vapor systems may be examined in the presence of a compressed gas. Such measurements have been made to a temperature of 250° and pressures to 300 atmospheres for the nitrogen–water system.

As predicted by Keunen and others, the solubility of nitrogen in water passes through a minimum point. This occurs in the neighborhood of 70 to 80°. Pressure causes a decided increase in the amount of dissolved nitrogen but Henry's law does not explain this effect quantitatively.

The concentration of water vapor in a given volume of the compressed gases is decidedly greater than that calculated by the usual methods. This effect increases with both temperature and pressure.

A method for the determination of the vapor phase density and compressibility is presented. The vapor density decreases with rising temperature at constant pressure. At temperatures above 150° where the concentration of water vapor in the gas phase reaches fairly large values, an additive rule for the calculation of the compressibility coefficient of the mixture does not hold.

It appears that liquid phase density measurements should be made in order to test the applicability of Poynting's relation in calculating the vapor phase compositions from the compressibility of the solution. They would also permit a test of the constancy of Ostwald's distribution coefficient calculated on a volume basis.

URBANA, ILL. RECEIVED OCTOBER 9, 1933

[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE UNIVERSITY OF NEBRASKA]

A Study of Solutions of Methyl Alcohol in Cyclohexane, in Water and in Cyclohexane and Water

BY E. ROGER WASHBURN AND HOWARD C. SPENCER

Recent work has been concerned with the solubility relationships involved in ternary systems of water, an alcohol and a hydrocarbon.[1] The present investigation, using water, methyl alcohol and cyclohexane, is a part of this systematic study of solubility behavior.

Materials

Water.—Distilled water of conductivity grade was used throughout the work.

Methyl Alcohol.—Synthetic methyl alcohol obtained from Merck and Company was refluxed over freshly burned lime and then fractionally distilled from an all-glass apparatus. The final product had a specific gravity of d_4^{25} 0.78673 and a refractive index of n_D^{25} 1.32660.

Cyclohexane.—The cyclohexane was the best grade obtainable from the Eastman Kodak Company. This was subjected to repeated alternate fractional crystallizations and distillations. Finally, it was dried over sodium and distilled from an all-glass apparatus. The best sample had a specific gravity of d_4^{25} 0.77354, a refractive index of n_D^{25} 1.42370, and a freezing point of 6.10°. Samples of slightly lower specific gravity were found to give the same results as the better grade in solubility determinations and were used in a few cases.

Experimental

Determination of the Ternary Solubility Curves.—The ternary solubility curves were determined in a manner similar to the procedure used in previous investigations of such systems.[1] The flask containing the weighed amounts of two of the liquids was suspended in a hand controlled water-bath and the third liquid added by means of a "medicine dropper" which was thrust through a cork stopper substituted for the ground-glass stopper of the flask. The use of this apparatus reduced the loss from evaporation to a minimum, and also made it possible to introduce very small amounts of the titrating liquid. The flask was shaken after each addition of the third liquid and sufficient time allowed for equilibrium to be reached. In order to ensure complete saturation near the end-point, the bath was warmed a few tenths of a degree so that complete solution occurred and then cooled to exactly 24.8°.

Representative results of these titrations are tabulated in Table I and are shown graphically in Fig. 1. Titrations numbered 1 to X form one of the curves, while Y, 12, and 13 form the other curve which when drawn to scale is hardly discernible in the figure. The composition is expressed in terms of weight per cent. rather than the more common mole per cent. or mole fraction since in these solutions the molecular form of the components is not known.

While methyl alcohol and water are miscible in all proportions at 25° and water and cyclohexane are practically immiscible, methyl alcohol has *only a limited miscibility with cyclohexane.* The

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[1] Washburn, Hnizda and Vold, THIS JOURNAL, **53**, 3237 (1931); Vold and Washburn, *ibid.*, **54**, 4217 (1932).

TABLE I

SOLUBILITIES OF METHYL ALCOHOL, CYCLOHEXANE AND WATER AT 25°

No.	C_6H_{12}, g.	CH_3OH, g.	H_2O, g.	Refr. index
1	0.0125	2.8555	9.8755	1.33838
2	.0294	5.4948	9.9300	1.34083
3	.0555	7.7729	9.9073	1.34167
4	.1103	7.7508	4.9642	1.34117
5	.3263	13.2856	4.9529	1.33953
6	.2760	7.0175	1.8852	1.33876
7	.4788	8.6026	1.8672	1.33860
8	.8520	11.1167	1.8965	1.33838
9	.9519	8.6042	0.9519	1.33911
10	1.4762	8.1968	.5204	1.34106
11	1.8943	7.8472	.3786	1.34388
12	2.9639	7.7553	.1342	1.34963
X	(35.55 wt.%)	(64.45 wt.%)		
Y	(96.22 wt.%)	(3.78 wt.%)		
13	8.7854	0.1404	.0397	1.42259
14	7.6861	.0704	.0142	1.42262
	Water saturated with cyclohexane			1.33255
	Cyclohexane saturated with water			1.42348

critical solution temperature of the binary system methyl alcohol–cyclohexane has been investigated by Jones and Amstell.[2] Since solubilities at 25° are not recorded, these were determined by graphical interpolation of data obtained by the method of Jones and Betts.[3] Points X and Y recorded in Table I were determined in this way.

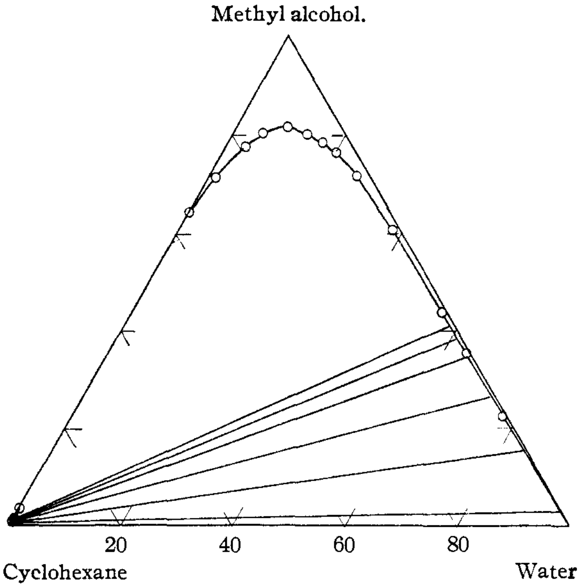

Fig. 1.—Concentration in wt. %.

Titrations 1, 2 and 3 were very difficult to determine since a very small amount of cyclohexane caused phase separation. Likewise, 13 and 14 were difficult due to the small amount of water that might be added before the end-point was reached. Nevertheless, the real value of these determinations lies in their use in determining the curve in Fig. 2, in which refractive index is plotted against weight per cent. alcohol. Even if a small excess of the titrating liquid should be present, the refractive index of the solution would not be affected, and, in turn, the curve in Fig. 2 would be unchanged.

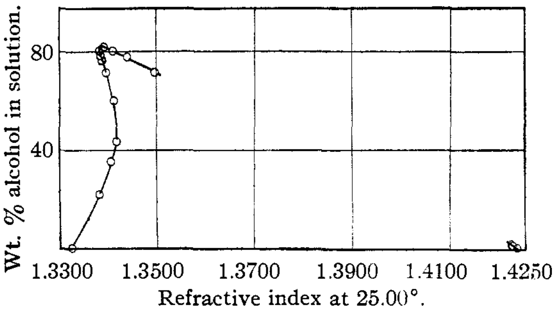

Fig. 2.—Methyl alcohol–cyclohexane–water.

After each titration was made the refractive index of the equilibrium mixture was taken by means of an immersion refractometer, which was dipped directly into a thermostatically controlled water-bath maintained at 25.00 ± 0.05°. The results are tabulated in Table I and shown graphically in Fig. 2. The refractive index of water saturated with cyclohexane is the first point on the left-hand side of the curve, and the refractive index of cyclohexane saturated with water lies farthest to the right. As the per cent. of alcohol in the water-rich portion of the curve is increased, there is a decided dip in the curve. This phenomenon has been observed in similar systems.[1] This curve is continuous until it terminates at the point of saturation of alcohol with cyclohexane and then it continues from the point of saturation of cyclohexane with alcohol.

Distribution of Methyl Alcohol between Water and Cyclohexane.—The tie-lines were determined as recorded in previous investigations. The distribution ratio was found by merely taking the quotient of the weight per cent. of alcohol in the water-rich layer divided by the weight per cent. of alcohol in the cyclohexane-rich layer. The results are given in Table II, and are plotted in Fig. 1.

Freezing Point Studies.—This investigation is necessarily quite restricted since at the freezing point of cyclohexane, methyl alcohol is only soluble in this solvent to the extent of approxi-

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(2) Jones and Amstell, *J. Chem. Soc.*, 1316 (1930).

(3) Jones and Betts, *ibid.*, 1177 (1928).

TABLE II

SUMMARY OF DATA ON TIE-LINES

In all cases the alcohol was distributed between approximately 20 cc. of water and 20 cc. of cyclohexane.

No.	Total cc. CH_3OH added	Refr. ind. of water layer	Wt. % CH_3OH	Refr. ind. of cyclohexane layer	Wt. % CH_3OH	Distribution ratio
A	1	1.33346	3.2	1.42345	0.05	64
B	5	1.33662	15.1	1.42331	.25	60
C	10	1.33934	26.8	1.42324	.40	67
D	15	1.34075	34.9	1.42317	.50	70
E	20	1.34127	38.8	1.42306	.65	61
F	25	1.34144	41.8	1.42302	.70	60

mately 1.1 weight per cent. of alcohol. In the determination of the freezing points of solutions of methyl alcohol in cyclohexane the standard Beckmann apparatus was used.

The familiar equation for the determination of the molecular weight of a solute by the depression of the freezing point was used.[1]

The molal freezing point constant was taken as 20. This is the value given in the "International Critical Tables,"[4] and is the average value obtained from a large number of experimental determinations by Mascarelli and his associates.[5] Many solutes including naphthalene and normal hexane gave a value of 20 for the molal freezing point constant of cyclohexane as a solvent. However, data on this point are conflicting, and in an earlier paper this constant was calculated to be 14 on the basis of data given by Mascarelli and Pestalozza for solutions of benzene in cyclohexane and the data of Baud[6] for solutions of ethylene dibromide in cyclohexane. Nevertheless, the preponderance of data undoubtedly favors the value 20.

The results are tabulated in Table III. In Fig. 3 there is given a graphical representation of the variation between the actual lowering of the freezing point of the cyclohexane by the addition of methyl alcohol (Curve A) and the calculated depression (Curve B) for such solutions.

TABLE III

FREEZING POINTS OF METHYL ALCOHOL-CYCLOHEXANE SOLUTIONS

No.	Wt. % CH_3OH in C_6H_{12}	Obs. depression, °C.	Calcd. depression, °C.	App. mol. wt. of alc.
1	0.21	0.35	1.32	121
2	.28	.50	1.75	112
3	.36	.65	2.26	111
4	.65	1.03	4.09	127
5	.75	1.10	4.72	137
6	1.11	1.42	7.02	158

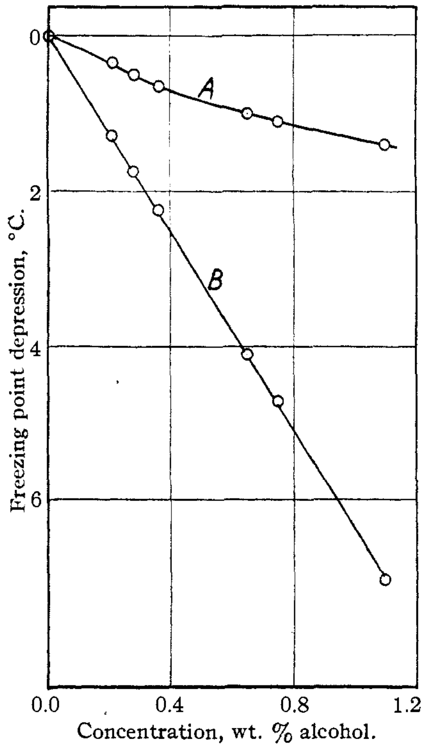

Fig. 3.—Methyl alcohol-cyclohexane: Curve A, observed depression; Curve B, calculated depression.

Discussion

A nearly constant distribution ratio may indicate that methyl alcohol has the same molecular form in the water saturated with cyclohexane layer as it has in the cyclohexane saturated with water layer.

Although all variations from the freezing point law cannot be attributed to association of the solute,[7] the results obtained in the study of the freezing points of solutions of methyl alcohol in cyclohexane indicate that the alcohol is highly associated. However, methyl alcohol in water solution is normal over a large concentration range.[8]

Thus, the conclusion from the experimental facts must be that methyl alcohol has a different molecular form in pure water than it has in pure cyclohexane, but that the difference is lessened when the alcohol-water mixture contains cyclo-

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(4) "International Critical Tables," The McGraw-Hill Book Co., Inc., New York, 1928, Vol. IV, p. 183.

(5) Mascarelli and Benati, *Gazz. chim. ital.*, **37**, II, 527 (1907); Mascarelli and Pestalozza, *ibid.*, **38**, I, 38 (1908); Mascarelli and Benati, *ibid.*, **39**, II, 642 (1909); Mascarelli and Musatty, *ibid.*, **41**, II, 73 and 82 (1911).

(6) Baud, *Ann. chim. phys.*, **29**, 124 (1913).

(7) Hildebrand, "Solubility," The Chemical Catalog Co., New York, 1924, p. 160.

(8) Pickering, *J. Chem. Soc.*, **63**, 998 (1893).

hexane or the alcohol–cyclohexane mixture contains water.

A study of the polarity of the liquids used may throw some light on their solubility behavior. It is generally accepted that polar liquids are soluble in polar liquids, and non-polar liquids are miscible in each other, while substances distinctly non-polar are immiscible in polar liquids. Thus the highly polar nature of water and the lesser polarity of methyl alcohol as compared with the extremely non-polar nature of cyclohexane may account for the miscibility of methyl alcohol and water, the immiscibility of water and cyclohexane, and the partial miscibility of methyl alcohol and cyclohexane.

In considering the ternary systems consisting of water, an alcohol and a hydrocarbon, the liquids may be listed in the order of their dielectric constants: water 81, methyl alcohol 33.1, ethyl alcohol 26, benzene 2.28 and cyclohexane 2.05.[9]

By distribution experiments the greater amount of the alcohol is found in the water-rich layer in each case. The alcohol thus functions chiefly in tending to bring the polarity of the water nearer to that of the hydrocarbon. Since methyl alcohol is more polar than ethyl alcohol, it might be expected that there would be a greater area beneath the binodal curve in the case of methyl alcohol–cyclohexane–water than with ethyl alcohol–cyclohexane–water.[1] This is substantiated by experiment. Similarly, the binodal curve for methyl alcohol–benzene–water[10] is higher than that for ethyl alcohol–benzene–water.[1]

Since benzene is slightly more polar than cyclohexane, the binodal curves of the two systems containing cyclohexane are above those containing benzene.

If these binodal curves are re-drawn, the concentration being expressed in mole per cent. using the usual molecular weights rather than in weight per cent., these differences are even more pronounced.

Summary

1. The equilibrium concentrations for the system methyl alcohol–cyclohexane–water at 25°, and tie-lines for this system have been determined.

2. The freezing point curve for solutions of methyl alcohol in cyclohexane has been determined.

3. It has been shown that a consideration of polarity gives a means of locating in a relative manner the binodal curves of some analogous ternary systems.

[9] "International Critical Tables," The McGraw-Hill Book Co., Inc., New York, Vol. VI, 1928, pp. 83–91.

[10] Barbaudy, *Compt. rend.*, **182**, 1279 (1926).

LINCOLN, NEBR. RECEIVED OCTOBER 13, 1933

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

The Thermal Reaction between Chlorine Trioxide and Ozone

BY G. K. ROLLEFSON AND A. C. BYRNS

Some time ago an investigation of the chlorine sensitized photochemical decomposition of ozone was started in this Laboratory. The preliminary experiments indicated that the system involved several parallel reactions so our attention has been concentrated on the isolation and study of these component reactions. The first indication that one of these could be isolated came from a study of the pressure change *vs.* time curves obtained when mixtures of chlorine and ozone were illuminated with blue light. These curves showed a marked decrease in the rate with time of illumination similar to that reported by Heidt, Kistiakowsky and Forbes.[1] At the same time a comparison of the oxygen pressure as calculated from the pressure change with the value obtained by freezing out all the other gases with liquid air revealed that much more oxygen was being formed than corresponded to the observed pressure change. Obviously this indicated the presence of another reaction which was causing a pressure decrease. A typical run illustrating this behavior is given in Table I. An examination of the

TABLE I

Initial Cl_2, 61 cm.; initial O_3, 69 cm.

Time, min.	Δp	O_2 from Δp	O_2 from freeze-out	Difference
90	7.49	22.5	40.6	18.1
175	11.97	35.9	67.3	31.4
220	14.90	44.7	82.8	38.1

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[1] Heidt, Kistiakowsky and Forbes, THIS JOURNAL, **55**, 223 (1933).