

# MOLECULAR CLUSTERING IN BINARY LIQUID MIXTURES.

(Variation with Composition and Temperature.)

BY R. S. KRISHNAN.

(From the Department of Physics, Indian Institute of Science, Bangalore.)

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## 1. Introduction.

It is well known that when certain pairs of liquids are brought together in suitable proportions, two liquid phases result; for example, in the case of phenol and water, the upper phase is a solution of phenol in water and the lower phase a solution of water in phenol. As the temperature is slowly raised, the compositions of the two phases tend to equality until at a particular temperature (called the critical solution temperature), the line of separation disappears and the whole mass presents the appearance of a single homogeneous phase. At this temperature the mixture exhibits a very marked turbidity or opalescence. The intensity of opalescence is markedly a function of temperature, being greatest at the critical solution temperature and becoming very weak as the temperature is removed from it in either direction. The earlier investigators in this field suggested as an explanation of the opalescence that the liquid mixture in the vicinity of the critical solution temperature behaves as an emulsoid. Smoluchowski was the first to propose a thermodynamic theory of the phenomenon which later was elaborated by Einstein. Einstein's formula for the intensity of opalescence received experimental support from the quantitative studies of Fürth and Zernike. 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 opalescence remains finite instead of tending to zero as the critical solution temperature is approached. In a recent paper<sup>1</sup> in these *Proceedings*, the present author presented evidence that large molecular clusters exist in such liquid mixtures in the neighbourhood of the critical solution temperature. The finite value of the depolarisation of the opalescent light arises from the fact that the size of the clusters is not small in comparison with the wave-length of light. The existence of such clusters could be demonstrated by the simple optical method developed

<sup>1</sup> R. S. Krishnan, *Proc. Ind. Acad. Sci.*, 1934, 1A, 211.

by the author. This consists in examining through a double-image prism, the light scattered in the transverse horizontal direction by the mixture when it is illumined with light polarised with electric vector horizontal. If clusters of size comparable with the wave-length of light are present, the horizontal component of the scattered light would be distinctly brighter than the vertical component. In a more recent paper<sup>2</sup> the author has reported the results of a detailed study of the opalescence of a series of binary mixtures over a wide range of temperature above the critical point. These results fully confirm the author's preliminary report, and demonstrate the existence of clusters in liquid mixtures—not only at the critical solution temperature but also at temperatures considerably removed from it. In the present investigation, a comparative study has been made of the intensity and depolarisation of the light scattered by mixtures of phenol and water in different proportions and at different temperatures, with a view to ascertain the influence of the composition and of the temperature of the mixture on the formation of clusters. The experimental results have an important bearing on other physical properties of the mixture, such as viscosity, magnetic birefringence, etc.

### 2. *Experimental Details.*

For the study of the effect of composition on the formation of clusters, mixtures of phenol and water were chosen as the most suitable, as it had been found from the previous investigation that the phenomenon is most pronounced in this case. Pure crystallised phenol was melted and was mixed with pure double distilled water in the requisite proportion, and the mixture was directly transferred to a clean and dry double bulb. The double bulb was then exhausted and sealed. The mixture was then got dust-free in one of the bulbs by repeated slow distillation and washing back into the other bulb. The bulb containing the dust-free mixture was then sealed off from the other. Six different mixtures of phenol and water containing respectively (a) 15% by weight of phenol, (b) 28% of phenol, (c) 34% of phenol, (d) 50% of phenol, (e) 60% of phenol and (f) 70% of phenol, were prepared dust-free in the manner indicated. The bulbs containing these mixtures were approximately of the same capacity and the quantity of mixture contained in each was also the same.

### 3. *Measurement of the Depolarisation of the Scattered Light.*

The experimental arrangement employed in the present investigation was similar to that previously employed\* for the measurement of the

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<sup>2</sup> R. S. Krishnan, *Ibid.*, 915.

\* *Loc. cit.*

depolarisations  $\rho_u$ ,  $\rho_v$  and  $\rho_h$  with the incident light respectively unpolarised, polarised with the electric vector vertical and with the electric vector horizontal. The ordinary lens of long focus used for condensing the light was replaced by a photographic lens of the same focal length provided with an iris diaphragm. The bulb containing the particular mixture to be studied was kept immersed in the water-bath. The temperature of the water in the bath was slowly raised and was kept steady at about  $30^\circ$  above the temperature of complete miscibility. The mixture was properly shaken. The depolarisations  $\rho_u$ ,  $\rho_v$  and  $\rho_h$  were measured by the usual method of Cornu, with the help of a double-image prism and nicol mounted on a stand so as to be capable of independent rotation about the same axis. The mixture was then slowly cooled down and the observations were repeated for a series of temperatures up to the critical point at which the mixture separated into two layers. The errors in the depolarisation measurements arising from the background illumination were avoided by viewing the two components of the scattered light against the same background. The error due to the finite convergence of the incident beam was almost negligible since the angle of convergence was less than  $3^\circ$ . The values of  $\rho_u$ ,  $\rho_v$  and  $\rho_h$  for various mixtures are tabulated below.

#### 4. Intensity Measurements.

The method usually adopted by the earlier investigators in this field for the comparison and measurement of intensities of scattered light was visual photometry. Although visual photometry has been recognised as one of the accurate methods for the comparison of intensities, it is defective in that the process is tedious and at the same time subjective in nature. The advantages of using a photocell together with a direct current amplifier for comparison and measurement of feeble intensities, *e.g.*, that of light scattered by a fluid, have already been pointed out by Mr. R. Ananthakrishnan.<sup>3</sup> The convenience of using a photocell in such experiments lies in the fact that the state of polarisation of the light has no influence on the photoelectric current which is a direct measure of the energy of light falling on the cell. Moreover, in contrast with the visual method it is objective in nature and is less tedious. In the present investigation, therefore, the photoelectric method was employed for comparing the intensities of light scattered by the mixtures of phenol and water at various temperatures.

The experimental arrangement used for the measurement of intensity was similar to that employed for the depolarisation measurements. But the following alterations were made. The nicol and double-image prism

<sup>3</sup> R. Ananthakrishnan, *Proc. Ind. Acad. Sci.*, 1934, 1A, 201.

were removed from the observation side. The transversely scattered light after passing through the side tube attached to the wooden box which contained the scattering substance was allowed to fall on the V-shaped plate of the Osram CMG 8 (gas-filled) cell manufactured by the General Electric Company, Ltd., of England. The photocell was suitably mounted inside a wooden case (well insulated) which was painted dull black. The leading tube through which the scattered light passed, was also painted dull black inside and projected into the wooden case of the photocell. The distance of the photocell from the scattering substance was about nine inches. The scattered light entering the cell was limited by a series of apertures. The whole arrangement was such that when the mixture was illuminated, only the light scattered in the exact transverse horizontal direction entered the cell.

The photocell was connected to the Valve Bridge Amplifier as shown in Fig. 1.

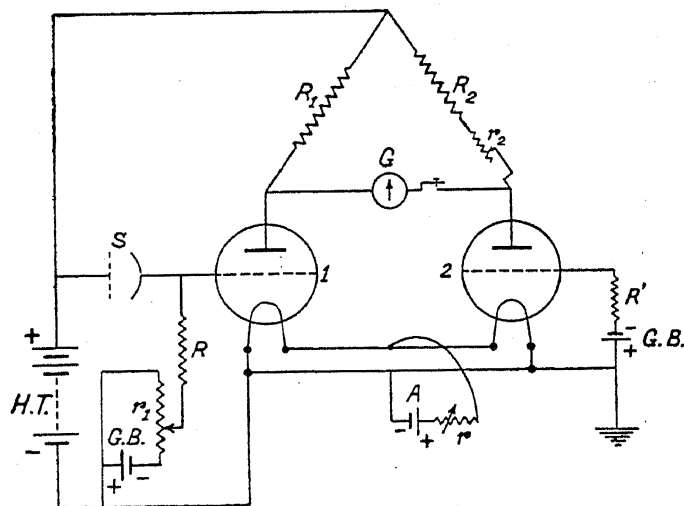


FIG. 1.

- 1, 2 .. L610 Marconi Dull Emitter Valves.
- $R_1, R_2$  .. 10000 ohm resistances.
- $R, R'$  .. 20 meg ohm grid leaks.
- $r_1$  .. Varley Potentiometer (1200 ohms).
- $r_2$  .. Adjustable rheostat (400 ohms).
- $r$  .. Filament rheostat (5 ohms).
- A .. Filament battery (6 volts).
- H. T. .. High tension battery (115 volts).
- G. B. .. Grid bias battery (2 volts).
- S .. Osram CMG8 Photocell.
- G .. Microammeter.

This amplifier was originally set up by Mr. R. Ananthakrishnan to whom the author's thanks are due. The leads from the photocell were properly insulated to avoid disturbances in the amplifier. The amplifier was of the simplest type possible without elaborate controls and the details of its working

had already been fully described by Mr. R. Ananthakrishnan<sup>4</sup> in his paper on the "Photoelectric Photometry of Light Scattering in Liquids". It was found that by the use of good storage batteries, a steady state could be reached in the bridge within a short time after switching on the various connections.

The particular mixture under examination was maintained at the requisite temperature. The incident light was cut off by a shutter before it entered the mixture. The various connections in the amplifier circuit were switched on and the bridge was brought to a balance by adjusting the rheostat  $r_2$  (see Fig. 1). The reading of the micro-ammeter was taken. The incident light was then let into the mixture and the final steady deflection of the micro-ammeter was again read off. The observations were repeated with the same mixture for a series of temperatures up to the critical solution temperature and also with the other mixtures. When the intensity of scattering was found to increase to large values as would be the case near the critical solution temperature, the intensity of the incident beam was proportionately reduced by means of the iris diaphragm attached to the long-focus lens so that the deflections of the micro-ammeter were always of the same order of magnitude.

The possible sources of error in the experiment are the following: (a) the want of linearity in the response of the amplifier, (b) the want of steadiness of the intensity of the light of the projection lantern which was used as the source of light, and (c) the absorption and reflections at the various surfaces. The linearity in the response of the amplifier was tested out by noting the deflections of the galvanometer using the same mixture as the scattering substance when the intensity of the incident light was reduced by known amounts. It was found that the deflections registered by the galvanometer in the bridge circuit when scattered light of a certain small intensity was allowed to fall on the photocell could be taken to be proportional to the intensity of light falling on the cell.

The intensity of light emerging out of the square aperture was measured in a foot-candle meter at regular intervals keeping the distance between the two standard carbon rods used in the projection lantern constant. It was found that the projection lantern could be taken as a fairly steady source of light within the limits of experimental error.

No account was taken of the absorption of light since the distances involved were small. In this case of the comparison of intensities, errors arising from the reflections at the various surfaces, etc., were automatically

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<sup>4</sup> R. Ananthakrishnan, *loc. cit.*

eliminated by the use of bulbs of the same capacity for all the mixtures and by keeping the rest of the experimental arrangement undisturbed.

From the observed deflections of the micro-ammeter and from a knowledge of the proportions in which the intensity of the incident light was reduced in each case, the relative intensities of light scattered by the mixtures at various temperatures were calculated. The results are tabulated below.

TABLE I.

(a) 15% Phenol.

Temperature of the mixture °C.	$\rho_h$ %	$\rho_v$ %	$\rho_u$		Relative intensity of transversely scattered light
			(observed) %	(calculated) %	
88	100	1.5	3.1	3.0	1.0 (assumed)
78	100	1.1	2.3	2.2	1.3
69	100	0.75	1.4	1.5	2.0
64	100	0.55	1.1	1.1	3.8
60	100	0.5	1.0	1.0	8.3

TABLE II.

(b) 28% Phenol.

Temperature of the mixture °C.	$\rho_h$ %	$\rho_v$ %	$\rho_u$		Relative intensity of transversely scattered light
			(observed) %	(calculated) %	
90	100	0.9	1.7	1.8	1.0 (assumed)
87	84	0.7	1.5	1.5	1.2
81	70	0.5	1.0	1.2	1.7
77	59	0.34	0.84	0.9	2.4
74	49	0.27	0.76	0.82	3.9
72	35	0.23	0.7	0.88	5.8
68.5	22	0.15	0.62	0.83	23.8

TABLE III.  
(c) 34% Phenol.  
(Critical Composition Mixture.)

Temperature of the mixture °C.	$\rho_h$ %	$\rho_v$ %	$\rho_u$		Relative intensity of the transversely scattered light
			(observed) %	(calculated) %	
95	75	1.0	2.2	2.3	1.0 (assumed)
90	66	0.7	1.5	1.7	1.2
87.5	61	0.6	1.4	1.6	1.3
83	51	0.43	1.1	1.3	2.1
80	47	0.34	0.93	1.0	2.9
77	39	0.27	0.77	0.96	3.8
74	31	0.23	0.75	1.0	7.8
71	26	0.19	0.7	0.93	24.6
69.5	16	0.12	0.62	0.87	45.0
69	12	0.07	0.62	0.65	53.0

TABLE IV.  
(d) 50% Phenol.

Temperature of the mixture °C.	$\rho_h$ %	$\rho_v$ %	$\rho_u$		Relative intensity of the transversely scattered light
			(observed) %	(calculated) %	
90	100	2.1	4.0	4.1	1.0 (assumed)
85	95	1.6	3.3	3.2	1.3
80	93	1.2	2.5	2.5	1.7
75	80	0.84	2.1	1.9	2.1
70	70	0.62	1.5	1.3	3.2
66.5	51	0.32	1.0	0.95	4.8
64.5	41	0.27	1.0	0.93	8.2

TABLE V. (e) 60% Phenol.

Temperature of the mixture °C.	$\rho_h$ %	$\rho_v$ %	$\rho_u$		Relative intensity of the transversely scattered light
			(observed) %	(calculated) %	
89	100	4.5	8.2	8.6	1.0 (assumed)
79	100	3.8	7.2	7.3	1.2
70	100	2.8	5.3	5.5	1.6
65	100	2.4	4.8	4.7	2.3
61	100	1.9	3.8	3.7	3.7

TABLE VI. (f) 70% Phenol.

Temperature of the mixture °C.	$\rho_h$ %	$\rho_v$ %	$\rho_u$		Relative intensity of the transversely scattered light
			(observed) %	(calculated) %	
59	100	9.3	16.3	17.0	1.0 (assumed)
49	100	8.2	14.9	15.1	1.2
40	100	6.9	12.2	12.9	1.3
30	100	6.0	11.0	11.3	1.5

TABLE VII.

Composition of the mixture i.e., % by weight of Phenol	Temperature of miscibility °C.	$\rho_h$ %	$\rho_v$ %	$\rho_u$ %	Relative intensity of opalescence
15	60	100	0.5	1.0	6.6
28	68.5	22	0.15	0.62	71
<b>34</b>	<b>69</b>	<b>12</b>	<b>0.07</b>	<b>0.62</b>	<b>186</b>
50	64.5	41	0.27	1.0	15
60	61	100	1.9	3.8	3
70	30	100	6.0	11.0	1 (assumed)



## 5. Discussion of Results.

In the tables given above the numbers given in the fifth column are the values of  $\rho_u$  calculated from the observed values of  $\rho_h$  and  $\rho_v$  using the reciprocity formula.<sup>5</sup> The observed values of  $\rho_u$  are in satisfactory agreement with the calculated values.

The experimental results show some very striking characteristics. For a mixture having any composition whatsoever, the values of the depolarisations  $\rho_u$ ,  $\rho_v$  and  $\rho_h$  are minimum at the critical point, while the intensity of light scattered transversely is a maximum at this temperature. Again the depolarisations  $\rho_u$ ,  $\rho_v$  and  $\rho_h$  attain minimum values and the intensity of scattering attains the maximum value for the mixture having the exact critical composition, *i.e.*, in this case for a mixture containing 34% by weight of phenol (see Table VII). The temperature of complete miscibility, as is well known, is also maximum for this concentration. As we go away from the critical composition on either side, the temperature of complete miscibility decreases, the depolarisation values increase suddenly at first and then gradually. In the same manner, the intensity of scattering falls off suddenly to less than half its value for the critical solution mixture, when the composition differs from the critical composition even by a small amount. For any mixture and especially for a critical composition mixture, there is a very rapid increase in the intensity of scattering as the critical solution temperature is approached. If curves are drawn showing (1) the dependence of depolarisation on composition, (2) the temperature of complete miscibility on composition, and (3) the intensity of scattering on composition, they will have approximately the same parabolic form.

It is seen from the results obtained that  $\rho_h$  for mixtures containing 15% by weight of phenol, 60% phenol and 70% phenol *has always the limiting value* of 100% showing thereby that no detectable clusters are present in these mixtures. In the case of the other three mixtures (*i.e.*, mixtures containing 28% phenol, 34% phenol and 50% phenol) detectable clusters are formed as is seen from the fall in the value of  $\rho_h$  from 100%. The range over which such clusters are detectable is less than 20° C. for mixtures containing 28% phenol and 50% phenol, while the range is more than 30° C. for a 34% phenol mixture. The values of  $\rho_h$  and  $\rho_v$  for the 34% phenol mixture at the critical solution temperature are considerably lower than the corresponding values for other mixtures. But the values of  $\rho_u$  is of the same order of magnitude. These definitely indicate that not only is the tendency for the formation of molecular clusters a maximum for the critical composition

<sup>5</sup> R. S. Krishnan, *Proc. Ind. Acad. Sci.*, 1935, 1A, 782.

mixture, but also that the size of the clusters formed is greatest for this mixture. These results are in accordance with the remark made by H. S. Taylor<sup>6</sup> in his book on Physical Chemistry, that *it is only with the critical composition in a system containing two partially miscible liquids that a critical state can be reached.*

#### 6. Relation to Other Physical Properties.

Various other physical properties such as viscosity, flow birefringence, magnetic birefringence, etc., have been extensively studied by numerous investigators. Ostwald and Malss<sup>7</sup> have determined the coefficient of viscosity for a series of binary mixtures of the type phenol and water both above and below the critical solution temperature. Only mixtures having the exact critical composition have been studied by them. They find an abnormal increase in the viscosity at the critical point. They try to explain the same by saying that liquid mixtures at the critical solution temperature are emulsoid systems of approximately colloidal degree of dispersion. Ostwald and Erbring<sup>8</sup> further found a marked streaming double refraction for a mixture of carbon disulphide and methyl alcohol within a definite region of temperature in the neighbourhood of the critical solution temperature.

A. Piekara<sup>9</sup> has investigated the variation of magnetic birefringence with temperature at different concentrations in mixtures of nitrobenzene and normal hexane. He finds that the thermal coefficient of magnetic birefringence increases with concentration, the coefficient becoming abnormally large at the critical solution point. The results are explained by him by assuming that the increase in the molecular association causes an increase in the molecular and magneto-optic anisotropy. These abnormal properties exhibited by critical composition mixtures near the critical point are in all probability due to the formation of molecular clusters under these conditions.

Critical composition mixtures near the critical point cannot be regarded as colloidal solutions or emulsoids since some important characteristics of a colloidal solution are not exhibited by these mixtures. A colloidal system progressively changes with time. But it is a fact of observation that the critical opalescence and such other phenomena exhibited by critical solution mixtures are invariant with time and depend only on the temperature. Moreover, if liquid mixtures at the point of complete miscibility behave like emulsoid systems, then all the phenomena which are characteristic of

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<sup>6</sup> H. S. Taylor, *A Treatise on Physical Chemistry*, Vol. 1, 530.

<sup>7</sup> W. Ostwald and A. Malss, *Koll. Zeits.*, 1933, 63, 61.

<sup>8</sup> W. Ostwald and Erbring, *Koll. Zeits.*, 1933, 64, 229.

<sup>9</sup> A. Piekara, *Jour. de Phys.*, 1934, 5, 54.

the critical composition mixture should also be exhibited by mixtures whose compositions are widely different from the critical composition. But this is not so. Although large molecular clusters are formed in binary liquid mixtures at the critical solution temperature, there seems to be no justification for regarding them as colloidal systems.

In conclusion, the author wishes to record his indebtedness to Prof. Sir C. V. Raman, Kt., F.R.S., N.L., for his kind and helpful interest in the work.

#### 7. *Summary.*

This paper deals with a comparative study of the intensity and depolarisation of the light scattered transversely by mixtures of phenol and water in different proportions and at different temperatures. The lowest values for the depolarisations  $\rho_u$ ,  $\rho_v$  and  $\rho_h$  are obtained with the critical composition mixture (in this case 34% phenol mixture) at the critical solution temperature, where  $\rho_u$ ,  $\rho_v$  and  $\rho_h$  are the depolarisations of the light scattered transversely when the incident light is (1) unpolarised, (2) polarised with electric vector vertical, and (3) polarised with electric vector horizontal respectively. The photoelectric method was employed for the comparison of intensities of scattering by these mixtures at various temperatures above the critical solution temperature. The intensity of scattering is found to increase considerably for the 34% phenol mixture as the critical solution temperature is approached. It is found that the tendency for the formation of clusters and the size of the clusters formed depend on the temperature and composition of the mixture. These phenomena are found to be most pronounced for the critical composition mixture at the critical solution temperature. The bearing of these results on the anomalies of viscosity, magnetic birefringence, etc., noticed in the vicinity of the critical conditions is also pointed out.