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Note

Solubility studies in aqueous media

III. Solubility product of silver benzoate and standard electrode potentials of silver-silver benzoate electrode in aqueous media

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In previous communications[1,2], we reported the solubility, and the solubility product of sparingly soluble silver salts in aqueous media over a range of temperatures. The present investigation deals with similar studies made on silver benzoate in aqueous solutions of sodium perchlorate at 20, 25, 30, and 35°C. The solubility of silver benzoate in aqueous solutions containing added electrolytes has received considerable attention. A survey of the literature shows that its solubility has been determined by numerous workers[3–7] in aqueous solutions in presence of different electrolytes at a number of single temperatures. But the thermodynamic parameters, such as ΔH°, and ΔS° for the dissolution of silver benzoate as well as the standard potentials of the silver–silver benzoate electrode in aqueous media are lacking. The present work has been undertaken with a view to evaluating the standard thermodynamic quantities as well as the standard potentials of the silver–silver benzoate electrode at 20, 25, 30 and 35°C in aqueous media.

EXPERIMENTAL

Sodium perchlorate was prepared according to the standard procedure given in the literature[8]. A stock solution of sodium perchlorate was prepared by dissolving a weighed quantity of sodium perchlorate in triply distilled water.

Sodium benzoate was prepared by the method[9] similar to that of potassium benzoate and dried at 110–120°C. Silver benzoate was prepared by mixing dilute solutions of silver nitrate (B.D.H., AnalaR) with the calculated amount of sodium benzoate. The crystals were washed with conductivity water and finally dried in a vacuum desiccator over calcium chloride for several weeks. The dried, colourless crystals, gave on analysis by standard methods a purity of 99.5%.

The solubility was determined by the method described earlier[1]. The solute contents were analysed by Volhard's method of determination of silver using a 0.01 M potassium thiocyanate solution and a calibrated microburette. The potassium thiocyanate solutions were standardized against silver nitrate which was previously standardized against potassium chloride (B.D.H. AnalaR). The titrations were accurate to ±0.2%.

RESULTS AND DISCUSSION

The experimental results of the solubility measurements are recorded in Table 1. The first column gives the molarity, c, of sodium perchlorate, the second the solubility, s of silver benzoate in moles per litre, averaged in each case, from three closely agreeing results; the third column lists the total salt concentration, $(c+s)$, which is the same as the ionic strength of the solution.

TABLE 1

SUMMARY OF SOLUBILITY DATA FOR SILVER BENZOATE
IN AQUEOUS SODIUM PERCHLORATE SOLUTIONS
AT DIFFERENT TEMPERATURES

$c \times 10^2$ $(mol\ l^{-1})$	$s \times 10^2$ $(mol\ l^{-1})$	$(c+s) \times 10^2$ $(mol\ l^{-1})$	$(c+s)^{\frac{1}{2}} \times 10^2$ $(mol\ l^{-1})^{\frac{1}{2}}$	$\dfrac{A(c+s)^{\frac{1}{2}} \times 10^2}{1+a^{\circ}B(c+s)^{\frac{1}{2}}}$	$-\log s$ $(mol\ l^{-1})$	$-\log s^{\circ\prime}$ $(mol\ l^{-1})$
Temperature 20°C						
0.75	1.1724	1.9224	13.87	6.564	1.9311	1.9967
0.50	1.0708	1.5708	12.51	5.835	1.9706	2.0289
0.25	0.9690	1.2190	11.09	5.218	2.0131	2.0652
0.10	0.8700	0.9800	9.90	4.690	2.0605	2.1074
0.01	0.8477	0.8577	9.26	4.409	2.0717	2.1158
					$-\log s^{\circ\prime}$ extrapolated	2.2140
					B' (l mol^{-1})	−11.54
Temperature 25°C						
0.75	1.2598	2.0098	14.17	6.601	1.9000	1.9660
0.50	1.1150	1.6150	12.71	5.974	1.9527	2.0124
0.10	0.9298	1.0298	10.14	4.845	2.0314	2.0798
0.05	0.9047	0.9547	9.76	4.676	2.0435	2.0902
0.025	0.8923	0.9173	9.57	4.507	2.0495	2.0945
					$-\log s^{\circ\prime}$ extrapolated	2.2001
					B' (l mol^{-1})	−11.73
Temperature 30°C						
0.75	1.3385	2.0885	14.45	6.659	1.8578	1.9243
0.50	1.2686	1.7686	13.29	6.287	1.8969	1.9597
0.25	1.0931	1.3431	11.60	5.437	1.9614	2.0157
0.15	1.0708	1.2208	11.05	5.194	1.9702	2.0221
0.10	1.0390	1.1390	10.68	5.126	1.9824	2.0336
					$-\log s^{\circ\prime}$ extrapolated	2.1676
					B' (l mol^{-1})	−11.70
Temperature 35°C						
0.75	1.6158	2.3658	15.38	7.247	1.7920	1.8644
0.50	1.4268	1.9268	13.88	6.601	1.8460	1.9120
0.15	1.1824	1.3324	11.54	5.676	1.9274	1.9702
0.10	1.1601	1.2601	11.23	5.424	1.9355	1.9897
0.01	1.0520	1.0620	10.30	5.007	1.9780	2.0280
					$-\log s^{\circ\prime}$ extrapolated	2.1248
					B' (l mol^{-1})	−11.88

The method of calculating the solubility is the same as in our previous papers[1,2], assuming that the salts employed are completely dissociated, the solubility, s, of silver benzoate at any salt concentration, c, may be written as

$$sf_{\pm} = s^{\circ} \tag{1}$$

which may be further written as

$$\log s^{\circ} = \log s + \log f_{\pm} \tag{2}$$

where the symbols have their usual significance.

As usual by following the Debye–Hückel theory, the mean activity coefficient may be expressed by

$$\log f_{\pm} = -A \frac{(c+s)^{1/2}}{1+a^{\circ}B(c+s)^{1/2}} + B'(c+s) \tag{3}$$

where A, B, and B' are the usual constants of the equation and a° is the ion-size parameter.

Combining eqns (2) and (3), the following equation is obtained

$$\log s - A \frac{(c+s)^{1/2}}{1+a^{\circ}B(c+s)^{1/2}} = \log s^{\circ} - B'(c+s) \tag{4}$$

By plotting the left-hand side of eqn (4) which is represented by the expression $\log s^{\circ\prime}$ against the total salt concentration $(c+s)$, a straight line should be obtained yielding an intercept equal to $\log s^{\circ}$ and a slope equal to $-B'$. Plots of such type at different temperatures are shown in Fig. 1. The values of $-\log s^{\circ}$ as obtained from the intercepts of these plots and those of B' as obtained from the slopes of these plots are shown in Table 1.

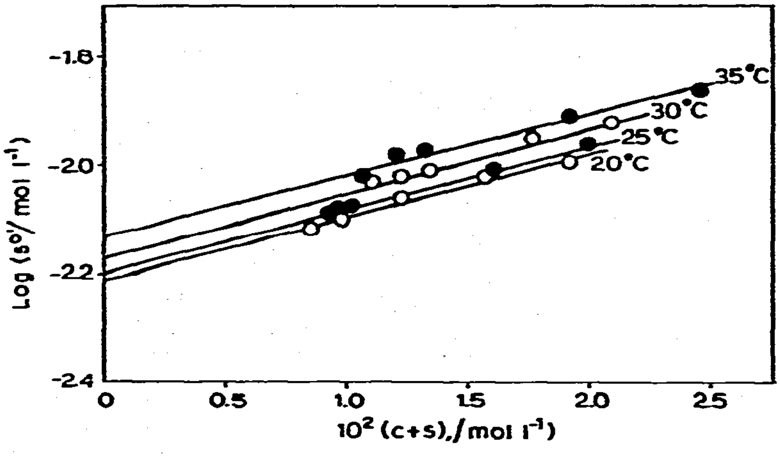

Fig. 1. Plot of $\log s^{\circ\prime}$ versus salt concentration.

The values of A and B, needed for the calculation of $\log s^{\circ\prime}$, were taken from the literature[10]. The ion-size parameter, a° has been calculated from the experimental data by the method used by Bates and Bower[11], which consisted of fitting eqn (4) to the data by the method of least squares for several values of a°, and then choosing as the best fit the value of a° which made the root-mean-square deviation a minimum. Since the a° parameter is probably almost insensitive to temperature[12], we therefore sought a single value of a° which would minimize the root-mean-square deviations for the whole body of data. The value of a° meeting this requirement was very close to 2A°. Essentially the same value was obtained by seeking the minimum mean deviation.

The values of s at rounded molarities of the salt, i.e., sodium perchlorate have been evaluated from eqn (5)

$$\log s = \log s^\circ + \frac{A(c+s)^{1/2}}{1+a^\circ B(c+s)^{1/2}} - B'(c+s) \tag{5}$$

by the method described earlier[1,2]. From the value of s, the mean activity coefficient, $f_\pm$ at the corresponding rounded molarity of the salt has been calculated using either eqn (1) or (3). The values of s and $f_\pm$ obtained are shown in Table 2.

TABLE 2

SUMMARY OF ACTIVITY COEFFICIENTS FOR SILVER BENZOATE IN AQUEOUS SODIUM PERCHLORATE SOLUTIONS AT DIFFERENT TEMPERATURES

$c \times 10^2$ (mol l^{-1})	$s \times 10^2$ (mol l^{-1})	$f_\pm$ from eqn (1)	$f_\pm$ from eqn (3)	$f_\pm$ from eqn (6)
Temperature 20°C				
0	0.8459	0.7221	0.7221	0.8986
1	1.3320	0.4585	0.4588	0.7505
2	2.5010	0.2442	0.2435	0.7798
Temperature 25°C				
0	0.8904	0.7084	0.7084	0.8952
1	1.4400	0.4382	0.4382	0.8328
2	3.6130	0.1726	0.1726	0.7575
Temperature 30°C				
0	0.9922	0.6852	0.6852	0.8888
1	1.6490	0.4122	0.4120	0.8247
2	19.9100	0.0520	0.0520	0.6507
Temperature 35°C				
0	1.1630	0.6451	0.6451	0.8790
1	2.1400	0.3505	0.3505	0.8090
2	30.1700	0.0460	0.0460	0.6657

As expected the $f_\pm$ values calculated with the help of eqn (1) agree well with those calculated from eqn (3). In the last column of Table 2, the $f_\pm$ values computed by Debye–Hückel's limiting expression

$$-\log f_{\pm} = A\sqrt{\mu} \tag{6}$$

are also shown. It will be observed that the activity coefficients calculated from the limiting Debye–Hückel equation are much higher than the experimental values.

The solubilities of silver benzoate in water in the absence of any added salt are found to be 0.8459×10^{-2}, 0.8904×10^{-2}, 0.9922×10^{-2} and 1.1630×10^{-2} mol l^{-1} at 20, 25, 30, and 35°C, respectively. Comparing the present set of data with the values reported earlier from solubility measurements in water by Holleman[3] (0.770×10^{-2} M) at 14.5°C, by Larson and Adell[4] (1.038×10^{-2} M) at 18°C, by Ephriam and Pfister[5] (0.948×10^{-2} M) at 20°C, by Noyes and Schwartz[6] (1.44×10^{-2} M) and by Kolthoff and Bosch[7] (1.162×10^{-2} M) at 25°C it is found that our values are in good agreement with those values reported earlier.

The solubility product is obtained by using the equation, $K_s = (s^\circ)^2$. The variation of K_s with temperature may be expressed by the equation

$$\log K_s = -23.9390 + 0.03796\,T + 2540.79/T \tag{7}$$

The standard free energy change ΔG°, for the dissolution process, $\mathrm{AgOBz(s)} \rightarrow \mathrm{Ag^+(aq)} + \mathrm{OBz^-(aq)}$ is obtained by the relation, $\Delta G^\circ = -RT\ln K_s$. A plot of $\log K_s$ against $1/T$ yields a straight line, from the slope of which the heat of solution (ΔH°) of silver benzoate has been calculated. 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 dissolution process may be evaluated from the relation,

$$\Delta S^\circ = (\Delta H^\circ - \Delta G^\circ)/T$$

These standard thermodynamic quantities are shown in Table 3.

TABLE 3

STANDARD THERMODYNAMIC QUANTITIES OF SILVER BENZOATE IN WATER AT DIFFERENT TEMPERATURES

Temp. (°C)	*$K_s\times10^4$* (mol^2 l^{-2})	*$\Delta G^\circ\times10^{-3}$* (J)	*$\Delta H^\circ\times10^{-3}$* (J)	*ΔS°* (J deg^{-1})
20	0.7158	23.26	31.79	29.11
25	0.7929	23.40	31.79	28.29
30	0.9845	23.24	31.79	28.21
35	1.3530	22.81	31.79	29.15

The standard potentials of the Ag–AgOBz electrode have been calculated at different temperatures by using the equation

$$E^\circ_{\mathrm{Ag-AgOBz}} = E^\circ_{\mathrm{Ag}} + \frac{RT}{F}\ln K_s \tag{8}$$

The standard electrode potential of silver, E°_{Ag} in water needed for this purpose was obtained from the empirical equation available in the literature[12a]. The standard potentials of the Ag–AgOBZ electrode can be represented by the equation

$$E^{\circ}_{t} = 0.5565 - 9.7 \times 10^{-4}(t-25) + 6.2 \times 10^{-5}(t-25)^2 \quad (9)$$

which predicts the values observed from 20–35°C with a maximum deviation of ±0.3 mV.

REFERENCES

1 U. N. Dash and J. Mohanty, *Thermochim. Acta*, 12 (1975) 189.
2 U. N. Dash, J. Mohanty and K. N. Panda, *Thermochim. Acta*, 16 (1976) 55.
3 A. F. Holleman, *Z. Phys. Chem.*, 12 (1893) 135.
4 E. Larson and B. Adell, *Z. Anorg. Chem.*, 196 (1931) 354.
5 E. A. Ephriam and Z. Pfister, *Z. Phys. Chem.*, 59 (1925) 196.
6 A. A. Noyes and D. Schwartz, *Z. Phys. Chem.*, 27 (1899) 279.
7 I. M. Kolthoff and W. Bosch, *J. Phys. Chem.*, 36 (1932) 1702.
8 H. H. Willard and G. F. Smith, *J. Am. Chem. Soc.*, 44 (1922) 2816.
9 U. N. Dash and B. Nayak, *Aust. J. Chem.*, 25 (1972) 941.
10 R. A. Robinson and R. H. Stokes, *Electrolyte Solutions*, Butterworth, London, 2nd. ed., 1959, p. 468.
11 R. G. Bates and V. E. Bower, *J. Res. Natl. Bur. Stand.*, 53 (1954) 283.
12 H. S. Harned and B. B. Owen, *The Physical Chemistry of Electrolytic Solutions*, Reinhold, New York, 3rd ed., 1967, Chap. 11 and 12, (a) p. 451.