ion. The other two formed compounds which have been compared with those of ethylenediamine.

The dichloro salts $[\mathrm{Co\ tn_2Cl_2}]\mathrm{Cl}$ and $[\mathrm{Co\ dan_2Cl_2}]\mathrm{Cl}$, which could be obtained only in the *trans* form, are more soluble in water and alcohol than is the analogous ethylenediamine compound. They react with water almost instantly. The mixed salt $[\mathrm{Co\ en\ tnCl_2}]\mathrm{Cl}$ is intermediate in properties between $[\mathrm{Co\ en_2Cl_2}]\mathrm{Cl}$ and $[\mathrm{Co\ tn_2Cl_2}]\mathrm{Cl}$.

The luteo type salts $[\mathrm{Co\ tn_3}]\mathrm{Cl_3}$, $[\mathrm{Co\ dan_3}]\mathrm{Cl_3}$ and $[\mathrm{Co\ en\ tn\ dan}]\mathrm{Cl_3}$ are much more soluble in water than is $[\mathrm{Co\ en_3}]\mathrm{Cl_3}$. Unlike most luteo cobaltic salts, they are pink in the solid state.

The mixed salt $[\mathrm{Co\ en\ tn\ dan}]\mathrm{Cl_3}$ is the first coördination compound which has been prepared having molecules of three different diamines attached to a single metallic ion.

URBANA, ILLINOIS RECEIVED JULY 31, 1944

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

The Ternary System: *t*-Butyl Alcohol, Benzene and Water at 25°

BY DAVID R. SIMONSEN[1] AND E. ROGER WASHBURN

A number of investigations[2,3,4,5,6] have been made of ternary systems involving an alcohol, benzene and water with the purpose of increasing our knowledge of solubility and distribution behavior. The system *t*-butyl alcohol, benzene and water, is also of interest because of some of the unique properties of the alcohol. It has the highest molecular weight of the monohydroxy saturated alcohols which are completely miscible with water at 25°. The other butyl alcohols have definitely higher dielectric constants, each about 18, while *t*-butyl alcohol has a dielectric constant of 11.8 and yet it is the only butyl alcohol completely miscible with water at 25°.

Measurements were made of the specific gravities and relative viscosities of saturated solutions throughout the complete range of concentration. Thus a calculation of the changes in volume and fluidity resulting from the mixing of these liquids was possible. As in previous investigations refractive indexes of saturated solutions were measured in order to provide a means of quickly analyzing the conjugate solutions formed when insufficient alcohol was present to bring about homogeneity of the liquid phases.

Materials

The *t*-butyl alcohol was obtained from Eastman Kodak Company. It was recrystallized several times with constant shaking. The final, constant, values of freezing point, specific gravity and refractive index for the alcohol used in this study are recorded in Table I. Evidence of a second crystalline form of this alcohol with a freezing point of 25.0° was obtained several times during the purification. This has been observed by other workers[7,8] although they do not indicate the freezing points of the two forms.

Benzene of reagent quality from Coleman and Bell was dried with sodium and slowly distilled. The middle fraction was slowly recrystallized several times until the constants listed in Table I were obtained.

Redistilled water was used.

TABLE I

Material	Specific gravity, d^{25}_4	Refractive index, n^{25}_D	Freezing point, °C.
t-Butyl alcohol	0.78043	1.38483	25.66
Benzene	.87366	1.49807	5.53

Procedure and Results

The ternary solubility curve was determined by titrating to the appearance of a second phase in a method similar to that described previously.[2,3,4] The titrations were carried out in 50 ml. volumetric flasks which were mounted in a mechanical shaker in a constant temperature bath. The temperature of the bath was controlled to ±0.04°. The capillary-tipped pipets from which water was added as the titrant were coated with bakelite lacquer, so that very small drops (about 5 mg.) could be added. When benzene was added as the titrant, untreated droppers were used which produced drops weighing around 4 mg. Titrations were handled so that less than 50 mg. of the titrant was added dropwise, thereby lessening evaporation losses. An hour of shaking after the addition of the last drop was considered sufficient in all cases for complete saturation.

The measurements of specific gravities and relative viscosities were made on the same solutions but a different series of titrations was carried out to provide solutions for the refractive indexes. The measurements were made immediately after each of the titrations. An Abbe refractometer was used in determining the refractive indexes. Glass-stoppered, capillary-stemmed pycnometers having a capacity of 5 ml. were used in the determinations of the specific gravities. Viscosity measurements were made by the use of two ordinary Ostwald viscometers. These values are recorded in Tables II and III. An immersion re-

---

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

[2] Washburn, Haizda and Vold, THIS JOURNAL, **53**, 3237 (1931).

[3] Washburn and Strandskov, *J. Phys. Chem.*, **48**, 241 (1944).

[4] Alberty and Washburn, *ibid.*, **49**, 4 (1945).

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

[6] Olsen and Washburn, THIS JOURNAL, **57**, 303 (1935).

[7] Atkins, *J. Chem. Soc.*, **99**, 10 (1911).

[8] Getman, THIS JOURNAL, **62**, 2179 (1940).

fractometer was used with the pure materials to obtain the values listed in Table I.

TABLE II

SOLUBILITIES AND REFRACTIVE INDEXES AT 25.0°

Wt. % alcohol	Wt. % benzene	Refractive index	Wt. % alcohol	Wt. % benzene	Refractive index
9.90	89.63	1.4830	49.61	7.62	1.3805
20.03	78.49	1.4687	39.67	4.06	1.3709
29.47	67.44	1.4552	29.74	1.84	1.3622
39.41	54.94	1.4402	20.01	0.52	1.3537
49.60	40.09	1.4233	15.01	.41	1.3487
54.81	30.51	1.4125	9.88	.27	1.3433
57.09	24.29	1.4050	Benzene satd. with water		1.4978
57.68	21.67	1.4018			
57.94	18.65	1.3979	Water satd. with benzene		1.3330
56.40	12.92	1.3904			

TABLE III

SOLUBILITY, SPECIFIC GRAVITY, VISCOSITY, CHANGE IN VOLUME, DEVIATION IN FLUIDITY

Wt. % alcohol	Wt. % benzene	d^{25}_4	Relative viscosity	% Change volume	% Deviation fluidity
0.00	99.93	0.8736	0.674	+0.026	+ 0.02
9.76	89.74	.8614	.687	+ .31	+ 8.44
15.74	83.31	.8553	.719	+ .37	+10.65
21.77	76.38	.8500	.779	+ .40	+ 9.64
29.48	67.37	.8441	.885	+ .36	+ 6.61
39.45	54.83	.8383	1.122	+ .20	− 2.65
49.65	40.00	.8362	1.616	− .24	−18.61
57.14	24.32	.8422	2.604	− .76	−38.42
57.95	19.00	.8483	3.117	−1.04	−45.65
56.02	12.38	.8630	3.881	−1.50	−54.86
48.73	7.24	.8878	4.463	−1.95	−62.69
39.76	4.24	.9135	4.449	−2.23	−65.81
30.02	1.90	.9406	3.543	−2.39	−61.20
20.24	0.51	.9648	2.602	−2.21	−52.39
10.14	.26	.9817	1.681	−1.26	−33.96
0.00	.15	.9970	1.001	−0.01	− 0.18
0.00	100.00	.8737	0.6743	.....	.....
100.00	0.00	.7804	4.970	.....	.....

The changes in volume were calculated on the basis of the differences between the actual volumes of mixtures and the sum of the volumes of the components used to form the mixtures. The deviations in fluidity are the differences between the actual fluidities of the solutions and the fluidities calculated from the fluidities of the pure components and the volume compositions of the solutions. The differences are expressed in per cent. of the theoretical, or calculated, values.

Graphs were prepared showing how refractive index varied with the percentage of each of the components in the saturated solutions. The scale was such that 1.0 mm. represented 0.1% of the component and 0.0002 in refractive index. These curves were used to determine the compositions of the conjugate solutions formed in the study of distribution.

The mixtures forming the conjugate solutions were made up by adding calculated amounts of each component successively to 25 ml. glass-stoppered volumetric flasks. The total amount of each mixture was such that it could be effectively shaken in the flasks. The shaking, in an automatic shaker in a constant temperature bath, was continued until further shaking of the solutions caused no measurable change in the refractive indexes of either of the phases. The solutions were then allowed to remain quiet for about half an hour in order to permit the complete separation of the phases. The refractive indexes of the conjugate liquids were then measured and by comparison with the graphs previously mentioned their compositions were determined. These values are recorded in Table IV.

TABLE IV

REFRACTIVE INDEXES AND CONCENTRATIONS OF CONJUGATE SOLUTIONS AT 25.0°

Benzene layer			Water layer		
Refractive index	Wt. % alcohol	Wt. % benzene	Refractive index	Wt. % alcohol	Wt. % benzene
1.4968	0.65	99.22	1.3347	1.62	0.17
1.4944	2.24	97.56	1.3381	4.90	.22
1.4877	6.70	92.94	1.3428	9.40	.27
1.4715	17.98	80.79	1.3468	13.17	.33
1.4536	30.54	66.13	1.3488	15.08	.38
1.4381	40.76	53.13	1.3501	16.36	.40
1.4251	48.61	41.67	1.3512	17.44	.43
1.4121	54.97	30.18	1.3523	18.58	.47
1.3984	57.93	18.97	1.3548	21.23	.60
1.3883	55.37	11.72	1.3584	25.26	1.08
1.3831	51.78	8.88	1.3613	28.67	1.64

Discussion

The solubility curve of this system is similar to the solubility curves of other alcohol–benzene–water systems.[2,5,6] The curve is almost symmetrical and reaches a maximum at 58% alcohol and 19% benzene. The per cent. of alcohol in the mixture represented by the maximum in the solubility curve is the minimum concentration of alcohol which is capable of bringing about homogeneity of any mixture of benzene and water. For the other alcohol–benzene–water systems at 25° the minimum concentrations of alcohol in per cent. by weight are isopropyl 51,[6] ethyl 52,[2] methyl 62,[5] *n*-butyl 79[3] and isobutyl 83.[4] These figures show that isopropyl and ethyl alcohols are more effective than *t*-butyl alcohol in bringing about miscibility in benzene–water mixtures, but that *t*-butyl alcohol is better than methyl, *n*-butyl and isobutyl alcohols.

Curves representing the distribution of the different alcohols between the benzene and water phases are given in Fig. 1. The curves for methyl and ethyl alcohols show that in these systems the alcohols are present in greater proportions in the water phase for all concentrations of the alcohols while isobutyl and *n*-butyl alcohols are always in greater proportion in the benzene phase. Isopropyl and *t*-butyl alcohols, however, tre found mainly in the water phase at low concenarations of the alcohol and are present in greater proportion in the benzene phase at higher concentrations of alcohol. On a ternary diagram this change in distribution of the alcohol is shown by a change in sign of slope of the tie-lines. A change in sign of slope has also been observed in other isopropyl alcohol–hydrocarbon–water systems in which the hydrocarbon was benzene,[6] toluene,[9] cyclohexane[10] and cyclohexene.[11]

It may be noted in Fig. 1 that for the lower concentrations of alcohol all of the curves are concave upward in varying degrees of curvature. This means that in each of the systems as the concentration of the alcohol is increased there is a greater tendency for the alcohol to go into the benzene phase.

It has been shown[12] that, throughout the complete concentration range, binary mixtures of isopropyl alcohol and benzene show expansions in volume on mixing, and fluidities greater than those calculated from the equations of Bingham and Brown.[13] Binary mixtures of isopropyl alcohol and water show contractions in volume and lower than calculated fluidities throughout the concentration range.

It is therefore not entirely surprising that in Table III expansions in volume are noted when benzene and *t*-butyl alcohol made up 94% or more of the mixture while contractions resulted with lower concentrations of the organic liquids. Because of the lack of knowledge concerning the molecular units in these ternary systems it was not considered justifiable to make use of free volumes in the calculation of theoretical fluidities for the mixtures. The measured fluidities, however, are greater than those calculated for all ternary mixtures containing 97% or more of alcohol and benzene. When the combined percentage of organic liquids was less than 95%, however, the measured fluidities were less than the calculated values.

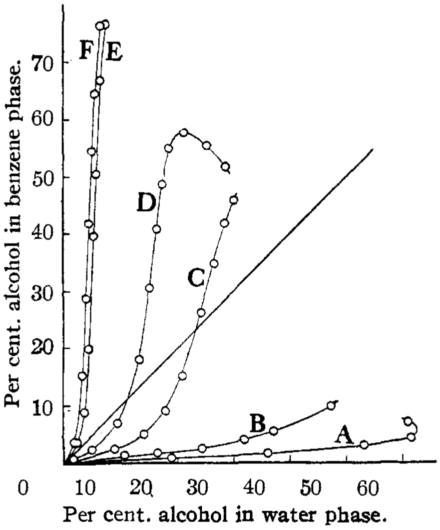

Fig. 1.—Distribution of alcohols between benzene and water at 25°: A, methyl alcohol; B, ethyl alcohol; C, isopropyl alcohol; D, tertiary-butyl alcohol; E, isobutyl alcohol; F, *n*-butyl alcohol.

The changes in volume and fluidities in the solutions resulting from the introduction of water seem disproportionately large compared with the amount of water introduced. Referring again to the binary solutions of isopropyl alcohol and water and isopropyl alcohol and benzene, we notice that there is not a great difference in the magnitude of the contractions noted with water and the expansions noted with benzene.

Summary

The solubility curve of the ternary system, *t*-butyl alcohol, benzene and water, has been determined at 25.0°. The refractive indexes, specific gravities and relative viscosities have been recorded. Comparisons have been made of this system with other alcohol–benzene–water systems which have been studied.

LINCOLN, NEBRASKA RECEIVED NOVEMBER 1, 1945

---

(9) Beguin and Washburn, THIS JOURNAL, **62**, 579 (1940).

(10) Washburn, Brockway, Graham and Deming, *ibid.*, **64**, 1886 (1942).

(11) Washburn, Graham, Arnold and Transue, *ibid.*, **62**, 1454 (1940).

(12) Olsen and Washburn, *J. Phys. Chem.*, **42**, 275 (1938).

(13) Bingham and Brown, *J. Rheol.*, **3**, 95 (1932).