

Estimation of Apparent Molal Compressibilities of Ions, Salts & Mixtures in Pure Water & Sea Water Using Brønsted-Guggenheim Theory

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The Brønsted-Guggenheim theory has been used for estimating apparent molal compressibilities of ions, salts and mixtures and sound velocities in pure water and sea water at 25°C. The cation-anion interactions are considered predominant and cation-cation and anion-anion interactions are completely neglected. The interaction coefficients obtained from single salt analysis are used in calculations for mixtures of salts in pure water and sea water.

We have recently shown¹ that Brønsted-Guggenheim (B-G) theory can accurately predict the apparent molal volumes and densities of ions, salts and mixtures in pure water and sea water at 25°C. In the present paper, this theory has been extended to estimate the other volume properties, viz. apparent molal compressibilities (ϕ_λ) of ions, salts and mixtures and relative sound velocities ($U - U_0$) in the multicomponent mixtures of NaCl–CaCl₂ in pure water and sea water. The parameters obtained from single salts are employed for mixtures in pure and sea water media. For this purpose, the moderate ionic strengths of 0.3, 0.5 and 1.0 mol kg⁻¹ are chosen and higher concentrations completely avoided.

Proposed Version of B-G Theory and Method of Calculations

The equation of apparent molal volume¹ can be differentiated with respect to pressure to obtain the expression for the apparent molal compressibility (ϕ_λ) of a salt M_{v_M} X_{v_X} as

$$\phi_K = \phi_K^0 + \frac{A_K \sum_i v_i Z_i^2 \cdot I^{1/2}}{3(1 + I^{1/2})} + \frac{v_M}{2} \sum_X B_{MX}^K m_X + \frac{v_X}{2} \sum_M B_{MX}^K m_M \quad \dots (1)$$

where ϕ_K and ϕ_K^0 are apparent molal compressibilities (cm³ mol⁻¹ bar⁻¹) at a given molality and at infinite dilution. A_K is Debye Huckel limiting slope (2.41 × 10⁻⁴ cm³ kg¹ mol^{-3/2} bar⁻¹) and I refers to the ionic strength (in mol kg⁻¹).

B_{MX}^K is the B-G interaction coefficient, accounting for cation-anion interactions and is given by Eq. (2).

$$B_{MX}^K = B^K(0) + B^K(1)I + B^K(2)I^2 \quad \dots (2)$$

v_M and v_X are mol of M and X per mol of salt respectively.

$$v = v_M + v_X \quad \dots (3)$$

Ionic apparent molal compressibility can be expressed by Eq. (4)

$$\phi_{Ki} = \phi_{Ki}^0 + \frac{Z_i^2 A_K I^{1/2}}{3(1 + I^{1/2})} + \frac{1}{2} \sum_j B_{ij}^K m_j \quad \dots (4)$$

where B_{ij}^K is B-G parameter or coefficient for cation-anion pair, m_j is molality and Z_i is the charge on ion. The summation is over all the ions with charge opposite to that on ion i .

Single salt analysis

ϕ_K data of a salt are fed into computer along with their respective molality. Equation (1) is then used to give interaction parameter B_{MX}^K in terms of $B^K(0)$, $B^K(1)$ and $B^K(2)$ using a least square programme. These parameters can now be used in calculations for mixtures in pure water and sea water.

Calculations in pure water

The B_{MX}^K coefficients for each pair are used in Eq. (4) to give ionic apparent molal compressibility. One can use Young rule⁴ to give ϕ_{KJ} , the apparent molal compressibility of a salt in the mixture as in Eq. (5)

$$\phi_{KJ} = \sum_i v_i \phi_{Ki} \quad \dots (5)$$

ϕ_{KJ} gives the mean apparent molal compressibility (ϕ_K^*) as

$$\phi_K^* = \frac{\sum_j m_j \phi_{KJ}}{\sum_j m_j} \quad \dots (6)$$

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Table 1—Brønsted-Guggenheim Coefficients Calculated using Eq. (1)

Salt	$-\phi_K$ $\text{cm}^3 \text{mol}^{-1} \text{bar}^{-1}$	$B^k(0) 10^4$	$B^k(1) 10^5$	$B^k(2) 10^6$	$\sigma \times 10^4$ $\text{cm}^3 \text{mol}^{-1} \text{bar}^{-1}$
NaCl	48.30 ± 0.20	8.33 ± 0.39	-12.96 ± 0.18	10.26 ± 2.34	0.21
CaCl ₂	91.25 ± 0.71	9.70 ± 0.55	-4.50 ± 0.64	0.89 ± 0.20	0.81

Table 2—R M S D (σ) for Relative Sound Velocities ($U - U_0$) and Mean Apparent Molal Compressibilities (ϕ_K^*) in Pure Water and Sea Water

Ionic Strength†	R M S D (σ) in			
	$U - U_0$ (cm s^{-1})		$\phi_K^* \times 10^4$ ($\text{cm}^3 \text{mol}^{-1} \text{bar}^{-1}$)	
	Pure water	Sea water	Pure water	Sea water
0.3	28	32	0.80	0.80
0.5	50	55	0.95	0.96
1.0	80	89	0.99	1.05

†Values in pure water

Table 3—Apparent Molal Compressibilities of NaCl and CaCl₂ (ϕ_{KJ}) in Pure Water and Sea Water at 25 C

Yb	$-\phi_K \times 10^4$ NaCl (cm ³ mol ⁻¹ bar ⁻¹)		$-\phi_K \times 10^4$ CaCl ₂ (cm ³ mol ⁻¹ bar ⁻¹)	
	Pure water	Sea water	Pure water	Sea water
	Ionic strength† = 0.3			
0.35	48.06	43.19	89.19	80.56
0.55	48.24	43.49	89.51	81.11
0.75	48.42	43.79	89.82	81.67
Ionic strength = 0.5				
0.35	46.88	42.13	87.00	80.43
0.55	47.16	42.43	87.50	80.94
0.75	47.44	42.76	88.00	81.52
Ionic strength = 1.0				
0.35	44.26	38.91	83.45	74.02
0.55	44.76	40.44	84.35	75.00
0.75	45.27	41.97	85.26	75.94

†Values in pure water (mol kg⁻¹)

where m_j is the molality of a salt and the sum is over salts.

Sound velocity (U , cm s^{-1}) is calculated by the expression (7),

$$U = \frac{1000}{d} \left[\frac{1000 + \sum_j m_j M_j}{\frac{10^9}{U_0^2 d_0^2} + \sum_j m_j \phi_{KJ}} \right]^{\frac{1}{2}} \quad \dots (7)$$

where d = density of solution, U_0 = sound velocity in pure water at 25 C (149669 cm s^{-1}) and d_0 = density of pure water at 25 C ($0.997047 \text{ g cm}^{-3}$).

U can be converted into relative sound velocity $U - U_0$ for further use.

Table 4— ϕ_K^* and $U - U_0$ in Pure Water and Sea Water

[Yb are in the same order as in Table 3]			
$-\phi_K^* \times 10^4$ ($\text{cm}^3 \text{mol}^{-1} \text{bar}^{-1}$)		$U - U_0$ (cm s^{-1})	
Pure water	Sea water	Pure water	Sea water
Ionic strength† = 0.3			
54.35	20.12	1586	4102
60.23	20.47	1398	3964
69.17	20.77	1212	3818
Ionic strength = 0.5			
53.03	20.15	2620	5046
58.88	20.55	2314	4794
67.74	20.98	2006	4539
Ionic strength = 1.0			
50.35	19.17	5194	7071
56.29	19.23	4643	6792
65.27	20.83	4076	6296

†Values in pure water (mol kg⁻¹)

Calculation in sea water

The procedure is exactly the same as in the case of apparent molal volume. Sea water recipe of Millero⁵ was used and final concentrations of the systems after adding aq. NaCl—CaCl₂ of ionic strengths of 0.3, 0.5 and 1.0 mol kg⁻¹ were calculated. The calculations were performed for each experimental point of Kumar *et al.*⁶ but for the sake of illustration only three experimental points (Yb = 0.35, 0.55 and 0.75, where Yb is the ionic strength ratio of CaCl₂) were chosen.

The B-G coefficients for Na⁺, Ca²⁺ and Cl⁻ obtained from single salt analysis were used along with those of SO₄²⁻, HCO₃⁻, CO₃²⁻, B(OH)₄⁻, Br⁻, F⁻, Mg²⁺, Sr²⁺ and K⁺ reported by Millero⁵. The contribution of HCO₃⁻, CO₃²⁻, B(OH)₄⁻, Br⁻ and F⁻ towards total apparent molal compressibility was found very small and hence neglected.

One can now use Eq. (4) to give ϕ_{Ki} of Na⁺, Ca²⁺ and Cl⁻ in a mixture. ϕ_{Ki} values thus obtained can be converted to give ϕ_{KJ} for NaCl and CaCl₂ using Eq. (5). The mean apparent molal compressibility, ϕ_{KS}^* is calculated by Eq. (8).

$$\phi_{KS}^* = \frac{\sum_i m_i \phi_{Ki}}{\sum_i m_i} \quad \dots (8)$$

$$\text{as } \sum_j m_j \phi_{KJ} = \sum_i m_i \phi_{Ki}$$

Sound velocity in sea water (U_s) is then expressed by Eq. (9)

$$U_s = \frac{1000}{d} \left[\frac{1000 + \sum_i m_i M_i}{\frac{10^9}{U_0^2 d_0^2} + \sum_i m_i \phi_{Ki}} \right]^{\frac{1}{2}} \quad \dots (9)$$

where sum is over ions and M_i is molecular weight of ion.

Results and Discussion

Table 1 lists the B-G coefficients for NaCl and CaCl_2 along with the standard deviation (σ). Data for NaCl and CaCl_2 were taken from elsewhere^{6,7}. ϕ_K data for NaCl fit better than those for CaCl_2 . The poor fit in the case of CaCl_2 is due to the change in hydration sphere of Ca^{2+} ions in the concentration range above 1 molal⁸. This has been confirmed by neutron scattering studies of Hewish *et al.*⁹, and activity coefficient studied¹⁰. The mathematical function for such a change is not easy to be accommodated in B-G theory. All the coefficients inspite of the error involved for both the salts are retained for performing the pairwise calculations.

The performance of this theory in pure water is summarised in Table 2, where calculated values of the density and mean apparent molal volumes are compared with experimental data⁶, in terms of root mean square deviation (σ) for $U - U_0$ and ϕ_K^* to within 2 and 1% respectively. The predictions in terms of the theory can be further improved, if the cation-cation interactions are taken into account. However, it has been neglected for the sake of simple and straightforward calculations of interaction coefficients in sea water media.

The results of calculations in sea water are shown in Table 2. It is clear from σ values that the predicted $U - U_0$ and ϕ_K^* values are fairly in good agreement with experimentally observed values¹¹. Table 3 lists ϕ_{Ki} of NaCl and CaCl_2 in pure water and sea water while Table 4 shows the $U - U_0$ and ϕ_K^* in pure water and sea water at the concentrations studied. The trend in the values of the ionic properties can be explained on the basis as has been done in the case of apparent molal volume¹.

In conclusion, it has been demonstrated that B-G theory predicts the apparent molal compressibility fairly accurately and it is hoped that this theory will equally apply in estimating the expansibility of such mixtures.

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