[CONTRIBUTION FROM THE CHEMISTRY DIVISION, ARGONNE NATIONAL LABORATORY]

Heats of Solution of Uranyl Nitrate Hydrates in Water and in Organic Solvents[1]

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The present paper reports an investigation of the heats of solution of uranyl nitrate hexahydrate, trihydrate and dihydrate in water and in isobutyl alcohol, diethyl ether, tetrahydrofuran, ethylene glycol monoethyl ether, ethylene glycol diethyl ether, tetrahydrofurfuryl alcohol, acetone, methyl ethyl ketone, methyl isobutyl ketone, ethyl malonate, ethyl propionate, ethyl oxalate and tributyl phosphate. The relative values of the heats of solution in the pure solvents are related to the base strengths of the solvents, with formation of undissociated uranyl nitrate tetrasolvate in solution. Experiments with mixed solvents show the effects of hexasolvate formation in water and in isobutyl alcohol.

Evidence is accumulating that strong electrolytes are more commonly soluble in organic solvents of low dielectric constant than was once assumed. Recent evidence suggests strongly that formation of a neutral solvated molecule maintaining the coördination number of the metal atom is an important factor in this solubility behavior.[2-5] Differences in the "base strength" (electron donating ability) of the molecular solvent groups present, and the relation of the lattice energies of the possible solid solvates to the strength with which solvent groups are held are also factors in the behavior.

Although more familiarity is being gained with these salt–solvent systems, there is a scarcity of thermochemical data which might aid elucidation of the relationships. An investigation of the heats of solution of the uranyl nitrate hydrates was therefore undertaken, since sufficient data are available on other aspects of their behavior with respect to a number of oxygenated organic liquids to make the findings of possible general significance. Data were obtained for water as well as for a sampling of alcohols, ethers, ketones and esters.

An analysis of the data leads to the conclusion that in general the product in solution, with the organic solvents tested, is the neutral tetrasolvate molecule. With the stronger bases, such as the ethers, tributyl phosphate and isobutyl alcohol, the amount of water held by a salt molecule in solution may be insensitive to whether the starting solid is uranyl nitrate dihydrate, or the hexahydrate. For the weaker bases, such as the ketones and esters, heat effects suggestive of a greater sensitivity to water are found. In the case of isobutyl alcohol (presumably typical of other simple alcohols), evidence is found for a considerable amount of hexasolvate formation in uranyl nitrate solutions in the pure solvent. Dilution, *e.g.*, with acetone, reduces the amount of hexasolvate formation. Solutions of uranyl nitrate in water sufficiently diluted with acetone seem in a large part also to contain tetrahydrated rather than hexahydrated uranyl nitrate.

Experimental

Highest purity Mallinckrodt uranyl nitrate was recrystallized from distilled water, and only the middle fraction of the solid crystallizing was used. The hexahydrate so obtained was maintained in a desiccator over 35–40% sulfuric acid, at about 24° after being pulverized in a ball mill. The trihydrate was prepared from this by equilibration over 60–65% sulfuric acid, and dihydrate by equilibration over 95% acid. Desiccators were maintained at reduced pressure (*ca.* 1 cm.) to facilitate equilibration. When thin layers of pulverized salt were used, the dehydration period to obtain the lower hydrates was about two weeks. The acid concentrations used agree roughly with the stability regions deduced from the vapor pressures of the hydrates as given by Germann and Frey.[6]

Uranyl nitrate hexahydrate loses water readily to the average atmosphere, the trihydrate is only relatively more stable, and the dihydrate will absorb water from humid atmospheres. Control of the composition of the solids used in the heat of solution determinations is therefore of prime importance. For this reason, the uranium and water contents of all solids were checked the day they were used. Uranium was determined by ignition to the solid U_3O_8; water was determined by titration with Karl Fischer reagent as in earlier work.[2] With 0.1% accuracy of the U_3O_8 determinations, and 0.5–1% for the water analyses, the hydrates used in the measurements could have contained 1 mole % of another hydrate without detection. Such a contamination could introduce an uncertainty approaching 2% for the heats of the hexahydrate and dihydrate in water, and 5% for the trihydrate, because of its relatively low numerical value.

The solvents were in general redistilled at atmospheric pressure from the commercial pure product; tetrahydrofurfuryl alcohol[7] was distilled at 70° under reduced pressure. All ethers were tested for peroxide impurities before use. Acetone was dried over potassium carbonate and redistilled. The methyl isobutyl ketone was a special purified Shell Oil Company product. The water content of all solvents was checked by titration with Karl Fischer reagent, and in general ranged from 0.3% to zero values.

The calorimeter consisted of a cylindrical dewar flask (685-ml. capacity) immersed in a water-bath at 25 ± 0.1°. The flask was fitted with a lucite lid through which a calibrated Beckmann thermometer, a bell-type glass stirrer, a nichrome wire heater of known resistance, and a closed tube for introducing the sample were mounted. When the solute was water, a 1- or 2-ml. portion was pipetted into the calorimeter. All openings were sealed with Apiezon "Q" compound. In all cases 200 ml. of solvent was used. The precision of the measurements was tested by measuring the heat of solution of sodium carbonate at a dilution of 1 mole of salt to 200 moles of water. Two determinations agreed to less than 1%, and the average deviated from the value 5.88 kcal./mole[8] by about 1%.

Heat capacities of the calorimeter and the solutions were determined by electrical heating, using a calibrated milliammeter to read currents. In the case of uranyl nitrate solutions in water, heat capacities were read from a plot of composition *vs.* heat capacity based on data of our own combined with those of Lister.[9] The plot is linear, from 0.770 cal./deg.-g. at 25% by weight of uranyl nitrate to the value

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[1] Presented at the Chicago Meeting of the American Chemical Society, Sept. 3–8, 1950.

[2] L. I. Katzin and J. C. Sullivan, *J. Phys. Colloid Chem.*, **55**, 346 (1951).

[3] L. I. Katzin and E. Gebert, THIS JOURNAL, **72**, 5455 (1950).

[4] L. I. Katzin and J. R. Ferraro, *ibid.*, **72**, 5451 (1950).

[5] L. I. Katzin and E. Gebert, *ibid.*, **72**, 5464 (1950).

[6] F. E. E. Germann and P. R. Frey, *J. Colo.-Wyo. Acad. Sci.*, **1**, 54 (1929).

[7] We are indebted to the Quaker Oats Company for a sample of the alcohol.

[8] F. R. Bichowsky and F. D. Rossini, "Thermochemistry of Chemical Substances," Reinhold Publishing Corp., New York, N. Y., 1936, p. 144.

[9] M. Lister, Canadian Atomic Energy Project, Report No. MX-234 (1946).

TABLE I

HEATS OF SOLUTION OF URANYL NITRATE HYDRATES IN VARIOUS SOLVENTS AT 25° (KCAL./MOLE)[a]

Solvent	Solute → $UO_2(NO_3)_2 \cdot 6H_2O$	$UO_2(NO_3)_2 \cdot 3H_2O$	$UO_2(NO_3)_2 \cdot 2H_2O$	H_2O
Water	5.48 ± 0.03 (10)	−1.66 ± 0.05 (4)	− 5.37 ± 0.06 (8)	0.0
Isobutyl alcohol	10.01 (4)	1.93 (2)	−2.58 (3)	.72
Diethyl ether	1.78 (2)	−6.54 (3)	−10.60 ± 0.18 (7)	.23
Tetrahydrofuran	0.73 (2)	....	−10.71 (3)	.51
Ethylene glycol diethyl ether	0.58 (2)	−7.21 (2)	−10.87 (5)	.80
Ethylene glycol monoethyl ether	..	....	−8.97 (2)	− .23
Tetrahydrofurfuryl alcohol	..	....	−8.51 (2)	− .40
Acetone	3.46 (4)	−3.23 (2)	−6.67 (3)	0.79
Methyl ethyl ketone	..	....	−5.98 (3)	1.09
Methyl isobutyl ketone	6.92 (2)	−2.01 (3)	−6.46 (5)	1.36
Ethyl propionate	..	....	−6.03 (2)	1.63
Diethyl malonate	..	....	−4.55 (2)	1.53
Diethyl oxalate	..	....	−3.05[b] (2)	1.18
Tributyl phosphate	0.80 (2)	....	−10.46 (4)	0.14

[a] Mole ratio, solute/solvent, 1/80. In case of solvent water, 1/180; tetrahydrofuran, 1/150. Numbers in parentheses are number of determinations averaged. Heat lost to the surroundings is given the minus sign. [b] Probably includes contribution from the reaction: $UO_2(NO_3)_2 \cdot 2H_2O + Et_2C_2O_4 \rightarrow UO_2C_2O_4 + 2EtOH + HNO_3$.

for pure water. In use a correction was of course made for the heat capacity of the calorimeter system, which was determined using a measured quantity of distilled water, and was about 5% of the total experimental heat capacities. All standard thermometer and leak corrections were made in the heat measurements.

Results

Heats of Solution in Water.—The heats of solution of the uranyl nitrate hydrates at a dilution of 1:180 are shown in Table I. The convention is followed of giving heat evolved the negative sign. Our value of 5.40 kcal./mole for the hexahydrate agrees better with the 5.45 kcal. found for 12° by de Forcrand[10] than the 5.25 kcal. of Coulter, Pitzer and Latimer[11] for 25° although both sets of data are for a terminal concentration approximately five times as dilute as ours. The best trihydrate values[10,12] fall 0.3 kcal. on either side of our value, −1.66 kcal./mole. For the dihydrate, our value of −5.37 kcal./mole agrees with the −5.42 kcal. value of Markétos[12] but not with the −5.05 kcal. of de Forcrand.[10]

Heats of Solution in Organic Solvents.—The outstanding feature of the data for the organic solvents, shown in Table I, is the relation between the functional group of the solvent and the value of the heat of solution, most clearly shown for the dihydrate. Diethyl ether, tetrahydrofuran and ethylene glycol diethyl ether show heat values between −10.60 and −10.87 kcal./mole, while acetone, methyl ethyl ketone and methyl isobutyl ketone show heats of −6.67, −5.98 and −6.46 kcal. Ethyl propionate has a value like that of the ketones, while ethyl malonate shows a slightly smaller value. The ester of an inorganic acid, tributyl phosphate, dissolves the dihydrate with a heat like that of the ethers. The dihydrate dissolves in isobutyl alcohol with a heat of −2.58 kcal./mole, and in tertiary butyl alcohol it tends toward a similar value (the two alcohols tend toward similar heats in the several cases, but the rate of solution of the uranyl nitrates in tertiary butyl alcohol has been found to be too slow for good heat measurements by the present technique). Ethylene glycol monoethyl ether and tetrahydrofurfuryl alcohol have the functional groups of both ether and alcohol, and give very similar heats of solution for the dihydrate which are close to those of the ethers, rather than to those of the butyl alcohols. The only comparative literature with which the authors are acquainted is the recent report of Mathieson[13] that the heat of solution of the trihydrate in methyl ethyl ketone is −3.06 kcal./mole, which is close to our −3.23 kcal. for acetone.

Apparent Heat Capacities of Uranyl Nitrate and Water in Organic Solvents.—From the heat capacity values obtained during the course of the heat of solution measurements, it should be possible to calculate apparent molal heat capacities for the solutes. However, the heat capacity differences here are rather small, so that reliability is not great. The best data have been obtained for diethyl ether solution, in which uranyl nitrate dihydrate has an apparent molal heat capacity of 390 cal./deg., the trihydrate 420, and the hexahydrate, 630 cal./deg.; water shows a molal heat capacity of 90 cal./deg. in the solvent. In the other ethers one finds lower numerical values, 110–330 cal./deg. for the dihydrate and 11–35 cal./deg. for water. Solutions in methyl isobutyl ketone and the esters give values from 500–650 cal./deg. for the dihydrate, and from 110–170 cal./deg. for water. Both acetone and isobutyl alcohol solutions show low values for the dihydrate and for water, and values of about 200 cal./deg. for the hexahydrate. For comparison with these numbers, one may cite the value of 112 cal./deg. found by Coulter, Pitzer and Latimer[11] for solid uranyl nitrate hexahydrate at 25°, and the well-known value 18 cal./deg. for liquid water. The values of the heat capacity of aqueous solutions of uranyl nitrate given earlier in the paper indicate a molal value of about 32 cal./deg. for the salt in dilute aqueous solution.

Discussion

The ternary phase studies of Katzin and Sullivan[2] have shown that uranyl nitrate usually is accompanied by four molecules of water when extracted from an aqueous phase into an organic phase. Likewise, the solid phases met in these systems, aside from the hexahydrate and the hexasolvated solids found with *t*-butyl alcohol, showed four or fewer solvent groups coördinated (*e.g.*, the trihydrate–monoetherate, dihydrate–dietherate, etc.) Cobalt salts in organic solvents take the anions into the coördination sphere of the metal atom, with displacement of a corresponding number of solvent groups,[3–5] and it seems most probable that this happens in the uranyl nitrate case also. It has further been shown in the work with uranyl nitrate and other salts, that there is a competition between the various solvent groups present (water, organic molecules) for the remaining coördination positions around the metal atom. In the case of uranyl nitrate,[2] groups such as the ethers seem unable to displace the ultimate two water groups attached to the salt, while the butyl alcohols accomplish this readily. This is shown by the fact that the ethers in the ternary systems never have shown solids with less than two molecules of water per salt molecule, and the equilibrium liquid phases have

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[10] M. de Forcrand, *Compt. rend.*, **156**, 1207 (1913); *Ann. chim.*, [9] **3**, 3 (1915).

[11] L. V. Coulter, K. S. Pitzer and W. M. Latimer, THIS JOURNAL, **62**, 2845 (1940).

[12] M. Markétos, *Compt. rend.*, **155**, 210 (1912).

[13] A. R. Mathieson, *J. Chem. Soc.*, Suppl. 2, S294 (1949).

never shown less than 2 molecules of water per salt molecule (although the value 2 may be approached extremely closely), while with the alcohols anhydrous alcoholated solids are met, and in the liquid phases water–salt ratios are frequently much lower than in the solid phases with which they are in equilibrium. The behavior with the ketones seems to fall between these two extremes.

The solution of a given hydrate in an organic solvent therefore entails (among other things) loss of a fraction of its water and addition of another (not necessarily equal) number of solvent molecules to the neutral salt. The measured heat of solution is affected by the difference in binding energy of the solvent groups and water, and by the equilibrium number of water and solvent groups attached to the molecule in solution. If the binding of the organic group is strong, relative to water, addition of another small fraction of water should shift the equilibrium very little, and show very little heat effect; if the binding of the organic group is weak, the equilibrium should be sensitive to the water concentration, and a perceptibly greater heat effect on adding water might be anticipated.

An experimental test of these relations may be obtained by comparing the heat effect on dissolving a fixed portion of water in a pure solvent, and in an equal portion of solvent in which uranyl nitrate dihydrate has been dissolved. The results of a series of such experiments are exhibited in Table II. Uranyl nitrate dihydrate (0.01–0.03 mole) was dissolved in 200 ml. of the solvent to be tested, and the heat effect of adding approximately 4 moles of water per mole of salt was measured. The ΔH values in the first two columns are kilocalories per mole of water in the experiment, the last column is the nominal heat of reaction per mole of salt. As can be seen, the ethers and alcohols are, by the heat criterion, distinctly stronger competitors with water than are the ketones and esters. As a class, the alcohols (isobutyl alcohol, presumably *t*-butyl alcohol, and the two ether–alcohols) seem slightly better water competitors than the ethers. Tributyl phosphate is almost as strong a water competitor, according to the heat values, as diethyl ether and isobutyl alcohol.

TABLE II

HEATS OF REACTION OF WATER WITH URANYL NITRATE DIHYDRATE IN ORGANIC SOLVENTS

$UO_2(NO_3)_2{\cdot}2H_2O(soln.) + 4H_2O(l)$

Solvent	Water to pure solvent, kcal./mole	Water to dihydrate solvent, kcal./mole	Mole ratio, added water to uranyl nitrate	Heat of reaction kcal./mole
Diethyl ether	0.23	0.21	4.7	0.09
Isobutyl alcohol	.72	.70	5.0	.10
Tributyl phosphate	.14	.06	3.7	.35
Ethylene glycol monoethyl ether	−0.23	− .39	4.3	.68
Tetrahydrofurfuryl alcohol	−0.40	− .67	4.0	1.08
Ethylene glycol diethyl ether	.80	.52	4.0	1.12
Tetrahydrofuran	.51	.14	4.0	1.48
Methyl isobutyl ketone	1.36	.74	4.0	2.48
Acetone	0.79	.10	4.0	2.76
Methyl ethyl ketone	1.09	.31	4.0	3.12
Ethyl propionate	1.63	.70	4.0	3.72
Ethyl malonate	1.53	.76	4.0	3.08
Ethyl oxalate	1.18	.37	5.9	(4.9)

It is interesting to compare such a criterion of base strength with values derived in other ways. An extensive series of measurements has been made by Gordy and Stanford,[14] in which the criterion of base strength has been the displacement of the infrared bands of deutero-methanol on mixing this reagent with the base to be tested. Their results also show that the esters are weaker bases than the ketones, which in turn are weaker than the ethers and than methyl alcohol. Within the ester class, their results show diethyl oxalate weaker than esters of monocarboxylic acids, and *n*-butyl phosphate a stronger base than organic esters or ketones, and almost as strong a base as ethyl ether. Among the ketones, the Gordy and Stanford results show methyl ethyl ketone to be a weaker base than acetone, with methyl isobutyl ketone of about the same base strength as methyl ethyl ketone. In our phase studies[2] as well as in the heat results, methyl isobutyl ketone seems to behave as equal to or perhaps slightly stronger than acetone. Ethyl ether, by both criteria, is the strongest base of the ethers tested, and the over-all agreement in order of base strengths is excellent.

Correlation of the actual heats of solution (*e.g.*, of the dihydrate) in the various solvents is more difficult. Both the ethers and the butyl alcohols appear as strong bases, but show opposite extremes in the heat of solution series. A possible factor is formation of a considerable proportion of hexasolvate in the butyl alcohols, as witness the mixed hexasolvated solid phases found in the ternary system uranyl nitrate–water–*t*-butyl alcohol.[2,4] To form hexasolvate from the tetrasolvate, according to the point of view followed here, it is necessary to break the cation–anion bonds, and then displace the anions from the cation by the diameter of a solvent molecule, against the electrostatic attraction, a process which should absorb energy which might otherwise appear as heat. A lesser amount of formation of hexasolvate ($[UO_2S_6]^{++}(NO_3)_2$) and more of the tetrasolvate ($[UO_2S_4(NO_3)_2]$) could explain why ethylene glycol monoethyl ether and tetrahydrofurfuryl alcohol, both with alcoholic groups, give heats of solution of uranyl nitrate dihydrate like those of the ethers rather than those of the butyl alcohols.

If this variance in the proportion of hexasolvate formation is the principal reason for the ether–alcohol difference in heat of solution, it should be possible to find a mixture of isobutyl alcohol with a weak base solvent (*e.g.*, acetone) in which the hexasolvate formation is minimized and which shows a heat of solution more like that in the ethers. Such a test has been made (see Table III) and in fact shows that although the heats of solution of uranyl nitrate dihydrate in isobutyl alcohol and acetone are −2.58 and −6.67 kcal., respectively, a mixture of equal volumes of acetone and

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(14) W. Gordy and S. C. Stanford, *J. Chem. Phys.*, **8**, 170 (1940).

isobutyl alcohol dissolves uranyl nitrate dihydrate with a heat evolution of 10.30 kcal./mole. In contrast, addition of acetone to tributyl phosphate reduces the heat of solution of the dihydrate in the direction of the heat of solution in acetone, to -8.72 kcal. for 25% acetone and -8.29 kcal. for 50% acetone by volume.

TABLE III

HEAT OF SOLUTION OF URANYL NITRATE DIHYDRATE IN ACETONE-ISOBUTANOL MIXTURES

Vol. % iso-BuOH	Heat of solution, kcal./mole
100	−2.58
87.5	−7.06
75	−8.84
50	−10.30
0	−6.65

The heat effects of adding water to solutions of uranyl nitrate dihydrate in the weaker bases show that at low water levels, where hexasolvate formation is minor, one should get an effect analogous to that exhibited by the acetone–alcohol mixtures. Experimental values for water–acetone mixtures (Table IV) confirm this. The -10.98 kcal. at 3.25% water represents a minimal value for the heat of solution of uranyl nitrate dihydrate in water to give undissociated uranyl nitrate tetrahydrate; the process of dissociation of the nitrates and coördination of two more molecules of water thus absorbs a net minimum of 5.6 kcal., to give the over-all value for pure water of -5.37 kcal. That the heat difference in the water case, for a lesser distance of separation of cation and anions, is 2.1 kcal. greater than for the alcohol–acetone mixtures *vs.* pure alcohol may be attributed in part to a greater binding energy for water, since the difference under discussion is the resultant of the exothermic solvent binding process, and the endothermic ion separation process. Considering this, the true value for the heat of solution to give the undissociated tetrahydrate runs ahead of the heats for the ethers, in agreement with what one would anticipate from the relative base strengths.

TABLE IV

HEAT OF SOLUTION OF URANYL NITRATE DIHYDRATE IN ACETONE-WATER MIXTURES

Vol. % H_2O	Heat of solution, kcal./mole
0.2-0.25	−6.67
0.5	−7.99
0.75	−8.68
1.25	−9.21
2.25	−9.99
3.25	−10.98
5.25	−10.26
7.75	−9.94

In view of the statements of Mathieson[13] it apparently needs to be stressed that in the absence of values for the lattice energies of the solids involved, one cannot equate solvation reaction heat values with binding energies for the molecular bases involved.

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[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

The Reduction of Nickel Oxide by Hydrogen

BY GIUSEPPE PARRAVANO

The reduction of nickel oxide by hydrogen has been studied in the range of 150–350° and initial pressures of hydrogen from 200 to 500 mm. The addition of foreign ions to nickel oxide affects both the rate and activation energy for reduction. These effects have been related to the change in the electronic properties of the oxide.

The problem of the extent to which chemical interactions involving a solid phase are affected by the energetic structure of that phase has been the subject of considerable experimental and theoretical work. These studies proceeded through different approaches, mainly centered on the elucidation of the mechanism of heterogeneous catalysis.

Theoretical advances and successful applications of the band theory of the solid state have recently led to a better understanding of the electronic properties of metallic oxides. In the field of catalysis the production of oxide semi-conductors with controlled electronic characteristics by Verwey and his school[1] discloses new possibilities, and affords a sound basis for attacking the problem of the relation between electronic states of oxides and their activity to catalyze chemical reactions.

As a preliminary study in this field, the reduction process of nickel oxide by hydrogen was investigated in order to obtain information on the effect of ionic and electronic defects in the solid phase on its reductive properties. The extensive investigations of Pease and Taylor[2] in the case of copper oxide, of Garner in the case of zinc oxide,[3] of Taylor and Starkweather[4] and Benton and Emmett[5] in the case of nickel oxide have shown that the reduction processes of metallic oxides involve several different stages. In the case of nickel oxide, after an initial auto acceleration of the reduction rate, a constant value is obtained up to relatively high conversions. The present data refer mainly to this latter stage of the reductive process and clearly show how the reaction can be greatly affected by the defective structure of the solid phase.

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(1) E. J. Verwey, P. W. Haaijman, P. C. Romeijn and G. W. Osterhout, *Philips Res. Reports*, **5**, 173 (1950).

(2) R. N. Pease and H. S. Taylor, THIS JOURNAL, **43**, 2179 (1921).

(3) W. E. Garner, *J. Chem. Soc.*, 1239 (1947).

(4) G. B. Taylor and H. W. Starkweather, THIS JOURNAL, **52**, 2314 (1930).

(5) A. F. Benton and P. H. Emmett, *ibid.*, **46**, 2728 (1924).