

These results, when compared with those obtained in using an ether solution, show clearly that the sodium ethylate reactions with the alkyl haloid also go much slower in benzene solution.

Summary.

1. An attempt has been made to measure the rate of reaction of metallic sodium in powder form with isoamylbromide dissolved in ether, in dimethylaniline and in benzene.

2. The rate in ether was faster than in benzene, while in dimethylaniline the rate was much greater than in either of the other two.

3. This can be explained by the formation of ammonium and oxonium (very slight) salts and by the sodium replacing the less positive organic basic radical in the salt. It cannot be explained if dissociation of the alkyl haloid alone is used and if the dissociating power of a solvent is proportional to its dielectric constant.

4. Chemically this result would be expected, as the dimethylaniline would certainly add the haloid and the ether would tend to do so, while benzene would not.

5. The effect of some impurities on the rate of reaction has been shown. That of alcohol and acetone is enormous.

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THE DETERMINATION OF ACETONE IN SYSTEMS OF METHYL ALCOHOL, WATER AND POTASSIUM FLUORIDE, AND EQUILIBRIA IN SYSTEMS OF METHYL ETHYL KETONE, WATER AND INORGANIC SALTS.

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In the study of the equilibria in the systems water, acetone and inorganic salts, it was found that the amount of acetone present in an aqueous solution can be determined. It was also found that methyl alcohol cannot be salted out of an aqueous solution by means of potassium fluoride. It was thought that acetone could be then accurately determined in the presence of methyl alcohol. When the methyl alcohol did not exceed 5%, its function was found to be the same as water, and from a study of the binodal curve, the amount of acetone in a solution could be determined. It was found, however, that when larger amounts of methyl alcohol were used the alcohol did not act the same as the water, and loci of points found by experiment did not fall on the binodal curve. A more or less comprehensive study of the effect of the alcohol was then made. Solutions containing from 5-95% methyl alcohol in water were made up and the salting out effect of potassium fluoride was again tried. The

method used is the same as the one described,¹ only in this case the alcohol and water mixtures were used in place of water.

If a careful study is made of Table I, it will be seen that it does not seem to be the amount of methyl alcohol, but rather the amount of acetone that gives discordant results. When the percentage of acetone does not exceed 18, the acetone can be determined as in the method described. If the amount of acetone present exceeds 18% the solution must be diluted and the acetone can then be determined, the methyl alcohol not interfering in this determination.

TABLE I.

1. KF.	2. Water.	3. Methyl alcohol.	4. Acetone.	5. Acetone.	6. Water.
17.65	29.80	44.70	7.85	8.00	74.50
16.35	51.28	21.97	10.40	10.00	74.00
15.91	59.89	14.97	9.23	9.50	74.00
14.57	44.59	29.73	11.11	11.50	74.00
13.75	43.48	28.98	13.79	13.50	73.50
10.67	42.60	28.40	18.33	18.00	70.50
9.75	48.57	20.81	20.87	24.00	66.50
9.29	28.54	42.80	19.37	25.00	66.00
8.92	35.15	35.15	20.78	25.00	66.00
7.33	40.17	26.77	25.73	29.50	63.00
7.02	43.06	10.76	39.16	31.00	62.00
7.62	28.02	42.04	22.32	29.50	63.00
5.78	42.30	10.57	41.35	37.00	58.00
5.30	32.53	32.53	29.64	37.00	58.00
5.16	26.35	39.53	28.96	39.00	56.00
4.97	41.10	10.27	43.66	40.00	55.00
5.19	37.91	25.28	31.62	39.00	56.00
4.21	39.83	9.96	46.00	44.00	52.00
4.12	40.96	17.54	37.38	45.00	51.00
4.46	31.28	31.28	32.98	42.00	54.00
4.05	24.83	37.25	33.87	45.00	51.00
3.99	35.90	23.93	36.18	45.00	51.00
3.82	14.72	44.16	37.31	47.00	50.00
3.65	30.14	30.14	36.08	47.00	49.00
3.37	39.20	16.80	40.63	50.00	47.00
3.10	23.59	35.38	37.93	50.00	47.00
3.03	33.97	22.65	40.35	50.00	47.00
2.75	28.00	28.00	41.25	52.00	46.00
2.43	36.20	15.52	45.85	52.00	46.00
2.42	35.82	8.96	52.80	52.00	46.00
2.10	25.79	25.79	46.32	54.00	44.00
1.93	34.22	8.55	55.30	58.00	41.00
1.72	11.30	33.92	53.06	58.00	41.00

In the table, Columns 1, 2, 3, 4, respectively, indicate the weight in grams of KF, water, alcohol and acetone in 100 g. of the solution. Columns 5 and 6 show the weight of acetone and water, respectively, in grams

¹ THIS JOURNAL, 36, 1103-34 (1914).

that should be present in 100 g. of the solution, if no methyl alcohol were present. The data from 5 and 6 were found in a former experiment.¹ The data in 1, 2, 3, 4 are those just determined.

Equilibria in Methyl Ethyl Ketone Systems.—The methyl ethyl ketone which was used in the following experiments came from the firm of C. A. F. Kahlbaum, of Berlin, and was labelled highest purity. An examination showed, however, that it was by no means pure, although of better quality than a sample of the same supposed purity from another factory. The Kahlbaum sample began to boil at 78° and rose to 84° before it had all distilled over. After fractioning several times, that part which passed over between 79.5° and 80.5° was collected and treated with magnesium, amalgam and finally with metallic sodium. It was again fractioned, practically all passing over between 79.6–80.2° at 745 mm. pressure. The purified sample was then weighed. It represented about 60% of the total sample taken; the remaining 40% included impurities and loss sustained in the purification. It was again redistilled, a very small amount passing over below 80°. The remaining part distilled at 80 to 80.2 at 752 mm. The specific gravity was taken at 20° in a specially designed and standardized vacuum pycnometer and gave 0.8054 and 0.8051^{20/4}.

The refractive index was taken with the latest Pulfrich refractometer using the newly designed hydrogen tube. The average of three determinations gave the following indices:

Alpha.... 1.38308; Beta.... 1.37023; Gamma.... 1.36178

Compared with the physical constants determined by others these are in fairly close accord, as will be seen by the following table:

Sp. gr. 0.82961 at 0°; 0.8125 at 13°; 0.8045 at 19.8°; 0.80526 average of two determinations.

Boiling point 80.6; 80.6; 80–80.2°; 80–80.2.

The last numbers were taken by the authors. It will be seen that the specific gravities agree fairly well but there is a slight difference in the boiling points. As the atmospheric pressure is not given in the determinations made by others we may assume that the pressure was normal or perhaps higher than that under which we work. This could easily account for the difference. The purified sample was kept in a double stoppered bottle away from the light until it was used in the accompanying experiments.

Methyl ethyl ketone can be salted out from its aqueous solution by the salts sodium chloride, potassium fluoride and potassium carbonate. The percentage of ketone in the aqueous solution can be approximately determined by means of these salts. For accurate determinations, this method would not be satisfactory.

The systems water, methyl ethyl ketone, water and sodium chloride;

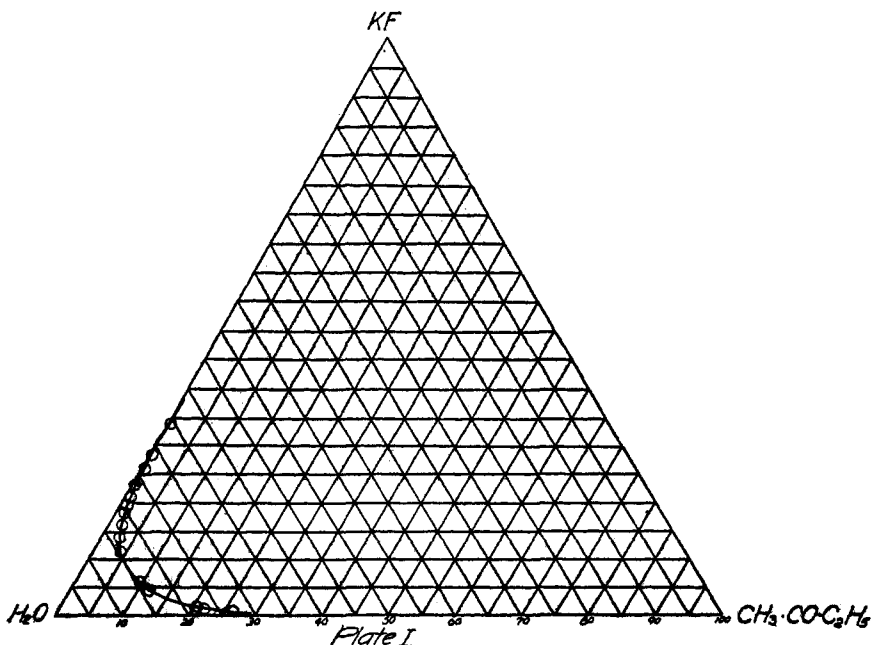
¹ *Loc. cit.*

ethyl methyl ketone, water and potassium fluoride; ethyl methyl ketone, water and potassium carbonate were studied and the binodal curve for each is given. The data for the systems are given in Tables II, III and IV. The results with potassium carbonate were not satisfactory.

TABLE II.
System Potassium Fluoride, Water and Methyl Ethyl Ketone.

Total wt. of subst. present.				% in 100 g. of sol.		
KF.	Ketone.	Water.	Total.	KF.	Ketone.	Water.
10.869	0.870	45.691	57.430	18.93	1.51	79.56
10.896	5.06	87.541	103.47	10.50	4.87	84.63
10.869	5.05	87.54	103.45	10.50	4.87	84.63
10.869	19.82	160.671	190.46	5.70	9.93	84.37
1.99	6.24	42.003	50.233	3.96	12.42	83.61
0.647	16.363	60.077	77.087	0.84	21.23	77.93
0.647	46.063	148.957	195.667	0.34	23.55	76.11
47.156	1.00	151.53	199.686	23.63	0.50	75.87
47.156	1.55	170.66	219.366	21.49	0.70	77.81
29.454	0.15	56.096	85.700	34.38	0.17	65.45
29.454	2.37	126.396	158.22	18.62	1.49	79.89
29.454	4.07	151.646	185.170	15.91	2.19	81.90
29.454	6.37	177.546	213.37	13.80	2.98	83.22

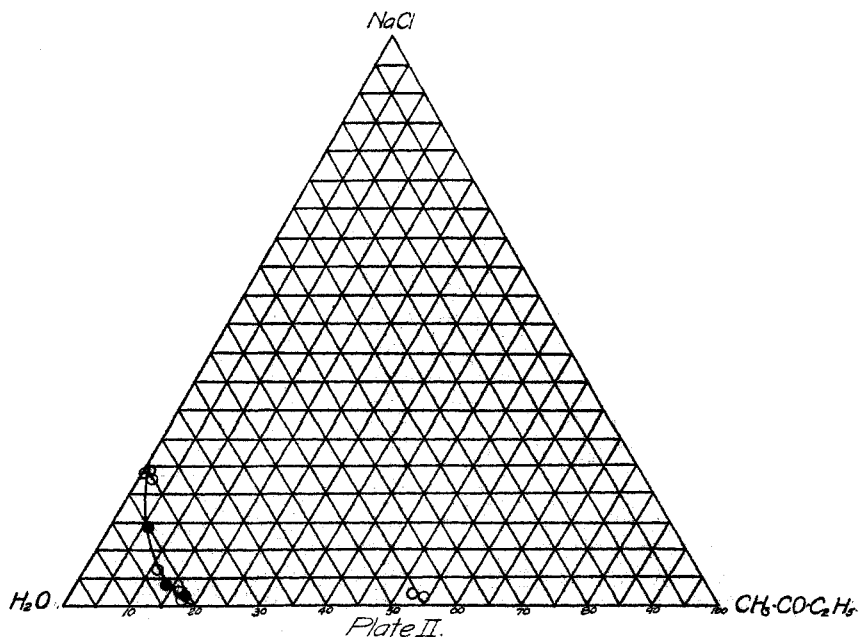
In all the studies we have so far made the two liquids in the systems have been miscible in all proportions. There is a limit to the solubility of methyl ethyl ketone in water and water in ethyl methyl ketone.



The solubility of the 2 liquids in each other is not only influenced by the temperature but also by the presence of inorganic salts. The influence of potassium fluoride is shown by Table II and Plate I. The effect of sodium chloride is shown in Plate II and Table III.

TABLE III.
System Sodium Chloride, Water and Methyl Ethyl Ketone.

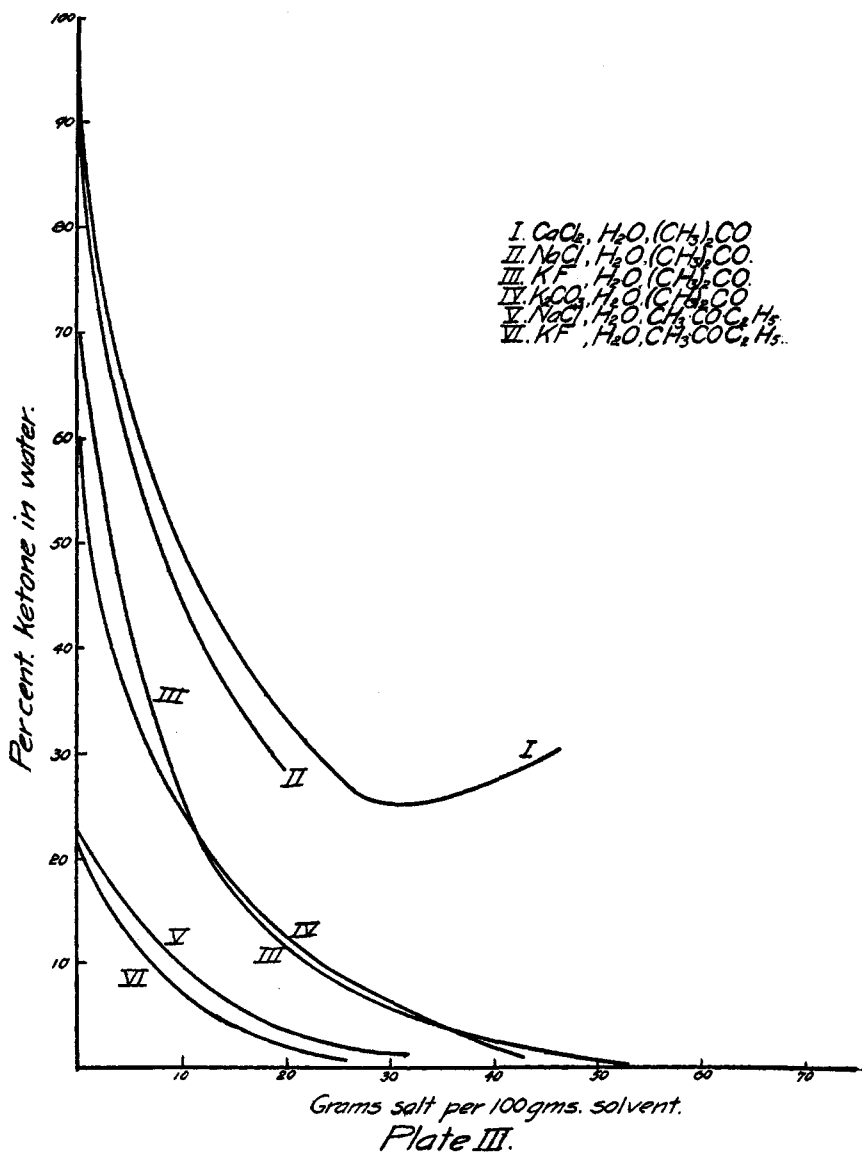
Total wt. of subst. present.				% in 100 g. of the sol.		
NaCl.	Ketone.	Water.	Total.	NaCl.	Ketone.	Water.
2.737	0.718	15.235	18.69	14.65	3.83	81.52
2.737	2.085	22.375	27.197	10.07	7.65	82.28
2.737	4.380	33.445	40.562	6.75	10.80	82.45
2.737	8.87	54.89	66.497	4.11	13.34	82.55
2.737	18.02	90.17	110.927	2.47	16.24	81.29
2.737	26.69	121.55	150.98	1.80	17.70	80.50
0.501	5.828	28.943	35.272	1.42	16.52	82.06
0.501	18.118	73.113	91.732	0.55	19.75	79.70
0.501	28.918	114.263	143.682	0.35	20.13	79.52
15.740	0.605	48.847	65.192	24.14	0.94	74.92
15.740	1.425	50.847	68.012	23.15	2.08	74.77
15.740	5.9	88.272	109.912	14.32	5.36	80.32



In Plate III, the data already given in the various tables¹ for the equilibria in the systems water, ketones and inorganic salts, have been re-plotted, with the solvent and the grams of salt per 100 g. of solvent as

¹ *Loc. cit.*

rectangular coördinates. The object of this was to show, if possible, the influence exerted by the acid radical on the salting out property. No.



relationship is apparently indicated by these curves. That hydration has an influence is indicated by the break in the calcium chloride curve.