Volume change on the formation of the complex EDTA—Mg^{2+} in water at 25 °C

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The volume of the chelate formation between ethylenediaminetetraacetic acid tetrasodium salt and the Mg^{2+} cation in water was measured for the first time. The volume of the complex formation increases with dilution of the solution and reaches the limit of 29.9±3 cm^3 mol^{-1} at 25 °C. The changes in the volume during the chelation and the entropy of the complex formation were compared.

Key words: magnesium sulfate, ethylenediaminetetraacetic acid, chelation volume, electrostriction volume.

The formation of molecular (π,π- and *n*,*v*-) complexes in solution is generally accompanied by an increase in the bond energy, a decrease in the intermolecular distances, and a decrease in the volume.[1,2] The equilibrium constants for these complexes substantially increase at elevated pressure due to the contribution of $p\Delta V$ to the free energy of the process. However, an increase in the compactness upon complexation is accompanied by the partial displacement of solvent molecules from the intermolecular interaction region in the complex. If the energies of intermolecular solvent—solvent and solvent—dissolved substance interactions are only slightly different, the change in the free energy is generally controlled by the change in the enthalpy of the complexation. It is known that the dissociation in solution giving ions is accompanied by an increase in the intrinsic volume of the substance due to the bond cleavage and by a sharp decrease in the volume due to the electrostriction of the solvent upon solvation of these ions.[2—4] For solutions of salts in *n*-donor solvents, no correlation between the change in the enthalpy of the dissolution and the change in the partial molar volume was found.[5]

The reaction of the tetrasodium salt of ethylenediaminetetraacetic acid (EDTA) with metal salts in aqueous solution produces unstable complexes with alkali metal cations ($\log K \approx 3$), much more stable complexes with alkaline earth metal cations ($\log K \approx 10$—12), and very stable complexes ($\log K > 20$) with M^{3+} cations.[6,7] Recently, the enthalpies of the dissolution and the partial molar volumes were measured in a series of *n*-donor solvents for lithium[5] and magnesium[8] perchlorates. The data on the volume of the complex formation between the Mg^{2+} cation and the tetrasodium salt of EDTA are absent in the literature.

In the present study, the apparent molar volumes of magnesium sulfate, the tetrasodium salt of EDTA (Na_4Y), and their equivalent mixture in water were determined in the concentration range of 0.01—0.2 mol L^{-1}:

$$Mg^{2+}\cdot n_1H_2O + SO_4^{2-}\cdot n_2H_2O + 4\ Na^+\cdot n_3H_2O + Y^{4-}\cdot n_4H_2O \longrightarrow [Y^{2-}—Mg]\cdot n_5H_2O + SO_4^{2-}\cdot n_2H_2O + 4\ Na^+\cdot n_3H_2O + (n_1 + n_4 - n_5)H_2O \quad (1)$$

or

$$Mg^{2+}\cdot n_1H_2O + Y^{4-}\cdot n_4H_2O \longrightarrow [Y^{2-}—Mg]\cdot n_5H_2O + (n_1 + n_4 - n_5)H_2O, \quad (2)$$

where n_i is the number of water molecules in the solvation shell of the charged species (with different energies of interaction and partial molar volumes for each ion). The results of this study are given in Table 1.

From these experimental data, the following concentration dependences were obtained:

$$\varphi(MgSO_4) = -197.47C^2 + 74.46C - (6.4\pm0.6), \quad (3)$$

$$\varphi(Na_4Y) = -394.13C^2 + 153.33C + (145.8\pm1.3), \quad (4)$$

$$\varphi(MgSO_4 + Na_4Y) = -1153.9C^2 + 243.11C + (169.3\pm1.1), \quad (5)$$

where φ/cm^3 mol^{-1} are the apparent molar volumes.

The smoothed values of the reaction volume (see Table 1) are described by the equation

$$\Delta\varphi = -562.3C^2 + 15.32C + (29.9\pm3). \quad (6)$$

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Table 1. Experimental values of the apparent molar volumes (φ) of $MgSO_4$, Na_4Y, and their equimolar mixtures at different concentrations in water at 25 °C

$MgSO_4$		Na_4Y		$(MgSO_4 + Na_4Y)$		ΔV	
C/mol L^{-1}	φ/cm^3 mol^{-1}	C/mol L^{-1}	φ/cm^3 mol^{-1}	C/mol L^{-1}	φ/cm^3 mol^{-1}	C/mol L^{-1}	Δφ/cm^3 mol^{-1}
(0)	(−6.4±0.6)	(0)	(145.8±1.3)	(0)	(169.3±1.1)	(0)	(29.9±3)
0.01230	−5.91	0.01032	146.2	0.009864	171.0	0.01	29.84
0.02002	−4.49	0.01461	147.9	0.020050	174.7	0.02	29.82
0.09952	−1.00	0.02048	150.7	0.049860	178.4	0.05	29.10
0.20001	0.63	0.09968	157.0	0.071620	180.6	0.07	28.06
		0.20005	160.9	0.100200	182.2	0.10	25.65

Note. The limiting values of the volume at $C \to 0$ are given in parentheses.

Evidently, the structural contribution to the volume of the reaction resulting in the formation of new bonds in the chelate $[Y^{2-}—Mg]$ should be negative. This contribution can be estimated[3] at −(10–20) cm^3 mol^{-1}. The displacement of water molecules ($(n_1 + n_4 - n_5)H_2O$) from the solvation shells $Mg^{2+} \cdot n_1H_2O$ and $Y^{4-} \cdot n_4H_2O$ in the course of the complexation accompanied by the neutralization of four charges is, apparently, the main factor responsible for the experimentally observed increase in the volume of this reaction. The total increase in the volume due to the neutralization of the charges upon chelation can be estimated at 40—50 cm^3 mol^{-1}. The equilibrium parameters of the $[Y^{2-}—M]$ complex formation in water at 25 °C are available for some M^{2+} cations (Table 2).

It should be noted that for the Mg^{2+} cation, the gain in the enthalpy of the formation of new bonds in the $[Y^{2-}—Mg]$ complex is smaller than the loss of the energy of the bond between water and charged species. This difference accounts for the endothermic complex formation and a large increase in the entropy. As can be seen from Table 2 and Eq. (2), the unusual parameters for the formation of the complex $[Y^{2-}—Mg]$ are consistent with the high enthalpy of hydration of the Mg^{2+} cation (ΔH = −1874, −1515, −1397, and −1205 kJ mol^{-1} for Mg^{2+} Ca^{2+}, Sr^{2+}, and Ba^{2+}, respectively[10]).

Table 2. Enthalpies (ΔH), entropies (ΔS), and free energies (ΔG) of the complexation of M^{2+} cations with EDTA in water at 25 °C

M^{2+}	ΔH	ΔG	ΔS	Reference
	kJ mol^{-1}		/J mol^{-1} K^{-1}	
Mg^{2+}	13.0	−51.9	218	9
	14.6	−49.0	213	6
Ca^{2+}	−10.5	−62.9	176	10
	−24.3	−63.0	130	9
	−27.4	−60.6	111	6
Sr^{2+}	−17.2	−49.6	109	10
	−17.6	−50.0	109	9
Ba^{2+}	−17.6	−45.1	92	6
	−21.3	−43.8	75	10

Experimental

The molar volumes of the reactants and their equimolar mixtures were calculated from the densities of aqueous solutions with known concentrations. Data on the vibration frequency of the mechanical resonator (Anton Paar DMA 602) with a solution at 25±0.002 °C were used in experiments. The calibration of the instrument and the order of operations have been described earlier.[5]

Magnesium sulfate solutions were prepared by diluting its standard titer. Solutions of ethylenediaminetetraacetic acid tetrasodium salt were prepared in the same way from the standard titers of the disodium salt of EDTA and NaOH. Equimolar mixtures with different concentrations were prepared from these solutions, and their densities were determined. Earlier, the influence of the salt buffer (up to 0.15 *N*) on the volume effects of the neutralization of polyelectrolytes[11] and proteins[12] has been analyzed, and it was shown that these additives have only a slight effect (<2%) on the volume of these processes. In the present study, salt buffers were not added to the reaction mixtures.

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