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

The Ternary System: Isopropyl Alcohol, Toluene and Water at 25°

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Continuing a series of previously described investigations[2] of similar systems, solubility and distribution studies have been carried out with the system isopropyl alcohol, toluene and water at 25.0°.

Materials.—Carefully purified water was used. It was prepared by the partial condensation of steam from an alkaline permanganate solution.

The toluene was the better of the two grades obtainable from the Eastman Kodak Company. As efforts to purify this material further failed to alter its physical constants it was used as received. The specific gravity $d^{25}{}_4$ was 1.4938.

The isopropyl alcohol, from Eastman Kodak Company, was refluxed for many hours with fresh lime. It was then distilled into a carefully dried all glass still from which it was fractionally distilled. The middle portion of the distillate, boiling from 81.7 to 81.9° was used. It had a specific gravity $d^{25}{}_4$ of 0.78087 and a refractive index $n^{25}{}_D$ of 1.3748.

Procedure and Results.—The details of the experimental work which seem to different workers to be most suitable for different ternary systems differ so that it is hardly possible to state that one system was studied by a previously described procedure and give an entirely truthful impression. The procedure followed in this investigation was like that described previously[3] with the following modifications. The titrations were carried out at 25.0° in small Erlenmeyer flasks which were shaken mechanically in the constant temperature bath except when additions of water or toluene were made from weight pipets. The values obtained with toluene as a titrant agreed with those obtained with water as the added liquid as closely as the water titrations agreed with each other. Preliminary titrations were carried out with materials not of the highest purity so that in the final titrations dropwise addition of all but the last few tenths of a gram of titrant was avoided.

The appearance of the end-point varied with different proportions of alcohol and toluene in the liquid titrated. At the lower end of the water rich part of the binodal curve relatively large droplets of the second phase appeared at the end-point; both phases appeared perfectly clear even after separation. As points further up on the curve were determined the droplets of the toluene rich phase separating out at the end-point became smaller and smaller until at an alcohol concentration of about 35% the mixture had the appearance of a fine mist. Above about 43% alcohol across the top of the curve and down to about 42% alcohol on the toluene rich side a still finer state of subdivision, a "milkiness," appeared at the end-point. In this region the first indication that the end-point was being approached was an opalescence, probably like that noted on cooling certain two component systems just before they separate into two liquid phases at the critical temperature. The remainder of the toluene rich side presented end-points similar to those on the lower part of the water rich side.

The end-points consisting of droplets and mists were easily observed by looking through the solution at a light bulb behind the bath. The "milky appearing" end-points were studied by light reflected from smooth black background suspended back of the titration flask. It was necessary to have the water-bath filled with very clear water when these titrations were carried out.

A special technique was developed in order to obtain reproducible results for the extreme lower ends of the solubility curve or more particularly for the important first and last parts of the refractive index–concentration curves used for the analysis. Flasks presenting a very small air space were employed since the amount of titrant used to saturate the air was important. The amounts of the first two liquids added to the small flasks were determined by weight, and the third liquid was added drop by drop from a fine pipet. The weight was determined from the number of drops added. The flask was carefully stoppered and if after about an hour the third liquid had all dissolved the process was repeated with one more drop of titrant.

The refractive indices of these saturated solu-

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[1] Present address: Eastman Kodak Company, Rochester, New York.

[2] See THIS JOURNAL, **61**, 1694 (1939).

[3] THIS JOURNAL, **54**, 4217 (1932); **56**, 361 (1934); **61**, 1694 (1939).

tions were determined with an Abbe refractometer at a temperature of 25.00 ± 0.01°. Representative values are listed in Table I. The concentrations determine the solubility curve in Fig. 1. Only the values marked with an asterisk are plotted.

TABLE I

SOLUBILITIES AND REFRACTIVE INDICES AT 25.0°

Wt. % toluene	Wt. % alcohol	Refractive indices	Wt. % toluene	Wt. % alcohol	Refractive indices
0.13	4.25	1.3359	27.73	50.89	1.4032
* .18	10.76	1.3419	*33.50	49.61	1.4102
.30	16.50	1.3473	37.36	48.14	1.4148
* .38	23.40	1.3530	*42.70	45.59	1.4213
*1.07	30.16	1.3583	47.09	42.55	1.4266
1.88	34.38	1.3616	*52.63	39.05	1.4332
*4.22	39.44	1.3669	59.28	34.30	1.4415
6.75	43.64	1.3724	*68.72	27.45	1.4525
*10.74	47.53	1.3789	75.50	21.76	1.4619
14.13	49.57	1.3845	*82.43	15.97	1.4703
*18.27	51.01	1.3906	*88.48	10.64	1.4784
*22.55	51.17	1.3963	95.30	4.31	1.4878

Toluene saturated with water 1.4937
Water saturated with toluene 1.3322

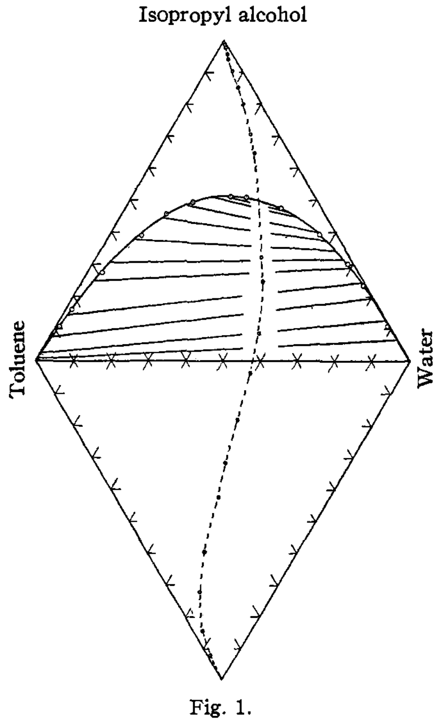

Fig. 1.

The tie lines were determined by adding varying amounts of alcohol to two liquid phase water–toluene mixtures. The amounts of alcohol were kept below that necessary to bring about complete miscibility. The mixtures were shaken from time to time during the twenty-four hours they were kept in the constant temperature bath. The deep but narrow flasks used for this work were constructed from 25-mm. test-tubes and 6-mm. glass tubes fitted with glass stoppers. The refractive index of each of the layers in the equilibrum mixture was determined. The concentration of these solutions was then read from large curves obtained by plotting refractive index against concentration for each of the three components in the saturated solutions. The fact that the sum of the percentages of the three components in each of the layers equaled 100.0 ± 0.1 indicates something of the precision of the analysis. Similar precision by these methods is not possible in several of the ternary systems that we have studied. Typical values are given in Table II and the marked values are used in locating the tie lines and the conjugation curve in Fig. 1. The intersection of the conjugation curve with the solubility curve locates the plait point.

TABLE II

REFRACTIVE INDICES AND CONCENTRATIONS OF ALCOHOL IN CONJUGATE SOLUTIONS AT 25.0°

Water layer			Toluene layer		
Refractive index	Wt. % alcohol	Wt. % water	Refractive index	Wt. % alcohol	Wt. % toluene
1.3383	6.87	93.12	*1.4925	0.89	99.14
1.3433	12.16	87.54	*1.4905	2.27	97.64
1.3501	19.77	79.95	*1.4829	7.45	91.84
1.3537	24.14	75.34	*1.4729	14.34	84.30
1.3574	29.00	69.98	*1.4570	24.90	71.90
1.3591	31.40	67.35	*1.4477	30.62	64.35
1.3616	34.34	64.20	*1.4351	37.90	54.20
1.3646	37.40	59.64	*1.4234	44.23	44.35
1.3675	39.92	55.75	*1.4137	48.57	36.35
1.3702	42.10	52.32	1.4088	49.95	32.60
1.3730	44.13	48.78	*1.4023	51.00	27.16
1.3739	44.73	46.80	1.4013	51.05	26.40
1.3769	46.50	44.00	*1.3972	51.20	23.56

If the solubility curve for this system is compared with those for the systems containing methyl alcohol[4] and ethyl alcohol[2] in place of isopropyl alcohol, certain interesting differences will be observed. The isopropyl alcohol is the most efficient and the methyl alcohol is least efficient in bringing about miscibility in toluene–water systems. The maximum amounts (wt. %) of the alcohols necessary to bring about homogeneity are isopropyl 51, ethyl 57, methyl 67.5. When the curves are plotted with mole % instead of wt. % the differences become even greater, isopropyl 41, ethyl 47, methyl 68.

(4) L. S. Mason and E. Roger Washburn, THIS JOURNAL, 59, 2076 (1937).

Beech and Glasstone[5] came to the same conclusion in regard to the relative efficiency of these alcohols in bringing about miscibility of ethyl acetate and water although a simple study of their binodal curves alone does not indicate the relation.

Methyl alcohol has the highest values for internal pressure, dielectric constant and dipole moment, and isopropyl alcohol has the lowest values for these constants among these alcohols. Since water has very high values and toluene very low values we may consider that the above solubility studies support the idea that liquids of high internal pressure and polarity tend to "squeeze out" relatively non-polar liquids.

A comparison of the tie lines is also interesting. The alcohols dissolve chiefly in the water layer, especially when they are present in relatively small proportions. As the amounts of the alcohols increase, increasing proportions are found in the toluene layer. The proportion of ethyl alcohol in the toluene layer increases more rapidly with increasing proportions of alcohol than is noted with methyl alcohol, but the proportion of isopropyl alcohol increases most rapidly of all. This increase in the case of isopropyl alcohol continues to such an extent that a horizontal tie line finally results, after which more alcohol is found in the toluene layer than in the water layer.

Inasmuch as the alcohols have values of internal pressure, etc., nearer to the values for toluene than to the values for water, we might expect more alcohol to be found in the toluene layer. The isopropyl alcohol, however, is most like toluene, and the relatively greater tendency which it has to enter the toluene is what would be expected.

Summary

The solubility relationships for the ternary system toluene, isopropyl alcohol and water have been determined at 25.0°.

The refractive indices of these saturated solutions have been determined and used to study the distribution of isopropyl alcohol between toluene and water at 25.0°.

This system has been briefly compared with similar systems containing methyl and ethyl alcohols in place of isopropyl alcohol.

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(5) D. G. Beech and S. Glasstone, *J. Chem. Soc.*, 67 (1938).

[CONTRIBUTION FROM COLUMBIA UNIVERSITY]

The Vapor Pressures, Heats of Vaporization and Melting Points of N^{14} and N^{15} Ammonias

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It has been observed previously[1,2] that the nitrogen isotopes are concentrated to a slight extent by the distillation of liquid ammonia, indicating that the N^{14} ammonia has the higher vapor pressure. However, the vapor pressure difference between N^{14} and N^{15} ammonia can now be measured directly since high concentrations of N^{15} have been obtained.[3] In this paper a simple apparatus is described for measuring the vapor pressure difference between two isotopic samples of liquid ammonia. With this apparatus the vapor pressure difference, and the difference in melting points between ordinary NH_3 and 70.6% $N^{15}H_3$, have been measured and the results reported.

Experimental

The ammonia used in this investigation was prepared by the action of a saturated solution of potassium hydroxide on C. P. ammonium chloride. The gas was subjected to preliminary drying by passing it through a vertical glass column containing potassium hydroxide pellets. The ammonia was then condensed over sodium in one of a series of distillation bulbs. About 1 g. of NH_3 was treated in this way. Following each distillation the sample was cooled to the temperature of liquid nitrogen and the apparatus was then evacuated to 10^{-4} mm. or better. The 70.6% $N^{15}H_3$ samples were treated in a similar manner, except that the original samples had to be recrystallized from ethyl alcohol to remove traces of amines which concentrated along with the N^{15} in the chemical separation process. The samples were considered pure when further purification produced no change, within experimental error, in the vapor pressure difference between the two samples.

The apparatus is shown diagrammatically in Fig. 1. It consists of an 8-mm. glass tube C, divided into two com-

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(1) M. K. Wahl, J. R. Huffman and J. Hipple, *J. Chem. Phys.*, **3**, 434 (1935).

(2) H. C. Urey and A. H. W. Aten, Jr., *Phys. Rev.*, **50**, 575 (1936).

(3) H. G. Thode and H. C. Urey, *J. Chem. Phys.*, **7**, 34 (1939).