five minutes at 50–55°, and was then poured slowly into 2000 ml. of hot water. The crude product was isolated as described in previous experiments, and amounted to 98.4 g. of oil. Distillation through a Podbielniak column at 50 mm. pressure gave a small fore-run (4.8 g.) and the following fractions: (a) 5.0 g., b.p. 150–153°, of material which solidified and which was identified as starting 1,2,3-trimethoxybenzene; (b) 4.5 g., b.p. 153–179°, of intermediate material; (c) 77.2 g., b.p. 179°, of 1,2,3-trimethoxy-4-bromobenzene (78% yield); (d) 4.5 g. of residue. The product turned dark on standing, and carbon analyses were consistently low. Freshly prepared material was used in Ullmann reactions to yield the expected products.

4-Bromoveratrole.—Veratrole was brominated by this method to provide 4-bromoveratrole, b.p. 164–167° (50 mm.), in 84% yield. This compound has been prepared previously by a variety of methods, including direct bromination,[8] with bromine diluted with air,[9] cyanogen bromide,[10] N-bromosuccinimide,[11] and by methylation[8] of bromoguaiacol.

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[9] M. Gaspari, *Gazz. chim. ital.*, **28**, **II**, 230 (1896).

[10] G. Bargellini and F. Madesani, *ibid.*, **61**, 684 (1931).

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An Unusual Salting-out Effect of Hydrohalogen Acids on Water–Dioxane Mixtures

BY W. T. GRUBB AND ROBERT C. OSTHOFF

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In the course of some reaction studies in the solvent system water–dioxane, it was found that the addition of hydrogen chloride or hydrogen bromide caused the formation of two phases over a limited concentration range. This behavior has not been previously reported despite the extensive use of water–dioxane as a medium for reactions under acidic conditions. Infinite miscibility of water with dioxane is ordinarily presumed,[1] although the 1-1-2 ternary compound $H_2O–HClO_4–O(CH_2CH_2)_2O$ has been reported.[2]

The authors therefore undertook a phase study of the ternary system water–dioxane–HX at 25° and atmospheric pressure.

Experimental

1,4-Dioxane.—Fisher Scientific Co. "Purified" 1,4-dioxane was further purified according to the general method which has been described by Kraus and Vingee.[3] However, during the final distillation a stream of dry nitrogen was passed through the condenser and over the collected dioxane to protect the material from atmospheric oxygen.[4] The dioxane was stored in a dark-colored bottle under dry nitrogen. The dioxane prepared in this manner was essentially free of peroxides, as indicated by a test with potassium iodide and acetic acid in the presence of Dry Ice; m.p. 11.78 ± 0.02° (previous value, 11.80[5]), $n^{21}D$ 1.4218 (previous value, $n^{21}D$ 1.4219[4]).

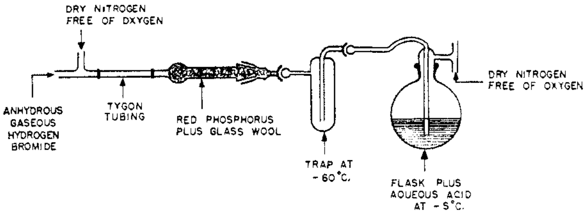

Fig. 1.—Apparatus for production of bromine-free aqueous hydrobromic acid.

Hydrogen Chloride.—du Pont analytical reagent grade hydrochloric acid was used without further purification. In some cases where higher concentrations were required Matheson anhydrous hydrogen chloride was added to the system.

Hydrogen Bromide.—Because reagent grade hydrobromic acid is available in only 42% concentration and may be contaminated by free bromine from atmospheric oxidation, the hydrogen bromide solution for these experiments was prepared by passing gaseous hydrogen bromide into distilled water employing the apparatus indicated in Fig. 1. The red phosphorus was used to remove bromine from the hydrogen bromide and the trap ensured the removal of phosphorus(III) bromide and any other high-boiling substances. At the start of the run dry nitrogen was allowed to pass through the system for 24 hours in order to sweep all oxygen from the lines and from the sample of distilled water. Then the hydrogen bromide was allowed to flow until a saturated solution was obtained (65% by wt.[6] was attained in approximately 5 hours). The colorless solution was stored under nitrogen until used.

Preliminary experiments showed that if a fairly concentrated aqueous acid solution was added with stirring into a sample of pure dioxane, the mixture remained clear up to a certain volume of acid, passed through a region of incom-

TABLE I

COMPOSITIONS OF THE SYSTEM H_2O–HCl–DIOXANE AT THE MISCIBILITY LIMITS

Aqueous acid added				
Volume,[a] ml.	Normality	Wt. % H_2O	Wt. % HCl	Wt. % Dioxane
0.65	12.00	1.87	1.04	98.08
.42	9.69	1.29	0.57	98.15
.53	7.08	1.73	.52	97.75
.90	4.87	3.06	.60	96.35
.96	2.42	3.44	.32	96.27
.90	3.13	3.18	.39	96.45
.86	4.09	2.98	.48	96.54
3.18	2.57	10.43	1.03	88.54
1.30	1.87	4.61	0.33	95.06
1.53	1.92	5.38	.39	94.30
2.05	2.12	7.05	.56	92.39
4.33	2.97	13.49	1.56	84.95
9.52	4.60	24.05	4.46	71.49
5.58	3.61	16.43	2.34	81.27
0.62	13.35	1.68	1.15	97.18
9.70	12.00	19.49	11.45	69.06
10.86	9.69	22.74	10.08	67.18
11.51	7.08	25.60	7.75	66.64
10.17	4.87	25.08	4.94	70.00
2.72	2.42	9.10	0.84	90.04
4.74	3.13	14.52	1.76	83.70
8.40	4.09	22.30	3.63	74.07
11.03	8.26	23.94	8.74	67.48
11.48	7.17	24.03	4.46	71.51
8.61	13.35	17.09	11.67	71.23
		5.10	7.26[b]	87.63
		7.32	8.81[b]	83.86
		13.22	10.96[b]	75.78
		11.38	10.37[b]	78.21
		14.72	12.98[b]	72.30

[a] Volume of acid added to 25.0 ml. of dioxane in each case. [b] Gaseous hydrogen chloride added to attain these concentrations (Method I).

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[1] F. Hovorka, R. A. Schaefer and D. Dreisbach, THIS JOURNAL, **58**, 2264 (1936).

[2] C. Smeets, *Naturw. Tijdschr.*, **19**, 12 (1937).

[3] C. A. Kraus and R. A. Vingee, THIS JOURNAL, **56**, 511 (1934).

[4] K. Hess and H. Frahm, *Ber.*, **71**, 2627 (1938).

[5] P. C. Teague and W. A. Felsing, THIS JOURNAL, **65**, 484 (1943).

[6] H. S. Booth, "Inorganic Synthesis," Vol. I. McGraw-Hill Book Co., Inc., New York, N. Y., 1939, p. 156.

TABLE II

COMPOSITION OF THE SYSTEM H_2O–HBr–DIOXANE AT THE MISCIBILITY LIMITS

Aqueous acid added				
Volume,[a] ml.	Normality	Wt. % H_2O	Wt. % HBr	Wt. % dioxane
0.71	14.70	1.58	3.15	95.27
3.78	14.70	6.99	13.93	79.09
0.60	13.85	1.41	2.52	96.06
4.49	13.85	8.42	15.04	76.53
0.48	11.97	1.24	1.76	97.00
5.85	11.97	11.34	16.06	72.60
0.43	10.70	1.18	1.41	97.41
6.49	10.70	13.04	15.62	71.35
0.46	8.99	1.35	1.28	97.37
6.95	8.99	14.82	14.07	71.13
0.44	7.59	1.34	1.02	97.63
7.08	7.59	16.00	12.17	71.83
0.48	6.20	1.53	0.91	97.56
6.54	6.20	16.01	9.52	74.46
0.65	4.34	2.19	0.86	96.97
3.57	4.34	10.57	4.15	85.29
1.66	3.69	5.46	1.74	92.78
7.20	7.75	16.05	12.59	71.37
0.84	3.64	2.86	0.93	96.20
7.02	8.37	15.35	13.25	71.40
1.28	3.40	4.31	1.29	94.39
2.72	4.02	8.43	3.07	88.51
5.22	5.00	14.11	6.48	79.41
2.12	3.64	6.82	2.25	90.93
		2.46	5.59[b]	91.98
		3.55	7.91[b]	88.57
		4.56	10.13[b]	85.29
		5.52	11.76[b]	82.70
		6.44	3.19[b]	80.38
		8.22	14.88[b]	76.90

[a] Volume of acid added to 25.0 ml. of dioxane in each case.
[b] Gaseous hydrogen bromide added to attain these concentrations (Method I).

plete miscibility indicated by marked visual cloudiness and then suddenly cleared as the acid addition was continued.

The cloud and clear points were determined quantitatively at various acid concentrations in the following manner:

Acids of various known concentrations were added from a buret to a 250-ml. glass-stoppered erlenmeyer flask containing 25 ml. of dioxane and thermostated at 25.0 ± 0.1°. Stirring was accomplished magnetically using a Teflon-covered bit. A cloud point and a clear point were obtained at each acid concentration with a reproducibility of ± 0.05 ml. A blanket of dry nitrogen above the system was provided during these operations. By the addition of acid in this manner, the region of incomplete miscibility is crossed along a line parallel to the volume axis. Two other methods were used to obtain additional points:

I.—The addition of gaseous hydrogen halide to a system containing known amounts of water and dioxane was employed to determine the miscibility limits along a line approximately parallel to the concentration axis. In these cases the entire sample was analyzed by titration with standard sodium hydroxide solution.

II.—The addition of aqueous acid to a system of water and dioxane or the addition of water to a system of aqueous acid plus dioxane was used to obtain points on the curve at intermediate acid concentrations.

The data for hydrogen chloride and hydrogen bromide are summarized in Tables I and II, respectively, on a volume basis. For a constant amount of dioxane (25 ml.) in each of these tables the compositions of the respective system at the miscibility limit is also expressed in terms of wt. per cent. of each component. Conventional phase diagrams for ternary systems are presented in Figs. 2 and 3.

In converting the composition of the systems from a volume basis to a weight per cent. basis, the densities of aqueous hydrochloric acid and hydrobromic acid for the various normalities were obtained by interpolations of the data of the "International Critical Tables."[7]

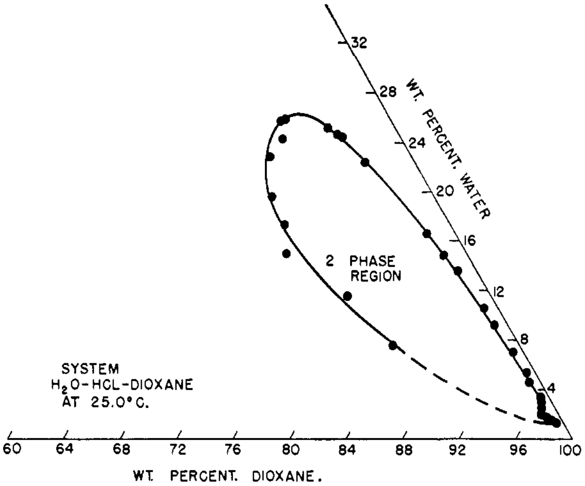

Fig. 2.—The ternary system water–hydrogen chloride–1,4-dioxane at 25.0°.

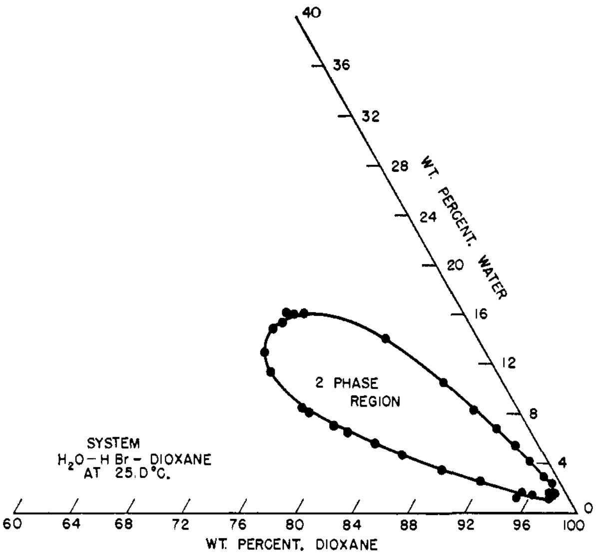

Fig. 3.—The ternary system water–hydrogen bromide–1,4-dioxane at 25.0°.

In Figs. 4 and 5 are presented directly the solubility limits in ml. for various concentrations of aqueous acid in 25 ml. of 1,4-dioxane. The boundary of the two-phase region is actually a closed curve. However, the portions of each curve at higher concentrations of aqueous acid have been omitted from Figs. 4 and 5 because they were obtained by addition of gaseous hydrogen chloride or hydrogen bromide (*cf.* Method I above) to the entire system and represent aqueous acids of concentrations unattainable at atmospheric pressure.

A surprisingly small quantity of aqueous acid is required to produce a two-phase system, *i.e.*, less than 2% of 9.69 *N* hydrochloric acid will cause the formation of two phases (less than 3% of 10.70 *N* hydrobromic acid). However, hydrogen chloride in any concentration will not cause the formation of two phases in the case of a system consisting of at least 34% water in dioxane (at least 29% water in the dioxane in the case of hydrogen bromide).

The data of Figs. 4 and 5 indicate that the maximum range of immiscibility occurs at concentrations corresponding to the approximate composition of the constant boiling acids, as well as the fact that hydrochloric acid solutions

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(7) "International Critical Tables," Vol. III, pp. 54–55.

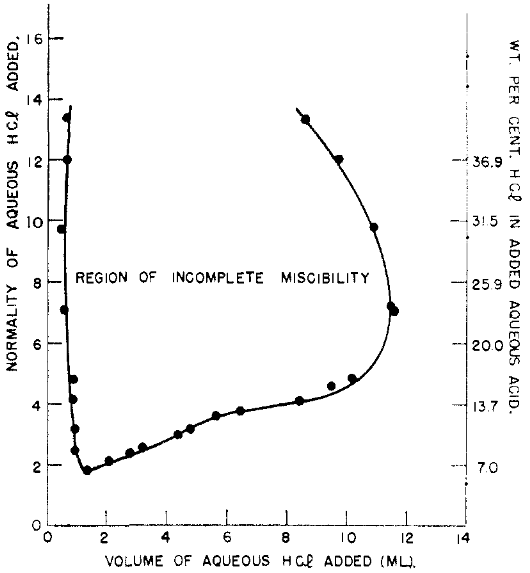

Fig. 4.—Solubility of aqueous hydrochloric acid of various concentrations on 25 ml. of 1,4-dioxane at 25.0°.

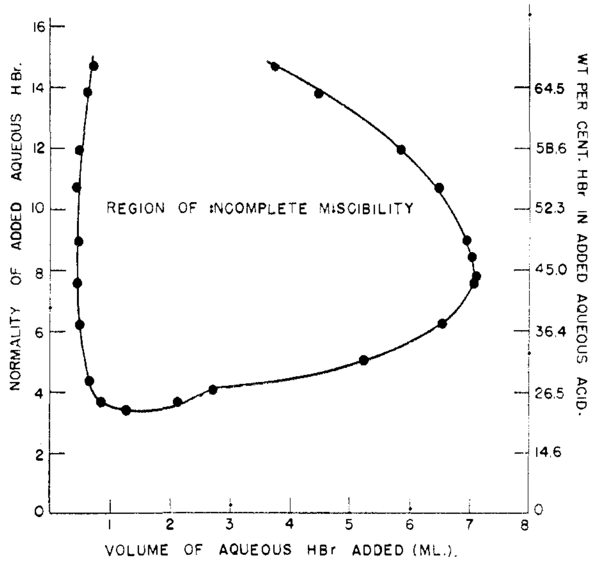

Fig. 5.—Solubility of aqueous hydrobromic acid of various concentrations in 25.0 ml. of 1,4-dioxane at 25.0°.

less than 1.87 *N* and hydrobromic acid solutions less than 3.64 *N* are completely miscible with 1,4-dioxane.

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Reactions of Quinolinium Compounds with Malononitrile and Ethyl Cyanoacetate

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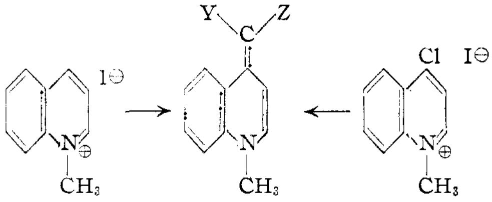
Our finding[1] that the product resulting from the condensation of 1-methylquinolinium iodide (I) with nitromethane in the presence of base is 1-methyl-4-nitromethylenequinolane (IIa), a correction of the structure suggested earlier by Kaufmann,[2] prompted the investigation of the reaction of 1-methylquinolinium iodide with other active methylene compounds. Malononitrile and ethyl cyanoacetate, of activity commensurate with that of nitromethane, have now been found to undergo reaction with quinolinium compounds to give similar condensation products (II). The reaction is related to that used for the preparation of dyes of the cyanine and isocyanine type,[3] which possess 4,α-unsaturation.



I II III

a, Y = H; Z = NO_2;
b, Y = CN; Z = CN;
c, Y = CN; Z = COOEt

Combination of 1-methylquinolinium iodide (I) with malononitrile in ethanolic sodium ethoxide gave a yellow product, m.p. 291.5–292.5°, in low yield. The analysis was correct for its formulation as 1-methyl-4-(α,α-dicyanomethylene)-1,4-dihydroquinoline (IIb), analogous to the established structure of the product (IIa) from nitromethane. The infrared absorption spectrum was also consistent with structure IIb. This structure was established unequivocally by the synthesis, in quantitative yield, of 1-methyl-4-(α,α-dicyanomethylene)-1,4-dihydroquinoline from 1-methyl-4-chloroquinolinium iodide (III) and malononitrile in alkaline solution. The products from the two reactions were identical. The device of comparing products obtained from 1-alkylquinolinium iodide with those from either the 4-chloro- or 4-iodo-1-alkylquinolinium iodide[4,5] has been useful for proving 4-substitution in the isocyanine dyes.

Malononitrile reacted with 1,2-dimethylquinolinium iodide in the presence of sodium ethoxide to produce 1,2-dimethyl-4-(α,α-dicyanomethylene)-1,4-dihydroquinoline in 34% yield. The structure of the product as the 2-methyl derivative of IIb was assigned on the basis of homology and effective blocking of the 2-position from attack by the malononitrile anion. The condensation of 1-methylquinolinium iodide with ethyl cyanoacetate gave 1-methyl-4-(α-carbethoxy-α-cyanomethylene)-1,4-dihydroquinoline (IIc), the structure of which was assigned on the basis of elemental analysis, analogy with the preceding examples, and similarity of the infrared spectrum with that of IIb. Similarly, 1,2-dimethylquinolinium iodide and ethyl cyanoacetate yielded 1,2-dimethyl-4-

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[1] N. J. Leonard, H. A. DeWalt, Jr., and G. W. Leubner, THIS JOURNAL, **73**, 3325 (1951).

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