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SOLUBILITY STUDIES IN FORMAMIDE

IV. IONIZATION CONSTANTS OF IODIC AND BROMIC ACIDS IN FORMAMIDE FROM SOLUBILITY MEASUREMENTS

U. N. DASH

Department of Chemistry, G.M. College, Sambalpur (India)

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ABSTRACT

The ionization constants of iodic and bromic acids in formamide have been determined at 25, 30, and 35°C from solubility measurements. The ionization constants of iodic acid are found to be 9.83×10^{-2}, 12.02×10^{-2} and 12.14×10^{-2}, respectively, and those of bromic acid, 9.56×10^{-2}, 9.70×10^{-2}, and 10.15×10^{-2}, respectively, at 25, 30 and 35°C. Thermodynamic parameters associated with the ionization processes have also been determined.

INTRODUCTION

Ionization constants of some organic acids from solubilities in aqueous medium have been determined by Albert[1], and Krebs and Speakman[2]. Li and Tulo[3] have reported the ionization constant of iodic acid at 25, 30, and 35°C from the solubility of silver iodate in water, in potassium nitrate and nitric acid solutions. However, the ionization constants of acids such as, iodic and bromic, have not been determined so far in any non-aqueous solvents. It was considered worthwhile to determine them in formamide, a solvent having a dielectric constant greater than that of water, chosen for the series of the present study[4–6].

EXPERIMENTAL

The general experimental details were essentially similar to those described earlier[5,6]. Formamide (Riedel, pure) was further purified as described in a previous communication[4]. Perchloric acid used was of G.R. quality.

The solutions of perchloric acid were prepared by dissolving appropriate and weighed amounts of acid in known weights of formamide at the ice-cold temperature to avoid decomposition of formamide during preparation of the solutions[7]. The method of solubility measurements, technique of the measurements and accuracy of analysis was also exactly similar to that described earlier[5]. The values of solubility of silver iodate and silver bromate in formamide in sodium perchlorate solutions at 25, 30 and 35°C were taken from our previous work[5,6].

RESULTS AND DISCUSSION

The experimental results of the solubility measurements are given in Tables 1 and 2 for silver iodate and silver bromate, respectively. In each table, the first column gives the molarity, c, of perchloric acid, the second the solubility, s, of silver salt in mol l^{-1}, averaged in each case from three closely agreeing results; the third column lists solubility, s', of silver salt in the same molarity of sodium perchlorate as reported in previous studies[5,6].

It is seen that the solubility of silver salts in solutions of perchloric acid is higher than that in solutions of sodium perchlorate of the same molarity. This might be due to the incomplete dissociation of iodic and bromic acids formed by the double decomposition of silver iodate and silver bromate with perchloric acid, respectively. Considering the similar assumptions as that of Naidich and Ricci[8], in formamide that the mean activity coefficient of a slightly soluble salt is the same in solutions of the same total ionic strength, regardless of whether the electrolyte is an acid or the sodium salt of a given anion, the solubility product of silver salts in solutions of perchloric acid may be equal to their solubility product in sodium perchlorate solutions of the same ionic strength.

TABLE 1

SOLUBILITY DATA FOR SILVER IODATE IN PERCHLORIC ACID AND SODIUM PERCHLORATE SOLUTIONS IN FORMAMIDE AT 25, 30 AND 35°C

$c \times 10^2$ ($mol\ l^{-1}$)	$s \times 10^4$ ($mol\ l^{-1}$)	$s' \times 10^4$ ($mol\ l^{-1}$)	$-\log s$ ($mol\ l^{-1}$)
Temperature: 25°C			
1.592	2.511	2.360	3.6063
1.836	2.540	2.371	3.5952
3.200	2.656	2.388	3.5760
5.912	2.984	2.471	3.5256
6.089	3.015	2.490	3.5210
9.568	3.452	2.585	3.4620
Temperature: 30°C			
1.665	2.849	2.690	3.5452
2.980	3.027	2.788	3.5190
3.134	3.053	2.862	3.5153
9.918	4.166	3.133	3.3806
14.240	5.028	3.383	3.2986
Temperature: 35°C			
1.029	3.273	3.142	3.4851
2.629	3.475	3.208	3.4591
6.726	4.133	3.416	3.3837
8.196	4.363	3.492	3.3602
9.668	4.732	3.545	3.3250

TABLE 2

SOLUBILITY DATA FOR SILVER BROMATE IN PERCHLORIC ACID AND SODIUM PERCHLORATE SOLUTIONS IN FORMAMIDE AT 25, 30 AND 35 °C

$c\times10^2$ (mol l^{-1})	$s\times10^2$ (mol l^{-1})	$s'\times10^2$ (mol l^{-1})	$-\log s$
Temperature: 25 °C			
2.735	2.080	1.890	1.6820
3.543	2.118	1.905	1.6740
4.645	2.185	1.940	1.6605
6.352	2.291	1.950	1.6401
8.539	2.442	1.955	1.6122
9.315	2.501	1.960	1.6019
10.420	2.570	1.965	1.5901
Temperature: 30 °C			
2.876	2.236	2.034	1.6507
4.860	2.338	2.054	1.6311
5.945	2.393	2.076	1.6211
9.342	2.626	2.086	1.5806
10.812	2.762	2.101	1.5588
11.992	2.858	2.121	1.5440
Temperature: 35 °C			
2.625	2.344	2.152	1.6301
3.225	2.396	2.165	1.6204
5.226	2.493	2.170	1.6033
6.180	2.570	2.178	1.5901
7.185	2.637	2.211	1.5789
9.766	2.754	2.220	1.5601

Thus, the various ionic concentrations in perchloric acid solutions may be calculated by the following equations[3]:

$$c_{XO_3^-} = K_s/s_a = s_s^2/s_a \tag{1}$$

$$c_{HXO_3} = s_a - c_{XO_3^-} \tag{2}$$

$$c_{H^+} = c_{HClO_4} - c_{HXO_3} \tag{3}$$

$$\begin{aligned} \mu &= s_a + c_{H^+} \\ &= c_{HClO_4} + c_{XO_3^-} \end{aligned} \tag{4}$$

Where XO_3^- stands for IO_3^- or BrO_3^-, s_s, the observed solubility in sodium perchlorate solutions, and s_a that in perchloric acid solutions of the same ionic strength. An illustration of the method of calculation is described for silver iodate as follows:

Temp. 25 °C, $c_{NaClO_4} = c_{HClO_4} = 1.592\times10^{-2}$

From Table 1, $s_s = 2.360\times10^{-4}$; $s_a = 2.511\times10^{-4}$

By means of eqn (1), $c_{IO_3^-}$ is calculated to be 2.218×10^{-4}, but this value is only a first approximation, since the uncorrected value of μ in acid solution is used. Taking into account the incomplete dissociation of iodic acid, the first corrected value of μ in perchloric acid solution is then given by eqn (4) and equal to 1.614×10^{-2}. Taking the value of s_s and interpolating this value to correspond with the correct value of μ (1.614×10^{-2}), a new value of s_s (2.334×10^{-4}) is obtained and a second approximation for $c_{IO_3^-}$ (2.169×10^{-4}). Further by means of eqn (4) and taking the second approximation value for $c_{IO_3^-}$, the second corrected value of μ is obtained which is equal to 1.614×10^{-2}. Thus, the first and the second corrected values of μ become equal and no further reiteration is required. The final values of s_s and other concentrations thus obtained are shown in Tables 3 and 4, for silver iodate and silver bromate, respectively. In Figs. 1 and 2, the logarithms of the solubility (s_a) in perchloric acid solutions and that of the corrected values of solubility (s_s) in sodium perchlorate solutions are plotted against $\sqrt{\mu}$, for silver iodate and silver bromate, respectively. For the sake of convenience these solubility values in electrolyte solutions are represented as s in the figures. The ionization constants, K_m, for iodic and bromic acids calculated in terms of concentration have been tabulated in the last column of Tables 3 and 4, respectively.

The solubility data presented in this paper are subject to the following source of error. Unfortunately, at present, there seems to be no suitable method for preparing

TABLE 3

CALCULATION OF K_m FOR IODIC ACID IN FORMAMIDE AT 25, 30 AND 35°C

$c_{HClO_4} \times 10^2$ (mol l^{-1})	$s_a \times 10^4$ (mol l^{-1})	$s_s \times 10^4$ (mol l^{-1})	$c_{IO_3^-} \times 10^4$ (mol l^{-1})	$c_{HIO_3} \times 10^4$ (mol l^{-1})	$c_{H^+} \times 10^2$ (mol l^{-1})	$\sqrt{\mu}$	K_m
Temperature: 25°C							
1.592	2.511	2.334	2.169	0.342	1.589	0.1271	0.1008
1.836	2.540	2.346	2.166	0.374	1.832	0.1363	0.1061
3.200	2.656	2.407	2.181	0.475	3.195	0.1795	0.1467
5.912	2.984	2.497	2.089	0.895	5.903	0.2435	0.1377
6.089	3.015	2.501	2.075	0.940	6.080	0.2472	0.1342
9.568	3.452	2.588	1.940	1.512	9.553	0.3096	0.1225
Temperature: 30°C							
1.665	2.849	2.707	2.572	0.277	1.662	0.1300	0.1543
2.980	3.027	2.798	2.586	0.441	2.976	0.1734	0.1745
3.134	3.053	2.807	2.580	0.473	3.129	0.1777	0.1706
9.918	4.166	3.148	2.382	1.784	9.900	0.3154	0.1321
14.240	5.028	3.334	2.210	2.818	14.212	0.3762	0.1114
Temperature: 35°C							
1.029	3.273	3.120	2.974	0.299	1.026	0.1029	0.1021
2.629	3.475	3.241	3.024	0.451	2.624	0.1630	0.1759
6.726	4.133	3.442	2.866	1.267	6.713	0.2599	0.1518
8.196	4.363	3.498	2.805	1.558	8.180	0.2867	0.1473
9.668	4.732	3.551	2.665	2.067	9.647	0.3114	0.1244

TABLE 4

CALCULATION OF K_m FOR BROMIC ACID IN FORMAMIDE AT 25, 30 AND 35°C

$c_{HClO_4} \times 10^2$ ($mol\ l^{-1}$)	$s_a \times 10^2$ ($mol\ l^{-1}$)	$s_s \times 10^2$ ($mol\ l^{-1}$)	$c_{BrO_3^-} \times 10^2$ ($mol\ l^{-1}$)	$c_{HBrO_3} \times 10^2$ ($mol\ l^{-1}$)	$c_{H^+} \times 10^2$ ($mol\ l^{-1}$)	$\sqrt{\mu}$	K_m
Temperature: 25°C							
2.735	2.080	1.916	1.764	0.316	2.419	0.2120	0.1350
3.543	2.118	1.923	1.745	0.373	3.170	0.2299	0.1483
4.645	2.185	1.932	1.708	0.477	4.168	0.2521	0.1492
6.352	2.291	1.942	1.646	0.645	5.707	0.2828	0.1456
8.539	2.442	1.952	1.560	0.882	7.657	0.3178	0.1354
9.315	2.501	1.955	1.528	0.973	8.342	0.3293	0.1310
10.420	2.570	1.958	1.491	1.079	9.341	0.3450	0.1291
Temperature: 30°C							
2.876	2.236	2.055	1.888	0.348	2.528	0.2183	0.1371
4.860	2.338	2.074	1.838	0.500	4.360	0.2587	0.1602
5.945	2.393	2.082	1.811	0.582	5.363	0.2785	0.1668
9.342	2.626	2.100	1.679	0.947	8.395	0.3320	0.1488
10.812	2.762	2.105	1.604	1.158	9.654	0.3524	0.1337
11.992	2.858	2.109	1.556	1.302	10.690	0.3681	0.1277
Temperature: 35°C							
2.625	2.344	2.179	2.025	0.319	2.310	0.2157	0.1467
3.225	2.396	2.185	1.946	0.456	2.719	0.2274	0.1160
5.226	2.493	2.202	1.944	0.549	4.677	0.2677	0.1656
6.180	2.570	2.208	1.897	0.673	5.507	0.2842	0.1552
7.185	2.637	2.213	1.857	0.780	6.405	0.3007	0.1524
9.766	2.754	2.223	1.794	0.960	8.806	0.3400	0.1645

pure anhydrous perchloric acid. Perchloric acid of G.R. quality (70%) was used in the determination of solubility of silver salts in formamide solutions. As described in earlier papers of this series, formamide is thermally unstable to some extent and ammonia is one of the decomposition products. It is possible that the free ammonia thus produced, coming in contact with aqueous perchloric acid neutralizes the acid. It thereby decreases the acid concentration as well as the formation of iodic or bromic acid which could be produced by double decomposition of silver iodate or silver bromate with perchloric acid, and the expected solubility of silver salt in pure perchloric acid–formamide solution will be less than that obtained in aqueous acid solution. However, the smooth linear plots (Figs. 1 and 2) of solubility in perchloric acid–formamide solutions against the ionic strength and comparison with that obtained in the presence of sodium salt seem to suggest that the error arising from this source is not at all significant.

The thermodynamic ionization constant, K_a, of acid is related to K_m by equation

$$\log K_a = \log K_m - 2A\sqrt{\mu} \qquad (5)$$

where the values of A used were the same as reported by Agarwal and Nayak[9]. The

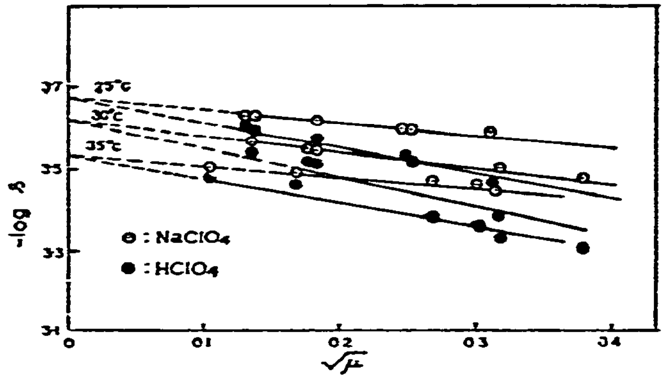

Fig. 1. Solubility of silver iodate in electrolyte solutions.

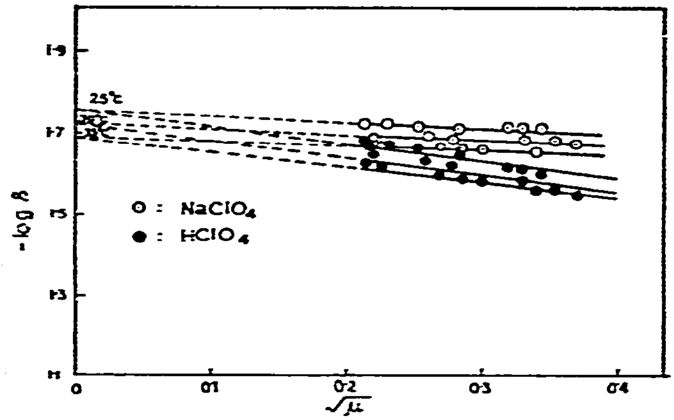

Fig. 2. Solubility of silver bromate in electrolyte solutions.

values of K_a were determined from eqn (5) for each molarity. These values, as expected, did not remain constant with change of molarity and have been tabulated as K_a'. Tables 5 and 6 list the values of K_a' for iodic and bromic acids, respectively. The true K_a value was obtained[10,11] by plotting the K_a' values against the ionic strength, $\sqrt{\mu}$, and extrapolating to zero ionic strength (not shown in Figure). The K_a values for iodic and bromic acids are shown in Tables 5 and 6, respectively.

For the sake of comparison, the K_a values for iodic acid in water have been calculated from eqn (5) by using the solubility data of Li and Tulo[3]. It is seen that the K_a values did not remain constant with change of ionic strength, so these values have been tabulated as K_a' and the extrapolation of these K_a' values to zero ionic strength yields the true K_a values for iodic acid. These values are presented in Table 5 along with the data obtained in formamide.

The K_a values for iodic acid in formamide are found to be 0.0983±0.01, 0.1202±0.01, and 0.1214±0.01, and for bromic acid in formamide 0.0956±0.01, 0.0970±0.02, and 0.1015±0.02 at 25, 30 and 35°C, respectively. The K_a values for iodic acid may be compared with those in water as reported by Li and Tulo[3] (0.164, 0.153 and 0.144, respectively, and recalculated by means of eqn (5): 0.1536±0.004, 0.1438±0.002, and 0.1367±0.002, respectively) at 25, 30 and 35°C. Thus the K_a values are found to be lower in formamide than those obtained in water and are in agreement with a general behaviour as shown by weak acids studied in this solvent[10,11].

Increasing the temperature leads to an increase in K_a values for both acids in formamide, whereas the reverse is the case in water medium as it is observed from the available data for iodic acid in that solvent. The standard free energy change, $\Delta G°$, for the ionization process of the acids is obtained by the relation, $\Delta G° = -RT \ln K_a$. The values of K_a as well as of $\Delta G°$ are shown in Table 7 together with similar data calculated in water (for iodic acid only) for the sake of comparison.

Plots of $\log K_a$ against $1/T$ yield straight lines in each case and the heats of ionization ($\Delta H°$) of iodic and bromic acids calculated from the slopes of these plots are 21.19 and 5.46 J, respectively. It is of interest to compare the heat of ionization of iodic acid in formamide with that in water, calculated in a similar manner from the

TABLE 5

VALUES OF K_a FOR IODIC ACID IN FORMAMIDE AND WATER AT 25, 30 AND 35°C

In formamide				*In water*			
$c_{HClO_4} \times 10^2$ (*mol* l^{-1})	$\mu^{\frac{1}{2}}$ (*mol* $l^{-1})^{\frac{1}{2}}$	K'_a	K_a	$c_{HNO_3} \times 10^2$ (*mol* l^{-1})	$\mu^{\frac{1}{2}}$ (*mol* $l^{-1})^{\frac{1}{2}}$	K'_a	K_a
Temperature: 25°C							
1.592	0.1271	0.0842		0.6503	0.082	0.1557	
1.836	0.1363	0.0875		1.410	0.120	0.1492	0.1536±
3.200	0.1795	0.1139	0.0983	7.050	0.266	0.1137	0.004
5.912	0.2435	0.0976	±0.01	12.130	0.349	0.1014	(0.164)[3]
6.089	0.2472	0.0946		25.280	0.503	0.0898	
9.656	0.3096	0.0791		50.500	0.711	0.0754	
				87.380	0.935	0.0567	
Temperature: 30°C							
1.665	0.1300	0.1283		0.6503	0.082	0.1343	
2.980	0.1734	0.1364	0.1202	1.410	0.120	0.1274	0.1438±
3.134	0.1777	0.1326	±0.01	7.050	0.266	0.1209	0.002
9.918	0.3154	0.1184		12.130	0.349	0.1023	
14.240	0.3762	0.0853		25.280	0.503	0.0849	(0.153)[3]
				50.500	0.711	0.0643	
Temperature: 35°C							
1.029	0.1029	0.0881		0.6503	0.082	0.1316	
2.629	0.1630	0.1395	0.1214	1.410	0.120	0.1211	0.1367±
6.726	0.2599	0.1049	±0.02	7.050	0.266	0.1086	0.002
8.196	0.2867	0.0980		12.130	0.349	0.0930	(0.144)[3]
9.668	0.3114	0.0799		25.280	0.503	0.0815	
				50.500	0.711	0.0595	

TABLE 6

VALUES OF K_a FOR BROMIC ACID IN FORMAMIDE AT 25, 30 AND 35°C

$c_{HClO_4} \times 10^2$ ($mol\ l^{-1}$)	$\mu^{\frac{1}{2}}$ ($mol\ l^{-1})^{\frac{1}{2}}$	K'_a	K_a
Temperature: 25°C			
2.735	0.2120	0.1000	
3.543	0.2299	0.1072	
4.645	0.2521	0.1044	0.0956
6.352	0.2828	0.0976	±0.01
8.539	0.3178	0.0864	
9.315	0.3293	0.1038	
10.420	0.3450	0.0793	
Temperature: 30°C			
2.876	0.2183	0.1007	
4.860	0.2587	0.1110	
5.945	0.2785	0.1124	0.0970
9.342	0.3320	0.0929	±0.02
10.812	0.3524	0.0812	
11.992	0.3681	0.0758	
Temperature: 35°C			
2.625	0.2157	0.1078	
3.225	0.2274	0.0840	
5.226	0.2677	0.1132	
6.180	0.2842	0.1036	0.1015
7.185	0.3007	0.0993	±0.02
9.766	0.3400	0.1014	

TABLE 7

STANDARD THERMODYNAMIC QUANTITIES OF IODIC AND BROMIC ACIDS IN FORMAMIDE AND WATER AT 25, 30 AND 35°C

Temp. (°C)	$K_a \times 10^2$	$\Delta G° \times 10^{-3}$ (J)	$\Delta H° \times 10^{-3}$ (J)	$\Delta S°$ ($J\ deg^{-1}$)	*Solution*
Iodic acid					
25	9.83	5.745	21.19	51.88	formamide
25	16.40	4.644	10.39	19.25	water
30	12.02	5.339	21.19	52.34	formamide
30	15.30	4.888	10.39	18.13	water
35	12.14	5.401	21.19	51.30	formamide
35	14.40	5.095	10.39	17.16	water
Bromic acid					
25	9.56	5.820	5.463	−1.053	formamide
30	9.70	5.882	5.463	−1.243	formamide
35	10.15	5.861	5.463	−1.154	formamide

values of K_a in water[3]. The resulting value is found to be 10.39 J which is less than that found for iodic acid in formamide (21.19 J). If ΔH° is assumed to remain constant over the range of temperatures employed, which appears to be the case, the standard entropy change, ΔS° for the ionization process may be evaluated from the relation, $\Delta S^\circ = (\Delta H^\circ - \Delta G^\circ)/T$. These values are also shown in Table 7 together with the corresponding values in water for iodic acid.

The ΔG° values are positive indicating that ionization is not spontaneous. The positive values of ΔH° show that the reaction is endothermic. Both acids show a similar trend in their ΔG° and ΔH° values, but differ in their ΔS° values. The negative values of ΔS° for bromic acid indicate that there is more order in the ionized form than in the unionized form, but the reverse is the case for iodic acid. This may be due to the lower solvation energy of silver iodate in formamide than that of silver bromate in this solvent[6]. A comparison of the present data for iodic acid with the corresponding values in water shows that the ΔG°, ΔH° and ΔS° values are on the higher side in formamide than in water. This indicates that the ionization process is more energy-consuming and the ionized form is more disordered in formamide than in water.

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