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Determination of the Partial Molar Volume of $Al(OH)_4^-$ at Infinite Dilution in Water at 25 °C

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The densities of $NaAlO_2$ salt have been measured at 25 °C in the molality range 0.01–0.06 mol·kg^{-1}, in several NaOH concentrations (0.1–1 mol·kg^{-1}). Apparent molar volumes were derived. We were able to determine the apparent molar volume for infinite dilution only for the three lowest NaOH concentrations (0.1, 0.15, and 0.25 mol·kg^{-1}). The partial molar volume of $NaAlO_2$ in water at infinite dilution and the standard-state partial molar volume of $Al(OH)_4^-$ ion were then derived. Our value for $V°[Al(OH)_4^-] = 42.3 \pm 1.7$ cm^3·mol^{-1} agrees with published semiempirical correlations.

Introduction

Aluminum is one of the most abundant elements in the earth. According to the low solubility of its compounds, aluminum concentrations in water are controlled by reactions between minerals and aqueous solutions. A lot of work has been recently carried out in order to improve the thermodynamic data base of both aqueous species and solid compounds of aluminum in a wide range of temperature and pressure (*1–7*).

In many natural waters, the dominant species is $Al(OH)_4^-$. To our knowledge, no data on the partial molar volume of this ion are available. This study is an attempt to determine the partial molar volume of the aluminate ion at 25 °C from density measurements.

Experimental Section

In a preliminary experiment, we used $NaAlO_2$ prepared by the technique of Hemingway and Robie (*8*). But this compound dissolves very slowly. Finally, we used a commercial sodium aluminate supplied by Prolabo (France) which was dried in a furnace at 80 °C and stored in a desiccator. The product was analyzed by a gravimetric method: Al was precipitated by 8-hydroxyquinoline, as described by Claasen and Bastings (*9*) (accuracy about 0.7%); Na was analyzed by ionic chromatography (Waters columns and Dionex apparatus; accuracy better than 1%) and water by a gravimetric technique. The stoichiometric formula derived from the analyses is $NaAlO_2$, 0.23 NaOH, 0.77 H_2O. As sodium aluminate is hydrolyzed into alumina in pure water, solutions were made in NaOH solutions.

All solutions were prepared by weighing. Initial products were water, supplied by a Milli-Q (Millipore) apparatus (dissolved CO_2 was removed by nitrogen bubbling) a 1 mol·L^{-1} "Merck Titrisol" NaOH solution, and sodium aluminate. First, five NaOH solutions of molality 0.096 35, 0.144 64, 0.241 79, 0.489 51, and 0.996 74 mol·(kg of water)$^{-1}$ were prepared; they were used (i) or dilute aluminate solutions in the same medium and (*ii*) as the reference solvent for determining the apparent molar volume. We will refer to these solutions as solvents S_j. Second, five 0.06 mol·(kg solvent)$^{-1}$ sodium aluminate stock solutions in sodium hydroxide at the previous molalities (0.096 35, 0.144 65, 0.241 79, 0.489 51, and 0.996 7 mol·(kg water)$^{-1}$) were also prepared. Amounts of NaOH and water provided by the sodium aluminate solid were taken into account in the calculation of NaOH molality of each solution. The five solutions were analyzed for Al and Na and the results are in agreement with the predicted value within 0.6%. These five aluminate solutions (A_j) were mixed with the corresponding solvent S_j by weighing the solutions and density of the resulting solutions were measured. The molality range for each set was restricted because the low solubility of the salt (<0.06 mol·(kg of solvent)$^{-1}$) and because below 0.01 mol·kg^{-1} measurements of molar volumes are not precise enough.

Table I. Aluminum Molality, Density, and Apparent Molar Volumes of the Solutions

set	m(Al), 10^{-2} mol·(kg of solvent)$^{-1}$	d, g·cm^{-3}	ϕ_V, cm^3·mol^{-1}
I. NaOH, 0.1 M	0	1.001 382	
	5.73	1.005 740	5.98
	5.21	1.005 355	5.84
	4.72	1.004 974	5.94
	3.49	1.004 041	5.91
	2.40	1.003 308	5.96
	1.38	1.002 435	5.52
II. NaOH, 0.15 M	0	1.003 512	
	5.70	1.007 823	6.55
	5.29	1.007 540	6.01
	4.70	1.007 072	6.46
	3.69	1.006 299	6.58
	2.44	1.005 358	6.50
	1.22	1.004 438	6.12
III. NaOH, 0.25 M	0	1.007 749	
	5.71	1.012 070	6.80
	5.09	1.011 593	6.91
	4.57	1.011 215	6.73
	3.47	1.010 391	6.47
	2.44	1.009 599	6.59
	1.24	1.008 695	6.29
IV. NaOH, 0.5 M	0	1.018 358	
	5.70	1.022 603	8.65
	5.06	1.022 151	8.21
	4.56	1.021 775	8.19
	3.55	1.021 039	7.75
	2.41	1.020 194	7.11
	1.17	1.019 260	6.22
V. NaOH, 1 M	0	1.039 340	
	5.69	1.043 318	14.10
	4.88	1.042 777	13.68
	4.52	1.042 561	12.93
	3.35	1.041 731	12.79
	2.35	1.041 015	12.94
	1.24	1.040 244	11.19

Density measurements were performed at 25 °C using a Sodev O3D flux densitometer. The densitometer was calibrated at 25 °C against water (ρ_{25} = 0.997 047 g·cm^{-3} (*10*)) and argon (ρ_{25} = 0.001 783 7 g·cm^{-3}). Temperature was maintained at 25 ± 0.001 °C by a Setaram temperature regulator. The uncertainty in the density measurement is about 2×10^{-6} g·cm^{-3}.

Results

The results of the measurements are presented in Table I. The apparent molar volume ϕ_V of a salt can be calculated from the density by

$$\phi_V = (1000/m)(1/d - 1/d_0) + M/d \qquad (1)$$

where m is the salt molality in moles per kilogram of solvent, M is the molar mass of the salt (81.97 g), d is the density of

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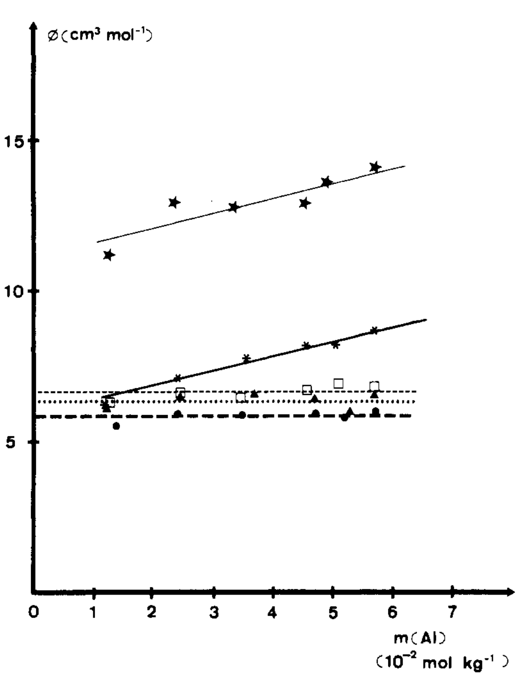

Figure 1. Apparent molar volumes versus sodium aluminate molality: (●) set I, NaOH 0.096 35 mol·(kg of water)$^{-1}$; (▲) set II, NaOH 0.144 64 mol·(kg of water)$^{-1}$; (□) set III, NaOH 0.241 79 mol·(kg of water)$^{-1}$; (*) set IV, NaOH 0.0489 51 mol·(kg of water)$^{-1}$; (★) set V, NaOH 0.996 74 mol·(kg of water)$^{-1}$.

the solution, and d_0 is the density of the solvent, i.e., water + NaOH at a given molality. Values of the apparent molar volumes for each set of measurements, at constant NaOH concentration, are given in Table I.

Uncertainties in apparent molar volumes are related to (i) uncertainty in molality, (ii) uncertainty in density measurements, and (iii) uncertainty in the NaOH molality. The influence of density uncertainty increases strongly as molality decreases. In our experiments an uncertainty of 2×10^{-6} g·cm^{-3} in the density implies an uncertainty in ϕ_V of 0.03 cm^3·mol^{-1} for the highest aluminate molality and of 0.15 cm^3·mol^{-1} for the lowest. Uncertainty in the aluminate molality is mainly due to the ill-defined nature of the salt; with $\Delta m/m = 0.6\%$, the uncertainty in ϕ_V is about 0.5 cm^3·mol^{-1}. As the salt contains NaOH, the molality of NaOH in the aluminate solution can be slightly different from the NaOH molality in the corresponding solvent, because the amount of sodium hydroxide brought by the salt is not known with a sufficient accuracy; the two molalities can differ by about 2×10^{-4} mol·(kg of water)$^{-1}$. This implies an uncertainty in the density of the solvent of about 2×10^{-5} g·cm^{-3} for the high aluminate solutions and about 6×10^{-6} g·cm^{-3} for the most dilute. The corresponding uncertainty in ϕ_V is about 0.4 cm^3·mol in both cases. Finally, the total uncertainty is about 1.2 cm^3·mol^{-1}.

Discussion

Partial Molar Volume of NaAlO$_2$ in Sodium Hydroxide Solutions. In the data sets corresponding to the sodium hydroxide molalities of 0.1, 0.15, and 0.25 mol·kg^{-1}, the apparent molar volumes of NaAlO$_2$ do not depend on the aluminate concentration. As the NaOH concentration is significantly higher than the aluminum concentration, the ionic strength is mainly fixed by NaOH and ϕ_V varies in a very restricted range. The partial molar volume $\bar{V}^\circ_1$ at infinite dilution in the medium is equal to the constant value of the apparent molar volume. Values of $\bar{V}^\circ_1$ found for the 0.1, 0.15, and 0.25 mol·kg^{-1} of NaOH are (5.9 ± 1.2), (6.4 ± 1.2), and (6.6 ± 1.2) cm^3·mol^{-1}.

For the two sets corresponding to the higher NaOH concentrations, we observe a dependency of ϕ_V on the NaAlO$_2$ molality (Figure 1). The variations are linear and the two straight lines corresponding to the two highest NaOH molalities are parallel. This trend could be tentatively related to an eventual polymerization of aluminate ion in a strongly basic medium; but we will not discuss any further these two sets of results.

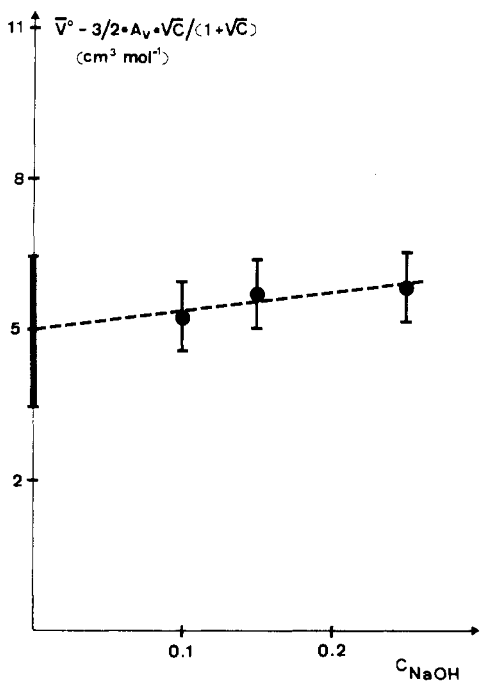

Figure 2. Plot of $\bar{V}^\circ - {}^3/_2 A_V \cdot c^{1/2}/(1 + c^{1/2})$ versus NaOH concentrations. $\bar{V}^\circ$ is the partial molar volume of NaAlO$_2$ derived from Figure 1 for sets I, II, and III.

Partial Molar Volume of NaAlO$_2$ in Water. For the equations developed by Redlich and Mayer (*11*) and by Swaddle and Mack (*12*), the partial molar volume $\bar{V}^\circ$ of NaAlO$_2$ in water can be derived from the values of $\bar{V}^\circ_1$ measurement in NaOH solutions. The three values of $\bar{V}^\circ_1$ are plotted in a diagram, $\bar{V}^\circ_1 - {}^3/_2 A_V c^{1/2}/(1 + c^{1/2})$ versus NaOH concentration, c (Figure 2). At 25 °C, A_V = 1.87 cm^3·L$^{1/2}$·mol$^{-3/2}$ (*13*). By extrapolation to zero NaOH concentration, we obtain an estimation of NaAlO$_2$ partial molar volume in water:

$$\bar{V}^\circ = 5.0 \pm 1.7 \text{ cm}^{-3}\cdot\text{mol}^{-1} \qquad (2)$$

Following Helgeson et al. (*13*), the conventional partial molar volume of Na$^+$ (i.e., molar volumes computed by assigning H$^+$ zero volume) is −1.3 cm^3·mol^{-1} and then $\bar{V}^\circ$(AlO$_2^-$) = 6.3 cm^3·mol^{-1}.

The structure and formula of aluminate in aqueous solution seem to correspond better to Al(OH)$_4^-$ (*14*). As pointed out by Sillen (*15*), for thermodynamic parameters, we cannot distinguish ions differing only by the number of solvent molecules. Thus

$$\bar{V}^\circ[\text{Al(OH)}_4^-] = \bar{V}^\circ(\text{AlO}_2^-) + 2\bar{V}^\circ(\text{H}_2\text{O}) = 42.3 \pm 1.7 \text{ cm}^3\cdot\text{mol}^{-1} \qquad (3)$$

This value is not very different from the value of 38 cm^3·mol^{-1} (*16*) estimated by a semiempirical correlation between entropy and molar volume of ions (*13*).

In spite of its low accuracy, the $\bar{V}^\circ$ obtained in this study is very useful for geochemical purposes; for a pressure of 1 kbar, which is the maximal pressure for natural waters at ordinary temperature, an uncertainty of 2 cm^3·mol^{-1} implies an error in log K less than 0.03 and at this pressure the compressibility of the ion cannot be neglected. But measurements of partial molar volume of aluminate ion at higher temperature are still needed.

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Registry No. $Al(OH)_4^-$, 14485-39-3; $NaAlO_2$, 1302-42-7.

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Excess Thermodynamic Properties for the Binary System 1,4-Dioxane–Acetonitrile at 40 °C

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Vapor–liquid equilibrium (VLE) and heat of mixing data for the binary system 1,4-dioxane–acetonitrile were determined at 40 °C. Measurements of vapor pressure and density were taken on pure components. The excess thermodynamic properties G^E and TS^E were calculated from the experimental data, which were correlated by means of Redlich–Kister expressions. Thermodynamic consistency of the VLE data is checked by the area test.

Introduction

Isothermal vapor–liquid equilibrium (VLE) data and liquid-phase enthalpy of mixing data were determined for the binary mixtures of 1,4-dioxane and acetonitrile at 40 °C. The measurements reported in this paper, together with the VLE data from the system 1,3-dioxolane–1,4-dioxane, previously obtained (*1*), and from 1,3-dioxolane–acetonitrile (following article in this issue), constitute a complete study of the three binary mixtures and supply a thermodynamic basis for the description of the corresponding ternary mixture. Furthermore, a comparison between thermodynamic properties of the binary mixtures of acetonitrile with 1,3 dioxolane and 1,4 dioxane is of interest due to the size of dipole moments of the three molecules considered. In fact, acetonitrile has an unusually large dipole moment, 3.4 D(*2*), to be compared with the one of 1,2 dioxolane, 1.47 D (*3*), whereas the symmetric molecule 1,4-dioxane has no appreciable dipole moment.

The experiments were carried out at 40 °C, which is the maximum working temperature for the calorimetric equipment. Since the enthalpy of mixing H^E is necessary to test correctly the thermodynamic consistency of isobaric VLE data, values of H^E at high temperatures are generally needed over the range of pressure 100–760 mmHg, which is usually explored. Isothermal VLE at 25 °C for 1,4 dioxane–acetonitrile mixtures was investigated by D'Avolio et al. (*4*).

Table I. Refractive Index–Composition Data for the Mixture Dioxane–Acetonitrile

X_1	n^{25}_{D}	X_1	n^{25}_{D}	X_1	n^{25}_{D}	X_1	n^{25}_{D}
0.000	1.3417	0.123	1.3567	0.396	1.3835	0.911	1.4163
0.005	1.3423	0.155	1.3603	0.455	1.3881	1.000	1.4206
0.038	1.3467	0.205	1.3658	0.527	1.3935		
0.074	1.3510	0.289	1.3740	0.736	1.4069		

Experimental Section

Chemicals Used. 1,4-Dioxane (dioxane) and acetonitrile were C. Erba (Milan, Italy) RPE-ACS 99.9% products. The major impurity, water 0.1% for acetonitrile and 0.02% for dioxane, was removed by distillation. The refractive indexes n^{25}_{D} of purified products are for dioxane 1.4206, (literature value 1.4202 (*4*, *5*)) and for acetonitrile 1.3417 (literature values 1.3419 (*4*), 1.3416 (*5*)). Dioxane is component 1. Molecular sieves 3A were added to the solvents to prevent moisture from contaminating them. Syringes were used to fill the still and to bring microsamples of liquid and condensed vapor to the refractometer. Since acetonitrile is toxic in contact with skin, use of gloves was necessary in handling this compound. Ordinary precautions were taken against inflammability of both materials.

VLE Measurements. The isothermal VLE data P-X-Y at 40 °C were obtained with the equilibrium still manufactured by Fritz GmbH (Normag) Hofheim (West Germany) described in detail by Gmehling (*6*). Equilibrium temperature t and pressure P in the still were measured with digital instruments declaring accuracy of 0.1 °C and 1 mbar (0.75 mmHg), respectively. These values were confirmed by repeated experiments on pure water and are assumed as the estimated errors for VLE data of this paper. A check of the equipment was performed following the procedure given in ref *7*.

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