

RAMAN EFFECT IN BINARY LIQUID MIXTURES THE SYSTEM PYRIDINE-ACETIC ACID

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SUMMARY

The effect of concentration on the Raman spectrum of a mixture of pyridine and acetic acid has been investigated over a wide range of concentrations. The 990–1,029 doublet of pyridine exhibits a conspicuous variation in intensity and structure. For a mixture containing 30 mol. % acid a new line appears at 1,006 cm.^{-1} and is of maximum intensity for 80 mol. % acid. Some other minor changes are also reported. The observed changes indicate the formation of a complex with the formula $4 \text{CH}_3\text{COOH}-\text{C}_5\text{H}_5\text{N}$.

1. INTRODUCTION

Two different liquids having an affinity for each other combine to form a chemical complex when mixed. Such complex formations can be detected by certain singularities in the physical properties of the mixture, like density, viscosity, vapour pressure, surface tension, freezing point and heat of solution. The complex formation is indicated by a maximum in the viscosity concentration curve for the mixture at or around a particular concentration or a maximum in the density concentration curve or a minimum in the vapour pressure concentration curve. The Raman spectrum of a substance is a significant physical property which is useful in solving many physico-chemical problems, the problem at hand being one of them.

The study of compound formation between pyridine and acetic acid has engaged the attention of a number of investigators. Tsakalatos (1908) found that at approximately 78 mol. % acetic acid of this mixture, the viscosity curve showed a maximum and approximately at 84 mol. % acid the density curve showed a maximum. From these observations he suggested the formation of a complex at about 80 mol. % acetic acid. The vapour pressure vs. concentration curves for this mixture obtained by Zawidzki (1900) showed two points of inflexion, one at 30 mol. % and the other at 80 mol. % acid. He explained these by postulating the existence of two compounds, one containing more of pyridine corresponding to the first point of inflexion and another containing more of acid molecules corresponding to the second point of inflexion. Swearingen and Heck (1934)

have determined the viscosity of this mixture at different temperatures over a wide range of concentrations. They too observed that the viscosity reached a maximum value at about 80 mol. % of the acid. In addition, the electrical conductance measurements on this mixture reported by Trifonov and Cherlov (1929) and Swearingen and Ross (1934) indicated the formation of a complex around 80 mol. % of the acid. On the other hand, the depolarisation and intensity measurements of the scattered light and magnetic susceptibility measurements of this mixture by Venkataraman (1940) indicated the formation of a complex at 60 mol. % acid. But his results failed to explain either the vapour pressure concentration curve of Zawidzki (1900) or the density concentration curve of Tsakalatos (1908). However, the results on the determination of the compressibility of this mixture from ultrasonic velocity measurements carried out recently by Balachandran (1953) favour the formation of two complexes, one at 30 mol. % and another at 80 mol. % of the acid. Though the Raman spectrum of a mixture of 66 mol. % was studied by Whiting and Martin (1931) they failed to detect any change. In view of the interesting but contradictory results obtained by the various workers, it was felt desirable to investigate the effect of concentration on the Raman spectrum of a mixture of pyridine and acetic acid using modern methods of Raman spectroscopy.

2. EXPERIMENTAL DETAILS

The usual Wood's tube arrangement has been employed in the present investigation. Both pyridine and acetic acid were pure Merck's and were distilled twice or more before use. The Raman spectra of pyridine, acetic acid and their mixture of different concentrations were photographed on the same plate by means of a Hartmann diaphragm so that they could be compared easily. The Fuess spectrograph used in the investigation had a dispersion of about 20 A°U per millimetre in the 4358 A°U region and gave satisfactory spectra. The concentrations studied were 20, 30, 60, 80 and 90 mol. % of the acid. The exposure was adjusted suitably to allow for the variation in intensity of the lines of the individual components due to the different concentrations studied. From the negatives, only those Raman lines whose character change with concentration were measured on a Hilger cross-slide micrometer.

3. RESULTS

Photographs of the Raman spectra of this mixture at different concentrations are reproduced in Plate (XII) at the end of this paper. Significant changes occur in the case of certain Raman lines of both acetic acid and pyridine. The observations can be summed up as follows,

1. *The strong doublet 990 and 1029 of pyridine.*—This doublet is due to the $c-c$ oscillation of the pyridine molecule. The conspicuous changes observed with this doublet indicate complex formation. This doublet is unaffected at 20 mol. % of the acid. At 30%, in addition to the doublet, a faint Raman line appears close to 990. This has a frequency shift of 1006 cm.^{-1} . At 60%, this component becomes brighter while 990 becomes feeble and 1029 is almost absent. At 80 mol. %, the line 1006 cm.^{-1} is very intense and asymmetric and more diffuse towards longer wavelength. The original doublet is not at all seen. At 90% this new line again becomes faint and it disappears in the pure acid.

2. *The lines 1572 and 1594 cm.^{-1} of pyridine.*—These lines are somewhat broad and nearly of equal intensity and remains unchanged for concentrations up to 20%. At 30% the Raman line 1594 becomes less intense and more sharp than it is in pure pyridine, while 1572 cm.^{-1} is unaffected. At 60% the change undergone by 1572 cm.^{-1} is quite similar to that observed with 1594 cm.^{-1} at 30%, while at 80 mol. % of acid both are extremely feeble in intensity but very sharp.

3. *The line 3054 due to pyridine.*—This is the aromatic C-H oscillation. This appears as a very strong and slightly broad line in the spectrum of pure pyridine as also in the spectra of mixtures containing 20, 30 and 60 mol. % of acid. For a mixture of 80 mol. % alone it splits into two sharp but much less intense lines 3054 and 3070. At 90% again only 3054 cm.^{-1} line is present although quite faint.

4. *C-C oscillation 894 cm.^{-1} of acetic acid.*—This has in the pure acid a very faint component, detectable only with very long exposures which remains unaltered in mixtures of 20 and 30% concentration. But at 60% and 80% this component is much more intense and is almost of the same intensity as the 894 line. At 90%, once again it becomes very faint, as in the pure acid.

5. *C = O frequency of the acid.*—In the pure acid, three lines of frequency 1670, 1707 and 1750 are observed in this region. The first line is relatively strong and slightly broad, while the latter two are extremely feeble. At 80% concentration 1670 becomes very weak, while 1707 and 1750 become more intense than the former. The author has not been able to record these lines with sufficient intensity at other concentrations for want of longer exposures and as such the changes could not be observed continuously from 20% onwards. But as the results listed above show the alterations in the spectra to be most evident at 80% it is assumed that, that should be the case here as well.

4. DISCUSSION

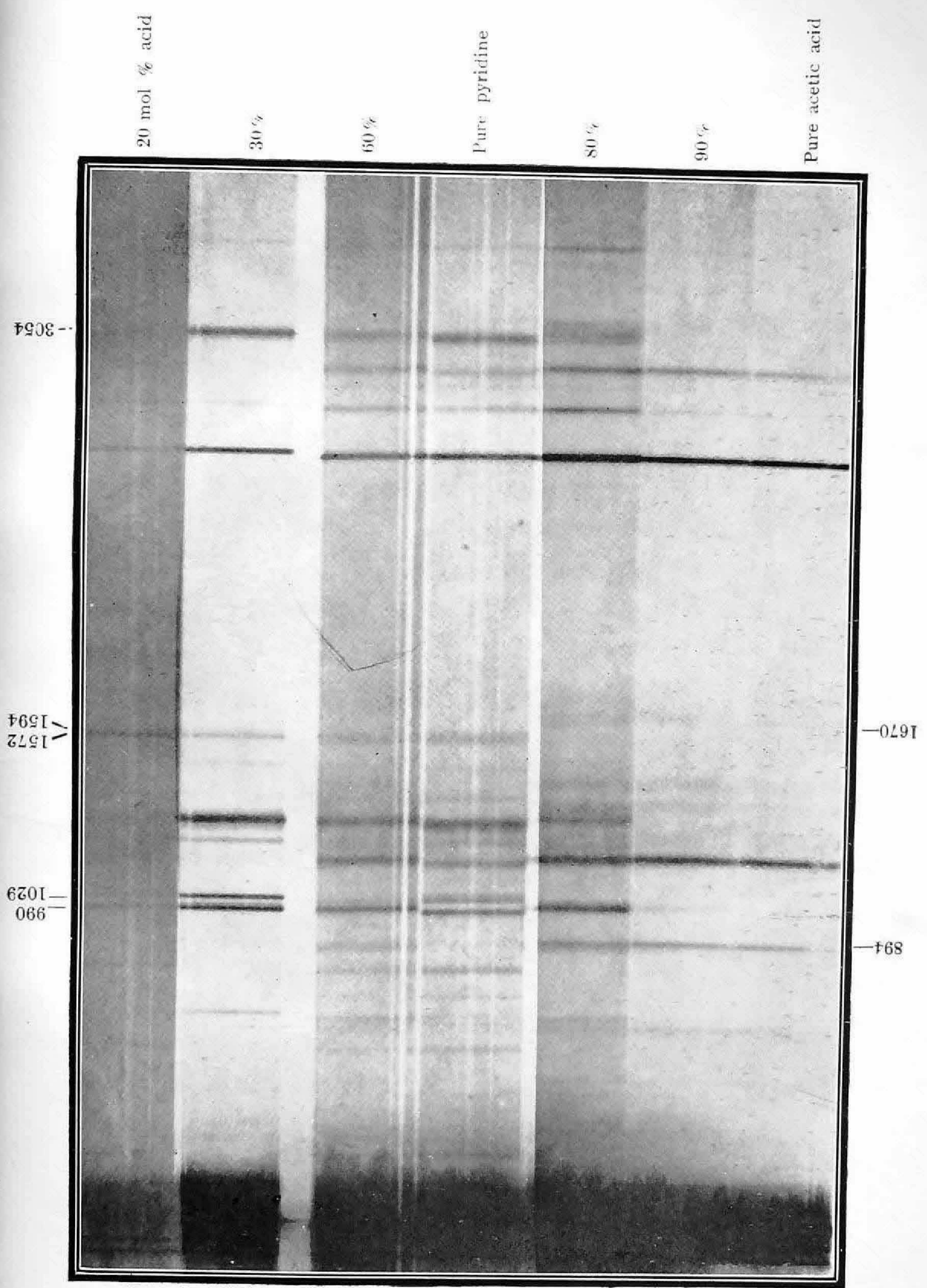
According to Raoult's law, the isothermal relation between the total vapour pressure of solutions of two liquid components and the molar composition is linear. Such multicomponent systems are called solutions. But for certain other multicomponent systems the total vapour pressure curves either fall far below or rise far above the straight line position. That is, they show large negative or positive deviations respectively and such solutions are non-ideal solutions and pyridine-acetic acid mixture is a non-ideal one showing a negative deviation from Raoult's law. The negative deviations are explained by assuming that a compound is formed when the liquid components are dissolved in each other. So pyridine-acetic acid mixture should show evidence of a complex formation on the basis of this assumption. This means that the Raman spectrum of this mixture should be different if not entirely, at least in some respects from that of the components.

The observations recorded above show that changes in the Raman spectrum of the mixture are observable from 30% concentration onwards and are most conspicuous at 80 mol. % of the acid. The fact that there exists a concentration after which no further appreciable changes are observable suggests the formation of a complex, and the concentration gives the molecular formula of the complex as $4 \text{CH}_3 \text{COOH} - \text{C}_5\text{H}_5\text{N}$. This result falls in line with those obtained from vapour pressure, viscosity, density, electrical conductance and compressibility measurements. In addition, the present investigation gives the characteristic C—C frequency of the complex as 1006 cm.^{-1} . The mechanism of this complex formation seems to be that acetic acid, an associated liquid in the pure state, containing mostly dimers, splits up into monomers on mixing with pyridine. These monomers form complexes with the pyridine molecules, 4 molecules of the acid combining with a single molecule of pyridine.

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