The Absorption Spectra of the Ketal and Ketone.—In absolute ethanol solution p-nitrobenzophenone and its diethylketal showed ultraviolet absorption maxima at 265 and 282 mμ, respectively. The molecular extinction coefficients at these wave lengths (based on the expression $d = \epsilon lc$ in which c represents the molar concentration of the absorbing substance, l the light path length (1 cm.) and d the measured optical densities of the solutions) were 20,100 and 10,200, respectively. At 265 mμ the extinction coefficient of ketal solutions was 9030. The absorption of these solutions followed Beer's law.

DAVIS, CALIFORNIA

The Ternary System: Isopropyl Ether–HCl–H₂O[1]

BY D. E. CAMBPELL, A. H. LAURENE AND H. M. CLARK

RECEIVED APRIL 11, 1952

The ternary system isopropyl ether–HCl–H₂O has been studied at 20°. A complete ternary diagram is presented along with plots of (1) the distribution coefficient of HCl as a function of the equilibrium concentration in the aqueous phase, (2) the variation in the equilibrium concentration of HCl in the aqueous phase as a function of the initial hydrochloric acid concentration for equal volume extraction and (3) density data used for analysis of the aqueous phase in the equilibrium study. The system is of interest in connection with the extraction from hydrochloric acid solution by isopropyl ether of inorganic substances such as ferric chloride. In the light of the results obtained, it is possible to interpret the known fact that optimum conditions for extraction of inorganic chlorides exist over a narrow range of hydrochloric acid concentration.

Introduction

The ether extraction of certain metallic chlorides from aqueous hydrochloric acid solutions has been known for some time. In particular, studies have been made of the ether extraction of $AuCl_3$,[2] $GaCl_3$,[3,4] $TlCl_3$,[5] $SbCl_5$[6] and $FeCl_3$[7–9] from strong hydrochloric acid solutions.

In the course of studying the extraction of ferric chloride by isopropyl ether in this Laboratory, it appeared advisable to undertake this investigation of the ternary system, isopropyl ether, hydrogen chloride and water in order to determine the effect of hydrogen chloride on the mutual solubility of isopropyl ether and water.

Experimental

Materials.—The hydrochloric acid used was du Pont, C.P. The isopropyl ether, Eimer and Amend, C.P., alcohol free, was purified by treatment with saturated ferrous sulfate solution followed by sodium hydroxide solution. It was dried over silica gel and distilled twice over calcium hydride. The middle fraction (b.p. 67.4–67.9° uncor.) was collected for use. Its purity was checked by examination of the ultraviolet spectrum. The average of the densities of seven different lots of the purified isopropyl ether was 0.7234 with a mean deviation of a single value from the average of ±0.0001. Standard sodium hydroxide solutions were made from Eimer and Amend, reagent grade material, and were standardized with certified analytical reagent grade sulfamic acid obtained from the G. Frederick Smith Co.

Methods of Analysis.—Isopropyl ether and hydrochloric acid in the aqueous phase were determined by direct analysis. In the ethereal phase, hydrochloric acid and water were determined directly. The third component in each phase was found by difference.

All acid analyses were carried out by titration with standard sodium hydroxide using methyl orange–indigo carmine indicator (pH at transition, 4.2).

The ethereal phase was analyzed for water by the Karl Fischer titration method.[10,11]

The analysis for ether in the aqueous phase proved to be the principal problem associated with the determination of the ternary diagram. Two chemical methods of analysis are available for the quantitative determination of ether—the combustion analysis, and the Zeisel alkoxy method.[12] Since neither of these methods is feasible for solutions containing preponderant amounts of water and hydrochloric acid, recourse was made to physical methods for the determination of the ether content.

The surface tension, refractive index, density and viscosity were measured for several solutions for which the ether and hydrochloric acid concentrations were known. Measurements of the surface tension were made by the capillary rise method and were not satisfactorily reproducible because of the poor wetting characteristics of these solutions on glass. The index of refraction shows large changes with respect to hydrochloric acid concentrations, but very small changes with respect to the ether content. This property, therefore, was not used. The viscosity was found to be extremely sensitive to the quantity of ether present in the acid. The precision of the viscosity measurements, however, was not adequate for analytical purposes. Reasonable changes in density result when isopropyl ether is added to aqueous hydrochloric acid. Furthermore, density measurements can be made precisely. Thus, of the four properties examined, the density proved to be the most readily applicable to the analysis of the aqueous phase for ether.

Procedure.—Five stock solutions were prepared in all-glass dispensing bottles and kept refrigerated to maintain constant composition. For each stock solution, three liters of aqueous hydrochloric acid (approximately 11 molar) was placed in the dispensing bottle and the density and the precise concentration were determined. (All density determinations were made with calibrated 250-ml. LeChatelier specific gravity flasks at 20.00 ± 0.01°.) A predetermined quantity of freshly purified ether of known density was then added to the hydrochloric acid. After thorough mixing, samples of this solution were withdrawn for the determinations of density and the concentration of HCl. The molar ratio Et/HCl for the stock solution was calculated from equations (1) and (2), combined in equation (3).

$$1000d_a + Xd_{Et} = (1000 + X + Y)d_s \qquad (1)$$

$$1000M_a = (1000 + X + Y)M_s \qquad (2)$$

$$R = \frac{1000(M_a d_s - M_s d_a)}{102.17 M_s M_a} \qquad (3)$$

(1) Abstracted from portions of the Ph.D. Theses of D. E. Campbell and A. H. Laurene.

(2) F. Mylius, Z. anorg. Chem., **70**, 203 (1911).

(3) E. H. Swift, THIS JOURNAL, **46**, 2375 (1924).

(4) N. H. Nachtrieb and R. E. Fryxell, ibid., **71**, 4035 (1949).

(5) A. A. Noyes, W. C. Bray and E. B. Spear, ibid., **30**, 559 (1908).

(6) F. C. Edwards and H. F. Voigt, Anal. Chem., **21**, 1204 (1949).

(7) R. W. Dodson, G. J. Forney and E. H. Swift, THIS JOURNAL, **58**, 2573 (1936).

(8) N. H. Nachtrieb and J. G. Conway, ibid., **70**, 3547 (1948).

(9) R. J. Meyers, D. E. Metzler and E. H. Swift, ibid., **72**, 3767 (1950).

(10) K. Fischer, Angew. Chem., **48**, 394 (1935).

(11) J. Mitchell and D. M. Smith, "Aquametry," Interscience Publishers, Inc., New York, N. Y., 1948.

(12) Pregl–Grant, "Quantitative Organic Micro Analysis," The Blakiston Company, Philadelphia, Pa., 1946, p. 146.

The symbols used in these equations are defined below

R = molar ratio Et/HCl
X = ml. of isopropyl ether added to 1000 ml. of HCl
V = ml. of volume change on mixing; (1000 + X + V) = total volume after mixing
M_a = molarity of the aqueous HCl
d_a = density of the aqueous HCl
M_s = molarity of HCl in ether–HCl solution
d_s = density of the ether–HCl solution
d_{Et} = density of the isopropyl ether
102.17 = molecular weight of isopropyl ether

The five stock solutions were made up to have the following values of R: 0.0330, 0.0433, 0.0889, 0.1745 and 0.2447. From each solution a series of samples was prepared by withdrawing different amounts of the solution into LeChatelier density flasks and diluting with triply distilled water. The weights of stock solution and water added were known, and the volume of the final mixture was read after equilibration for one hour in a constant temperature-bath. The molarity of HCl in each diluted sample was calculated from the weight and density of the solution added and the final volume of the mixture.

The density data obtained from the five stock solutions are shown in Fig. 1. Also shown are equilibrium data obtained from two-phase systems to be described later.
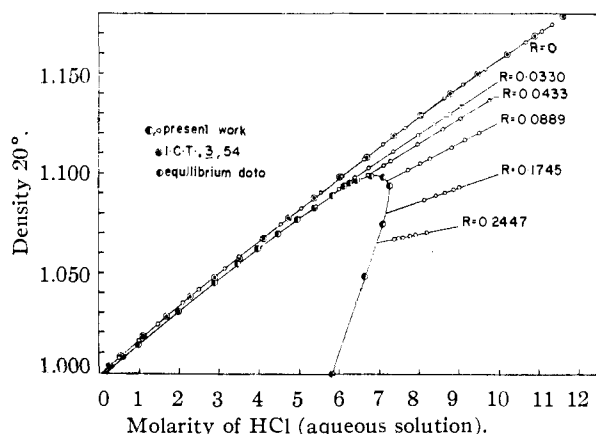

Fig. 1.—Densities of pure hydrochloric acid, aqueous solutions of isopropyl ether–HCl–H₂O and the aqueous phases of the heterogeneous isopropyl ether–HCl–H₂O system.

A mathematical analysis of the density data leads to a general expression which relates the density and molarity of HCl for a solution to its ether content.

$$R = \frac{d_s - 0.01417M_s - 1.0112}{0.1065 - 0.0414M_s} \quad (4)$$

Equation (4) has been found to hold for the following range; ($R = 0.035$ and $M_s > 6.5$) to ($R = 0.848$ and $M_s > 5.6$). This range can be more clearly visualized as the region on Fig. 1 to the right of the maximum of the equilibrium data curve.

Equation (4) does not involve the initial concentration or density of the hydrochloric acid used in making an ether–HCl solution. Values of R found by this equation agree with the correct values of R calculated by equation (3) in the limiting case for homogeneous solutions. Table I shows agreement between these values.

TABLE I

A COMPARISON OF VALUES OF R CALCULATED FROM EQUATION (3) AND THE EMPIRICAL EQUATION (4)

M_a	d_a	M_s	d_s	Eq. (3)	Eq. (4)
10.38	1.1628	9.76	1.1363	0.0433	0.0445
10.69	1.1657	9.48	1.1201	.0889	.0891
11.32	1.1746	8.99	1.0929	.1745	.1724
11.07	1.1711	8.19	1.0703	.2447	.2452

The Heterogeneous System.—A series of two-phase samples was prepared by using different initial concentra-

tions of hydrochloric acid for each sample. The initial concentrations of HCl were known accurately for all samples through 8.5 molar. To attain initial concentrations of HCl greater than 12 molar, dry hydrogen chloride was passed into two-phase systems.

The two-phase samples were equilibrated at 20°, and each flask was shaken vigorously at 12-hour intervals. After an equilibration time of 48 hours, the phases were separated and analyzed.

The concentration of ether in the aqueous phase was found by three different methods, depending on the concentration of the aqueous hydrochloric acid used to make up the two-phase sample. For heterogeneous systems which were made with starting hydrochloric acid concentrations between 0 and 7 molar, equation (3) was used to calculate the ether content from the density and the concentration of the initial hydrochloric acid. The use of equation (3) introduces a small error when two phases are present since some hydrochloric acid passes from the aqueous to the ether phase. Analyses have shown that this error is negligible when the starting hydrochloric acid concentration for equal volume extraction is less than 7 molar. When the initial concentration of hydrochloric acid is above 7 molar, the concentration of hydrochloric acid in the ethereal phase at equilibrium rises sharply. Thus, the error resulting from the use of equation (3) becomes appreciable. From 7 to 11.5 molar initial hydrochloric acid concentration, equation (4) has been shown to hold. Above 11.5 molar starting hydrochloric acid concentration, the water was determined and the ether calculated by difference.

The data for all the samples are presented in Table II, and the mole fractions are plotted on the ternary diagram in Fig. 2.
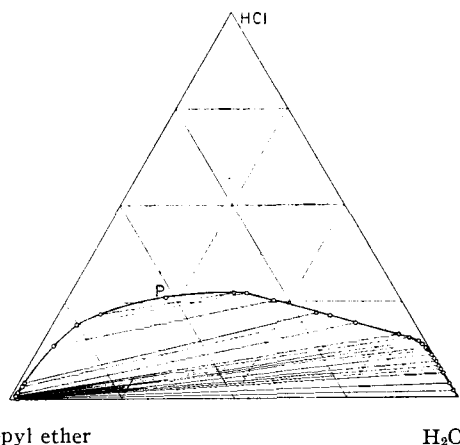

Isopropyl ether   H₂O

Fig. 2.—Mole fraction ternary plot of the system isopropyl ether–HCl–H₂O at 20°. P is the experimentally obtained plait point.

Discussion

The effect which HCl has on the mutual solubility of water and isopropyl ether at 20° is shown by the ternary diagram in Fig. 2. With no HCl present, the solubility of water in isopropyl ether is 0.87 g. per 100 g.,[11] corresponding to 0.047 mole fraction of water. The solubility of isopropyl ether in water is 0.2 g. per 100 g., or 0.0002 mole fraction of ether. As the over-all mole fraction of HCl is increased the solubility of ether in water increases slowly at first, then rises sharply. This sharp rise begins when the mole fraction of ether in the aqueous phase reaches 0.007. For equal volume extraction, this mole fraction obtains when the initial hydrochloric acid is 7 molar.

As the initial concentration of hydrochloric acid is increased to 7 molar, the concentration of HCl in the ethereal phase at equilibrium increases only

TABLE II

DATA FOR THE HETEROGENEOUS ISOPROPYL ETHER–HCl–H₂O SYSTEM

Initial vol. ratio ether: acid	Molarity HCl initial	Density of equilibrium aq. phase	Density of equilibrium ether phase	Aqueous phase			Ether phase		
				Molarity HCl	Molarity Ether	Molarity H₂O	Molarity HCl	Molarity Ether	Molarity H₂O
1:1	7.64	1.0980	0.7253	7.10	0.523	43.6	0.0321	7.07	0.091
1:1	7.11	1.0985	.7248	6.79	0.346	45.3	.0204	7.07	.096
1.3:1	8.09	1.0934	.7251	7.26	0.77	41.6	.0426	7.07	.088
1.3:1	8.63	1.0752	.7255	7.12	1.40	37.4	.0559	7.07	.085
1.5:1	9.5	1.0480	.7256	6.65	2.27	31.9	.0645	7.06	.084
1.7:1	10.5	0.9997	.7264	5.85	4.07	20.6	.0964	7.06	.084
2.9:1	11.5	0.9840	.7270	5.62	4.76	16.3	.1257	7.06	.084
1:1	6.70	1.0961	.7249	6.45	0.278	46.2	.0150	7.07	.123
1:1	5.99	1.0888	.7248	5.83	.203	47.5	.0096	7.07	.133
1:1	5.47	1.0827	.7249	5.37	.137	48.5	.0073	..	...
1:1	4.53	1.0698	.7252	4.46	.131	49.7	.0021	..	...
1:1	4.01	1.0621	.7250	3.95	.107	50.4	.0015	..	...
1:1	5.06	1.0770	.7249	4.95	.164	48.9	.0063	7.07	.130
1:1	3.0	1.0452	.7252	2.87	...	..	.0007	7.07	.166
1:1	2.00	1.0307	.7253	1.988	.079	52.8	....	..	.175
1:1	1.002	1.0138	.7255	0.995	.054	54.0	.0005	7.07	.188
1:1	3.51	1.0544	.7254	3.46	.118	50.9	.0057	7.06	.159
1:1	5.51	1.0831	.7248	5.40	.150	48.4	.0072	7.07	.117
3.7:1	6.27	1.0919	.7248	6.09	.216	47.1	.0120	7.07	.106
...	12.5	0.9761	.7275	5.51	...	...	.1498	7.05	.091
...	...	.9187	.7491	5.09	5.52	9.4	1.132	6.83	.258
...	...	.9608	.7298	5.35	4.83	15.1	0.236	7.04	.099
...	...	.9546	.7313	5.30	5.02	13.9	0.312	7.03	.108
...	...	.8905	.7632	4.74	5.81	6.9	1.740	6.76	.505
...	...	.8760	.7761	4.49	5.92	5.98	2.14	6.67	.94
...ᵃ	...		.8165ᵃ	...	...	...	3.20ᵃ	6.38ᵃ	2.67ᵃ

ᵃ The isothermal critical point.

slightly and the solubility of water decreases. A marked increase in the HCl content of the ethereal layer begins when the starting hydrochloric acid concentration exceeds 7 molar. The solubility of water in the ether layer reaches a minimum and then increases markedly with increasing HCl concentration in this layer.

Existing hydration theories furnish a basis for a possible interpretation of these phenomena. Hydronium ions in the aqueous layer may be expected to be preferentially solvated by water molecules.
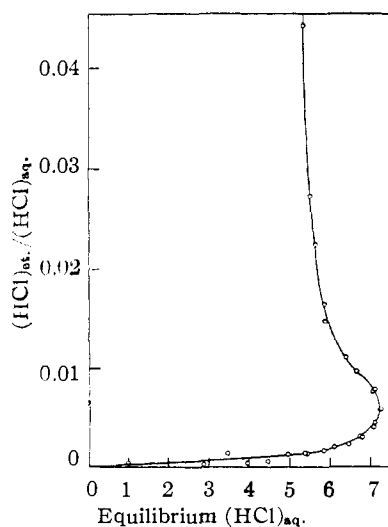
The hydration theory of Stokes and Robinson[13] indicates that essentially all the water in about 7 molar hydrochloric acid is combined with the ions and little exists as free solvent. The sharp increase in the solubility of ether in hydrochloric acid at this initial concentration indicates that solvation of hydronium ions by ether takes place. The increase in the concentration of water in the ethereal phase af-

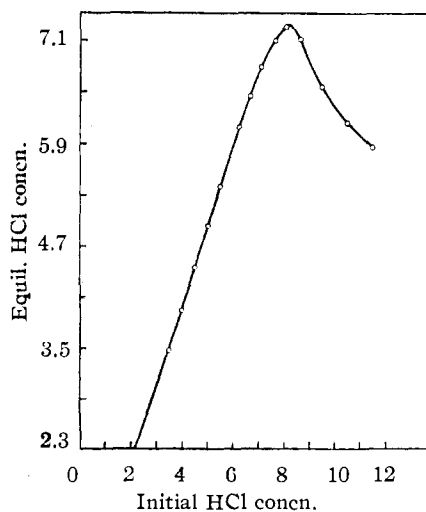Fig. 3.—Molar distribution of HCl between isopropyl ether and water at 20°.

Fig. 4.—Variation of the equilibrium concentration of HCl in the aqueous phase when equal volumes of hydrochloric acid and isopropyl ether are mixed at 20°.

(13) R. H. Stokes and R. A. Robinson, THIS JOURNAL, 70, 1870 (1948).

ter it has passed through the minimum is apparently due to the large concentration of HCl in the organic solvent. With the continued increase in solubility of water in the ethereal phase, this layer becomes similar to the denser phase.

While the molar distribution coefficient of HCl between the two layers, which is shown in Fig. 3, increases continuously, the equilibrium HCl concentration reaches a maximum and then decreases. This decrease is due to the enhanced solubility of ether in the aqueous phase. The location of a maximum in the equilibrium hydrochloric acid concentration of the aqueous phase suggests an explanation for the decrease in extraction efficiency of ferric chloride by isopropyl ether when the initial hydrochloric acid exceeds 8.5 molar. The plot shown in Fig. 4 is very similar in shape to a plot of the log $(Fe)_{Et}/(Fe)_{Aq}$ against the initial concentra-

tion of hydrochloric acid for equal volume extraction given by Nachtrieb and Conway.[8] The equilibrium concentrations for initial hydrochloric acid of 9.5, 10.5 and 11.5 molar in Fig. 4 have been calculated for equal volume extraction from tie line data on the ternary diagram.

The results of this investigation are being applied in a study of the ferric chloride extraction system.

# The Thermochemistry of Calcium and Calcium Iodide in Ammonia at −33°[1]

BY SUMNER P. WOLSKY, EDWARD J. ZDANUK AND LOWELL V. COULTER

For the solution reaction of calcium metal and calcium iodide in liquid ammonia, $\Delta H = -19.7$ and -62.8 kcal., respectively, at $-33°$. For the reaction of calcium metal with NH_4^+(am), $\Delta H = -99.3$ kcal. From these thermochemical data for calcium metal, $\Delta H = -79.7$ kcal. has been calculated for the reaction: e_2^-(am) $+ 2NH_4^+$(am) $= 2NH_3$(l) $+ H_2$(g). This result is in agreement with that previously obtained for the same reaction based on the thermochemistry of the alkali metals, and signifies two-electron ionization of the calcium atom in ammonia rather than one-electron ionization and the presence of Ca_2^{++} previously proposed. In ammonia, $\bar{S}^0_{Ca^{++}} = -129$ e.u. relative to $\bar{S}^0_{H^+} = 0$. If two-electron ionization of calcium is assumed, the solvation energy difference for the gas ion pair, I^- and e^-, based on the thermochemistry of calcium and calcium iodide is 32.8 kcal. which compares favorably with 31.5 and 31.4 kcal. obtained from the thermochemistry of sodium and potassium and their iodides. The large negative ionic entropy of Ca^{++}(am) and the larger heats of ammoniation of electrolytes compared with heats of hydration are qualitatively correlated with the differences in the nature of the solvents.

Moderately dilute solutions of the alkali metals in liquid ammonia react with NH_4^+(am) according to the equation

$$\tfrac{1}{2}e_2^-(am) + NH_4^+(am) = NH_3(l) + \tfrac{1}{2}H_2(g) \quad (1)$$
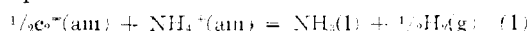
with the liberation of 40.4 ± 1 kcal. per equivalent.[2] The constancy of this value for the alkali metal solutions has confirmed the observed similarity of the state of the electron in these solutions and, in addition, now serves as a basis for comparison of the alkaline earth metal solutions with the alkali metal solutions. This is of particular interest in the case of calcium solutions since the low magnetic susceptibility of these solutions relative to barium solutions[3] has been interpreted by Yost and Russell[4] as an indication of one-electron ionization for the solution reaction, Ca(s) $= \frac{1}{2}Ca_2^{++}$(am) $+ \frac{1}{2}e_2^-$-(am), rather than two-electron ionization, Ca(s) $= Ca^{++}$(am) $+ e_2^-$(am). As a part of the objective of this research, it has been of interest to make a thermochemical distinction between the two different modes of ionization with the use of the re-

action represented by equation 1. For two-electron ionization in calcium solutions, reaction 1 should liberate 40.4 kcal. per equivalent of calcium, whereas, a considerably lower value would be anticipated for the heat of reaction of the system resulting from one-electron ionization. The direct determination of this heat of reaction has not appeared feasible because of experimental difficulties. As a consequence, we have obtained it indirectly from the heat of solution of calcium in liquid ammonia and the heat of reaction of calcium with NH_4^+(am).

Comparison of the nature of calcium and alkali metal solutions may also be accomplished by a consideration of the differences of solvation energy in liquid ammonia of the gas ion pairs, I^-(g) and e^-(g), derived from the appropriate thermochemical data for alkali metal–iodide systems and the corresponding calcium systems. This comparison has entailed the experimental determination of the heats of solution of Ca and CaI_2 in liquid ammonia.

Experimental Procedures

The calorimetric procedure followed in this research has been described previously.[2] The total heat capacity of the calorimeter varied from 85 to 165 cal. per degree and reaction times varied from 5 to 70 minutes depending upon the experiment. Crystals of calcium metal of appropriate size were selected from a high purity preparation of the metal

(1) Part of this paper was presented before the Division of Physical and Inorganic Chemistry, American Chemical Society Meeting, Cleveland, Ohio, April 11, 1951.

(2) L. V. Coulter and R. H. Maybury, THIS JOURNAL, 71, 3394 (1949); L. V. Coulter and L. Monchick, ibid., 73, 5867 (1951).

(3) S. Freed and N. Sugarman, J. Chem. Phys., 11, 354 (1943).

(4) Don M. Yost and Horace Russell, Jr., "Systematic Inorganic Chemistry," Prentice-Hall, Inc., New York, N. Y., 1944, p. 148.