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BOILING-POINT-COMPOSITION DIAGRAM OF THE SYSTEM DIOXANE-WATER

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ABSTRACT

Dioxane and water form a positive homoazeotrope which has an azeotropic decrease in temperature sufficiently large to effect the complete removal, by fractional distillation through an efficient column, of water present as an impurity. The boiling-point-composition diagram, including the composition of the vapor in equilibrium with the boiling liquid, was determined. The normal boiling point of dioxane was found to be 101.320° C.

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I. INTRODUCTION

During the past few years, the system dioxane (1,4-diethylene dioxide)-water has received considerable attention, for several reasons. The boiling point, freezing point, and density of dioxane are not very different from those of water and, what might be least expected considering its symmetrical ether structure and nonpolar character, it is miscible with water in all proportions. These mixtures are of particular interest in electrochemistry because the low dielectric constant of dioxane permits the preparation of a mixture having any desired dielectric constant between the values of about 2 and 80. Åkerlöf and Short [1]² measured the dielectric constants of dioxane-water mixtures over the temperature range 0 to 80° C. Kraus and Fuoss [9] used mixtures of dioxane and water in a study of the conductance of electrolytes as influenced by the dielectric constant of the solvent medium. Grady [6] measured the infrared absorption spectra of this system. From a study of the freezing points of solutions of normal water and of deuterium oxide in dioxane, Bell and Wolfenden [3] were able to show that the association factor for D₂O is about 3 percent more than for H₂O at the same concentrations. Gillis and Delaunois [5] measured the freezing points, boiling points, densities, and indices of refraction of the system water-dioxane. Their measurements of boiling point, however, were reported only to 0.1° C and were not corrected to normal pressure. They made no attempt to establish the composition of the vapor phase in equilibrium with the boiling

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² The figures in brackets here and throughout the text refer to the references at the end of the paper.

liquid for any point of the system. Hovorka, Schaefer and Dreisbach [8] measured densities, surface tensions, and total vapor pressures in the system from 10 to 80° C and, in addition, the partial vapor pressures and indices of refraction at 25° C, and the freezing points. Geddes [4] measured the fluidity of dioxane-water mixtures over the whole range of composition between 20 C and 80° C. Scatchard and Benedict [12] measured the freezing points of dilute solutions of dioxane in water and the effect of added salts on the freezing points. Hertz and Lorentz [7] measured the densities, viscosities, surface tensions, and refractive indices of the system over the whole range of composition at several temperatures.

In the present investigation the boiling-point-composition diagram at normal pressure for the system dioxane-water was determined over the complete range of composition.

II. MATERIALS AND APPARATUS

Three kilograms of the best grade of 1,4-dioxane sold by the Eastman Kodak Co. was distilled through a vacuum-jacketed, 40-bulb, glass rectifying column [15] equivalent to about 30 theoretical plates. Dioxane and water form a positive homoazeotrope (homogeneous mixture of minimum boiling point) which contains about 52 mole percent of water. The boiling point of this azeotrope (87.82° C) is so much lower than the boiling point of dioxane (101.32° C) that water, if present in not too large an amount, can be removed completely in the head portions of a fractional distillation, thus permitting the collection of anhydrous dioxane in the middle and tail fractions. The anhydrous dioxane prepared in this way was found to be of a high degree of purity when tested in a standard differential ebulliometer [15].

The water used for preparing the mixtures of dioxane and water, and for the comparative standard for the boiling-point determinations, was prepared by redistillation with alkaline permanganate of the distilled water supplied to the laboratory, following this by a simple distillation, rejecting the first and last portions in each case.

For the determination of the boiling points two ebullimeters were used. One of these was a simple barometric ebulliometer containing the redistilled water for the reference standard. The other was a standard differential ebulliometer containing the dioxane or the mixtures of dioxane and water under investigation. These ebullimeters, together with their accessories, have been described in connection with the determination of the boiling-point-composition diagram for dilute aqueous solutions of deuterium oxide [13]. The same platinum-resistance thermometer and Mueller thermometer bridge were used in this investigation.

III. PROCEDURE AND RESULTS

First, the boiling point of dioxane of a known degree of purity was determined. To remove moisture absorbed by the hygroscopic dioxane during its transfer to the ebulliometer, several portions of 2 to 3 ml were distilled from the side tube of the condenser.³ After this was done, the difference between the boiling point and condensation temperature, Δt , was only 0.003° C, which corresponds to the fifth or highest degree on the Świątosławski scale of purity [15]. The boiling point was next determined at the prevailing atmospheric pressure and

³ Reference [13] figure 2.

at two other pressures, one slightly below and one slightly above 1 atmosphere. By this procedure the value of the change in boiling point of the dioxane, Δt_s , and the change in boiling point of water, Δt_w , corresponding to the same change in pressure were obtained at pressures slightly above and slightly below 1 atmosphere. The ratio $\Delta t_s/\Delta t_w$ at 1 atmosphere was then computed and the normal boiling point of the preparation was calculated by the formula [16] $t_s = t'_s + (100 - t'_w)\Delta t_s/\Delta t_w$, in which t_s is the normal boiling point of the preparation under investigation and t'_s and t'_w are the boiling points of the preparation and of water, respectively, measured under the same actual pressure. The normal boiling point thus obtained for this sample was 101.321°C . The boiling point found for a second fraction of the dioxane, having $\Delta t = 0.004^\circ$, was 101.319°C .

A series of mixtures of dioxane and water were prepared, and the values of their normal boiling points and of the differences between their boiling points and the temperatures of condensation of their vapors were measured in the differential ebulliometer, using the same procedure. It was shown in a previous investigation [13] that the amount of fractionation which occurs in this differential ebulliometer is very nearly equivalent to that of one theoretical plate of a fractionating column. With this knowledge it is a simple matter to construct the vapor-composition curve as well as the liquid-composition curve from the boiling point and Δt data. However, over most of the range the vapor has a composition considerably different from the liquid, and the composition of the latter is thereby altered from its original value, since the amount of the vaporized mixture in the dead space above the boiling liquid is appreciable. To make the necessary correction, the volume of the dead space and the amount of condensed vapor in the drop counters and upper boiling tube were determined roughly. Then from a preliminary boiling-point-composition diagram, in which the original compositions were plotted as abscissa, the compositions of the vapor phase were determined for each mixture with sufficient accuracy to make the required small correction to the liquid compositions.

TABLE 1.—Data for the boiling-point-composition diagram

Mole percent dioxane (corr.)	Boiling point	Δt	Condensation temperature	$\Delta t_s/\Delta t_w$	$\Delta t_s/\Delta p$
	$^\circ\text{C}$	$^\circ\text{C}$	$^\circ\text{C}$		$^\circ\text{C}/\text{mm}$
0.00	100.000	0.000	100.000	1.000	0.03685
2.12	97.29	7.09	90.20	0.992	.0366
4.42	94.00	5.06	88.94	.975	.0359
7.33	91.97	3.62	88.35	.980	.0361
11.33	90.52	2.43	88.09	.984	.0363
15.76	89.41	1.53	87.88	.988	.0364
24.44	88.44	0.599	87.84	.993	.0366
32.44	88.04	.244	87.80	.998	.0368
37.41	87.90	.114	87.79		
43.54	87.84	.059	87.78	1.000	.0369
45.27	87.83	.047	87.78	1.002	.0369
46.91	87.82	.039	87.78		
57.55	87.95	.124	87.83	1.010	.0372
67.77	88.44	.444	88.00	1.021	.0376
79.99	90.09	1.17	88.92	1.055	.0389
87.96	92.70	2.89	89.81	1.122	.0414
95.75	97.24	3.01	94.23		
100.00	101.320	0.003	101.317	1.173	.0432

The data obtained are given in table 1. The first column contains the corrected mole percentage of dioxane in the liquid phase, the second the normal boiling point of the liquid, the third the difference between the boiling point of the liquid and the condensation temperature of the vapor, the fourth the condensation temperature (boiling point $-\Delta t$), the fifth the value of the ratio $\Delta t_s/\Delta t_w$ at 1 atmosphere, and the sixth the value of $\Delta t_s/\Delta p$ at 1 atmosphere obtained by multiplying $\Delta t_s/\Delta t_w$ by the value of $\Delta t_w/\Delta p$, $0.03685^\circ/\text{mm}$ [14].

The boiling-point-composition diagram for the system at 1 atmos-

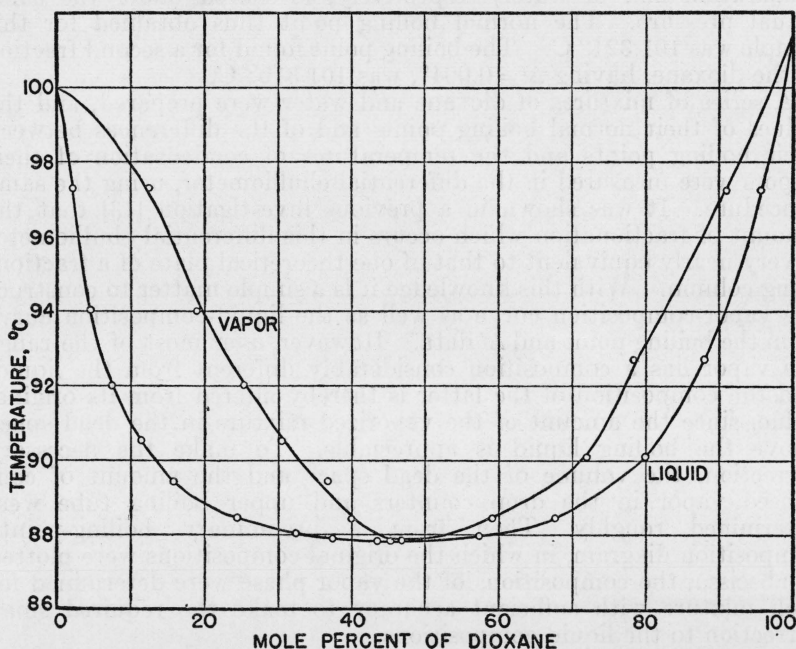


FIGURE 1.—Boiling-point-composition diagram for the system dioxane-water.

phere is shown in figure 1. The composition of the positive homoazeotrope lies between 47 and 48 mole percent of dioxane. An interesting observation here, that has been noted previously for other systems [15], is that the degree of purity of the azeotrope, as indicated by its Δt , is markedly lower (third degree) than the purity of the components (fifth degree). This is due to the high sensitivity of the azeotropic mixture towards very small amounts of impurities, which seems to be a general phenomenon. It is also noteworthy that the boiling point of dioxane is very much lowered by a small amount of water. Thus, 1 percent of water by weight (4.7 mole percent) lowers the boiling point by 4° . Accordingly each 0.001° lowering corresponds to 0.00025 percent by weight of water. A comparison of the values for the normal boiling point of dioxane obtained by different investigators is shown in table 2.

TABLE 2.—Boiling point of dioxane

Observer	Normal boiling point	$(dt/dp)_{760\text{mm}}$
	°C	° C/mm
Anschütz and Broeker [2].....	101.2 to 101.4	-----
Gillis and Delaunois [5].....	101.4	-----
Hertz and Lorentz [7].....	100.2 to 100.4	-----
Kraus and Vingee [10].....	¹ 101.24	-----
Milone [11].....	100.7	-----
Scatchard and Benedict [12].....	101.22	-----
Smith and Wojciechowski.....	101.32 ₀	0.0432

¹ At 761 mm.

On standing at room temperature in a bottle having its ground-glass stopper covered by a paraffin-sealed hood to prevent contamination, dioxane was found to undergo a slow change, probably a polymerization, which increases its boiling point. One sample, after standing in this way for 12 weeks, had a normal boiling point of 101.44° C, the increase amounting on the average to about 0.01° per week. The value of Δt for this sample was 0.094°. To obtain accurate measurements on dioxane it is, therefore, necessary to use freshly purified samples as well as to take precautions to exclude moisture.

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