

roughly half as great, about 1-3 v. e. The hydrogen molecule-ion,  $\text{H}\cdot\text{H}^+$ , triatomic hydrogen ion,  $\text{H}\cdot\text{H}\cdot\text{H}^+$ , boron hydrides  $\text{H}:\overset{\text{H}}{\underset{\text{H}}{\text{B}}}\cdot\overset{\text{H}}{\underset{\text{H}}{\text{B}}}\cdot\text{H}$ , etc., lithium molecule-ion,  $\text{Li}\cdot\text{Li}^+$ , etc., contain one-electron bonds. The helium molecule and molecule-ion,  $\text{He}\cdot\cdot\cdot\text{He}$  and  $\text{He}\cdot\cdot\cdot\text{He}^+$ , nitric oxide,  $:\text{N}\overset{\cdot\cdot}{\text{O}}:$ , nitrogen dioxide,  $:\overset{\cdot\cdot}{\text{O}}\text{N}::\text{O}:$ , and oxygen molecule,  $:\overset{\cdot\cdot}{\text{O}}\overset{\cdot\cdot}{\text{O}}:$ , contain three-electron bonds. A discussion of nitroso compounds, in particular dealing with their magnetic moments, is also given.

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## A STUDY OF SOLUTIONS OF ETHYL ALCOHOL IN BENZENE, IN WATER, AND IN BENZENE AND WATER

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The results of several investigations<sup>1</sup> have indicated that the molecular weight of ethyl alcohol in dilute aqueous solutions as determined by the freezing point method is normal. Curve A in Fig. 1, plotted from Pickering's data<sup>1</sup> shows the range in concentration through which the deviation from the theoretical freezing point lowering Curve ( $T_A$ ), is not large.

Similar investigations<sup>1a,2</sup> of solutions of ethyl alcohol in benzene show that above extremely low concentrations of alcohol the observed freezing point lowering is much less than would be expected from the freezing point law. Curve (B) in Fig. 2, is plotted from Pickering's data, curve (B<sup>1</sup>) is plotted from our data, while curve ( $T_B$ ) is the theoretical freezing point lowering curve for solutions of alcohol in benzene. Peterson and Rodebush<sup>3</sup> have shown that for concentrations up to 2.262 g. of alcohol in 1000 g. of benzene the molecular weight of alcohol as calculated from freezing point data is normal. They state that above this concentration, however, the usual freezing point formulation does not apply.

It would seem from these investigations that ethyl alcohol exists in a different molecular form when dissolved in benzene than when dissolved in water. It has been suggested by some workers that evidence as to whether or not this is true should be obtained by the study of the distribution of alcohol between the two nearly immiscible solvents, water and benzene.

<sup>1</sup> (a) S. V. Pickering, *J. Chem. Soc.*, **63**, 998-1027 (1893); (b) R. Abegg, *Z. physik. Chem.*, **15**, 209-261 (1894); (c) F. M. Raoult, *Compt. rend.*, **124**, 885-890 (1897); (d) E. H. Loomis, *Z. physik. Chem.*, **32**, 578-606 (1900).

<sup>2</sup> F. Viala, *Bull. soc. chim.*, **15**, 5-11 (1914); N. Perrakis, *Compt. rend.*, **176**, 1137-1140 (1923).

<sup>3</sup> J. M. Peterson and W. H. Rodebush, *J. Phys. Chem.*, **32**, 709-718 (1928).

S. F. Taylor<sup>4</sup> studied the ternary system ethyl alcohol, water and benzene. He measured the refractive indices of single phase, saturated solutions of these substances and next prepared mixtures of such composition that two layers were formed. He then determined the refractive index of each liquid layer and by comparisons with the refractive indices of the single phase systems he determined the composition of each liquid layer. Considering that the alcohol was distributed between the water and the benzene he calculated the distribution coefficients on the assumption that the alcohol exists in the same molecular form in the two layers. Throughout the concentration range in which he worked the coefficients were fairly constant, which he thought justified the assumption.

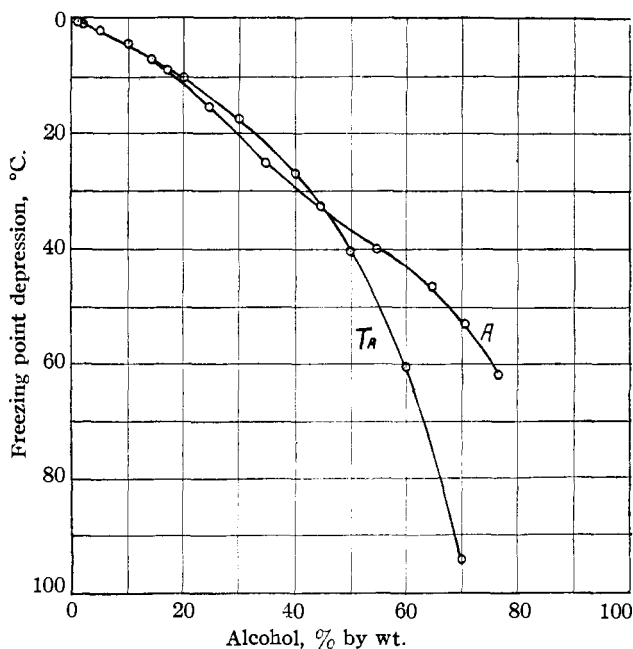


Fig. 1.—Ethyl alcohol-water.

Lincoln confirmed<sup>5</sup> the results of Taylor, "in a general sort of way" but gave no data as to the value of the constants or, perhaps what is more important, as to the concentrations of alcohol in benzene with which he worked.

Morgan and Benson<sup>6</sup> made a brief study of this system. They determined the concentration of the alcohol in the benzene layer by extracting the benzene with ether and sodium chloride and determining the density

<sup>4</sup> S. F. Taylor, *J. Phys. Chem.*, 1, 461-473 (1897).

<sup>5</sup> A. T. Lincoln, *ibid.*, 4, 161-187 (1900).

<sup>6</sup> J. L. R. Morgan and H. K. Benson, *THIS JOURNAL*, 29, 1176-1179 (1907).

of the remaining alcohol-water mixture after it had been separated from the salt by distillation. Four different amounts of alcohol were distributed between equal volumes of water and benzene. The most concentrated solution of alcohol in benzene was approximately 22% alcohol by weight. The distribution coefficients calculated on the assumption that alcohol has the same molecular form in water that it has in benzene showed only a slight trend with changing concentration. The variation in the con-

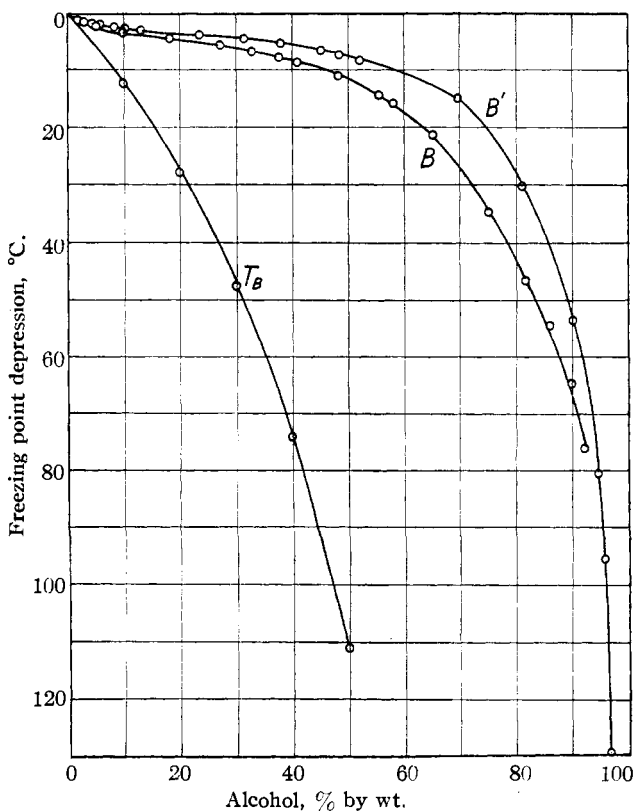


Fig. 2.—Ethyl alcohol-benzene.

stants was far less than would be expected if alcohol in benzene is polymerized as much as freezing point data seem to indicate, providing the effects due to polymerization are not negated by other changes in the system.

These researches present a problem in regard to the physical and chemical nature of the following, and similar solutions: ethyl alcohol-water, ethyl alcohol-benzene, ethyl alcohol-water-benzene. It is difficult to conceive that the answer to this problem lies in a consideration of interionic attraction and yet the answer should be of fundamental importance,

certainly for solutions of non-electrolytes, and possibly for solutions of electrolytes. As one of the initial steps in the study of solutions such as these, parts of these investigations have been repeated and extended.

### Materials

**Water.**—Ordinary laboratory distilled water was redistilled from alkaline permanganate solution in a Pyrex flask connected by constricted ground glass connectors with a block tin condenser, and receiving bottle.

**Ethyl Alcohol.**—A standard commercial grade of absolute alcohol was used. This was dried with calcium oxide and metallic calcium until density measurements showed it to be better than 99.3% alcohol.

**Benzene.**—Mallinckrodt's reagent quality benzene was dried with sodium and redistilled. Its density compared favorably with the value given in the "International Critical Tables."

**Freezing Point Study.**—In order to determine whether alcohol produced a normal lowering of the freezing point of benzene in concentrations much greater than those studied by Peterson and Rodebush,<sup>3</sup> and in order to establish the shape of the freezing point lowering-composition curve, we measured the freezing point of solutions ranging from nearly pure benzene to nearly pure alcohol. The usual Beckmann method was employed, taking special care to avoid errors due to supercooling. Ice, salt and ice and liquid air were used as cooling agents. For the smaller lowerings a Beckmann thermometer was used, for the larger lowerings a tenth degree mercury thermometer, and for the very large lowerings a 1.0° pentane-filled thermometer was used. These instruments were compared with each other and with a Bureau of Standards calibrated thermometer. The proper stem corrections were made. The results are collected in Table I, and plotted as Curve B<sup>1</sup> in Fig. 2.

TABLE I

EXPERIMENTAL RESULTS			
Wt. % alcohol in benzene	Freezing point lowering, °C.	Wt. % alcohol in benzene	Freezing point lowering, °C.
1.8	1.1	46.4	6.5
2.9	1.5	48.6	7.2
4.4	1.7	52.3	8.4
5.8	2.0	69.8	14.9
8.5	2.3	81.4	30.2
10.3	2.5	90.2	53.7
13.3	2.8	94.9	80.7
23.5	3.7	95.8	95.7
31.5	4.5	96.9	129.7 <sup>a</sup>
38.1	5.2		

<sup>a</sup> Alcohol was very viscous, so it is doubtful if it actually crystallized at this temperature.

As found by earlier workers, the range of concentration through which the freezing point lowering is normal is very short. For higher concen-

trations of alcohol the freezing point lowerings are much too small; for example, when alcohol makes up 30% by weight of the solution, the freezing point is still above 0°, whereas we would calculate the freezing point to be -42°, using the formula  $\Delta f. p. = wt. alc. \times 1000 \times 5.12 / wt. ben. \times 46.05$ .

**Distribution of Alcohol between Benzene and Water.**—In order to measure the concentration of alcohol in conjugate layers of water and benzene, a procedure similar to that employed by Taylor<sup>4</sup> and more recently by Barbaudy was used.<sup>7</sup> With the aid of calibrated pipets mixtures of alcohol and benzene in the following proportions (Table II) were prepared in 125-cc. glass-stoppered bottles. The liquids when mixed were at 25.0°; after mixing they were allowed to come to room temperature, which, during the final experiment and the one here reported, was 24.5°. Each of the mixtures was then titrated with water to a permanent cloudiness, time being allowed during the titration for the temperature to return to 24.5°. The volume of water used in mixtures 1-11 was read from a 10-cc. buret graduated to 0.01 cc. and for mixtures 12-16 a calibrated 50-cc. buret was used. After each solution was titrated the bottle containing it was suspended in a constant temperature bath at 25.0 ± 0.1°. This slight increase in temperature was sufficient to clear up or nearly clear up the emulsion. The refractive index of each solution was then measured with an Abbé refractometer, the lenses of which were kept at 25.0° by water siphoned from a constant temperature bath. The results of this study are given in Table II and plotted in Figs. 3 and 4.

TABLE II  
EXPERIMENTAL RESULTS

No.	Ethyl alcohol, cc.	Benzene, cc.	Water, cc.	Wt. % alcohol	Wt. % benzene	Refractive index at 25.0°
1	10.0	100.0	0.66	8.2	91.1	1.4824
2	10.0	80.0	0.72	10.0	89.0	1.4792
3	10.0	60.0	0.87	12.9	85.7	1.4747
4	10.0	40.0	1.11	17.9	79.5	1.4660
5	10.0	25.0	1.40	25.3	70.2	1.4519
6	10.0	20.0	1.68	29.1	64.6	1.4443
7	10.0	15.0	2.00	34.3	57.0	1.4340
8	10.0	10.0	2.32	41.6	46.2	1.4193
9	10.0	8.0	2.70	44.8	39.8	1.4114
10	10.0	5.0	3.39	50.4	27.9	1.3960
11	10.0	4.0	3.84	51.8	23.0	1.3890
12	10.0	2.0	5.77	51.2	11.4	1.3735
13	20.0	2.0	17.1	46.6	5.1	1.3642
14	20.0	1.0	25.5	37.4	2.1	1.3573
15	40.0	1.0	73.0	29.9	0.83	1.3522
16	50.0	1.0	112.7	25.8	0.57	1.3494

Water saturated with benzene 1.3325

Benzene saturated with water 1.4965

<sup>7</sup> J. Barbaudy, *Rec. trav. chim.*, **45**, 207-213 (1925).

The curve in Fig. 3 shows the variation of refractive index with the change in concentration of alcohol in the equilibrium mixture, the concentrations being expressed in weight per cent. The curve intersects the horizontal axis at the refractive index of water saturated with benzene on the side nearest the origin, and at the refractive index of benzene saturated with water at the other end.

Although the curve must obviously intersect the horizontal axis at these points, an error is possibly introduced in extending the curve through such a large concentration range, from 0.0% alcohol to 25.8% alcohol, with no intermediate points. It is difficult to determine accurately the end-point with these mixtures of low benzene content because of the great solubility of water in these mixtures and the resulting difficulty of telling

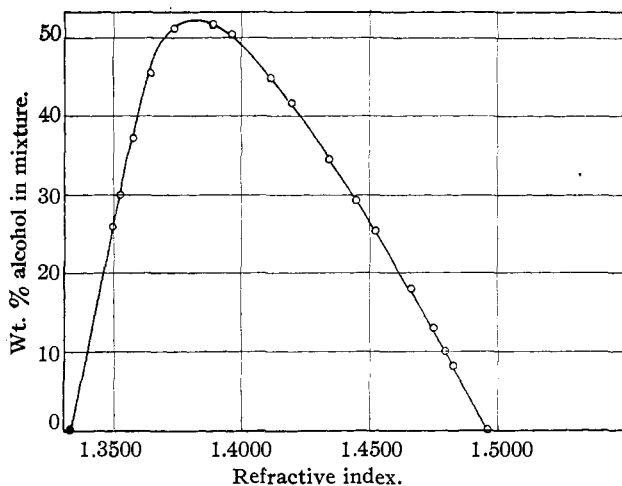


Fig. 3.—Refractive index at 25.0°.

just when a cloudy emulsion is first formed. There seems to be a slight tendency for the curve to drop too rapidly to meet squarely the refractive index of water saturated with benzene without undergoing a change of slope. We have not drawn it this way, however, for we are not certain that such an inflection is necessary; furthermore, we have no information as to where it should start if it is necessary. There is a still smaller tendency, almost unmeasurable, for the other end of the curve likewise to drop too rapidly to meet the refractive index of benzene saturated with water. We have not been able to find that other investigators have noted this peculiarity, although it would seem that any complete discussion of the system should take it into account.

Figure 4 shows the concentrations of the saturated, single-phase system. All mixtures, the gross compositions of which are represented by points above the curved line, are unsaturated single-phase systems. Those repre-

sented by points beneath the curve will separate into two conjugate layers, each saturated and each represented by a point on the curve.

The following mixtures having gross compositions which would place them beneath the curve were then prepared, each in a small glass-stoppered bottle. Since in each case 25.0 cc. of water and 25.0 cc. of benzene were used, only the amount of alcohol distributed in the system is listed in the table. The volumes were measured at 25.0°. The mixtures were carefully shaken and then suspended in the constant temperature bath. When sufficient time had elapsed for the systems to reach equilibrium the two layers were clear and transparent. Samples of each layer were then withdrawn with small pipets and refractive indices were measured. The results are recorded in Table III, and the tie-lines are indicated in Fig. 4.

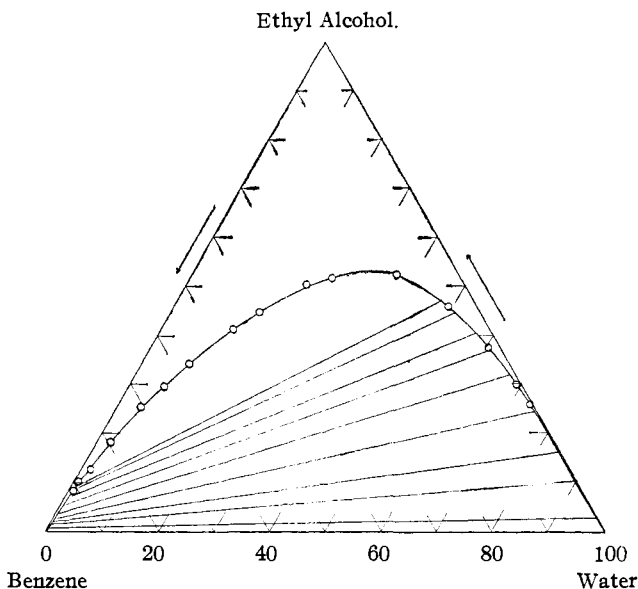


Fig. 4.—Concentrations in wt., %.

### Discussion

Since it is impossible, at the present time, to separate the effects of possible polymerization from the effects of changing thermodynamic environment, the theoretical treatment of this problem necessarily will be brief.

If alcohol is polymerized when dissolved in benzene, as freezing point data would seem to indicate, and if the change in thermodynamic environment is small enough to be ignored, then constant values for the distribution ratios would be obtained, not by use of the above formula, but by use of  $(\text{concn. of alc. in water})^x / \text{concn. of alc. in benzene} = K$ , where  $x$  refers

TABLE III  
 EXPERIMENTAL DATA

Ethyl alcohol, cc.	Refractive index of water layer	Wt. % alc. in water layer	Refractive index of benzene layer	Wt. % alc. in benzene layer	Distribution ratio
1.0	1.3340	2.5	1.4960	0.7	3.6
4.0	1.3391	10.6	1.4951	1.2	8.8
6.0	1.3427	16.4	1.4944	1.6	10.2
10.0	1.3479	24.3	1.4930	2.4	10.1
15.0	1.3530	31.8	1.4920	3.9	8.1
20.0	1.3569	37.0	1.4876	5.4	6.8
25.0	1.3597	40.5	1.4848	7.0	5.8
30.0	1.3629	44.3	1.4821	8.4	5.2
35.0	1.3659	57.3	1.4798	9.8	4.9

The "distribution ratios" were calculated from the simple relationship  $\text{Wt. \% alc. in water} / \text{Wt. \% alc. in benzene} = K$ .

to the number of simple molecules of alcohol combining to form one molecule of polymerized alcohol. Although the values for the distribution ratios as calculated (Table III) are not constant, they do not vary nearly as much as one would expect them to vary if the concentration of alcohol in the water should be raised to some power in order to satisfy conditions.

In another investigation by one of us it has been shown that the presence of a small<sup>8</sup> amount of water in ethyl alcohol alters to a rather large extent the temperature and volume changes which accompany the mixing of alcohol and benzene in different proportions. It may be that when water is present in benzene the equilibrium between the simple alcohol molecules and the polymerized molecules shifts so that the simple molecules predominate. This might account for the variation observed between the results of freezing point studies and the results of the distribution studies; it may also account for the effect of water on the changes in temperature and volume already mentioned.

This work is being continued and the effects of small but known amounts of water on the viscosities of alcohol-benzene mixtures are being studied.

### Summary

The freezing points of ethyl alcohol-benzene mixtures throughout nearly the complete range of concentration have been determined.

The equilibrium concentrations for the system ethyl alcohol-water-benzene and tie-lines relating to this system have been determined.

Some of the difficulties encountered in attempts to correlate these results are pointed out.

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<sup>8</sup> E. R. Washburn and A. Lightbody, *J. Phys. Chem.*, **34**, 2701-2710 (1930).