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Compound	Frequencies of absorption regions in cm. $^{-1}$														
2-Monosubstd.	1377	1299-	$1225^{a}$		1146-		1050-	_		995ª			743-		
	1383	1311			1152		1052						750		
3-Monosubstd.	1377-	1312-	1239-	1180-	1117-				1021-			789-			712-
	1383	1318	1253	1196	1131				1034			810			715
4-Monosubstd.	1377-	1299-	1222-			1067-				995-		785-			
	1383	1311	1253			1072				1000		822			
Disubstd.	1377-	1300-	1226 -		1099-				$1028^{b}$	988-	816-			725-	
	1383	1330	1250		1136					998°	833			743	
Trisubstd.	1377	1280 -	1222 -					1032-		996-				724 -	
	1383	1330	1231					1040		1001				732	

TABLE II

1400-650 Cm.  $^{-1}$  Infrared Absorption Peaks of Pyridines

<sup>a</sup> The position of this band was constant; hence, no range is given. <sup>b</sup> Present only in spectra of 2,5-disubstituted pyridines.

4-monosubstituted compounds the band appeared at 785–822 cm.<sup>-1</sup>. The disubstituted pyridines showed two such bands in the 650–1000 cm.<sup>-1</sup> region. These occurred at 816–833 cm.<sup>-1</sup> and 725– 743 cm.<sup>-1</sup>. The trisubstituted compounds examined had only one strong peak (725–732 cm.<sup>-1</sup>) in the low-frequency region. In each instance the out-of-plane vibration bands were the strongest observed in the 650–1000 cm.<sup>-1</sup> region.

#### Summary and Conclusions

Peaks near 1600, 1570 and 1000 cm.<sup>-1</sup> are characteristic of an alkyl-pyridine system. In 3alkylpyridines and 2,5-dialkylpyridines the 1000 cm.<sup>-1</sup> peak is removed to 1021–1034 cm.<sup>-1</sup>. Peaks in the regions 1280–1330 cm.<sup>-1</sup> and 1222–1253 cm.<sup>-1</sup> are strong confirmatory evidence of the presence of an alkylpyridine.

The separation of the two peaks near 1600 and 1570 cm.<sup>-1</sup> is approximately 40 cm.<sup>-1</sup> for 4-monoalkylpyridines. This distinguishes the 4-monoalkylpyridines from the other monosubstituted pyridines; in these spectra the two peaks are separated by only 20 cm.<sup>-1</sup>.

In the region 1050–1200 cm.<sup>-1</sup> peaks at 1050 cm.<sup>-1</sup> and at 1146–1152 cm.<sup>-1</sup> characterize 2monoalkylpyridines; peaks at 1117–1131 cm.<sup>-1</sup> and 1180–1196 cm.<sup>-1</sup> indicate 3-monoalkylpyridines; and a peak at 1067–1072 cm.<sup>-1</sup> indicates 4-monosubstitution. All the disubstituted pyridines examined have peaks in the 1099–1136 cm.<sup>-1</sup> region. This overlaps the vibration of 3-monoalkylpyridines. The distinction between these two types would have to be made from other regions of the spectrum. As no correlations were made in this region for trisubstituted pyridines, the characterization of these must also be made from other spectral regions.

Out-of-plane deformation vibrations for 2-monoalkylpyridines were found in the region 743-750 cm.<sup>-1</sup>; for 3-monoalkylpyridines in the regions 789-810 cm.<sup>-1</sup> and 712-715 cm.<sup>-1</sup>; for 4-monoalkylpyridines in the region 785-822 cm.<sup>-1</sup>; for disubstituted pyridines in the regions 816-833 cm.<sup>-1</sup> and 725-743 cm.<sup>-1</sup>; and for trisubstituted pyridines in the region 724-732 cm.<sup>-1</sup>. The location and relative intensity of the peaks

The location and relative intensity of the peaks in the 1667–2080 cm.<sup>-1</sup> region are characteristic of position of substitution for monoalkylpyridines. Changes in size and branching of the substituent group have little effect on the over-all appearance of the spectrum in this region. Assignments of typical substitution patterns for some disubstituted compounds are included. These may need modification as additional compounds of the types become available.

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## INTERFACIAL TENSION AND COMPLEX FORMATION

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The interfacial tension method, proposed by Kazi and Desai for the study of complex formation in aqueous solution, has been examined critically and the effect of experimental variables on the results determined. The drop volume technique originally proposed was found to give results which were too erratic and unreliable to allow correlation with solution composition. Measurement of interfacial tension by the ring method, which was found to be much more accurate, showed no evidence of changes in interfacial tension due to complex formation alone.

During the last few years several workers have reported, in a long series of articles,<sup>1-4</sup> studies on

 H. J. Kazi and C. M. Desai, J. Indian Chem. Soc., **30**, 287, 290, 291, 421, 423, 424, 426, 872, 873 (1953);
 **31**, 163, 165, 329, 331, 332, 415, 416, 418, 633, 636, 638, 640, 769 (1954); Science and Culture, **19**, 259 (1953). complex formation in aqueous salt solutions carried out by measurement of the interfacial tension between the solutions and organic liquids "having

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(3) C. M. Desai, ibid., 31, 957 (1954).

(4) H. V. Barat and C. M. Desai, ibid., 32, 61 (1955).

April, 1957

an unstable H-bond ring structure." According to these workers, mixtures of salts corresponding to stoichiometric compound or complex formation showed strikingly higher interfacial tension against liquids such as n-butyl acetate than did similar mixtures which did not correspond to stoichiometric ratios. A typical set of their results is shown in the lower curve of Fig. 1. The observed effect persisted even in very dilute solutions and it was claimed in many instances that a larger number of complexes was formed in dilute (e.g., 0.01 M) than in relatively more concentrated (0.5 M) solutions. The effects reported were large, sometimes as much as 3 dynes/cm. between peak and trough, and about the same for nearly all systems studied. Usually more complexes were reported for a given system than had been found by other workers using wellestablished potentiometric and spectrophotometric methods. From a study of the published results, it was evident that either the interfacial tension method must be a remarkable tool of hitherto unsuspected sensitivity, or it must be a trap for the unwary. In order to determine which, we have undertaken to repeat and extend some of the studies reported by previous workers, concentrating on systems the characteristics of which had also been well worked out by other investigators using established methods.

#### Experimental

The first measurements of interfacial tension were made using the "drop volume" method as described by Kazi and Desai<sup>s</sup> and duplicating their technique as closely as possible. A Gilmont microburet was used to discharge and measure the drops of organic liquid. Tips of both glass and stainless steel were used to form the drops, with no significant differences being observed. Later experiments were performed by the ring method utilizing a du Noüy interfacial tensiometer as marketed by Central Scientific Company of Chicago, Illinois, under their catalog No. 70545. Measurements were performed in a constant temperature room at 23°, although it was observed that small temperature changes had very little effect.

Reagents and chemicals used were the best quality commercially available. Distilled, deionized water was used throughout. In order to avoid chance contamination by detergents or other surface-active agents, all glassware was cleaned with hot nitric-sulfuric acid and washed with distilled water.

#### **Results and Discussion**

Several systems, of which the one involving mercuric and potassium chlorides is typical, were investigated following the procedure of Kazi and Desai. It was immediately observed that although satisfactory agreement could be obtained between successive observations of the volume of ten drops of *n*-butyl acetate delivered from the tip as long as the tip and solution remained undisturbed, emptying and refilling the apparatus often resulted in considerable changes in the apparent interfacial tension. Figure 2 shows the results of three independent runs made with the mercuric chloridepotassium chloride system, all supposedly identical.

In these runs the standard deviation of the measurements as estimated from the agreement between duplicate measurements made in immediate succession without any alteration or disturbance in experimental conditions, was 0.20 dyne/cm., based on 59 separate samples. On this basis, a

(5) H. J. Kazi and C. M. Desai, J. Indian Chem. Soc., 30, 209 (1953).



Fig. 1.—Interfacial tension between n-butyl acetate and mixtures of mercuric bromide and sodium bromide: upper curve, data of this investigation obtained by ring method, lower curve, data of Kazi and Desai.<sup>1</sup>



Fig. 2.—Interfacial tension between n-butyl acetate and mercuric chloride-potassium chloride mixtures, determined by the drop-volume method. Three separate runs are shown. The arrows correspond to the positions of peaks reported by previous workers.

difference of 0.56 dyne/cm. between two single observations would be statistically significant at the conventional 5% level. This, however, is not a valid way of estimating experimental error, inasmuch as it is always necessary in the actual experiments to compare results obtained on different solutions. Accordingly, the precision of the measurements was estimated by comparison of measurements on sets of identical replicate solutions. Here, the standard deviation was found to be 1.70 dynes/cm., based on 20 sets of triplicate samples. In order, then, to attribute statistical significance to a difference between two samples, the observed difference between them would have to be 4.8 dynes/cm. or more. Such differences were not observed in our work. The differences between solutions of different compositions were no greater than the differences between solutions of the same composition. Other systems investigated, including the lead nitrate-potassium nitrate and mercuric bromide-sodium bromide pairs, gave similar results. The range of values obtained in the present investigation was about the same as that previously reported.

It was noted that the drop volume, and therefore the apparent interfacial tension, was sensitive to small differences in the rate of delivery of the organic liquid through the capillary tip. When solutions of known composition were being used, an unconscious tendency on the part of the operator to measure stoichiometric mixtures with greater care than solutions of less significance resulted in the occasional appearance of small peaks at stoichiometric compositions. When the samples were prepared by another person and run in random order under a blind code, these regularities disappeared and a random distribution of drop volumes with solution composition was obtained as in Fig. 2.

Although this result seemed clear-cut, we were far from satisfied, because as already indicated the precision of the drop-volume method was in our hands, rather low. The reproducibility was often not better than about  $\pm 0.5$  dyne/cm., and quite a number of the peaks shown in the literature are of that order of magnitude. Experimentation with various sizes, shapes and materials for the tips used and methods of manipulation led us to conclude that a significant increase in precision could only be achieved by a major effort in apparatus building, and this did not seem justified in view of the fact that the Indian workers had obtained their results apparently without difficulty using quite simple equipment. Room temperature changes were shown to be almost without effect. In an effort to get more reproducible data, we abandoned the drop-volume method and carried on the rest of the work with a du Nouv tensiometer. This instrument utilizes the well-known ring method of measuring surface tension and is adaptable both to ordinary surface tension and to interfacial tension measurements. In addition to being faster and more convenient than the drop-volume apparatus, it was found in our hands to be far more reproducible. For both surface tension and interfacial tension measurements, a precision of  $\pm 0.05$ dyne/cm. was obtained in regular use, in good agreement with the manufacturer's claims. The systems previously studied by the drop-volume method were then re-examined using the new apparatus. In the mercuric chloride-potassium chloride system, detailed examination of the region in the immediate vicinity of the alleged HgCl4= peak, using solutions of composition known to the investigator, showed at the most a difference of 0.2



Fig. 3.—Interfacial tension between *n*-butyl acetate and 12.0 ml. of 0.025 M mercuric nitrate during titration with 0.30 M potassium iodide.

dyne/cm. between the stoichiometric mixture and the lowest parts of the curve. Other experiments over a wide range of compositions and using solutions of composition unknown to the investigator showed no detectable differences between stoichiometric solutions and solutions of other compositions. A typical result is given in Fig. 1 in which the results of this investigation are compared with those of Kazi and Desai for the 80/M mercuric bromide-sodium bromide system. Our 36 observations showed no peaks whatever, and all the points lay within  $\pm 0.05$  dyne/cm. of the average value of 14.95 dynes/cm. Similar results were obtained with the mercuric chloride-potassium chloride system, although the scatter of points was a little greater. Control runs in which concentrations of potassium chloride alone and mercuric chloride alone were measured against nbutyl acetate showed only a slight trend of interfacial tension with concentration.

Potentiometric studies by a number of workers had indicated that although some complex formation between mercuric and potassium chlorides or bromides does take place, changes in physical properties of the solutions might not be great when dilute solutions were mixed. The ions  $HgX_3$ and  $HgX_4^-$  are much less stable, relatively speak-ing, than the un-ionized  $HgX_2$ .<sup>6</sup> To give the interfacial tension method a greater chance of success, we used it to follow the addition of the first two chlorides to the mercuric ion by studying mixtures of mercuric nitrate and potassium chloride. This is a quantitative reaction which is used for analytical purposes and which gives a very striking endpoint break in the potentiometric titration curve. Almost no effect was detected at the stoichiometric point, although a very slight rise just on the borderline of statistical significance could be seen.

It was reasoned that more definite results might be obtained using iodide ions, inasmuch as the capillary activity of iodide is greater than that of chloride or bromide. Addition of potassium iodide to water produced a small but definite drop in the interfacial tension. Mercuric nitrate was then titrated with potassium iodide and a very large drop (2 dynes/cm.) was indeed found at the stoichiometric point of HgI2 (Fig. 3). This, however, was not a clear-cut case of detection of complex formation; for, as is well known, HgI<sub>4</sub><sup>-</sup> forms im-mediately on addition of iodide and HgHgI<sub>4</sub> is precipitated. After the stoichiometric point, the red precipitate begins to dissolve, forming yellow HgI<sub>4</sub><sup>--</sup> ions, and it was observed that the yellow color of the complex was being extracted into the organic phase. This fact is, in itself, sufficient to explain the change in interfacial tension. Not even the titration of calcium ions with sodium palmitate gave a clear-cut end-point by interfacial tension measurements. A rapid drop in interfacial tension was observed at the beginning of the titration, and very little further change took place in the vicinity of the end-point.

Parallel with a number of the interfacial studies, measurements were made on the surface tension of the solutions using the ring method. The results

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were quite analogous and no evidence was found of the sharp drops at stoichiometric compositions which have been reported in surface tension *versus* composition curves by some previous workers.<sup>7-9</sup>

From all the evidence we have been able to gather, we can only conclude that within the pre-

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cision of our measurement, the interfacial tension of aqueous salt mixtures with liquids such as *n*butyl acetate does not assume peak values at stoichiometric compositions corresponding to complex formation, and that previous workers have been misled by unrecognized procedural bias and a failure to evaluate observed differences in terms of a validly estimated experimental error.

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# DILUTE SOLUTION MEASUREMENTS OF MOLAR KERR CONSTANTS OF SOME HALOBENZENES, MONOHALOBENZOTRIFLUORIDES AND BENZOTRIFLUORIDE<sup>1,2</sup>

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The Kerr constants of three halobenzenes, benzotrifluoride and nine monohalobenzotrifluorides were measured by a relative method in benzene at concentrations below 0.015 mole fraction of solute. In this range the Kerr constants were found to vary linearly with concentration. A method developed by Otterbein for calculating molar Kerr constants of disubstituted benzene derivatives has been modified by use of the Silberstein molecular model to include effects of possible interaction between substituents on the benzene ring. The molar Kerr constants calculated by this method are generally in better agreement with experimental values than those calculated by the Otterbein method without correction. The principal polarizabilities of all compounds studied were calculated from the Kerr constants and refractivity data on benzene and its monohalogen derivatives. The results for benzene and the monohalobenzenes agreed with the values reported by LeFèvre and LeFèvre, on the average, to within  $\pm 3\%$ .

Theoretical treatments of the Kerr effect relate the Kerr constant of a molecule to its polarizability and the components of the permanent dipole moment in the directions of the principal polarizabilities of the molecule. As shown mathematically by Langevin<sup>3</sup> and Born,<sup>4</sup> it is these quantities which determine the orientation of the molecule in an external electric field. The relation between the Kerr constant and the above mentioned molecular properties can be used, as Stuart<sup>5</sup> has pointed out in his excellent review article, to provide a considerable amount of information concerning molecular structure.

The objective of the present investigation was to learn how reliably the Kerr constant and polarizabilities of disubstituted benzene derivatives can be predicted by combination of appropriate properties of the corresponding monosubstituted benzenes. The compounds chosen for the study were benzotrifluoride,  $C_6H_5CF_3$ , the halobenzenes,  $C_6H_5X$ , and the monohalobenzotrifluorides,  $CF_3C_6H_4X$ , where X = F, Cl or Br.

Measurements were made in dilute solution since this offered a good compromise between the theoretically favorable gaseous state and the experimentally favorable pure liquid state. No sys-

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tematic observations of the Kerr constant have been reported on a well-defined series of compounds in the dilute concentration range (mole fraction  $\leq 0.015$ ) although many solution measurements on benzene derivatives have been reported by Briegleb,<sup>6</sup> Otterbein,<sup>7</sup> and others.<sup>8-11</sup>

#### Experimental

Materials.—Reagent-grade Jones and Laughlin benzene was refluxed overnight over sodium, then distilled twice over sodium through a 6-ft. Dufton column. The middle fraction boiling over a range of less than 0.02° was used. The benzene was recovered by essentially the same treatment.

Eastman Kodak Co. white label fluorobenzene, chlorobenzene and bromobenzene were shaken first with portions of cold concentrated sulfuric acid, then with dilute sodium bicarbonate solution, and finally with water. After storage for two days over anhydrous magnesium sulfate, the liquids were distilled, as were all the other substances studied through a 60-cm. jacketed column packed with glass helices. There were sufficient quantities of most materials to permit redistillation of the middle cuts obtained from the first fractionation.

Samples of benzotrifluoride and the three chlorobenzotrifluorides, obtained from the Hooker Electrochemical Company, were distilled without treatment.

The o-bromobenzotrifluoride and o-fluorobenzotrifluoride were prepared using the method of Jones.<sup>12</sup>

The m- and p-fluorobenzotrifluoride were synthesized by the method of Booth, Elsey and Burchfield.<sup>13</sup>

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<sup>(1)</sup> Presented before the Division of Physical and Inorganic Chemistry of the American Chemical Society at the 130th National Meeting, Atlantic City, September, 1956.

<sup>(2)</sup> Taken in part from a dissertation submitted by L. V. Cherry to the Graduate School of Duke University in partial fulfillment of the requirements for the degree of Doctor of Philosophy, June, 1953.

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