structure and the border between distinct and diffuse bands, and shows that the diffuse bands extend at least to 2730 Å.

2. The quantum yields of polymerization and decomposition, and their variations with wave length, pressure and light intensity, have been determined.

3. Fluorescence is found to extend throughout the regions of distinct and diffuse bands, but to be absent in the continuum.

4. The absorption spectrum is interpreted as consisting of bands underlaid by continuous absorption, and the photochemical reactions produced are explained on this basis.

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Equilibrium in Liquid Systems of Three Components

BY WILLIAM T. REBURN AND WILLIAM N. SHEARER

Equilibrium curves for ternary systems involving polar liquids, water and halogen hydrides were needed. Very few published data on such systems of which the non-aqueous phases are fair conductors of electricity could be found. We were compelled therefore to secure the data in the laboratory. This paper presents data and curves for the equilibrium in a few such systems.

The experimental procedure was as follows. Glass-stoppered bottles containing measured portions of aqueous acid solutions of known concentration were placed in an agitator in a bath maintained at the desired temperature. When bath temperature was attained the organic liquid was delivered from a buret until the first appearance of permanent turbidity indicated saturation. In a few instances only, subsequent agitation caused the solution to clear, whereupon turbidity was restored by addition of a drop or two more. The percentage composition of the phase could then be calculated. Saturation points for the non-aqueous phases were obtained by delivering water from the buret to a solution of aqueous acid in the organic liquid until turbidity developed. End-points were sharper and were satisfactorily duplicated. No appreciable chemical reaction was noticeable during the time required for attainment of physical equilibrium except in the non-aqueous phases involving cyclohexanone with hydrogen bromide and hydrogen iodide.

The materials were obtained from the following sources. The hydrochloric acid was the C. P. product of commerce. The hydrobromic and hydriodic acids were prepared by the usual laboratory process from red phosphorus and bromine and from phosphorus iodide, respectively. These acids were preserved in colored bottles in the dark and remained colorless throughout the course of the experiments. The isoamyl and isobutyl alcohols and the cyclohexanone were of the highest grade furnished by the Eastman Kodak Company. The normal butyl alcohol was C. P. from the J. T. Baker Chemical Company. The liquids were all dried and redistilled and their purity established by boiling point, specific gravity and refractive index determinations.

In some cases tie-lines were determined by agitating, in the thermostat bath, mixtures containing suitable amounts of the three constituents, the two phases then being separated and titrated with baryta solution and phenolphthalein. From these data the coördinate tie-line points could be fixed on the curve.

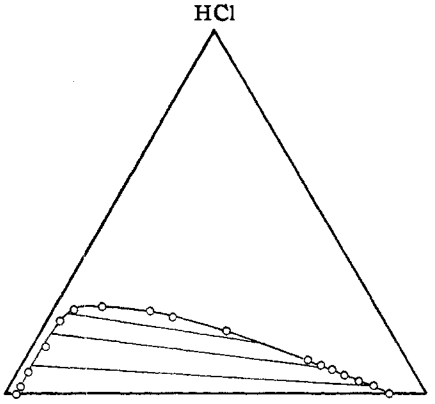

Fig. 1.—Water-HCl-isoamyl alcohol.

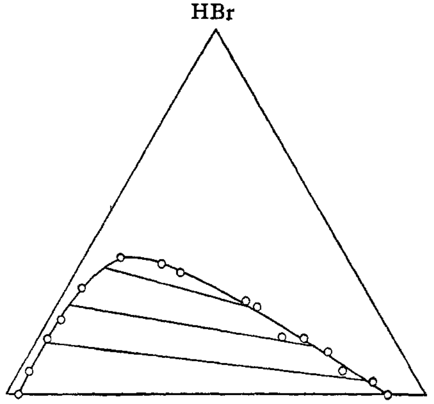

Fig. 2.—Water-HBr-isoamyl alcohol.

Experimental Data[1]

TABLE I

SYSTEM WATER, HCl AND ISOAMYL ALCOHOL PERCENTAGES BY WEIGHT, 25°

Water	Isoamyl alcohol
8.9	91.1
11.38	86.7
14.15	82.5
16.67	78.4
18.90	74.6
21.00	71.2
23.10	67.7
38.80	44.1
49.5	29.8
54.3	23.6
64.9	11.3
72.0	5.16
76.7	3.50
83.6	3.60
91.4	2.79
95.2	2.86
97.1	2.90

Tie-Line Data

HCl in water phase	HCl in alcohol phase
7.83	1.99
16.13	7.30
21.7	14.1

TABLE II

SYSTEM WATER, HBr AND ISOAMYL ALCOHOL AT 25°

Water	Isoamyl alcohol
9.00	91.0
11.36	85.3
16.90	76.8
17.7	70.6
21.2	63.2
26.4	57.6
28.4	47.8
30.2	44.2
42.0	25.0
45.8	19.1
54.7	8.17
67.7	3.39
76.9	3.00
83.0	2.84
91.7	2.58
97.0	3.00

Tie-Line Data

HBr in water phase	HBr in alcohol phase
13.5	3.5
24.0	13.0
34.1	23.5

TABLE III

SYSTEM WATER, HI AND ISOAMYL ALCOHOL AT 25°

Water	Isoamyl alcohol
8.50	91.5
12.0	82.8
21.0	58.8
24.0	52.6
25.8	47.5
27.8	43.2
29.1	40.1
43.2	15.7
62.3	2.76
76.6	2.55
77.5	3.03
91.2	2.98
97.2	2.80

Tie-Line Data

HI in water phase	HI in alcohol phase
16.84	9.45
30.0	21.1
41.1	30.5

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(1) The work on isoamyl alcohol was done by William T. Reburn, the remainder by William N. Shearer.

TABLE IV

SYSTEM WATER, HCl AND ISOBUTYL ALCOHOL AT 25°

Water	Isobutyl alcohol
16.1	83.9
27.3	68.4
35.4	58.3
40.0	52.3
44.6	46.6
49.6	40.9
53.2	36.7
56.4	33.1
59.2	30.0
61.5	27.5
69.5	18.7
79.8	10.3
84.8	8.4
91.2	8.8

Tie-Line Data

HCl in water phase	HCl in alcohol phase
10.4	6.3
7.7	3.6
4.2	1.3

TABLE V

SYSTEM WATER, HBr AND ISOBUTYL ALCOHOL AT 25°

Water	Isobutyl alcohol
16.1	83.9
22.6	72.2
29.1	61.8
35.1	53.1
48.9	35.0
57.3	25.7
62.4	20.0
66.9	15.4
70.8	12.6
75.5	11.0
82.8	8.7
91.2	8.8

Tie-Line Data

HBr in water phase	HBr in alcohol phase
10.8	6.0
8.7	4.3

TABLE VI

SYSTEM WATER, HI AND ISOBUTYL ALCOHOL AT 25°

Water	Isoamyl alcohol
16.1	83.9
24.9	67.0
32.0	54.7
37.8	46.7
39.6	44.3
61.9	19.3
69.2	16.7
91.2	8.81

Tie-Line Data

HI in water phase	HI in alcohol phase
11.6	8.3
4.8	4.0

TABLE VII

SYSTEM WATER, HCl AND ISOBUTYL ALCOHOL AT 40°

Water	Isobutyl alcohol
17.9	82.1
26.6	69.6
42.6	49.3
53.5	36.5
64.0	25.0
68.4	20.4
71.5	17.2
74.0	14.7
78.1	11.6
81.2	10.0
88.2	8.2
92.0	8.0

TABLE VIII

SYSTEM WATER, HCl AND ISOBUTYL ALCOHOL AT 55°

Water	Isobutyl alcohol
21.8	78.2
29.2	67.2
37.0	56.8
50.6	40.5
64.3	24.8
72.4	16.6
80.7	10.5
91.2	8.8

TABLE IX

SYSTEM WATER, HCl AND *n*-BUTYL ALCOHOL AT 25°

Water	*N*-Butyl alcohol
21.9	78.1
29.2	67.1
39.7	54.3
51.9	39.4
66.4	23.3
75.4	13.9
84.9	8.5
91.7	8.3

TABLE X

SYSTEM WATER, HCl AND CYCLOHEXANONE AT 25°

Water	Cyclohexanone
7.5	92.5
22.1	74.4
34.6	59.8
43.4	49.6
50.2	41.9
54.4	36.9
56.5	34.0
62.8	27.0
68.1	21.7
72.8	17.2
81.4	12.3
87.8	12.2

Tie-Line Data

HCl in water phase	HCl in cyclohexanone phase
9.5	2.3
8.8	1.1

Discussion

A study of the curves reveals one or two facts worthy of comment. The curves show, for example, that the increase in the solubility of the alcohol (or ketone) in the aqueous phase is built up very slowly as compared with the increase in the solubility of the water in the non-aqueous phase, with increase in the content of halogen acid; whereas at high concentrations of acid the solubility of the alcohol in the aqueous phase increases very rapidly.

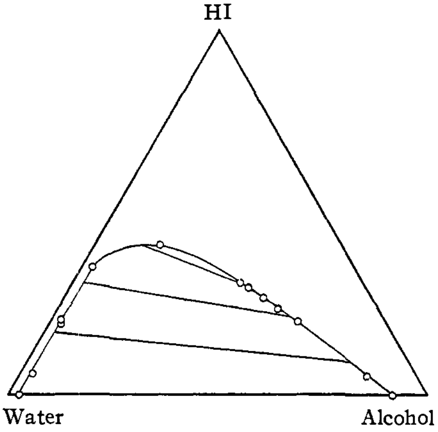

Fig. 3.—Water-HI-isoamyl alcohol.

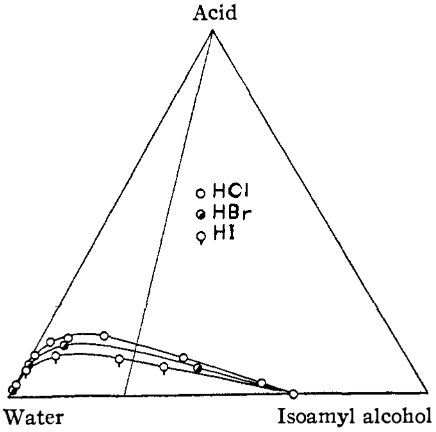

Fig. 4.—Mole percentage.

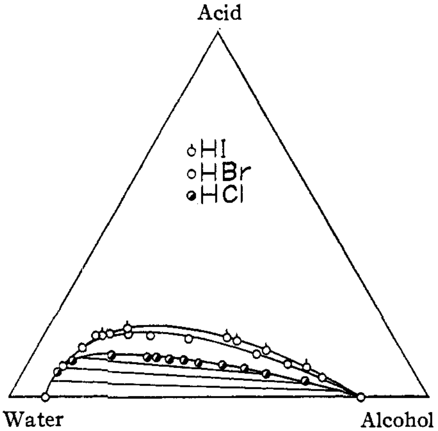

Fig. 5.—Water-halogen acids-isobutyl alcohol.

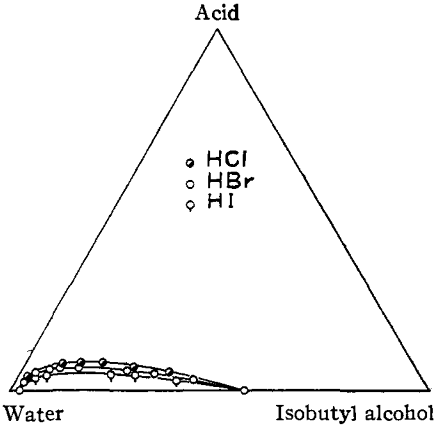

Fig. 6.—Mole percentage.

A possible explanation is suggested by a consideration of the effect of the halogen acids on the cohesive forces or internal pressure particularly in the water phase. Two liquid phases become the more miscible the more nearly their cohesive forces attain to comparable magnitudes.[2] Isoamyl alcohol, for instance, and water are but slightly miscible because the internal pressure of the water is so much greater than that of the alcohol. Any factor which functions to lower this cohesive force will favor miscibility. The halogen hydrides have but little effect in reducing the internal pressure of water in dilute solutions (some of the curves even suggest a slight increase at the lowest concentrations) but this effect becomes considerable at relatively high concentrations of acid. On this basis it seems possible to explain the steepness of the curve on the aqueous side.

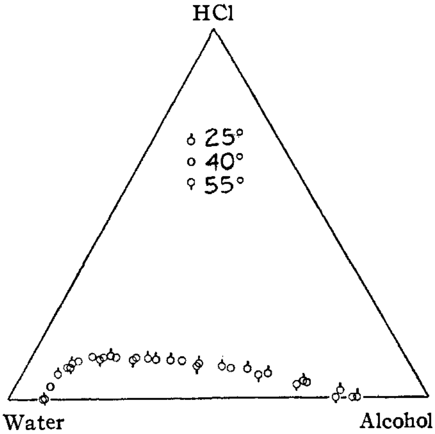

Fig. 7.—Effect of temperature on the system, water–HCl–isobutyl alcohol.

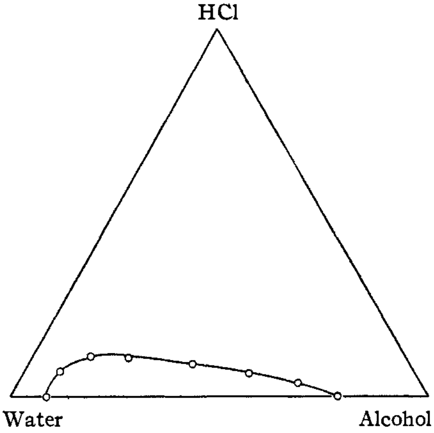

Fig. 8.—Water–HCl–*n*-butyl alcohol.

On the other hand, one would expect the presence of the halogen hydrides to bring about a measurable increase of the cohesive forces prevailing in the alcohol phase, due to their strongly polar character. The water which dissolves doubtless engages much of the acid, thereby suffering a decrease in internal pressure, these factors reinforcing one another in the direction of increased miscibility, thus accounting for the markedly rapid increase in the solubility of water in the alcohol phase.

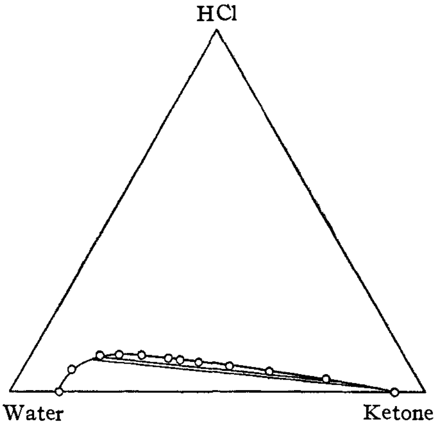

Fig. 9.—Water–HCl–cyclohexanone.

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(2) Harkins and King, THIS JOURNAL, **41**, 970 (1919).

Again, when the concentrations are expressed in mole percentages rather than weight percentages, the curves show a progressively increasing potency of the halogen hydride in inducing miscibility as one passes from hydrogen chloride through hydrogen bromide to hydrogen iodide. This would seem to be associated with the greater tendency of the hydrogen iodide in the water phase to enter into covalency relationship, due to its size and correspondingly weaker external field of force.[3] The covalent bonding doubtless predominates in the non-aqueous phase and miscibility is favored by an increase in the non-polar molecules in the aqueous phase.

Orton and Jones[4] present a curve for the system water, hydrogen chloride and *n*-butyl alcohol, for which they give no data and which appeared to be somewhat in error. Their work was repeated and a somewhat different curve obtained, Fig. 8. It is, as was to be expected, substantially identical with that for isobutyl alcohol.

Finally, temperature changes between the limits of 25 and 55° scarcely seem to affect the equilibria. This accords with expectation since the thermal changes accompanying the mixing appear to be substantially zero.

Summary

The mutual solubility of water and some polar organic liquids is increased by addition of the hydrogen halides. Equilibrium data and curves for a few such ternary systems have been worked out.

It is pointed out that the equilibrium relationships appear to be in qualitative agreement with theories of miscibility advanced by Harkins and others.

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[3] Fajans, *Z. Physik*, **23**, 1 (1924).

[4] Orton and Jones, *J. Chem. Soc.*, **115**, 1194 (1919).