

[CONTRIBUTION FROM THE MORLEY CHEMICAL LABORATORY, WESTERN RESERVE UNIVERSITY]

The System Dioxane and Water

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Introduction

There has been a considerable interest shown in the use of symmetrical dioxane (1,4) after it was recommended by Anschütz and Broeker¹ as an excellent organic solvent for molecular weight determinations. The first important workers, Herz and Lorentz,² unfortunately overlooked the highly hygroscopic nature and the slow decomposition with time of dioxane. These two properties were later pointed out by Roth and Meyer³ and consequently some of the results of Herz and Lorentz are in error because of the questionable purity of their dioxane.

Since dioxane is completely miscible with water it cannot only serve as a solvent for investigating the properties of the various solutes in it, but can also be used when it is desirable to know the properties of solutes in the mixed solvents, dioxane and water. Thus in view of the importance of dioxane in its various applications it was thought desirable to determine various physical properties not only in the pure state but also in its various mixtures with water over a wide range of temperatures.

Experimental

Materials.—The dioxane was purified by a modification of the Kraus and Vingee⁴ method. Commercial dioxane was refluxed over sodium hydroxide and after distillation boiled for a long period over metallic sodium, fresh metal being added from time to time. It was then crystallized several times. The final product melted at $11.78 \pm 0.01^\circ$.

The water used in this investigation was prepared by repeated crystallizations from selected pieces of ice.⁵ The fifth crop proved very pure. The conductivity of the liquid from this ice was 0.95×10^{-6} mhos at 25° .

Procedure.—The apparatus was cleaned and dried and allowed to stand overnight in dry air. The different concentrations were prepared by weighing the desired amounts in small glass-stoppered bottles. Transfer of liquids and all the weighings were performed in an atmosphere of purified air. The dioxane was recrystallized each time before being used.

Temperatures in all cases were kept constant to 0.01° up to 40° and $\pm 0.02^\circ$ above 40° , and were referred to a thermometer calibrated by the Bureau of Standards.

(1) Anschütz and Broeker, *Ber.*, **59**, 2844 (1926).

(2) Herz and Lorentz, *Z. physik. Chem.*, **A140**, 406 (1929).

(3) Roth and Meyer, *Z. Elektrochem.*, **39**, 35 (1933).

(4) Kraus and Vingee, *THIS JOURNAL*, **56**, 511 (1934).

(5) Ephraim, "Inorganic Chemistry," translated by P. C. Thorne, Gurney and Jackson, London, 1932, p. 356.

Densities were determined by the dilatometer method. The dilatometer was calibrated with purified mercury. The working volume was 7.7 to 8.7 cc. and the total height 23.3 cm. The smallest volume capable of being read was 0.0001 cc., which corresponds to an accuracy of approximately one part in fifty thousand.

The capillary rise method was used for surface tension measurements as outlined by Richards and Coombs.⁶ The large tube had a diameter of 3.8 cm. and the capillary tube a radius of 0.01815 cm. as determined by careful calibration with a mercury thread. The length of the thread was measured by means of a precision micrometer.

A static method similar to the one previously described by Hovorka and Dreisbach⁷ was used for measuring the vapor pressure.

For the measurements of the three properties above a cathetometer with a reproducible accuracy of ± 0.01 mm. was used. All of the determinations were carried out with the apparatus sealed off *in vacuo*.

The index of refraction was determined with an Abbé refractometer accurate to ± 0.0001 . Measurements were carried out at $25 \pm 0.05^\circ$ using sodium light as a source of illumination.

The freezing point curve was investigated with the usual Beckmann apparatus. The temperature was controlled by cooling ethyl alcohol with solid carbon dioxide in a gallon (4-liter) Dewar flask and was maintained three degrees lower than the freezing point of the solution under investigation. Precautions were taken to prevent moisture from entering the freezing point tube.

Experimental Results.—The experimental results are summarized in Tables I–VI and Figs. 1–3. The temperature is in degrees centigrade and vapor pressure in mm. of mercury. The vapor pressure data, Table III, are for round values of concentration obtained by graphical interpolation.

Discussion of Results

The results obtained deviate widely from the ideal solution laws as was to be expected, since dioxane is non-polar while water is a highly polar substance. A study of the experimental data shows a pronounced difference in internal pressures of the dioxane and water. Table IV of the partial molal volumes of the 25° isotherm shows this phenomenon exceedingly well. ($\bar{V} - V^0$ is the partial molal volume of each constituent, \bar{V} , less the molal volume of that constituent in the pure state, V^0 .) From the curves in Fig. 1 we see that the maximum change in the partial molal

(6) Richards and Coombs, *THIS JOURNAL*, **37**, 1656 (1915).

(7) Hovorka and Dreisbach, *ibid.*, **56**, 1664 (1934).

TABLE I
 SURFACE TENSION OF THE DIOXANE-WATER SYSTEM

Dioxane mole fr.	Temperature, °C.								
	10	20	25	30	40	50	60	70	80
0.1011	48.09	46.52	45.73	44.91	43.44	42.24	40.62	39.09	37.71
.1916	42.66	41.38	40.45	39.81	38.29	36.92	35.56	34.22	33.02
.3219	39.30	37.99	37.13	36.52	35.26	33.98	32.73	31.41	30.16
.4065	38.09	36.82	36.25	35.52	34.28	32.89	31.69	30.39	29.05
.4319	37.87	36.69	36.05	35.32	34.02	32.75	31.40	30.14	
.5251	36.94	35.77	35.31	34.63	33.21	32.08	30.58	29.43	28.11
.6091	36.55	35.38	34.74	33.96	32.72	31.34	30.08	28.86	27.42
.7417		34.62	34.06	33.31	32.45	30.60	29.20	27.78	
.8748	35.21	34.02	33.52	32.80	31.25	30.11	28.57	27.09	
1.0000		33.39	32.85	32.19	30.73	29.35	27.81	26.25	24.76

 TABLE II
 DENSITY OF THE DIOXANE-WATER SYSTEM

Dioxane mole fr.	Temperature, °C.								
	10	20	25	30	40	50	60	70	80
0.1011	1.03324	1.02738	1.02447	1.02136	1.01491	1.00860	1.00176	0.99439	0.98858
.1916	1.04467	1.03708	1.03314	1.02961	1.02208	1.01388	1.00553	.99669	.99006
.3219		1.02420	1.03722	1.03355	1.02468	1.01464			
.4065		1.04063	1.03634	1.03123	1.02164	1.01161	1.00140	.99091	.98054
.4319	1.05015	1.04042	1.03553	1.03063	1.02034	1.01025	1.00001	.98721	.97902
.5021		1.03785	1.03296	1.02790	1.01758	1.00690	0.99601	.98648	.97558
.6074	1.04486	1.03521	1.02995	1.02427	1.01416	1.00315	.99168	.98233	.97107
.7633	1.04379	1.03361	1.02806	1.02285	1.01094	1.00038	.98981	.97840	.96766
.8760	1.04307	1.03328	1.02788	1.02210	1.01074	0.99974		.97733	.96598
1.0000		1.03318	1.02766	1.02189	1.01045	.99948	.98781	.97693	.96486

 TABLE III
 VAPOR PRESSURE OF THE DIOXANE-WATER SYSTEM
 (Corrected to 0°)

Dioxane mole fr.	Total pressure Temperature, °C.								Partial pressure 25°C.		
	10	20	25	30	40	50	60	70	80	Dioxane	Water
0.000	9.2	17.5	23.8	31.8	55.4	92.6	149.6	233.8	355.1	0.0	23.8
.100	14.8	27.7	37.0	49.2	84.1	138.8	218.8	336.1	501.5	11.1	25.9
.200	18.0	32.9	42.8	57.6	95.7	156.8	245.4	373.7	550.0	17.7	25.1
.300	19.5	35.4	45.7	61.3	101.8	164.0	255.9	387.9	569.5	22.5	23.2
.400	20.1	36.5	47.3	62.5	104.3	165.1	257.7	390.8	575.5	26.2	21.1
.500	20.3	36.7	47.7	62.9	104.6	165.3	257.9	390.9	576.5	28.6	19.1
.600	20.4	36.8	47.7	62.9	104.6	165.3	257.9	390.7	571.0	30.1	17.6
.700	20.5	36.9	47.7	62.9	104.4	165.0	257.4	386.7	556.0	31.6	16.1
.800	20.6	36.7	47.5	62.4	103.0	163.6	252.0	374.1	526.5	33.2	14.3
.900	19.5	34.4	45.2	59.0	97.4	150.2	230.9	345.2	476.0	35.0	10.2
1.000	17.0	28.1	36.9	47.6	76.6	119.8	181.3	266.9	382.8	36.9	0.0

 TABLE IV
 PARTIAL MOLAL VOLUME IN CC.

Dioxane mole fr.	Water	Dioxane
0.0000	18.05	79.78
.1011	17.95	82.77
.1916	17.77	83.84
.3219	17.46	84.72
.4065	16.92	85.65
.4319	16.76	85.97
.5021	16.75	85.95
.6074	16.78	85.88
.7633	17.20	85.75
.8760	17.43	85.70
1.0000	17.48	85.69

 TABLE V
 REFRACTIVE INDEX

Dioxane mole fr.	Refr. index	Dioxane mole fr.	Refr. index
0.0000	1.3325	0.5021	1.4080
.0132	1.3380	.6052	1.4116
.1011	1.3670	.7417	1.4153
.1916	1.3840	.7633	1.4155
.3219	1.3980	.8760	1.4173
.4065	1.4038	1.0000	1.4198
.4319	1.4049		

volume of water is about 8%, whereas that of the dioxane is about 4%. The greatest deviation is in the region of low concentration of dioxane.

TABLE VI
FREEZING POINTS OF DIOXANE-WATER SYSTEM

Dioxane mole fr.	Freezing point, °C.	Eutectic temp., °C.
0.0000	0.0	
.0855	-10.1	-14.9
.0905	-10.8	
.1011	-11.6	-14.9
.1140	-12.7	-14.9
.1515	-14.9	-14.9
.1830	-11.1	
.2500	-3.6	
.3219	-0.7	
.4007	1.0	
.4285	1.5	-14.9
.5202	2.8	
.6074	3.7	
.6351	3.9	
.7296	5.0	
.7633	5.4	
.8760	7.5	-14.9
.9208	8.7	
1.0000	11.78	

The partial pressure of water, Fig. 2, is abnormally high in this neighborhood, while dioxane follows the natural course for systems having a maximum vapor pressure. There is also a decided maximum

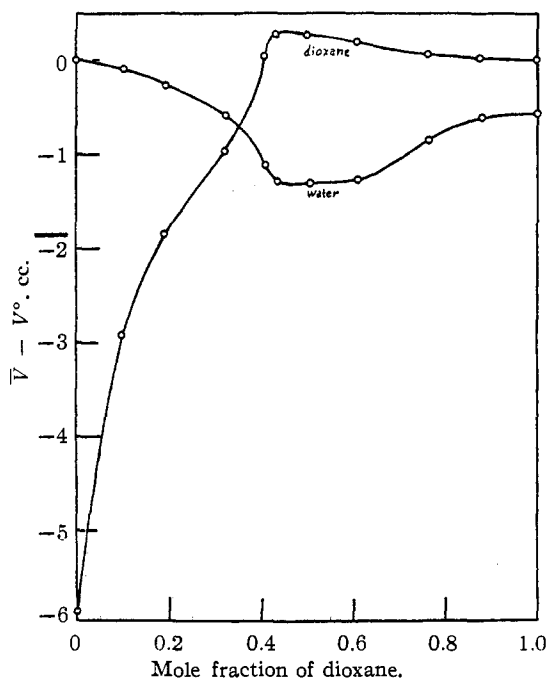


Fig. 1.—Partial molal volumes of dioxane and water.

in the density curve of this system. Geddes⁸ reports a maximum in the viscosity of this system as well as an inflection point in the fluidity curve. The latter is "an unusual type of behavior." It

(8) Geddes, *THIS JOURNAL*, **55**, 4832 (1933).

is to be noted that this point of inflection may be due entirely to the densities given by Geddes. In the region between 0 and 5% water he gives

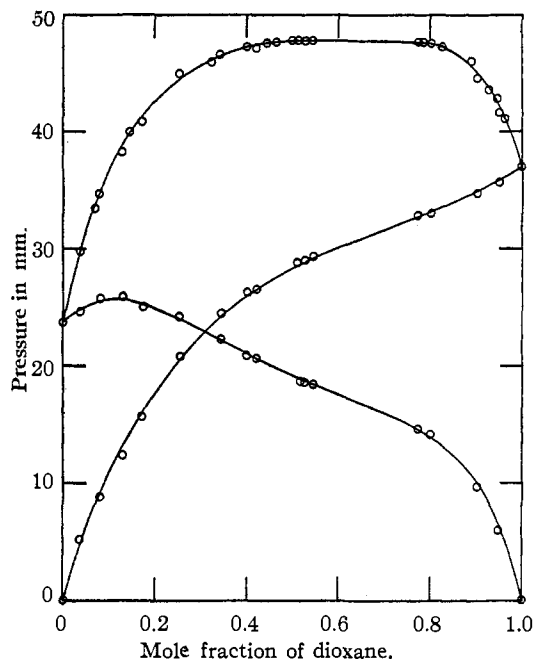


Fig. 2.—Total and partial vapor pressure curves of dioxane-water mixtures at 25°.

two points which are decidedly higher than his values at 0 and 5%. No such high values were found in this work nor in that of Gillis and

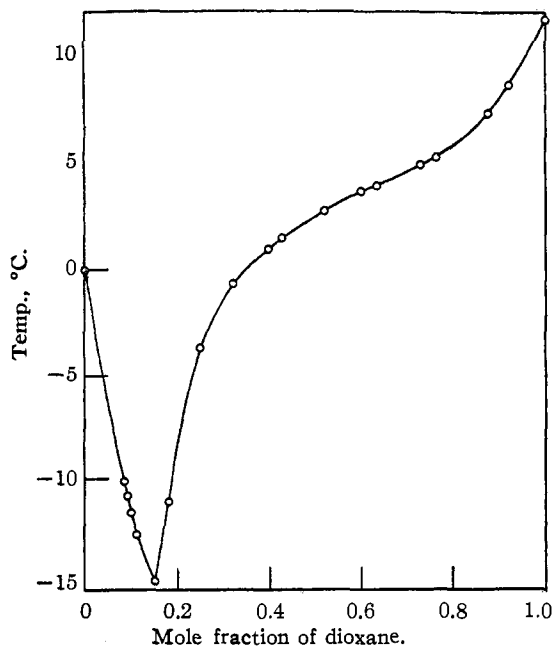


Fig. 3.—Freezing point curve of dioxane-water mixtures.

Delaunoy.⁹ The density curve is quite normal in this region.

The refractive index does not possess a maximum but for both refractive index and surface tension the deviations from the ideal are very great.

The eutectic point at 0.152 mole fraction of dioxane and a temperature of -14.9° agrees well with that found by Gillis and Delaunoy. However, these workers report a peculiar trend in the curve between 0.8 and 1.0 mole fraction dioxane. This has not been confirmed and the results obtained here are in excellent agreement with those found by Bell and Wolfenden.¹⁰ Gillis and Delaunoy in calling attention to this peculiar irregularity base their conclusions on one point only which may well be in error by 10%. Further, it is difficult to understand why they report two densities for their pure dioxane at 20° , namely, 1.0345 and 1.03215. The maximum deviation from the ideal linear freezing-point curve, Fig. 3, occurs at 0.37 mole fraction of dioxane corresponding to the maximum found in the density measurements.

Values for the vapor pressure of pure dioxane, Table III, are higher at low temperatures and lower at higher temperatures than the corresponding values given by Herz and Lorentz.² The vapor pressure may be expressed by means of the equation

(9) Gillis and Delaunoy, *Rec. trav. chim.*, **53**, 186 (1934).

(10) Bell and Wolfenden, *J. Chem. Soc.*, 822 (1935).

$$\log_{10} P \text{ (mm.)} = -1933.8/T + 8.0588$$

with a maximum deviation of one per cent. over the temperature range 10 to 80° .

Dioxane itself is a very normal liquid. The Eötvös constant as calculated is 2.11 for the temperature range investigated. The parachor is 205.7, which agrees fairly well with the calculated value of 202.1. The molecular refraction according to the expression of Lorentz and Lorenz gives an experimental value of 21.678, which is in excellent agreement with the theoretical value of 21.690.

The authors wish to express their appreciation to Dr. J. O. Morrison, of Yale University, for furnishing the purified dioxane.

Summary

1. The density, surface tension and total vapor pressure of the dioxane-water system were investigated for the temperature range 10 to 80° .
2. The partial vapor pressure and the index of refraction for this system were determined at 25° .
3. The freezing point curve of the dioxane-water system was studied.
4. The dioxane-water system was discussed and the possible errors of other workers in the case of freezing points, density and fluidity were pointed out.

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The Reaction of 2,3-Epoxybutane with the Grignard Reagent

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The rearrangement of certain ethylene oxides in Grignard reactions is well known. Among the simple alkyl or aryl substituted ethylene oxides, 2,3-epoxybutane,¹ 1,2-epoxy-2-methylpropane,² 1,2-epoxy-2-methylbutane,³ 1,2-epoxy-2-phenylpropane,⁴ and styrene oxide,⁵ have been reported to rearrange in Grignard reactions to produce one alcohol, while 1,2-epoxypropane⁶⁻⁸ and 1,2-epoxybutane⁸ have been reported not to rearrange.

(1) L. Henry, *Compt. rend.*, **145**, 406 (1907).

(2) L. Henry, *ibid.*, **145**, 21 (1907).

(3) Fourneau and Tiffeneau, *ibid.*, **145**, 438 (1907).

(4) Tiffeneau, *ibid.*, **140**, 1460 (1905).

(5) Fourneau and Tiffeneau, *ibid.*, **146**, 698 (1908).

(6) Hess, *Ber.*, **46**, 3117 (1913).

(7) Levene and Walti, *J. Biol. Chem.*, **90**, 81 (1931).

(8) Levene and Walti, *ibid.*, **94**, 367 (1931).

In order to explain the rearrangement of cyclohexene oxide in a methylmagnesium iodide reaction reported by Bedos, Bartlett and Berry⁹ adopted the Blaise¹⁰ structure for the primary intermediate.^{11,12}

(9) Bartlett and Berry, *This Journal*, **56**, 2683 (1934).

(10) Blaise, *Compt. rend.*, **134**, 552 (1902).

(11) This theory was criticized by Grignard [*Bull. soc. chim.*, [3] **29**, 944 (1903)] who preferred to depict the oxide ring as breaking at much higher temperatures. Boord and Summerbell readvanced the Blaise theory (Columbus, Ohio, meeting of The American Chemical Society, May, 1929) and Ribas and Tapia placed it on a more secure basis as a result of extensive experiments with ethylene oxide, epichlorohydrin and 3-methoxy-1,2-epoxypropane [*Anal. soc. españ. fis. quím.*, **30**, 778 (1932); **30**, 944 (1932)].

(12) Boord and Summerbell and Ribas and Tapia suggested as likewise possible the structures $\text{BrMgOCH}_2\text{CH}_2\text{Br}$ and $\text{Mg}(\text{OCH}_2\text{CH}_2\text{Br})_2$ for ethylene oxide intermediates.