

THE RAMAN SPECTRA OF ORGANIC COMPOUNDS : BINARY LIQUID MIXTURES

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It is now well established that the marked blue opalescence of binary liquid mixtures at the critical solution temperature is due to the formation of molecular clusters of size comparable to the wave-length of light. In order to find out the exact nature of these aggregates, an investigation of the Raman spectra of such mixtures has been undertaken. Two typical systems are chosen. They are made up of (1) a polar and a non-polar liquid, *viz.*, cyclohexane and aniline, and (2) two polar liquids, *viz.*, iso-butyric acid and water. The critical mixture of cyclohexane and aniline contains 54% by weight of the former and 46% of the latter, the critical temperature being 30° C. and of water and isobutyric acid contains 50% by weight of each, the critical temperature being 26° C. The two liquids are immiscible below the critical temperature. In each case the liquids are mixed together in the proper proportion and distilled over completely into the experimental tube. The tube is heated by a cylindrical electric heater and when the critical temperature is attained, the liquids are thoroughly mixed up by shaking to form a homogeneous fluid, and this temperature is maintained throughout the exposure. The spectra of the two liquids and their mixture are recorded separately. Since the unmodified scattering is very intense in the case of the critical mixtures, their Raman spectra are accompanied by a fairly strong continuous background. In fact, due to this latter cause, Bogros and Rocard (1928) and Martin (1928) failed to record any Raman line for a critical mixture of phenol and water, and Ziemecki and Jodko (1929) for a mixture of *iso*-butyric acid and water. In the case of cyclohexane-aniline mixture, this background is considerably suppressed and the discolouration due to photo-decomposition is prevented by using a solution of sodium nitrite as filter. For *iso*-butyric acid-water mixture, the spectra were obtained with unfiltered radiation as well as with 4047 A.U. alone by using a filter of iodine in CCl₄ and with 4358 A.U. by using the nitrite filter. The spectrum of the mixture in each case was compared with those of the component liquids both by superposition and by careful comparison with the iron arc spectrum recorded alongside of every picture.

Results

The results of the investigation are given in Tables I and II. In the case of *iso*-butyric acid, the polarisation characters of the spectrum of the pure liquid and of the mixture were also studied and are recorded in the table. The spectrum of *iso*-butyric acid-water mixture taken with 4046 A.U. radiations of the arc is reproduced in Plate XVII along with that of the pure acid.

TABLE I. *Cyclohexane - Aniline Mixture*

Cyclohexane	Aniline	Mixture	Cyclohexane	Aniline	Mixture
..	234 (4)	234 (1)	1348 (1)	1340 (1)	1342 (0)
384 (½)	387 (4 b)	387 (2)	1442 (5 b)	..	1445 (2)
426	1456 (2)	1456 (0)
600	532 (5)	532 (1)	..	1499 (2)	..
..	619 (5)	619 (0)	..	1538 (2)	..
..	757 (3)	757 (0)	..	1590 (2)	..
802 (10)	..	802 (3)	..	1601 (10)	1601 (6)
..	810 (8)	810 (5)	..	1612 (2)	1612 (0)
..	830 (8)	830 (5)	2854 (10 b)	..	2854 (5)
..	996 (10)	996 (5)	2922 (8 b)	..	2922 (4)
1029 (6)	1029 (5)	1029 (3)	..	3046 (10)	3046 (5)
1156 (3)	1149 (3)	1149 (1)	..	3066 (4)	3066 (2)
..	1168 (2)	1162 (1)	..	3362 (3 b)	3362 (1)
1265 (5)	1272 (4 b)	1270 (4)	..	3423 (2 b)	3423 (0)

TABLE II. *Iso-Butyric Acid-Water Mixture*

<i>Iso</i> -butyric Acid	Polarisation	Mixture	Polarisation	<i>Iso</i> -butyric Acid	Polarisation	Mixture	Polarisation
130 (2)	D	1224 (2 b)	P
253 (2)	D	253 (0)	..	1234 (0)
342 (2 b)	D	342 (1)	D	1253 (0)
435 (1)	1300 (2)	D	1300 (1)	..
510 (5)	P	Disappears	..	1313 (0)
..	..	519 (2 b)	P	1430 (2)	P	Disappears	..
540 (1)	D	540 (3)	D	1457 (5 b)	D	1453 (4)	D
603 (2)	D	603 (1)	D	1654 (4 b)	P	Disappears	..
690 (0)	1715 (2 b)	D
710 (1)	2732 (1)
743 (2)	P	743 (3)	P	2763 (2)
800 (10)	P	800 (4 b)	P
..	..	Broader and weaker	..	2815 (0)
854 (1)	D	2874 (6)	P	2874 (5)	P
909 (5)	D	909 (5)	D	2920 (4)	P	2920 (2)	P
930 (0)	2978 (6)	D	2978 (4)	D
962 (3)	D	962 (3)	D
..
991 (1)	D
1010 (0)
1042 (1)
1092 (2 b)	..	1092 (1)
1106 (2 b)	..	1106 (1)

Discussion of Results

1. *Cyclohexane-aniline mixture*.—It will be noticed from Table I that all but the very weak lines of the two molecules have been recorded in the mixture. There is neither any shift of frequencies, nor any change in the relative intensities of the lines. It is, however, observed that in spite of the fact that cyclohexane forms 61% by volume (56% by weight) of the mixture, its spectrum is very much less intense than that of aniline as judged from the intensities of lines in the neighbourhood of 800 cm.^{-1} . In the mixture, the spectra of the liquids are photographed under identical experimental conditions, and this difference in the intensity of the Raman lines due to the same mode of vibrations is presumably due to the lower scattering power of cyclohexane. As the spectrum of the mixture is only a superposition of the spectra of the two liquids, we have to conclude that the inter-molecular forces between the molecules forming clusters should be assumed to be too weak to influence the intra-molecular vibrations to any extent.

2. *Iso-butyric acid-water mixture*.—The striking changes that take place in the Raman spectrum of *iso*-butyric acid when it forms a critical mixture with water are the disappearance of three strong lines 510 (5), 1430 (2) and 1654 (4 b) and the appearance of two broad lines at 519 (2 b) and 1715 (2 b). The Raman band at 3460 of the pure water is shifted slightly towards higher frequency in the mixture. These changes are illustrated by the microphotometric curves given in Fig. 1 and indicated by arrows in the spectra of the acid and the mixture. The most intense and well polarised line of the acid at 800 cm.^{-1} is also slightly broadened and rendered relatively weak, while the line 909 has gained somewhat in intensity. These variations suggest that unlike cyclohexane-aniline mixture, *iso*-butyric acid molecule undergoes configurational changes when it forms a critical composition mixture with water. It has been shown by Sunanda Bai (1940) that when pure *iso*-butyric acid is heated to its boiling point the line at 1654 which is due to the carbonyl linkage, weakens and a new broad line 1726 makes its appearance. These changes are attributed to the breaking up of some of the dimer molecules into single molecules at the higher temperature. The hydrogen bond formed between C=O and O-H in the dimer lowers the carbonyl frequency from its normal value of 1726 to 1654. The disappearance of the line at 1650 and the appearance of a line at 1720 in its place has also been observed by Edsall (1936) in aqueous solutions of formic and acetic acids and by Saxena (1940) in trichloro-acetic acid and explained on the same basis as given above. Saxena (1940) has also shown that the carbonyl frequency of the monomer at 1720 is polarised and of the dimer at 1650 is depolarised. These observations are fully supported by the

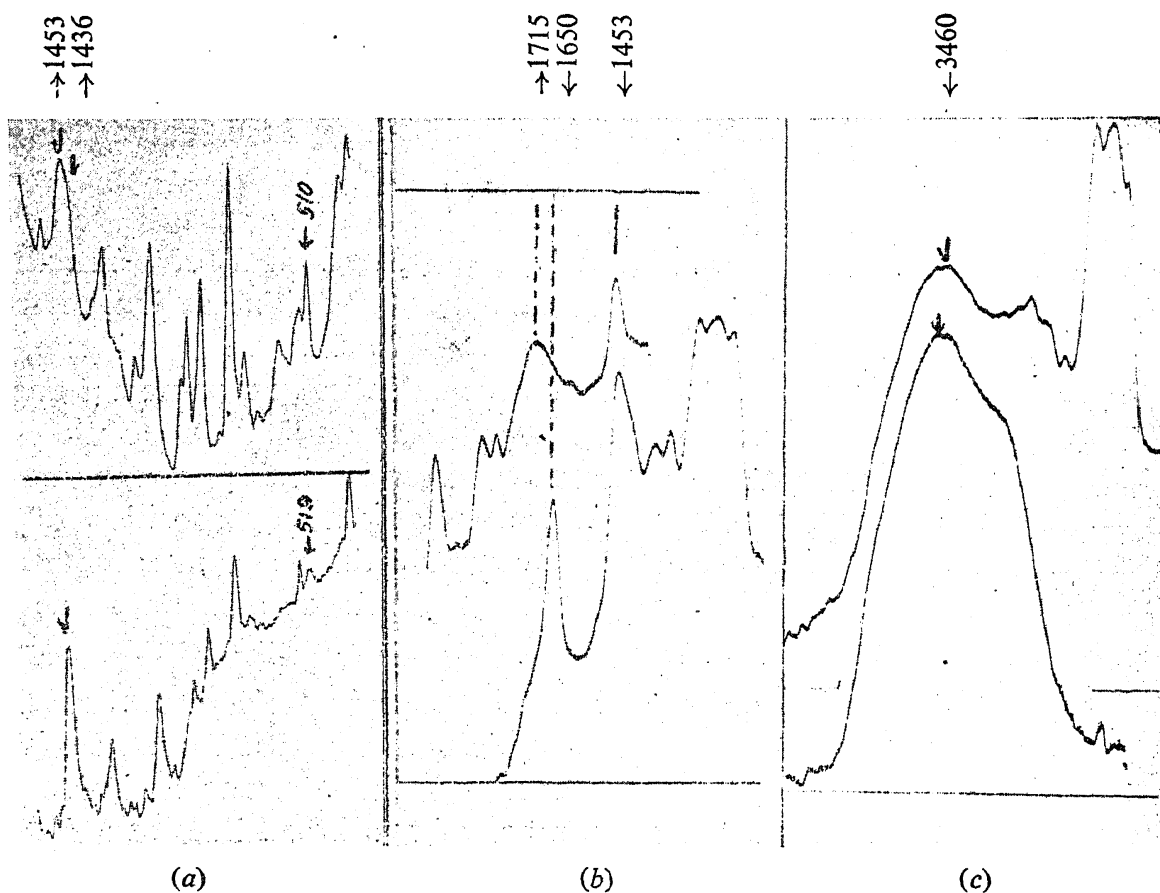


FIG 1. Microphotometric records of horizontal and vertical components for *iso*-butyric acid at room temperature.

(a) Above : Pure Acid
Below : Mixture

(b) Below : Pure Acid
Above : Mixture

(c) Below : Pure Water
Above : Mixture

polarisation measurements of these lines in the present investigation. Besides, according to Saxena, we should expect one polarised line at about 1400 for the dimer corresponding to the symmetrical oscillation of the carboxyl group. The line at 1436 in *iso*-butyric acid is polarised and is evidently to be assigned to this mode of vibration of the dimer, and its disappearance in the critical solution mixture is readily understood as arising from depolymerisation. The changes taking place for the line at 510 is analogous to that observed by Edsall in dilute aqueous solutions of formic and acetic acids and by Saxena for trichloroacetic acid. In formic acid the line at 678 (3) is replaced by 708 (1 b) in 35% aqueous solution, in acetic acid the line at 623 (4) by 630 (3 b) in 33% solution and in trichloroacetic acid, the line at 675 by a diffuse one at 695. It should, however, be mentioned that the lines 678 of formic acid and 623 of acetic acid are depolarised according to Saxena (1940), while we have observed that the line 506 of *iso*-butyric acid is partially polarised. The changes in this region are also due to the dissociation of the acid molecule to smaller units.

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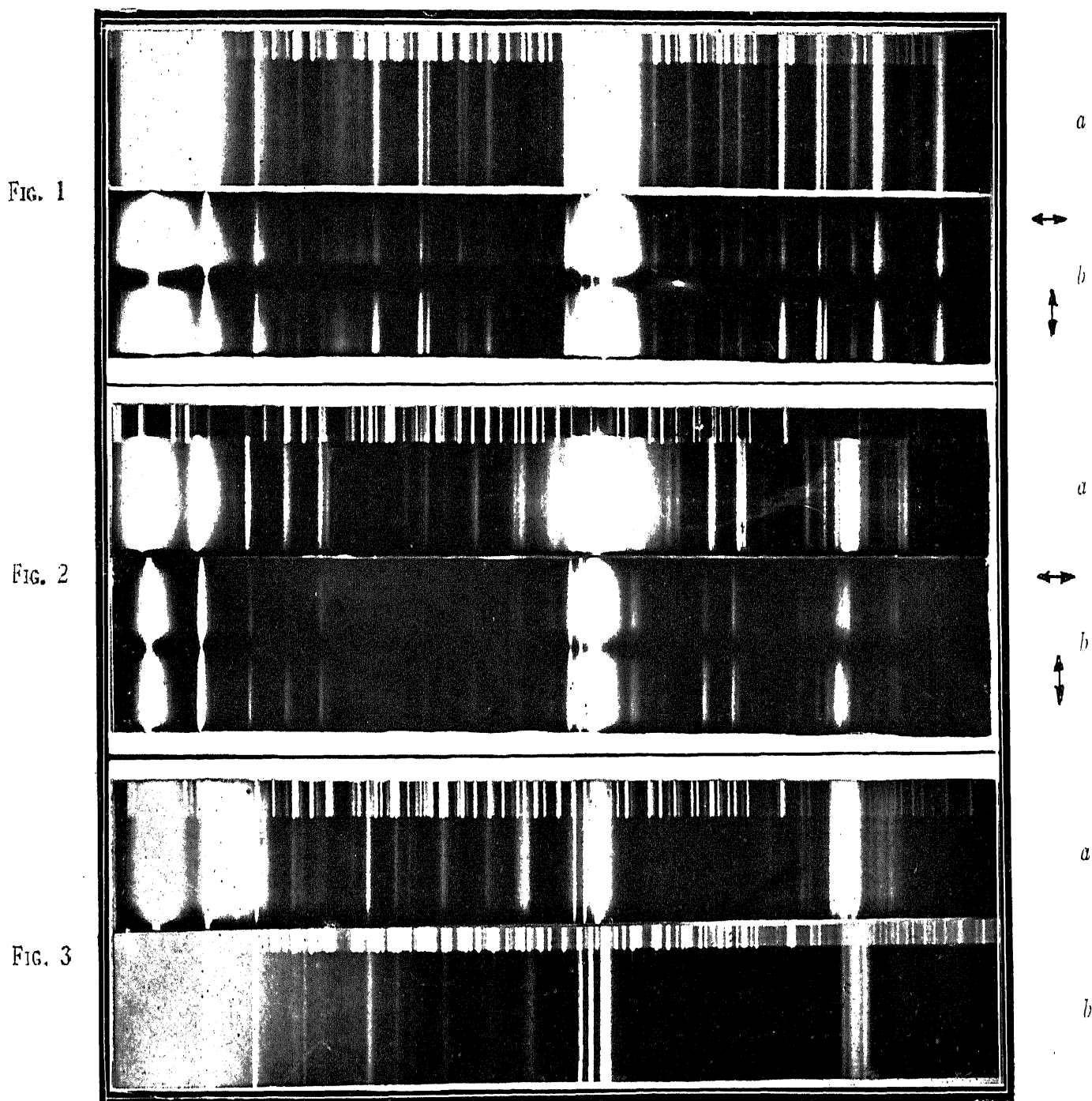


FIG. 1. (a) Aniline; (b) Polarisation of Aniline
FIG. 2. (a) Diethyl disulphide; (b) Polarisation of Diethyl disulphide
FIG. 3. (a) Iso-butyric Acid; (b) Iso-butyric acid-Water mixture



Since the changes in the spectrum mentioned above can be brought about only by an interaction of the acid and the water molecules, we have to conclude that *iso*-butyric acid which is immiscible with water below 26° C, forms an intimate solution above that temperature accompanied by the attendant changes such as depolymerisation and dissociation. The opalescence of the critical mixture should, therefore, arise from clusters composed of molecules of the acid and water together. The hydrogen bond in the dimer in the pure acid presumably opens up, resulting in effect in the simultaneous formation of single molecules and of weaker bonds between the latter and the water molecules in larger numbers. This also accounts for the shift of the water band at 3460 cm.⁻¹ to a higher frequency.

The polarisation characters of the intense lines in *iso*-butyric acid remain the same in the mixture so far as could be ascertained. The hydroxyl frequency does not appear in the pure acid. Four new lines, *viz.*, 1234, 1253, 1313 and 2763 cm.⁻¹ are observed for the liquid in addition to those reported by Sunanda Bai (1940).

Summary

The Raman spectra of two critical solution mixtures, namely cyclohexane-aniline and *iso*-butyric acid-water, are obtained and compared with the spectra of the component liquids. No changes are observed in the cyclohexane-aniline mixture. In the *iso*-butyric acid-water mixture the following changes are observed: Three fairly intense lines at 510, 1430 and 1654 cm.⁻¹ of the acid disappear in the mixture and instead, broad lines appear at 519 and 1715. The strongest line of the acid at 800 cm.⁻¹ becomes slightly broader and less intense. The strong water band at 3460 appears to be shifted to a slightly higher frequency. From a comparison of these changes with those reported for formic, acetic and trichloroacetic acids, it is concluded that at the critical temperature, the acid molecules change over from dimer to monomer state. This indicates that at or above the critical temperature, the two liquids in the mixture become homogeneous as in solutions. The results are discussed in relation to the cluster formation in the binary liquid mixtures.

In conclusion we wish to place on record our thanks to Prof. C. V. Raman for his interest in the work.

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