Results

The data obtained are tabulated in Table I, and plotted in Fig. 1. The saturated solutions lying along portion AB of the curve are in equilibrium with the hexahydrate crystals; along BC, with the tetrahydrate; along CD, with the dihydrate, and along DE, with the monohydrate. These are the same hydrates that were found by the freezing point method for the binary system zinc nitrate–water.[1] No evidence was obtained of the existence of the trihydrate.

Summary

The equilibrium diagram for the ternary system zinc nitrate–nitric acid–water at 25° has been established.

The forms of zinc nitrate in stable equilibrium with nitric acid at 25° are the hexahydrate, the tetrahydrate, the dihydrate and the monohydrate.

BETHLEHEM, PENNSYLVANIA RECEIVED AUGUST 7, 1933
PUBLISHED DECEMBER 14, 1933

[CONTRIBUTION FROM THE GAYLEY CHEMICAL LABORATORY OF LAFAYETTE COLLEGE]

The Fluidity of Dioxane–Water Mixtures[1]

BY JOHN A. GEDDES

I. Introduction

Because of the wide range of dielectric constants which can be obtained by the use of dioxane–water mixtures, these have become of considerable importance in the study of dilute electrolytic solutions.[2] The viscosity is also a contributing factor in this study, and although some measurements have already been made,[3] it is evident that corrections are necessary, the value of a 10% water–90% dioxane mixture at 20° being obviously in error. In addition, the fluidity–temperature plot of pure dioxane does not give the smooth curve which should be obtained. This is doubtless caused by incomplete purification, the melting point of the dioxane used having been reported as 11.0°, whereas a later method[4] affords a compound melting several tenths of a degree higher.

This investigation was undertaken to examine the effect of addition of water on the fluidity of dioxane, to correct existing data, and to furnish data at 25° in particular for application to the study of the conductivity of dilute solutions in these mixtures.

(1) The author wishes to express his appreciation to Dr. Eugene C. Bingham, who afforded the facilities of his laboratory for this investigation.

(2) Kraus and Fuoss, THIS JOURNAL, **55**, 21 (1933); Fuoss and Kraus, *ibid.*, **55**, 476 (1933); **55**, 1019 (1933).

(3) Herz and Lorentz, *Z. physik. Chem.*, **140**, 407 (1929).

(4) Vingee, Thesis, Brown University, 1931.

II. Apparatus and Materials

Viscosities were measured in a variable pressure viscometer[5] number 1–33, calibrated at 20° with pure distilled dust-free water, a viscosity of 1.005 C. P. being assumed at that temperature. The values of the instrument constants[6] obtained were $C = 1.70756 \times 10^{-7}$, $C' = 0.01593$, $m_l = 1.43$, and $m_r = 1.32$.[7] The hydrostatic head correction[7,8] was negligible. The value of C was the average of eight determinations on two samples of water, the extreme deviation being 0.08%. The m's were averaged from nine determinations of flow in each direction, three samples being used for this purpose.

Temperatures were kept constant within 0.02° by the use of thermometer number 36,715, calibrated at the Physikalisch-Technische Reichsanstalt and the U. S. Bureau of Standards. Stem corrections were made when necessary.

Densities were determined by the use of pycnometer 2-33, except in the case of pure dioxane, which was measured in pycnometer 1-31, calibrated by means of water, and corrected to vacuum.

Dioxane was purified by a modified form of Vingee's method.[4] The technical product was cooked with caustic soda, dried over barium oxide and then twice boiled with metallic sodium. The dioxane was then distilled, and fractionally crystallized, the first fraction being refluxed for several hours over sodium–lead alloy, and finally distilled over this before use. The melting point after removal from the viscometer was 11.6°.

III. Results

The experimental results are summarized in Tables I–III, where the temperature is in degrees centigrade, the viscosity is in centipoises, and

TABLE I

VISCOSITIES OF DIOXANE–WATER MIXTURES

% Water	20°	25°	30°	40°	60°	80°
0.000	1.3076	1.1964	1.0990	0.9416	0.7146	0.5625
(Pure dioxane)	1.3079	1.1966	1.0992	.9414	.7149	.5624
	1.3071	1.1976	1.1003	.9415	.7145	.5629
	1.3072	1.1969	1.1005	.9414	.7149	.5626
0.975	1.3055	1.1962	1.0978	.9391	.7121	.5618
	1.3060	1.1959	1.0984	.9391	.7116	.5615
2.079	1.3200	1.2067	1.1077	.9443	.7138	.5619
	1.3199	1.2067	1.1068	.9440	.7135	.5613
5.018	1.3992	1.2745	1.1627	.9839	.7338	.5706
	1.3998	1.2739	1.1629	.9835	.7341	.5707

(5) Bingham, *Proc. A. S. T. M.*, **18**, Pt. II, 373 (1918); also U. S. Bur. of Standards, Bull. **298**, 14 (1917).

(6) Bingham, "Fluidity and Plasticity," Appendix A.

(7) Bingham and Geddes, *Physics*, **4**, 203 (1933).

(8) Corrected for typographical error, this equation should read $h_l = [(t_l - t_r)/(t_l + t_r)][p/\rho + C'/Ct_lt_r]$.

TABLE I (*Concluded*)

% Water	20°	25°	30°	40°	60°	80°
10.96	1.6215	1.4578	1.3215	1.0998	0.8007	0.6079
	1.6191	1.4581	1.3212	1.0997	.7996	.6075
21.33	1.9816	1.7606	1.5743	1.2790	.8956	.6611
	1.9810	1.7609	1.5739	1.2787	.8951	.6608
44.26	2.2637	1.9760	1.7383	1.3774	.9246	.6632
	2.2632	1.9748	1.7381	1.3761	.9242	.6624
56.94	2.0599	1.7962	1.5797	1.2505	.8433	.6100
	2.0598	1.7962	1.5790	1.2506	.8430	.6099
75.91	1.5768	1.3802	1.2213	0.9756	.6713	.4949
	1.5762	1.3807	1.2211	.9755	.6707	.4949
88.55	1.2579	1.1090	0.9855	.7973	.5584	.4189
	1.2585	1.1084	.9853	.7976	.5587	.4191
100.00	1.0044	0.8928	.7983	.6547	.4681	.3566
(Pure water)	1.0048	.8924	.7984	.6550	.4682	.3570

(The viscosity of pure dioxane was also measured at 50°, these values being 0.8158, 0.8160, 0.8154 and 0.8161. The fluidity averaged from these is 122.58 rhes.)

TABLE II

SPECIFIC VOLUMES OF DIOXANE-WATER MIXTURES

% Water	20°	25°	30°	40°	60°	80°
0.000 (Pure dioxane)	0.9667	0.9722	0.9774	0.9882	1.0118	1.0363
0.975	.9679	.9733	.9788	.9895	1.0120	1.0367
2.079	.9677	.9728	.9786	.9894	1.0117	1.0359
5.018	.9666	.9718	.9769	.9875	1.0097	1.0335
10.96	.9644	.9693	.9741	.9843	1.0054	1.0285
21.33	.9616	.9662	.9708	.9799	0.9993	1.0212
44.26	.9630	.9667	.9706	.9782	.9949	1.0140
56.94	.9680	.9713	.9747	.9815	.9964	1.0136
75.91	.9809	.9831	.9858	.9912	1.0038	1.0181
88.55	.9914	.9931	.9951	.9997	1.0098	1.0227

TABLE III

FLUIDITIES OF DIOXANE-WATER MIXTURES

% Water	20°	25°	30°	40°	60°	80°
0.000	76.48	83.55	90.93	106.21	139.92	177.75
.975	76.59	83.61	91.07	106.49	140.49	178.06
2.079	75.76	82.87	90.31	105.92	140.13	178.08
5.018	71.46	78.49	86.00	101.66	136.25	175.25
10.96	61.72	68.59	75.68	90.93	124.98	164.55
21.33	50.47	56.80	63.53	78.20	111.69	151.30
44.26	44.18	50.62	57.53	72.64	108.18	150.88
56.94	48.55	55.67	63.32	79.97	118.61	163.94
75.91	63.43	72.44	81.89	102.51	149.03	202.07
88.55	79.48	90.20	101.48	125.41	179.05	238.66
100.00	99.54	112.03	125.26	152.71	213.63	280.29

the fluidity in rhes. It will be noted that the greatest deviation between right and left limb determinations is only 0.15% for the 10.96% water mixture at 20°, and as the majority of the determinations are well within this figure, it is believed that a precision higher than the customary 0.1% has been obtained. (In Table I, left and right limb determinations are given alternately.) The viscosities of water are not absolute values, but were obtained by the use of the instrument constants derived from calibration with water at 20°, a viscosity of 1.005 c. p. being assumed at that temperature.

IV. Discussion of Results

The relationship between the fluidity of dioxane and the temperature in degrees centigrade is expressed over the range of temperature covered by the equation

$$\varphi = \frac{T - 171.97 + (T^2 - 146.58T + 39{,}264.2)^{1/2}}{0.51894} \qquad (1)$$

Observed and calculated values are compared in Table IV.

TABLE IV

COMPARISON OF OBSERVED VALUES OF FLUIDITY OF DIOXANE WITH VALUES CALCULATED FROM EQUATION 1

Temp., °C.	20	25	30	40	50	60	80
Observed	76.48	83.55	90.93	106.21	122.58	139.92	177.75
Calculated	76.48	83.55	90.86	106.22	122.56	139.92	177.77

By rearrangement of equation 1, we may calculate the absolute temperatures required for fluidities of 50, 100 and 200 rhes. These are listed in Table V, together with the values calculated from the atomic temperature constants,[9] and the association "n."

(n = Observed absolute temperature/calculated absolute temperature)

Extrapolated values are given in parentheses.

TABLE V

ASSOCIATION OF DIOXANE BY FLUIDITY METHOD

Fluidity in rhes	Absolute temperature Observed	Absolute temperature Calculated	Association n
50	(272.6)	179.2	(1.52)
100	309.0	199.6	1.55
200	(364.0)	230.7	(1.58)

It is observed that the association increases with the temperature. On the other hand, the fluidity-specific volume plot shows positive curvature, thus indicating a breaking down of association. Also, this value is rather high for a compound of this type, so that some doubt is cast upon the values of the atomic temperature constants—particularly that of the oxygen atom.

The fluidity is plotted against the composition by weight of the mixtures in Fig. 1. There is an inflection point in the curves at about 5% of water—an unusual type of behavior, Bingham and Rogers[10] having found

(9) Bingham and Spooner, *J. Rheol.*, **3**, 221 (1932).

(10) Bingham and Rogers, *ibid.*, **3**, 113 (1932).

only two examples out of one hundred and thirty-one mixtures studied. Between 5 and 100% water, the curves follow the usual course of mixtures of two liquids in which a volume contraction occurs. It has been previously noted[3] that the minimum in these curves shifts toward the region of higher dioxane concentration with increasing temperature. This effect is also seen here, the minimum being at 45% water at 20°, and at 32.5% water at 80°. This, however, is to be expected in mixtures of this type,

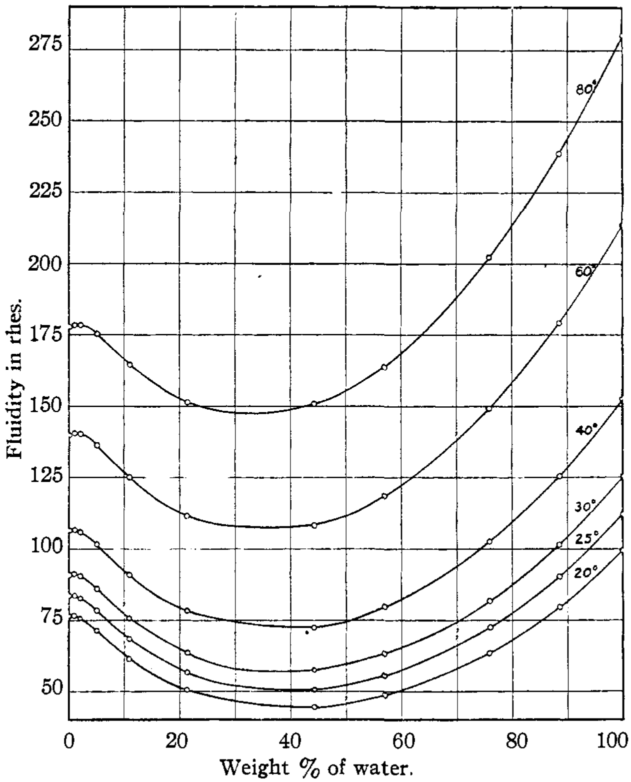

Fig. 1.—Fluidity–concentration curves of dioxane–water mixtures.

and the minimum has no meaning. The important factor is the point of greatest deviation from linearity,[11] or in other words, the point at which the slope of the experimental curve is equal to that of the straight line connecting the fluidities of the pure components. The mean value determined from the six curves is 49.9% of water, which corresponds, within the error of reading, to a mixture of the composition $C_4H_8O_2 \cdot 5H_2O$. Assuming that the dioxane and water present uncombined have not been dissociated, it is possible to calculate the amount of the hydrate formed.

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

From the atomic temperature constants[9] it appears that this compound should have a fluidity of 100 rhes at an absolute temperature of 771.6°. By interpolation from the curves, a mixture of this composition is found to have a fluidity of 100 rhes at 326.4°. Pure dioxane and pure water attain this fluidity at 309.0 and 293.2°, respectively, so that if the mixture were wholly uncombined, the absolute temperature necessary for a fluidity of 100 rhes (using volume % of components) would be $309.0° \times 0.4918 + 293.2° \times 0.5082 = 301.0°$. Letting x represent the fraction of the volume of the mixture which is combined, we obtain $771.6°x + 301.0° (1-x) = 326.4°$, and $x = 0.054$, so that approximately 5.4% by volume of the mixture is in combination.

This value serves to indicate the order of magnitude of combination, but may be appreciably in error, because of the uncertainty of the value of the atomic temperature constants previously noted, and in a greater degree, because of the negative curvature between pure dioxane and 5% water. This indicates an increase in fluidity which is ascribed to dissociation of the highly associated water and moderately associated dioxane in this region. It will also be noted that the specific volume varies in the same manner as the fluidity; the addition of small amounts of water results in an increase in volume, whereas larger amounts result in a volume contraction.

V. Summary

1. The viscosities of dioxane, water and of nine dioxane-water mixtures have been measured over the temperature range 20-80°.

2. The variation of the fluidity of dioxane with temperature is expressed by the equation $\varphi = [T - 171.97 + (T^2 - 146.58T + 39{,}264.2)^{1/2}]/0.51894$.

3. The fluidity-concentration curves are all inflected in the neighborhood of 5% water, showing that addition of small amounts of water results in an increase in fluidity, whereas larger amounts produce the customary decrease.

4. The points of maximum deviation from linearity of the fluidity-concentration curves indicate the presence of approximately 5% of a hydrate of the formula $C_4H_8O_2 \cdot 5H_2O$.

EASTON, PENNA.

RECEIVED AUGUST 7, 1933
PUBLISHED DECEMBER 14, 1933