zoic acid series. Here, again, the results indicate that the largest resonance effects are found for the anilinium ions.

TABLE XIII

LOG $K_{A_xB_0}$ FOR SUBSTITUTED ANILINIUM IONS AND ANILINE

	Water Obsd.	Water Calcd.	Methanol Obsd.	Methanol Calcd.	Ethanol Obsd.	Ethanol Calcd.
m-NO₂	2.604	2.550	2.909	2.639	3.243	2.686
m-Cl	1.257	1.256	1.532	1.288	1.554	1.302
m-F	1.204	1.216	1.455	1.247	1.468	1.261
m-CH₃	−0.091	−0.174	−0.187	−0.180	−0.292	−0.184
p-NO₂	3.604	1.181	4.519	1.273	5.207	1.323
p-Cl	0.772	0.826	1.004	0.867	1.068	0.888
p-F	.061	.823	0.320	0.863	0.348	.883
p-CH₃	− .495	− .123	−0.538	−0.132		− .136

TABLE XIV

RESONANCE CONTRIBUTIONS TO THE PARA POSITION

Substituent	Anilinium ions	$\Delta \log K_{A_xB_0}$ Phenols[22]	Benzoic acids[28]
F	−0.75	−0.40	−0.18
Cl	− .05	− .07	− .05
CH₃	− .29	− .20	− .13
NO₂	2.37	1.81	.29

Table XV presents a Δ' log $K_{A_xB_0}$ which is the change in log $K_{A_xB_0}$ with change in solvent. This emphasizes the structural change in the solvent as against change in dielectric constant. From water to methanol, Δ' log $K_{A_xB_0}$ observed is about an order of magnitude greater than the calculated. There is close agreement between the observed and

calculated change for the halogens from methanol to ethanol. This correlates with the fact that the greatest structural change takes place where a methyl group is substituted for a hydrogen in water. These data also indicate the nitro group interacts with the solvent to a greater extent than do the halogens. The dielectric constant, therefore, is insufficient to account for medium effects except where solvents are closely related in structure and interactions between solute and solvent are small. The Sarmousakis or any analogous electrostatic treatment can give consistent results in any given solvent but it contains no structural parameters for the solute–solvent interaction and, therefore, it does not successfully bridge solvents.

TABLE XV

CHANGE IN LOG $K_{A_xB_0}$ WITH SOLVENT

	Methanol–water Δ' log $K_{A_xB_0}$ Obsd.	Methanol–water Calcd.	Ethanol–methanol Obsd.	Ethanol–methanol Calcd.
m-NO₂	+0.305	+0.029	+0.334	+0.047
m-Cl	+ .275	+ .032	+ .022	+ .014
m-F	+ .251	+ .031	+ .013	+ .014
m-CH₃	− .089	− .006	− .105	− .004
p-NO₂	+ .915	+ .092	+ .688	+ .050
p-Cl	+ .232	+ .041	+ .064	+ .021
p-F	+ .259	+ .040	+ .024	+ .020
p-CH₃	− .043	− .009		

CHICAGO 16, ILLINOIS

Heats of Solution of the Cobaltous Chloride Hydrates in Water and Certain Organic Solvents .

BY LEONARD I. KATZIN AND JOHN R. FERRARO

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The heats of solution of cobaltous chloride and its hydrates in water and a number of oxygenated organic solvents are presented. Some relations to heats of solution of other salts are pointed out.

In previous papers we have reported on measurements of the heats of solution of the hydrates of uranyl nitrate[1] and cobaltous nitrate[2] in a series of organic solvents. From these data it has been possible to estimate energies of binding of solvent groups by the metal atom.[2] This report covers the extension of heat of solution measurements to cobaltous chloride and its hydrates and provides data for refining some of the binding energy values, and extension of some of the relations previously noted.

Experimental

The heat measurements and analytical procedures have been described previously.[1,2] The cobaltous chloride hydrates were prepared from commercial chemically pure salt by recrystallization of the hexahydrate, and dehydration of the hexahydrate to the lower hydrates. The crystals of hexahydrate were analyzed, ground in a ball mill and reanalyzed. The lower hydrates were prepared by desiccation of the hexahydrate over sulfuric acid. The anhydrous salt was prepared by heating the monohydrate in a stream of hydrogen chloride gas. Composition of the final product

(1) L. I. Katzin, D. M. Simon and J. R. Ferraro, THIS JOURNAL, 74, 1191 (1952).

(2) L. I. Katzin and J. R. Ferraro, ibid., 74, 6040 (1952).

was always checked by analysis at the time of the heat measurements.

Heats of Solution.—The heats of solution of the hydrates and anhydrous salt in the solvents water, dimethylformamide, monoethyl ether of ethylene glycol, tetrahydrofuran, tetrahydrofurfuryl alcohol, tributyl phosphate, acetone and isobutyl alcohol are given in Table I. Measurements were also attempted with methyl isobutyl alcohol, methyl ethyl ketone, diethyl ether of ethylene glycol, diethyl ether and ethyl propionate, but the solubilities in the pure solvents were too limited for satisfactory measurements. In the cases of ethylene glycol diethyl ether and methyl ethyl ketone, heats of solution could be calculated, when solution of the salt was sufficiently complete, from the analysis of the liquid phase. This procedure gave values of −2.58 kcal./mole for the dihydrate in ethylene glycol diethyl ether, and 0.97 kcal./mole in methyl ethyl ketone. Since there is no assurance that the solid phase in contact with the solution was of the same composition as that originally added, these values must be regarded with caution.

TABLE I

HEATS OF SOLUTIONS OF THE COBALTOUS CHLORIDE HYDRATES IN WATER AND IN VARIOUS ORGANIC SOLVENTS

(KCAL./MOLE)

Solvent	CoCl₂	CoCl₂· H₂O	CoCl₂· 2H₂O	CoCl₂· 4H₂O	CoCl₂· 6H₂O
Water	18.92	−14.64	−9.79	−3.22	2.83
Dimethylformamide		−13.56	−10.42		−1.29
Tetrahydrofurfuryl alcohol		−10.85	−8.55ᵃ		1.77ᵃ
Monoethyl ether of ethylene glycol		−8.12	−5.23		4.90
Diethyl ether of ethylene glycol			−2.58ᵃ		
Tetrahydrofuran		−5.60	−2.36		9.81
Tributyl phosphate		−4.16	−2.09ᵃ		9.39ᵃ
Acetone		−3.47	0.35		11.94
Methyl ethyl ketone			0.97ᵃ		
Isobutyl alcohol		−2.90ᵃ	1.45		11.90ᵃ
Pyridine			−23.15ᵇ		

ᵃ Small residue or precipitate at end of measurement. ᵇ Rose precipitate, probably CoCl₂·6Py.

Anhydrous cobaltous chloride was freely soluble only in water. In dimethylformamide, the best of the organic solvents, it dissolved slowly and incompletely. The solubility in isobutyl alcohol, tetrahydrofurfuryl alcohol, acetone, tributyl phosphate, tetrahydrofuran and ethylene glycol diethyl ether was at best slight or the solution process quite slow. In pyridine the solubility was low, and the solid very quickly took on the rose color of the cobaltous chloride pyridinates.[3] There was a suspicion in the case of the alcohols that with
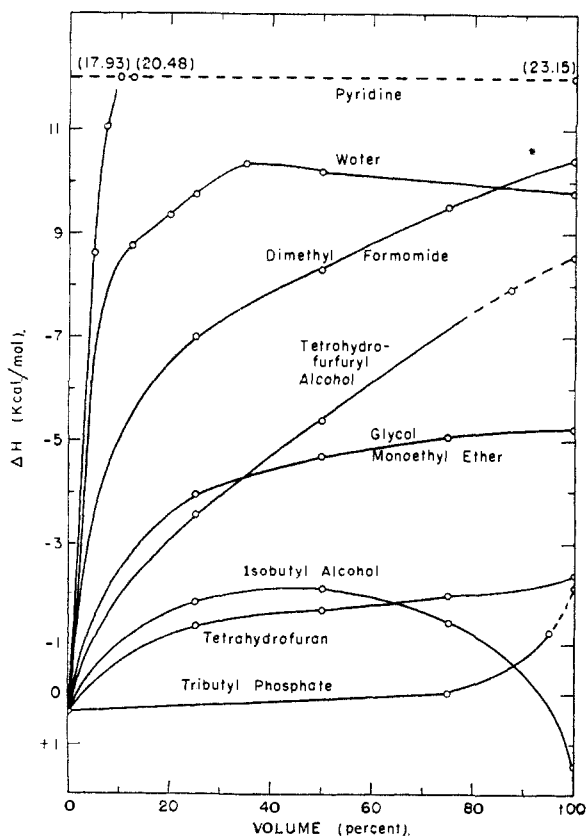

Fig. 1.—Heats of solution of CoCl₂·2H₂O in mixtures of acetone with solvents designated.

(3) L. I. Katzin, J. R. Ferraro and E. Gebert, THIS JOURNAL, 72, 5471 (1950).

time the solid phase was changing to blue alcoholates. No analytical confirmation was attempted, but study of the ternary system cobaltous chloride–water–t-butyl alcohol[4] is under way.

In some instances measurements in mixtures of the solvents with acetone were successful where insolubility hindered the measurements of the heat of solution of the dihydrate in the pure solvents (see Table II), and in the case of the alcohols as well as pyridine the suggestion is strong that the insoluble form is a hexasolvate[4] of cobaltous chloride. As in the studies with uranyl nitrate and cobaltous nitrate, evidence is found in the heats of solution in acetone mixtures for hexasolvate formation with water, isobutyl alcohol and pyridine (Fig. 1). With pyridine, precipitation of salt commences at between 5 and 12.5 volume per cent. of pyridine. As little as 5% by volume of ethylene glycol diethyl ether, 12.5% of diethyl ether or 25% of methyl ethyl ketone, cause incomplete solubility using the standard salt–solvent ratio. The check on base-strengths of the solvents relative to water,[1,2] made by addition of 4 equivalents of water to a solution of cobaltous chloride dihydrate in the solvent, gives in general the expected order, in agreement with previous findings, with the possible displacement of isobutyl alcohol from the other alcohols (Table III).

TABLE II

HEAT OF SOLUTION OF CoCl₂·2H₂O IN MIXTURES OF ACETONE WITH OTHER SOLVENTS (KCAL./MOLE)

Second solv.	Vol. per cent.	ΔH	Second solv.	Vol. per cent.	ΔH
Water	0.0	0.35	Tetrahydrofuran	25	−1.36
	12.5	−8.77		50	−1.67
	20	−9.35		75	−1.97
	25	−9.74	Isobutyl alcohol	25	−1.83
	35	−10.37		50	−2.09
	50	−10.19		75	−1.41
Dimethylformamide	25	−6.98	Tributyl phosphate	75	0.00
	50	−8.32		95	−1.22
	75	−9.52	Pyridineᵇ	5	−8.62
Tetrahydrofurfuryl alcohol	25	−3.58		7.5	−11.05
	50	−5.40		10.0	−17.93ᶜ
	87.5	−7.88ᵃ		12.5	−20.48ᵈ
Ethylene glycol monoethyl ether	25	−3.98			
	50	−4.71			
	75	−5.08			

ᵃ Small precipitate or residue at end of experiment. ᵇ Salt, solvent, 1:175. ᶜ Small precipitate. ᵈ Significant precipitate.

TABLE III

HEAT OF REACTION OF WATER WITH COBALTOUS CHLORIDE DIHYDRATE IN VARIOUS SOLVENTS

Solvent	ΔH₁, water to pure solv. (kcal./mole water)	water to dihydrate soln. (kcal./mole water)	Mole ratio water/ salt	Heat effect (kcal./mole salt)
Dimethylformamide	−0.74	−0.88	3.60	0.56
Tetrahydrofurfuryl alcohol	−.40	−.53	4.24	0.52
Monoethyl ether of ethylene glycol	−.23	−.48	4.10	1.0
Tributyl phosphate	.14	−.27	3.42	1.6
Tetrahydrofuran	.51	.03	3.98	1.9
Isobutyl alcohol	.70	.06	3.98	2.5
Acetone	.79	.08	4.0	2.9

(4) L. I. Katzin and J. R. Ferraro, unpublished data.

TABLE IV

DIFFERENCES IN HEATS OF SOLUTION OF URANYL NITRATE, COBALTOUS NITRATE AND COBALTOUS CHLORIDE DIHYDRATES
IN ORGANIC SOLVENTS

Solvent	1 $UO_2(NO_3)_2\cdot$ $2H_2O$	(2) − (1)	2 $Co(NO_3)_2$ $2H_2O$	(3) − (2)	3 $CoCl_2\cdot$ $2H_2O$	(3) − (1)
Tetrahydrofuran	−10.71	6.41	−4.30	1.94	−2.36	8.35
Ethylene glycol diethyl ether	−10.87	5.98	−4.89	2.31	−2.58	8.29
Tributyl phosphate	−10.46	5.72	−4.74	2.65	−2.09	8.37
Ethylene glycol monoethyl ether	− 8.97	2.41	−6.56	1.33	−5.23	3.74
Tetrahydrofurfuryl alcohol	− 8.51	(−1.0)	(−9.54)	(1.0)	−8.55	−0.04
Isobutyl alcohol	− 2.58	1.30	−1.28	2.73	1.45	4.03
Isobutyl alcohol–acetone mixture (max. heat)	−10.30	6.10	−4.20	2.11	−2.09	8.21
Acetone	− 6.67	5.02	−1.65	2.00	0.35	7.02

It has been remarked previously[2] that the heats of solution of the dihydrates of uranyl nitrate and cobaltous nitrate in a given organic solvent differ by approximately a constant 6.1 kcal. per mole, the alcohols constituting exceptions to this rule because of presumed hexasolvate formation. A similar relationship holds for the heats of solution of cobaltous chloride dihydrate and the other two salts, as is seen in Table IV. An explanation for the approximately constant difference in the case of the two nitrates was based on the correspondence in type of the solute in both sets of solutions (i.e., the entities $(UO_2(NO_3)_2\cdot 2H_2O\cdot 2S)$ and $(Co(NO_3)_2\cdot 2H_2O\cdot 2S)$ and an apparent equality of energy released in binding the two solvent groups. The same explanation will not serve for the chloride, since in the solutions in question it is predominantly in its 4-coördinate blue form as $(CoCl_2\cdot 2H_2O)$, but the appearance of the constant difference can be explained in another way.

Consider the process of dissolution of one of the nitrate dihydrates in a specified solvent to proceed through the steps of (a) vaporization of the solid to the ionic gas; (b) evaporation of two equivalents of solvent S; (c) combination of the solvent with the gaseous cation; (d) combination of cations and anions to give gas of neutral molecules; and (e) solution of the gas in the solvent. The corresponding steps for the chloride dihydrate would be (a) vaporization of the solid to the ionic gas; (b) rearrangement of the electronic configuration from that of the six-coördinate type to the four-coördinate; (c) combination of cations and anions to give gas of neutral molecules; and (d) solution of the gas in the solvent. Heat equations for these two examples may be written as

$$\Delta H_a = U_a + 2H_v − 2E − _aH_d + _aH_s \qquad (1)$$

$$\Delta H_b = U_b + _bH_c − _bH_d + _bH_s \qquad (2)$$

The subscripts a and b serve to designate quantities relating to the nitrate compound and the chloride compound, respectively. The symbols refer to heat of solution (ΔH), lattice energy (U), energy of dissociation of the neutral gaseous molecule (H_d) and its heat of solution (H_s), energy to rearrange the electronic configuration (H_c), heat of vaporization of the solvent (H_v) and the energy to dissociate it from the gaseous cation (E). The difference in the two heats of solution, which is the quantity with which we are concerned, is given in the following expression, in which the subscript S has been used to mark off those terms dependent

on the particular solvent involved from those which are determined by the salts alone

$$(\Delta H_a − \Delta H_b) = (U_a − U_b) − (_aH_d − _bH_d) +$$
$$(_aH_s − _bH_s)_S + 2(H_v − E)_S − _bH_c \qquad (3)$$

The latter constitute a constant, and if one makes the assumption discussed in the previous paper[2] of essential invariance of the H_s terms, the solvent-dependence of the heat of solution difference is determined by the $2(H_v − E)$ term.

It develops, on inspecting the $(H_v − E)$ values[2] for tetrahydrofuran, ethylene glycol diethyl ether, tributyl phosphate and isobutyl alcohol, which show concordant values for the difference in heat of solution of uranyl nitrate dihydrate and cobaltous chloride dihydrate (the maximum acetone mixture value being used for isobutyl alcohol), that the difference between the lowest and the highest $(H_v − E)$ value for the group is only 0.35 kcal. The $(H_v − E)$ value for acetone is about 1.5 kcal. less than for this group, and it is noticed that the difference value for this solvent is significantly lower than for the other four. The three pure alcohols cannot be compared because of the factor of hexasolvation. There therefore appears to be a reasonable explanation of the constant difference phenomenon in this case, even though its basis is different than for comparison of the two nitrates.

Binding Energies for Water and Pyridine.— It has been shown[2] that the mean binding energy for the $(a − b)$th solvate groups of the salts Mx·aS and Mx·bS, E (defined as the energy to dissociate these groups from the gaseous cation), can be derived from the lattice energies (U), the heats of solution (ΔH) of the solvates, and the heat of vaporization of S, through the relation

$$\Delta H_a − \Delta H_b = U_a − U_b − (a − b)H_v + (a − b)E \qquad (4)$$

It has further been found, for 2-1 salts, that the lattice energy may be calculated by an equation in which the parameters are the specific gravity of the solid, and the Madelung constant for the crystal type. Comparison between cobaltous nitrate and literature data on cobaltous chloride showed that concordant data for binding of water and of pyridine could be obtained using a layer-structure Madelung constant of 6.21 for all the chlorides (except the hexammines, which are known to be of the fluorite structure pattern) and the fluorite structure constant 7.33 for the nitrates.

The calculations with respect to the cobalt chloride hydrates and pyridinates were based largely on literature values of heats of solution and/or

TABLE V

WATER BINDING ENERGIES OF HYDRATES OF COBALTOUS CHLORIDE

Solid	Density	$U,^a$ (kcal./mole)	$\Delta H,$ (kcal./mole)	Transition	Water binding energy (kcal.)
CoCl$_2$·6H$_2$O	1.91	317.7	2.83	Hexa → tetra	53.9
CoCl$_2$·4H$_2$O	2.11	344.6	− 3.22	Tetra → dihydrate	63.7
CoCl$_2$·2H$_2$O (violet)	2.43	380.7	− 9.79	Dihyd → mono	38.2 ⎫ 101.1
CoCl$_2$·H$_2$O	2.64	403.5	−14.64	Mono → anhydrous	62.9 ⎭
CoCl$_2$	3.41	451.6	−18.92		

^{a} Layer lattice structure.

specific gravity. There were therefore gaps in the data available, and questions of reliability and consistency of the values in the literature. With the present data on the heats of solution of the hydrates, it is possible to correct the values calculated previously for the water binding energies, and to extend them (Table V). Measurements have also been made on the cobaltous chloride pyridinates (Table VI), for which literature values had been used previously; the heats of solution in general checked the literature[5] to better than 0.1 kcal./mole. The biggest discrepancy 'was found with CoCl$_2$ itself, for which a heat of solution 0.5 kcal.-mole greater than the literature was found, which correspondingly affects the binding energies calculated against the unsolvated state. A larger correction on the same values is due to the correction of the specific gravity value for CoCl$_2$ from the apparently erroneously low value of Clark, Quick and Harkins.[6] These corrections do not affect the general conclusions drawn already as to the significance of the values for binding energies obtained previously.

TABLE VI

ENERGY OF BINDING OF PYRIDINE TO COBALTOUS ION

Solid	Density	$U,^a$ (kcal./mole)	$\Delta H_s,$ (HCl)	Transition	Pyridine binding energy (kcal.)
CoCl$_2$·6Py	1.30	211.5	−20.07	Hexa → tetra	53.4
CoCl$_2$·4Py	1.36	235.9	−12.46	Tetra → di	81.7
CoCl$_2$·2Py (violet)	1.64	286.0	− 7.42	Di → mono	70.6
CoCl$_2$·1Py	2.00	335.0	−10.76	Mono → anhyd.	143.0
CoCl$_2$		451.6	−18.92		

^{a} Layer lattice structure.

Apparent Heat Capacities of Solutes.—Apparent heat capacities per mole for the hydrates in solution are given in Table VII. Values are rounded to the nearest multiple of 5, and those for which only single determinations are available, or for which duplicates vary badly, are given in parentheses. It is to be understood that these are by-products of the heat of solution determinations, and are based on small differences in heat capacity with and without the solute. For cobaltous chlo-

(5) W. Hieber and A. Woerner, Z. Elektrochem., 40, 256 (1934).

(6) G. L. Clark, A. J. Quick and W. D. Harkins, THIS JOURNAL, 42, 2483 (1920).

ride in water, the molal heat capacity calculated on the basis of the hexahydrate is close to 387 cal. per degree.

TABLE VII

APPARENT MOLAL HEAT CAPACITIES OF CoCl$_2$ HYDRATES IN ORGANIC SOLVENTS (CAL. MOLE^{-1} DEG.$^{-1}$)^a

Solvent	CoCl$_2$·H$_2$O	CoCl$_2$·2H$_2$O	CoCl$_2$·6H$_2$O
Tetrahydrofuran	(25)	120	185
Tetrahydrofurfuryl alcohol	(175)		
Ethylene glycol monoethyl ether	(5)	235	(250)
Isobutyl alcohol	(105)	(240)	(500–600)
Acetone	200	380	380
Dimethylformamide	(225)	310	460
Tributyl phosphate	(65)		

^{a} Values rounded to nearest multiple of 5. Those for which only single determinations are available or for which duplicates disagree badly are given in parenthesis.

Appendix. Heats of Solution of Uranyl Nitrate Hydrates in Dimethylformamide.—Dimethylformamide differs from the other organic solvents in these studies in that its dielectric constant,[7] 36.7 at 25°, is higher than any of the others. Ionic dissociation of the solute is therefore much more likely. Values for the heats of solution of the cobaltous salts are contained in this paper and the preceding publication of this series,[2] but values for the uranyl nitrate hydrates have not appeared. They are therefore appended here. Details of the measurements are as previously described.[1]

Hydrate	ΔH (kcal.)
UO$_2$(NO$_3$)$_2$·6H$_2$O	− 8.95
UO$_2$(NO$_3$)$_2$·3H$_2$O	−12.74
UO$_2$(NO$_3$)$_2$·2H$_2$O	−15.45
+ (25 vol. % acetone)	−14.04
+ (50 vol. % acetone)	−12.79
+ (75 vol. % acetone)	−11.53
+ (87.5 vol. % acetone)	−10.63

Apparent molal heat capacities of the dihydrate, trihydrate and hexahydrate in dimethylformamide are 115, 140 and 175 cal. mole^{-1} deg.$^{-1}$, rounded to the nearest multiple of 5.

LEMONT, ILLINOIS

(7) G. R. Leader and J. F. Gormley, ibid., 73, 5731 (1951).