	ρ_v	ρ_u (observed)	ρ_u (calculated)
2° C.	81 %	17 %	35 %	33 %
5° C.	76 %	14 %	28 %	29 %
9°·5 C.	70 %	9·3 %	20 %	21 %
12° C.	66 %	8·5 %	16 %	20 %
14°·5 C.	63 %	5·3 %	13 %	13 %
16°·5 C.	55 %	2·7 %	6·7 %	7·4 %
18° C.	42 %	0·85 %	3·1 %	2·9 %
19° C.	33 %	0·38 %	1·3 %	1·5 %

temperature above the critical solution temperature at which ρ_h was equal to unity up to the critical solution temperature. This range of temperature was about 25° for most of the mixtures. In the case of phenol-water mixture the temperature of the bath which contained water could not be raised up to the point at which ρ_h was equal to 1. In the case of triethyl amine water mixture the temperature had to be lowered instead of being raised, since the temperature of 19° C. corresponded to its lower consolute point. The opalescence of this mixture was rather weak probably owing to the concentration being slightly different from the critical concentration. As the temperature approaches the critical solution point, ρ_u, ρ_v and ρ_h for all the mixtures fall down in value considerably attaining the minimum value at that temperature. The values of ρ_u, ρ_v and ρ_h at the critical solution temperature vary from mixture to mixture. ρ_h is of the order of 15% to 25%, ρ_v of the order of 0·2% to 0·3%, while ρ_u is of the order of 0·8% to 1·5%. Phenol-water mixture gives the lowest values of ρ_u, ρ_v and ρ_h and the range of temperature over which ρ_h is less than one is maximum for this mixture. The intensity of the horizontal component of the transversely scattered light when the incident electric vector is horizontal was found to increase as the temperature approached the critical solution temperature. As soon as the critical solution temperature was passed and the critical fog or the emulsion had begun to appear, a considerable increase in the value of ρ_u was observed.

4. *Validity of the Optical Reciprocity Principle in Liquid Mixtures.*

With the aid of two double-image prisms, one in the path of the incident light and the other in the path of the scattered light, the scattered light was visually observed and subsequently photographed. One of the mixtures was examined thus at various temperatures. It was visually observed that the two middle tracks (out of the four tracks observed) which were respectively the horizontal component of the scattered light arising from the vertical component of the incident light and the vertical component of the scattered light arising from the horizontal component of the incident light were equal in intensity, proving the applicability of the very general "Principle of Reciprocity" to light scattering in liquid mixtures.

Four photographs are reproduced in Plate XLVII, obtained with a carbon disulphide-methyl alcohol mixture and the arrangement mentioned above, one at about 41° C., the second at about 44° C., the third at about 48° C. and the fourth at about 60° C. In Fig. 4 the last two tracks are almost equal, *i.e.*, ρ_h is equal to unity. The first track is very intense because it is the vertical component of the scattered light arising from the incident vertical vibrations. A slight difference in intensity between the second and the third tracks will be noticed in the pictures. This is due to the fact that the photographic halation has slightly increased the apparent intensity of the second component since it happens to be very near the intense first component. A comparative study of the photographs shows that as we approach the critical temperature, the fourth component increases in brightness in comparison with the middle two and consequently the value of ρ_h falls down below unity. Since the reciprocity principle holds good in the case of mixtures the relation

$$\rho_u = (1 + {}^1/\rho_h) \,/\, (1 + {}^1/\rho_v)$$

should be satisfied. In the tables appearing above, the last column gives the values of ρ_u calculated from the observed values of ρ_v and ρ_h. In all cases satisfactory agreement is obtained between the observed and the calculated values of ρ_u.

5. *Relation to X-ray Evidence.*

X-ray evidence[8] goes to show that there are, broadly speaking, two types of liquid mixtures, one type giving X-ray diffraction rings due to the two components separately at approximately the same angles as in the pure liquids, the other type giving an X-ray diffraction pattern consisting mainly of only one ring, the ring due to one component having contracted and the ring due to the second component having expanded. Phenol-water mixture and such pairs of partially miscible liquids belong to the first type, while completely miscible liquids such as ethyl alcohol-water mixture, etc., belong to the second type. The tendency for the formation of two distinct rings in the case of the first class of mixtures is explained by postulating the formation of large molecular clusters. The present optical evidence offers full support to this view. In this connection it should be remarked that no evidence was obtained for the existence of large molecular clusters in completely miscible liquids such as benzene and chlorobenzene, benzene and carbon tetrachloride, etc.

6. *Relation to Theories of Critical Opalescence.*

Smoluchowski[9] and Einstein[10] were the first to propose a theoretical explanation of the opalescence in liquid mixtures in the immediate neighbourhood of the critical solution temperature. These authors regarded the opalescence in liquid mixtures as due to local fluctuations in composition and consequent optical inhomogeneity. The theory of Smoluchowski and Einstein predicts an infinite intensity of scattering and also complete polarisation of the opalescent scattering. The results of the present experiment show clearly that the theories of Smoluchowski and Einstein are inadequate

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[8] P. Krishnamurti, *Ind. Jour. of Phys.*, 1929, **3**, 331.

[9] M. Smoluchowski, *Ann. der Phys.*, 1908, **25**, 205.

[10] A. Einstein, *Ann. der Phys.*, 1910, **33**, 1275.

to explain the observed phenomena. Ornstein and Zernike[11] put forward a modified theory of opalescence which takes into account the mutual influence of fluctuations in density in neighbouring small elements of volume in the fluid. This theory has already been adversely criticised by Rocard and Ponte[12] and it has been shown that some of the conclusions derived from the Ornstein-Zernike theory do not agree with the observed results. An attempt has been made by Rocard[13] to explain the finite value of the depolarisation of the opalescent scattering. He takes into consideration the scattering arising from the fluctuations in the molecular field which according to him become appreciable at the critical solution temperature. According to Rocard, the law of distribution in direction of this "fluctuation scattering" is the same as that of the orientation scattering and consequently if the incident light is polarised with electric vector horizontal the light scattered by the mixture in the transverse horizontal direction must be completely unpolarised, *i.e.*, ρ_h should be equal to 1. The results obtained by the present author however indicate a definite fall in value of ρ_h from 1 to about 0·2. Any value of ρ_h less than unity can only be explained by the formation of molecular clusters of size not small compared with the wavelength of light. From the results obtained it is clear that molecular clusters are formed at the critical solution temperature, T_c. The clusters have their maximum size at T_c and the size progressively diminishes as we go away from T_c.

The total scattering in liquid mixtures in the neighbourhood of the critical solution temperature is made up of (1) the scattering due to the fluctuations in composition which is completely polarised, (2) the scattering arising from the varying orientations which is depolarised to the extent of 6/7, and (3) the scattering arising from the finite size of the clusters which is also depolarised if the incident light is unpolarised. At the critical solution temperature the composition scattering becomes large and the scattering due to the finite size also becomes appreciable. The combined effect gives a finite value for the depolarisation ρ_u. Owing to the preponderance of the composition scattering which is proportional to λ^{-4} over the size-scattering which is proportional to λ^{-2}, the λ^{-4} law is found to be in better agreement with the observed result[14] than λ^{-2} law.

Further experimental work with pure liquids in the immediate neighbourhood of the critical temperature is in progress.

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[11] Ornstein and Zernike, *Proc. Amsterdam,* 1914, **17**, 793; 1916, **18**, 1520; *Phys. Zeits.*, 1918, **19**, 134; 1926, **27**, 761.

[12] Y. Rocard and M. Ponte, *Nature,* 1928, **126**, 746.

[13] Cabannes-Rocard, *La Diffusion Moleculaire de la Lumiere*, 1929.

[14] Rocard and Ponte, *loc. cit.*

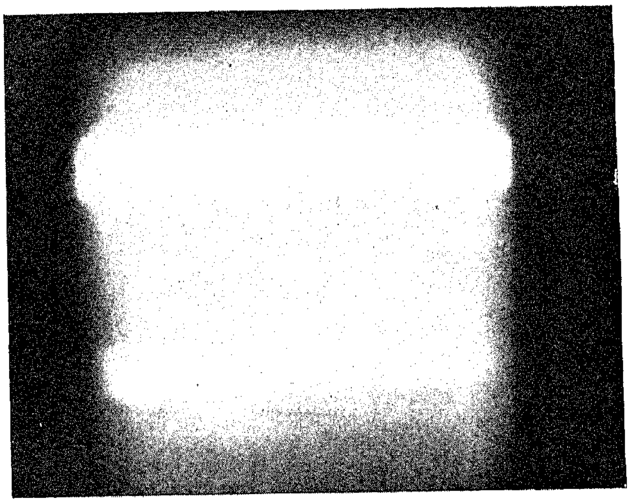

FIG. 1.
CS_2+CH_3OH at 41° C.

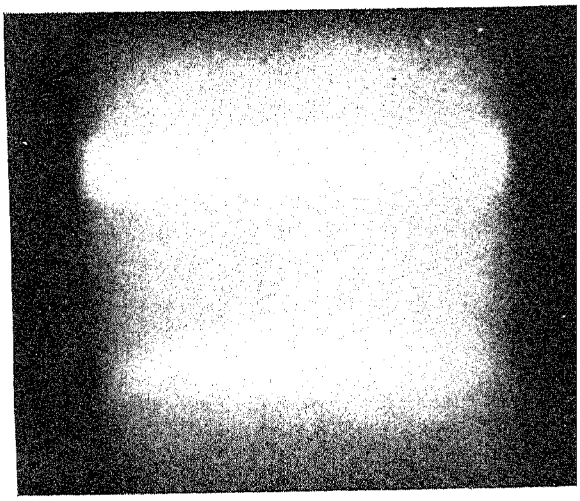

FIG. 2.
CS_2+CH_3OH at 44° C.

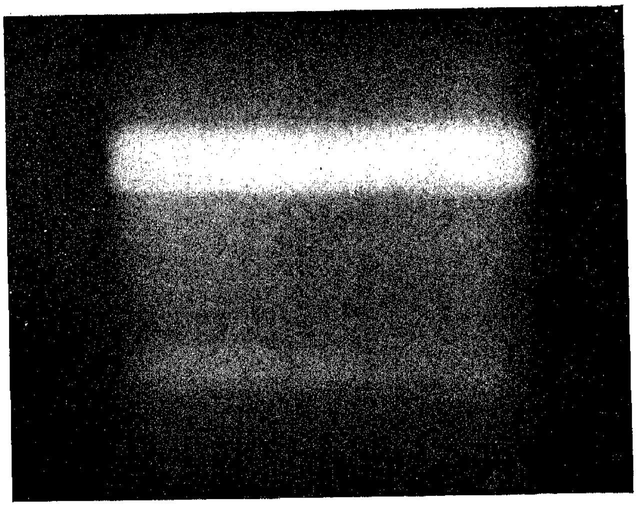

FIG. 3.
CS_2+CH_3OH at 48° C.

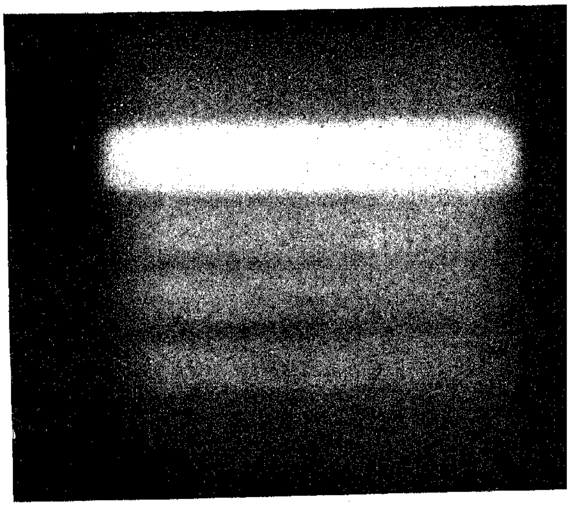

FIG. 4.
CS_2+CH_3OH at 60° C.

In conclusion the author takes this opportunity to express his grateful thanks to Prof. Sir C. V. Raman, Kt., F.R.S., N.L., for suggesting the problem and for rendering valuable help and guidance during the progress of this investigation.

7. *Summary.*

The earlier investigations on the intensity and depolarisation of the transversely scattered light in liquid mixtures in the neighbourhood of the critical solution temperature are briefly reviewed. It is pointed out that it is important to make comparative studies of the state of polarisation of the transversely scattered light with the incident light in different states of polarisation in order to get a correct idea of the state of dispersion of the scattering elements in the medium. Measurements of the depolarisation ρ_u, ρ_v and ρ_h were made, using, respectively, incident unpolarised light and incident light polarised with vibrations vertical and horizontal, for mixtures of eight different pairs of liquids over a range of temperature of about 30° above the critical solution temperature. The results obtained fully confirm the author's preliminary 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 validity for such mixtures of the optical reciprocity principle has been verified experimentally. It is also shown that the observed values of ρ_u, ρ_v and ρ_h satisfy the relation

$$\rho_u = (1 + {}^1/\rho_h) \,/\, (1 + {}^1/\rho_v)$$

The X-ray evidence regarding the state of dispersion of the molecules in liquid mixtures of the type phenol and water is in agreement with the optical evidence presented in this paper. The bearing of the experimental results on the various theories of critical opalescence including those which have been put forward subsequent to the work of Smoluchowski and Einstein is also discussed in the paper.