THERMODYNAMICS OF SILVER SALICYLATE IN WATER AND WATER + 10, + 20, AND + 40 MASS PERCENT OF DIOXANE AT DIFFERENT TEMPERATURES

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(Received 5 May 1978)

ABSTRACT

The solubility studies on silver salicylate at different temperatures were made to derive (a) the standard electrode potential of the silver–silver salicylate electrode, (b) the mean activity coefficient of silver salicylate, (c) the dissociation constant of salicylic acid, and (d) the standard thermodynamic quantities, ΔG_t^0, ΔH_t^0, ΔS_t^0, and ΔC_{pt}^0, for the transfer of silver salicylate from the standard state in water to the standard state in water + 10, + 20, and + 40 mass percent of dioxane. The results are discussed in terms of the preferential solvation of the ions.

INTRODUCTION

Although the determinations of the solubility product of a number of sparingly soluble silver salts in aqueous and non-aqueous solvents have been made[1-9], little information is available regarding the effects of medium change upon the thermodynamic quantities of the silver salts. The present investigation aims at determining the standard electrode potential of the silver–silver salicylate electrode and the related thermodynamic quantities in aqueous and mixed solvents at temperatures ranging from 20 to 35°C, from the solubility measurements. The results are interpreted in terms of selective solvation of the two ions, the silver ion and the salicylate ion, with molecules of two species, water and dioxane. Also, the dissociation constants of salicylic acid have been determined in aqueous medium at these temperatures from the solubility measurements.

EXPERIMENTAL

Potassium salicylate was prepared by neutralizing a known weight of salicylic acid (E. Merck) with the required quantity of potassium bicarbonate (G.R.) solution, evaporating the solution to dryness, 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. Silver salicylate was precipitated in the

dark by mixing dilute solutions of silver nitrate (E.M., G.R.) and potassium salicylate. The precipitate was repeatedly washed with conductivity water and finally dried in a vacuum desiccator over calcium chloride in the dark for several weeks. The dried, white amorphous powder gave, on analysis by standard method, a purity of 99.5%.

The purification of dioxane (G.R., Merck) was done by treating it with beads of NaOH (G.R.) and refluxing for about 48 h. The refluxed product was distilled and subsequently refluxed again with shining pieces of sodium metal for 6 h. This sodium-treated dioxane was redistilled at the time of preparation of solutions to avoid the presence of peroxide which is formed on storing.

Stock solutions of sodium perchlorate (G.R.) were prepared by dissolving known weights of it in conductivity water and in water + 10, + 20, and + 40 mass percent of dioxane. Approximately 0.1 N solution of perchloric acid was prepared by using a G.R. sample of perchloric acid, and was standardized against a previously standardized sodium hydroxide (G.R.) solution. From the stock solutions of sodium perchlorate and perchloric acid, solutions of required strength were prepared by the method of double dilution.

The detailed description of the solubility measurements has been discussed in earlier work[1-9]. The solute contents of the solutions were analysed by Volhard's method of determining the silver ion using 1×10^{-3} M potassium thiocyanate solution. The potassium thiocyanate solutions were standardized against a standard silver nitrate solution which was previously standardized against potassium chloride (BDH, AnalaR).

RESULTS AND DISCUSSION

The hypothetical solubility s^0 of silver salicylate 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 was introduced[10] for the activity coefficient of silver salicylate over the experimental range of molarities c. This procedure is essentially the same as that used in our earlier studies[1-9].

From the solubility and activity coefficient relations, the function log s' is defined by

$$\log s' = \log s - \frac{A\,I^{1/2}}{1\,+\,Ba^0 I^{1/2}} = \log s^0 - b\,I \tag{1}$$

where A and B are the Debye–Huckel constants obtained from the literature for water[11] and water + 10, + 20, and + 40 mass percent of dioxane[12], a^0 is the ion-size parameter 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 versus the ionic strength I when extrapolated to infinite dilution, $I = 0$, assuming proper values of a^0 are chosen. By following the principle adopted by Roy et al.[13], the

values of a^0 were found to be 2.5, 4.5, 5, and 4 Å in water and water $+10$, $+20$, and $+40$ mass percent of dioxane, respectively.

The solubilities of silver salicylate at rounded molarities (e.g., $c = 0$, 0.01, 0.02 or 0.03 mole l^{-1}, etc.) were calculated from the equation[1-7, 9]

$$\log s = \log s^0 + \frac{A\,I^{1/2}}{1 + Ba^0 I^{1/2}} - b\,I \tag{2}$$

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 the same as that described in our earlier studies[1-7, 9]. The solubility product K_s has been calculated from the relation $K_s = (s')^2$, where s' is the solubility of silver salicylate at $c = 0$ mole l^{-1}. The values of K_s at various temperatures were fitted by the method of least squares to an equation of the form

$$-\log K_s = A/T + B + CT \tag{3}$$

where T is the thermodynamic temperature in degrees Kelvin. The parameters A, B, and C in eqn. (3) are presented in Table 1 for water and water $+$ dioxane compositions. The average deviation between the observed (experimental) values and the values calculated from eqn. (3) for different media is within ± 0.0008 logarithm units.

Using the K_s value, the standard electrode potential of the silver–silver salicylate electrode ($E^0_{Ag-AgSal}$) has been calculated in water medium from the equation

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

where E^0_{Ag} is the standard potential of the silver electrode in water and is known[11] over the temperature range under investigation. The value of E^0 thus obtained were fitted into the equation

$$E^0_t = 0.5356 - (1.58 \times 10^{-3})(t - 25) + (3.00 \times 10^{-6})(t - 25)^2 \tag{5}$$

over the temperature range 20 to 35°C within a deviation of ± 0.5 mV from the observed values.

TABLE 1

PARAMETERS OF EQN. (3)

Mass percent of dioxane	A	B	$10^2 C$
0	-984.29	12.495	-1.590
10	1762.57	-5.060	1.226
20	25 794.92	-164.172	27.570
40	0.3254	7.244	-0.853

The mean activity coefficients of silver salicylate calculated at rounded molarities[1-7, 9] by means of the following equations

$$sf_\pm = s^0 \tag{6}$$

$$\log f_\pm = \frac{-AI^{1/2}}{1 + Ba^0 I^{1/2}} + bI \tag{7}$$

and

$$\log f_\pm = -AI^{1/2} \tag{8}$$

show that there is good agreement between these values but beyond ca. 0.01 molar the values calculated by eqn. (8) show deviation from the observed values (e.g., calculated from eqns. (6) and (7)).

K_a (the thermodynamic dissociation constant of acid for the process HA $\rightleftharpoons$ H$^+$ + A$^-$) is related to K_c by the equation

$$\log K_a = \log K_c - \frac{2A\,I^{1/2}}{1 + Ba^0 I^{1/2}} \tag{9}$$

where K_c is the dissociation constant in terms of concentration and I is the ionic strength, and A, B, and a^0 have their usual significance (eqn. (1)). The "concentration dissociation constant" K_c was calculated from the expression

$$K_c = \frac{C_{H^+} \times C_{A^-}}{C_{HA}} \tag{10}$$

where $C_{A^-} = s_s^2/s_a$ (s_s is the observed solubility of silver salicylate in sodium perchlorate solutions and s_a is that in perchloric acid solutions of the same ionic strength) $C_{HA} = s_a - C_{A^-}$, $C_{H^+} = C_{HClO_4} - C_{HA}$ and $I = s_a + C_{H^+} = C_{HClO_4} + C_{A^-}$

TABLE 2

CORRECTED SOLUBILITY VALUES ($10^3 s_s$, MOLE L^{-1}) OF SILVER SALICYLATE IN AQUEOUS SODIUM PERCHLORATE SOLUTIONS FROM 20 TO 35°c

$10^2 C$ (mole l^{-1})	t (°C)			
	20	25	30	35
0.5			6.210	
1.5		6.244	6.449	
2.5	6.282		6.637	
3.5		6.585	6.795	6.984
4.5	6.564	6.717	6.937	7.131
5.5	6.683			7.259
6.5	6.790	6.952		7.382
7.5	6.892	7.071		7.492

Equation (10) is obtained from the concentrations of the species designated by following a reiteration procedure similar to that adopted by Dash[8] for obtaining the exact values of I and the corrected value of the solubility s_s of silver salicylate in sodium perchlorate solutions.

The corrected values of the solubility s_s of silver salicylate in sodium perchlorate solutions of the same molarity as that of perchloric acid calculated by following the reiteration procedure[8] are entered in Table 2. The pK_a values obtained from the extrapolation of the right-hand side of eqn. (9) to $I = 0$ were found to be 2.92 $\pm$ 0.01, 2.89 $\pm$ 0.06, 2.90 $\pm$ 0.05, and 2.91 $\pm$ 0.06, at 20, 25, 30 and 35°C, respectively. The pK_a of salicylic acid has earlier been reported from conductance measurements to be 2.973 at 25°C in aqueous medium[14]. This is slightly different from our value of 2.89 at the same temperature. Such differences exist even in very accurate determinations of equilibrium constants by the same or different physical methods, examples are plentiful in the literature[15]. Further, the pK_a values at different temperatures show that there is slightly uneven variation or these values with change of temperature. A similar trend is also observed in the pK_a values of benzoic acid reported earlier in aqueous medium[16].

The various thermodynamic quantities ΔG^0, ΔH^0, ΔS^0, and ΔC_p° for the dissolution process of silver salicylate in water and water $+10$, $+20$ and $+40$ mass percent of dioxane have been evaluated from the usual relations at different temperatures using the parameters A, B, and C of eqn. (3). The value of ΔH^0 of the dissociation process of salicylic acid has been calculated from the slope of the plot of pK_a vs. $1/T$, assuming it to be independent of temperature[8]. The ΔG^0, ΔH^0, and ΔS^0 values of dissociation of salicylic acid at 25°C were found to be 16 490 J mole^{-1}, 735.88 J mole^{-1}, and -52.84 J deg^{-1} mole^{-1}, respectively. Our value for ΔS^0 of dissociation is in good agreement with the value -46.44 J deg^{-1} mole^{-1} reported in the literature[17], whereas the ΔH^0 of dissociation (735.88 J mole^{-1}) shows poor agreement with the literature value[17] (3050.32 J mole^{-1}). Such discrepancy is generally not

TABLE 3

STANDARD THERMODYNAMIC QUANTITIES OF THE DISSOLUTION PROCESS

Ag Sal(s) $\rightarrow$ Ag$^+$ (solvated) + Sal$^-$ (solvated)

IN WATER AND WATER + DIOXANE MIXTURES AT 25°C

Mass percent of dioxane	$\Delta G^0 \times 10^3$ (J mole^{-1})	$\Delta H^0 \times 10^{-3}$ (J mole^{-1})	ΔS^0 (J mole^{-1} deg^{-1})	ΔC_p^0 (J mole^{-1} deg^{-1})
0	25.41	8.19	−57.79	181.44
10	25.73	12.89	−43.06	−139.94
20	25.94	25.11	−2.78	−3146.00
40	26.83	14.51	−41.36	97.33

TABLE 4

STANDARD THERMODYNAMIC CONSTANTS FOR THE TRANSFER OF SILVER SALICYLATE FROM WATER TO
WATER + DIOXANE MIXTURES AT 25°C

Mass percent of dioxane	ΔG_t^0 (J mole^{-1})	ΔH_t^0 (J mole^{-1})	ΔS_t^0 (J mole^{-1} deg^{-1})	$\Delta C_{P_t}^0$ (J mole^{-1} deg^{-1})
10	320	4700	14.73	−321.38
20	530	16 920	55.01	−3327.44
40	1420	6320	16.43	−84.11

uncommon in the determinations of the thermodynamic properties of the electrolytes
by different physical methods.

It is of interest to compare the results of the standard entropy of dissolution
of silver salicylate in water and in different water + dioxane mixtures (Table 3). The
values of ΔS^0 in these solvents are expected to be negative, but in water + dioxane
mixtures they appear to be less negative. This might be due to the fact that the degree
of reorientation and partial immobilization of the dioxane and water molecules by
Ag^+ ion and salicylate ion is not greater in the mixed solvents than in water.

The thermodynamic constants ΔG_t^0, ΔH_t^0, ΔS_t^0 and ΔC_{pt}^0 for the transfer of
silver salicylate from water to the mixed solvents of various compositions have been
derived from the usual relations[18] and these values at 25°C are listed in Table 4.
The values of ΔG_t^0 appear to be positive for all compositions, increasing sharply to
a more positive value for +40 mass percent of dioxane. The positive values of ΔG_t^0
lend support to the view that silver salicylate is more strongly stabilized by solvation
with water molecules in mixed solvents than in water. Further, the transfer enthalpy
and entropy for water + dioxane mixtures appear to be positive and these positive
values indicate that for a transfer of silver salicylate from water to water + dioxane
mixtures, the silver ion and the salicylate ion will orient solvent molecules less readily
in mixed solvents than in pure water. Consequently, the degree of solvent orientation
is less in water + dioxane mixtures than in aqueous medium.

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 U. N. Dash and P. C. Rath, *Thermochim. Acta*, 16 (1976) 407.
4 R. C. Das, U. N. Dash and K. N. Panda, *Acta Chim.*, (1977) in press.
5 B. Nayak and U. N. Dash, *Thermochim. Acta*, 6 (1973) 223.
6 U. N. Dash and B. Nayak, *Thermochim. Acta*, 11 (1975) 17.
7 U. N. Dash, *Thermochim. Acta*, 12 (1975) 197.
8 U. N. Dash, *Thermochim. Acta*, 11 (1975) 25.
9 U. N. Dash, U. K. Nayak, S. K. Nayak and S. P. Pattnaik, submitted to *Aust. J. Chem.*
10 E. A. Guggenheim and J. E. Prue, *Physicochemical Calculations*, North-Holland, Amsterdam,
   1956, pp. 228–30.

11 H. S. Harned and B. B. Owen, *The Physical Chemistry of Electrolytic Solutions*, Reinhold, New York, 1967, pp. 165, 451.
12 U. C. Mishra, *Ph.D. Thesis*, Utkal University, Orissa, India, 1976.
13 R. N. Roy, R. A. Robinson and R. G. Bates, *J. Am. Chem. Soc.*, 95 (1973) 8231.
14 J. L. Ernst, R. J. Erving and J. Menashi, *Trans. Faraday Soc.*, 66 (1964) 56.
15 L. G. Sillen and A. E. Martell (Editors), *Stability Constants of Metal Ion Complexes*, 2nd edn., Chemical Society, Publication, London, 1964.
16 A. V. Jones and H. N. Parton, *Trans. Faraday Soc.*, 48 (1952) 8.
17 J. J. Christensen, R. M. Izatt and L. D. Hansen, *J. Am. Chem. Soc.*, 89 (1967) 213.
18 F. Franks (Ed.) *Physico-Chemical Processes In Mixed Aqueous Solvents*, Heinemann Educational Books Ltd., London, 1969.