The values of K_2 do not agree as well as the previous set, but since the data are given in the order of increasing ionic strength, it is obvious that there is no correlation with ionic strength. With the help of Dr. Paul F. Derr it was discovered that the values marked with an asterisk were either obtained before the technique was perfected, or were uncertain because of variation in the analytical results. They were all included in the previous table because of apparent agreement with the more reliable later data, while one or two results which had appeared to be much too low were disregarded. If the values marked with the asterisk are omitted, the average value of K_2 is 6.2×10^{-5}, while the average of all is 6.3×10^{-5}. It is believed that the former figure is the more reliable. An error of 10% in the value of k_1 would make an error of 0.8% in K_2 in the least favorable case, and not more than 0.4% in any of the values used for the average 6.2×10^{-5}. The values for the more concentrated solutions would not be affected appreciably. Bjerrum's value for K_2 is 5.9×10^{-8}.

Summary

Measurements of the solubilities of silver sulfate, silver bromate, and silver iodate in very dilute ammonia solutions confirm the conclusion that a monammine silver ion exists. Its instability constant has been found to be 4.3×10^{-4} in satisfactory agreement with Bjerrum's value 4.8×10^{-4}. Recalculation of previous data gives a value of 6.2×10^{-8} for the equilibrium constant for the dissociation of the diammine silver ion into silver ion and ammonia.

DURHAM, N. C. RECEIVED FEBRUARY 18, 1943

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF DELAWARE]

The Ternary System: Dioxane–Ethanol–Water

BY CHARLES H. SCHNEIDER AND CECIL C. LYNCH

The system dioxane–ethanol–water is completely miscible, and the three binary systems from these components each shows a minimum azeotrope; a ternary minimum azeotrope should be expected for the system. It is the purpose of this investigation to obtain analysis data for the ternary system and to estimate its minimum azeotropic composition and corresponding boiling point.

The binary system ethanol–water has been examined by several workers.[1,2] Lecat[3] gives for the binary minimum azeotrope the composition 89.43 mole per cent ethanol with boiling point 78.15°. The binary system dioxane–water has been studied by Smith and Wojciechowski[4] by the ebulliometric method. They report the binary minimum azeotrope at 48–49 mole per cent. dioxane with boiling point 87.82°. The binary system dioxane–ethanol has been reported from this Laboratory,[5] with the minimum azeotrope at 5.1 mole per cent. dioxane with boiling point 78.13°.

Preparation of Materials

Dioxane.—Technical 1,4-dioxane from the Eastman Kodak Co. was purified by the method described by Eigenberger.[6] The product was kept over metallic sodium, from which it was distilled when needed; density d^{25}_4 1.0276, n^{25}_D 1.4201.

Ethanol.—Commercial absolute ethanol was refluxed for twenty-four hours over lime and barium oxide, and distilled from the mixture. The product was treated with metallic sodium to remove remaining water and the redistilled product was used; density at 25° of 0.7852, n^{25}_D 1.3597.

Ordinary distilled water was redistilled for use in all solutions.

The Binary System: Dioxane–Water.—Smith and Wojciechowski,[4] using the ebulliometer, have investigated this binary system. Our method has been to examine vapor–liquid equilibria using the apparatus of Othmer[7]; therefore, the study of this binary system using the Othmer still was made. Mixtures of approximate composition were introduced into the apparatus and runs were made until equilibrium had been established. This required three to four hours for each run. Temperatures were measured with a (0–110°) thermometer with 0.1° division, which was checked frequently for accuracy, the precision ±0.03°. Pressure correction to 1 atmosphere and stem correction were made for all readings. The equilibrium residue and distillate were analyzed through refractive index. Data are given in Table I, and Fig. 1 shows the boiling point–composition diagram for the system. The

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[1] Doroszewski and Polansky, *Z. physik. Chem.*, **73**, 192 (1910).

[2] Noyes and Warfel, THIS JOURNAL, **23**, 463 (1901).

[3] Lecat, "La tension de vapeur des mélanges de liquides l'azéotropisme," Brussels, 1918.

[4] Smith and Wojciechowski, *J. Research Natl. Bur. of Standards*, **18**, 461 (1937), Research Paper 985.

[5] Hopkins, Yerger and Lynch, THIS JOURNAL, **61**, 2460 (1939).

[6] Eigenberger, *J. prakt. Chem.*, **130**, 75 (1931).

[7] Othmer, *Ind. Eng. Chem.*, **20**, 743 (1928).

binary minimum azeotrope occurs at 48.5 mole per cent. dioxane with boiling point at 87.59°.

TABLE I

VAPOR-LIQUID EQUILIBRIUM DATA AT ONE ATMOSPHERE PRESSURE FOR THE DIOXANE-WATER SYSTEM

Boiling poing, °C.	Refractive index, $n^{25}D$ Vapor	Liquid	Mole fraction of dioxane Vapor	Liquid
97.17	1.3689	1.3369	0.103	0.008
93.90	1.3890	1.3442	.227	.024
90.97	1.3990	1.3550	.335	.052
89.37	1.4027	1.3661	.390	.091
88.61	1.4045	1.3760	.425	.135
88.21	1.4055	1.3860	.443	.203
87.93	1.4064	1.3960	.460	.298
87.59	1.4076	1.4054	.490	.442
87.65	1.4078	1.4099	.493	.540
87.85	1.4091	1.4138	.523	.688
89.57	1.4121	1.4173	.618	.865
94.80	1.4161	1.4190	.790	.963
100.00	....	1.3326	Water	
101.07	....	1.4201	Dioxane	

Refractive index-composition values for the dioxane water mixtures were taken from the data of Lynch.[8]

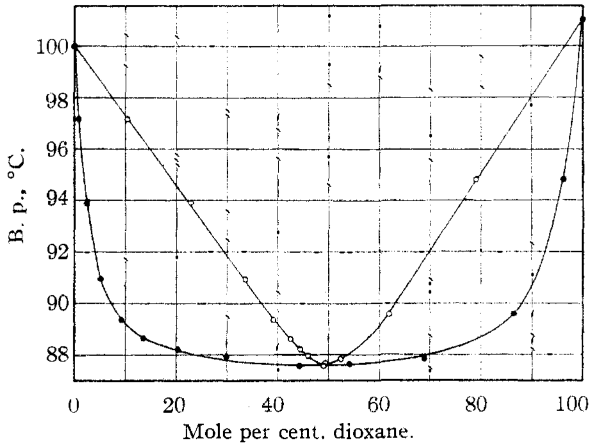

Fig. 1.—Boiling point-composition diagram for the system dioxane-water.

Min. b. p. = 87.59°C., azeotrope: 48-49% dioxane.

The Ternary System

Analysis.—We have employed the same method for analyzing this three component system as was used by Berl and Ranis[9] for the system methanol-ethanol-water, and by J. Barbaudy[10] for the benzene-ethanol-water system. This method consists of measuring refractive index and density for a sufficiently large number of carefully prepared solutions of the three components covering the complete composition range, so that lines of common density and lines of common refractive index may be constructed on a triangular chart. All measurements are isothermal (at 25°). Table II includes the data of composition, refractive index, and density for the system. Figure 2 is the analysis diagram. Refractive index was determined with an Abbe refractometer of precision ±0.0002 unit; density was determined with the Westphal balance, the precision ±0.0002 unit.

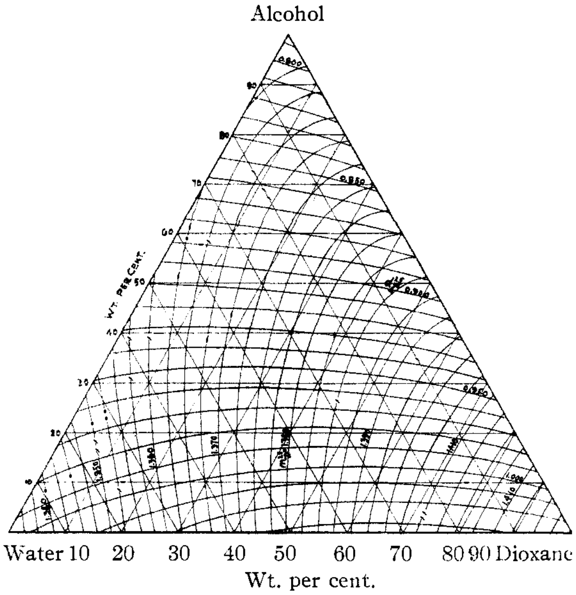

Fig. 2.—Analysis diagram for the system dioxane-ethanol-water at 25°.

The precision of analysis from the diagram was determined by taking several known mixtures of the three components, compositions being chosen to cover a wide range, and the average variation was found to be ±0.3 unit in weight per cent. for any component.

Vapor-Liquid Equilibria.—The vapor-liquid equilibria of the ternary system were studied with the same apparatus and in the same fashion as described under the binary

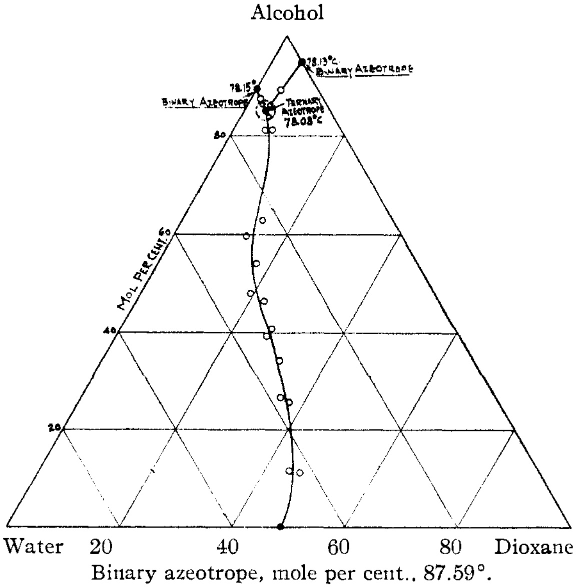

Fig. 3.—Ternary azeotrope for the system dioxane-ethanol-water.

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(8) Lynch, *J. Phys. Chem.*, **46**, 366 (1942).

(9) Berl and Ranis, *Ber.*, **60B**, 2225 (1917).

(10) J. Barbaudy, *Bull. soc. chim.*, (4) **39**, 371 (1926).

TABLE II

ANALYSIS DATA FOR THE TERNARY SYSTEM AT 25°

DIOXANE–ETHANOL–WATER

Refract. index	Density	Calculated percentage by weight % Dioxane	% Water	% Alc.
1.3485	0.9907	10.03	80.59	9.38
1.3570	.9996	19.83	71.81	8.36
1.3668	1.0090	30.60	62.17	7.23
1.3747	1.0155	39.96	53.80	6.24
1.3830	1.0206	50.63	43.91	5.46
1.3908	1.0257	59.36	36.41	4.23
1.3988	1.0279	69.42	27.40	3.18
1.4063	1.0289	80.51	17.47	2.02
1.4147	1.0290	90.99	8.05	0.96
1.3540	0.9756	9.43	72.42	18.15
1.3628	.9861	20.64	63.45	15.91
1.3704	.9947	30.36	55.68	13.96
1.3788	1.0024	41.21	47.00	11.79
1.3857	1.0085	50.42	39.64	9.94
1.3929	1.0146	59.99	31.99	8.02
1.4000	1.0189	69.93	24.06	6.01
1.3593	0.9606	9.71	60.65	29.64
1.3665	.9706	20.67	55.52	23.81
1.3740	.9798	30.82	48.26	20.92
1.3802	.9888	41.38	41.03	17.59
1.3870	.9970	51.29	34.11	14.60
1.3931	1.0042	59.04	28.68	12.28
1.3998	1.0113	70.80	20.44	8.76
1.4058	1.0178	79.87	14.10	6.03
1.3629	0.9430	11.94	53.15	34.91
1.3691	.9535	20.37	48.13	31.50
1.3758	.9644	31.24	41.49	27.26
1.3820	.9749	42.30	34.83	22.88
1.3870	.9832	50.00	30.18	19.82
1.3941	.9933	60.16	24.05	15.79
1.3990	1.0008	69.07	18.68	12.25
1.4124	1.0201	89.76	6.18	4.06
1.3653	0.9234	10.36	45.04	44.60
1.3717	.9356	21.63	39.37	39.00
1.3771	.9462	31.17	34.59	34.24
1.3822	.9572	40.44	29.94	29.62
1.3885	.9700	51.43	24.42	24.15
1.3938	.9801	59.96	20.12	19.92
1.3994	.9903	69.23	15.46	15.31
1.4062	1.0046	80.54	9.78	9.69
1.3671	0.9011	10.71	35.73	53.57
1.3722	.9144	20.85	31.67	47.48
1.3776	.9274	30.63	27.75	41.63
1.3830	.9410	40.84	23.66	35.50
1.3880	.9539	49.90	20.03	30.06
1.3940	.9687	61.04	15.58	23.38
1.4001	.9825	70.01	11.99	17.99
1.3677	.8784	10.04	27.41	62.55
1.3728	.8938	20.38	24.25	55.39
1.3779	.9090	30.38	21.20	48.41
1.3827	.9229	39.68	18.38	41.95
1.3882	.9404	50.73	15.01	34.26
1.3931	.9590	59.05	12.48	28.47
1.3989	.9699	68.63	9.55	21.83
1.4050	.9880	78.91	4.97	16.13
1.4125	1.0087	90.09	3.03	6.88
1.3680	0.8568	10.14	18.47	71.40
1.3730	.8720	19.91	16.46	63.63
1.3798	.8951	33.44	13.68	52.88
1.3847	.9104	42.45	11.83	45.73
1.3895	.9278	51.73	9.92	38.36
1.3952	.9474	62.07	7.81	30.12
1.3967	.9538	65.21	7.15	27.65
1.3681	.8351	11.61	8.97	79.42
1.3730	.8559	22.18	7.91	69.92
1.3884	.9125	52.13	4.86	43.00

system. However, the residue and distillate samples were analyzed through refractive index and density by means of the analysis diagram.

We were concerned chiefly with boiling points in the vicinity of the binary azeotropes and along the minimum trace lines from binary to ternary minima. By preparing mixtures on both sides of the estimated trace lines, the vapor composition was found to shift closer to the trace lines to such an extent that the approximate trace could be drawn from the dioxane–water azeotrope to a point in the vicinity of the ternary azeotrope. Data for such a plot are given in Table III and the plot is found in Fig. 3 (only the vapor points are plotted). Two points are included along the other trace lines. Points in the vicinity of the ternary azeotrope showed a flat area where no change in boiling point or composition resulted even after five hours were allowed for equilibrium in the still. We have indicated this region approximately by the dotted circle in Fig. 3. The ternary azeotrope estimated from these data occurs at 4.2 mole per cent. dioxane, 85.3 mole per cent. ethanol, 10.5 mole per cent. water and has a boiling point 78.08°.

TABLE III

VAPOR–LIQUID EQUILIBRIA IN THE TERNARY SYSTEM: DIOXANE–ETHANOL–WATER

Composition of vapor, mole % Dioxane	Ethanol	Water	Composition of liquid, mole % Dioxane	Ethanol	Water	Boiling point, °C.
46.4	11.3	42.3	49.2	6.1	44.7	86.36
37.4	25.3	37.3	47.2	13.6	39.2	84.37
31.9	33.7	34.4	41.2	21.7	37.1	83.09
26.4	41.1	32.5	36.8	29.0	34.3	81.75
22.5	46.7	30.8	31.1	35.2	33.7	81.30
17.6	54.6	27.8	26.1	44.6	29.3	80.13
14.3	63.1	22.6	18.7	54.7	26.6	79.40
8.7	81.6	9.7	9.3	78.1	12.6	78.61
4.5	89.8	5.7	5.0	92.1	3.1	78.30
43.7	11.8	44.5	46.1	5.5	48.4	86.16
34.8	27.0	38.2	40.4	15.5	44.1	83.91
26.1	39.3	34.6	31.3	25.7	43.0	82.22
19.0	48.2	32.8	25.8	36.5	37.7	80.80
13.0	59.9	27.1	17.4	51.0	31.6	79.57
6.9	81.7	11.4	7.9	78.0	14.1	78.43
1.8	87.7	10.5	1.2	88.3	10.5	78.11
2.9	86.2	10.9	2.9	86.2	10.9	78.08
5.0	84.2	10.8	5.0	84.2	10.8	78.08
4.1	86.4	9.5	4.1	86.4	9.5	78.08

Summary

1. Vapor–liquid equilibria for the binary system dioxane–water at one atmosphere have been presented. The minimum azeotrope of

this system was found to have a composition 48.5 mole per cent. dioxane with a boiling point at 87.59°.

2. Refractive index and density data for the analysis of the ternary system: dioxane–ethanol–water have been obtained. An analysis diagram for the system is included.

3. Some vapor–liquid equilibria data at one atmosphere for the ternary system are presented, which permit the estimation of a ternary minimum azeotrope.

NEWARK, DELAWARE RECEIVED MARCH 23, 1943

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY, POLYTECHNIC INSTITUTE OF BROOKLYN]

Magneto-optic Rotation. IV. Acetic and Chloroacetic Acids in Polar and Non-polar Solvents

BY CHAS. E. WARING, SAMUEL STEINGISER[1] AND HERBERT H. HYMAN[1]

In the last two papers of this series, the molecular Verdet constants were determined for solutions of carbon disulfide in various organic liquids and an interpretation proposed for the irregularity of the function plotted against mole per cent. concentration.[2,3] In order to establish the abnormality of this observed behavior and to demonstrate the possible causes for its presence or its absence, several other systems were studied. It was suspected, although not previously definitely established, that ordinary dipole association, simple hydrogen bonding and addition type complex formation without intramolecular rearrangement would not produce any effect. That is, the rotation per individual molecular group would remain constant if there were no internal bond rearrangements, regardless of how the density and direct Faraday rotation were altered by intermolecular combinations.

As a result of our present investigations, we now believe that when any alterations in intramolecular structure are produced in solution, whether by virtue of solvation, resonance or disturbed resonance effects, this method will reveal that change. On the other hand, the magneto-optic method will also show the absence of any such changes in the internal bond configuration even in cases where other physical methods, such as density, viscosity, molar volume, etc., indicate the probability of solvate formation.

Experimental

Materials and Apparatus.—The acids were the best grades of C. P. material available. The acetic acid was purified with a single distillation and fractional crystallization to reduce the water content, but no attempt to obtain really anhydrous material was thought necessary. The carbon disulfide was the same as previously described.[3] An important improvement has been made in the apparatus over that described in a previous paper.[2] Instead of measuring the current directly with an ammeter, the *IR* drop in a fixed resistance in the circuit is balanced against an e. m. f. in an auxiliary circuit and the small deflections of a galvanometer in that circuit used to measure the current.

Since the error in measuring the current is now solely the error in measuring impressed voltage with the potentiometer and the galvanometer deflection, it is considerably smaller than that of the direct ammeter method.

Densities and refractive indices were measured with conventional instruments as previously described.[3] The solutions were made up to approximately the concentrations desired and titrated against standard alkali. Potassium acid phthalate was used as the primary standard. The procedure was to neutralize weighed portions of the acid with weighed excess of standard alkali, back titrate with known hydrochloric acid, and finally titrate to the end-point with dilute alkali using phenol red as indicator. All concentrations are the result of, at least, two analyses with a deviation of less than 0.1% by weight.

Measurements.—The primary standard and the technique of measurements were the same as before.[3] Table I is a summary of all the experimental measurements. Included in this tabulation are the recalculated results taken from Schwers[4] for the acetic acid–carbon tetrachloride systems. The molecular Verdet constants as given in the table are plotted against mole per cent. composition in Fig. 1.

Discussion.—Studies of viscosity and density on acetic acid-water mixtures show wide deviations from linearity at 50 mole per cent., which indicate interaction between the acetic acid and water molecules. Studies of infrared and Raman spectra[5] in this system also indicate interactions of a type readily interpreted as due to hydrogen bonding.

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[1] Submitted in partial fulfillment for the Master of Science degree.

[2] Waring, Hyman and Steingiser, THIS JOURNAL, **62**, 2028 (1940).

[3] *Ibid.*, **63**, 1985 (1941).

[4] Schwers, *Bull. class. Sci. Acad. Roy. Belg.*, 648 (1912).

[5] Krishnamurthi, *Nature*, **128**, 639 (1931).