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Note

THERMODYNAMICS OF SILVER BENZOATES AND THE STANDARD ELECTRODE POTENTIALS OF THE SILVER—SILVER BENZOATE ELECTRODES IN AQUEOUS MEDIUM

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A survey of the literature shows that the solubility products of a number of sparingly soluble silver salts of inorganic acids have been determined in aqueous [1—3], non-aqueous [4—9] and mixed-solvent media [10] either at a single temperature, 25°C, or over a range of temperatures, and, using the solubility product value, the standard electrode potentials of the silver salt electrodes have also been reported. Excepting silver acetate and silver chloroacetate [11] no work seems to have been done on the determination of the solubility product of the silver salts of organic acids in aqueous medium. The present work has been undertaken as part of our programme for the determination of the solubility product and other thermodynamic parameters of the silver salts of a number of substituted benzoic acids in aqueous and mixed solvents in the presence of sodium perchlorate. Recently, it has been shown by Dash et al. [9,12—14] in this laboratory that the solubility method can be satisfactorily used for the determination of the standard electrode potentials of the silver salt electrodes in aqueous and non-aqueous media.

The present work also aims at determining the standard electrode potentials of the silver benzoate electrodes which have hitherto not been determined in aqueous medium.

EXPERIMENTAL

Sodium salts of the substituted benzoic acids were prepared by a method similar to that of potassium benzoate described earlier [15]. Silver benzoates were prepared by mixing dilute solutions of silver nitrate and the corresponding sodium benzoate in the dark at ice-cold temperature. The precipitates were repeatedly washed with conductivity water, and finally dried in a vacuum desiccator over anhydrous $CaCl_2$ for several weeks in the dark. The purity of these silver salts was tested by standard method.

The method of determining the solubility, the analysis of the solute contents and the accuracy of the analysis have been adequately described [1—10,14,16,17]. The calorimetric titration of determining the heat of solution of silver salts was done by standard method [18].

RESULTS AND DISCUSSION

The hypothetical solubility, s^0, of silver salts was obtained by means of an extrapolation technique involving a function of the determined solubility, s, which was determined experimentally at any sodium perchlorate molarity, c, taken to the limit of zero ionic strength, I. A linear function of I was observed when the Debye—Huckel equation [19] was introduced for the activity coefficient of the silver salt over the experimental range of molarities, c. This procedure is essentially the same as that used in our earlier determinations [1—10,16].

From the solubility and activity coefficient relations [3,19], the function $\log s'$ is defined by

$$\log s' = \log s - \frac{AI^{1/2}}{1 + Ba^0 I^{1/2}} = \log s^0 - bI \qquad (1)$$

where the symbols have their usual significance and the ionic strength $I = c + s$. It is evident from eqn. (1) that $\log s^0$ is the intercept, and b is the slope of a plot of the middle terms of the equation vs. the ionic strength, I, when extrapolated to infinite dilution, $I = 0$, assuming the proper values of a^0 are chosen [20].

The required values of A and B at different temperatures were taken from the literature [21]. The exact values of a^0 for silver benzoates were obtained by following the principle adopted by Roy et al. [22]. At each temperature about six to eight solubility measurements for each silver benzoate were made with c_{NaClO_4} in the range $1.0—8.0 \times 10^{-2}$ mole l^{-1} and I between $1.0—8.0 \times 10^{-2}$. The solubilities of silver salts at rounded molarities (e.g., c = 0, 0.01, 0.02 or 0.03 mole l^{-1} etc.) were calculated from the equation

$$\log s = \log s^0 \times \frac{AI^{1/2}}{1 + Ba^0 I^{1/2}} - bI \qquad (2)$$

by substituting the appropriate constants along with simultaneous substitution of the rounded molarity value, and the appropriate and reasonable value of s for I. The method of calculation is exactly similar to that described in our earlier studies [1—10,14,16,17]. The solubility product, K_s, has been calculated from the relation, $K_s = (s'^0)$ [2], where s'^0 is the solubility of a particular silver salt at c = 0 mole l^{-1}.

The values of K_s for a particular silver benzoate at different temperatures may be expressed by an equation of the form

$$-\log K_s = \frac{A}{T} + B + CT \qquad (3)$$

where T is any temperature in degrees Kelvin. The parameters A, B, and C of eqn. (3) for different silver benzoates are presented in Table 1. Equation (3) predicts the K_s values observed from 20 to 35°C with a maximum deviation of ±0.001 units. The values of a^0 for different silver benzoates are entered in Table 1. The solubility products of silver benzoate and silver salicylate (silver salt of *ortho*-hydroxy-benzoic acid) determined earlier [16,17] are also included in Table 1 for the sake of comparison.

TABLE 1

Parameters of eqn. (3) and values of a^0 for different silver benzoates

Silver benzoate	*A*	*B*	$c \times 10^3$	a^0 (Å)
	2540.80	23.94	37.96	2.5
o-Chloro	−10746.5	76.90	−127.74	2.5
m-Chloro	−7402.8	57.43	−93.00	2.5
p-Chloro	−4119.9	38.91	−63.70	2.5
o-Nitro		2.71		2.5
m-Nitro	7701.1	−41.41	67.61	2.5
p-Nitro	1952.4	−5.14	10.39	2.5
o-Hydroxy	−984.3	12.49	−15.90	2.5
m-Hydroxy	1833.3	−6.74	11.82	4.0
p-Hydroxy	2857.3	−13.76	26.54	4.5
o-Amino	18134.3	106.46	171.90	3.5
m-Amino	21561.7	−127.48	201.52	4.0
p-Amino	−27602.6	196.06	−331.48	6.0

Using the K_s values, the standard electrode potential E^0 of the particular silver—silver benzoate electrode can be calculated [1—10] by using the equation

$$E^0_{\mathrm{Ag-AgX}} = E^0_{\mathrm{Ag}} + 2.3026\,(RT/F)\log K_s \qquad (4)$$

where X is the benzoate or substituted benzoate, and E^0_{Ag} is the standard potential of the silver—silver ion electrode, and is known [21] over the temperature range under investigation. The variation of $E^0_{\mathrm{Ag-AgX}}$ with temperature has been expressed through an equation of the form

$$E^0_{\mathrm{Ag-AgX}} = a + b\,(T - 25) + c\,(T - 25)^2 \qquad (5)$$

where T is any temperature in °C. In Table 2, the values of the constants, a, b, and c of eqn. (5) are presented. The values of K_s have been expressed on the molar scale, therefore the $E^0_{\mathrm{Ag-AgX}}$ values calculated from eqn. (4) have also been expressed on the molar scale (E^0_{c}). Values of $E^0_{\mathrm{Ag-AgX}}$ on the molal (E^0_{m}) and mole-fraction scale (E^0_{N}) which are inter-related by equations

$$E^0_{\mathrm{N}} = E^0_{\mathrm{c}} - 2\,k\log - 2\,k\log(1000/M),\ \text{and}\ E^0_{\mathrm{m}} = E^0_{\mathrm{c}} - 2\,k\log\rho \qquad (6)$$

where M and ρ are the molecular weight and density, respectively, of water, and $k = 2.3026\,RT/F$, at 25°C, given in Table 2.

The thermodynamic quantities, ΔG^0, ΔH^0, ΔS^0, and ΔC^0_p for the dissolution process of silver benzoates have been calculated by the usual equations [14] using the parameters *A*, *B*, and *C* of eqn. (3). These quantities for different silver benzoates at 25°C are shown in Table 3. In the case of the silver *ortho*-nitrobenzoate, as the solubility product has been determined at a single temperature, 25°C, the ΔH^0 value could not be evaluated and so the calorimetric titration was done for its determination at this temperature. To check the reliability of this result, the ΔH^0 of silver benzoate was also redetermined calorimetrically at 25°C and was found to be in reasonably good agreement with the value reported earlier [16].

TABLE 2

Constants of eqn. (5), and standard electrode potentials on the molar ($E^0_c = a$), molal (E^0_m), and mole-fraction scale (E^0_N) for different silver—silver benzoate electrodes in water at 25°C

Silver—silver benzoate	a	$b \times 10^3$	$c \times 10^5$	E^0_m (V)	E^0_N (V)
	0.5565	—0.970	6.200	0.5567	0.3503
o-Chloro-	0.6321	—1.131	1.750	0.6323	0.4259
m-Chloro-	0.5108	—1.378	1.880	0.5110	0.3046
p-Chloro-	0.4978	—1.157	1.115	0.4980	0.2916
o-Nitro-	0.6391			0.6393	0.4329
m-Nitro-	0.5287	—0.769	1.200	0.5289	0.3225
p-Nitro-	0.6322	—1.100	1.500	0.6324	0.4260
o-Hydroxy-	0.5356	—1.581	30.000	0.5358	0.3294
m-Hydroxy-	0.5350	—1.703	6.520	0.5352	0.3288
p-Hydroxy-	0.5778	—1.390	0.600	0.5780	0.3716
o-Amino-	0.4674	—0.017	3.700	0.4676	0.2612
m-Amino-	0.5078	0.483	40.000	0.5080	0.3016
p-Amino-	0.5238	0.701	6.400	0.5240	0.3176

The values of the solubilities of the silver salts of benzoic, *ortho*-, *meta*-, and *para*-substituted chloro-, nitro-, hydroxy-, and amino-benzoic acids as determined in the present study and reported earlier [16,17] are found to be in the following order: *ortho*-nitrobenzoate > *ortho*-chlorobenzoate > *meta*-hydroxybenzoate > *para*-hydroxybenzoate > benzoate > *ortho*-hy-

TABLE 3

Standard thermodynamic quantities for the silver benzoates at 25°C

Silver benzoate	ΔG^0 (kJ mole^{-1})	ΔH^0 (kJ mole^{-1})	ΔS^0 (J deg^{-1} mole^{-1})	ΔC^0_p (J deg^{-1} mole^{-1})
	23.40	31.79 [a] 29.07 [b]	28.29	
o-Chloro-	15.82	11.45	—14.73	1457
m-Chloro-	27.81	16.37	38.38	1061
p-Chloro-	29.06	23.68	18.05	727
o-Nitro-	15.44	19.29 [b]	12.90	
m-Nitro-	26.11	32.49	21.41	—771
p-Nitro-	25.75	19.71	—20.48	—118.6
o-Hydroxy-	25.41	8.19	—57.79	181.4
m-Hydroxy-	21.35	9.57	—134.91	—302.9
p-Hydroxy-	16.77	15.00	—5.93	—39.5
o-Amino-	32.09	54.77	76.09	—196.3
m-Amino-	28.11	70.19	141.21	—2299
p-Amino-	26.54	35.15	28.72	3783

[a] Ref. 3.

[b] From calorimetric titration.

droxybenzoate > *para*-aminobenzoate > *para*-nitrobenzoate > *meta*-chlorobenzoate > *meta*-aminobenzoate > *meta*-nitrobenzoate > *para*-chlorobenzoate > *ortho*-aminobenzoate.

A comparison of the relative solubilities of the silver salts with the relative strengths of the benzoic acids in water [23] at 25°C which are in the order *ortho*-nitrobenzoic > *ortho*-chlorobenzoic > *ortho*-hydroxybenzoic > *para*-nitrobenzoic > *meta*-nitrobenzoic > *meta*-chlorobenzoic > *para*-chlorobenzoic > *meta*-hydroxybenzoic > benzoic > *para*-hydroxybenzoic > *meta*-aminobenzoic > *para*-aminobenzoic > *ortho*-aminobenzoic acid, shows that the dissolution of the silver salts depends on the dissociation of the corresponding acids, although in some cases deviations occur. The specific solute—water interaction may be the cause of such deviation in the relative solubilities of the silver salts from the relative strengths of acids.

There is no doubt that the relative solubilities of the silver salts do depend to a considerable extent on the nature of the substituents present, and as is seen from the results it may perhaps be possible to explain their differences qualitatively by taking the effect of the substituents alone into account, but nevertheless the effect always seems to get mixed up with the nature of the silver salts, which possibly arises from the specific solute—water interaction. With a few exceptions, the relative solubilities of the silver salts of benzoic and substituted benzoic acids seem to be in general agreement with the qualitative theory of substituents effects on the dissociation constants of acids [23].

It is found that a simple relationship of the form [15,24]

$$-\log K_s = C + S/d$$

correlates the solubility product data for silver benzoate and the three amino-substituted silver benzoates, where d is taken as the distance between the polar bond joining the —COOAg group to the ring and the polar bond connecting the amino-substituent to the ring, the distance being measured along the carbon skeleton of the ring. A plot of $-\log K_s$ vs. $1/d$ yields straight lines at all temperatures studied and fits four points to within ±0.08 logarithm units. The values of c and s at different temperatures are summarized as follows

	20°C	25°C	30°C	35°C
c	4.292	4.207	4.025	3.829
s	1.521	1.416	1.455	1.539

As apparent in Table 3, the positive values of ΔG^0 and ΔH^0 indicate that the dissolution processes for all silver salts are non-spontaneous and endothermic. The negative values of ΔS^0 for *ortho*-chloro-, *para*-nitro-, and *ortho*-, *meta*-, and *para*-hydroxy-silver benzoates indicate that there is more order in the ionized form than in the unionized form in the corresponding dissolution processes of these silver salts. The negative values of ΔS^0 for these silver salts, as compared with other silver benzoates, might indicate that the stabilization of the water structure causes an increased order in the proximity of Ag^+ and $PhCOO^-$ ions, where Ph is the substituted phenyl group. The contrary variation of ΔS^0 and ΔC_p^0 for the dissolution processes of some silver benzoate might be due to the specific interactions between the silver benzoate and the water structure which may lead to both a decrease in the entropy and an increase in the heat capacity, lending support to the deviation of the relative solubilities of the silver benzoates from the relative strengths of the acids.

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