ISSN 1070-3632, Russian Journal of General Chemistry, 2006, Vol. 76, No. 6, pp. 881–884. © Pleiades Publishing, Inc., 2006.
Original Russian Text © M. Kopacz, B. Bujonek, A. Kuzniar, S. Kopacz, 2006, published in Zhurnal Obshchei Khimii, 2006, Vol. 76, No. 6, pp. 921–924.

Complexes of Barium Ions with Quercetin-5'-sulfonic Acid and Sodium Salt of Morin-5'-sulfonic Acid

M. Kopacz, B. Bujonek†, A. Kuzniar, and S. Kopacz

Rzeszow Polytechnic Institute,
pr. Powstancow Warszawy 6, Rzeszow, 39-959 Poland

Received August 28, 2004

Abstract—Complex formation of Ba^{2+} ions with quercetin-5'-sulfonic acid and sodium salt of morin-5'-sulfonic acid was studied by potentiometry. Solid complexes were obtained, and their composition and physicochemical properties were studied.
DOI: 10.1134/S1070363206060077

Quercetin-5'-sulfonic acid (QSA) and sodium salt of morin-5'-sulfonic acid (NaMSA) [1] are readily soluble in water, unlike quercetin and morin. These compounds are nontoxic and form chelates with toxic metal ions, such as barium. In the present work we studied the stability of barium complexes of QSA and NaMSA with the aim to assess the feasibility of the latter reagents as antidotes. It should be noted that Ba^{2+} complexes of QSA and NaMSA have not so far been reported. We previously studied [2] complex formation of Mg^{2+} and Ca^{2+} ions with NaMSA and obtained an estimate of 2.90 ± 0.06 for the $\log\beta_1$ of the Mg^{2+} complex.

To find conditions for complex formation of Ba^{2+} with QSA and NaMSA, we titrated aqueous solutions of QSA and NaMSA in the absence or in the presence of barium ions at varied ligand:metal ratios ($c_L : c_M$), with 0.1 M NaOH. The ligand concentration was ~10^{-3} M. The ionic strength of the solution of 0.1 was maintained constant with $NaClO_4$ solution (c 1 M). All experiments were performed under constant stirring at 25 ± 1°C. Solutions of QSA and mixtures of QSA with Ba^{2+} ions were titrated at $c_L : c_M = 2:1$ and pH 2.3–8 (Fig. 1). The fact that the titration curves at pH > 6 for the two titrates differed from each other gave evidence for the complex formation between Ba^{2+} and QSA.

Solutions of NaMSA and NaMSA with Ba^{2+} ions at $c_L : c_M = 2:1$ were titrated at pH 2.5–11. The titration curves were identical over the entire pH range. During titration of a mixture of NaMSA and Ba^{2+} at $c_L : c_M = 4:1$ in a weakly acidic medium, the solutions got turbid, and further addition of NaOH caused precipitate formation. At pH > 6, the solutions were transparent. The titration curves of NaMSA and a solution of NaMSA containing Ba^{2+} ions at pH 6–8 were identical and got different at pH > 8, on account of complex formation (Fig. 1).

In the course of titration of QSA with Ba^{2+} at pH 5.5–6.8, for each experimental concentration of

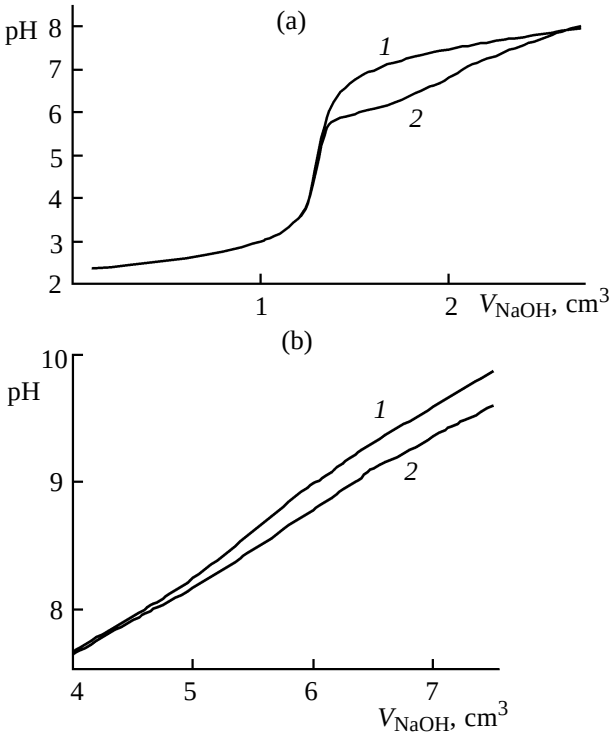

Fig. 1. Titration curves of solutions: (a) (*1*) QSA (c 3.5×10^{-3} M) and (*2*) QSA (c 3.5×10^{-3} M) in the presence of Ba^{2+} (c 1.7×10^{-3} M); and (b) (*1*) NaMSA (c 7×10^{-3} M) and (*2*) NaMSA (c 7×10^{-3} M) in the presence of Ba^{2+} (c 1.7×10^{-3} M).

† Deceased.

hydrogen ions we calculated the equilibrium concentration of the ligand ([L]), as well as the number of ligands ($\bar{n}$) bound to the metal ion, by Eqs. (1) and (2) [3].

$$[L] = \frac{c_{QSA} + c_Z - [H^+]}{[H^+](K_{a_1})^{-1}}, \quad (1)$$

$$\bar{n} = \frac{c_Z + [H^+] - [L]}{c_M}. \quad (2)$$

Here [L] is the concentration of the ligand; $\bar{n}$, average number of ligands; c_Z, concentration of NaOH; and K_{a1} 3.39×10^{-8}, dissociation constant of QSA [4].

The [L] and $\bar{n}$ values for solutions of NaMSA containing Ba^{2+} ions were calculated by Eqs. (3) and (4) [5].

$$[L] = \frac{(3 - a)c_L - [H^+] + [OH^-]}{[H^+](K_{a_1})^{-1} + 2[H^+](K_{a_2})^{-1} + 3[H^+](K_{a_1})^{-1}(K_{a_2})^{-1}(K_{a_3})^{-1}}, \quad (3)$$

$$\bar{n} = \frac{c_L - [L]\{1 + [H^+](K_{a_1})^{-1} + [H^+]^2(K_{a_2})^{-1}(K_{a_3})^{-1} + [H^+]^3(K_{a_1})^{-1} + [H^+]^2(K_{a_2})^{-1}(K_{a_3})^{-1}\}}{c_M}. \quad (4)$$

Here [L] and $\bar{n}$ are the same as in Eqs. (1) and (2); c_L, analytical concentration of the ligand; a, titration fraction; $[H^+]$, equilibrium concentration of hydrogen ions; $[OH^-]$, equilibrium concentration of hydroxide ions; c_M, analytical concentration of metal ions; and K_{a1} 3.31×10^{-5}, K_{a2} 2.04×10^{-8}, and K_{a3} 3.39×10^{-10}, step dissociation constants of NaMSA [6].

From [L] and $\bar{n}$, we obtained $\bar{n} = f(pL)$ dependences and on their basis, for $\bar{n}$ 0.5, determined $\log\beta_1$ 3.99+0.02 for the complex BaQSA and $\log\beta_1$ 2.97 ± 0.01 for the complex BaMSA, where MSA is the anion of NaMSA. To define more exactly the stability constants obtained by the Bjerrum method from [L] and $\bar{n}$, we also made use of the Rossoti method [7]. In the

$$\frac{\bar{n}}{(1 - \bar{n})[L]} = f\frac{(2 - \bar{n})[L]}{(1 - \bar{n})}$$

coordinates, straight lines described by general equation (5) were obtained.

$$y = ax + b. \quad (5)$$

The a and b coefficients were calculated by the least-squares method: for BaQSA, $y = 6.89 \times 10^6 x + 9.93 \times 10^3$, and BaMSA, $y = 1.74 \times 10^5 x + 9.32 \times 10^2$.

The stability constant of BaQSA is 9.93×103, which an order of magnitude higher than that of BaMSA. This result implies that QSA forms a stronger complex with Ba^{2+} than NaMSA, and, therefore, can better remove barium ions from human organism.

Previously we showed that QSA is an active antidote against cadmium(II), mercury(II), and lead(II) ions [8].

Our present results provide evidence to show that QSA and NaMSA in aqueous solutions form with Ba^{2+} complexes of composition ML. Group IIA metal ions do not form strong hydroxo complexes in aqueous solutions [9]. Thus, the condition $pH \leq 14 - 2 - \log\beta_1$ is fulfilled [3], and the fraction of hydroxo complexes at pH < 11.3 is smaller than 1%. These data suggest that the complex formation of Ba^{2+} with QSA and NaMSA occurs by reactions (6) and (7).

QSA (H_4L^-):

$$Ba^{2+} + H_5L^- \rightleftarrows [Ba(H_4L)] + H^+, \quad (6)$$

NaMSA (H_3L^{3-}):

$$Ba^{2+} + H_3L^{3-} \rightleftarrows [Ba(H_2L)]^{2-} + H^+. \quad (7)$$

Using aqueous solutions with Ba^{2+}, QSA, and NaMSA concentrations of 0.01 M, we synthesized complexes at pH 1.3–1.5 and varied molar concentration ratios of Ba^{2+} (c_M) and ligand (c_L): c_M: c_L = 1 : 3, 1 : 5, and 5 : 1. In all the cases, yellow precipitates formed, which were separated, washed, air-dried, and analyzed for carbon, hydrogen, sulfur, barium, sodium, and water.

The following elemental analyses were obtained. For BaQSA: found, %: C 35.84; H 2.80; Ba 13.38; S 6.39; H_2O 10.54. $Ba(C_{15}H_9O_{10}S)_2 \cdot 6H_2O$. Calculated, %: C 35.75; H 3.00; Ba 13.62; S 6.36; H_2O 10.72. For BaMSA: found, %: C 34.27; H 3.08; Ba 13.74; S 6.18; H_2O 13.90. $Ba(C_{15}H_9O_{10}S)_2 \cdot 8H_2O$. Calculated, %: C 34.51; H 3.28; Ba 13.15; S 6.14; H_2O 13.80.

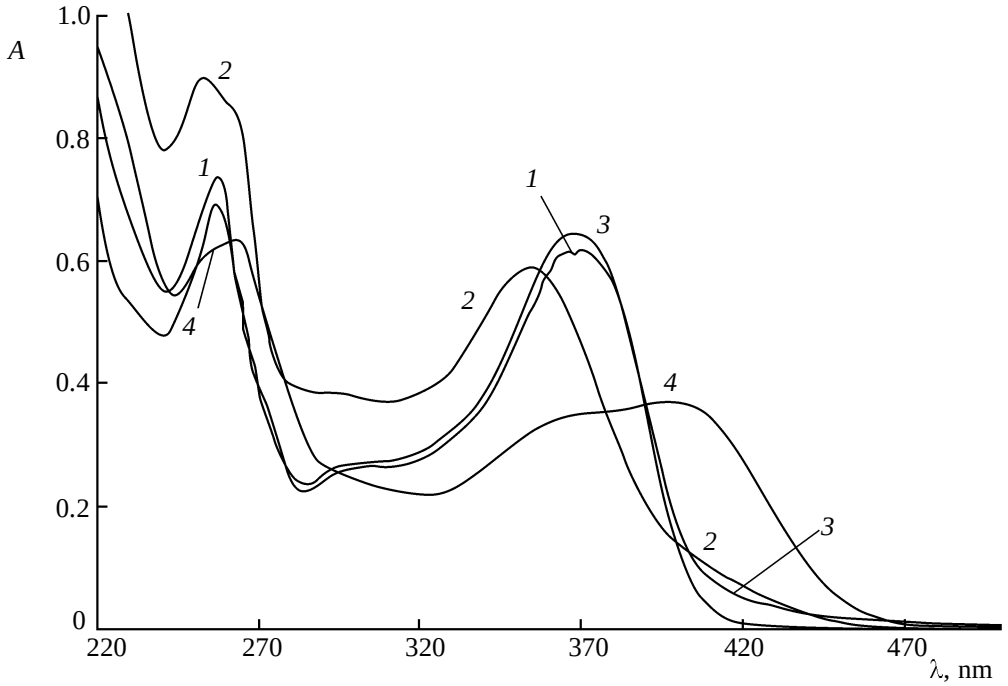

Fig. 2. Electronic absorption spectra in methanol: (*1*) QSA (c 3.28×10^{-5} M); (*2*) NaMSA (c 4.25×10^{-5} M); (*3*) comlex of Ba^{2+} with QSA, saturated solution; and (*4*) complex of Ba^{2+} with MSA, saturated solution.

It was shown that Ba^{2+} forms with QSA the complex $Ba(C_{15}H_9O_{10}S)_2\cdot6H_2O$ at $c_M:c_L$ = 5:1, 3:1, and pH 1.3. The compositions of complexes formed under the other conditions were not determined. The composition the complex of Ba^{2+} with NaMSA, isolated at pH 1.5 and $c_M:c_L$ = 1:3 and 1:5, is $Ba(C_{15}H_9O_{10}S)_2\cdot8H_2O$, and it differs from the QSA complex by the number of water molecules only. The complex of Ba^{2+} with NaMSA at pH 1.5 precipitates in the acid form with an SO_3H group, rather than as sodium salt with an SO_3Na group. These complexes are scarcely soluble in water and poorly soluble in methanol and methanol.

The electronic absorption spectra (Fig. 2) show two strong ligand bands ($\pi\rightarrow\pi^*$) at 258 and 371 nm for the complex with QSA and at 263 and 370 nm for the complex with NaMSA. Furthermore, the band of the complex BaQSA at ~420 nm has an inflection point, whereas the complex BaMSA gives a strong band at ~410 nm. These bands are associated with ligand-to-metal charge transfer. Figure 2 also shows the absorption spectra of the ligands QSA and NaMSA. The $\pi\rightarrow\pi^*$ bands of the ligands are at 257 and 368 nm for QSA and at 253 and 356 nm for NaMSA.

Our and published [10] data suggest that Ba^{2+} is coordinated to the 3-OH and 4-CO groups of the corresponding ligand.

EXPERIEMNTAL

Quercetin-5'-sulfonic acid and NaMSA were prepared by the procedures in [11, 12], respectively. The complex formation was studied by potentiometry at the ionic strength I 0.1 at 25±0.1°C. The ionic strength was maintained constant with a solution of $NaClO_4$ (c 1 M). Chemical grade $Ba(NO_3)_2$, NaOH, $HClO_4$, and NaClO4 were used. Potentiometric titration was performed using an N-5172 pH-meter with an OSH-10-00 electrode calibrated by titration of 0.01, 0.02, and 0.04 M HCl with 0.1 M NaOH.

The stability constants were determined by Bjerrum and Rossoti. Solutions of QSA and NaMSA and their mixtures with Ba^{2+} ions were titrated with 0.1 M NaOH.

Solid complexes were isolated from aqueous solutions of QSA and NaMSA, containing Ba^{2+} ions. Starting solutions of Ba^{2+} (c 0.01 M) were prepared by dissolving 2.614 g of $Ba(NO_3)_2$ in 1 l of doubly distilled water. Starting solutions of QSA and NaMSA (c 0.01 M) were prepared by dissolving 4.724 g of QSA and 4.403 g of NaMSA in 1 l of doubly distilled water. Further the solution of $Ba(NO_3)_2$ was mixed with the corresponding solution of the ligand at 60°C to obtain the $c_M:c_L$ ratio of 1:3, 1:5, 3:1, or 5:1. The pH values of the solutions within the range

1.3–1.5 were adjusted with NaOH and HNO_3 (*c* 0.1 M). After isolation and drying in air the precipitates were yellow. The compositions of the complexes were determined by elemental analyses on a Carbo-Erba EA-1108 instrument. Barium was determined by gravimetry as $BaSO_4$ [13] and sodium, by atomic absorption spectroscopy on a Perkin–Elmer-3100 instrument. The UV-Vis spectra in methanol were measured on a Beckman DU-640 spectrophotometer.

REFERENCES

1. Kopacz, M., Nowak, D., and Nitka, B., *Stud. Mat. Monogr. IMP Lodz,* 1989, vol. 34, p. 152.
2. Bujonek, B., Kopacz, M., and Nowak, D., *Zh. Obshch. Khim.,* 1999, vol. 69, no. 12, p. 2033.
3. Inczedy, J., *Rownowagi kompleksowania w chemii analitycznej* (Complex-Formation Equilibria in Analytical Chemistry), Warsaw: PWN, 1979, p. 46.
4. Kopacz, M., Bujonek, B., Nowak, D., and Kopacz, S., *Chem. Anal. (Warsaw),* 2001, vol. 46, p. 621.
5. Bjerrum, N., *Z. Anorg. Allg. Chem.,* 1921, no. 119, p. 179.
6. Bujonek, B., *Polish. J. Chem.,* 1993, vol. 67, p. 1339.
7. Rossoti, H., *Rownowagi jonowe* (Ionic Equilibria), Warsaw: PWN, 1983, p. 708.
8. Kopacz, M., Nowak, D., Kopacz, S., and Sliwoska, M., *Zeszyty Naukowe Politechniki Rzeszowskiej,* no. 194, Chemia, p. 18, Rzeszow, 2002, p. 41.
9. Gimblett, F.G.R. and Monk, C.B., *Trans. Faraday Soc.,* 1954, vol. 50, p. 965.
10. Kopacz, M., *Zeszyty Naukowe Politechniki Rzeszowskiej,* no. 55, Chemia, p. 4, Rzeszow, 1989, p. 31.
11. Terpilowski, J., Manczyk, R., and Kopacz, M., *Dissert. Pharm. Pharmacol.,* 1970, vol. 22, p. 389.
12. Kopacz, M., *Pol. J. Chem.,* 1981, vol. 55, p. 227.
13. Minczewski, J. and Marczenko, Z., *Chemia analityczna,* Warsaw: PWN, 1985, vol. 2, p. 167.