Measurements of Dissociation Constants of Carbonic Acid in Synthetic Seawater by Means of a Cell without a Liquid Junction

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The first and second apparent dissociation constants of carbonic acid have been determined in synthetic seawater for temperature and salinity ranges of 273 to 303 K and 1.5 to 40 respectively, using the conventional activity coefficient of the individual ion scale (Pitzer scale) [1]. The values of the first dissociation constants have been measured by means of a cell without a liquid junction, which was equilibrated with $CO_{2(gas)}$ at 1 atm total pressure and was composed of a pH glass electrode and silver/silver-chloride electrode. The cell was calibrated by means of 0.01 M HCl solutions. The same cell was used for the determination of the second dissociation constants. However, in this case, part of the dissolved CO_2 was removed by purging with nitrogen gas until a pH of about 8.3 was reached. Dissolved inorganic carbon was measured by the coulometric method and the total alkalinity known from the preparation of synthetic seawater and pH measurements provided the data required for the calculations of values of the second dissociation constants. Estimated precision is about 0.003 pK and uncertainty is less than 0.01 pK for the first constants, and both are two times higher for the second constants. Obtained apparent dissociation constants move towards the thermodynamic values at zero salinity on the plots of constants versus salinity. The results, including the thermodynamic constants at zero salinity, have been fitted by empirical equations as a function temperature and salinity.

The comparison shows that our first dissociation constants agree with the Mehrbach *et al.* data [2] within ~ 0.01 for pK(1) in the 20 to 40 salinity range. Our second dissociation constants agree with the Mehrbach *et al.* data [2] as well (within ~ 0.01 for pK(2) in the 30 to 40 salinity range), but become progressively lower as the salinity decreases. The comparison with obtained constants by Lueker *et al.* [3] shows excellent agreement, within ~ 0.002, for pK(1) for salinities of 30 and 35 psu, and there is a good agreement, within ~ 0.01 in pK(2) for the 30 to 40 psu salinity range for the second dissociation constants.

Since the obtained constants are reliable for a high salinity range (30 to 40) and the trend is towards the thermodynamic constants at zero salinity, they can be used for the study of carbonate systems in estuaries. The determined dissociation constants of carbonic acid in the Pitzer pH scale together with cells without a liquid junction for pH measurements [4] create a strict basis study of carbonate systems in marine environments.

[1] K.S.Pitzer, In: *Activity Coefficients in Electrolyte Solutions.* K. S. Pitzer Ed.; 2nd Edition; CRC Press: Roca Raton, Ann Arbor, Boston, London, 1991, pp. 75-153.
[2] A.G.Dickson, and F.J.Millero, *Deep-Sea Res.* **34**, 1733 (1987).
[3] T.J.Lueker, A.G.Dickson, and C.D.Keeling, *Mar. Chem.* **70**, 105 (2000).
[4] P.Ya.Tishchenko, C.S.Wong, G.Yu.Pavlova *et al. Okeanologiya* **41**, 849 (2001) (in Russian).