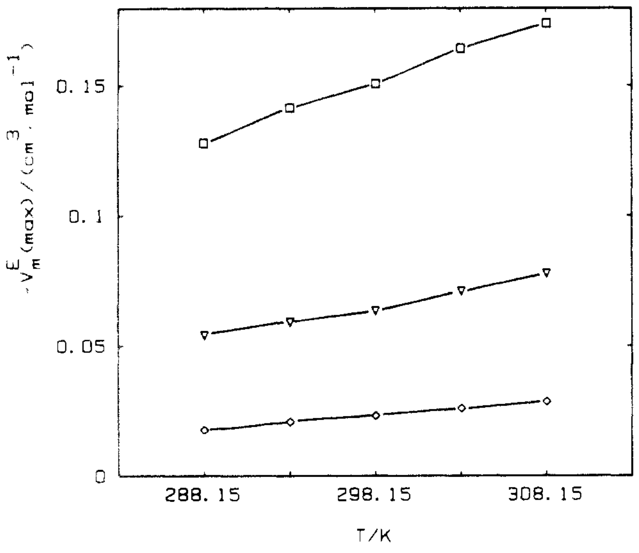

Figure 2. Maximum values of V_m^E: (□) n-heptane + n-undecane, (▽) n-octane + n-undecane, (◇) n-nonane + n-undecane.

the present study are compared with previously published values (*7*).

In Figure 2 we present the maxima of V_m^E versus temperature for the three mixtures studied. These results allow to draw qualitative conclusions concerning the dependence of excess molar entropy S_m^E on pressure. Note that the maximum values of $-V_m^E$ increase with the difference between the chain lengths of the mixture's components and with the temperature.

According to Maxwell's equation

$$(\partial S_m^E/\partial P) = -(\partial V_m^E/\partial T) \quad (4)$$

and the previous paragraph, we get a positive derivative $(\partial S_m^E/\partial P)$, and the deviation from ideal behavior thus increases with pressure and with the difference in chain length of the components.

Registry No. Nonane, 111-84-2; undecane, 1120-21-4.

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Received for review January 30, 1987. Accepted October 1, 1987.

Estimation of Ion Product of Water in Sea Water

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The equations of Sweeton, Mesmer, and Baes, of Marshall and Mesmer, and of Marshall and Franck, which were found useful in estimating the ion product of pure water at different temperatures and pressures, have now been applied for predicting the ion product of water in sea water at 0 and 25 °C and up to 1000 bar pressure. By introduction of the density of sea water at a given pressure, the equation of Marshall and Franck describes some reliably calculated values for the ion product of water in sea water. The equation of Sweeton, Mesmer, and Baes with an added density relationship based on the equation of Marshall and Franck also provides these values.

Introduction

The self-ionization of water is a fundamental property for aqueous systems and is frequently used by electrolyte chemists, chemical oceanographers, and geochemists in their evaluations. In the past few years, a large number of equations representing the self-ionization of water in pure water and in aqueous NaCl solution under different conditions have been proposed. However, equations are not available for estimating the ion product of water in sea water up to high pressures. In this note, we examine two sets of equations given by (1) Sweeton, Mesmer, and Baes (*1*) and Marshall and Mesmer (*2*) and by (2) Marshall and Franck (*3*) for estimating values of the ion product of water in sea water (log K_w), applicable to high pressures. Throughout this study, we refer to K_w on the molality scale.

Equations

The equation of Sweeton, Mesmer, and Baes (SMB) (*1*) for the ionization of pure water at temperatures from 25 to 300 °C and at saturated pressure is given as

$$\ln K_w^0(\text{SMB}) = 2.303(-606.52 - 2.1710 \times 10^6 T^{-2} + 3.1286 \times 10^4 T^{-1} - 9.7610 \times 10^{-2} T + 94.973 \ln T) \quad (1)$$

This expression can be combined with the equation of Marshall and Mesmer (SMARME) (*2*) to give

$$\ln K_w^0(\text{SMARME}) = \ln K_w^0(\text{SMB}) + 2.303(k - 1) \log \rho_p/\rho_1 \quad (2)$$

where according to Marshall and Franck (*3*)

$$k = 13.957 - 1.2623 \times 10^3 T^{-1} + 8.5641 \times 10^5 T^{-2} \quad (3)$$

and where ρ_p and ρ_1 are the densities at pressure p and 1 bar, respectively.

Marshall and Mesmer (*2*) expressed the ion product of pure water in terms of density at various pressures. According to Quist (*4*) and also Sweeton, Mesmer, and Baes (*1*), the density (ρ) describes the ion product of water more simply than pressure.

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Table I. Comparison of K'_p/K'_1 As Calculated by MARFRA and SMARME Equations with Those Tabulated by Millero (*8*) at 0 and 25 °C for Sea Water

press., bar	Millero (0 °C)[a]	MARFRA or SMARME[a]	Millero (25 °C)[b]	MARFRA or SMARME[b]
1	1.00	1.00	1.00	1.00
200	1.19	1.19	1.15	1.15_5
400	1.40	1.42	1.33	1.34
600	1.63	1.66	1.51	1.54
800	1.88	1.91	1.72	1.75_5
1000	2.16	2.20	1.95	1.99

[a] Average difference = 0.024. [b] Average difference = 0.024.

Marshall and Franck (*3*) have published a generalized equation (MARFRA) for estimating the ion product of water, and proposed its applicability up to 1000 °C and 10 000 bar. This equation has been found to be in good agreement with the reported values (*1*, *5*, *6*). The equation is

$$\log K_w{}^0(\text{MARFRA}) = -4.098 - 3.2452 \times 10^3 T^{-1} + 2.2362 \times 10^5 T^{-2} - 3.9840 \times 10^7 T^{-3} + (13.937 - 1.2623 \times 10^3 T^{-1} + 8.5641 \times 10^5 T^{-2}) \log \rho_w \quad (4)$$

where ρ_w is the density of pure water.

In order to use eq 2 (SMARME) and eq 4 (MARFRA) for estimating the ion product of water in sea water, we substitute the density of pure water by the density of sea water. The remaining portions of the equations do not change. We use a prime for sea water in order to distinguish it from that for pure water. Densities of sea water can be taken from UNESCO tables (*7*).

Results and Discussion

According to Millero (*8*), the directly measured experimental values of the ion product of water in sea water are not available at high pressures. He obtained them by using ΔV and Δk values which are the experimentally determined values of volume and compressibility changes. He also listed the values of K'_p/K'_1 at different pressures at 0 and 25 °C.

In Table I, we list the values of K'_p/K'_1 obtained from the uses of eq 2 and 4, along with those obtained by Millero (*8*) at both 0 and 25 °C for ready comparison. The values of log K'_w used in these calculations were −14.386 and −13.776 at 0 and 25 °C, respectively, and at 1 bar pressure.

An inspection of Table I shows that both SMARME and MARFRA yield the same predictions of log K'_w. The average difference between the calculated values and those obtained by Millero are 0.02 and 0.007 units for K'_p/K'_1 and log K'_w, respectively.

The log K'_w values thus obtained from either equation, when differentiated with respect to pressure and temperature, yield the change in molar volume (ΔV^*) and enthalpy (ΔH^*), respectively, upon ionization. The ΔV^* thus obtained is −18.07 cm^3 mol^{-1}, which agrees closely with that of Millero (−18.10 cm^3 mol^{-1}). The ΔH^* is 13.63 kcal mol^{-1}, which is nearly 0.30 kcal mol^{-1} higher than that of pure water.

Thus, it is clear that by introduction of the density of sea water at a given pressure, the equation of Marshall and Franck describes some reliably calculated values of the ion product of water in sea water. The equation of Sweeton, Mesmer, and Baes with an added density relationship based on the Marshall and Franck equation also provides these values.

Acknowledgment

I thank Professors E. U. Franck and Loren G. Hepler for many suggestions to improve the quality of the manuscript. I also thank an anonymous reviewer for pointing out errors in the manuscript through his excellent reviews.

Registry No. Water, 7732-18-5.

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Received for review September 30, 1985. Revised manuscript received June 1, 1987. Accepted August 18, 1987.

Densities of Binary Aqueous Solutions of 306 Inorganic Substances

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Constants of equations expressing the density of binary aqueous solutions as a function of concentration, and where possible also of temperature, are given for 306 inorganic substances. The goodness of fit and limits of the equation validity are indicated for each system.

Introduction

The density of aqueous solutions of inorganic substances and its dependence on solution concentration and/or temperature represents important information for chemical engineering and physical chemistry. A comparatively large volume of relevant data for a wide variety of systems is available in the periodical literature and the existing monographs. However, the presentation of density data, even in the recent monographs (*1*, *2*), is not very suitable for direct use as they are given for particular concentrations and temperatures, which rarely cover the whole interval required. Moreover, different sources present mutually inconsistent sets of data for most systems.

We have, therefore, critically evaluated the existing density data for binary aqueous solutions of inorganic substances and those regarded as reliable, correlated in a consistent manner.

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