RAMAN SPECTRA STUDIES.[1] II. THE RELATIVE INTENSITIES OF CHARACTERISTIC LINES IN RAMAN SPECTRA OF BENZENE–TOLUENE MIXTURES

BY ELIZABETH A. CRIGLER

Introduction

Shortly after the discovery of the Raman effect, Daure[2] pointed out that the Raman spectrum of a mixture of benzene and toluene was the superposition of the spectra of the individual components. Dadieu and Kohlrausch[3] studied the Raman spectra of fifteen binary liquids and found no change in the characteristic frequencies of the components, except in a few cases where a slight shift occurred in a Raman line associated with a group having a high dipole moment.

Since the intensities of Raman lines produced under a given set of conditions depend upon the molecular density, it seemed probable that Raman spectra should prove useful not only for indicating the quality, but also for estimating the quantity, of substances present in mixtures. As previously noted[4] the Raman spectra of benzene–toluene mixtures of varying concentrations were photographed, the intensities of the lines recorded, and the relative heights of the intensity curves compared with the corresponding concentrations of the components taken. Benzene and toluene were chosen for this investigation, primarily because these substances furnish excellent Raman lines for intensity study; also, because they belong to a class of compounds commonly occurring in fractions of light oil mixtures.

In photographing Raman spectra for intensity measurements several factors which condition the density of spectral lines were considered. Experiments of Read and Johnson[5] show that the blackening produced on a photographic plate is a function of the intensity of light producing the blackening, the time of exposure, the wave length of light, the kind and age of the plate, and the conditions under which the plate is developed. Obviously, optimum results for the comparison study of Raman lines necessitated control of these variables. A method was adopted, therefore, by which as many conditions as possible could be maintained constant.

Apparatus.—The mercury arc was a Hanovia Advanced Research

[1] From the dissertation submitted by Elizabeth A. Crigler to the Faculty of Philosophy, The Johns Hopkins University, in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] Daure, *Compt. rend.*, **186**, 1833 (1928).

[3] Dadieu and Kohlrausch, *Physik. Z.*, **31**, 514 (1930).

[4] Crigler, *Phys. Rev.*, **38**, 1387 (1931).

[5] Read and Johnson, *Phil. Mag.*, **11**, 1152 (1931).

Model. This type, encased with a cooling coil and aluminum reflector and connected with a variable resistance, produced a steady light source for intensity work. The Raman tube was the same as used in Part I. Both the arc and Raman tube were cooled by a small electric fan. A Bausch and Lomb glass prism spectroscope analyzed the scattered light.

A Moll densitometer was used for recording the intensity of the Raman lines. The lines of each spectrum were focused on the face of the thermocouple tube and, as they passed between the light source and the slit of the tube, the intensity of the light falling on the thermocouple varied with the density of the intervening lines. The thermocouple was connected to a galvanometer, and every time a Raman line intercepted the light falling on the thermocouple the mirror of the galvanometer was deflected. This deflection was recorded by a narrow beam of light reflected from the mirror to photographic paper which was mounted on a revolving drum. The drum, in gear with the holder carrying the Raman plate, was run by an electric motor.
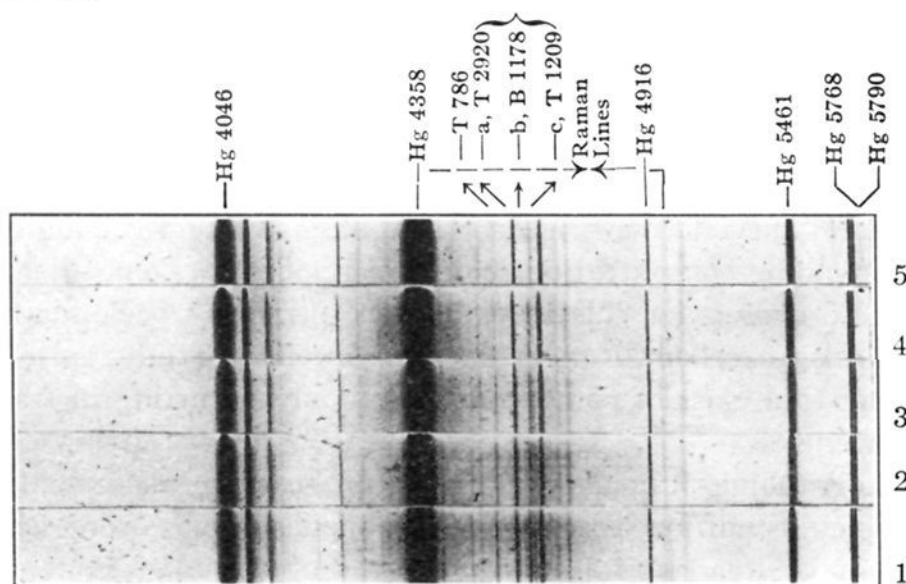

Plate I.—% Benzene–toluene: 1, B 0, T 100; 2, B 25, T 75; 3, B 50, T 50; 4, B 75, T 25; 5, B 100, T 0.

Materials.—Freshly distilled samples of Baker's c. p. benzene, specific gravity 0.88, and Baker's c. p. toluene, specific gravity 0.87, were used in making all mixtures.

The same kinds of photographic materials were used for this work as were used in Part I. Eastman's P. M. C. bromide paper, No. 2, smooth, was used in the densitometer for photographing the intensity curves.

Adjustment and collimation of the spectroscope were first secured. After the metal pieces forming the slit were carefully polished, and placed parallel to ensure spectral lines of uniform width, the spectroscope was leveled and the collimator and camera adjusted so that when the mercury

arc was placed in front of the spectroscope a horizontal spectrum of mercury lines was projected on the ground glass plate of the camera. The Raman tube, firmly supported by an iron clamp, was brought in line with the collimator by focusing an image of the tube in the center of the spectroscopic field. The light from the mercury arc was reflected back and forth through the liquid by a tin-foil reflector. The face of the Raman tube was almost tangent to the end of the spectroscope. This arrangement prevented stray light from entering the slit. The proximity of the tube to the spectroscope increased the intensity of the incident light.

After alignment of the apparatus, all parts except the Raman tube were left intact for each series of photographs made. In changing the material in the tube it was found more convenient to leave the tube clamped to the ring stand and to move the stand and Raman tube as a unit. In this way, each time the tube was emptied and refilled, it could readily be placed in the original position by adjusting the position of the stand. Shadows of the Raman tube formed on the box of the mercury arc and reflections from the uneven edges of the Raman tube face served as excellent reference marks for adjusting and replacing the tube.

The voltage across the mercury arc was regulated by a rheostat in series with the arc, and did not vary more than one or two volts during any exposure.

After the apparatus was in line with the spectroscope and the voltage across the arc carefully regulated, the width of the slit and time of exposure were varied alternately until a combination of the two yielded spectra showing marked and measurable variations with small changes in concentration. With two-hour exposures the best results were procured when the mercury arc was maintained at 50 volts, the temperature of the Raman tube was kept at 35°, and the width of the slit was 0.07 mm.

All plates were developed under the same conditions. The solutions used in developing and in fixing the image and the water used for washing the plates were kept at 0° by immersing the developing trays in an ice-bath. Each plate was developed for ten minutes in 100 cc. of Rhodinal solution, 1 to 20 dilution, then rinsed in ice
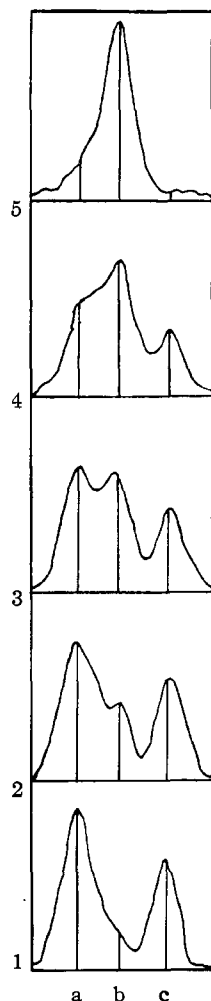

Fig. 1.—Section of photometric curve. % Benzene–toluene: 1, B 0, T 100; 2, B 25, T 75; 3, B 50, T 50; 4, B 75, T 25; 5, B 100, T 0. $\Delta\nu$ Raman line: a, T 2920 [Hg 4046]; b, B 1178 [Hg 4358]; c, T 1209 [Hg 4358].

water and fixed in a solution of Eastman's hypo for ten minutes. Care was taken to wash the plate free from the salt left by the hypo solution.
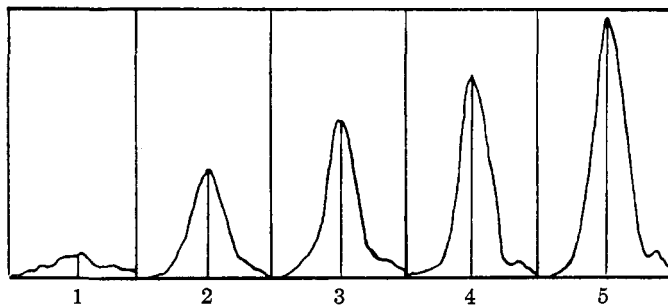

Fig. 2.—Intensity curve of toluene line $\Delta\nu$ 786. % Benzene–toluene: 1, B 100, T 0; 2, B 75, T 25; 3, B 50, T 50; 4, B 25, T 75; 5, B 0, T 100.

The trays in which the plate was developed were agitated to keep the solution constantly washing the gelatin surface in order to leave an even film on the glass. Plates treated in this manner and carefully dried showed a uniform, fine-grained background, with well-developed lines suitable for photometric measurements.
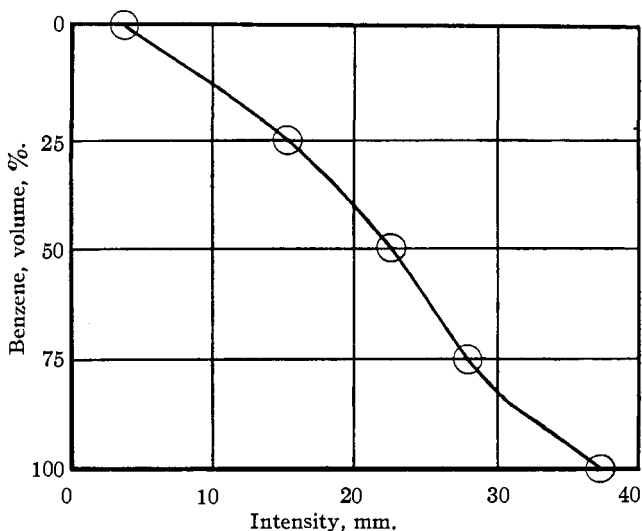

Fig. 3.—Relative intensity of characteristic benzene line [$\Delta\nu$ = 1158] with change in concentration.

In measuring the relative heights of the Raman lines the same horizontal section of each spectrum was chosen for each series of photographs in order that any gradation or imperfection in one spectrum, due to experimental conditions, would be recorded for every spectrum.

Halation around the stronger mercury lines and a slight continuous background prevented the use of a single standard line for measuring all of the Raman lines. Instead, a line for each group of Raman lines was chosen, and this same line used as reference throughout a series of measurements.
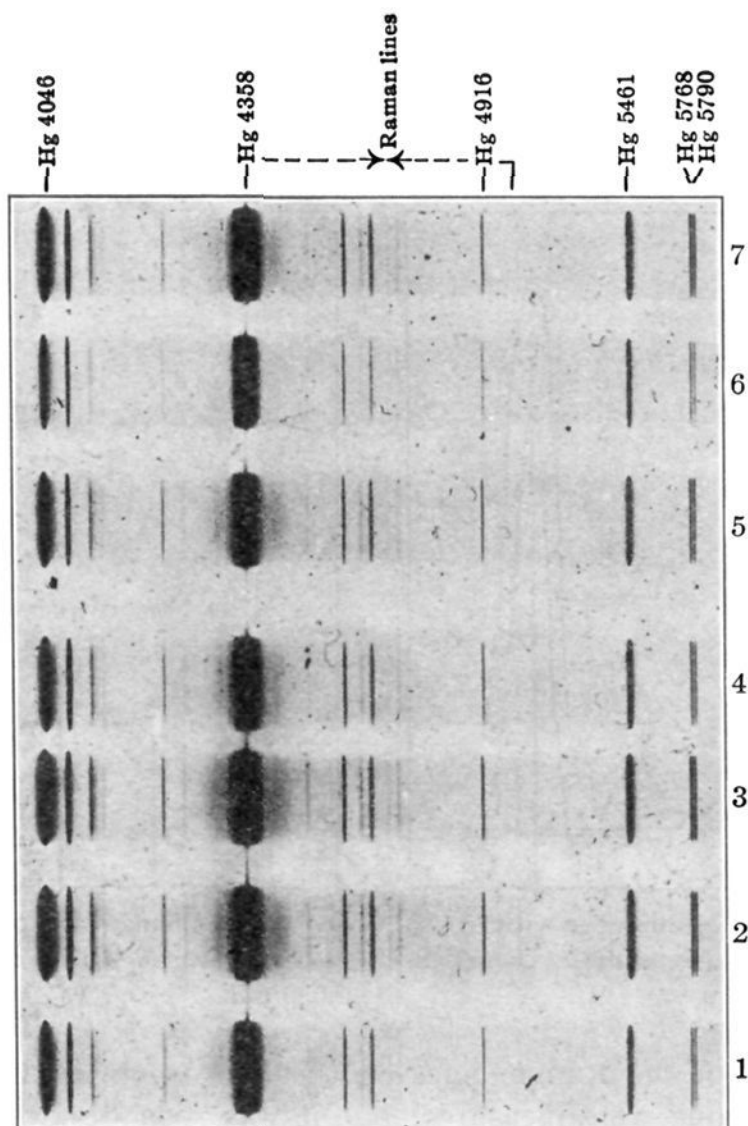

Plate II.—Variation of slit and exposure: 1, [−2]— 1 hr.; 2, [−2]—2 hrs.; 3, [−4]—2 hrs.; 4, [−4]—1 hr.; 5, [+2]—2 hrs.; 6, [+2]—1 hr.; 7, [−7]—1 hr.

Good intensity measurements seemed to depend largely upon the nature of the photographs and the technique of using the densitometer. After spectra of sharp contrast and uniform background were obtained it was necessary, due to the sensitivity of the densitometer, to duplicate the photometric curves before making final intensity measurements. Raman photographs were duplicated which gave photometric curves in which the height of the most intense lines varied less than 1 mm. Likewise,

duplicate intensity curves of the same photograph showed less than a 0.5 mm. change for any Raman line.

Results

Photographs of the first Raman spectra of mixtures of 25% variation in concentration are reproduced in Plate I where the appearance, disappearance, and the change in density of certain Raman lines can be observed. Further evidence of these intensity changes is shown by the photometric curves in Figs. 1 and 2 and by the intensity curves plotted in Fig. 3.
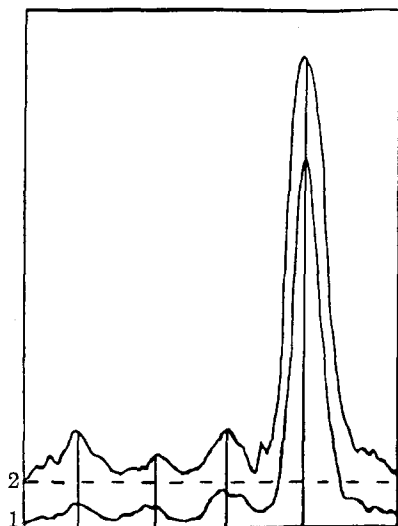

Fig. 4.—Change of curve with length of exposure: 1, exposure, 1 hour; 2, exposure, 2 hours.
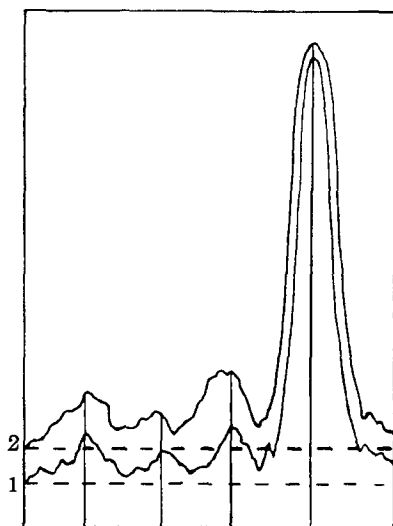
Fig. 5.—Change of curve with width of slit: 1, slit, 0.071 mm.; 2, slit, 0.089 mm.

At first, all of the Raman lines on the long wave length side of the 4358 mercury line were measured, but it was soon discovered that the group of Raman lines in the region between 600 and 1000 cm.$^{-1}$ exhibited the greatest variations in intensity with change in concentration. The work, therefore, was devoted to measuring and comparing lines falling within this particular region.

The fact that the first results did not show measurable differences for small changes in concentration suggested improvement in technique. The importance of finding a favorable combination of slit and exposure, in photographing Raman spectra for intensity study, is strikingly brought out in the gradations shown in the spectra of Plate II and in the photometric curves of Figs. 4 and 5. From these illustrations it is evident that a narrow slit with long exposure is preferable to a wide slit with short

exposure. Spectrum (5) in Plate II proved the most satisfactory type for the present work.
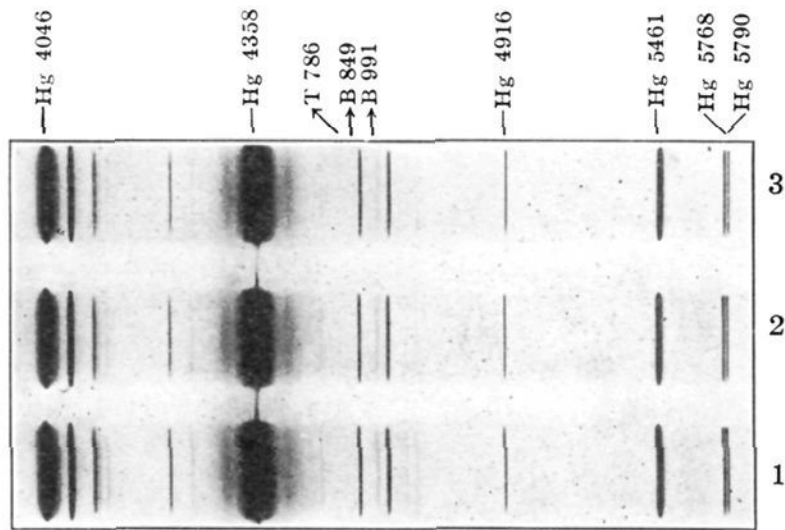

Plate III.—% Benzene–toluene: 1, B 95, T 5; 2, B 90, T 10; 3, B 85, T 15.
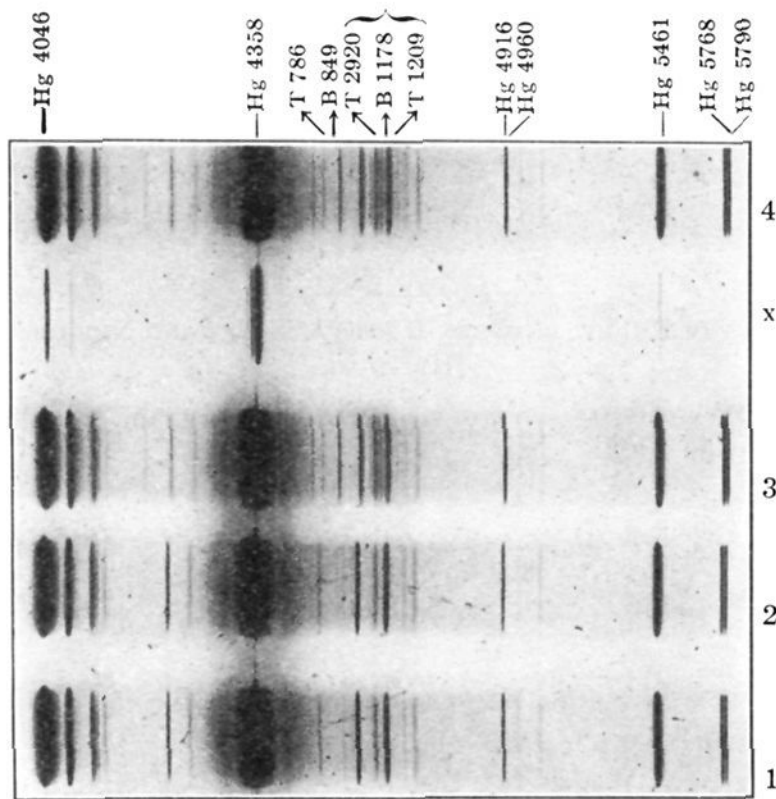

Plate IV.—% Benzene–toluene: 1, B 95, T 5; 2, B 95 T 5; 3, B 0, T 100; 4, B 5, T 95; x, Hg lines.

Plates III and IV, Figs. 6 and 7, and Tables II, III and IV give results obtained under the optimum conditions and show that 5% changes in concentration are easily measurable.

TABLE I
RELATIVE INTENSITY OF RAMAN LINES FOR 25% CHANGE IN CONCENTRATION OF BENZENE-TOLUENE

Exciting mercury line		4358		4046		4358		4358	
Raman line		T 786		T 2920		B 1178		T 1209	
% (vol.) B-T	Mole, % B-T	ΔI		ΔI		ΔI		ΔI	
100-0	100-0	2.7		8.5		37.2		1.5	
			17.2		10.2		9.0		11.7
75-25	78-22	19.9		18.7		28.2		13.2	
			7.1		6.9		5.6		2.1
50-50	54-46	27.0		25.6		22.6		15.3	
			8.2		2.2		7.5		3.7
25-75	28-72	35.2		27.8		15.1		19.0	
			10.5		4.4		11.4		3.6
0-100	0-100	45.7		32.2		3.7		22.6	

TABLE II
RELATIVE INTENSITY OF RAMAN LINES [HT. IN MM.]

Exciting mercury line	4358		4358		4347		4358	
Raman line	T 786		B 849		B 991		B 991	
% (vol.) B-T	ΔI		ΔI		ΔI		ΔI	
95- 5	6.3		10.1		13.0		92.7	
		1.5		1.1		2.0		1.6
90-10	7.8		9.0		11.0		91.1	
		1.2		1.2		1.0		0.5
85-15	9.0		7.8		10.0		90.6	

TABLE III
DIFFERENCES IN HEIGHT BETWEEN B 991 [4358 Hg] AND NEIGHBORING LINES [HT. IN MM.]

Exciting mercury line	4358		4358		4347	
Raman line	T 786		B 849		B 991	
% (vol.) B-T	ΔI		ΔI		ΔI	
95-5	85.2		81.7		78.5	
		2.9		0.3		0.7
90-10	82.3		82.0		79.2	
		2.0		0.3		0.7
85-15	80.3		82.3		80.5	

TABLE IV
RELATIVE INTENSITY OF RAMAN LINES [HT. IN MM.]

Exciting mercury line	4358		4358		4046		4358		4358	
Raman line	T 786		B 849		T 2920		B 1178		T 1209	
% (vol.) B-T	ΔI		ΔI		ΔI		ΔI		ΔI	
0-100	31.2		54.0		39.0		11.7		23.2	
		3.7		3.5		3.7		4.8		0.7
5-95	27.5		50.5		35.3		16.5		27.5	

Discussion

As can be seen in the spectra photographed, the complete mercury spectrum was used in producing Raman lines for intensity measurements. In the section chosen for study the Raman lines were excited by the mercury lines λ4046, λ4339, λ4347 and λ4358. There was an advantage in using the high frequency Raman lines excited by the 4046 mercury line, as they were more intense than the corresponding lines excited by the 4358 mercury line. In the case of high frequency Raman lines the intensity increases with the frequency of the exciting line much more rapidly than the fourth power law.[6]

A study of Raman spectra and of intensity values shows that the Raman line at 786 cm.$^{-1}$ is by far the best indicator for toluene. This characteristic toluene line was perceptible in the spectrum of a mixture containing 5% toluene obtained after only one hour of exposure. However, short exposures necessitating a fairly wide slit are not suitable for intensity comparisons.

Fig. 6.—Section of photometric curve. % Benzene–toluene: 1, B 85, T 15; 2, B 90, T 10; 3, B 95, T 5. Δν Raman line: a, T 786 [Hg 4358]; b, B 849 [Hg 4358]; c, B 991 [Hg 4339]; d, B 991 [Hg 4347]; e, B 991 [Hg 4358].

The concentration of benzene in a mixture can be estimated from the intensity of either the 849 cm.$^{-1}$ frequency or the 991 cm.$^{-1}$ frequency, both strong Raman lines of benzene. It is interesting to note that the weak 4347 mercury line excites a Raman line at 991 cm.$^{-1}$ which apparently gives with the densitometer greater intensity variation with small changes in concentration than the same line excited by the strong 4358 mercury line.

In the case of benzene–toluene mixtures the toluene line at 1002 cm.$^{-1}$ might be expected to interfere somewhat with the actual height and contour of the benzene line at 991 cm.$^{-1}$. Although the shape of the curve for this line is slightly changed and the peak of the curve shifted with increase in toluene, it invariably decreases in height with decrease in the concentration of benzene.

Table III shows a method for measuring the intensities in terms of the differences in height between a given Raman line, chosen as standard,
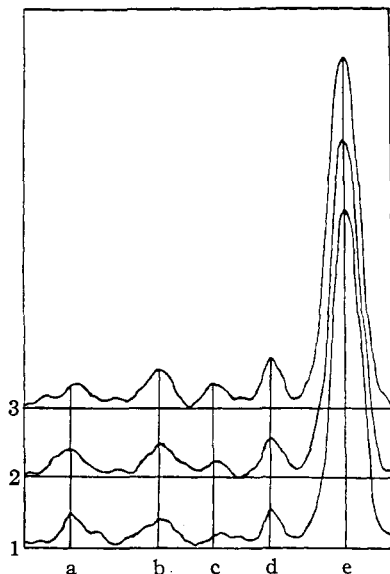
[6] Sirkar, *Indian J. Physics,* **5,** 593 (1930).

and each neighboring Raman line. Perhaps this method is less subject to error than the more direct method of measuring relative heights, because in using the differences between the peaks of lines the arbitrary choice of a reference line is eliminated. Since measurements of this kind show a difference of 50 mm. from the top of a strong toluene line in 100% toluene to the top of a strong benzene line in 100% benzene, surely much less than 5% change in concentration should be detectable from intensity measurements.
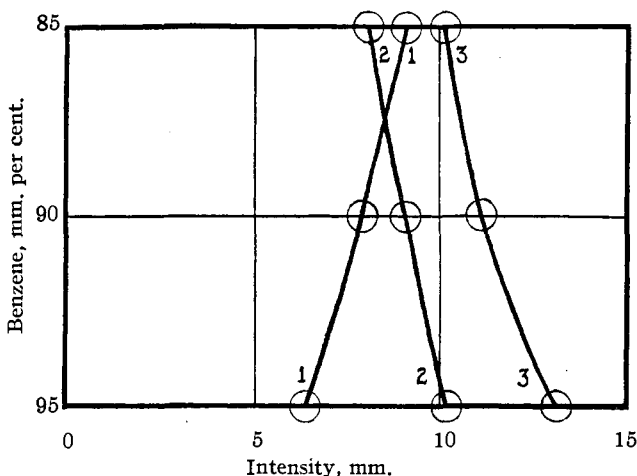

Fig. 7.—Relative intensity of Raman lines in benzene–toluene mixtures: 1, T 786; 2, B 849; 3, B 991.

The relative intensities of Raman lines, which depend upon molecular density,[7] intensity and frequency of the exciting line,[6] and experimental conditions under which the lines are produced,[8] offer excellent opportunity and possibility for investigating the nature and determining the composition of mixtures and solutions. Recently the sensitivity of Raman lines in testing for the presence of the double bond has been reported to be as high as 1.2–2.4%.[9]

The author wishes to express her appreciation to Professor D. H. Andrews for his many helpful suggestions.

Summary

By means of a simple experimental procedure, measurements of the relative intensities of characteristic Raman lines of benzene–toluene mixtures were obtained which show with 5% change in the concentration

[7] Cabannes and Daure, *Compt. rend.*, **186**, 1533 (1928).

[8] Merton and Nicholson, *Phil. Trans.*, **A217**, 237 (1918); Read and Johnson, *Phil. Mag.*, **11**, 1152 (1931).

[9] Lespieau, Bourquel and Wakeman, *Compt. rend.*, **193**, 238 (1931).

of either benzene or toluene a change of several millimeters in the height of the photometric curve.

BALTIMORE, MARYLAND

[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE UNIVERSITY OF NEBRASKA]

A STUDY OF SOLUTIONS OF ETHYL ALCOHOL IN CYCLOHEXANE, IN WATER, AND IN CYCLOHEXANE AND WATER

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The results of a previous investigation[1] have indicated some of the problems involved in a study of ternary solubilities and the distribution of ethyl alcohol between water and a hydrocarbon. In the previous work it was found that ethyl alcohol is monomolecular in water solutions and associated in benzene solutions according to freezing point data. On the other hand, according to distribution experiments it was found to have the same molecular form in both solutions. As a step toward the solution of similar problems this investigation was undertaken, substituting cyclohexane for benzene.

Materials

Ethyl Alcohol.—A standard commercial grade of absolute alcohol was refluxed over freshly burned lime and distilled from an all-glass apparatus until density determinations showed it to be 99.91% alcohol.[2]

Cyclohexane.—The best grade of cyclohexane obtainable from the Eastman Kodak Co. was further purified by alternate fractional crystallizations and distillations. Finally, it was dried over sodium and distilled from an all-glass apparatus. The final product had a density of 0.77379 g. per ml. and a freezing point of 6.20°. Several fractions of lower freezing point were obtained which were later found to give the same results as the better grade in solubility determinations.

Water.—Laboratory distilled water was redistilled from potassium permanganate in a tinned boiler provided with a block tin condenser. The specific conductance of the distillate at 25° was 2.51×10^{-6} mhos.

Ternary Solubilities and the Distribution of Ethyl Alcohol between Water and Cyclohexane.

—The distribution of alcohol between water and cyclohexane was determined by a procedure similar to that of other investigators of such systems.[3,4,5,1] Definite amounts of cyclohexane and alcohol were weighed into 100-cc. glass-stoppered Erlenmeyer flasks on an analytical balance. The flasks were suspended in a hand-operated bath maintained at 24.8° and water added from a weight pipet until phase

[1] Washburn, Hnizda and Vold, THIS JOURNAL, 53, 3237 (1931).

[2] "International Critical Tables," The McGraw Hill Book Co., New York, 1929, Vol. III, p. 116.

[3] Taylor, J. Phys. Chem., 1, 461 (1897).

[4] Barbaudy, Rec. trav. chim., 45, 207 (1925).

[5] Hand, J. Phys. Chem., 34, 1961 (1930).