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THERMODYNAMIC BEHAVIOUR OF THE SILVER–SILVER CHROMATE ELECTRODE IN FORMAMIDE

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ABSTRACT

The first and second ionization constants of chromic acid have been determined in formamide at 25, 30 and 35°C with the help of cells without liquid junction using platinum–hydrogen and silver–silver chloride electrodes. From the ionization constants of chromic acid at 25°C, the standard free energy changes, $\Delta G°$, of the ionization processes have been evaluated. Using the values of the ionization constants, the standard potentials of the $Ag(s)/Ag_2CrO_4(s)/CrO_4^{2-}$ electrode and the standard thermodynamic quantities for the process $H_2(g)+Ag_2CrO_4(s)\rightleftharpoons 2Ag(s)+H_2CrO_4$ (solvated) have been calculated in formamide at 25, 30 and 35°C.

INTRODUCTION

In previous communications[1–5], the first and second ionization constants of some organic dibasic acids such as, phthalic, oxalic, malonic, succinic, glutaric and adipic and the standard potentials of the silver–silver oxalate and the mercury–mercurous oxalate electrodes have been determined in formamide over a range of temperatures. No work seems to have been done so far on the study of the behaviour of inorganic dibasic acids as well as the second order electrodes of these acids in formamide. The present work deals with the study on the determination of the ionization constants of an inorganic dibasic acid, chromic acid, and the behaviour of the silver–silver chromate electrode in formamide at 25, 30, and 35°C. From the values of the standard potentials of the silver–silver chromate electrode, the standard thermodynamic quantities for the process, $H_2(g)+Ag_2CrO_4(s)\rightleftharpoons 2Ag(s)+H_2CrO_4$ (solvated) have been calculated in formamide at these temperatures.

EXPERIMENTAL

Potassium chloride (BDH, AnalaR) was dried above 100°C for 2 h before use. Formamide (BDH, L.R.) was purified as described earlier[6]. Chromium trioxide was dried at 120°C, weighed out of contact with air, and chromic acid solution was prepared by weight with conductivity water. The purity of the acid was checked by the iodometric determination of the chromate and was found to be 99.8%. Potassium hydrogen chromate was prepared by adding the calculated quantity of 1 N KOH solutions, prepared from KOH (Guaranteed reagent, pro analysi) and standardized against potassium hydrogen phthalate (BDH, AnalaR) to the known quantity of chromic acid prepared from chromium trioxide, evaporating the solution to dryness on a steam-bath, and recrystallizing the product from 95% alcohol. The salt was dried at 110–120°C for at least 2 h and kept in a vacuum desiccator over calcium chloride until required. Potassium chromate (BDH, AnalaR) was dried at 120°C for 2 h and kept in a vacuum desiccator.

Silver chromate was prepared by the method of Smith et al.[7] from chromic acid solution by adding silver oxide, and this precipitated silver chromate was repeatedly washed with hot water until the wash water no longer contained chromic acid. The product consisted of small dark green crystals which were kept in conductivity water in an amber coloured bottle for use.

Silver–silver chromate electrode was prepared by the method similar to that of the silver–silver oxalate electrode[5] by giving a paste of silver chromate on the spongy silver obtained by the thermal decomposition of silver oxide on a platinum spiral fused to a standard tapered glass joint. The electrodes thus prepared were stored in a 0.05 M aqueous chromic acid solution for 24 h and then rinsed with the chromic acid solution in formamide before use. Only those electrodes were used which showed a potential difference of 0.1 mV or less on being mutually compared with each other.

TABLE 1

DETERMINATION OF $-\log K_{1a}$ OF CHROMIC ACID IN FORMAMIDE

$m_1 \times 10^2$ (mol kg^{-1})	$m_2 \times 10^2$ (mol kg^{-1})	$m_3 \times 10^2$ (mol kg^{-1})	E (V)	$10^2 m'H^+$ (mol kg^{-1})	$\mu \times 10^2$ (mol kg^{-1})	$-\log K'_{1a}$
Temperature: 25°C						
0.756	0.843	2.223	0.4368	0.561	3.627	1.5180
1.634	0.771	2.422	0.4130	1.347	4.540	1.1417
2.342	1.287	2.206	0.4136	1.464	4.957	1.4836
1.703	0.737	5.876	0.3890	1.578	8.188	0.7209
2.261	2.157	4.946	0.3895	1.876	8.979	0.9014
2.840	1.331	5.502	0.3805	2.408	9.241	0.8795
				$-\log K_{1a}$ (extrapolated)		1.88 ± 0.15
Temperature: 30°C						
1.043	1.457	3.424	0.4150	0.870	5.755	1.0885
2.103	1.300	3.370	0.4000	1.596	6.266	1.2036
3.913	1.872	3.572	0.3825	3.132	8.579	0.8848
2.885	2.637	5.873	0.3847	1.832	10.342	1.3192
3.546	1.408	12.622	0.3579	2.716	16.746	1.1372
				$-\log K_{1a}$ (extrapolated)		1.08 ± 0.13
Temperature: 35°C						
1.261	0.868	1.942	0.4225	1.046	3.854	1.1595
0.925	0.853	2.218	0.4261	0.799	3.870	1.1084
3.838	2.769	5.042	0.3740	3.064	10.875	0.8523
3.996	1.492	5.598	0.3645	3.961	11.051	1.0078
3.558	0.984	17.047	0.3461	3.159	21.190	0.7853
				$-\log K_{1a}$ (extrapolated)		1.19 ± 0.04

Silver–silver chloride and hydrogen electrodes were prepared according to the method available in the literature[8,9]. Purification of hydrogen and nitrogen has been described earlier[8,10].

Solutions for e.m.f. measurements were prepared by dissolving the appropriate weighed amounts of salts and acids in known weights of formamide. For the determination of the first ionization constant of the acid and the standard potential of the electrode, the cell solutions were prepared at the ice-cold temperature to avoid decomposition of formamide by chromic acid during preparation of the solutions[8,11].

The cell measurements were carried out with electrodes set up as described earlier[3–5]. The results of the e.m.f. measurements of the cells

$$\text{Pt, } H_2|H_2CrO_4(m_1), KHCrO_4(m_2), KCl(m_3)|AgCl\text{–}Ag \qquad (A)$$

$$\text{Pt, } H_2|KHCrO_4(m_1), K_2CrO_4(m_2), KCl(m_3)|AgCl\text{–}Ag \qquad (B)$$

TABLE 2

DETERMINATION OF $-\log K_{2a}$ OF CHROMIC ACID IN FORMAMIDE

$m_1 \times 10^2$ (mol kg^{-1})	$m_2 \times 10^2$ (mol kg^{-1})	$m_3 \times 10^2$ (mol kg^{-1})	E (V)	$\mu \times 10^2$ (mol kg^{-1})	$-\log K'_{2a}$
Temperature: 25°C					
1.130	0.204	2.583	0.7692	4.325	8.9423
2.581	0.298	2.580	0.7615	6.055	9.0287
1.621	0.954	3.394	0.7900	7.877	8.9441
0.974	1.353	4.452	0.8041	9.485	8.9468
2.209	0.728	5.746	0.7655	10.139	9.0371
1.005	0.272	8.502	0.7401	10.323	8.8586
0.980	0.471	8.706	0.7468	11.099	8.7474
1.500	0.505	8.640	0.7556	11.655	9.0531
				$-\log K_{2a}$ (extrapolated)	9.02±0.09
Temperature: 30°C					
1.128	0.213	2.593	0.7680	4.360	8.8281
2.581	0.298	2.580	0.7602	6.055	8.9360
2.585	0.502	3.298	0.7538	7.389	8.7267
0.802	0.537	5.452	0.7707	7.955	8.7032
1.972	0.483	5.817	0.7345	9.238	8.5713
2.695	0.368	7.029	0.7320	10.828	8.8827
1.929	0.196	9.115	0.7160	11.632	8.8655
				$-\log K_{2a}$ (extrapolated)	8.81±0.12
Temperature: 35°C					
1.130	0.204	2.583	0.7656	4.325	8.7307
2.781	0.330	2.686	0.7744	6.457	9.1039
1.617	0.362	8.067	0.7454	10.770	8.8787
2.068	0.446	13.370	0.7167	16.776	8.6985
2.260	0.548	14.438	0.7147	18.342	8.6611
2.469	0.580	20.200	0.7162	24.409	8.8877
2.569	0.523	22.841	0.7128	26.979	8.9637
				$-\log K_{2a}$ (extrapolated)	8.85±0.09

and

$$\mathrm{Pt,\ H_2|H_2CrO_4(m)|Ag_2CrO_4\text{–}Ag} \qquad \text{(C)}$$

for the determination of the first and second ionization constants of chromic acid and of the standard potential of the silver–silver chromate electrode, respectively, at 25, 30, and 35°C together with other data are presented in Tables 1, 2, and 3.

TABLE 3

SUMMARY OF e.m.f. DATA OF THE CELL:

$\mathrm{Pt,\ H_2\ |H_2CrO_4(m)|\ Ag_2CrO_4\text{–}Ag}$ (C)

m × *10*^{2} (*mol kg*$^{-1}$)	*E* (*V*)	*α*	*β* × *10*^{3}	*μ* × *10*^{3} (*mol kg*$^{-1}$)	*E*$^{\circ\prime}$ (*V*)	*E*$^\circ$ (*V*)
Temperature: 25°C						
0.582	0.9898	0.76097	0.6012	4.434	0.3523	
0.650	0.9838	0.74482	0.5835	4.848	0.3506	
0.734	0.9757	0.72652	0.5642	5.338	0.3473	
0.848	0.9668	0.70413	0.5414	5.978	0.3439	0.3663
1.035	0.9588	0.67226	0.5105	6.966	0.3430	±0.0008
1.106	0.9539	0.66145	0.5004	7.323	0.3404	
1.918	0.9233	0.56982	0.4208	10.940	0.3278	
2.440	0.9108	0.52977	0.3887	12.940	0.3227	
Temperature: 30°C						
0.389	0.9986	0.95911	0.7287	3.738	0.3472	
0.436	0.9906	0.95472	0.7099	4.167	0.3449	
0.708	0.9570	0.93099	0.6253	6.598	0.3353	0.3607
0.771	0.9527	0.92595	0.6101	7.139	0.3350	±0.0008
1.005	0.9343	0.90788	0.5617	9.133	0.3289	
2.389	0.8585	0.82473	0.4108	19.720	0.2887	
2.391	0.8578	0.82463	0.4107	19.730	0.2880	
Temperature: 35°C						
0.430	0.9985	0.94415	0.6971	4.065	0.3398	
0.436	0.9971	0.94347	0.6948	4.118	0.3393	
0.510	0.9857	0.93527	0.6678	4.775	0.3358	0.3547
0.560	0.9794	0.92991	0.6514	5.213	0.3343	±0.0009
0.839	0.9534	0.90225	0.5789	7.578	0.3273	
1.067	0.9337	0.88206	0.5356	9.421	0.3183	
3.152	0.8374	0.75417	0.3569	23.880	0.2643	

CALCULATION OF RESULTS

The method of calculation for the first and second ionization constants has been adequately described[1,3,4].

The first ionization constant, K_{1_a}, corresponding to the equilibrium $\mathrm{H_2CrO_4 + solvent \rightleftharpoons H^+(solvated) + HCrO_4^-(solvated)}$ may be defined in the usual way as

$$K_{1_a} = m(\mathrm{H^+})\cdot m(\mathrm{HCrO_4^-})/m(\mathrm{H_2CrO_4}) \times \gamma(\mathrm{H^+})\cdot\gamma(\mathrm{HCrO_4^-})/\gamma(\mathrm{H_2CrO_4}) \qquad (1)$$

where m and γ are the molalities and activity coefficients of the species designated in parentheses. The first ionization constant was obtained by linear extrapolation to zero ionic strength, ($\mu = 0$) of the apparent first ionization constant, $-\log K'_{1a}$, defined by eqn (2):

$$\log K'_{1a} = -2A(\mu d_0)^{1/2} + \log [m'(\mathrm{H}^+)\cdot\{m_2 + m'(\mathrm{H}^+)\}/\{m_1 - m'(\mathrm{H}^+)\}] \qquad (2)$$

where $m'(\mathrm{H}^+)$ is the apparent hydrogen ion molality[12] related to the e.m.f. E of the cell (A) through relation (3),

$$-\log \mathrm{m}'(\mathrm{H}^+) = (E - E^\circ)F/2.303RT + \log m(\mathrm{Cl}^-) - 2A(\mu \mathrm{d}_0)^{1/2} \qquad (3)$$

and $m(\mathrm{Cl}^-) = m_3$, $m(\mathrm{H_2CrO_4}) = m_1 - m'(\mathrm{H}^+)$ and $m(\mathrm{HCrO_4^-}) = m_2 + m'(\mathrm{H}^+)$ and μ is given by

$$\mu \approx m_2 + m_3 + m'(\mathrm{H}^+) \qquad (4)$$

The second ionization constant, K_{2a} corresponding to the equilibrium $\mathrm{HCrO_4^-} + \text{solvent} \rightleftharpoons \mathrm{H}^+(\text{solvated}) + \mathrm{CrO_4^{-2}}(\text{solvated})$ is given by

$$K_{2a} = [m(\mathrm{H}^+)\cdot m(\mathrm{CrO_4^{-2}})/m(\mathrm{HCrO_4^-})]\cdot[\gamma(\mathrm{H}^+)\cdot\gamma(\mathrm{CrO_4^{-2}})/\gamma(\mathrm{HCrO_4^-})] \qquad (5)$$

and the apparent second ionization constant K'_{2a} may be expressed by

$$-\log K'_{2a} = (E - E^\circ)F/2.303RT + \log (m_1 m_3/m_2) + 2A(\mu d_0)^{1/2} \qquad (6)$$

where m_1 is the molality of $\mathrm{HCrO_4^-}$, m_2 is the molality of $\mathrm{CrO_4^{-2}}$ and m_3 is the molality of $\mathrm{Cl^-}$ used in the cell (B), μ is the ionic strength given by

$$\mu = m_1 + 3m_2 + m_3 \qquad (7)$$

The second ionization constant was obtained by the linear extrapolation to zero ionic strength ($\mu = 0$) of the function $-\log K'_{2a}$.

The values of E°(Ag–AgCl), the Debye–Hückel constant, A, and the density d_0 of the solvent needed for calculations at 25, 30, and 35 °C were obtained from the literature[13,14].

The values of $\log K'_{1a}$ or $\log K'_{2a}$ thus calculated were found to vary linearly[1,4,15,16] with μ for different temperatures and the linear extrapolation to $\mu = 0$ of values of $\log K'_{1a}$ or $\log K'_{2a}$ yielded $\log K_{1a}$ or $\log K_{2a}$, respectively.

The standard potential E° of the silver–silver chromate electrode was obtained by the method of extrapolating[8,10,17] the auxiliary function $E^{\circ\prime}$ given by[18]

$$E^{\circ\prime} = E + (2.3026RT/2F)(-6A\sqrt{\mu}) + (2.3026RT/2F)$$
$$[2\log\{m\alpha(1+\beta)\} + \log(m\alpha\beta)] \qquad (8)$$

to ionic strength $\mu = 0$, where m is the molality of chromic acid solution, and α and β are the degrees of first and second ionization of chromic acid, respectively. Using the K_{1a} and K_{2a} values of chromic acid at 25, 30 and 35 °C obtained from e.m.f. measurements just described the degrees of ionization, α and β of chromic acid at the corresponding temperature were computed following a reiteration procedure[18], and the ionic strength, μ was thus obtained by

$$\mu = m\alpha(1+2\beta) \tag{9}$$

DISCUSSION

It has been described in the preceding paragraphs that the variation of the values of log K'_{1a} or log K'_{2a} with μ at the respective temperature is linear. But it is observed in case of the plot of log K'_{1a} versus μ that the slopes of the straight lines vary irregularly with temperature, that is in agreement with the slopes observed in cases of monobasic acids such as picric[19], chloroacetic[20] and in case of the first ionization constants of some dicarboxylic acids such as phthalic[1], oxalic[3] studied over a range of temperature in formamide.

The values of pK_{1a}, obtained were 1.88, 1.08, and 1.19, respectively, and those of pK_{2a}, 9.02, 8.81, and 8.85, respectively, at 25, 30, and 35°C. The variation of pK_{1a} and pK_{2a} with temperature is found to be irregular and in the range of temperature studied the minima are found in both cases at 30°C. From the values of pK_a for a number of mono- and dicarboxylic acids studied in formamide[2,3,19,21] at temperatures ranging from 5 to 45°C, it is found that the values of pK_a vary irregularly with temperature and cannot be represented by empirical equations of any form by using the least squares method pointing out the difficulties in ascertaining the maxima or minima in pK_a values in formamide medium. The values of pK_a for acids studied in formamide over a range of temperature further support the view that despite the irregular variation of pK_a with temperature in this medium, the observed pK_a values are only the precise values at the corresponding temperature. As in the present study, the determination of the pK_a values has been limited to the three temperatures. However, it is difficult to ascertain the minima (through the visual examination shows the minima to be at 30°C) in pK_a value at a particular temperature. The determination of pK_a values for a large number of acids over a temperature range in formamide supports to the fact that the pK_a values for chromic acid determined in formamide are the precise and only the precise values at the corresponding temperature.

A comparison of the present data with the corresponding values in water is difficult because of the lack of relevant data in water at all temperatures. However, available data for K_{1a} at a single temperature, i.e., at 25°C and for K_{2a} at some temperatures in water (by Neuss and Rieman[22], $K_{1a} = 0.18 \pm 0.04$ and $K_{2a} = 3.20 \times 10^{-7}$ at 25°C by Nancollas et al.[23]. $K_{2a} = 3.01 \times 10^{-7}$ from potentiometric measurement and $K_{2a} = 2.97 \times 10^{-7}$ from spectrophotometric maesurement at 25°C, by Jones et al.[24] $K_{2a} = 3.17 \times 10^{-7}$ and 2.93×10^{-7} at 25 and 35°C, respectively) show that the ionization constants of chromic acid are lower (pK_a values are higher) in formamide than those obtained in water. These results suggest that chromic acid, a strong inorganic acid, exhibits similar behaviour to weak organic acids in this solvent[1–4,15,16,19–21]. Further, in changing the solvent from water to formamide, the second ionization constant of chromic acid is depressed more than the first as is observed in cases of organic dicarboxylic acids studied in formamide[1–3], because of the fact that the electrostatic effect due to the negative charge on the bichromate ion is more readily transmitted to the chromate ion in formamide than that in water.

From the ionization constants of chromic acid at 25°C, the standard free energy changes, ΔG°, of the ionization processes have been evaluated, and are found to be 10, 730 and 51,460 J for the first and the second ionizations, respectively.

The E° values of the $Ag(s)/Ag_2CrO_4(s)/CrO_4^{-2}$ electrode are found to be 0.3663, 0.3607, and 0.3547 V with negative slopes of the values, 3.448, 3.658, and 3.784 V mol^{-1} kg^{-1} in formamide at 25, 30, and 35°C, respectively. The values of $E^\circ_{Ag\text{-}Ag_2CrO_4}$ in formamide may be compared with the values in water as reported by Cann and Mueller[25] (0.4463 V) by Hass and Jellineck[26] (0.4620 V), by Bolam and MacKenzie[27] (0.4504 V), by Abegg and Cox[28] (0.4480 V) at 25°C and by Jena and Prasad[29] (0.4468 V) at 35°C. The E° values are found to be lower in formamide than in water and are in agreement with the general behaviour exhibited by other electrodes of this class[5-10]. This lowering of E° values may be explained by the lower basicity of formamide which increases the ΔG° ($-70{,}689$ J at 25°C in comparison with $\Delta G^\circ = -86{,}128$ J at 25°C in water) of the cell reaction, $H_2(g) + Ag_2CrO_4(s) \rightleftharpoons 2Ag(s) + H_2CrO_4$(solvated) by increasing the free energy of H_2CrO_4(solvated) in formamide.

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