Densities and partial molal volumes of sodium tetrafluoroborate aqueous solutions at 20°C

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Densities of solutions of NaBF₄ in H₂O have been determined at 20.00 °C over the concentration range 0.05 to 9.0 molal (0 to 50 wt%) NaBF₄. The results are represented by \( d \) (g/mL, 20°C) = 9.726×10⁻³ m³ - 3.2157×10⁻⁵ m³ + 6.7447×10⁻⁷ m + 0.99843, where \( d \) is density and \( m \) is molality. This equation has been used to derive concentration properties for NaBF₄ solutions. The raw density data have been used to derive partial molal volumes. The partial molal volume at infinite dilution is 37.6 ± 2.7 mL/mol at 20°C. The partial molal volume at 20°C is represented by \( \bar{v}_2 \) = 37.5 + 9.22m² - 2.92m from 0 to 2.5 m NaBF₄ and \( \bar{v}_3 \) = 44.6 + 0.081m from 2.5 to 9 m NaBF₄.

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Analytical data and plant solution compositions are often reported in molarity units. Densities of salt solutions are needed to convert the concentrations to molal basis in order to utilize physical property data that have been established on a molal basis, for example, solution reaction equilibrium constants or activity coefficients. We report here the densities at 20.00°C of sodium tetrafluoroborate (NaBF₄) solutions from 0.05 molal to 9.0 molal, near saturation of 9.2 molal.

Experimental

Sodium tetrafluoroborate, 98%, Chemical Abstracts Service Registry Number 13755-29-8, an off-grey solid obtained from ACROS, was purified by recrystallization from water, according to the procedure of Platford. The NaBF₄ (125.8 g) was added to 60 mL of hot Millipore water to dissolve it. The cooled solution was separated from the precipitated crystals by suction filtration. A black solid deposited on the surface of the filter paper and white NaBF₄ crystals were on top of them. The white crystals (74.1 g, 59% recovery) were physically separated from the mixture of black solid and white crystals. This NaBF₄ was dried to a constant weight in a drying oven at 120°C and stored in a desiccator until use.

Solutions of NaBF₄ were prepared by weighing the dried crystals and adding degassed Millipore H₂O by weight. Masses were determined on an analytical balance of 0.1 mg sensitivity that was calibrated against NIST-traceable standard weights and were corrected for air buoyancy. The NaBF₄ masses ranged from 0.28 g to 5.93 g in 50 to 6.0 g H₂O, respectively. Thus, the solution molal concentrations were measured to an accuracy of 0.04% at the lowest concentration to 0.003% at the highest concentration. The individual solution concentration uncertainties are reported with the results.

Densities were determined with an Anton Parr DNA 4500 oscillating U-tube density meter. The technical specification for standard deviation in repeatability is stated to be 0.00001 g/cm³. Sources and magnitudes of error are discussed by Fitzgerald for the Anton Parr DMA 5000 density meter. For solutions with a limited viscosity range of less than 30 mPa·s, the maximum error is less than 0.000015 g/cm³. The DMA 5000 has a technical specification for standard deviation in repeatability of 1×10⁻⁶ g/cm³, an order of magnitude less than for the DMA 4500. Thus, a maximum error for the DMA 4500 of approximately 0.00015 g/cm³ might be conservatively assumed (less than 0.015% for the current measurements). The following precisions reflect actual measurement variabilities, which are slightly greater than these best possible specifications.

Three measurements were taken at each concentration and averaged for solutions up to 1.5 molal NaBF₄ and two measurements were averaged for higher concentrations. The maximum variability of an individual measurement from the average was 0.02% or less for all but one of the 23 data points, which had a maximum variability of 0.04%. The average standard deviation of measurements was 0.00016 g/mL (0.013%). The instrument calibration
was checked with boiled (degassed) Millipore H₂O (<18 MOhms) (density at 20°C, 0.998204 g/mL) after each series of measurements at a concentration. The calibration correction thus determined started at -0.01% and gradually changed in a regular fashion to +0.13% as the measurements progressed from the lowest concentration to the highest in order. This may be due to a slight corrosion of the cell by the NaBF₄ solutions. The calibration corrections are considered to be good to 0.01% of the measured value.

The results of the instrument were checked by determining the densities of the nominal 1.0 and 9.0 molal NaBF₄ solutions from the mass of solution contained in a 10 mL Gay-Lussac specific gravity bottle at 20.00 °C and by measuring the mass of solution delivered from a 1 mL pipette. The volumes of the bottle and pipette were calibrated with water (standard deviation of 5 measurements, 0.003% for the bottle and 0.025% for the pipette). Five determinations were made by each method for each solution, except that only one measurement was made on the 9 molal solution with the specific gravity bottle. The results agreed with the density meter measurements within 0.04% in all cases as follows: 1 m NaBF₄ (pipette 0.01% difference, standard deviation 0.06%; specific gravity bottle 0.04% difference, standard deviation 0.03%); 9 m NaBF₄ (pipette 0.02% difference, standard deviation 0.09%; specific gravity bottle 0.02% difference, single point). In all the cases, the density meter read higher than the others. These results validate the density meter measurements that are used in the analysis and data reduction.

Temperature (ITS-90) was controlled and measured to within 0.01°C with two integrated NIST-traceable 100 ohm platinum resistance thermometers. The temperature was controlled to 20.00±0.01°C. This corresponds to an uncertainty in density of ±0.0002%.

The overall uncertainty in the averaged density measurements is judged to be less than 0.03%, based on the pooling of 2 times the average standard deviation of measurement (0.02%) and 2 times the estimated error of calibration correction (0.02%). The combined uncertainties in individual measurements of molality and density (pooled) are less than 0.05% at the lowest concentration to less than 0.03% at the highest concentration.

Results and discussion

The experimental data are summarized in Table 1. Including the 0 molal data point of 0.99820 g/mL,

<table>
<thead>
<tr>
<th>NaBF₄ Conc., molal</th>
<th>Uncertainty in Conc., molal</th>
<th>Density, g/mL</th>
<th>Uncertainty in Density, g/mL</th>
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<td>8.9823</td>
<td>0.00003</td>
<td>1.4152</td>
<td>0.0003</td>
</tr>
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</table>

Notes:
1. Based on 0.0001 g uncertainty in measured masses of NaBF₄ and H₂O.
2. Based on the pooled errors of 2 times average standard deviation of measurement and 2 times the estimated error of instrument calibration correction.

The data are well fitted by the equation

\[ d \text{ (g/mL, 20°C)} = 9.726 \times 10^{-5} m^3 - 3.2157 \times 10^{-3} m^2 + 6.7447 \times 10^{-2} m + 0.99843, \text{ R}^2 = 0.99997 \]

where \( m \) is molality and \( d \) is density. This equation was used to derive concentrative properties for NaBF₄ solutions in tabular form (see Table 2) identical to those provided for solutions in the CRC Handbook of Chemistry and Physics\(^6\). The heading notations are identical to the CRC Handbook: \( p = \text{density, g/mL, } D_s^0 = \text{specific gravity at 20°C, } C_w = \text{NaBF}_4 \text{ concentration, g/L, } M = \text{molar concentration, g-mol/L, } C_w = \text{total water concentration, g/L and } (C_0 - C_w) = \text{water displaced by anhydrous solute, g/L).} \]
Partial molal volumes were determined from the density data as follows. The apparent molal volume, $\langle V \rangle$, was first derived from the raw density values $^7$:

$$
\langle V \rangle = \frac{1000}{md \rho} \left[ \frac{d_0 - d}{d} \right] M_2
$$

... (1)

where $d_0$ is the solvent (H₂O) density, 0.998204 g/mL at 20°C, and $M_2$ is the molecular weight of the solute NaBF₄, 109.794 g/mol. Extrapolation of the apparent molal volume data from 0.05 to 0.5 mol NaBF₄ to infinite dilution yielded $\langle V \rangle$, the value of $\langle V \rangle$ at infinite dilution, of 37.6 mL/mol. This is also the value of partial molal volume of NaBF₄ at infinite dilution, $\tau_{20}^w$ (ref. 7).
As discussed above, uncertainty in individual density values is estimated to be approximately 0.0003 g/mL, or less than 0.03%. The corresponding uncertainty in \( \Delta V \) is obtained by differentiating Eq. (1) with respect to \( d \), yielding a probable error in \( \Delta V \) of

\[
\frac{1000}{m + M_2} \frac{\delta d}{d^2}
\]

This would correspond to an experimental uncertainty in apparent molar volume at the lower limit of 0.05 mol \( NaBF_4 \) of 15\% (±5.7 mL/mol) and 1.4\% (±0.6 mL/mol) at 0.5 mol \( NaBF_4 \). (If one considers the pooled errors of density and molality measurements of 0.05\%, the total uncertainty in apparent molar volume from both sources of error becomes 26\% and 2.2\% at 0.05 and 0.5 mol \( NaBF_4 \), respectively.) Based on the uniformity of the series of density values and the good extrapolation to the infinitely dilute value of 0.9982 g/mL, the associated uncertainty for the extrapolated apparent molar volume is judged to be approximately 7\% (±2.7 mL/mol), corresponding to ±0.014% uncertainty in density at 0.05 mol \( NaBF_4 \).

In order to represent the apparent molar volumes analytically, two regions of data were fitted in overlapping ranges. The data from 0 to 6 molal \( NaBF_4 \) were fitted to the Redlich-Meyer function\(^7\,8\) to yield a function suitable to 2.5 molal. To obtain a suitable function above 2.5 molal, the data from 1 to 9 molal were fitted to a quadratic function.

Partial molar volume values, \( \overline{\Delta \nu} \), were then derived from these functions using the relationship\(^7\,9\)

\[
\overline{\Delta \nu} = \Delta V + m \frac{\partial \Delta V}{\partial m}
\]

The partial molar volume function derived from the quadratic partial molar volume equation had a curvature that did not quite match the Redlich-Meyer value at 2.5 molal and had a slight maximum at 8.5 molal \( NaBF_4 \). Considering that the actual values would continue a slight increase, an adequate representation above 2.5 molal was obtained by fitting a linear function to the two points of the 2.5 molal value from the Redlich-Meyer equation and the 8 molal value from the quadratic equation. This approach yielded a smooth transition between equations. The resulting representation of the partial molar volume (mL/mol at 20°C) is, thus,

\[
\overline{\Delta \nu} = 37.5 + 9.22 \overline{\Delta \nu}^2 - 2.92 \overline{\Delta \nu} \text{ from 0 to 2.5 mol NaBF}_4
\]

and

\[
\overline{\Delta \nu} = 44.6 + 0.081 \overline{\Delta \nu} \text{ from 2.5 to 9 mol NaBF}_4
\]

Considering variability in individual values and the inaccuracies of the fitted equations, the uncertainty in individual calculated values is approximately ±2.7 mL/mol at the lower end of the concentration range and ±1 mL/mol beyond 2.5 molal.

References

3. Fitzgerald D, Technical Assessment of the Anton Paar DMA 5000 Density Meter, 10 January 2000, H&D Fitzgerald Ltd., CEfn Du, Tremerchion, St. Asaph, LL 17 0US, UK. denis@density.co.uk.