[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NEBRASKA]

# A Study of Solutions of Isopropyl Alcohol in Benzene, in Water and in Benzene and Water

BY ALLEN L. OLSEN AND E. ROGER WASHBURN

As a part of a comparative study of binary and ternary systems made up of water, a hydrocarbon, and a lower alcohol, the following observations have been made on solutions of isopropyl alcohol in benzene, in water and in benzene and water.

### Materials

**Water.**—"Conductivity water" was used.

**Isopropyl Alcohol.**—A good grade of isopropyl alcohol was refluxed over lime and subjected to fractional distillations. The best product had a density of 0.78087 g./ml. ±0.00002 at 25.00 ± 0.05° which corresponds favorably with Brunel's value of 0.78084 g./ml.[1]

**Benzene.**—The purified benzene had a density of 0.87360 g./ml. ± 0.00005 at 25.00° as compared with the value of 0.87344 g./ml. given by the "International Critical Tables."[2]

## Experimental

**Freezing Point Determination.**—A modification of the familiar Beckmann apparatus was used in this study and an effort was made to avoid unnecessary supercooling. The theoretical freezing point lowering was calculated with the usual equation.[3] The results for the calculated and observed values are tabulated in Table I.

TABLE I

FREEZING POINT LOWERING OF BENZENE BY ADDED AMOUNTS OF ALCOHOL

| Wt. % alcohol in benzene | Δ f. p. obsd. | Δ f. p. calcd. | $\Delta T/N_w$ |
|---|---|---|---|
| 0.786 | 0.622 | 0.676 | 4.712 |
| 2.013 | 1.214 | 1.751 | 3.549 |
| 2.530 | 1.358 | 2.217 | 3.143 |
| 3.772 | 1.740 | 3.341 | 2.706 |
| 7.451 | 2.639 | 6.871 | 1.962 |
| 8.952 | 3.075 | 8.380 | 1.878 |
| 12.94 | 3.903 | 12.67 | 1.586 |
| 14.49 | 4.141 | 14.46 | 1.437 |
| 17.40 | 4.655 | 17.51 | 1.328 |
| 19.77 | 5.225 | 21.01 | 1.273 |

**Ternary Solubilities.**—Equilibrium Concentration. This work was carried out at a constant temperature of 24.8° in an apparatus similar in construction to that previously described.[3,4,5] The mixtures were purposely titrated at this temperature in order that the slight excess, necessary for the recognition of the end-point, might be dissolved at 25.00°, the temperature at which the refractive index was determined.

The solubilities of benzene in water and water in benzene were taken from the literature.[6] These values give the intersections of the solubility curve on the base line.

Results of these titrations are tabulated in Table II and are shown graphically in Fig. 1. The concentrations are expressed in terms of weight per cent.

**Refractive Index.**—After each titration was made, the refractive index of the ternary system was measured by means of an immersion refractometer. The instrument was dipped directly into a thermostatically controlled water-bath maintained at 25.00°. The results are listed in Table II.

TABLE II

TERNARY SOLUBILITY DATA

| Wt. % components Benzene | Alc. | Water | Ref. ind. | Density | Rel. visc. |
|---|---|---|---|---|---|
| 99.93 | 0.00 | 0.07 | 1.49750 | 0.8733 | 0.674 |
| 87.74 | 13.20 | .06 | 1.47588 | .8594 | .671 |
| 82.06 | 17.22 | .72 | 1.47295 | ... | ... |
| 68.63 | 28.54 | 2.83 | 1.45493 | .8467 | .813 |
| 57.81 | 37.95 | 4.24 | 1.44027 | .8392 | .935 |
| 44.55 | 46.00 | 9.46 | 1.42445 | .8405 | 1.247 |
| 35.30 | 50.28 | 14.42 | 1.41317 | .8442 | 1.552 |
| 29.40 | 51.00 | 19.59 | 1.40620 | .8516 | 1.893 |
| 27.17 | 51.36 | 21.47 | 1.40347 | .8543 | 2.024 |
| 23.63 | 50.42 | 25.95 | 1.39865 | .8619 | 2.302 |
| 17.59 | 48.16 | 34.25 | 1.39022 | .8771 | 2.830 |
| 8.71 | 41.79 | 49.50 | 1.37397 | .9084 | 3.419 |
| 6.25 | 39.11 | 54.64 | 1.37041 | .9165 | 3.328 |
| 2.21 | 32.51 | 65.28 | 1.36189 | .9386 | 3.061 |
| 0.80 | 25.16 | 74.04 | 1.35547 | .9571 | 2.654 |
| .15 | 0.00 | 99.85 | 1.33287 | .9974 | 1.008 |

**Viscosity.**—The viscosities of each equilibrium mixture were determined with a modification of the Ostwald viscometer designed to prevent evaporation, and the usual procedures were observed.[7] The viscometer was suspended in a

---

[1] R. F. Brunel, THIS JOURNAL, **45**, 1336 (1923).

[2] "International Critical Tables," McGraw-Hill Book Co., New York, 1929, Vol. III, p. 29.

[3] E. R. Washburn, V. Hnizda and R. Vold, THIS JOURNAL, **53**, 3237 (1931).

[4] R. Vold and E. R. Washburn, *ibid.*, **54**, 4217 (1932).

[5] E. R. Washburn and H. C. Spencer, *ibid.*, **56**, 361 (1934).

[6] "International Critical Tables," McGraw-Hill Book Company, New York, 1929, Vol. III, p. 389.

[7] Findlay, "Practical Physical Chemistry," Longmans, Green and Company, New York, p. 72.

thermostatically controlled water-bath, kept at 25.00°. The viscosities were calculated relative to water as unity at the same temperature.

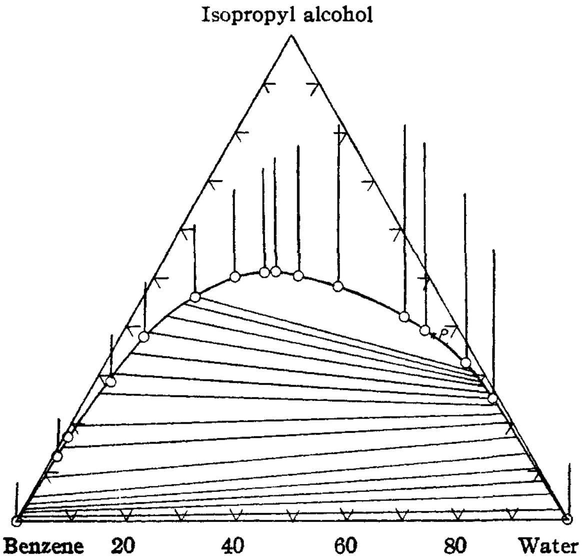

Fig. 1.—Concentrations in weight per cent.; *P* shows plait point.

**Distribution of Alcohol between Water and Benzene.**—Approximately 20 cc. each of benzene and water were pipetted into glass stoppered bottles and varying amounts of alcohol were added to the mixture. The flasks were suspended in the constant temperature water-bath (25.00°) for a period of twenty-four hours. An occasional shaking aided in reaching an equilibrium condition. At the end of this time, the liquid layers were analyzed by means of the refractometer. The distribution ratio was found by dividing the weight per cent. of alcohol in the water layer by the weight per cent. of alcohol in the benzene layer. The results are tabulated in Table III.

The allocation of the plait point, the point at which the solubility curves of benzene in water and water in benzene mixtures, produced by increasing amounts of alcohol, intersect, was determined by the method described in the "International Critical Tables."[8]

The ternary solubility of benzene-water-alcohol, the distribution of alcohol between mixtures of water and benzene, the relative viscosity of each equilibrium mixture and the plait point are represented in Fig. 1.

It was possible to represent the relative viscosity in a coördinate perpendicular to the triangular diagram, giving a triangular prism as the space configuration in which the two variables composition and relative viscosity are represented. This is represented on a two-dimensional diagram by drawing straight lines toward the top of the graph from the points indicating the composition of the mixtures. The magnitude of the relative viscosity is indicated by the lengths of these lines.

TABLE III

SUMMARY OF DATA ON TIE LINES

Alcohol was distributed between approximately 20 cc. of water and 20 cc. of benzene

| Approx. cc. alc. added | Water layer Ref. ind. | | Benzene layer Ref. ind. | | Dist. ratio |
|---|---|---|---|---|---|
| | Ref. ind. | % alc. | Ref. ind. | % alc. | |
| 1 | 1.33552 | 2.9 | 1.49638 | 0.8 | 3.6 |
| 2 | 1.33807 | 5.8 | 1.49551 | 1.5 | 3.9 |
| 3 | 1.34079 | 8.8 | 1.49445 | 2.3 | 3.9 |
| 4 | 1.34303 | 11.3 | 1.49317 | 3.3 | 3.4 |
| 5 | 1.34554 | 14.1 | 1.49103 | 4.9 | 2.8 |
| 7 | 1.34900 | 17.9 | 1.48574 | 8.9 | 2.0 |
| 10 | 1.35172 | 20.9 | 1.47741 | 15.0 | 1.4 |
| 12 | 1.35332 | 22.8 | 1.47018 | 19.8 | 1.2 |
| 15 | 1.35469 | 24.3 | 1.46062 | 26.1 | 0.9 |
| 17 | 1.35577 | 25.6 | 1.45410 | 30.1 | .8 |
| 20 | 1.35679 | 26.7 | 1.44599 | 34.8 | .7 |
| 22.5 | 1.35782 | 27.9 | 1.43914 | 38.6 | .7 |
| 25 | 1.35836 | 28.5 | 1.43440 | 41.9 | .6 |
| 27.5 | 1.35948 | 29.7 | 1.42801 | 44.3 | .6 |
| 30 | 1.35995 | 30.2 | 1.42476 | 45.9 | .6 |

## Discussion

The studies on the freezing point data indicate that isopropyl alcohol is associated in benzene, if such deviations be attributed to association, to quite a large extent. However, the theoretical and the observed lowering of the freezing points for isopropyl alcohol-water are normal over a wide range of concentration.[9] A comparison of the theoretical and the observed values for the depression of the freezing point for the two systems, at some specified concentration of alcohol, will clearly show these deviations. At weight per cent. alcohol = 10, the difference between the observed and the calculated values for the alcohol-benzene system is 6.32° and for the alcohol-water system is 0.26°.

In considering the ternary systems which have been studied in this Laboratory consisting of water, an alcohol and benzene, the liquids may be listed in the order of their dielectric constants: water 80, methyl alcohol 33.7, ethyl alcohol 22.0, isopropyl alcohol 15.7 and benzene 2.3.[10]

---

[8] "International Critical Tables," McGraw-Hill Book Company, New York, 1929, Vol. III, p. 398.

[9] "International Critical Tables," McGraw-Hill Book Co., New York, 1929, Vol. IV, p. 262.

[10] "International Critical Tables," McGraw-Hill Book Co., New York, 1929, Vol. VI, pp. 78, 83, 85, 86, 90.

The dielectric constants and the internal pressures for the two liquids, benzene and water, are sufficiently different to cause almost total immiscibility at 25.0°. It is observed that isopropyl alcohol is more nearly like benzene than either of the lower alcohols for which polarity data are given. The propyl alcohols are the last of the increasing homologous series, *i. e.*, methyl, ethyl, propyl, etc., to be infinitely soluble in water at 25.0°.

The effectiveness of the various alcohols, methyl, ethyl and isopropyl, in bringing about homogeneity of mixtures of benzene and water may be compared on the basis of the penetration of the solubility curve into the alcohol-rich region. If methyl, ethyl and isopropyl alcohols, expressing concentration in weight per cent. or in mole per cent., were to be listed in the order of effectiveness in bringing about miscibility, the order would be as follows: isopropyl alcohol > ethyl alcohol > methyl alcohol which corresponds to the order of the increasing dielectric constants.

When small additions of alcohol, a liquid of intermediate dielectric constant and internal pressure and one which is miscible in both layers, are first made, a greater part of it enters the water layer due to the fact that both alcohol and water are polar liquids. The presence of the alcohol increases the solubility of benzene in water and water in benzene. If the assumption is made that the alcohol in benzene is an aggregate and in water a monomer, then if there were no water present in the benzene or benzene in the water, the alcohol would retain its original form of aggregation. The presence of water in the benzene layer favors a simpler form for the alcohol molecules and the presence of benzene in the water favors a more complex form. At very dilute concentrations, the observed and the calculated lowering of the freezing points for the alcohol–benzene system were nearly identical. With increasing amounts of alcohol, the benzene layer tends to become more polar because an increasing amount of alcohol is found in the benzene layer. Further additions of alcohol result in a still greater fraction of alcohol to be found in the benzene layer. The increase in the fraction of alcohol in the benzene layer results in a change of direction of slope of the tie-lines and, of course, in the numerical value of the distribution ratio. The plait point, therefore, occurs at an entirely different part of the curve than one would predict from the direction of the first few tie-lines.

The maxiumum in viscosity occurs in the vicinity of the plait point. The complexity of a binary system is greatly increased with the addition of a third component. If alcohol is associated in benzene and monomolecular in water and if benzene in water causes the alcohol to associate and water in benzene causes the alcohol to dissociate, then at the plait point the molecular form of the alcohol must be exactly the same. It is impossible to say whether the maximum in viscosity is due to the further association of individual components or their respective unions.

## Summary

1. The freezing point data for solutions of isopropyl alcohol in benzene up to 19.8 weight per cent. of alcohol have been presented.

2. The equilibrium concentrations of the ternary system benzene–isopropyl alcohol–water have been determined at 25.0 ± 0.1°. Viscosities for the different equilibrium concentrations have been measured. The tie-lines for the system have been determined, the plait point has been located and the values of the distribution ratio between water and benzene have been calculated.

3. Attempts have been made to correlate the physico-chemical properties of this system with other investigations which were similar in nature.

LINCOLN, NEBRASKA RECEIVED NOVEMBER 19, 1934