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

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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).

separation just occurred, whether it was evidenced by drop formation, opalescence, mistiness or actual emulsification.   In order to ensure permanent phase separation after each addition of water, the flasks were alternately shaken for thirty seconds and allowed to stand for thirty seconds for at least five minutes. Titration to the appearance of a second phase was selected as the end-point rather than titration of a two-phase system to a homogenous solution since it has been found[6] to give a sharper end-point.   During the titrations the flasks were kept stoppered except during addition of water from the pipet. A study of the change in weight due to evaporation showed that at most it amounted to only two or three parts per thousand.

Hand[5] claims to have eliminated all uncertainty regarding the end-point in similar titrations by recording the amounts of titrating liquid definitely insufficient and then definitely in excess by working first at 22° and then at 25°.   In the present work it was found that such systems are very sensitive to temperature variations, a very small change in temperature being sufficient in some concentration ranges to produce a dense milkiness in the solution.   Consequently, it appears that there is no method for determining the end-point between the two extremes used by Hand.   Therefore, it is believed that direct observation of the point of phase separation provides a more accurate determination of the end-point despite its difficulty.

The results of these titrations are collected in Table I and shown graphically in Fig. 1. The starred values were extremely difficult to obtain.

TABLE I

SOLUBILITIES OF ETHYL ALCOHOL–CYCLOHEXANE AND WATER AT 25°

No.	C_6H_{12}, g.	Alc., g.	Water, g.	Wt. % C_6H_{12}	Wt. % alc.	Wt. % water	Refractive index
1*	0.0346	0.8248	9.9554	0.32	7.63	92.05	1.33749
2*.	.0739	2.5107	9.9377	.59	20.05	79.36	1.34622
3	.0402	19.6007	28.1032	.08	41.06	58.86	1.35707
4	.0971	7.7960	10.1346	.54	43.24	56.22	1.35799
5	.2511	15.6421	15.1538	.81	50.38	48.81	1.36012
6	.3951	15.6588	13.0224	1.36	53.85	44.79	1.36120
7	.7837	15.6074	8.9327	3.09	61.63	35.28	1.36339
8	.8103	7.7775	3.0218	6.98	66.99	26.03	1.36568
9	2.0129	15.5899	5.1660	8.84	68.47	22.69	1.36684
10	1.5615	7.7915	1.8890	13.88	69.31	16.81	1.36947
11	2.3427	7.8054	1.3486	20.38	67.89	11.73	1.37276
12	3.0952	7.7919	1.0258	25.98	65.41	8.61	1.37549
13	3.8837	7.8089	0.9863	30.63	61.59	7.78	1.37843
14	7.6998	7.8026	.6954	47.54	48.17	4.29	1.38816
15	7.6724	3.9236	.2455	64.79	33.14	2.07	1.39900
16	19.4184	3.9360	.2106	82.41	16.70	0.89	1.41051

Water saturated with cyclohexane   1.33255
Cyclohexane saturated with water   1.42348

⁶ Bogin, *Ind. Eng. Chem.*, **16**, 380 (1924).

Those solutions undoubtedly contained a small amount of undissolved cyclohexane but since it was in a few relatively large insoluble drops it had little or no effect on the refractive index of the solution. Therefore it caused no appreciable error in the later graph of amount of alcohol against refractive index of solution. Attention is called to the fact that composition is expressed in terms of weight per cent., rather than in mole fraction or mole per cent. This is advisable since in these solutions the molecular form of the alcohol is not only unknown but is probably changing.
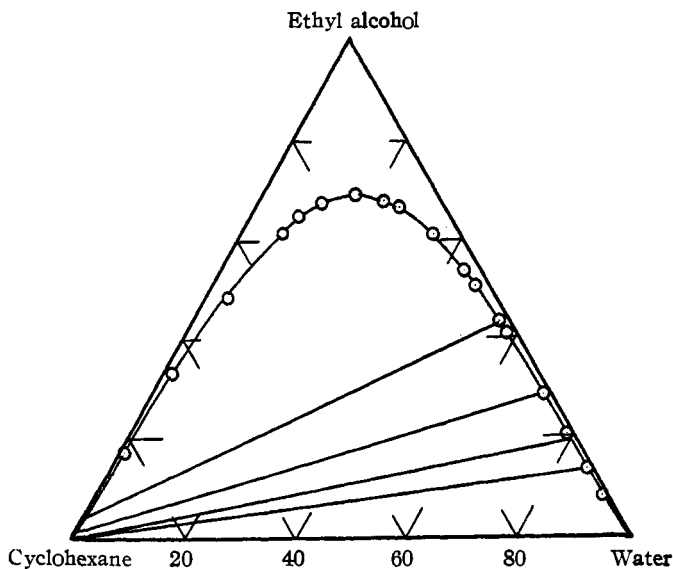

Fig. 1.—Concentration in wt. %.

The refractive indices at 25° of the saturated ternary solutions for the D line of sodium were then determined by an immersion refractometer equipped with a closed metal cup to prevent evaporation of the solutions. Temperature was kept at 25.00° during the determinations by dipping the whole lower end of the instrument directly into an electrically controlled thermostat. This temperature was selected 0.2° above the titration temperature in order to clear up the solutions so as to permit accurate determination of the refractive index. No appreciable error is introduced by this procedure since the excess water necessary to cause visible phase separation at 24.8° may be assumed to just dissolve at 25.00°, thus leaving a clear, saturated, single solution phase ternary solution. This information is also tabulated in Table I and is shown in Fig. 2.

The curve in Fig. 1 shows the composition of the various possible saturated ternary solutions of ethyl alcohol, cyclohexane, and water. This solubility curve is made up of two curves which approach and finally

meet, one giving the solubility of alcohol in cyclohexane saturated with water and the other the solubility of alcohol in water saturated with cyclohexane.

It can be shown from phase rule considerations that there are three degrees of freedom in this system which must be specified before the equilibrium is determined and the position of the curve fixed. In this work these were chosen as temperature, pressure, and an initial concentration ratio of cyclohexane to alcohol. Actually atmospheric pressure was used and it was assumed to remain constant throughout the experiment.
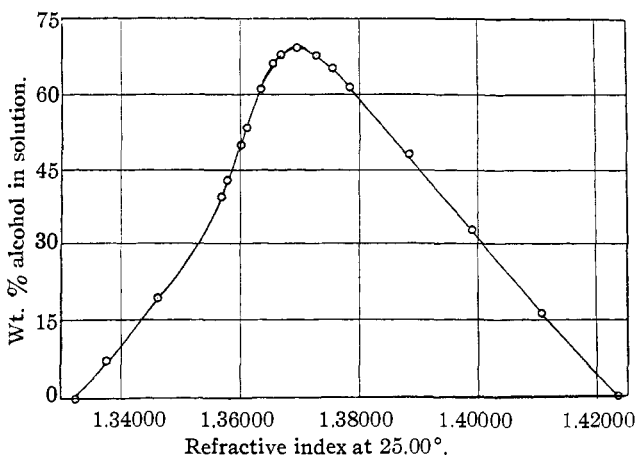

Fig. 2.—Ethyl alcohol–cyclohexane–water.

A change in the concentrations in the solution as a result of a change in external pressure is brought about by its effect on the vapor pressures of the liquids. This effect is given by the equation $dp/dP = v/V$, where p is the vapor pressure of the liquid, P the external pressure and v and V are, respectively, the molecular volumes of the substance as liquid and vapor. Consequently, since this is very small, even relatively large changes of external pressure would not noticeably affect the equilibrium concentrations of the three liquids in single phase saturated solution.

This conclusion seems to be a contradiction of an observation made by a previous worker,[5] who found that the composition of his saturated solutions in certain concentration ranges was very sensitive to changes of external pressure. In the present investigation a procedure similar to his was used except that any pressure variations were eliminated. Nevertheless, a result similar to that obtained by him was observed. In view of the fact that these systems are very sensitive to temperature changes in certain concentration ranges, it seems probable that the observed changes in the system are due to incidental temperature variations rather than to any effect of external pressure changes.

Figure 2 shows the variation of refractive index of saturated ternary solutions of ethyl alcohol, cyclohexane and water with the weight per cent. of alcohol present. At the one end of the curve is the refractive index of water saturated with cyclohexane and at the other end is the refractive index of cyclohexane saturated with water. In this, as in a similar system,[1] the curve has a dip in the water-rich solutions and does not rise to its maximum with uniformly changing slope.

To determine the distribution ratio of alcohol between cyclohexane and water, samples were made up of approximately 10 cc. of water and 10 cc. of cyclohexane mixed in glass-stoppered bottles. To these mixtures different amounts of alcohol were added and the bottles then suspended in the thermostat at 25.00° for twelve hours to ensure attainment of equilibrium. The refractive index of each of the two separated phases was then determined as before and from the graph of Fig. 2 the concentration of alcohol in each phase was found. The distribution ratio was calculated as the simple quotient of the weight per cent. of alcohol in the water layer divided by the weight per cent. of alcohol in the cyclohexane layer. The results appear in Table II.

TABLE II

IN ALL CASES THE ALCOHOL WAS DISTRIBUTED BETWEEN APPROXIMATELY TEN CC. OF WATER AND TEN CC. OF CYCLOHEXANE

No.	Ref. ind. of water layer	Wt. % alc.	Ref. ind. cyclo-hexane layer	Wt. % alc.	Total amt. alc.	Dist. ratio
A	1.33306	0.72	1.42351	0.0	0.1	..
B	1.33494	3.30	1.42351	0.0	0.5	..
C	1.33524	3.68	1.42340	0.0	0.6	..
D	1.33723	6.65	1.42334	?	1.0	?
E	1.34148	12.74	1.42321	0.20	2.0	63.7
F	1.34562	18.80	1.42311	0.37	3.0	50.8
G	1.35106	28.10	1.42280	0.64	5.0	43.9
H	1.35804	43.60	1.42230	1.20	10.0	36.3

Freezing Point Studies.—For this work a standard Beckmann apparatus was constructed and the usual precautions[7] observed in its use. A weighed amount of cyclohexane was placed in the inner tube and its freezing point determined. Weighed amounts of alcohol were then added from a weight pipet and the freezing points of the solutions determined. The molal freezing point constant for cyclohexane was calculated to be 14 from the data of Mascarelli and Pestalozza[8] and Baud[9] by the equation $K = mdW/w$, where m is the molecular weight of the solute, W the grams

[7] Findlay, "Practical Physical Chemistry," Longmans, Green and Co., New York, 5th ed., 1931, p. 120.

[8] Mascarelli and Pestalozza, "International Critical Tables," The McGraw-Hill Book Co., New York, 1929, Vol. IV, p. 133.

[9] Baud, *ibid.*, p. 107.

of cyclohexane, d the freezing point depression and w the grams of solute. Using this value for the constant the theoretical depression of the freezing point for each concentration of alcohol was calculated on the basis that the alcohol was monomolecular. The apparent molecular weight of the alcohol at each concentration was also calculated.

TABLE III

FREEZING POINTS OF ETHYL ALCOHOL-CYCLOHEXANE SOLUTIONS

Wt. % alc. in cyclohexane	Observed depression	Calculated depression	App. mol. wt. of alc.
1.15	1.56	3.54	104
1.18	1.57	3.63	106
3.11	2.92	9.78	154
4.25	3.53	13.49	176
4.61	3.68	14.71	184
6.09	4.32	19.72	210
8.56	5.06	28.48	259
16.60	6.74	60.58	414

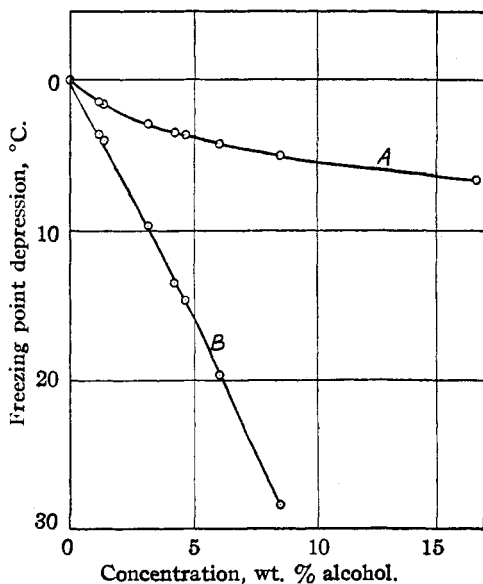These results appear in Table III. The variation of the observed from the calculated depression of the freezing point is shown in Fig. 3. Curve B is the theoretical freezing point lowering curve for solutions of ethyl alcohol in cyclohexane, while curve A shows the actual lowering.

Fig. 3.—Ethyl alcohol-cyclohexane.

Discussion

If absolutely constant values of the distribution ratio had been obtained it would have shown (1) that the alcohol had the same molecular form in the two solvents, (2) that the mutual solubility of the two solvents was equally affected by the presence of the alcohol and (3) that the deviations from the laws of perfect solutions were the same in both the water and cyclohexane solutions of alcohol. Actually, up to a certain concentration, practically all the alcohol dissolved in the water layer and above this the value of the ratio steadily decreased as the concentration of alcohol was further increased.

The steady decrease in the value is due to the fact that weight per cent.

was chosen as the method of expressing concentration. This is equivalent to using an expression of the form

$$K = \frac{A_1}{A_1 + B_1 + C_1} \bigg/ \frac{A_2}{A_2 + B_2 + C_2}$$

where A, B and C are the three liquids, the subscripts 1 and 2 denoting in which phase they are present. Since, as is shown by the solubility curve of Fig. 1, the solubilities of water in cyclohexane and of cyclohexane in water are unequally affected by the addition of alcohol, it is obvious that strictly constant values of the ratio will not be obtained even though the other conditions are fulfilled. The distribution law was developed in terms of the ratio of grams of A to grams of B divided by the ratio of grams of A to grams of C. Nevertheless, it seems more reasonable to use the expression with weight per cent., since the alcohol is actually distributed between saturated solutions of cyclohexane in water and water in cyclohexane and not between pure water and pure cyclohexane. Furthermore, some variation is probably due to the use of the improbable assumption that the alcohol has the same activity in water, a polar solvent of the same type as alcohol itself, that it has in cyclohexane, a non-polar hydrocarbon.

The fact that the change in the value of the ratio is relatively so small is therefore strong evidence that the alcohol has the same molecular form in the two phases.

On first consideration freezing point data seem to contradict this conclusion. Several investigators have shown that the freezing point depression caused by addition of alcohol to water is normal over a large concentration range.[10,11] Our results indicate that in cyclohexane the alcohol is highly associated, the apparent molecular weight varying from about one hundred to four hundred. Despite the uncertainty involved in attributing all variations from the freezing point law to association of the solute,[12] nevertheless, it is reasonable to assume that the alcohol is associated since even in dilute solutions the observed depression of the freezing point varied several hundred per cent. from the calculated value. Therefore, the conclusion is that alcohol has a different molecular form in water than it has in cyclohexane.

This conclusion is not a contradiction of that deduced from the distribution ratio if the presence of a small amount of a third liquid is sufficient to change the alcohol to simple molecules in the cyclohexane phase or to associated molecules in the water phase. This hypothesis is supported by the peculiar behavior of the system on addition of alcohol when the

[10] Pickering, *J. Chem. Soc.*, **63**, 998 (1893).

[11] Pictet, *Compt. rend.*, **119**, 678 (1894).

[12] Hildebrand, "Solubility," Am. Chem. Soc. Monograph, Chemical Catalog Co., New York, 1924, p. 160.

alcohol content is low. This is just the region where the value of the distribution ratio should be most nearly constant since the solutions are extremely dilute. Actually, however, it is in this region that the values of the distribution ratio would be changing most rapidly if a sufficiently delicate analytical method could be devised for determining the concentration of the alcohol in the cyclohexane so as to permit calculation of the ratio.

The peculiar dip in the curve of refractive index against weight per cent. of alcohol is possibly another indication of the validity of the assumption. Since refractive index depends not only on density but also on molecular complexity of the solution, this variation may indicate some change taking place in the molecular form of the dissolved alcohol. In any event, whether the explanation is correct or not, the fact remains that depression of the freezing point and calculation of distribution ratios cannot always be used as interchangeable methods for the determination of molecular form.

It is of interest to compare this system with the similar system ethyl alcohol–benzene–water[13] from the standpoint of differences in physicochemical properties of the various liquids involved. In general the phenomena are very similar for the two systems. Ethyl alcohol appears to be associated in benzene as it is in cyclohexane, judging from the results of freezing point data. In both systems the value of the distribution ratio for alcohol distributed between water and the hydrocarbon decreases as the concentration of alcohol is increased. In the cyclohexane system, however, much larger concentrations of alcohol are required to bring about formation of a one-phase solution than are required in the benzene system.

Comparison of physical properties shows that benzene has a relative internal pressure of 6.48[14] and cyclohexane of 5.56,[15] both calculated from surface tension divided by molecular volume to the one-third power. Alcohol and water, on the other hand, are both liquids of high internal pressure. According to the modern conception substances having like values of internal pressure are most soluble in each other and tend to form the more perfect solutions. Thus, ethyl alcohol and water are completely miscible while water and the hydrocarbons are but sparingly soluble. Ethyl alcohol and cyclohexane are completely soluble above $-15°$[16] but below this temperature form a two-phase system, indicating a large variation from ideality. Thus it is to be expected that more of the alcohol dissolves in the water phase than in the hydrocarbon phase in distribution experiments.

[13] Washburn, Hnizda and Vold, THIS JOURNAL, **53**, 3237 (1931).
[14] Hildebrand, Ref. 12, p. 111.
[15] Jones and Betts, *J. Chem. Soc.*, 1177 (1928).
[16] Jones and Amstell, *ibid.*, 1316 (1930).

Furthermore, addition of a third liquid of intermediate internal pressure increases the solubility of two liquids of greatly different internal pressures since each dissolves more in the third liquid than it could in the other. Thus, the increased solubility of water in cyclohexane and of cyclohexane in water is predicted by this theory since the internal pressure of alcohol is intermediate between those of cyclohexane and water. In addition, the fact that a greater concentration of alcohol is required to bring about complete solubility in the case of the cyclohexane system than in the case of the benzene system may be qualitatively predicted from the fact that cyclohexane has a lower relative internal pressure than benzene.

Consideration of the relative magnitudes of dielectric constant and entropy of vaporization, both measures of the relative polarity of a liquid, leads to identically the same qualitative conclusions as in the case of internal pressure. By both measurements water is by far the most polar liquid, alcohol next, benzene low and cyclohexane very low. Liquids of the same degree of polarity tend to be most soluble in each other and therefore the same conclusions may be drawn concerning the relative solubility relations as have been discussed under internal pressure.

This work is being continued on similar systems and certain related properties such as vapor pressures, viscosities and heat and volume changes on mixing are being studied.

Summary

1. The equilibrium concentrations of ethyl alcohol, cyclohexane, and water in single phase saturated ternary solutions at 25° have been determined.

2. The tie lines for the system have been determined and the values of the distribution ratio for ethyl alcohol distributed between water and cyclohexane calculated.

3. The freezing point curve for solutions of ethyl alcohol in cyclohexane up to sixteen weight per cent. alcohol has been determined.

4. It has been shown that lowering of the freezing point and distribution experiments cannot always be used interchangeably in the determination of molecular form in solution.

5. It has been shown that the observed solubility relations can be qualitatively predicted from the physico-chemical properties of the three components.

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