Thermochimica Acta, 30 (1979) 73–81

THERMODYNAMIC PROPERTIES OF SOLUTIONS OF BENZOIC AND CITRIC ACIDS IN FORMAMIDE AT DIFFERENT TEMPERATURES

U. N. DASH
Department of Chemistry, G.M. College, Sambalpur (India)
(Received 10 April 1978)

ABSTRACT

The standard thermodynamic quantities, ΔG^0, ΔH^0, and ΔS^0, associated with the ionization process of benzoic acid in formamide have been evaluated. The standard potentials of the $Ag(s)/AgCNS(s)/CNS^-$ and the $Ag(s)/Ag_3Ci(s)/Ci^{3-}$ electrodes, and the standard thermodynamic quantities for the electrode processes have been calculated in formamide, at different temperatures.

INTRODUCTION

In a previous communication[1] the ionization constant of benzoic acid in formamide at 25 °C has been reported from the study of the cell

$$\text{Ag–AgCl} \mid \text{KCl}(m_3), \text{KOBz}(m_2), \text{HOBz}(m_1), \text{QH}_2\text{–Q} \mid \text{Pt} \qquad \text{(A)}$$

The present investigation extends the study to other temperatures ranging from 5 to 45 °C. Using the values of the ionization constants of benzoic acid at different temperatures, the standard potentials of the silver–silver thiocyanate electrode have been determined in formamide at these temperatures from the study of the buffer cell

$$\text{Ag–AgCNS} \mid \text{KCNS}(m_3), \text{KOBz}(m_2), \text{HOBz}(m_1), \text{QH}_2\text{–Q} \mid \text{Pt} \qquad \text{(B)}$$

The cell

$$\text{Ag–AgCNS} \mid \text{KCNS}(m_3), \text{KOAC}(m_2), \text{HOAC}(m_1), \text{QH}_2\text{–Q} \mid \text{Pt} \qquad \text{(C)}$$

has also been studied in formamide at 25, 30, and 35 °C, with a view to having an independent check on the benzoic acid–benzoate buffer cell for the determination of the standard potential of the $Ag(s)/AgCNS(s)/CNS^-$ electrode. Further, the standard potential of this electrode has also been calculated in formamide from the solubility data of silver thiocyanate obtained in the presence of the added electrolyte, sodium perchlorate, in this solvent at temperatures ranging from 15 to 35 °C. The standard potentials of the $Ag(s)/Ag_3Ci(s)/Ci^{3-}$ electrode have been determined over the temperature range 5 to 45 °C from the study of the cell

$$\text{Pt/Q–QH}_2, \text{H}_3\text{Ci}(m)/\text{Ag}_3\text{Ci–Ag} \qquad \text{(D)}$$

EXPERIMENTAL

The preparation of the quinhydrone and the silver–silver chloride electrodes has been described earlier[2]. The silver–silver thiocyanate electrodes were of the thermal electrolytic type, and were made by anodizing[3] the silver electrodes prepared by the method described earlier[4] in a solution of 0.2 M potassium thiocyanate and 0.06 M perchloric acid. After preparation, the electrodes were allowed to equilibrate in a 0.1 M aqueous solution of potassium thiocyanate for about 48–72 h, and then rinsed either with the benzoate solution in formamide, or acetate solution in formamide, as needed before use. Only those electrodes which showed a potential difference of 0.1 mV or less on being compared with another of the same type were used.

Silver citrate was prepared by mixing dilute solutions of silver nitrate (B.D.H., AnalaR) with the calculated amount of sodium citrate (B.D.H., AnalaR), keeping it shielded from light during the process. The crystals were washed with conductivity water and finally dried in a vacuum desiccator in the dark over calcium chloride for several weeks. The silver–silver citrate electrodes were prepared by a method similar to that for the silver–silver acetate electrode[4]. The cell vessels were of the type recommended by Harned and Wright[5].

Potassium thiocyanate (B.D.H., AnalaR) was carefully dried at 150°C according to the procedure of Kolthoff and Lingane[6] and was kept in a vacuum desiccator before use. Benzoic acid, potassium benzoate, acetic acid, potassium acetate, citric acid and potassium chloride, anhydrous sodium perchlorate, and silver thiocyanate were the same samples as used in the previous studies[1, 4, 7–10]. Formamide (B.D.H., L.R.) was purified as described earlier[11].

Other experimental methods and procedures, such as those employed for the preparation of cell solutions, setting up of the cells, measurements of e.m.f., determination of solubility, and the analysis of the solute contents, were similar to those described in previous studies[1, 2, 4, 9, 10].

RESULTS AND DISCUSSION

As usual[2, 12], the pK_a values of benzoic acid were obtained from the e.m.f. of cell (A) by extrapolation of pK'_a to zero ionic strength, μ. The pK'_a is then defined by

$$pK'_a = [E - E^0(\text{Ag–AgCl}) + E^0(\text{QH}_2\text{–Q})]\, F/2.303RT + \log (m_1 m_3/m_2) \qquad (1)$$

Similarly, the standard potential, E^0, of the silver–silver thiocyanate electrode was obtained from the e.m.f. of the buffer cells (B) and (C) by extrapolation[13] of E' to zero ionic strength, μ. The E' is then defined by

$$\begin{aligned} E' &= E + E^0(\text{Q}H_2\text{–Q}) - 2.3026\,(RT/F)\text{p}K_a + 2.3026(RT/F)\log (m_1 m_3/m_2) \\ &= E^0 - 2.3026\,(RT/F)\log \gamma_{\text{HA}}\, \gamma_{\text{CNS}^-}/\gamma_{\text{A}^-} \\ &= E^0 + \text{f}\,(\mu) \qquad (2) \end{aligned}$$

where HA is benzoic or acetic acid. In eqns. (1) and (2), E is the observed e.m.f.[4, 18] and E^0 is the standard e.m.f., and is known[14] over the temperature range under investigation, m_1, m_2, and m_3 are the molalities of the species designated in cells (A), (B) and (C), and the ionic strength $\mu = m_2 + m_3$. Using the pK_a values of benzoic acid obtained in the present study, and of acetic acid obtained earlier[7], the function E' was calculated from eqn. (2).

From the solubility data, the standard potential of the Ag(s)/AgCNS(s)/CNS$^-$ electrode was calculated from the equation.

$$E^0 = E^0_{\mathrm{Ag}} + 2.3026\,(RT/F)\log K_s \tag{3}$$

where E^0_{Ag} is the standard potential of the silver electrode, and is known[15, 16] over the temperature range under investigation, and K_s is the solubility product of silver thiocyanate and was calculated from the relation, $K_s = s^2$, where s is the solubility of silver thiocyanate at $m = 0$ mole kg^{-1}. The solubilities of silver thiocyanate at rounded molalities (e.g., $m = 0, 0.01, 0.02$ mole kg^{-1} etc.) were calculated from the equation[10]

$$\log s = \log s^0 + \frac{A(m+s)^{\frac{1}{2}}}{1 + a^0B(m+s)^{\frac{1}{2}}} - b\,(m+s) \tag{4}$$

with the symbols having their usual significance. The method of calculation was exactly the same as that described in our earlier studies[9, 10, 15]. The value of the ion-size parameter[17], a^0, in eqn. (4) was taken to be 6 Å.

The standard potential, E^0, of the silver–silver citrate electrode was obtained by the method of extrapolating the auxiliary function E' given by

$$E' = E + E^0(\mathrm{QH_2\text{-}Q}) - 2.3026\,(RT/3F)\left(\frac{12A\sqrt{\mu}}{1 + a^0B\sqrt{\mu}}\right) + 2.3026\,(RT/3F)$$

$$\{3\log[m\alpha(1+\beta+\beta\delta)] + \log(m\alpha\beta\delta)\} \tag{5}$$

to ionic strength $\mu = 0$, where m is the molality of citric acid solution, E is the observed e.m.f.[4, 18] of cell (D), and α, β, and δ are the degrees of first, second and third ionization of citric acid, respectively. Using the K_{1a}, K_{2a} and K_{3a} values of citric acid reported earlier[8], over the temperature range under investigation, the degrees of ionization, α, β, and δ of citric acid were computed from the following equations

$$\alpha = [-K_{1a} + (K_{1a}^2 + 4\,m\,K_{1a})^{\frac{1}{2}}]/2m \tag{6}$$

$$\beta = \{-(m\alpha + K_{2a}) + [(m\alpha + K_{2a})^2 + 4m\alpha K_{2a}]^{\frac{1}{2}}\}/2m\alpha \tag{7}$$

$$\delta = \{-(m\alpha + m\alpha\beta + K_{3a}) + [(m\alpha + m\alpha\beta + K_{3a})^2 + 4m\alpha\beta K_{3a}]^{\frac{1}{2}}\}/2m\alpha\beta \tag{8}$$

and the ionic strength μ was thus obtained by

$$\mu = m\alpha(1 + 2\beta + 3\beta\delta) \tag{9}$$

TABLE 1

VALUES FOR pK_a OF BENZOIC ACID, E^0 OF THE SILVER–SILVER THIOCYANATE AND SILVER–SILVER CITRATE ELECTRODES AND K_s OF SILVER THIOCYANATE IN FORMAMIDE AT DIFFERENT TEMPERATURES

Temp. (°C)	*pK_a of benzoic acid*	*E^0 of the Ag(s)/AgCNS(s)/CNS$^-$ electrode (V)*		*From solubility product [eqn. (3)]*	*E^0 of the Ag(s)/Ag$_3$Ci(s)/Ci^{3-} electrode [cell (D)] (V)*	*$K_s \times 10^{10}$ of AgCNS (mole^2 kg^{-2})*
		From cell (B)	*From cell (C)*			
5	6.71 ± 0.06	0.1908 ± 0.0006			0.4963 ± 0.0006	
10	6.70 ± 0.03	0.1858 ± 0.0003			0.4927 ± 0.0002	
15	6.69 ± 0.01	0.1812 ± 0.0007		0.1788	0.4882 ± 0.0002	4.529
20	6.68 ± 0.05	0.1752 ± 0.0003		0.1730	0.4845 ± 0.0005	5.992
25	6.32 ± 0.02	0.1693 ± 0.0008	0.1714 ± 0.0008	0.1687	0.4803 ± 0.0006	8.563
30	6.38 ± 0.02	0.1639 ± 0.0006	0.1656 ± 0.0001	0.1661	0.4763 ± 0.0003	13.260
35	6.46 ± 0.02	0.1597 ± 0.0006	0.1602 ± 0.0008	0.1605	0.4718 ± 0.0002	18.400
40	6.12 ± 0.01	0.1547 ± 0.0008			0.4676 ± 0.0003	
45	6.17 ± 0.01	0.1491 ± 0.0001			0.4638 ± 0.0004	

In eqn. (5) the Debye–Huckel constants, A and B (on the molal scale), were either obtained from the literature or calculated in this solvent by following the usual method, and a^0 is the ion-size parameter and was taken[8] as 6 Å.

The pK_a values of benzoic acid, and the standard potentials of the Ag(s)/AgCNS(s)/CNS$^-$ electrode obtained from the three methods, and that of the Ag(s)/Ag$_3$Ci(s)/Ci^{3-} electrode obtained from the study of cell (D) in formamide at different temperatures are presented in Table 1, along with their accuracies. It has been shown earlier that the acetic acid–acetate buffer cell has been successfully employed in the accurate determination of the E^0's of the Ag(s)/AgBr(s)/Br$^-$ and Ag(s)/AgI(s)/I$^-$ electrodes in formamide[19]. An examination of Table 1 shows that the E^0 values obtained from the three independent methods are in reasonable agreement with each other, suggesting that the benzoic acid–benzoate buffer cell and the solubility measurements can also be employed satisfactorily for the determination of the E^0 of an electrode of the second kind in formamide.

The values of E^0 of the silver–silver thiocyanate and the silver–silver citrate electrodes obtained from the study of cells (B) and (D), respectively, at different temperatures were fitted by the method of least squares to equations

$$E^0_{\mathrm{Ag-AgCNS}} = 0.1711 - (1.048 \pm 0.0017) \times 10^{-3}(t - 25) - (6.608 \pm 1.284) \times 10^{-6} (t - 25)^2 \quad (10)$$

$$E^0_{\mathrm{Ag-Ag_3Ci}} = 0.4795 - (8.21 \pm 0.03) \times 10^{-4}(t - 25) + (4.261 \pm 0.78) \times 10^{-6} (t - 25)^2 \quad (11)$$

over the range 5 to 45°C, where t is any temperature in °C. The average deviation between the observed (experimental) values of E^0 and the values calculated from the above equations is within 0.8 mV.

The values of K_s of silver thiocyanate at different temperatures may be expressed by an equation of the form

$$-\log K_s = A/T + B + CT \quad (12)$$

where T is any temperature in degrees Kelvin. The parameters A, B, and C are given as

$$-\log K_s = -(355.87 \pm 0.08)/T + (19.6162 \pm 0.0132) - (0.03145 \pm 0.0005)T \quad (13)$$

Equation (13) predicts the K_s values obtained from 15 to 35°C with a maximum deviation of ± 0.001 units. The observed K_s values in formamide at different temperatures are listed in Table 1.

A comparison of the E^0 values of the Ag(s)/AgCNS(s)/CNS$^-$ electrode in formamide (0.1693 V) with that in water[10] (0.0895 V) at 25°C shows that the value of E^0 is greater in formamide than in water. The higher E^0 values in formamide lend support to the higher solubility of silver thiocyanate in formamide (2.925×10^{-5} mole kg^{-1}) than in water (0.976×10^{-6} mole kg^{-1}) at 25°C. It is thus seen that the behaviour of the silver–silver thiocyanate electrode is consistent with that of the silver–silver bromide and silver–silver iodide electrodes studied in formamide[19]. The E^0 value of the Ag(s)/Ag$_3$Ci(s)/Ci^{3-} electrode was found to be less in formamide (0.4803 V at 25°C) than that in water[20] (0.5046 V at 25°C), which is in agreement with the behaviour exhibited by the silver–silver oxalate[21], mercury–mercurous oxalate[21], silver–silver chromate[22] and silver–silver acetate[4] electrodes reported earlier in this solvent.

From the E^0 values of the Ag(s)/AgCNS(s)/CNS$^-$ and the Ag(s)/Ag$_3$Ci(s)/Ci^{3-} electrodes at different temperatures, the thermodynamic quantities ΔG^0, ΔH^0, and ΔS^0 for the cell reactions

$$\mathrm{AgCNS(s)} + \tfrac{1}{2}\mathrm{H_2} \rightleftharpoons \mathrm{Ag(s)} + \mathrm{HCNS(solvated)} \qquad (14)$$

and

$$2\mathrm{Ag_3Ci(s)} + 3\mathrm{H_2} \rightleftharpoons 6\mathrm{Ag(s)} + 2\mathrm{H_3Ci(solvated)} \qquad (15)$$

have been calculated in Joules at these temperatures. These quantities have been represented through the equations

$$\Delta G^0 = (51.63 \pm 0.08) \times 10^3 - (0.5667 \pm 0.01) \times 10^3 T + (1.13 \pm 0.09)T^2 \qquad (16)$$

$$\Delta H^0 = (-\ 45.72 \pm 0.04) \times 10^3 - (8.954 \pm 6.381) \times 10^{-3} T^2 \qquad (17)$$

and

$$\Delta S^0 = (-\ 91.58 \pm 0.03) - 0.0325T \qquad (18)$$

for the cell reaction (14), and

$$\Delta G^0 = (-\ 178.8 \pm 0.04) \times 10^3 + (45.71 \pm 0.12)T + (0.29 \pm 0.05)T^2 \qquad (19)$$

$$\Delta H^0 = (-\ 206.65 \pm 0.34) \times 10^3 - (0.0355 \pm 0.004)T^2 \qquad (20)$$

and

$$\Delta S^0 = (-\ 238.48 \pm 0.13) + 0.003\ T \qquad (21)$$

for the cell reaction (15), over the range 5 to 45°C, where T is any temperature in degrees Kelvin. The various thermodynamic quantities for the ionization of benzoic acid

$$\mathrm{HOBz} + \mathrm{solvent} \rightleftharpoons \mathrm{H^+(solvated)} + \mathrm{OBz^-(solvated)} \qquad (22)$$

and for the dissolution of silver thiocyanate

$$\mathrm{AgCNS(s)} + \mathrm{solvent} \rightarrow \mathrm{Ag^+(solvated)} + \mathrm{CNS^-(solvated)} \qquad (23)$$

have been evaluated in formamide, and the values of these at 25°C are entered in Table 2, along with their uncertainties. The values of these quantities in water[10, 20, 23] at 25°C have also been included in Table 2 for the sake of comparison.

TABLE 2

THERMODYNAMIC QUANTITIES (ON THE MOLAL SCALE) FOR THE IONIZATION OF BENZOIC ACID, CELL REACTIONS, AND DISSOLUTION PROCESS OF SILVER THIOCYANATE IN FORMAMIDE AND WATER AT 25°C (V DENOTES SOLVATED)

Process	ΔG^0 *(J mole⁻¹)*	ΔH^0 *(J mole⁻¹)*	ΔS^0 *(J mole⁻¹ deg⁻¹)*	$\Delta C_p{}^0$ *(J mole⁻¹ deg⁻¹)*	*Solution*
$HOB_z \rightleftharpoons H^+(v) + OBz^-(v)$	36,060 ± 10.4	26,180 ± 101	−33.17 ± 0.92		Formamide
	23,850	627.6	−78.24		Water
$\frac{1}{2}H_2(g) + AgCNS(s) \rightleftharpoons Ag(s) + HCNS(v)$	−16,340 ± 9.9	−46,510 ± 89	−101.3 ± 1.4		Formamide
	−8635.8	−11,506	−9.62		Water
$AgCNS(s) \rightarrow Ag^+(v) + CNS^-(v)$	51,622 ± 8.4	46,651 ± 76	−16.69 ± 0.86	358.8 ± 10.6	Formamide
	68,580	37,390	−103.3		Water
$3H_2(g) + 2Ag_3Ci(s) \rightleftharpoons 6Ag(s) + 2H_3Ci(v)$	−139,425 ± 98	−209,802 ± 124	−237.59 ± 3.4		Formamide
	−142,339	+218,530	−257.10		Water

Any change in ΔG^0 for various processes on passing from water to formamide will be due to variation of free energy of solvation. A comparison of the present data for benzoic acid with the corresponding values in water (Table 2) shows that the ΔG^0, ΔH^0, and ΔS^0 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. As the E^0 of the silver–silver thiocyanate electrode has been determined from the study of the benzoic acid–benzoate buffer cell (B), it is interesting to note a contrary variation of ΔG^0, ΔH^0 and ΔS^0 for the solvation of HCNS with that of the ionization process of benzoic acid in formamide. Further, it is seen from Table 2 that these thermodynamic quantities for the solvation of HCNS are on the lower side in formamide than in water. The thermodynamic behaviour of the process closely resembles that of HBr and HI studied in formamide. In other words, thiocyanate ion, a pseudo halide, like bromide and iodide ions, unlike their counterpart chloride ion[24], is large, and on passing from water to formamide the free energy of solvation tends to decrease as the anionic solvation is affected more because of its larger size. The more negative values of ΔH^0 and ΔS^0 for the solvation of HCNS in formamide suggest that the net amount of order created by both ions, the hydrogen ion and the thiocyanate ion, is more in formamide than in water. In other words, the formamide molecules become less associated than water, lending support to the fact that thiocyanic acid "breaks down more structure"[25] in water than in formamide.

Considering the dissolution process of silver thiocyanate, the ΔG^0, ΔH^0, and ΔS^0 for the process appear to be of similar order in both formamide and water but the less negative value of ΔS^0 in formamide indicates that the degree of re-orientation and partial immobilization of the formamide molecules by CNS^- is not greater in formamide than in water. This indicates that the behaviour of CNS^- in the dissolution process of silver thiocyanate is just the opposite of that for the solvation process of HCNS in formamide. One reason for this anomalous behaviour could be the greater solvating power of CNS^- in silver thiocyanate as opposed to HCNS.

The contrary variation of ΔH^0 for the solvation of citric acid in the cell process involving the silver–silver citrate electrode in formamide and water indicates that the solvation pattern is significantly altered on passing from water to formamide. The values of ΔS^0 in both solvents are expected to be negative, but in formamide they appear to be less negative, pointing to the fact that the net amount of order created by both ions, the hydrogen ion and the citrate ion, is not more in formamide than in water. Citric acid thus "breaks down more structure" in formamide than in water. On changing the solvent from water to formamide the free energy of solvation, ΔG^0, tends to increase. This is consistent with the solvation processes of benzoic[18], acetic[4], oxalic[21] and chromic[22] acids studied earlier in formamide. This increase in ΔH^0 is probably due to the fact that citric acid is more strongly stabilized by solvation with formamide molecules.

REFERENCES

1 U. N. Dash, *Aust. J. Chem.*, 28 (1975) 1653.
2 U. N. Dash and B. Nayak, *Aust. J. Chem.*, 26 (1973) 111.
3 C. E. Vanderzee and W. E. Smith, *J. Am. Chem. Soc.*, 78 (1956) 721.
4 U. N. Dash and B. Nayak, *J. Electroanal. Chem.*, 41 (1973) 323.
5 H. S. Harned and D. D. Wright, *J. Am. Chem. Soc.*, 55 (1933) 4849.
6 I. M. Kolthoff and J. J. Lingane, *J. Am. Chem. Soc.*, 57 (1932) 2126.
7 U. N. Dash, R. K. Agarwal and B. Nayak, *Indian J. Chem.*, 13 (1975) 923.
8 U. N. Dash, *J. Chem. Thermodyn.*, (in press).
9 B. Nayak and U. N. Dash, *Thermochim. Acta*, 6 (1973) 223.
10 U. N. Dash, J. Mohanty and K. N. Panda, *Thermochim Acta*, 16 (1976) 55.
11 U. N. Dash and B. Nayak, *Indian J. Chem.*, 8 (1970) 659.
12 U. N. Dash and B. Nayak, *Aust. J. Chem.*, 25 (1972) 941.
13 K. K. Kundu, D. Jana and M. N. Das, *J. Phys. Chem.*, 74 (1970) 2625.
14 U. N. Dash and B. Nayak, *Aust. J. Chem.*, 28 (1975) 793.
15 U. N. Dash and B. Nayak, *Thermochim. Acta*, 11 (1975) 17.
16 U. N. Dash, *Ph.D. Thesis*, Indian Institute of Technology, Kharagpur, India, 1973.
17 R. N. Roy, R. A. Robinson and R. G. Bates, *J. Am. Chem. Soc.*, 95 (1973) 8231.
18 U. N. Dash, *Electrochim. Acta*, 21 (1975) 279; 21 (1976) 1061.
19 U. N. Dash and B. Nayak, *Aust. J. Chem.*, 28 (1975) 1657.
20 P. B. Mathur and S. M. A. Naqvi, *Proceedings of the Symposium on Electrode Processes*, 1966, Karaikudi, India, pp. 39–45 (Eng.).
21 U. N. Dash and B. Nayak, *Aust. J. Chem.*, 28 (1975) 1373.
22 U. N. Dash, *Thermochim. Acta*, 16 (1976) 177.
23 J. J. Christensen, R. M. Izatt and L. D. Hansen, *J. Am. Chem. Soc.*, 89 (1967) 213.
24 R. K. Agarwal and B. Nayak, *J. Phys. Chem.*, 70 (1966) 2568.
25 D. Feakins, *Physico-chemical Processes in Mixed Aqueous Solvents*, American Elsevier Publishing Co., New York, 1967, p. 71.