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USING THE IONIC FORCE RULE AND THE HYPTHESIS OF THE DISTRIBUTION OF IONS WITH EQUAL PROBABILITY IN CALCULATING TEMPERATURE INFLUENCE ON SOUND VELOCITY IN SEA WATER

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The values of the deviations of sound velocity in sea water from sound velocity in pure water are calculated with the help of the method of calculating sound velocity in sea water based on the ionic force rule on the hypothesis of the distribution of ions with equal probability when sea water is considered as a solution containing 6 ions Na^+, Mg^{2+}, K^+, Ca^{2+}, SO_4^{2-}, Cl^- for 8 values of salinity. The calculated values of the deviations mentioned above are in agreement with the experimental values.

The description of the influence of the composition of the solutes on sea water properties with the help of salinity can be justified if the relations of concentrations of the ions are constant [1]. The mentioned constancy does not take place for isolated sea and for seas connected with the neighbour seas by narrow passes [2]. So the methods of calculating properties of sea water by using the known concentrations of ions based on the thermodynamic of isopiestic solutions, i.e. solutions having the same value of the chemical potential of water μ_W have been proposed [3, 4]. As the concentration dependence of μ_W for binary solutions of electrolytes mostly are known only for 25^0C the methods based on the thermodynamic of isopiestic solutions do not allow to find the dependence of sea water properties on temperature. The influence of temperature on sea water properties can be found with the help of the method based on the ionic force rule and the hypothesis of the distribution of ions with the equal probability [6]. The ionic force is determined by the equality

$$I = \frac{1}{2}\sum_{j=1}^{r}(\nu_{j+}z_{j+}{}^2 + \nu_{j-}z_{j-}{}^2)m_j \qquad (1)$$

where ν_{o+}, ν_{j-} are the number of the cations and the number of the anions having the charges $z_{j+}e$, $z_{j-}e$, respectively which appear at the dissociation of the molecule of the j-th electrolyte, e is the absolute quantity of electron charge, r is the number of electrolytes, m_j is the molality of the j-th electrolyte in considered mixed solution..

In the present work sea water is considered as a solution containing 6 ions Na^+, Mg^{2+}, K^+, Ca^{2+}, SO_4^{2-}, Cl^- , the molalities of the first five ions m_{Na}, m_{Mg}, m_K, m_{Ca}, m_{SO_4} are equal to the molalities of the pointed ions in the considered sea The molality of the Cl^- $m_{C\partial}$ is calculated from the electroneutrality condition. The molality of $CaSO_4$ is supported to be equal zero. The ions mentioned above are distributed between 7 salts NaCl, Na_2SO_4, $MgCl_2$, $MgSO_4$, KCl, K_2SO_4, $CaCl_2$. The quantities referring to the pointed salts are marked by the indexes 1, 2, 3, 4, 5, 6, 7 respectively. Accordingly to the formula (1) the ionic force of the considered mixed solution is connected with the molalities of the salts by the equality

$$I = m_1 + m_5 + 3(m_2 + m_3 + m_6 + m_7) + 4m_4 \qquad (2)$$

In accordance with the ionic force rule the sound velocity in considered mixed solution u_{mix} can be connected with the values of sound velocities in the binary solutions having the same value of I which the considered mixed solution has $u_i\,(I)$, by the relation

$$u_{mix} = I^{-1}\{m_1u_1(I) + m_5u_5(I) + 3[m_2u_2(I) + m_3u_3(I) + m_6u_6(I) + m_7u_7(I) + 4m_4u_4(I)]\} \qquad (3)$$

Because of the assumption concerning the absence of $CaSO_4$ in the mixed solution the SO_4^{2-} ions and the difference between the whole molality of Cl^- ions and double molality Ca^{2+} are distributed between the three ions Na^+, Mg^{2+}, K^+. Thanks to the hypothesis of the distribution of ions with the equal probability [7] it is not difficult to comr to the relations connecting the molalities of the salts and the molalities of the ilons [4]

$$m_1 = m_{Na}\widehat{m}_{Cl}(m_{Na} + m_K + 2m_{Mg})^{-1} \quad (4)$$

$$m_2 = m_{Na}m_{SO_4}(m_{Na} + m_K + 2m_{Mg})^{-1} \quad (5)$$

$$m_3 = m_{Mg}\widehat{m}_{Cl}(m_{Na} + m_K + 2m_{Mg})^{-1} \quad (6)$$

$$m_4 = 2m_{Mg}m_{SO_4}(m_{Na} + m_K + 2m_{Mg})^{-1} \quad (7)$$

$$m_5 = m_K\widehat{m}_{Cl}(m_{Na} + m_K + 2m_{Mg})^{-1} \quad (8)$$

$$m_6 = m_K m_{SO_4}(m_{Na} + m_K + 2m_{Mg})^{-1} \quad (9)$$

where $\widehat{m}_{Cl}$ is connected with the whole molality of Cl^- m_{Cl} by the equality

$$\widehat{m}_{Cl} = m_{Cl} - 2m_{Ca} \quad (10)$$

In accordance with the assumption mentioned above the molality of $CaCl_2$. is equal to the molality of Ca^{2+}. In the present work the formula (3) is applied for calculating the differences between the values of the sound velocity in sea water and in pure water u_W by using the known deviations of sound velocity in the binary solutions having the same value of I which the considered mixed solution has from the sound velocity in pure water

$$u_{mix} - u_W = I^{-1}\{m_1[u_1(I) - u_W] + m_5[u_5(I) - u_W] + 3m_2[u_2(I) - u_W] + 3m_3[u_3(I) - u_W] + $$
$$+ 3m_6[u_6(I) - u_W] + 3m_7[u_7(I) - u_W] + 4m_4[u_4(I) - u_W]\} \quad (11)$$

Because of absence of the values of sound velocity in isolated seas and seas connected with neighbour seas for which the mentioned above methods based on the thermodynamic of isopiestic solutions [3, 4,] and the method which is being proposed in the present work are made the calculations were realised for the sea water which quantities can be described with the help of salinity adequately. It sould be noted that the deviations $u_{mix} - u_W$ calculated in accordance with the formula (11) are compared with the experimental values of the pointed deviations for sea water in which the molalities of 5 ions pointed above are equal to the molalities of these ions in the considered mixed solution.

Table 1.

Calculated and experimental deviations of the values of sound velocity in sea water from the values of sound velocity in pure water

S ‰	25^0C	25^0C	30^0C	30^0C.
	$(u_{mix} - u_W)^{calc}$ m c^{-1}	$(u_{mix} - u_W)^{exp}$ m c^{-1}	$(u_{mix} - u_W)^{calc}$ m c^{-1}	$(u_{mix} - u_W)^{exp}$ m c^{-1}
5,024	5,34	5,20	5,51	5,31
10,057	10,74	10,47	10,95	10,59
15,142	16,15	15,75	16,45	15.94
20,000	21,26	20,73	21,60	20,93
24,943	26,50	25,84	26,91	26,01
30,031	31,97	31,12	32,42	31.34
35,003	37,33	36,31	37,73	36,48
40,025	42,65	41,48	41,48	41.73

The work [8] contains deviations $u_{mix} - u_W$ for some values of the salinity S and for two values of temperature. Taking into account the constancy of the relations of the ion concentrations which should take place in order salinity can be used it is njt difficult to come to the formula connecting the molalities of the ions and S.

$$m_{Na}\left[M_{Na}+\frac{m_{Mg}}{m_{Na}}M_{Mg}+\frac{m_K}{m_{Na}}M_K+\frac{m_{Ca}}{m_{Na}}M_{Ca}+\frac{m_{SO_4}}{m_{Na}}M_{SO_4}+\frac{m_{Cl}}{m_{Na}}M_{Cl}\right]=S(S+1) \quad (12)$$

where M_{Na}, M_{Mg}, M_K, M_{Ca}, M_{SO_4}, M_{Cl} are the mole masses of the corresponding ions..
The values of the molalities of five ions Na^+, Mg^{2+}, K^+, Ca^{2+}, SO_4^{2-}, corresponding to S = 35,004 ‰ [1] and the molality of Cl m_{Cl} found from the electroneutrality condition are chosen as a start point. The dependeces of sound velocities in binary solutions on concentrations and temperature are given in the works [9, 10].

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