blue with sodium methylate, the latter a delicate amethyst. In both cases the color is deeper in the presence of furil, benzofuril or benzil. On the other hand, neither piperoin nor anisoin give any color with methylate; neither does piperil nor anisil intensify the color of benzoins that do give color, namely, benzoin, furoin and benzofuroin.

Simple sugars are similar to benzoin inasmuch as they have a carbonyl group adjacent to hydroxyl. Levulose, however, does not respond to the color test; neither does butyroin, $C_3H_7CHOHCOC_3H_7$, a typical aliphatic acyloin.

We compared the delicacy of the color test against that of the Fehling test. The smallest amount of benzoin capable of yielding a significant precipitate of cuprous oxide in an hour was 0.01 g. An immediate color change on simple heating required 0.02 g. to 0.05 g. This is a poor test when compared with the color reaction with sodium methylate, which gives an immediate and conclusive purple color with 0.0002 g. of benzoin. The extreme limit of the Fehling test is 0.005 g. of benzoin. At this dilution the mixture must stand for two hours or more and the indication which finally results is very doubtful.

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Summary

1. Various analogs of benzil can be prepared by iodine oxidation of alkaline solutions of the corresponding benzoins. A mechanism involving stilbenediolate is suggested.

2. The frequently described delicate color test with alcoholic alkali is shown to be applicable to certain benzoins but not to others. It is suggested that the color is indicative of trivalent carbon.

MIDDLEBURY, VERMONT

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF ORGANIC CHEMISTRY,
MASSACHUSETTS INSTITUTE OF TECHNOLOGY, No. 44]

THE REACTIVITY OF ATOMS AND GROUPS IN ORGANIC COMPOUNDS. IX. THE VAPOR PRESSURES, DENSITIES AND REFRACTIVE INDICES OF CERTAIN BINARY MIXTURES

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In the seventh paper of this series the velocity constants of the reaction at 25° between pyridine and ethyl iodide in a number of solvents were presented. The relative values of the constants, indicating the adjuvance of the solvents, were as follows.

TABLE I

VELOCITY CONSTANTS

Benzene	1	*n*-Propyl alcohol	1.11
Nitrobenzene	25	*n*-Butyl alcohol	1.11
Acetone	12.8	*Iso*propyl alcohol	1.07
Methyl alcohol	2.5	*Sec.*-butyl alcohol	1.00
Ethyl alcohol	1.4	*Tert.*-butyl alcohol	0.93

In view of the differences in chemical behavior shown by benzene, *n*-butyl alcohol and *tert.*-butyl alcohol, it was regarded as noteworthy that these compounds possessed nearly the same adjuvance. It has been suggested that adjuvance may be related more to physical forces set up between the molecules involved than to chemical attractions.

The present investigation was undertaken to test the validity of this hypothesis. If physical forces are the important factor, it seemed to us that a study of the physical properties of several binary mixtures of each reactant with a few of the more adjuvant and less adjuvant solvents might yield significant results. Specifically, we hoped to show that the adjuvance of the solvent would bear a simple relation to the deviations, from ideal solution laws, of vapor pressures, densities and refractive indices of several binary mixtures of the solvent with each reactant. No simple relationship has been found which will apply to all the cases studied. However, it is felt that the data obtained in this study possess sufficient value, apart from the above-mentioned hypothesis, to warrant their publication.

During this investigation a simple apparatus has been devised for measuring the vapor pressures of liquid mixtures where only small quantities—5 cc. or less—are available for each determination. It is hoped that adaptations of this apparatus may also be found useful in other lines of work.

Vapor Pressures.—The vapor pressures at 20° were measured by a static method. A small glass ampoule containing 3 or 4 cc. of the liquid was broken in an evacuated space of small volume and the pressure developed was measured by means of a mercury manometer. In this way the vapor pressures of pyridine, ethyl iodide, two of the more adjuvant, and two of the less adjuvant solvents, together with those of several binary mixtures of each reactant with each solvent, were obtained.

A numerical expression of the deviation, when this is small, of the observed vapor pressures from Raoult's Law is given by the exponent A in the equations[1]

$$p_1 = p_1^{\circ}\mathrm{N}_1\, e^{A\mathrm{N}_2^2} \tag{1}$$

$$p_2 = p_2^{\circ}\mathrm{N}_2\, e^{A\mathrm{N}_1^2} \tag{2}$$

where p° is the vapor pressure of the pure component and p is its partial pressure over a solution in which its mole fraction is N. Where $A = 0$ the equations become the familiar expressions of Raoult's Law; positive and negative values of A correspond, respectively, to positive and negative deviations from the law.

The values of A, which when substituted in Equations 1 and 2 yielded values of $p_1 + p_2$ in fair agreement with the observed total vapor pressures, are given in Table II. In the first line are given the solvents studied

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[1] See Hildebrand, "Solubility," The Chemical Catalog Co., New York, **1924,** p. 45.

and in Line 2 their relative adjuvance in the reaction under consideration, as found by the previous determination of velocity constants; Line 3 gives the *A*-values for the system solvent–pyridine, and Line 4 the *A*-values for the system solvent–ethyl iodide.

TABLE II

A-VALUES

Solvent	Nitrobenzene	Acetone	*n*-Butyl alcohol	Benzene
Adjuvance	25	12.8	1.11	1.00
A, Pyridine	1.425	0.448	0.48	0.24
A, Ethyl iodide	1.17	0.76	1.70	0.65

No simple combinations of the *A*-values for pyridine and ethyl iodide have been found which give values in any way proportional to the values found for the relative adjuvance.

Densities and Indices of Refraction.—The density and refractive index of mixtures of each reactant with nitrobenzene, acetone, *tert.*-butyl alcohol and benzene, respectively, were measured. In these instances, also, no parallelism was found between the adjuvance of a given solvent and the deviation of the measured property from the value it would have if the solution were ideal. In general the deviations were small and of opposite sign to those found in the measurements of vapor pressure. The data are given in Tables V and VI in the experimental part of this paper.

Experimental Part

The vapor pressures were measured in the apparatus shown in Fig. 1b, constructed of pyrex glass. Connections were made through Q to a Cenco Hyvac pump, through T to a Langmuir diffusion pump backed up by the Hyvac pump through R, through S to a McLeod gage and through J to a water-jet aspirator. The chamber, O, served to break the ampule containing the liquid under investigation. It was provided with a ground joint to permit the removal of the lower portion and to enable the latter to be turned in the fixed member. Inward pointing knobs were made, as close as possible to the top and bottom, by heating a very small spot to a bright orange and pushing in the hot spot with a small stout wire. This chamber, together with a stirrer and a Beckmann thermometer, was immersed in a water-bath contained in a Dewar flask. The water-bath temperature was controlled by a heating coil and a cooling-water tube (not shown) also immersed in the bath. The setting of the Beckmann thermometer was effected through the use of a thermometer reading from 0 to 40° which had been standardized by the Berliner Reichsanstalt. A paper scale was placed behind the manometer.

The vapor space from O and M to the mercury surface at P, approximately 30 cc., corresponded to $30/22{,}400 \times 273/293 = 0.0012$ mole. As the internal diameter of the manometer tube was approximately 0.4 cm., the vapor space was increased by $0.4^2\pi/2 = 0.25$ cc., corresponding to 0.000010 mole for each centimeter of pressure. The corrections to be subtracted from the weights of each component taken were obtained by multiplying the number of moles of vapor, as above determined, by an approximate value of the pressure fractions, p_1/p and p_2/p, respectively.

Ampules having a capacity of about 4 cc. were made from 10 mm. o.d. soft glass tubing (Fig. 1a). The tip A was made quite fragile, and the shank D fairly heavy, with an internal diameter of 2 or 3 mm. A 5-cc. pipet was drawn out at the tip into a small tubule, about 0.5 mm. i.d., 1 mm. o.d., and 10 cm. long; by passing this tubule down the shank of the ampule, the latter could be filled with a liquid without wetting any part of the ampule above the level C.

A determination of the vapor pressure was carried out in the following manner. The desired mixture was first made up by weight, using a 5-cc. glass-stoppered weighing bottle. Enough of this was transferred to the ampule to bring the liquid to the level C, just above the shoulder. By bringing the tip of the tubulated pipet into contact with the inside wall of the ampoule and letting the liquid flow in very slowly at first, the tip A could be filled with liquid without entrapping any air.

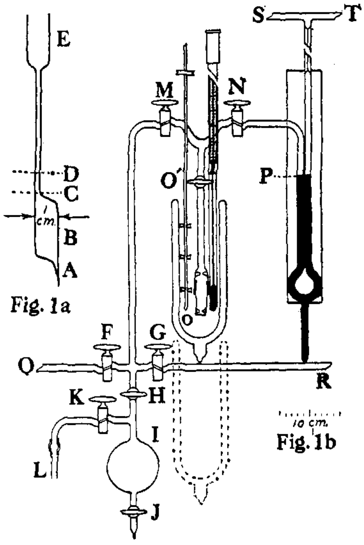

Fig. 1.

The ampule was next attached by means of the rubber tubing L to the Bulb I, which had been previously exhausted by means of a water-jet aspirator to a pressure of from 5 to 10 mm. of mercury. The ampule and contents were chilled by immersion in ice and concentrated hydrochloric acid, Stopcock K was opened and the ampule was sealed off at a point near the top of the shank, using a hand torch. The remaining long portion of the shank was removed by sealing at a point D such that when the ampule was subsequently placed in the chamber O the upper tip would project above the upper knobs without touching the wall directly above them.

The ground joint was next very sparingly greased, the ampule placed in the lower portion with the fragile tip resting on the bottom and the chamber put together as at O (ampule not shown), with the Dewar flask lowered. The right side of the manometer having been previously evacuated to less than 0.01 mm. as shown by the McLeod gage, the rest of the apparatus was evacuated through Q as far as Stopcocks H and G, until there was no further change in the level of mercury in the left arm that could be seen with the unaided eye.

Stopcock O′ was next turned so as to break the lower tip of the ampule, whereupon the liquid ran out into the chamber. The Dewar bath was placed in position and Stopcock M was closed; whereupon Stopcock O′ was slowly opened by a minute amount until the bulk of the vapor had formed, when it was opened wide. After the establishment of equilibrium, shown by repeatedly and slowly approaching the temperature, 20°, alternately from above and below, the vapor pressure was read and recorded.

Tables III and IV give the data thus found. Table III gives the vapor pressures of the individual components, in mm. of mercury, observed at 20.00°. In Table IV, Cols. 1 and 2 give the number of moles, × 100, of each component in the solution, as determined by weight; Col. 3 gives the mole fraction, N_2, of pyridine or ethyl iodide, corrected for vaporization; Cols. 4 and 5 give, respectively, the observed vapor pressure and that calculated from Equations 1 and 2, using the value of A given in the table for each system.

TABLE III

VAPOR PRESSURES OF THE COMPONENTS

									Average
Pyridine	17.4	21.0	21.5	22.7	19.9	21.2	22.3	22.0	21.0
Ethyl iodide			115.2	115.8	118.8	117.0	118.3		117.0
Nitrobenzene					0.0				0.0
Acetone				194.0	195.7	195.3			195.0
n-Butyl alcohol				12.2	13.3	14.3			13.3
Benzene				84.0	85.0				84.5

TABLE IV

EXPERIMENTAL DATA

Solvent, $n_1 \times 100$	Reactant, $n_2 \times 100$	N_2	p, obs. mm. of Hg	p, calcd., mm. of Hg
Nitrobenzene–Pyridine. A = 1.425				
1.00	4.00	0.79	19.1	17.7
2.00	3.00	.59	16.4	15.7
2.40	1.60	.38	13.6	13.8
3.21	0.81	.18	11.0	9.9
3.20	0.81	.18	8.5	9.9
Nitrobenzene–Ethyl Iodide. A = 1.17				
1.00	4.00	.79	100	97.5
1.00	4.00	.79	99	97.5
2.00	3.01	.58	85	84.0
2.70	1.80	.37	68	69.0
2.70	1.80	.37	68	69.0
3.60	0.90	.17	45	44.6
3.60	0.90	.17	45	44.6
Acetone–Pyridine. A = 0.448				
1.30	3.91	.77	73	75.0
2.50	2.50	.52	118	118.0
2.00	2.02	.53	118	116.5
3.31	1.10	.26	156	155.5
Acetone–Ethyl Iodide. A = 0.76				
0.50	4.50	.91	142.5	140.0
1.50	3.51	.71	169.0	171.5
2.50	2.50	.51	186.0	188.5
3.20	1.60	.34	196.0	196.0
4.00	1.00	.20	199.0	199.0
5.00	0.29	.05	196.5	196.5
n-Butyl Alcohol–Pyridine. A = 0.48				
1.00	4.00	0.799	21.5	20.71
1.00	4.02	.799	20.5	20.71
1.07	3.74	.775	20.5	20.67
2.50	2.51	.500	19.5	19.34
2.50	2.50	.500	19.5	19.34
4.00	1.00	.200	16.5	16.55
4.03	1.01	.195	16.0	16.49
n-Butyl Alc.–Ethyl Iodide. A = 1.70				
1.00	4.00	.795	111.5	107.9
1.01	4.00	.795	109.5	107.9
1.00	4.00	.795	106.5	107.9
2.00	4.00	.660	104.5	103.5
2.00	3.00	.590	105.0	101.8
2.00	3.00	.590	104.5	101.8
2.50	2.50	.480	101.0	99.2
2.50	2.50	.480	99.0	99.2
3.01	2.50	.425	95.0	97.7
3.00	2.00	.380	92.0	96.3
4.00	1.00	.170	69.0	75.7
Benzene–Pyridine. A = 0.65				
1.00	4.00	.81	39.0	42.0
2.00	3.00	.61	56.0	56.1
3.00	2.00	.41	69.0	66.4
4.00	1.01	.21	77.0	75.3
Benzene–Ethyl Iodide. A = 0.24				
1.00	4.00	.80	113	114.0
2.00	3.00	.60	109	109.6
3.00	2.03	.40	104	103.6
4.24	1.06	.20	96	95.6

Densities and Refractive Indices.—The densities of the pure components had been measured with especial care using a Sprengel pyknometer, yielding values which are believed fairly to indicate the degree of purity of the substances used (see below). However, for the purpose of comparing the densities of the binary mixtures studied, all that was required was a rapid, fairly accurate method which would give reproducible results. A pyknometer patterned after that described by Mulliken[2] was found to fulfil these requirements perfectly. Accordingly, the densities of the mixtures were measured and those of the pure components remeasured, at 25.0°, using this instrument. No excessive care was used in its calibration and no buoyancy corrections have been included in the density values as given. Nevertheless, it is evident from an inspection of the data that the main purpose of the density measurements—namely, a determination of the deviations from ideal solution laws—has been adequately fulfilled.

The refractive indices were measured at the same temperature, 25.0°, using an Abbé refractometer. The density and refractive index of the pure components and of 2 to 1 and 1 to 2 molecular mixtures of each reactant with each solvent were measured. The mixtures were made up by volume, in duplicate, and the number of moles of each component was calculated using the observed density of the latter. One determination of each property of each mixture was made. The agreement in the case of the pure components was within 1 or 2 units in the last decimal, for both properties. From the respective property and the mole fraction of each pure component were calculated the molecular volume and the molecular refraction of ideal solutions having the composition indicated, using the formulas

$$MV = \frac{1}{D}(M_1\mathrm{N}_1 + M_2\mathrm{N}_2), \text{ and } MR = \frac{n^2 - 1}{n^2 + 2} \times MV$$

where MV = molecular volume, MR = molecular refraction, D = mass/volume at 25.0°, M = molecular weight, N = mole fraction and n = refractive index at 25.0° using the D line. Tables V and VI give the data thus found.

TABLE V

EXPERIMENTAL DATA

Compound	M	D	MV	n	MR
Pyridine	79.1	0.975	81.2	1.5044	24.06
Ethyl iodide	156.0	1.922	81.2	1.5076	24.18
Nitrobenzene	123.1	1.200	102.6	1.5476	32.58
Acetone	58.1	0.781	74.4	....	...
Tert.-butyl alcohol	74.1	.781	94.9	....	...
Benzene	78.1	.871	89.7	1.4950	26.18

The materials used were of the best grade obtainable and were further purified before use. Pyridine was refluxed with quicklime, ethyl iodide with silver powder and lumps of marble, and they were then fractionally

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[2] Mulliken, "Identification of Pure Organic Compounds," John Wiley and Sons, Inc., New York, **1904**, Vol. I, p. 229.

Table VI

Results of Experiments

Solvent, cc.	Reactant, cc.	N_2	D	MV, obs.	MV, calcd.	n	MR, obs.	MR, calcd.
Nitrobenzene–Pyridine								
1.55	2.45	0.67	1.062	88.4	88.3	1.5166	26.78	26.88
1.55	2.45	.67	1.059			1.5180		
2.86	1.14	.33	1.134	95.6	95.6	1.5339	29.68	29.79
2.86	1.14	.33	1.136			1.5325		
Nitrobenzene–Ethyl Iodide								
1.55	2.45	.67	1.685	86.5	88.3	1.5307	26.70	26.96
1.55	2.45	.67	1.665			1.5278		
2.86	1.14	.33	1.404	95.7	95.6	1.5371	29.90	29.83
2.86	1.14	.33	1.398			1.5380		
Acetone–Pyridine								
1.24	2.76	.67	0.918	78.5	79.0			
1.24	2.76	.67	.918					
2.58	1.42	.33	.852	76.2	76.7			
2.58	1.42	.33	.854					
Tert.-butyl Alcohol–Pyridine								
1.47	2.53	.67	.904	85.6	85.7			
1.47	2.53	.67	.903					
2.79	1.21	.33	.840	90.2	90.4			
2.79	1.21	.33	.841					
Benzene–Pyridine								
1.42	2.58	.67	.943	83.4	84.0	1.5013	24.57	24.74
1.42	2.58	.67	.943			1.5016		
2.75	1.25	.33	.908	86.2	86.9	1.4987	25.30	25.47
2.75	1.25	.33	.907			1.4985		
Benzene–Ethyl Iodide								
1.42	2.58	.67	1.551	84.1	84.0	1.5007	24.78	24.82
1.42	2.58	.67	1.540			1.5012		
2.75	1.25	.33	1.193	86.8	86.9	1.4965	25.38	25.51
2.75	1.25	.33	1.202			1.4968		

distilled. Nitrobenzene was repeatedly frozen and distilled *in vacuo*. Acetone from the bisulfite compound was first refluxed with permanganate, then repeatedly with anhydrous carbonate of potash and then fractionally distilled. The alcohols were purified in general by the procedures used in this Laboratory in previous investigations. Benzene (thiophene free) was shaken with concentrated sulfuric acid, alkali and water, then refluxed with sodium and distilled from flasks containing this metal.

Table VII gives the physical constants of the materials used. The figures represent the maximum and minimum values of the constants for the different compounds used, and not the variation in the property for the individual compound. The boiling range, for example, was usually 0.1 or 0.2° for 90% distilled.

TABLE VII

PHYSICAL CONSTANTS OF MATERIAL

	d_4^{25}	M. p., °C.	B. p. (760 mm.), °C.
Pyridine	0.9775 to 0.9779	....	115.2 to 115.4
Ethyl Iodide	1.922 to 1.924	....	72.2 to 72.4
Nitrobenzene	1.197 to 1.199	5.7 to 5.8	
Acetone	0.7855 to 0.7863	....	56.1 to 56.3
n-Butyl alcohol	0.8058 to 0.8060	....	117.7 to 117.8
Tert.-butyl alcohol	0.7807	24.5	82.5 to 82.6
Benzene	0.8730 to 0.8736	5.4[a]	80.1 to 80.3

[a] The melting point was not determined for all the samples used.

The author is indebted to Professor J. F. Norris for his continued interest in this work, and to Professor George Scatchard for many helpful suggestions and criticisms, and especially for indicating the applicability of the Duhem–Margules equations to the problem in hand.

Summary

1. The vapor pressures of several binary mixtures of nitrobenzene, acetone, *n*-butyl alcohol and benzene with pyridine, and with ethyl iodide, have been measured at 20° by a static method.

2. The densities of similar mixtures of nitrobenzene, acetone, *tert.*-butyl alcohol and benzene with pyridine, and of nitrobenzene and benzene with ethyl iodide, and the refractive indices of mixtures of nitrobenzene and benzene with pyridine and with ethyl iodide, have been measured at 25°.

3. For the reaction between pyridine and ethyl iodide an attempt has been made to show that the adjuvance of the solvent, reported in paper No. VII of this series, would bear some relation to the deviation, from ideal solution laws, of vapor pressures, densities or refractive indices of binary mixtures of the solvent with each reactant. No such correlation, however, has been observed.

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