volts, a very large value of the junction potential appears to be unlikely.

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Hydration of Undissociated Salts in Acetonitrile[1]

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Abstract: An equation has been derived to calculate from the total and ionic solubilities of potassium picrate, salicylate, 3,5-dinitrobenzoate, and 3,5-dinitrophenolate in acetonitrile (AN) in the presence of known concentrations of water the individual formation constants $K^{\mathrm{f}}{}_{(\mathrm{MA})_\mathrm{w}}$ and $K^{\mathrm{f}}{}_{(\mathrm{MA})_{2\mathrm{w}}}$ of dissolved, undissociated mono- and dihydrated salts, $(\mathrm{MA})_\mathrm{w}$ and $(\mathrm{MA})_{2\mathrm{w}}$. Using these values and the previously determined values of formation constants of hydrated ions in AN, it has been possible to calculate the concentration of all species present in saturated solutions of the above salts in the presence of water. This allowed the calculation of the ionic dissociation constant $K^{\mathrm{d}}{}_{(\mathrm{MA})_\mathrm{w}}$ which was found to be greater than $K^{\mathrm{d}}{}_{(\mathrm{MA})_\mathrm{s}}$ (unhydrated salt). Unexplained is the result that $K^{\mathrm{d}}{}_{(\mathrm{MA})_{2\mathrm{w}}}$ of potassium salicylate was found smaller than the corresponding constant of the anhydrous salt. In the presence of water the dissociation constant of the anhydrous salt was found to be virtually unaffected up to a water concentration of 0.6 *M*. The red solid salt, potassium 3,5-dinitrophenolate, changes into a yellow solid in the presence of small concentrations of water in AN. This solid was found to be a monohydrate. No hydrated solid was formed with the other salts used. The ionic dissociation constant of the monohydrate was found greater than that of the anhydrous salt, while the constant of the dihydrate was found considerably greater than that of the monohydrate.

In a previous paper[2] the equilibrium constant of the hydration of several monovalent ions $\mathrm{I}^{\pm}$ was determined. In that study it was not necessary to consider a reaction between the dissolved undissociated anhydrous salt, $(\mathrm{MA})_\mathrm{s}$ (M^+ and A^- both being monovalent ions), and water.

In the present investigation the formation constants of the hydrates of the potassium salts of picric, salicylic, and 3,5-dinitrobenzoic acids and 3,5-dinitrophenol were determined. The potassium ion forms only a monohydrate with a formation constant of 1, while the sodium ion is much more strongly hydrated and forms at least a mono- and a dihydrate. For this reason sodium salts have not been used in the present study as they are expected to form higher hydrates than those of potassium. On the basis of the uncertainty in the assumptions made and in the experimental results, the hydration and dissociation constants calculated for sodium salts would be considerably more uncertain than those of hydrated potassium salts.

Denoting $(\mathrm{MA})_\mathrm{s}$ as the unhydrated potassium salt and $(\mathrm{MA})_{\Sigma y\mathrm{w}}$ as the hydrated salts, the following equilibria can be written

$$(\mathrm{MA})_\mathrm{s} + \mathrm{H_2O} \rightleftharpoons (\mathrm{MA})_\mathrm{w} \quad K^{\mathrm{f}}{}_{(\mathrm{MA})\mathrm{w}} = [\mathrm{MA}]_\mathrm{w}/[\mathrm{MA}]_\mathrm{s}[\mathrm{H_2O}] \tag{1}$$

$$(\mathrm{MA})_\mathrm{s} + 2\mathrm{H_2O} \rightleftharpoons (\mathrm{MA})_{2\mathrm{w}} \quad K^{\mathrm{f}}{}_{(\mathrm{MA})2\mathrm{w}} = [\mathrm{MA}]_{2\mathrm{w}}/[\mathrm{MA}]_\mathrm{s}[\mathrm{H_2O}]^2 \tag{2}$$

$$s_\mathrm{t} = i_\mathrm{t} + [\mathrm{MA}]_\mathrm{s} + [\mathrm{MA}]_{\Sigma y\mathrm{w}} \tag{3}$$

From the total molar solubility, s_t, and the total ionic solubility, i_t, in presence of known concentrations of water eq 3 results, $[\mathrm{MA}]_\mathrm{s}$ being the solubility of undissociated anhydrous salt in absence of water and $[\mathrm{MA}]_{\Sigma y\mathrm{w}}$ the total concentration of hydrated undissociated salts in presence of water. From the experimentally determined values of s_t, i_t, and $[\mathrm{MA}]_\mathrm{s}$, $[\mathrm{MA}]_{\Sigma y\mathrm{w}}$ is readily obtained. Assuming that the ratio of the solubility product and dissociation constant of $(\mathrm{MA})_\mathrm{s}$, $K_\mathrm{sp}/K^{\mathrm{d}}{}_{(\mathrm{MA})_\mathrm{s}}$, equal to $[\mathrm{MA}]_\mathrm{s}$, does not change with water content, the values of the individual formation constants K^f of the hydrates (eq 1 and 2) are found from the relation

$$\frac{s_\mathrm{t} - i_\mathrm{t} - [\mathrm{MA}]_\mathrm{s}}{[\mathrm{MA}]_\mathrm{s}[\mathrm{H_2O}]} = \frac{[\mathrm{MA}]_{\Sigma y\mathrm{w}}}{[\mathrm{MA}]_\mathrm{s}[\mathrm{H_2O}]} = K^{\mathrm{f}}{}_{(\mathrm{MA})_\mathrm{w}} + [\mathrm{H_2O}]K^{\mathrm{f}}{}_{(\mathrm{MA})_{2\mathrm{w}}} \tag{4}$$

which is derived by combining eq 1–3. A plot is made of $s_\mathrm{t} - i_\mathrm{t} - [\mathrm{MA}]_\mathrm{s}/[\mathrm{MA}]_\mathrm{s}[\mathrm{H_2O}]$ *vs.* $[\mathrm{H_2O}]$. If the slope of the linear plot is zero or close to zero, it is safe to conclude that $y = 1$ and only a monohydrate is formed. When the linear plot does not have a slope of 0, $y = 2$, the intercept being equal to $K^{\mathrm{f}}{}_{(\mathrm{MA})_\mathrm{w}}$ and the slope $K^{\mathrm{f}}{}_{(\mathrm{MA})_{2\mathrm{w}}}$.

From the experimental data it was also possible to calculate the dissociation constant of the salt $(\mathrm{MA})_\mathrm{w}$ and of $(\mathrm{MA})_{2\mathrm{w}}$ (eq 5 and 6). The over-all dissociation constant $K^{\mathrm{d}}{}_{\Sigma(\mathrm{MA})_{\mathrm{s+w}}}$ (eq 7) is calculated in the follow-

$$(\mathrm{MA})_\mathrm{w} \rightleftharpoons \mathrm{M_s}^+ + \mathrm{A_w}^- \quad K^{\mathrm{d}}{}_{(\mathrm{MA})\mathrm{w}} = [\mathrm{M_s}^+][\mathrm{A_w}^-]f^2/[\mathrm{MA}]_\mathrm{w} \tag{5}$$

$$(\mathrm{MA})_{2\mathrm{w}} \rightleftharpoons \mathrm{M_s}^+ + \mathrm{A_{2w}}^- \quad K^{\mathrm{d}}{}_{(\mathrm{MA})2\mathrm{w}} = [\mathrm{M_s}^+][\mathrm{A_{2w}}^-]f^2/[\mathrm{MA}]_{2\mathrm{w}} \tag{6}$$

$$K^{\mathrm{d}}{}_{\Sigma(\mathrm{MA})_{\mathrm{s+w}}} = i_\mathrm{t}{}^2f^2/s_\mathrm{t} = \frac{[[\mathrm{M_s}^+] + [\mathrm{M_w}^+]][[\mathrm{A_s}^-] + [\mathrm{A_w}^-] + [\mathrm{A_{2w}}^-]]f^2}{[\mathrm{MA}]_\mathrm{s} + [\mathrm{MA}]_{\Sigma y\mathrm{w}}} \tag{7}$$

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[1] This work was supported by the Directorate of Chemical Sciences, Air Force Office of Scientific Research, under Grant AF-AFOSR-28-65.

[2] M. K. Chantooni, Jr., and I. M. Kolthoff, *J. Am. Chem. Soc.*, **89**, 1582 (1967).

ing way. First $[M_s^+]$ is calculated from the ionic solubility, i_t, taking the value of $K^f_{K_w^+}$ equal to 1.0[2]. Then $[A_s^-]$ is found from the solubility product, K_{sp} ($K_{sp} = [M_s^+][A_s^-]f^2$). From the values of $[A_s^-]$ and the individual formation constants[2] $K^f_{A_w^-}$ and $K^f_{A_{2w}^-}$

$$K^f_{A_w^-} = [A_w^-]/[A_s^-][H_2O]$$

$$K^f_{A_{2w}^-} = [A_{2w}^-]/[A_s^-][H_2O]^2$$

$[A_w^-]$ and $[A_{2w}^-]$ become known, while $[MA]_w$ and $[MA]_{2w}$ are calculated from the values of $K^f_{(MA)_w}$ and $K^f_{(MA)_{2w}}$ (eq 1 and 2) and $[MA]_s$. Finally $K^d_{(MA)_w}$ and $K^d_{(MA)_{2w}}$ are evaluated from eq 5 and 6.

Experiments have been carried out to check the assumption that the ionic dissociation constant of the unhydrated salt $(MA)_s$ does not change in the presence of relatively small concentrations of water. For this purpose, water in known concentrations was added to a saturated solution of potassium salicylate in AN and the conductance measured. Using previously determined constants, $K^d_{(MA)_s}$ could be calculated, writing in eq 3 the total concentration C_s of the salt instead of s_t. From the relations

$$[K_s^+] = \frac{i_t}{1 + K^f_{K_w^+}[H_2O]} \tag{8}$$

$$[A_s^-] = \frac{i_t}{1 + K^f_{A_w^-}[H_2O] + K^f_{A_{2w}^-}[H_2O]^2} \tag{9}$$

and

$$[MA]_s = \frac{C_s - i_t}{1 + K^f_{(MA)_w}[H_2O] + K^f_{(MA)_{2w}}[H_2O]^2} \tag{10}$$

we obtain $K^d_{(MA)_s}$ in the presence of water

$$K^d_{(MA)_s} = \frac{i_t^2 f^2(1 + K^f_{(MA)_w}[H_2O] + K^f_{(MA)_{2w}}[H_2O]^2}{(C_s - i_t)(1 + K^f_{K_w^+}[H_2O](1 + K^f_{A_w^-}[H_2O] + K^f_{A_{2w}^-}[H_2O]^2)} \tag{11}$$

Experimental Section

Chemicals. Acetonitrile was purified and dispensed as described previously.[3] Potassium picrate,[4] 3,5-dinitrobenzoate,[5] and 3,5-dinitrophenolate[2] were used previously while potassium salicylate was prepared in a similar way as the sodium salt.[6]

The monohydrate of potassium 3,5-dinitrophenolate was prepared and analyzed in the following way. Approximately 0.5 g of the red anhydrous salt was introduced into 10 ml of AN, the solution made 1.6 *M* in water, and the mixture shaken until equilibrium was obtained. The orange-yellow solid was collected by filtering with suction on a sintered-glass filter crucible and left exposed to the air until constant weight was attained (2 hr). The water content of the salt was determined by heating 412.2 mg at 110° to constant weight. The loss in weight corresponded to $KA \cdot 0.96H_2O$. A blank experiment in the absence of water gave a loss in weight of 0.7 mg for 402.0 mg of air-dried salt. Under the same conditions as above, 947.2 mg of air-dried potassium salicylate lost 0.6 mg upon drying at 110°, while in the blank experiment 902 mg of air-dried salt lost 0.2 mg. Apparently undissociated potassium salicylate is not hydrated in acetonitrile containing 1.6 *M* water.

Ionic and Total Molar Solubility. Ionic solubilities were obtained from the conductance of the saturated solutions as described previously.[2]

The total molar solubility, s_t, was found by taking a 1-ml aliquot of the saturated solution containing water, after filtering, evaporating to dryness under an infrared lamp, dissolving the residue in 0.3 ml of anhydrous acetic acid, adding 3 ml of AN, and titrating with 0.450 *M* perchloric acid in acetic acid using dibromothymol benzein as indicator. A very sharp color change from yellow to red was obtained at the end point.[7]

Results

Ionic Mobilities and Dissociation Constants of Salts. The mobilities of the following ions were previously reported in AN; potassium, 86;[8] 3,5-dinitrobenzoate, 100;[5] 3,5-dinitrophenolate, 96;[9] salicylate, 78;[6] and picrate, 78.[8] It was found that with the exception of the picrate ion, the mobilities of the above ions did not change with the addition of water up to a concentration of at least 1.5 *M*.[2] The following values of the mobility of the picrate ion in the presence of water have been reported:[2] 0.55 *M* H_2O, 80; 1.94 *M* H_2O, 84; 2.13 *M* H_2O, 84; and 3.14 *M* H_2O, 84.

The dissociation constants and solubility products in anhydrous AN of the salts in Table I are: potassium picrate,[4,8] 6.7×10^{-3}, 2.8×10^{-5}; 3,5-dinitrobenzoate,[5] 2.6×10^{-4}, 5.3×10^{-8}; 3,5-dinitrophenolate,[2] 3.6×10^{-3}, 6.7×10^{-6}; and salicylate, 1.4×10^{-3}, 9.6×10^{-6}, respectively. The dissociation constants of the latter two salts were estimated from the Fuoss and Kraus plot of conductivity data in Table II.

Viscosity of AN in the Presence of Water. The viscosity of AN solutions containing water[2] is 0.352 cp in 0.46 *M* H_2O; 0.356 in 0.91 *M* H_2O; 0.366 in 1.88 *M* H_2O; and 0.382 in 3.13 *M* H_2O. All reported conductivities in the presence of water were corrected for viscosity.

Total and Ionic Solubility of Salts. Table I lists the total molar solubility, s_t, and total ionic solubility, i_t, at various concentrations of water up to 2 *M* in saturated solutions of the various salts. From the experimental data $K^f_{(MA)_w}$, $K^f_{(MA)_{2w}}$, $K^d_{(MA)_w}$, $K^d_{(MA)_{2w}}$ (the latter only for potassium salicylate), and $K^d_{\Sigma(MA)_{s+w}}$ (eq 7) were calculated as described in the introductory section, and the results are given in Table I. Values of $K^f_{A_w^-}$ and $K^f_{A_{2w}^-}$ reported in Table I have been taken from a previous publication.[2]

Of the salts in Table I potassium 3,5-dinitrophenolate is the only one which becomes hydrated in the solid phase. This occurs when the water concentration is equal to or greater than about 0.2 *M*. The product $[M_s^+][A_s^-]f^2$ then becomes smaller than K_{sp}. With the monohydrate as the solid phase, values of $[M_s^+]$, $[M_w^+]$, $[A_s^-]$, $[A_w^-]$, and $[A_{2w}^-]$ were found from the total ionic solubility, i_t, and the reported hydration constants of the ions, using eq 8 and 9, while $[MA]_s$ was calculated from the experimentally determined value of $s_t - i_t$ and the known value of $K^f_{(MA)_w}$ using eq 10. The molarity of water reported in Table I has been calculated in all instances from the amount of water added and that removed by the various hydrated species.

Table III presents the conductance of solutions obtained by adding water to a saturated solution of potassium salicylate in anhydrous AN. The last column

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[3] I. M. Kolthoff, S. Bruckenstein, and M. K. Chantooni, Jr., *J. Am. Chem. Soc.*, **83**, 3927 (1961).

[4] I. M. Kolthoff and M. K. Chantooni, Jr., *ibid.*, **87**, 4428 (1965).

[5] I. M. Kolthoff and M. K. Chantooni, Jr., *ibid.*, **85**, 426 (1963).

[6] I. M. Kolthoff and M. K. Chantooni, Jr., *J. Phys. Chem.*, **70**, 856 (1966).

[7] Details of the titration of carboxylates in AN with perchloric acid will be described elswehere.

[8] P. Walden and E. J. Birr, *Z. Physik. Chem.*, **144**, 269 (1929).

[9] I. M. Kolthoff, M. K. Chantooni, Jr., and S. Bhowmik, *J. Am. Chem. Soc.*, **88**, 5430 (1966).

Table I. Hydration Constants of Salts and Dissociation Constants of Hydrated Salts[a]

$[H_2O]$, M	s_t,[f] $M \times 10^3$	i_t,[g] $M \times 10^3$	$[K_s^+]$, $M \times 10^3$	$[K_w^+]$, $M \times 10^3$	$[A_s^-]$, $M \times 10^3$	$[A_w^-]$, $M \times 10^3$	$[A_{2w}^-]$, $M \times 10^3$	$[A_{3w}^-]$, $M \times 10^3$	f^2	$[MA]_w$, $M \times 10^3$	$[MA]_{2w}$, $M \times 10^3$	$K^d{}_{(MA)_w} \times 10^3$	$K^d{}_{(MA)_{2w}} \times 10^3$	$K^d{}_{\Sigma(MA)} \times 10^3$
Potassium Picrate, $K_{sp} = 2.8 \times 10^{-5}$, $K^d{}_{(KPi)_s} = 6.7 \times 10^{-3}$, $[KPi]_s = 4.2 \times 10^{-3}$, $K^f{}_{(KPi)_w} = 0$														
0	11.9	7.7					0	0	0.52	0	0			
0.55	14.1	10.0					0	0	0.50	0	0			
1.09	19.0	15.0					0	0	0.43	0	0			
Potassium Salicylate, $K_{sp} = 9.6 \times 10^{-6}$, $K^d{}_{(KSal)_s} = 1.4 \times 10^{-3}$, $[KSal]_s = 6.6 \times 10^{-3}$, $K^f{}_{(Sal^-)_w} = 4$, $K^f{}_{(Sal^-)_{2w}} = 4$, $K^f{}_{(KSal)_w} = 1.3$, $K^f{}_{(KSal)_{2w}} = 7.6$														
0	10.5	3.9	3.9	0	3.9 (3.9)[b]	0[b]	0[b]	0	0.65 (0.68)[b]	0	0	. . .[b]	. . .[b]	1.4 (1.5)[b]
0.089	14.5	5.0	4.6	0.4	3.4 (3.4)	1.2 (1.2)	0.1	0	0.65 (0.66)	0.76	0.4			1.6 (1.8)
0.176	17.4	5.75	4.9	0.8	3.34 (3.3)	2.3 (2.3)	0.4	0	0.59 (0.65)	1.5	1.6	4.4 (4.9)		1.7 (1.9)
0.275	21.9	7.2	5.65	1.55	3.0 (2.8)	3.5 (3.1)	1.05 (1.0)	0	0.58 (0.61)	2.4	3.8	4.7 (4.5)		2.0 (2.2)
0.495	35.4	10.4	6.95	3.45	2.8 (2.5)	5.6 (5.0)	2.7 (2.4)	0	0.49 (0.54)	4.2	12.2	4.5 (4.5)	0.8 (0.7)	2.1 (2.4)
0.77	59.4	15.8	8.94	6.9	2.56 (2.2)	7.9 (6.8)	6.05 (5.2)	0	0.42 (0.49)	6.6	29.5	4.5 (4.5)	0.8 (0.7)	2.4 (2.8)
1.28	134	29.7	13.0	16.7	2.4 (1.8)	12.2 (9.1)	15.6 (14.6)	0	0.31 (0.42)	11.0	82	4.5 (4.5)	0.8 (1)	2.6 (3.5)
Potassium 3,5-Dinitrobenzoate, $K_{sp} = 5.3 \times 10^{-8}$, $K^d{}_{(KDNB)_s} = 2.6 \times 10^{-4}$, $[KDNB]_s = 2.1 \times 10^{-4}$, $K^f{}_{(DNB^-)_w} = 6.4$, $K^f{}_{(DNB^-)_{2w}} = 5.4$, $K^f{}_{(DNB^-)_{3w}} = 4$, $K^f{}_{(KDNB)_w} = 2.5$														
0	0.47	0.25	0.25	0	0.25	0	0	0	0.87	0				0.26
0.55	1.21	0.82	0.52	0.30	0.13	0.44	0.21	0.08	0.82	(0.29)[c]		(0.64)[c]		1.4
1.32	3.01	2.14	0.92	1.2	0.080	0.67	0.76	0.73	0.72	(0.69)		(0.64)		3.8
1.54	3.68	2.76	1.1	1.66	0.071	0.70	0.93	1.0	0.69	(0.81)		(0.64)		5.7
Potassium 3,5-Dinitrophenolate, $K_{sp} = 6.7 \times 10^{-6}$, $K^d{}_{(KDNP)_s} = 3.6 \times 10^{-3}$, $[KDNP]_s = 1.9 \times 10^{-3}$, $K^f{}_{(DNP^-)_w} = 7$, $K^f{}_{(DNP^-)_{2w}} = 6$, $K^f{}_{(KDNP)_w} = 4$														
Anhydrous Solid Phase														
0	5.10	3.20	3.20	0	3.20	0	0	0	0.67	0				3.6
0.058	6.41	4.09	3.86	0.23	2.72	1.11	0.05	0	0.64	0.44		6		3.6
0.091	7.08	4.47	4.07	0.41	2.66	1.69	0.13	0	0.62	0.69		6		4.7
0.151	8.36	5.23	4.53	0.69	2.46	2.60	0.33	0	0.59	1.14		6		5.1
Monohydrate Solid Phase														
0.31	7.25	5.20	3.97	1.2	1.30	3.1	0.80	0	0.60	1.14[d]		7		7.9
0.53	8.00	6.20	4.0	2.2	0.91	3.7	1.6	0	0.58	1.14[e]		6		12.4

[a] $K^f{}_{K_w^+}$ taken as 1.0. [b] Values in parentheses obtained by using the extended Debye–Hückel expression (see Discussion). [c] Values very uncertain. [d] $[KDNB]_s = 0.87 \times 10^{-3}\,M$. [e] $[KDNB]_s = 0.56 \times 10^{-3}\,M$. [f] Total solubility. [g] Ionic solubility.

Table II. Conductance of Salts

Potassium 3,5-dinitrophenolate $M \times 10^3$	Λ	Potassium salicylate $M \times 10^3$	Λ
1.28	134	1.70	107
2.04	126	2.55	90
2.55	118	4.10	78.5
5.11	100	5.10	72
$\Lambda_0 = 181$		10.2	58
		$\Lambda_0 = 180$	

Table III. Effect of Water Added to Saturated Solutions of Potassium Salicylate on Conductivity and $K^d{}_{(KA)_s}$

$[H_2O]$, M	C_s, $M \times 10^2$	Specific conductance, L	Λ	i_t, $M \times 10^3$	$K^d{}_{(KA)_s} \times 10^3$
0	1.19	6.1	141	4.32	1.6
0.33	1.19	7.3	139	5.22	1.6
0.54	1.18	7.9	138	5.69	1.8
0.81	1.17	8.4	137	6.15	2.2
1.10	1.17	9.1	135	6.76	2.6

$K^f{}_{K_w^+} = 1.0$, $K^f{}_{A_w^-} = 4$, $K^f{}_{A_{2w}^-} = 4$; $K^f{}_{(KA)_w} = 1.3$, $K^f{}_{(KA)_{2w}} = 7.6$

lists the calculated values of $K^d{}_{(KA)_s}$ in the presence of water (*cf* eq 10).

Discussion

From the data in Table I it appears that undissociated potassium picrate does not become hydrated, at least up to a water concentration of 1 *M*. The most extensive study has been carried out with potassium salicylate. The solubility of this salt is great enough to determine the formation constants $K^f{}_{(KA)_w}$ and $K^f{}_{(KA)_{2w}}$ with reasonably accuracy. In the presence of 0.5 *M* or higher concentrations of water, the values of $[MA]_w$ and especially $[MA]_{2w}$ become considerably greater than the concentration of the unhydrated salt $[MA]_s$. It was expected that the ionic dissociation constants of the hydrated salts would be greater than that of the anhydrous salt due to the separation of center of charge on the cation and anion resulting from interposing one or two water molecules between them. This was found to be true for the monohydrate of potassium salicylate, its constant being of the order of 4.5×10^{-3} as compared to 1.4×10^{-3} for that of the anhydrous salt. Unexpectedly, the constant for the dihydrate was found to be 0.8×10^{-3} and smaller than that of the anhydrous salt. All calculations of the activity coefficients had been made using the limiting Debye–Hückel expression, which should yield only approximate values at the relatively high ionic strength of the solutions. All calculations were repeated using the extended Debye–Hückel expression

$$-\log f = \frac{1.53\sqrt{\mu}}{1 + (4.7 \times 10^7)a\sqrt{\mu}}$$

Using Kielland's[10] values in water for the ionic size *a* of potassium, 3×10^{-8} cm, and of salicylate, 6×10^{-8} cm, we obtain $-\log f_{K^+} = 1.53\sqrt{\mu}/(1 + 1.41\sqrt{\mu})$ and $\log f_{Sal^-} = 1.53\sqrt{\mu}/(1 + 2.82\sqrt{\mu})$.

The values in parentheses in Table I refer to those calculated with the aid of the extended Debye–Hückel expression. The values of $K^d{}_{(MA)_s}$, $K^d{}_{(MA)_w}$, and $K^d{}_{(MA)_{2w}}$ remained unchanged. The data in Table III indicate that $K^d{}_{(MA)_s}$ remains practically unchanged up to a water concentration of 0.6 *M*. All calculations in Table I were repeated taking into account the small effect of water on $K^d{}_{(MA)_s}$. The values obtained were almost the same as those reported in Table I up to a water concentration of 0.8 *M*. Considering the experimental uncertainty in the values of the four constants needed for the calculation of the dissociation constants and also the uncertainty in the assumptions made (especially that $[MA]_s$ remains unaffected by water), the values for the dissociation constants of the hydrated forms of potassium salicylate are no more reliable than to within 50%. However, it is fair to conclude that the ionic dissociation constant of the dihydrate is relatively small since its formation constant is large and the value of the "over-all" dissociation constant of potassium salicylate, reported in the last column of Table I, increases only very slightly with increasing water content because of formation of relatively large concentrations of the dihydrate. In the presence of 1.3 *M* water, the "over-all" dissociation constant is only twice as large as that of the unhydrated salt, while a similar "constant" of potassium 3,5-dinitrobenzoate was found to increase 15 times when the water concentration was 1.3 *M*.

The solubility product and the ionic dissociation constant of potassium 3,5-dinitrobenzoate in anhydrous AN are much smaller than those of the salicylate. In order to obtain results from eq 4 which are reasonably accurate it is necessary that $s_t - i_t - [MA]_s = [MA]_{\Sigma yw}$ be considerably greater than corresponds to the experimental error in the determination of s_t, i_t, and $[MA]_s$. This is not found to be the case with potassium 3,5-dinitrobenzoate. The sum of the concentrations of the three un-ionized hydrated forms $[MA]_{\Sigma yw}$ is so small that the formation constant of each hydrate cannot be calculated. Only the "over-all" dissociation constant is found with good accuracy; it is found to increase very much with increasing water concentration (last column, Table I). The solubility product and ionic dissociation constant of anhydrous potassium 3,5-dinitrophenolate are of the same order of magnitude as the corresponding constants of the salicylate. At the low water concentrations where the solid phase is anhydrous salt, formation of undissociated dihydrated salt can be neglected, as its concentration is proportional to $[H_2O]^2$. At the three lowest water concentrations used a constant value of $K^d{}_{(MA)_w}$ of 6×10^{-3} is found as compared to 3.6×10^{-3} for the anhydrous salt.

In saturated solutions, the monohydrate being the solid phase, $[MA]_s$ is no longer constant, but it decreases with increasing concentration of water. On the other hand, $[MA]_w$ is now a constant and equal to 1.14×10^{-3} *M* (Table I). Knowing $K^d{}_{(MA)_w}$ and $[K_s{}^+]$, the value of $[A_w{}^-]$ is readily obtained and found equal to 2.8×10^{-3} *M* at a water concentration of 0.55 *M*. From $K^f{}_{(MA)_w}$ we obtain $[MA]_s = 5 \times 10^{-4}$ and from $K^d{}_{(MA)_s}$, $[A_s{}^-] = 0.9 \times 10^{-3}$. From eq 3 we get that $[MA]_{2w}$ is 2×10^{-4} *M*. This small value is highly uncertain, but its order of magnitude should be correct. Using this value of $[MA]_{2w}$ we obtain for $K^d{}_{(MA)_{2w}}$ a value of the order of 3×10^{-2}, which is considerably greater than $K^d{}_{(MA)_s} = 3.6 \times 10^{-3}$. The formation constant of the dihydrate is of the order of 1.

The large increase of the "over-all" dissociation constant (last column, Table I) with increasing water concentration substantiates the conclusion that the dissociation constant of the dihydrate must be considerably greater than that of the anhydrous salt and greater than that of the monohydrate.

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(10) J. Kielland, *J. Am. Chem. Soc.*, **59**, 1675 (1937).