

A Potentiometric Study of the Complex Compounds between Silver and Benzoate Ions

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The object of this work was a quantitative determination of the complex compounds, formed by dissolving silver perchlorate and sodium benzoate in water and adding sodium perchlorate to a constant ionic strength. In one series an ionic strength of 0.2 C and in another 1 C was chosen.* Due to the careful work on the solubility of silver benzoate, carried out by Larsson and Adell¹, the activity coefficients are well known even in rather concentrated salt solutions, so an attempt has also been made to calculate the thermodynamic equilibrium constant of the formation of the simplest complex, *i. e.* the silver benzoate molecule itself.

EXPERIMENTAL DETAILS

Potentiometric measurements were carried out in a thermostat at 25.00° C, in the same manner as previously described by the author². The potentiometer was from Leeds & Northrup, type K₁.

The silver perchlorate was prepared by dissolving newly precipitated and carefully washed silver oxide in perchloric acid, *p. a.* The surplus of silver oxide was filtered away from the resulting neutral (pH ≈ 6) silver perchlorate solution, which was then analyzed by gravimetric determination of the silver ions as silver chloride. Due to the high solubility of silver perchlorate in water, no purification by recrystallization was attempted. The analyzed stock solution of silver perchlorate was about 3 C, and all the solutions of silver perchlorate were prepared from this stock by dilution.

The sodium perchlorate, *purum*, was purified by recrystallization until it became free from chloride. The recrystallization was carried out at such a high temperature (>60° C) that a nonaqueous salt resulted. From this product stock solutions were prepared.

* C stands for gram formula weight per liter.

Stock solutions of sodium benzoate were obtained by careful neutralization of a known amount of recrystallized benzoic acid, *p. a.*, with carbonate free sodium hydroxide solution. Attempts to recrystallize sodium benzoate directly seemed to indicate that it was very difficult to obtain a chloride free product in this way.

Mercury electrodes in 1 C or 0.2 C solutions of sodium perchlorate, saturated with mercurous sulphate, were used as reference electrodes.

Brown's³ silver-silver chloride electrodes were used to measure the silver ion concentrations. These electrodes functioned well also in benzoate solutions. The reproducibility of the electromotive forces decreased with increasing benzoate concentrations, but that was probably due to the increasing liquid junction potentials of the cells. When junction solutions were used, 1 or 0.2 C NaClO₄ respectively, the emf of a cell could be reproduced with an accuracy of 0.3–0.4 mV at the highest benzoate concentrations, but with less deviations with decreasing amounts of benzoate in the solution.

MEASUREMENTS AND CALCULATIONS OF THE EQUILIBRIUM CONSTANTS

The measurements at an ionic strength 1 C are shown in Table 1. The solutions in question were produced by adding portions of a 1 C sodium benzoate solution from a burette to an exactly known volume of an initial solution, containing 0.000950 C AgClO₄ + 0.999 C NaClO₄ or 0.00295 C AgClO₄ + 0.997 C NaClO₄ in the electrode vessel. After every portion added from the burette, the emf of the cell was measured. In Table 2 the measurements at the ionic strength 0.2 C are to be found. Here the 'titration' was performed in the same way with a 0.2 C solution of sodium benzoate in the burette and an initial solution in the electrode vessel of 0.00299 C AgClO₄ + 0.197 C NaClO₄. The emf E in the tables is the difference between the emf of the initial cell free from benzoate, and the emf of the same cell after the addition of benzoate.

c_{Ag} and c_{B} represents the total concentration of silver and benzoate respectively, while $[\text{Ag}^+]$ and $[\text{B}^-]$ is the concentration of free silver and benzoate ions. $[\text{Ag}^+]$ is calculated from Nernst's formula, which for our purpose may be written:

$$E_{\text{corr}} = 59.16 \log \frac{c_{\text{Ag}}^0}{[\text{Ag}^+]} \quad \text{I}$$

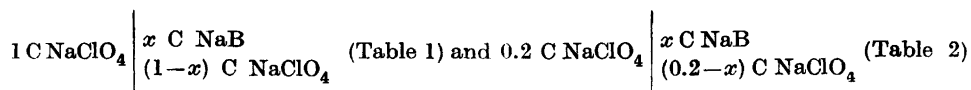
where c_{Ag}^0 is the silver concentration of the 'benzoate free' initial solution and E_{corr} the already mentioned emf E , corrected for the liquid junction potential according to Henderson (see *e. g.* Bjerrum and Unmack⁴). For the calculation of this correction the ionic mobility at infinite dilution has been used, *viz.* $u_{\text{Na}} = 50.1$, $v_{\text{ClO}_4} = 68$ and $v_{\text{B}} = 32.5$, *i. e.* the values in the tables of Landolt-Börnstein. In consequence of the great difference between the mobilities of benzoate and perchlorate ions, this correction becomes exceptionally great and probably rather uncertain. By putting in a suitable salt bridge between

Table 1. Titration with 1 C sodium benzoate. Ionic strength 1 C.

c_{Ag} mC	c_B mC	E mV	E_{corr} mV	$[Ag^+]$ mC	$[B^-]$ mC	$F_1(B^-)$ C^{-1}
0.950	0	0	0	0.950	0	× *
0.941	9.70	1.2	1.1	0.910	9.67	3.4
0.932	19.22	2.3	2.1	0.875	19.16	3.4
0.914	37.9	4.4	4.1	0.809	37.8	3.44
0.897	55.9	6.4	6.0	0.752	55.7	3.46
0.864	90.4	10.3	9.6	0.654	90.2	3.56
0.849	106.7	12.1	11.3	0.612	106.4	3.64
0.820	137.3	15.4	14.3	0.545	137.0	3.68
0.792	166.1	18.7	17.4	0.483	165.8	3.86
0.732	229.9	25.5	23.7	0.378	229.5	4.20
0.679	284.9	31.5	29.2	0.306	284.5	4.28
0.595	374	41.1	38.1	0.215	373	4.74
0.529	443	48.9	45.3	0.163	442	5.08
0.476	499	54.9	50.8	0.132	498	5.17
2.95	0	0	0	2.95	0	⊙ *
2.93	9.70	1.2	1.1	2.83	9.60	3.3
2.89	19.22	2.3	2.1	2.72	19.1	3.3
2.84	37.9	4.6	4.3	2.50	37.5	3.6
2.79	55.9	6.7	6.3	2.31	55.4	3.7
2.68	90.4	10.6	9.9	2.01	89.7	3.7
2.64	106.7	12.3	11.5	1.89	105.9	3.75
2.54	137.3	15.5	14.4	1.69	136.4	3.7
2.46	166.1	18.7	17.4	1.50	165.1	3.9
2.27	229.9	25.3	23.5	1.18	228.7	4.0
2.11	284.9	31.0	28.7	0.967	283.7	4.2
1.847	374	40.5	37.5	0.685	373	4.5
1.642	443	48.1	44.5	0.522	442	4.85
1.474	499	54.2	50.1	0.420	498	5.0
1.180	600	66.2	61.3	0.272	599	5.6

the two half-elements of the cells, the liquid junction potential might have been diminished, but at the same time it would have been quite impossible to estimate the necessary correction.

The liquid junction potential was calculated for the boundaries



* These signs are used to distinguish $F_1(B^-)$ -values, connected with different c_{Ag} (cf. Fig. 1).

Table 2. Titration with 0.2 C sodium benzoate. Ionic strength 0.2 C.

c_{Ag} mC	c_B mC	E mV	E_{corr} mV	$[Ag^+]$ mC	$[B^-]$ mC	$F_1(B^-)$ C^{-1}
2.99	0	0	0	2.99	0	●
2.96	1.94	0.5	0.4	2.94	1.90	3.6
2.93	3.84	1.2	1.0	2.88	3.77	4.5
2.88	7.58	2.2	2.0	2.78	7.47	4.8
2.82	11.18	3.0	2.6	2.70	11.03	4.0
2.72	18.08	4.9	4.2	2.54	17.87	4.0
2.67	21.34	5.8	4.9	2.47	21.08	3.8
2.58	27.5	7.6	6.5	2.32	27.2	4.1
2.49	33.2	9.2	7.9	2.20	32.8	4.0
2.30	46.0	12.8	11.0	1.95	45.5	4.0
2.14	57.0	16.3	14.0	1.73	56.5	4.2
1.872	74.8	22.3	19.2	1.42	74.2	4.3
1.664	88.6	27.1	26.2	1.20	88.0	4.4
1.498	99.8	31.3	27.2	1.04	99.2	4.4

for some round values of the benzoate concentration x . The correction was then drawn in a diagram as a function of $x = c_B$. In such a diagram, the correction could be interpolated for the c_B values of the tables. The influence upon the liquid junction potential by the small amounts of silver in the solutions has thus been neglected. The correction is largest at the ionic strength 0.2 C, where a greater percentage of perchlorate is exchanged for benzoate. One advantage of working at a high ion concentration, *e. g.* 3 C, is that there are less liquid junction potentials; but, on the other hand, the calculations of the activity coefficients turn out to be more difficult at increasing concentrations. The curves, describing the variation of the activity coefficients, regarded as functions of the ionic concentration, are perhaps also steeper at a concentration of 3 C, as the activity coefficients often have a minimum about 0.5 or 1 C, where it thus ought to be easiest to maintain constant activity conditions.

The benzoate ion concentration, $[B^-]$, has been calculated by the methods previously described². The calculation is very simple in the present case, since c_{Ag} is small and the complex compounds are weak, and therefore $[B^-]$ is nearly equal to c_B . The little correction that must be done, is limited by $(c_{Ag} - [Ag^+])$ and $2(c_{Ag} - [Ag^+])$, and as $(c_{Ag} - [Ag^+])$ is so small compared to c_B , it is of very little importance if c_B is corrected with $(c_{Ag} - [Ag^+])$ or twice this quantity when calculating $[B^-]$.

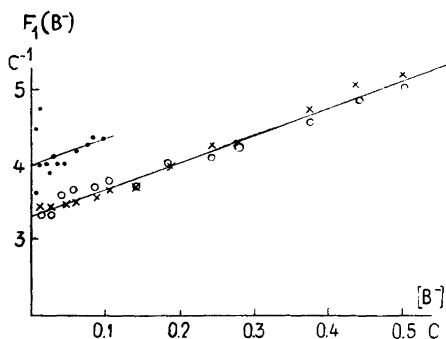


Fig. 1. $F_1(B^-)$ in the ion media 0.2 and 1 C NaClO_4 .

$$\text{The points: } F_1(B^-) = \frac{c_{\text{Ag}} - [\text{Ag}^+]}{[\text{Ag}^+] \cdot [B^-]}$$

The lower line (1 C): $F_1(B^-) = 3.3 + 3.6 [B^-]$. The upper line (0.2 C) is drawn parallel to the lower one, as β_2 is perhaps relatively independent of the ionic strength.

$F_1(B^-)$, in the tables, is the function previously used by the author to calculate the complexity constants β_n^2 . At the ionic strength 1 C, $F_1(B^-)$ can be described by a straight line within the limits of unavoidable errors of measurements (*q. v.* Fig. 1). The diagram gives $\beta_1 = 3.3 \pm 0.1 \text{ C}^{-1}$ and $\beta_2 = 3.6 \pm 0.5 \text{ C}^{-2}$ as values of the complexity constants of AgB and AgB_2^- respectively. The attainable range of measurements is too small to let us conclude with certainty that $F_1(B^-)$ does not deviate from a straight line. Such a deviation would mean that complex ions with more than two benzoate ligands should exist in the solutions. At the ionic strength 0.2 C the attainable range of c_B is still less, and therefore not even the slope of the line $F_1(B^-)$ can be settled. Thus only $\beta_1 = 4.0 \pm 0.2 \text{ C}^{-1}$ is calculated from the measurements in Table 2.

THE THERMODYNAMIC EQUILIBRIUM CONSTANT β_1^0

The calculated values of β_1 are concentration constants, valid only in the corresponding ionic conditions, *i. e.* 0.2 and 1 C sodium perchlorate solutions. Thus

$$\beta_1 = \frac{[\text{AgB}]}{[\text{Ag}^+][B^-]} \quad \text{II}$$

The real equilibrium constant β_1^0 is defined by $\beta_1^0 = \frac{(\text{AgB})}{(\text{Ag}^+)(B^-)}$, III

if, as usual, (s) means the activity and [s] the concentration of a substance s. β_1^0 can be calculated, if the activity coefficients, f_s , are known in the ionic media used, as

$$\beta_1^0 = \frac{f_{\text{AgB}}}{f_{\text{Ag}} \cdot f_B} \cdot \frac{[\text{AgB}]}{[\text{Ag}^+][B^-]} = \frac{f_{\text{AgB}}}{f_{\text{Ag}} \cdot f_B} \cdot \beta_1 \quad \text{IV}$$

The mean activity coefficient of silver benzoate, at 18° C $f = \sqrt{f_{\text{Ag}} \cdot f_{\text{B}}}$, has been determined by Larsson and Adell¹ in several salt solutions. At an ionic concentration of 0.2 C these authors found $-\log f = 0.14$, *i. e.* $f^2 = 0.52$, determined in solutions of sodium-, potassium- and barium nitrate with insignificant deviations. At the ionic concentration 1 C they found $-\log f = 0.21$, *i. e.* $f^2 = 0.38$, determined in sodium and potassium nitrate. The authors, it is true, assumed the silver benzoate to be completely dissociated, but their method of extrapolation might partly compensate the rather insignificant error that was caused by the small amounts of undissociated silver benzoate, which existed in their solutions notwithstanding the small concentrations of benzoate and silver ions.

The calculated mean activity coefficients thus seem to be rather independent of the nature of the ionic conditions and therefore ought to be valid in solutions of sodium perchlorate. The fact that Larsson and Adell apparently found very differing coefficients in acetate solutions, can now be accounted for by the formation of complex compounds between silver and acetate ions, taking place to a great extent in the concentrated acetate solutions also examined by the authors^{Cf. 2}. As activity coefficients are known to vary only slowly with changing temperature, the coefficients, determined by Larsson and Adell at 18°, can also be used at a temperature of 25° in the following approximate calculations.

The activity coefficient, f_{AgB} , of the uncharged compound AgB is not known, but its value is probably nearly equal to 1. Larsson⁵ determined the activity coefficient of the undissociated molecule HB of benzoic acid in several salt solutions and found that this coefficient was very little influenced even by great concentrations of sodium perchlorate, contrasting to other salt media investigated.

Thus if $f_{\text{AgB}} = 1$, and $f_{\text{Ag}} \cdot f_{\text{B}} = f^2$ is taken from¹, β_1^0 can be calculated from equation IV as follows. From the measurements at the ionic strength 0.2 C: $\beta_1^0 = 4.0/0.52 = 7.7 \pm 1$, and at 1 C: $\beta_1^0 = 3.3/0.38 = 8.7 \pm 0.5$, or as a mean $\beta_1^0 = 8.2 \pm 1 \text{ C}^{-1}$. The accordance of the two calculated values of β_1^0 is as good as can be expected, especially in view of the uncertainty of the liquid junction potential, which is most pronounced at an ionic strength of 0.2 C. The value of this potential, calculated according to Henderson (*l. c.*), is perhaps to be regarded more as an approximate measure of the possible error of the measured emfs than as a quantitatively reliable correction. By calculating β_1 at the ionic strength 0.2, without any correction for the diffusion potential, we arrive at a value of 4.6 instead of 4.0.

Kolthoff and Bosch⁶ have determined the silver ion activity by potentiometric measurements in solutions, saturated with silver benzoate. They

draw only the qualitative conclusion that silver benzoate is not completely dissociated. From their measurements, however, an approximate value of β_1^0 can be computed. By dissolving silver benzoate in distilled water at 25°, the authors determine the solubility $c_{\text{Ag}} = 0.01162$ C and the silver ion activity $(\text{Ag}^+) = 0.009462$ C. The latter value was assigned an uncertainty of 2 %, arising from an assumed fault of 0.5 mV in the emf measurements. From these figures the authors calculated the apparent activity coefficient of the silver ion to be $0.009462/0.01162 = 0.813$. This value is so much less than the theoretical value, calculated according to the limit law of Debye and Hückel, *i. e.* $-\log f_{\text{Ag}} = 0.5 \sqrt{0.01162}$, giving $f_{\text{Ag}} = 0.883$, that the authors concluded that the silver benzoate was incompletely dissociated. From the cited values, we can calculate β_1^0 , assuming that the real activity coefficients can be calculated from the limit law of Debye and Hückel and that AgB is the only complex compound in such a diluted solution ($[\text{AgB}_2^-]$ ought to be less than 1 % of $[\text{AgB}]$, if the values of β_1 and β_2 of the present paper are approximately correct). Then the following equations are valid:

$$\begin{cases} [\text{Ag}^+] \cdot f_{\text{Ag}} = 0.009462 \\ -\log f_{\text{Ag}} = 0.5 \sqrt{[\text{Ag}^+]} \end{cases}$$

an equation system, giving $[\text{Ag}^+] = 0.01066$ and $f_{\text{Ag}} = 0.887$. Thus the concentration of undissociated silver benzoate $[\text{AgB}] = c_{\text{Ag}} - [\text{Ag}^+] = 0.00096$, and $\beta_1^0 = [\text{AgB}]/(\text{Ag}^+)^2 = 10.7 \pm 2.5 \text{ C}^{-1}$, where the proposed uncertainty corresponds to an uncertainty of 2 % in (Ag^+) . The value, calculated from the measurements of Kolthoff and Bosch, thus coincides within the limits of experimental error with β_1^0 from the present paper.

SUMMARY

1. By 'potentiometric titrations' of silver perchlorate in 1 C NaClO_4 with 1 C sodium benzoate (NaB) the existence of the complex compounds AgB and AgB_2^- was proven and their complexity constants determined to $\beta_1 = 3.3 \pm 0.1 \text{ C}^{-1}$ and $\beta_2 = 3.6 \pm 0.3 \text{ C}^{-2}$ (concentration constants) at 25° C.

2. Complexes containing more than two ligands, *e. g.* AgB_3^{2-} , could not be discovered. It cannot, however, be absolutely denied that such compounds might exist in small concentrations in the solutions examined, and that they thus might be dominant at sufficiently high concentrations of benzoate ions.

3. Neither did binuclear compounds of the type Ag_2B^+ , Ag_2B_2 , Ag_2B_3^- etc. exist in detectable concentrations, as is seen from the fact that the function

$F_1(B^-)$ in Table 1 or Fig. 1 is independent of c_{Ag} ^{cf. 2}. As some of the solutions investigated are supersaturated with silver benzoate, such polynuclear compounds could never be formed in aqueous solutions in detectable concentrations, except possibly in those solutions made by dissolving silver benzoate in concentrated solutions of a very soluble silver salt.

4. In 0.2 C $NaClO_4$ β_1 has been determined to be $4.0 \pm 0.2 C^{-1}$.

5. By the aid of the mean activity coefficient of silver benzoate, found in the literature, the thermodynamic equilibrium constant β_1^0 has been calculated to be $8.2 \pm 1 C^{-1}$.

Finally I wish to express my gratitude to Prof. Erik Larsson, the head of the Institution of Organic Chemistry of Chalmers' Institute of Technology, who made the present work possible by placing the precious potentiometer of his institution at my disposal. I also wish to thank Mrs. Barbro Aggeryd, who has carried out a great part of the laboratory work for this paper.

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