Journal of Environmental Protection and Ecology 6, No 4, 771–777 (2005)

Water quality

THERMODYNAMIC MODELLING BY PITZER'S EQUATIONS OF BLACK SEA WATER ALONG THE CONSTANTZA HARBOR

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Abstract. We made a simulation by the Pitzer's model on the marine water of the Black sea. An equation has been developed with the guidance of statistical theories of electrolytes which is designed for convenient and accurate representation and prediction of the thermodynamic properties of aqueos electrolytes including mixtures with any number of components by Pitzer and collaborators. We obtained original results for activity and osmotic coefficients on the Black sea water samples for 6 different recoltation points on the Romanian sea coast.

Keywords: electrolyte, solution, marine water, the Pitzer's model, simulation.

AIMS AND BACKGROUND

The sea water represents a natural wealth which belongs to both anorganic and organic fields and being a potential source of raw materials.

Within sea waters it has been detected 77 elements, most of them in very small concentrations. Together with its hydrogen and oxygen, the marine water contains 13 major components whereas other elements are found only in 'traces' (minor components or oligoelements)[1].

Comparing to the planetary ocean waters, the Black sea is included in category of the seas with average salinity, but with significant variations, due to the sweet waters contribution (the Danube large rivers, the Danube – Black sea canal) and also some other effluents of the water treatment plants placed along the Romanian sea shore (as Petromidia, Fertil-Chim Navodari, Constantza and Mangalia water treatment plants)[1].

The thermodynamic properties of aqueous electrolytes have been extensively investigated both experimentally and theoretically. The monographs of Harned and Owen[2] and of Robinson and Stoches[3] provide excellent summaries. The best available system proposed by Brewer and Pitzer[4] was applied to dilute solutions by Guggenheim[5] with modifications and by Scatchard[6] for concentrated solu-

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tions. While this system was useful in providing a simple and compact summary of experimental data, it did not fully satisfy the other desired qualities.

An equation has been developed by Pitzer and collaborators[7] with the guidance of statistical theories of electrolytes which is designed for convenient and accurate representation and prediction of the thermodynamic properties of aqueos electolytes including mixtures with any number of components. The evaluation of parameters for the activity and osmotic coefficients of pure electrolytes at room temperature is given for 1-1, 2-1, 1-2, 2-2-electrolyte in which slightly different but compatible form of equation was used[1,8].

We made a simulation on the marine water of the Black sea by Pitzer's model.

EXPERIMENTAL

In this work we present a thermodynamic modelling of composition data, based on the Pitzer model for the Black sea surface water. Sea water samples for 6 different recoltation points on the Romanian sea coast were used. There have been processed composition data both for coast waters (2 m far from the shore) and open sea waters (at 45 km distance from the shore)[1].

The coast water samples were collected from the surface waters (a maximum depth of 2 m) in 1993 and 1994 in May, June and July from the following poins: 1 – Midia; 2 – Mamaia; 3 – Constantza port; 4 – Agigea port; 5 – Mangalia; 6 – Vama Veche.

The open sea water samples were collected from the marine petroleum platform zone (45 km far from the shore). The study for finding out the major ions concentrations – 4 anions (Cl^-, SO_4^{2-}, CO_3^{2-}, HCO_3^-) and 4 cations (Ca^{2+}, Mg^{2+}, Na^+ and K^+) – presenting the utilised analysis methods, was described in other previous works[1,9]. For the determinations we made use of analytical purity reactives delivered by MERC Company.

RESULTS AND DISCUSSION

The analysis of experimental results for the analysed ions are presented in the work cited in Refs 1, 9 and 10 as multimonthly average values for sea shore and open sea waters for every year (1993, 1994) being presented for the collecting points in meq/l. The thermodynamic sea water processing is difficult to achieve, the sea water being a multicomponent aqueous electrolyle solution.

By means of the attending study we have achieved for the first time a thermodynamic treatment of the Black sea water by mathematical modelling based on the Pitzer equations[11-13] with a proper program. This fact was possible because the program contains in its data the basic Pitzer interaction parameters for all the major ions analysed in the sea water samples[7,13,14]. From the results obtained for the Black sea water major ions we have chosen for all the collecting points a set of multimonthly medium concentrations from the open sea water, considering that the water composition variation would be less influenced by some elements as the contribution of sweet or plant waters.

"For the processing easing, we considered that the marine water samples have been thermostatically controlled in laboratory at 25°C, temperature close moreover to the collecting real one, talking about the warm months (May, June and July).

The program has 2 work moduls which are being started successively (Fig. 1).

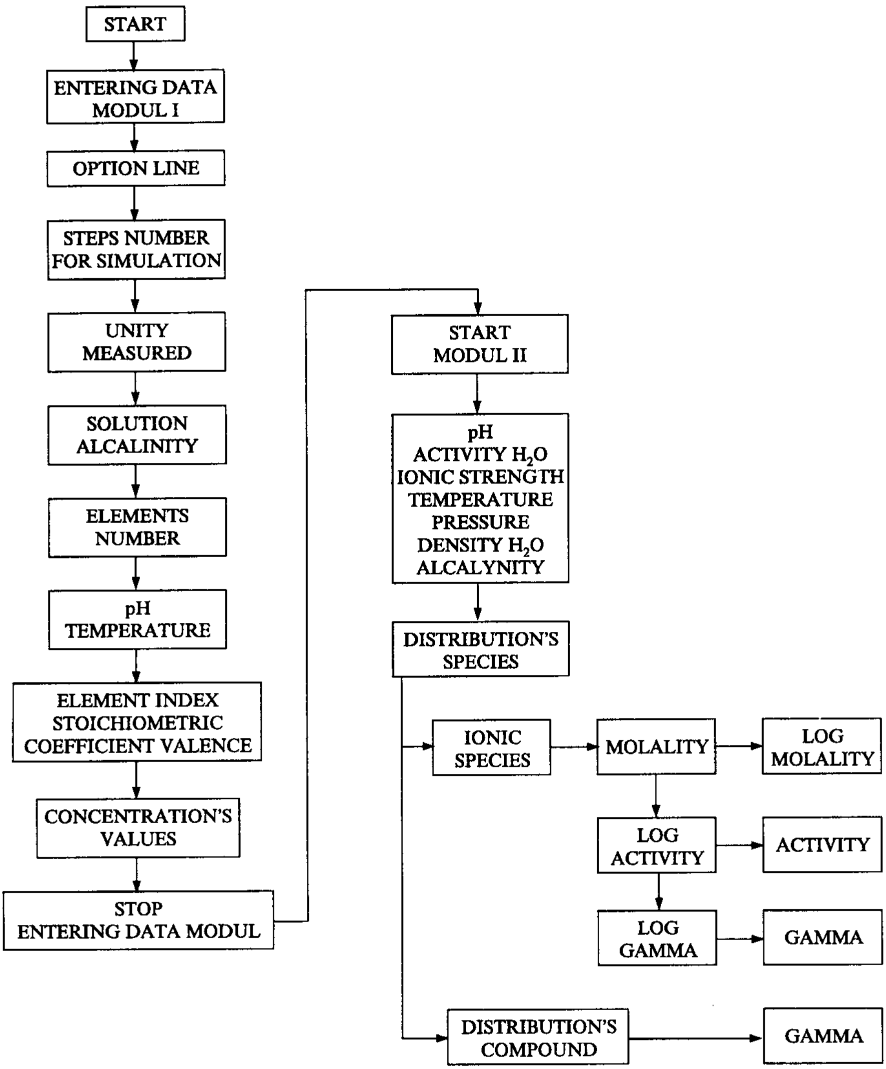

Fig. 1. Logical scheme for the Pitzer's modelling

In modulus I (entering data) we have introduced the ions concentration in mol/kg solvent, using the sea water density measured 1.014 g/l. Every ionic species from 4 anions (Cl^-, SO_4^{2-}, CO_3^{2-}, HCO_3^-) and 4 cations (Ca^{2+}, Mg^{2+}, Na^+ and K^+) has been introduced with its corresponding index from the program, with its valence and the concentration found in the sample experimentally analysed for each collecting point.

There have been established the simulation steps, the pH of the sea water sample, which have been sent for the calculations but we also needed the keywords (Elements, Species, Minerals, Gamma, Mean Gamma). Each sea water sample for the 6 collecting points has been distinctively named.

At the start of modulus II for every water sample there has been realised the description of the multicomponent electrolyte solution.

By modulus II running, in keeping with the Pitzer model equations[11-14], the program calculates: the individual ionic activity coefficients for 8 ionic species inroduced (10 species with the ionic of the water in fact).

In Figs 2 and 3 are presented the variation of ionic activity coefficients for water ions. In Figs 3-7 are presented the variations of ionic activity coefficients

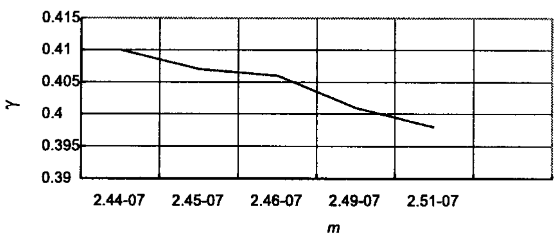

Fig. 2. Ionic activity coefficients for H^+ in the Black sea water

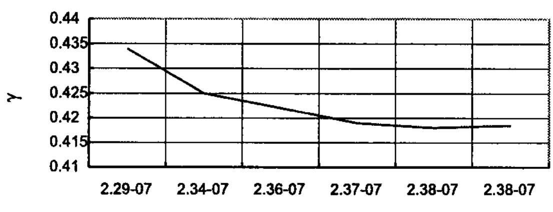

Fig. 3. Ionic activity coefficients for OH^- in the Black sea water

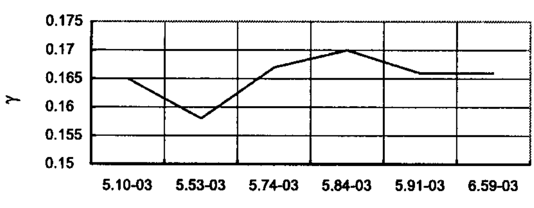

Fig. 4. Ionic activity coefficients for Ca^{2+} in the Black sea water

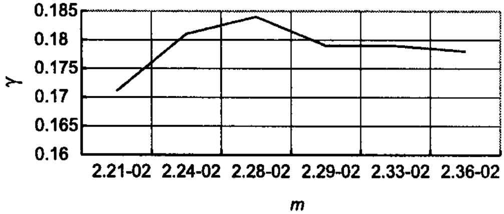

Fig. 5. Ionic activity coefficients for Mg^{2+} in the Black sea water

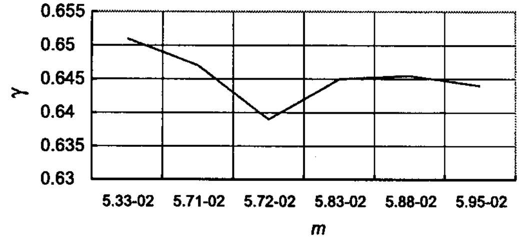

Fig. 6. Ionic activity coefficients for Na^+ in the Black sea water

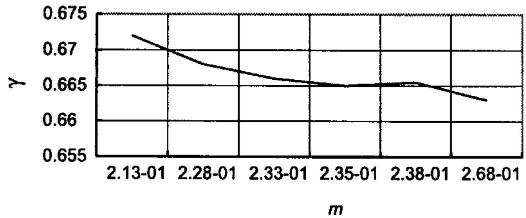

Fig. 7. Ionic activity coefficients for K^+ in the Black sea water

for 4 cations (Ca^{2+} , Mg^{2+}, Na^+ and K^+). We observed the most increased values for K^+ and Na^+ ions. The values of ionic activity coefficients for Mg^{2+} are over 0.170 and for Ca^{2+} are under 0.170.

In Figs 8-11 are presented the variations of ionic activity coefficients for 4 anions (Cl^-, SO_4^{2-}, CO_3^{2-}, and HCO_3^-). In this case we observed the most incresed values for Cl^- (over 0.718) and the small values are for the ionic activity coefficients of CO_3^{2-}. In Fig. 12 are presented the variations of thermodynamic activity with ionic strength of the Black sea water.

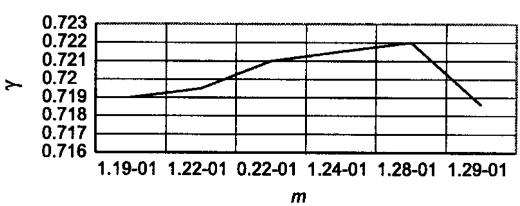

Fig. 8. Ionic activity coefficients for Cl^- in the Black sea water

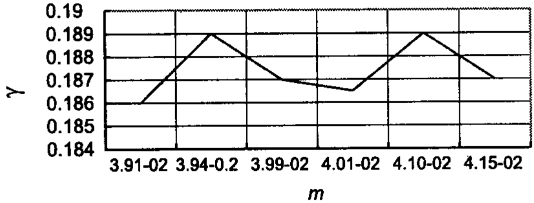

Fig. 9. Ionic activity coefficients for SO_4^{2-} in the Black sea water

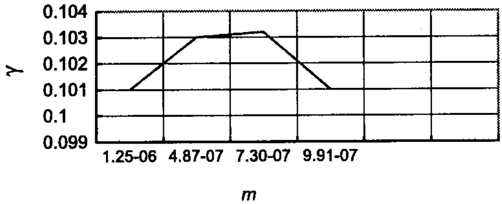

Fig. 10. Ionic activity coefficients for CO_3^{2-} in the Black sea water

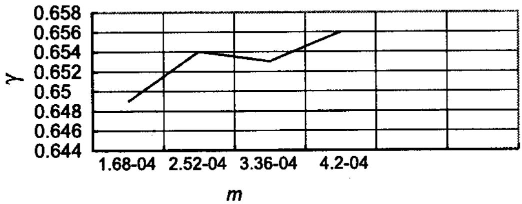

Fig. 11. Ionic activity coefficients for HCO_3^- in the Black sea water

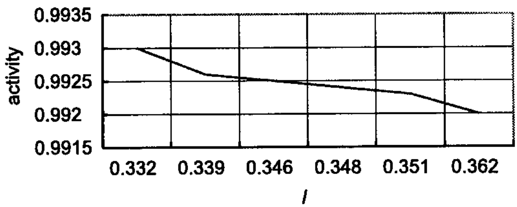

Fig. 12. Variation of thermodynamic acivity with ionic strength of the Black sea water

CONCLUSIONS

The importance of the study is based also on the fact that for the first time there has been achieved a physicochemical treatment of the Black sea waters by thermodynamic modelling. The results obtained using thermodynamic modelling consist in the values of the individual and mean activity and osmotic coefficients and thermodynamic activity of macro-ions of sea water. The analysis of the multicomponents solutions is hard to achieve due to both the reciprocal interactions of the ionic species contained and the difficulties of the thermodynamic calculations. The calculation will be easier both for the composition data processing and the thermodynamic properties obtained using the modelling method.

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Received 5 July 2004
Revised 10 October 2004