[CONTRIBUTION FROM THE LABORATORY OF CHEMICAL PRODUCTS DIVISION, STANDARD OIL CO. OF N. J.]

PROPERTIES OF MIXTURES OF ISOPROPYL ALCOHOL AND WATER.

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In working with aqueous solutions of *iso*propyl alcohol, it becomes necessary to know the relationship between the specific gravity, boiling point, composition of the solution and composition of the evolved vapors.

This article is divided into two parts, dealing first with specific gravity of *iso*propyl-alcohol—water mixtures and second with the distillation characteristic of the alcohol water mixtures. The word alcohol as used here denotes *iso*propyl alcohol only.

Part I. Specific Gravity of Isopropyl Alcohol and Its Water Solutions.

Several workers have in the past reported specific gravities for anhydrous *iso*propyl alcohol with more or less variance as follows: Thorpe[1] 0.7903, Doroshewski[2] 0.7898, Young[3] 0.7899, all at 15°/15°.

In making anyhdrous alcohol, the following procedure was used. Two liters of *iso*propyl alcohol was dehydrated as usual by mixing with fresh lime, and then distilled through an efficient rectifying column, the fraction boiling between 82° and 82.4° being separated and treated with anhydrous copper sulfate for two days with frequent shaking. This was then distilled thrice until a constant boiling point, 82.4° (corr.), was obtained. The alcohol was treated with anhydrous copper sulfate before each distillation. The distillate was collected in an air-tight receiver and the distilling flask heated by an air-bath. D_4^{20}, 0.7855, or D_{15}^{15}, 0.7902 (pycnometer).

It is believed that the alcohol so prepared contains less than 0.10% of water. *Iso*propyl alcohol does not appear to hold on to water as tenaciously as does ethyl alcohol. This quantity of water would make an error less than 0.0002 in the specific gravity of the anhydrous alcohol and a proportionally smaller error for the aqueous mixtures.

The alcohol—water mixtures were made by weighing the water and alcohol in stoppered bottles. The alcohol was delivered to the bottles from a pipet operated by an atomizer bulb, no alcohol coming in contact with rubber.

% Alcohol by weight.	D_4^{20}.	% Alcohol by weight.	D_4^{20}.
100.00%	0.78556	53.07%	0.89868
90.35	0.80866	43.02	0.92418
85.09	0.82282	33.17	0.94590
74.35	0.84828	21.39	0.96847
65.22	0.87003	9.58	0.98293

[1] Thorpe, *J. Chem. Soc.*, **71,** 920 (1897).
[2] Doroshewski, *Zentr.*, [I], **1910,** p. 157.
[3] Young, *J. Chem. Soc.*, **81,** 728 (1902).

No attempt was made to calibrate the weights used, on the basis of the absolute gram.

The results were plotted to a large scale on cross-section paper so that 0.1% could be easily read on the ordinate and 0.0002 sp. gr. on the abscissa. The points were connected by a smooth curve and from this, Table I was constructed giving the specific gravity at 20/4° for each percentage by weight and the corresponding volume percentage.

TABLE I.

SPECIFIC GRAVITY OF *iso*PROPYL-ALCOHOL—WATER MIXTURES AT 20°/4°.

Wt. %.	Vol. %.	D.	Wt. %.	Vol. %.	D.	Wt. %.	Vol. %.	D.
0	0	0.9983	34	41.1	0.9441	68	74.5	0.8633
1	1.3	0.9963	35	42.2	0.9420	69	75.4	0.8610
2	2.5	0.9945	36	43.3	0.9400	70	76.3	0.8585
3	3.8	0.9927	37	44.4	0.9378	71	77.2	0.9561
4	5.0	0.9910	38	45.5	0.9356	72	77.9	0.8538
5	6.2	0.9894	39	46.6	0.9334	73	78.8	0.8514
6	7.5	0.9878	40	47.7	0.9311	74	79.7	0.8490
7	8.7	0.9863	41	48.7	0.9288	75	80.5	0.8465
8	9.9	0.9848	42	49.7	0.9265	76	81.4	0.8440
9	11.0	0.9834	43	50.7	0.9240	77	82.3	0.8416
10	12.4	0.9821	44	51.6	0.9216	78	83.1	0.8392
11	13.5	0.9809	45	52.6	0.9192	79	83.9	0.8367
12	14.8	0.9798	46	53.6	0.9166	80	84.9	0.8343
13	16.0	0.9787	47	54.7	0.9142	81	85.7	0.8318
14	17.2	0.9777	48	55.6	0.9118	82	86.4	0.8293
15	18.4	0.9766	49	56.6	0.9094	83	87.2	0.8269
16	19.7	0.9755	50	57.6	0.9070	84	87.9	0.8244
17	20.8	0.9744	51	58.6	0.9045	85	88.2	0.8220
18	22.0	0.9732	52	59.5	0.9021	86	89.5	0.8195
19	23.2	0.9718	53	60.4	0.8997	87	90.3	0.8170
20	24.0	0.9704	54	61.4	0.8972	88	91.1	0.8146
21	25.7	0.9689	55	62.4	0.8947	89	91.8	0.8121
22	27.0	0.9670	56	63.3	0.8922	90	92.6	0.8097
23	28.2	0.9652	57	64.4	0.8897	91	93.3	0.8073
24	29.4	0.9635	58	65.2	0.8875	92	94.1	0.8048
25	30.5	0.9616	59	66.2	0.8851	93	94.7	0.8024
26	31.8	0.9598	60	67.2	0.8826	94	95.5	0.7999
27	33.0	0.9578	61	68.1	0.8801	95	96.3	0.7974
28	34.3	0.9559	62	69.0	0.8777	96	97.0	0.7950
29	35.4	0.9541	63	69.9	0.8752	97	97.7	0.7926
30	36.7	0.9521	64	70.8	0.8728	98	98.0	0.7902
31	37.8	0.9501	65	71.7	0.8703	99	99.2	0.7878
32	38.9	0.9482	66	72.6	0.8680	100	100.0	0.7855
33	40.0	0.9461	67	73.5	0.8657	....	....	.....

Table II shows the relation between temperature correction and strength of alcohol solution. This was constructed by taking specific gravity readings at three different temperatures between 10° and 30° on the standard solutions prepared above. Average values for change in specific gravity per degree were calculated from these readings and plotted against strength of alcohol. The table gives the correction for every even 10%. A Westphal balance was used to obtain these data.

TABLE II.—TEMPERATURE CORRECTION.

Change in sp. gr. per degree C.

Strength alcohol, %.	Correction.
10	0.00019
20	0.00042
30	0.00059
40	0.00068
50	0.00074
60	0.00078
70	0.00079
80	0.00080
90	0.00080
100	0.00080

Part II. Boiling and Condensing Points of Isopropyl-Alcohol—Water Mixtures.

The boiling point and composition of the vapor from any liquid mixture depend upon the composition of the liquid. Very little is to be found in the literature in regard to *iso*propyl-alcohol—water mixtures. Doroshewski[1] gives a few values which in general run higher than the boiling points reported here.

Like ethyl alcohol, *iso*propyl alcohol and water form a mixture boiling with constant composition for which Young[2] gives 80.37° as the boiling point and 87.90 the weight per cent. of the alcohol. Mixtures below this low-boiling mixture in alcohol content on boiling give off a vapor richer in alcohol than the liquid, while those having a higher alcohol content than the low-boiling mixture give off a vapor weaker in alcohol than the liquid in each case, the vapor composition tending to approach that of the low-boiling mixture.

The purpose of this work is to obtain the relation between liquid and vapor composition at the boiling point of alcohol—water mixtures which for all industrial purposes may be considered to represent equilibrium conditions. Laboratory distillations of *iso*propyl alcohol show that it rectifies with greater ease than does ethyl alcohol, which fact is borne out by the curves presented below.

Procedure.—The specific gravity and temperature of 700 cc. of nearly anhydrous alcohol were taken and the alcohol content determined from the specific gravity table given in Part I. This was placed in a short-neck liter distilling flask fitted with a thermometer graduated to 0.1°. Twenty cc. of alcohol was distilled at a rate of 50 to 70 drops a minute. The boiling point was read when 10 cc. of the distillate had been

[1] Doroshewski, *J. Russ. Phys. Chem. Soc.*, **42**, 1448 (1910).

[2] Young, *J. Chem. Ind.*, **81**, 728 (1902).

obtained. The average alcoholic content in the flask before and after distillation was taken as the composition at the time the boiling point was read. To the liquid in the flask 20 cc. of water was added and the distillation carried out as before. In some cases, more water was added but enough alcohol had been previously removed to bring the contents to 700 cc. A Westphal balance was used for determining the specific gravities.

The thermometer used was previously calibrated with water and with naphthalene recrystallized from alcohol and resublimed. A constant correction of +0.2° was found. The observed temperatures were corrected for exposed mercury column by adding $C(T - t)$ 0.000154 where C is the length of the exposed mercury, T is the observed temperature and t is the room temperature. For effect of pressure on boiling point, Young[1] gives for the value of dt/dp, 0.034°/mm. Doroshewski[1] gives values ranging from 0.033° for strong alcohol to 0.038° for weak alcohol. The value of 0.034° was used. The data are given in Table III.

The composition of the mixture boiling with constant composition was determined by numerous distillations of 250 cc. of various strengths of alcohol. These distillations were conducted with an efficient glass rectifying column the distillate being cut into two 115-cc. fractions and, the specific gravity of each being determined at 20°. A Westphal balance was used until the specific gravities became nearly equal when a pycnometer was employed. These points were plotted against total volume of distillate and a straight line was drawn between the points of a single distillation.

Data and Discussion.

Table III gives the data for the liquid and vapor compositions of boiling alcoholic solutions. This is shown in graphic form in Fig. 1, where the

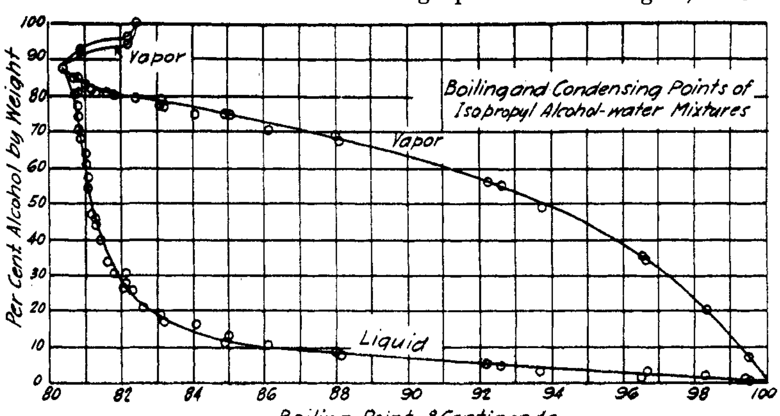

Fig. 1.

[1] *Loc. cit.*

average strength of the content in the flask before and after distillation and the strength of distillate are plotted against boiling temperature. The lower curve represents the liquid composition in equilibrium with the vapor composition shown by the upper curve. The mixtures above the

TABLE III.

BOILING AND CONDENSING POINTS OF *iso*PROPYL-ALCOHOL—WATER MIXTURES.

	Before distillation.			After distillation.			Distillate.							
No.	D.	*T.* °C.	Wt. % of alcohol	D.	*T.* °C.	Wt. % of alcohol.	D.	*T.* °C.	Wt. % of alcohol.	B. p. obs.	Bar. mm.	Stems and calibration corrections.	B. p. corr.	Av. % of alcohol in flask.
1	0.7957	20	96.6	0.7909	27	96.6	0.8000	22	94.2	81.4	760	0.83	82.2	96.6
2	0.8063	20	92.4	0.8048	21	92.7	0.8110	20	91.5	80.3	773	0.95	80.9	92.5
3	0.8146	21	88.7	0.8180	17	88.8	0.8160	21	88.2	80.1	773	0.88	80.5	88.7
4	0.8265	18	84.6	0.8231	22	84.8	0.8185	23	86.5	80.2	773	0.88	80.7	84.7
5	0.8305	22	81.8	0.8380	16	85.6	0.8220	21	85.6	80.3	773	0.88	80.8	81.1
6	0.8446	16	77.9	0.8430	19	77.5	0.8272	18	84.5	80.3	774	0.94	80.8	77.7
7	0.8497	20	74.5	0.8521	18	74.0	0.8301	18	83.3	80.3	774	0.94	80.8	74.3
8	0.8586	18	71.4	0.8572	22	70.5	0.8300	18	83.3	80.3	774	0.94	80.8	70.9
9	0.8635	22	67.9	0.8625	25	67.2	0.8280	22	82.7	80.4	774	0.94	80.9	67.5
10	0.8693	25	64.4	0.8736	22	63.6	0.8309	19	82.8	80.4	774	0.94	81.0	64.0
11	0.8663	21	60.7	0.8850	10	59.9	0.8345	16	82.1	80.3	769	0.95	81.0	60.3
12	0.8899	19	57.9	0.8916	20	57.5	0.8348	16	82.0	80.4	769	0.95	81.1	57.7
13	0.8967	20	54.9	0.9020	17	53.5	0.8318	19	82.0	80.4	769	0.95	81.1	54.2
14	0.9075	17	51.1	0.9071	22	49.9	0.8348	17	81.7	80.4	769	0.95	81.1	50.5
15	0.9116	22	48.0	0.9167	25	46.4	0.8357	16	81.6	80.5	766	0.95	81.2	47.2
16	0.9158	21	46.6	0.9179	22	45.4	0.8340	19	81.2	80.6	766	0.95	81.3	46.0
17	0.9214	20	44.6	0.9242	20	43.4	0.8410	17	79.0	80.6	766	0.95	81.3	44.0
18	0.9274	23	41.2	0.9396	15	38.5	0.8337	21	80.7	80.6	766	0.94	81.4	39.8
19	0.9424	23	34.7	0.9451	24	33.0	0.8366	20	79.9	80.4	759	0.95	81.3	33.8
20	0.9456	16	35.2	0.9453	24	33.2	0.8338	21	80.7	80.3	749	0.89	81.6	34.0
21	0.9490	24	31.3	0.9557	19	29.5	0.8345	22	80.2	80.6	749	0.89	82.8	30.4
22	0.9548	23	28.8	0.9648	14	26.4	0.8380	21	79.2	81.1	757	0.95	82.1	27.6
23	0.9653	15	25.7	0.9665	20	23.8	0.8394	19	78.3	81.1	757	0.95	82.1	24.7
24	0.9610	20	26.5	0.9636	21	24.7	0.8365	22	79.3	81.1	749	0.89	82.3	25.6
25	0.9675	22	22.3	0.9704	21	21.8	0.6375	22	78.8	81.4	749	0.89	82.6	20.5
26	0.9718	21	19.9	0.9747	20	18.0	0.8410	18	77.7	82.1	755	0.98	83.1	18.8
27	0.9740	21	18.3	0.9764	21	16.3	0.8440	22	76.2	82.0	749	0.89	83.2	17.3
28	0.9756	20	17.4	0.9774	22	13.7	0.8480	18	75.8	82.9	755	1.03	84.1	16.5
29	0.9778	22	14.7	0.9808	23	11.8	0.8487	19	75.0	83.8	755	1.05	85.0	13.2
30	0.9813	20	12.2	0.9830	23	10.6	0.8500	24	75.3	83.5	745	0.90	84.9	11.4
31	0.9815	23	11.5	0.9843	23	9.3	0.8662	23	70.7	84.9	755	1.05	86.1	10.2
32	0.9850	23	8.8	0.9857	20	7.9	0.8625	23	69.2	86.1	745	0.90	88.0	8.4
33	0.9846	23	9.2	0.9880	22	6.8	0.8665	19	67.6	86.9	755	1.05	88.1	8.0
34	0.9885	23	6.4	0.9910	24	4.6	0.8944	19	56.2	90.0	755	1.16	92.2	5.0
35	0.9896	20	5.8	0.9928	20	3.8	0.8953	19	55.0	90.5	745	0.90	92.6	4.8
36	0.9915	24	4.2	0.9943	21	3.0	0.9098	17	49.4	92.6	764	1.22	93.7	3.6
37	0.9943	20	2.7	0.9958	23	1.8	0.9448	18	34.8	95.0	745	0.90	96.6	2.2
38	0.9943	21	2.9	0.9960	22	1.9	0.9430	17	35.3	95.4	764	1.30	96.5	1.6
39	0.9963	22	1.7	0.9974	24	0.8	0.9720	18	19.7	98.2	764	1.34	99.3	1.3
40	0.0074	24	0.8	0.9984	21	0.2	0.9872	19	7.1	98.4	764	1.34	99.5	0.5

low boiling mixture in alcoholic content are represented by the two short curves between 80.4° and 82.4° and are reversed, the liquid curve being above and vapor curve below. In Table IV are given the boiling and condensing points of *iso*propyl–alcohol—water mixtures containing less alcohol than the low-boiling mixture. These values are taken from the curves of Fig. 1. The data will differ from true equilibrium conditions by the small amount of fractionation that takes place in the flask.

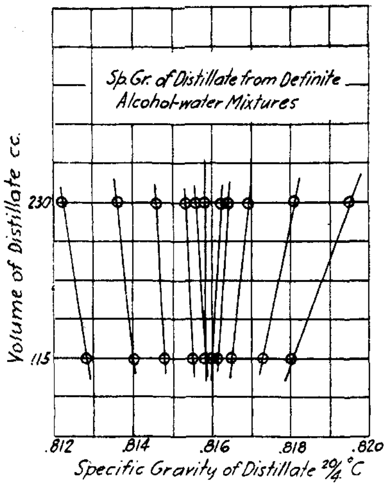

Fig. 2.

The data for the distillations used in the determination of the mixture boiling with constant composition are all given in graphic form in Fig. 2. The curves for distillation of mixtures stronger in alcohol than the mixture of constant composition slope to the left, the constant-composition mixture tending to

TABLE IV.

BOILING AND CONDENSING POINTS OF *iso*PROPYL–ALCOHOL—WATER MIXTURES.

Temp. °C.	Strength of liquid. %.	Strength of vapor. %.	Temp. °C.	Strength of liquid %.	Strength of vapor. %.
80.4	87.7	87.7	88.5	8.4	67.3
80.6	82.9	85.7	89.0	8.1	65.9
80.8	75.4	84.1	89.5	7.8	64.6
81.0	64.5	82.9	90.0	7.3	63.1
81.2	49.6	82.0	90.5	7.0	61.7
81.4	42.2	81.2	91.0	6.7	60.1
81.6	37.1	80.7	91.5	6.3	58.3
81.8	33.2	80.1	92.0	6.0	56.8
82.0	29.8	79.8	92.5	5.7	54.9
82.2	27.2	79.6	93.0	5.2	53.1
82.4	24.9	79.4	93.5	4.9	51.1
82.6	23.1	79.2	94.0	4.6	48.9
82.8	21.4	79.0	94.5	4.2	46.5
83.0	20.0	78.8	95.0	3.9	43.9
83.5	17.4	78.0	95.5	3.5	41.2
84.0	15.4	77.2	96.0	3.1	38.3
84.5	13.8	76.3	96.5	2.8	35.2
85.0	12.5	75.6	97.0	2.4	31.6
85.5	11.3	74.6	97.5	2.1	27.6
86.0	10.6	73.4	98.0	1.8	23.1
86.5	9.9	72.2	98.5	1.4	18.8
87.0	9.4	71.1	99.0	1.0	13.2
87.5	9.0	69.9	99.5	0.5	7.3
88.0	8.8	68.6	100.0	0.0	0.0

come over first and stronger alcohol later. For the mixture boiling with constant composition the curve should be vertical showing that the composition did not change while for mixtures weaker in alcohol the slope would be to the right the mixture of constant composition tending to distil first and weaker mixtures later. The boiling point was read at the end of each fraction and corrected as related before. The vertical curve representing the low boiling mixture is plotted from the following gravities of the two fractions, D^{20}_{4} 0.81582 and 0.81586. On repeated distillation the value of 0.81583 was obtained. The observed constant boiling point was 79.6° at 756 mm. Adding 0.6° stem correction and 0.2° calibration correction gives 80.4° as the boiling point of the constant-boiling mixture. By interpolation between the original data for the specific gravity table a composition of 87.70% by weight and 91.09% by volume is obtained for the alcoholic content of this mixture. A number of samples taken from a run on a large rectifying column gave an average specific gravity of 0.81583, and ranging from 0.81570 to 0.81587.

The greatest accuracy is obtained for the low boiling mixture, being limited only by the accuracy of the specific gravity table of Part I.

Summary.

The specific gravity of *iso*propyl alcohol was found to be 0.7855 at 20/4°, its boiling point 82.4° at 760 mm. pressure. A table for specific gravity of alcohol—water mixtures is given.

The specific gravity of the mixture boiling with constant composition was found to be 0.8158 at 20/4°, its boiling point 80.4° and its composition 87.70% alcohol by weight and 91.09% by volume.

Curves showing the boiling points of alcohol—water solutions and the composition of the evolved vapor are given. These curves when compared with like curves for ethyl alcohol show that *iso*propyl alcohol is rectified more easily than is ethyl alcohol.

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[CONTRIBUTION FROM THE DEPARTMENT OF SOILS, UNIVERSITY OF WISCONSIN.]

THE EFFECT OF FINELY DIVIDED MATERIAL ON THE FREEZING POINTS OF WATER, BENZENE AND NITROBENZENE.[1]

BY F. W. PARKER.

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In a study of the salt content of the soil solution by different methods, including the freezing-point method of Bouyoucos and McCool,[2] results

[1] Part of a thesis submitted to the University of Wisconsin in partial fulfilment of the requirements for the degree of Doctor of Philosophy. Published with the permission of the Director of the Wisconsin Agricultural Experiment Station.

The writer wishes to express his appreciation for the helpful suggestions and criticisms tendered by Prof. E. Truog.

[2] Bouyoucos and McCool, Mich. Agr. Exp. Sta., *Tech. Bull.* **24** (1915); **31** (1917).