[CONTRIBUTION FROM THE CHEMISTRY DIVISION, ARGONNE NATIONAL LABORATORY]

Solvent Effects in the Iodide–Iodine–Triiodide Complex Equilibrium[1]

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The triiodide complex ion is shown by a spectrophotometric technique to be much more stable in dry *t*-butyl alcohol solution than in water. Up to 50 mole % water the equilibrium is well-represented by $I^- + I_2 \cdot \text{Solvent} = I_3^- + \text{Solvent}$, while another factor enters at higher water concentrations to make the complex less stable than would be predicted. The possible nature of this factor is discussed. Comparison of sodium triiodide and tetrabutylammonium triiodide in dry alcohol solution shows a sodium hydration effect and a spectral change of the triiodide on coördination to unhydrated sodium.

Two factors, among others, generally recognized to play an important role in the formation of cation–anion complexes in solution are solvation of the cation, and dielectric constant effects on the attraction between the oppositely charged ions. For weak complexes these factors are most clearly brought out in solvent mixtures, in particular when one of the solvents is water. In such mixtures the stronger base solvent generally makes its presence in minor concentrations felt to a disproportionate extent. The first action is the displacement of the weaker base solvent from the coördination sphere of the cation, and the second (not always to be resolved from the first) is the displacement of the anion from its place in the coördination sphere. The latter effect is most marked with weakly coördinated anions, and at higher dielectric constants. At lower dielectric constants the electrostatic attraction between the ions increases the effective competitive strength of the anion.

With complexes between a cation and molecular electron donors, only the factor of competition between bases for the coördination positions of the cation enters, and this has received detailed study in some cases. A type of complex which has been little investigated is that between an anion and a neutral electron acceptor which is not itself an ionic complex. An example of the type of reaction under consideration is that between a halide ion and halogen to give the trihalide complex, *e.g.*, $I^- + I_2 = I_3^-$.

It is probably a fair summary to say that studies which have been directed toward the determination of the hydration number of ions in solution, by a considerable variety of techniques, are largely agreed that the iodide ion may be considered to be without primary coördinated water in aqueous solution, and even more certainly so in alcoholic solution.[2–5] In the case of the iodine, modern studies are rather uniformly agreed that the behavior of iodine in solutions of solvents other than carbon tetrachloride, carbon disulfide, aliphatic hydrocarbons, etc., which give "violet" solutions, conforms to its presence largely as a monosolvated entity[6–12] (see however, Bayliss and Rees).[13–15] The triiodide equilibrium might therefore be expected to lend itself readily to analysis of solvent effects in this equilibrium. Comparison of the behavior of the equilibrium in mixed water–*t*-butyl alcohol solutions with the predictions of this picture is the subject of this paper.

Experimental

Solutions of iodine in carbon tetrachloride, sodium iodide or tetrabutylammonium iodide in *t*-butyl alcohol, potassium iodide in water and potassium iodate in water were made up after weighing out the solutes. Perchloric acid solutions were made by dilution of the concentrated acid. All reagents were chemically pure. The commercial synthetic *t*-butyl alcohol was analyzed for water by titration with Karl Fischer reagent, and generally contained in the neighborhood of 0.1–2 g. of water per liter.

Spectrophotometric measurements were made in quartz cells with the Beckman DU quartz spectrophotometer and a hydrogen lamp source. Attention was concentrated on the longer wave length peak of the triiodide absorption spectrum which falls at 350–360 $m\mu$, and is essentially free of interference by absorption of either iodide or iodine. Triiodide solutions to be measured were generated shortly before observation by aliquoting the reagents into a volumetric flask and diluting to volume with the appropriate solvent mixture. Concentrations of the reagents were adjusted to allow simple pipetting to give stoichiometric ratios of iodide and iodine in the final solutions equivalent to pure triiodide solutions.

Results

The round points in Fig. 1 show the optical density at 360 $m\mu$ of *t*-butyl alcohol solutions 4.54×10^{-5} *M* in tetrabutylammonium triiodide, as a function of water concentration (% by volume). These solutions contain also 1% by volume of carbon tetrachloride, which has no noticeable effect on the results. The corresponding optical density of an aqueous solution of the same triiodide, from literature dissociation constants[16] and molal extinction coefficient[17] would be 0.030. With sodium triiodide rather than tetrabutylammonium triiodide, densities corresponding to the square points in the low water region are found. From 10% water on, both salts agree within experimental error.

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[1] Presented in part at meeting of American Chemical Society, Chicago, Ill., September, 1953.

[2] (a) J. W. Ingham, *J. Chem. Soc.*, 1917 (1928); (b) H. Uhlich, *Z. Elektrochem.*, **36**, 497 (1930).

[3] M. Cordier, *Compt. rend.*, **214**, 707 (1942); *J. chim. phys.*, **43**, 93 (1946); *ibid.*, **43**, 134 (1946).

[4] H. Spandau and G. Spandau, *Z. physik. Chem.*, **192**, 211 (1943).

[5] J. I. Fernandez and A. Hidalgo, *Anal. real. soc. espan. fis. y quim.*, **46B**, 5, 17 (1950).

[6] J. H. Hildebrand and B. L. Glascock, THIS JOURNAL, **31**, 26 (1909).

[7] J. Groh, M. Radvanyi, L. Urbanek and K. Lanyi, *Z. anorg. Chem.*, **162**, 287 (1927).

[8] F. Fairbrother, *Nature*, **160**, 87 (1947); *J. Chem. Soc.*, 1051 (1948).

[9] J. Kleinberg and A. W. Davidson, *Chem. Revs.*, **42**, 601 (1948).

[10] H. A. Benesi and J. H. Hildebrand, THIS JOURNAL, **71**, 2703 (1949).

[11] R. S. Mulliken, *ibid.*, **72**, 600 (1950).

[12] J. A. A. Ketelaar, C. van de Stolpe and H. R. Gersmann, *Rec. trav. chim.*, **70**, 499 (1951).

[13] N. S. Bayliss and A. L. G. Rees, *J. Chem. Phys.*, **8**, 377 (1940).

[14] A. L. G. Rees, *ibid.*, **8**, 429 (1940).

[15] N. S. Bayliss, *Nature*, **163**, 764 (1949).

[16] G. Jones and B. B. Kaplan, THIS JOURNAL, **50**, 1845 (1928).

[17] A. D. Awtrey and R. E. Connick, *ibid.*, **73**, 1842 (1951).

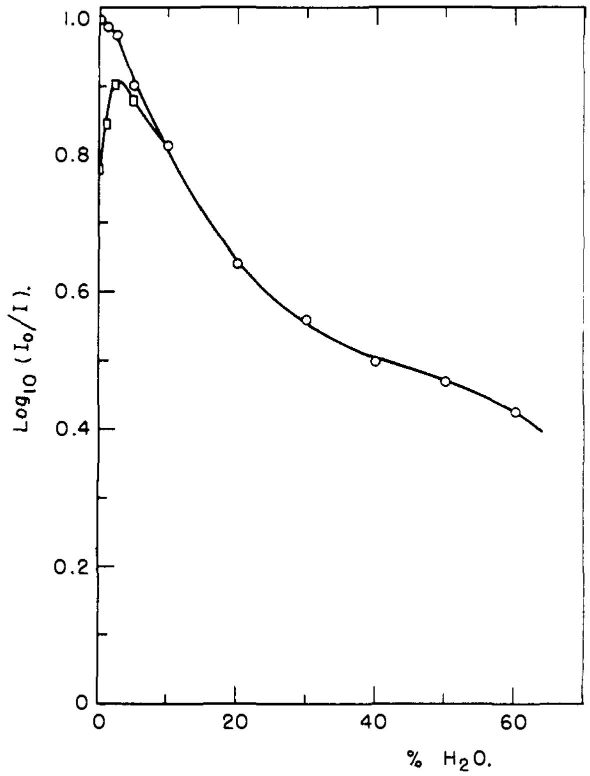

Fig. 1.—Optical density at 360 mμ of 4.54 × 10^{-5} *M* triiodide in *t*-butyl alcohol as function of water concentration: ○, tetrabutylammonium triiodide; □, sodium triiodide.

To elucidate the factors in the absorption behavior, dissociation constants for the triiodide in the various solutions were determined by a dilution technique. It can be readily demonstrated, for a substance dissociating into two components, that comparison of two solutions in the same solvent which have the relationship $m_1 = m_2V$, where V is a dilution factor and m is the formal concentration of the dissociable substance, gives for the undissociated fraction in the undiluted solution, F, the expression

$$F = \frac{r}{V(r-1)}\left[(V-1) - \left\{(V-1)^2 - (r-1)\left(\frac{V^2}{r} - 1\right)\right\}^{1/2}\right]$$

in which r is the ratio of concentration of the undissociated species in the more concentrated solution to that in the less concentrated solution. The dissociation constant is then given by

$$K = m_1(1 - F)^2/F = (I^-)(I_2)/(I_3^-)$$

In our experiments, on the reasonable assumption that dilution with solvent of the same composition should not change the molal extinction coefficient of the triiodide, the ratio of the two optical densities should give the triiodide concentration ratio directly. Knowing m_1 and F, it is also possible to calculate the triiodide extinction coefficient in the solution from the optical density.

Application of this procedure to the solutions with less than 10% by volume of water gave the results shown in Table I. In actual practice, a series of dilutions is made (2, 4, 10 and 20 times), and the F values found from these constitute checks for the value. The lowest dilution is usually too sensitive to small changes in the optical density, for this particular system, to give more than a semi-quantitative check. It is seen that the dissociation con-

TABLE I

DISSOCIATION PRODUCT OF TRIIODIDE BY DILUTION TECHNIQUE

Salt	Water added, vol. %	Concn., M × 10^5	Optical density D	Dilution factor V	Cell length, cm.	F	$10^6 \times \frac{(I^-)(I_2)}{(I_3^-)}$	ϵ_{360}
Bu_4NI_3	...	4.54	0.998	1	1	...		
			.486	2	1	(0.931)		
			.433	4	2	.869		
			.370	10	5	.870		
			.291	20	10	.852		
						.864	0.97	25,600
	...	4.40	0.962[a]	1	1	...		
			.454	2	1	0.863		
			.408	4	2	.847		
			.345	10	5	.855		
			.286	20	10	.858		
						.856	1.07	25,500
	...	5.06	1.107	1	1	...		
			.407	10	5	0.865		
			.338	20	10	.864		
						.865	1.06	25,300
	2.5	3.80	0.841	1	1	...		
			.374	2	1	.752		
			.315	4	2	.744		
			.230	10	5	.747		
			.172	20	10	.759		
						.750	3.2	29,500
	5	4.40	0.878	1	1	...		
			.389	2	1	(0.742)		
			.335	4	2	.759		
			.244	10	5	.754		
			.185	20	10	.766		
						.760	3.3	26,500
NaI_3	...	4.54	0.717	1	1	...		
			.344	2	1	(0.843)		
			.321	4	2	.895		
			.286	10	5	.895		
			.249	20	10	.899		
						.896	0.55	17,500
	...	4.68	0.705	1	1	...		
			.346	2	1	(0.962)		
			.316	4	2	.897		
			.279	10	5	.897		
			.237	20	10	.888		
						.894	0.59	16,900
	3.5	4.46	0.892[a]	1	1	...		
			.399	2	1	(0.762)		
			.355	4	2	.794		
			.275	10	5	.795		
			.207	20	10	.792		
						.794	2.4	25,200
	5	4.35	0.833[a]	1	1	...		
			.376	2	1	0.781		
			.315	4	2	.751		
			.246	10	5	.777		
			.182	20	10	.777		
						.772	3.0	24,800

[a] Density values in this series are averages of several repetitions.

stants for the sodium and the tetrabutylammonium triiodides even in the anhydrous solutions are comparable, and if anything the sodium salt is *less* dissociated than the tetrabutylammonium salt. As water is added to the system, this small difference vanishes. The difference shown in Fig. 1 can therefore be traced to a difference in extinction coefficient of the anion in the presence of the two cations. With sodium, the triiodide extinction is about 17,000, and with tetrabutylammonium as cation, about 25,500. With the latter cation the extinction varies only slowly with water concentration, being about 26,200 in pure water.[17,18] For converting the data of Fig. 1 to dissociation constants, therefore, one may use the optical density data together with interpolated values of the extinction coefficient.

For water concentrations greater than 60% by volume it was necessary to use iodide–iodate reaction in acid solution to generate the triiodide, due to insolubility of carbon tetrachloride in the solutions. The perchloric acid needed to bring the reaction to completion causes reaction with alcohol added, introducing a complication. By experimentation it was found that with 0.025 *M* acid the iodide–iodate reaction proceeded rapidly enough in solutions containing alcohol to give a maximum optical density. At higher acidities lower optical densities were obtained because of side reactions. The third-power dependence of the back reaction on water activity undoubtedly helped to make the slightly low acid concentration sufficient. A few tests with added acid in the lower water regions showed no noticeable difference from the iodide-plus-iodine solutions without acid. At 60% water, agreement in dissociation constant calculated was found for both procedures. It is to be remarked also that it is in this region, from 60–100% water, that the wave length of the peak absorption shifts from 360 mμ, characteristic of the high-alcohol solution, to the 352 mμ characteristic of the water solution.

Although the temperature was not closely controlled in these experiments, it was fairly close to 25°, being limited on the low side by the tendency of the solution to solidify (equilibrium freezing point, 25.5°). In some experiments the temperature was controlled and deliberately modified, to see if occasional difficulties in reproducing results might be due to temperature sensitivity, and incidentally to estimate the ΔH for the association reaction. With a restricted temperature range available, and with I_3^-, which is the form measured, already 85–90% associated, a very few percentage change makes a large change in the constant. Such small changes may be masked by experimental variability, minute traces of reactive impurities in solutions in which the solute is about 5×10^{-5} *M*, etc. There was found, however, the suggestion of a trend toward stronger association at higher temperatures (30° as compared with 24–25°) which was perhaps more marked with the sodium triiodide than the tetrabutylammonium triiodide. What was unmistakably obvious, however, was the change in the extinction coefficient of the triiodide with temperature. Thus, at the same over-all concentrations, sodium triiodide solutions at 23.9° and at 28.9° might show optical densities of 0.828 and 0.777, respectively, with the degree of dissociation being if anything less in the second solution. Similar alterations could be observed in the absorption of the tetrabutylammonium triiodide solutions. Expansion of the solution would account only for 0.5% change.

In water solution, with a larger temperature range available, the effects of temperature variation were even more striking. Thus, a solution with an optical density of 1.01 at 20.1° gave a reading of 0.85 at 30.1°. Determination of the dissociation constant and the extinction coefficient of the triiodide in 1 *M* perchloric acid, generating the triiodide by the iodide–triiodide reaction, gave the results shown in Table II. Both the dissociation constant and the extinction coefficient decreased by a factor close to 2 in changing the temperature from 20 to 27°. The striking feature, besides the mutability of the extinction coefficient, is that the temperature coefficient of the dissociation constant appears to be oppo-

TABLE II

EFFECTS OF ACIDITY AND TEMPERATURE ON TRIIODIDE IN AQUEOUS SOLUTION

$HClO_4$ concn., *M*	Temp., °C.	KI_3 concn., *M* × 10^4	Optical density *D*	Dilution factor *V*	Cell length, cm.	*F*	$10^3 \times \frac{(I^-)(I_2)}{(I_3^-)}$	ε_{352}
1	19.9	2.50	0.994[a]	1.00	1.00	. . .		
			.531	2.00	2.00	(0.068)		
			$.238_5$	5.00	5.00	.112		
			$.273_5$	6.67	10.00	.115		
			.191	8.00	10.00	.114		
						.114	1.72	34,900
	27.2	2.50	0.843[a]	1.00	1.00	. . .		
			.506	2.00	2.00	.192		
			.228	5.00	5.00	.182		
			.267	6.67	10.00	.191		
			$.196_5$	8.00	10.00	.214		
						.195	0.83	17,300
0 1	19.7	2.50	0.926[a]	1.00	1.00	. . .		
			.514	2.00	2.00	.107		
			$.225_5$	5.00	5.00	.121		
			.262	6.67	10.00	.130		
			.194	8.00	10.00	.159		
						.129	1.46	28,750
	27.2	2.50	0.813[a]	1.00	1.00	. . .		
			.478	2.00	2.00	.170		
			$.210_5$	5.00	5.00	.157		
			.246	6.67	10.00	.167		
			.179	8.00	10.00	.185		
						.170	1.01	19,150
0.05	19.8	2.50	0.929	1.00	1.00	. . .		
			.525	2.00	2.00	.126		
			.226	5.00	5.00	.120		
			.267	6.67	10.00	.139		
			.183	8.00	10.00	.127		
						.128	1.48	29,000
	27.2	2.50	0.811	1.00	1.00	. . .		
			.494	2.00	2.00	.209		
			.206	5.00	5.00	.145		
			.256	6.67	10.00	.189		
			.176	8.00	10.00	.178		
						.180	0.93	18,000

[a] Density values in this series are average of two runs.

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(18) J. J. Custer and S. Natelson, *Anal. Chem.*, **21**, 1005 (1949).

site in sign to the values appearing in the literature, which were determined by different techniques.[16,19,20] Since no other determinations had used acid concentrations as high as ours,[21] lower concentrations were tried (Table II). At 0.1 *M* acid, the high and low temperature constants agreed more closely with each other, as did the corresponding extinction coefficients, but the sign of the temperature coefficient was still the same. Reduction of the acid to 0.05 *M* showed no significant difference, while at lower acidities the iodide–iodate reaction became too slow for reliable use. Whether the sign of the temperature coefficient is altered at zero acid could not be checked in the present experiments.

Discussion

If iodine were monosolvated, iodide unsolvated, and the formation of triiodide resulted from displacement of solvent by iodide, one would have for mixtures of solvents S and Σ the equilibrium constants

$$k_a = (I_2S)(I^-)/(S)(I_3^-) \text{ and } k_b = (I_2\Sigma)(I^-)/(\Sigma)(I_3^-) \quad (1a.1b)$$

Dividing one equation by the other leads to the relationship

$$(I_2\Sigma) = (k_b/k_a)(\Sigma/S)(I_2S) \quad (2)$$

An over-all dissociation constant for triiodide in these solutions, K, is

$$\begin{aligned} K &= ((I_2S) + (I_2\Sigma))(I^-)/((S) + (\Sigma))(I_3^-) \\ &= ((I_2S) + (I_2S)(\Sigma/S)(k_b/k_a))(I^-)/((S) + (\Sigma))(I_3^-) \\ &= (k_a(S) + k_b(\Sigma))/((S) + (\Sigma))k_a\cdot(I_2S)(I^-)/(S)(I_3^-) \\ &= k_a(S)/((S) + (\Sigma)) + k_b(\Sigma)/((S) + (\Sigma)) \quad (3) \end{aligned}$$

through substitution of equations 2 and 1a at appropriate places. In words, the over-all constant K found, for these dilute solutions, is the sum of the individual pure solution constants multiplied by the mole-fraction of the appropriate solvent.

If k_b is much larger than k_a, it can be seen that with small additions of Σ to the systems originally containing pure S, K will rapidly rise from the initial value k_a toward the value k_b, which will then be approached asymptotically as the solvent approaches pure Σ. It readily can be shown mathematically that neither the function K nor ln K (taking mole fraction of one of the solvents as the independent variable) shows an inflection point. It is seen that the low water end of curve I, Fig. 2 corresponds to this sort of behavior, but that the second portion, in the region 50–100% water, introduces an inflection point, which is at variance with the behavior of ln K. Since the plot suggests that there may be two stages of complexing involved, one should consider the possibility that the iodine is disolvated (see also reference 12), and that the triiodide may be solvated also. The following equilibria involving solvents S and Σ then apply.

$$I_2S_2 + I^- = I_3{}^-S + S: \quad k_4 = (I_2S_2)(I^-)/(I_3S^-)(S) \quad (4)$$

$$I_2\Sigma_2 + I^- = I_3\Sigma^- + \Sigma: \quad k_5 = (I_2\Sigma_2)(I^-)/(I_3\Sigma^-)(\Sigma) \quad (5)$$

$$I_3S^- + \Sigma = I_3\Sigma^- + S: \quad k_6 = (I_3\Sigma^-)(S)/(I_3S^-)(\Sigma) \quad (6)$$

$$I_2S_2 + \Sigma = I_2S\Sigma + S: \quad k_7 = (I_2S\Sigma)(S)/(I_2S_2)(\Sigma) \quad (7)$$

$$I_2S\Sigma + \Sigma = I_2\Sigma_2 + S: \quad k_8 = (I_2\Sigma_2)(S)/(I_2S\Sigma)(\Sigma) \quad (8)$$

The over-all equilibrium constant for the dissociation of triiodide, K, is

$$K = ((I_2S_2) + (I_2S\Sigma) + (I_2\Sigma_2))(I^-)/((I_3S^-) + (I_3\Sigma^-))((S) + (\Sigma)) \quad (9)$$

Through equations 4–8, and the substitution $x = (\Sigma)/((S) + (\Sigma))$, one arrives at the final equation

$$K = k_4\cdot[(1 - x)^2 + k_7x(1 - x) + k_7k_8x^2]/[(1 - x) + k_6x] \quad (10)$$

the logarithm of which can be shown to have an inflection point (second derivative equal to zero, third derivative not equal to zero) which for appropriate ranges of values of the equilibrium constants k can be made to fall in the region $0 < x < 1$ to which the physical problem is restricted. (A second inflection point falls at $x < 0$, not of physical interest.) Equation 10 is readily shown to be analogous to equation 3, since for low values of x, K approximates k_4, for values of x near unity, K approximates $k_4k_7k_8/k_6$, and for intermediate values of x the exact shape of the curve is dependent on the relative values of the constants. In particular may be noted the fact that when both k_6 and k_8 are very small, values of x less than the maximum give the approximate relation

$$K = k_4((1 - x) + k_7x) \quad (11)$$

which is of the same form as equation 3.

The value for k_4 may be taken as K for the driest solution, k_7 can be evaluated for some low value of x through equation 11, and from K in pure water can be obtained k_8/k_6. Arbitrary choice of a point (*e.g.*, at $x = 0.78$) to match the experimental curve can then give individual values for k_8 and k_6 for the first approximation. These values of the constants k_6, k_7, k_8 can then be varied to obtain the best fit of equation 10 to the experimental points. The transfer of the data from volume % to mole % is made on the approximation that the volume change on mixing is zero.

It turns out that the values of k_6 are in general too small (around 0.01) significantly to affect the points below the very highest values of x, and that so long as the value of k_7 chosen is about 11, a fair match to the experimental points up to some 70–80 mole % water results (see Fig. 2). This is almost equally true if equation 11 is followed. The fit at higher values of x is very poor under all conditions, however, and it is seen that a term in x^3 is needed to introduce another adjustable constant. In fact, the experimental curve itself shows a second inflection in the region of x greater than 0.9. More constants, however, reduce the significance of any fit obtained. One must say therefore that either the solvation relations are even more complicated than the disolvated iodine monosolvated triiodide which led to equation 10 (*e.g.*, that a trisolvated iodine is involved), or that there is something else not allowed for in the concept of the species affecting the equilibrium in the solutions under consideration.

The fact that equation 11 = equation 3 gives an excellent fit to experiment in the region up to x =

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(19) H. M. Dawson, *J. Chem. Soc.*, 238 (1901).

(20) C. Winther, *Z. physik. Chem.*, B**3**, 299 (1929).

(21) E. W. Washburn and E. K. Strachan, THIS JOURNAL, **35**, 681 (1913).

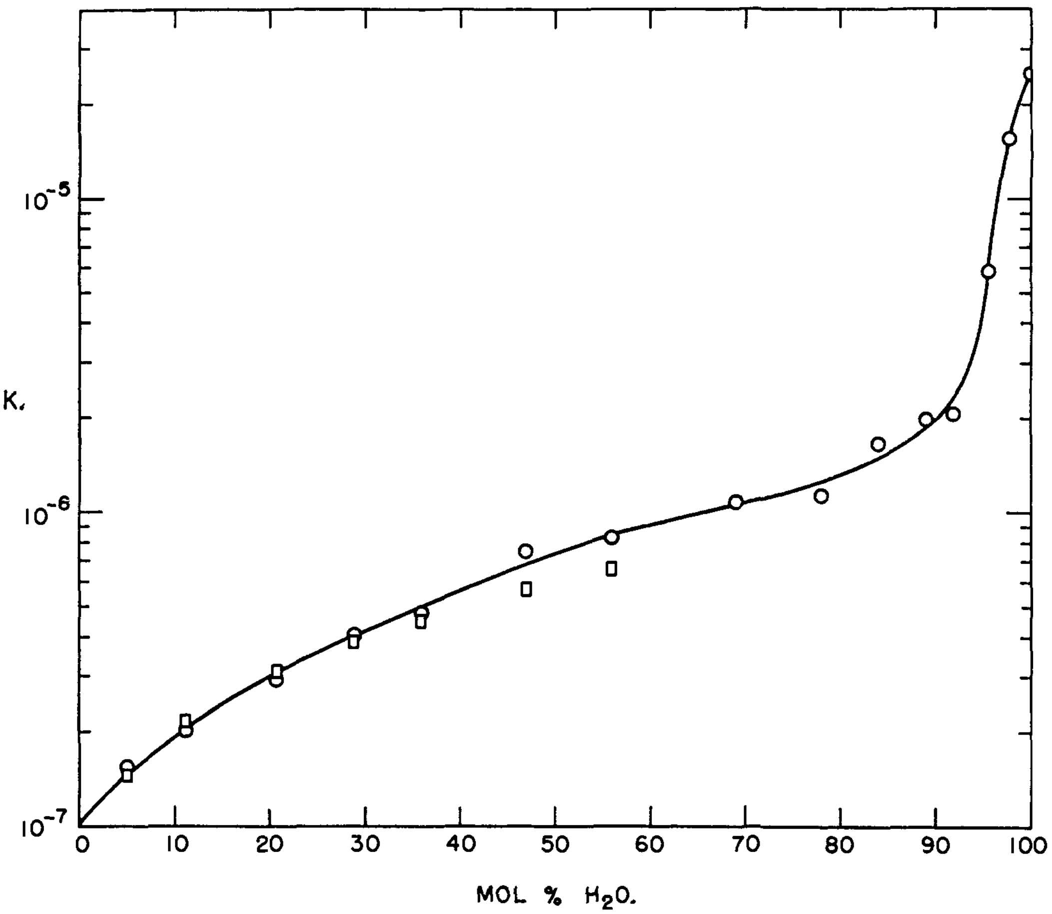

Fig. 2.—Over-all dissociation constant, K, of triiodide in *t*-butyl alcohol, as function of water concentration: ○ and curve, experimental; □, calculated from $K = k_4((1 - x) + k_7x)$ with $k_4 = 1 \times 10^{-7}$, $k_7 = 11$.

0.5 suggests that fundamentally the reaction *is* that of competition between iodide and a mole of solvent for the single coördination position of the iodide, but that at higher water concentrations something new intervenes. This "something new" could conceivably be the "cage effect" proposed by Bayliss and co-workers[13-15] to account for the absorption shifts of iodine with solvent, which other workers[6-12] have shown seem to be better described as due to monosolvate formation. It is possible that as water becomes the dominant solvent in the mixture, and the structure goes over toward the highly lattice-like situation of pure water, the large fundamentally linear[22,23] triiodide structure becomes strained due to lack of match with the interstices of the water structure, resulting both in shift of the peak absorption wave length from the 360 mμ of the "alcoholic absorption" to the 352 mμ of the "aqueous absorption," and in interference with stability of the complex, to give a greater chemical dissociation. It might also be noted that though in general the wave length of the *iodine* absorption decreases as base strength of the solvent increases, the peak absorption wave length of iodine in water is *higher* than that of iodine in alcohol, perhaps another sign of solvent peculiarity, if not actually a symptom of structural influence on the $I_2 \cdot H_2O$ stability. Possible dielectric constant influences on stability of the triiodide are difficult to evaluate because of uncertainty as to the cause of the dipole moment of iodine in solution.[8,11]

The difference between the wave length and extinction coefficient of anhydrous sodium triiodide solution on the one hand, and tetrabutylammonium triiodide or hydrated sodium triiodide solution on the other hand, has analogs in the modifications of anion absorption spectra on coördination with cations[24-26] and its reversal in the presence of water.[24,25] In the triiodide case it might be linked to a change in the geometrical arrangement of the three iodine atoms. They are presumably symmetrically spaced in a linear arrangement in solution, but in the solid state there seems to be a differentiation, the "iodide" atom being further separated from its nearest neighbor in the triiodide ion than the two "iodine" atoms.[22,23] A similar alteration might be pictured to take place with the close approach of the sodium cation in solution, a shift in position of the iodine atoms resulting in a change in the absorption. With hydration of the cation, the relations between cation and anion approach those for the

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[22] R. C. L. Mooney, *Z. Krist.*, **90**, 143 (1935).

[23] R. J. Hach and R. E. Rundle, THIS JOURNAL, **73**, 4321 (1951).

[24] L. I. Katzin, *J. Chem. Phys.*, **18**, 789 (1950).

[25] L. I. Katzin, *ibid.*, **20**, 1165 (1952).

[26] M. Linhard and M. Weigel, *Z. anorg. allgem. Chem.*, **266**, 49 (1951).

large tetrabutylammonium cation, and spectral differences should vanish as they do.

Analogous solvent dependence of the stability of the trihalide ion is found in the literature on tribromide ion.[27-33] This is consistent with the literature on solvent complexes of bromine which is parallel to that for iodine.[34]

The acid effect noted on the triiodide equilibrium, in the region of acidity 1 M $HClO_4$ is apparently the first evidence for a difference in the dissociation constants for HI and HI_3. The temperature variation in the peak extinction coefficient of triiodide is probably related to the origin of the absorption. This is a modified absorption of the iodide ion, which will be discussed elsewhere.

LEMONT, ILLINOIS

(27) A. A. Jakowkin, *Z. physik. Chem.*, **20**, 19 (1896).

(28) S. Bugarszky, *ibid.*, **48**, 63 (1904).

(29) R. O. Griffith, A. McKeown and A. G. Winn, *Trans. Faraday Soc.*, **28**, 101 (1932).

(30) L. Farkas, B. Perlmutter and O. Schächter, THIS JOURNAL, **71**, 2829 (1949).

(31) S. Bugarszky, *Z. physik. Chem.*, **38**, 561 (1901).

(32) S. Bugarszky, *ibid.*, **71**, 705 (1910).

(33) R. E. Buckles, A. I. Popov, W. F. Zeleszy and R. J. Smith, THIS JOURNAL, **73**, 4525 (1951).

(34) R. M. Keefer and L. J. Andrews, *ibid.*, **72**, 4677 (1950).

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Dissociation Pressures and Related Measurements in the System Aluminum Sulfate–Water[1]

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Published data on the system aluminum sulfate–water are incomplete and contradictory. A static manometric method was used to measure the vapor pressures of known aluminum sulfate–water compositions at fixed temperatures as known quantities of water were withdrawn. Measurements were made at 25, 14 and 0°, and the sample size was varied. Equilibrium could be reached only for the higher hydrates. Within the range of conditions studied both of the compounds $Al_2(SO_4)_3 \cdot 16H_2O$ and $Al_2(SO_4)_3 \cdot 17H_2O$ appear to exist and are, furthermore, mutually soluble. The $17H_2O$ is thus capable of losing up to one mole of zeolitic water. Dissociation pressures for the systems vapor–liquid–$17H_2O$ and vapor–$16H_2O$–lower hydrate, and for a metastable system, were obtained at each temperature. A log P *vs.* $1/T$ plot was linear for each. The ice curve and eutectic point were redetermined giving results markedly different from the only previous values. The solubility curve of the $17H_2O$ was extended. Melting points of hydrated aluminum sulfate in various stages of hydration indicated transition temperatures at ~111° and ~128°. Previous boiling point elevation values have been improved upon and extended to higher concentrations.

The phase relations in the system aluminum sulfate–water are, surprisingly, not well established considering the widespread use of the hydrates. There is, for instance, no complete agreement as to the identity of the highest hydrate[2] although the existence of (1) a hydrate or hydrates with 18, 17 or 16 moles, and (2) a hydrate with 10 or 9 moles of water of hydration is generally conceded. Smith and others[3] showed the highest hydrate at 25° to be the 17 but Bassett and others[4-6] still regard it as the 16 (see Discussion). The second highest hydrate would appear to be the 10 from the work of Gee[7] but 9 from that of Henry and King.[2] If, as Gee claims, the highest hydrate is the 10 (or 9) at 80° but the 16 at 30° there should be a break in the aqueous solubility curve between these two temperatures. This is not evident in the measurements of Taylor and Bassett.[6] Furthermore, the only published boiling point elevation data[8] were obtained by the crudest of methods, the authors themselves suggesting that their measurements be repeated.

Dissociation Pressures

To resolve the problem of the identity of hydrates it would appear that isothermal measurements of the equilibrium pressure of the system as water is gradually withdrawn would provide the best means, by noting the compositions of solid at which marked changes in pressure are observed. Such dissociation pressure measurements at 20° are described by Kremann and Hüttinger[9] using equilibration over sulfuric acid solutions, and the hydrates 18, 16, 12 and 2 were claimed. Their results are open to alternative interpretations, however, and their pressures do not agree with those reported below. Taylor and Bassett[6] give a brief reference to dissociation pressure measurements at 25° using a static manometric method. Equilibrium was approached from the direction opposite[10] to that used by us and their results differ from, and are less complete than, ours.

Experimental

In the present work pressures were measured by a method patterned after that of Logan.[11] The sample (A, Fig. 1) was contained in a thermostated 50-ml. glass bulb B leading directly to one arm of a mercury manometer C. The other arm led to a Hyvac pump and McLeod gage, and to a means of introducing or removing measured quantities of water. Air-free water was introduced by drawing water into E (previously evacuated) through F, boiling out the air through

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(1) Presented before the Division of Physical and Inorganic Chemistry of the American Chemical Society at Chicago, Ill., September, 1953.

(2) *Cf.* J. L. Henry and G. B. King, THIS JOURNAL, **71**, 1142 (1949).

(3) N. O. Smith, *ibid.*, **64**, 41 (1942); H. A. Horan and J. A. Skarulis, *ibid.*, **61**, 2689 (1939); W. F. Ehret and F. J. Frere, *ibid.*, **67**, 68 (1945).

(4) H. Bassett and T. H. Goodwin, *J. Chem. Soc.*, 2239 (1949).

(5) H. Bassett and W. Watt, *ibid.*, 1408 (1950).

(6) D. Taylor and H. Bassett, *ibid.*, 4431 (1952).

(7) E. A. Gee, THIS JOURNAL, **67**, 179 (1945).

(8) W. L. Badger and J. S. France, *Ind. Eng. Chem.*, **15**, 364 (1923).

(9) R. Kremann and K. Hüttinger, *Jahrb. k.k. Geol. Reichsanstalt*, **58**, 637 (1908).

(10) Private communication.

(11) T. S. Logan, *J. Phys. Chem.*, **36**, 1035 (1932).