Measurement of Partial Molar Volumes

In this laboratory exercise, we will measure the partial molar volumes of NaCl and Water for Aqueous NaCl solutions of varying concentrations. We will use these quantities to determine the Volume of Mixing for these substances. Deviation of this quantity from the Ideal of zero indicates the presence of strong solution non-idealities.

Preparing an Aqueous NaCl Solution

The volume of a solution is dependent on its temperature (T), pressure (P) and the amount of each component (n₁, n₂, ...) used to form the mixture; V(T, P, n₁, n₂, ...). For a binary system held at constant temperature and pressure, the differential volume change upon an incremental addition or removal of either component is determined by:

\[ dV = \left( \frac{\partial V}{\partial n_1} \right)_{T,P,n_2} \, dn_1 + \left( \frac{\partial V}{\partial n_2} \right)_{T,P,n_1} \, dn_2 \]  

(Eq. 1)

Defining the Partial Molar Volume of each component as:

\[ \bar{V}_i = \left( \frac{\partial V}{\partial n_i} \right)_{T,P,n_j \neq i} \]  

(Eq. 2)

allows us to write this differential volume change for the solution as:
\[ dV = \bar{V}_1dn_1 + \bar{V}_2dn_2 \] (Eq. 3)

Importantly, integration of the differential volume expression above (Castellan, 1983) yields an "additivity rule" which allows us to determine the solution’s volume, given the amount of each component used to prepare it and each component's partial molar volume:

\[ V = n_1 \bar{V}_1 + n_2 \bar{V}_2 \] (Eq. 4)

Beyond being useful in its own right, this determination is useful because many other thermodynamic quantities depend on system volume measurements.

For any extensive property like \( V \), or \( U \), H, S, etc., of a solution, generally denoted as \( \Phi \), the partial molar quantity of that property, for each component, is defined as:

\[ \bar{\Phi}_i = \left( \frac{\partial \Phi}{\partial n_i} \right)_{T,P,n_j \neq i} \]

At constant \( T \) and \( P \), \( \Phi \) then adheres to an Additivity Rule:

\[ \Phi = \sum n_i \bar{\Phi}_i \]

**Details Concerning Partial Molar Volumes**

It must be emphasized, the partial molar volume of a substance in a solution is not equal to the Molar Volume of the substance when pure; \( \bar{V}_i \).

**Point of Illustration**

The molar volumes of Water and Ethanol at 20\(^\circ\)C are:

- \( \bar{V}_{\text{H}_2\text{O}}^* = 18.0 \text{ mL/mole} \)
- \( \bar{V}_{\text{EtOH}}^* = 58.0 \text{ mL/mole} \)

Parenthetically, the molar volume of a pure substance is related to its density via its molar mass (\( M_i \)); \( \bar{V}_i = M_i / \rho_i \). For Water, we have:

\[ \bar{V}_{\text{H}_2\text{O}} = \frac{(18.0 \text{ g/mole})}{(1.0 \text{ g/mL})} = 18.0 \text{ mL/mole} \]

If the molar volumes of Ethanol and Water did not change upon mixing, we would predict an Aqueous Ethanol solution prepared from 2 moles of each of these components would have a total volume of:

\[ V = (2 \text{ mole}) (18.0 \text{ mL/mole}) + (2 \text{ mole}) (58.0 \text{ mL/mole}) = 152 \text{ mL} \]

But these molar volumes do change. At a mole fraction of \( x_{\text{EtOH}} = 0.5 \), the partial molar volumes of Ethanol and Water are measured to be:
Thus, for our example solution, we instead have a total volume of:

\[ V = (2 \text{ mole}) (16.9 \text{ mL/mole}) + (2 \text{ mole}) (57.4 \text{ mL/mole}) = 148.6 \text{ mL} \]

In other words, the system experiences a 3.4 mL contraction when the components are mixed. This situation should not be unexpected. Liquid Water has a fairly open structure; not being too different from that of Ice. The voids in its structure can be “filled” with the non-polar hydrocarbon portion of the Ethanol molecule (CH₃CH₂OH).

Thus, the volume of the mixture will be less than the volume of the components separately.

It is observed partial molar volumes typically vary with concentration. This is illustrated below for the Water-Ethanol system (Moore, 1972):
The states indicated by $\bar{V}_{i}^{**}$ represent the molar volume of the solute $i$ in a state of infinite dilution in the solvent. The “molecular” situation is as illustrated below:

We should not get too carried-away with our discussion, however. As noted by Adamson, Water is anomalous:
For most ordinary organic liquids the average molar volume \( V/n \) varies almost linearly with composition. In the acetone-chloroform system, for example, the volume change on mixing amounts to a few tenths of a percent at the most. The molar volume of acetone is 72.740 cm\(^3\) mole\(^{-1}\) at 25°C and the partial molal volume increases slightly on dilution with chloroform to a limiting dilute solution value of 73.993 cm\(^3\) mole\(^{-1}\). Solutions involving water are often anomalous; there is almost a 3% volume change when a water-methanol solution is made up, and an actual shrinkage in total volume may occur when an electrolyte is dissolved in water. The explanation for this last is that ions attract water molecules so strongly that the resulting compaction more than compensates for the added volume of the ions themselves.

A Textbook of Physical Chemistry
Arthur W. Adamson

**How to Measure Partial Molar Volumes**

It is relatively easy to show that solution density (\( \rho \)) measurements are sufficient to determine the partial molar volumes of the components in a binary liquid solution.

For the Aqueous NaCl solutions we wish to examine, we can write the total solution volume in terms of the partial molar volumes as:

\[
V = n_{H_2O} \bar{V}_{H_2O} + n_{NaCl} \bar{V}_{NaCl} \tag{Eq. 5}
\]

We will define an Apparent Molar Volume for NaCl (\( \varphi_{NaCl} \)) according to:

\[
V = n_{H_2O} \bar{V}_{H_2O}^+ + n_{NaCl} \varphi_{NaCl} \tag{Eq. 6}
\]

This quantity represents the “apparent” volume of NaCl required to bring the Water’s volume up to the solution volume.

**Example**

For the 50:50 Ethanol-Water mixture of the example above, we have:

\[
V = n_{H_2O} \bar{V}_{H_2O}^+ + n_{EthOH} \varphi_{EthOH}
\]

Or,

148.6 mL \( = \) (2 mole) (18.0 mL/mole) \( + \) (2 mole) \( \varphi_{EthOH} \)

Giving us an apparent molar volume of:

\( \varphi_{EthOH} = 56.3 \text{ mL/mole} \)

(Note: This compares to Ethanol’s molar volume of 58.0 mL/mole and its partial molar volume in this mixture of 57.4 mL/mole.)
The partial molar volumes for \( \text{H}_2\text{O} \) and \( \text{NaCl} \) can now be written in terms of the apparent molar volume:

\[
\bar{V}_{\text{NaCl}} = \left( \frac{\partial V}{\partial n_{\text{NaCl}}} \right)_{T,P,n_{\text{H}_2\text{O}}} = \varphi_{\text{NaCl}} + n_{\text{NaCl}} \left( \frac{\partial \varphi_{\text{NaCl}}}{\partial n_{\text{NaCl}}} \right)_{T,P,n_{\text{H}_2\text{O}}} \tag{Eq. 7}
\]

\[
\bar{V}_{\text{H}_2\text{O}} = \frac{V - n_{\text{NaCl}}\bar{V}_{\text{NaCl}}}{n_{\text{H}_2\text{O}}}
\]

\[
= \frac{1}{n_{\text{H}_2\text{O}}} \left[ n_{\text{H}_2\text{O}}\bar{V}_{\text{H}_2\text{O}} - n_{\text{NaCl}}^2 \left( \frac{\partial \varphi_{\text{NaCl}}}{\partial n_{\text{NaCl}}} \right)_{T,P,n_{\text{H}_2\text{O}}} \right] \tag{Eq. 8}
\]

To relate \( \varphi_{\text{NaCl}} \) to the solution density \( \rho \), we write:

\[
\varphi_{\text{NaCl}} = \frac{V - n_{\text{H}_2\text{O}}\bar{V}_{\text{H}_2\text{O}}}{n_{\text{NaCl}}}
\]

\[
= \frac{1}{n_{\text{NaCl}}} \left[ n_{\text{H}_2\text{O}}M_{\text{H}_2\text{O}} + n_{\text{NaCl}}M_{\text{NaCl}} \rho - n_{\text{H}_2\text{O}}\bar{V}_{\text{H}_2\text{O}} \right] \tag{Eq. 10}
\]

The solution’s mole numbers \( n_i \) can be written in terms of the solution’s molality:

\[
n_{\text{H}_2\text{O}} = \frac{1000g}{M_{\text{H}_2\text{O}}} \tag{Eq. 11}
\]

\[
n_{\text{NaCl}} = m \times 1 \text{ kg} \tag{Eq. 12}
\]

This allows us define \( \varphi_{\text{NaCl}} \) in terms of this more conventional concentration scheme:

\[
\varphi_{\text{NaCl}} = \frac{1}{m} \left[ \frac{1000 + mM_{\text{NaCl}}}{\rho} - \frac{1000}{(M_{\text{H}_2\text{O}}/\bar{V}_{\text{H}_2\text{O}})} \right] \tag{Eq. 13}
\]

However, the density of pure Water is just \( \rho_{\text{H}_2\text{O}}^* = M_{\text{H}_2\text{O}}/\bar{V}_{\text{H}_2\text{O}}^* \). So, our final form for \( \varphi_{\text{NaCl}} \) is:

\[
\varphi_{\text{NaCl}} = \frac{1000}{m\rho_{\text{H}_2\text{O}}^*} (\rho_{\text{H}_2\text{O}}^* - \rho) + \frac{M_{\text{NaCl}}}{\rho} \tag{Eq. 14}
\]

Further details concerning these derivations can be found at (Crockford et al, 1975).

Now we have come to it. Density measurements at various concentrations \( m \) will yield \( \varphi_{\text{NaCl}} \) via Equation 14. This determination can then be used in Equations 7 and 8 to obtain our desired results, \( \bar{V}_{\text{NaCl}} \) and \( \bar{V}_{\text{H}_2\text{O}} \).

**The Volume of Mixing**

Finally, the Volume of Mixing is defined as:
\[ \Delta V_{mxg} = \frac{\nu - n_{H_2O} \tilde{V}_{H_2O} - n_{NaCl} \tilde{V}_{NaCl}}{n_{H_2O} - n_{NaCl}} \quad (Eq. 15) \]

**Example**

Again, for our 50:50 Ethanol-Water solution, we have:

\[ \Delta V_{mxg} = \frac{148.6 \text{ mL} - (2 \text{ mole}) \left(18 \frac{\text{mL}}{\text{mole}}\right) - (2 \text{ mole}) \left(58 \frac{\text{mL}}{\text{mole}}\right)}{2 \text{ mole} + 2 \text{ mole}} \approx -0.85 \text{ mL/mole} \]

Using appropriate substitutions, this becomes:

\[ \Delta V_{mxg} = \frac{mM_{H_2O} (\varphi_{NaCl} - \tilde{V}_{NaCl})}{1000 + mM_{H_2O}} \quad (Eq. 16) \]

By definition \( \Delta V_{mxg,Id} = 0 \) for an Ideal Solution. Hence, the Excess Volume of the solution, the volume of mixing in excess of the Ideal case, is:

\[ \bar{V}^E = \Delta V_{mxg} - \Delta V_{mxg,Id} = \Delta V_{mxg} \quad (Eq. 17) \]

\( \bar{V}^E \) is a measure of the magnitude of the non-idealities inherent in the solution. When a solution forms, solvent-solute interactions may be different in quality when compared with the solvent-solvent or solute-solute interactions. This difference will lead to non-ideal solution behavior. For Ethanol-Water mixtures, non-idealities are significant because of Ethanol’s non-polar hydrocarbon tail. However, mixtures of Benzene \((C_6H_6)\) and Toluene \((C_7H_8)\) are relatively Ideal because of the similarity in their chemical structures. Hence \( \bar{V}^E \) will be approximately zero over the entire concentration range for these mixtures.

We will determine \( \bar{V}^E \) for NaCl/H_2O mixtures over a range of concentrations. The results can then be interpreted in terms of the strong ion-dipole interactions which exist within the solution.
Procedure

We will be making the required density measurements using a pycnometer:

The pycnometer is first calibrated against Water. The pycnometer is cleaned, dried and weighed empty. Then it is filled with Water. Using the density of Water at the measuring temperature and the mass of the Water required to fill the pycnometer, the volume of the pycnometer can be calculated. The pycnometer is then filled with the solution whose density is to be determined and weighed. This mass, along with the calibration volume, gives us the desired density measurement.

Week 1

Dry Primary Standard grade NaCl overnight in a drying oven at 110°C. Allow the salt to cool in a desiccator before weighing it out.

Prepare sufficient 3.0 molar NaCl stock solution to make the needed dilutions for this experiment. Dilute this in half successively for a total of five dilutions. These dilutions will be your “samples.”

Pre-Lab Preparation

1. Determine how much stock solution will be required. Assume each pycnometer holds between 25 – 50 mL of liquid.
2. Prepare a scheme for making the stock solution.

Week 2

It is critical that the mass measurements of the pycnometers be very accurate. Even minute errors in the mass measurement will cascade through to give very large errors in the partial molar volume results.
After you remove the pycnometer from the water bath, it should be rinsed and dried with a Kimwipe. Because small variations in the handling of the pycnometer can result in unacceptable variations in the mass measurement, the pycnometer should be handled by the same person for all measurements. And it should be handled identically for each measurement.

You will be provided with two pycnometers. Prepare and calibrate each pycnometer. After the pycnometer is clean, do not handle it directly. For the calibration, use Distilled Water and calibrate the pycnometer in a 25°C water bath. Allow the pycnometer to equilibrate for 15 minutes in the water bath using the copper baskets provided. (Be sure to read the actual temperature of the bath.)

After the system has equilibrated, draw off the bead of Water that has formed at the top of the pycnometer’s bore with a Kimwipe. (It is critical that you do this consistently.)
Carefully wash and dry the outside of the pycnometer after you remove it from the water bath. Allow the pycnometer to equilibrate in the balance room for 20 - 30 minutes (always use the same waiting period) before making a mass measurement. **Use the 5-place analytical balance in the Instrument Room in Jones Annex to make all mass measurements.** All measurements should be made in duplicate and should agree to within ± 0.01%.

**The calibration should be made in triplicate in order to determine ΔV.**

Once each pycnometer has been calibrated, fill them with the solutions whose density is to be measured, equilibrate them in a 25°C water bath, draw off the bead at the top of the pycnometers' bore, and then remove, wash and dry the pycnometers. Allow the pycnometers to equilibrate in the balance room and then make the needed mass measurements.
Data Analysis

All results must be accompanied by an appropriate error estimate.

1. Determine the density of each sample. Include appropriate error estimates.

2. Convert each solution’s concentration from Molarity \((M)\) to molality \((m)\):

\[
m = \frac{1}{1 - \left(\frac{M}{\rho}\right)\left(\frac{M_{\text{NaCl}}}{1000}\right)} \frac{M}{\rho} = \frac{1}{1 - \left(\frac{M_{\text{NaCl}}}{\rho}\right)\left(\frac{1000}{1000}\right)}
\]

3. Calculate \(\varphi_{\text{NaCl}}\) for each solution using Eq. 14 and then plot \(\varphi_{\text{NaCl}}\) vs. \(m^{1/2}\); empirically it is found this plot is linear for aqueous ionic solutions of reasonably low concentration. Include appropriate error bars. Perform a linear least squares fit to the data. Determine the slope of the line, along with an appropriate error estimate. This slope can be used to determine:

\[
\left(\frac{\partial \varphi_{\text{NaCl}}}{\partial m}\right)_{T,P,n_{\text{H2O}}} = \frac{1}{2m^{1/2}} \left(\frac{\partial \varphi_{\text{NaCl}}}{\partial m^{1/2}}\right)_{T,P,n_{\text{H2O}}} = \frac{1}{2m^{1/2}} \text{(plot slope)}
\]

The trendline should also be used to determine improved values for \(\varphi_{\text{NaCl}}\) at each measured concentration:

\[\varphi_{\text{NaCl}} = \text{(plot slope) } m + \text{(plot intercept)}\]

4. The relationship above:

\[
\left(\frac{\partial \varphi_{\text{NaCl}}}{\partial n_{\text{NaCl}}}\right)_{T,P,n_{\text{H2O}}} = \frac{1}{2m^{1/2}} \left(\frac{\partial \varphi_{\text{NaCl}}}{\partial m^{1/2}}\right)_{T,P,n_{\text{H2O}}}
\]

can be used to show that \(\bar{V}_{\text{H2O}}\) of Eq. 8 and \(\bar{V}_{\text{NaCl}}\) of Eq. 7 can be written in terms of the solution molality \(m\), instead of \(n_{\text{H2O}}\) and \(n_{\text{NaCl}}\) (Sime, 1990). This allows us to determine \(\bar{V}_{\text{H2O}}\) and \(\bar{V}_{\text{NaCl}}\) as:

\[
\bar{V}_{\text{H2O}} = \frac{M_{\text{H2O}}}{\rho_{\text{H2O}}} - \frac{m^{3/2}}{111.02} \left(\frac{\partial \varphi_{\text{NaCl}}}{\partial m^{1/2}}\right)_{T,P,n_{\text{H2O}}}
\]

and:

\[
\bar{V}_{\text{NaCl}} = \varphi_{\text{NaCl}} + \frac{m^{1/2}}{2} \left(\frac{\partial \varphi_{\text{NaCl}}}{\partial m^{1/2}}\right)_{T,P,n_{\text{H2O}}}
\]

Using this modification, determine \(\bar{V}_{\text{NaCl}}\) and \(\bar{V}_{\text{H2O}}\) for each solution. Include an appropriate error estimate for each quantity determined. Prepare a plot of each quantity; \(\bar{V}_l\) vs. \(m\).
5. Use your plot of $\bar{\nu}_\text{NaCl}$ vs. $m$ to determine $\bar{\nu}^{**}_\text{NaCl}$. Again, include an appropriate error estimate.

6. Determine $\Delta \bar{\nu}_\text{mg}$ for each solution using Eq. 16. Plot these values as $\Delta \bar{\nu}_\text{mg}$ vs. $m$. Interpret and discuss the results.
## Glossary

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Meaning</th>
</tr>
</thead>
<tbody>
<tr>
<td>$n_i$</td>
<td>Number of Moles of component $i$</td>
</tr>
<tr>
<td>$\bar{V}_i$</td>
<td>Partial Molar Volume of component $i$</td>
</tr>
<tr>
<td>$\bar{V}_i^*$</td>
<td>Molar Volume of Pure of component $i$</td>
</tr>
<tr>
<td>$\bar{V}_i^{**}$</td>
<td>Molar Volume of Pure of component $I$ at Infinite Dilution</td>
</tr>
<tr>
<td>$\varphi_i$</td>
<td>Apparent Molar Volume of component $i$</td>
</tr>
<tr>
<td>$M_i$</td>
<td>Molar Mass of component $i$</td>
</tr>
<tr>
<td>$\rho$</td>
<td>Density of the Solution</td>
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<tr>
<td>$m$</td>
<td>molality of the Solution</td>
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References


