

## **Freezing Point Depression**

CHEM 445 - 025L

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## ABSTRACT

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In this experiment, the freezing point depression of a solution of hydrochloric acid, HCl, was determined as a function of the molality of the solution. The freezing point of water was measured twice and the average was determined to be  $4.561 \pm 0.003$  °C. Consequently, to determine the freezing point depression for each data point, the following equation was used:

$$\Delta T_{F,calc} (^{\circ}\text{C}) = vK_F m$$

where  $v$  is the number of moles of ions per mole of electrolyte in solution,  $m$  is the molality of the solution, and  $K_F$  is the freezing point depression constant which for the solvent used, water in this case, is  $1.860 \frac{^{\circ}\text{C}}{m}$ . Furthermore, to compare the experimental freezing point depression, for each value of molality, with its theoretical, calculated counterpart, the osmotic coefficient was determined using the following equation:

$$g = \frac{\Delta T_{F,exp}}{vK_F m}$$

## INTRODUCTION

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Colligative properties are those properties of solutions which solely depend on the number of particles dissolved in solution irrespective of the identities of said particles. One such property is the freezing point depression; whereby, the presence of particles, in this case dissolved hydrogen ions,  $H^+$ , and chloride ions,  $Cl^-$ , lowered the freezing point of the solution relative to that of the pure solvent, water. By gradually increasing the concentration of the hydrochloric acid, HCl, in solution, the corresponding, constant temperature was recorded, from which the difference between the freezing point of the pure water slurry and the recorded temperature was calculated. This difference is the freezing point depression. Additionally, for each data point collected, the freezing point depression was determined using the associated equation, which presents the freezing point depression as a function of molality. Consequently, from both the calculated and experimental freezing point depression, the osmotic coefficient,  $g$ , was determined. The osmotic coefficient quantifies the magnitude of deviation of the real solution, experimentally prepared, and the ideal solution, theoretically obtained. From  $g$  the activity coefficient,  $\gamma$ , which is a thermodynamic factor that accounts for the non-ideality of a solution, can be determined. However, there are several models that relate these two parameters,  $g$  and  $\gamma$ . Therefore, the experimental values were compared with two such models, the Debye-Hückel Limiting Law and Davies equations, to determine which provided the better fit to the data points.

## PROCEDURE

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The freezing point of water was determined by using a differential thermometer. A slurry, a mixture of ice and water added alternately, was prepared in a Dewar flask. The slurry was stirred vigorously and the temperature was observed and recorded after several minutes of stirring until a constant value was achieved. The process was repeated with a second batch of slurry and the temperature was recorded. The average of these two values was obtained and used to compute the freezing point depression of twelve solutions.

Twelve snap top jars with caps were labeled and weighed on an analytical balance. These jars were used to contain the solutions. About 10 mL of hydrochloric acid, HCl, solution was added into the Dewar flask and mixed well. The solution was stirred continuously until a constant temperature was achieved. The temperature was recorded and immediately about 50 mL of this solution was pipetted into the first snap top jar by using a volumetric pipet. The pipet was first rinsed with the solution prior to its use. The top jar with its cap was reweighed and the mass of the solution was computed. After leaving the solution to cool down to room temperature, it was quantitatively transferred to an Erlenmeyer flask where two drops of phenolphthalein were added. A buret was filled with sodium hydroxide, NaOH, solution and the initial buret reading was recorded. The HCl solution was titrated to its end point (marked with a color change from colorless to faint pink) and the final buret reading was recorded. The volume of NaOH titrated was calculated to find the molality of HCl. This process was repeated for the remaining eleven solutions, all the while ensuring that the volume of the solution pipetted out of the Dewar flask was consistently less than the previous aliquot.

After the experiment ended, the dilute solutions were poured down the sink and the buret and Dewar flask were rinsed with distilled water.

## RESULTS AND DISCUSSION

**Table 1: Freezing Point of Distilled Water**

<b>Trial</b>	<b>Temperature (°C)</b>	<b>Uncertainty (°C)</b>	<b>Agreement (°C)</b>
1	4.561	0.002	0.001
2	4.560	0.002	
<b>Average</b>	<b>4.561</b>	<b>0.003</b>	

The temperature of the distilled water was recorded for two trials in Table 1. The values agreed within 0.001 °C and the average freezing point of distilled water was calculated to be 4.561 °C.

**Table 2: The Freezing Points and Corresponding Weights of 12 Solutions**

<b>Set #</b>	<b>t (°C) *</b>	<b>W<sub>1</sub> (g) **</b>	<b>W<sub>2</sub> (g) ***</b>	<b>W (g) ****</b>
1	4.395	75.8819	95.4469	19.5650
2	4.235	105.5287	139.9110	34.3823
3	4.089	73.3786	103.3099	29.9313
4	3.955	76.6974	110.0465	33.3491
5	3.805	76.9648	106.8735	29.9087
6	3.659	76.4136	101.5943	25.1807
7	3.640	106.1132	124.8147	18.7015
8	3.515	74.7786	85.2392	10.4606
9	3.410	105.1332	109.4806	4.3474
10	3.280	106.9373	113.6304	6.6931
11	3.200	106.9892	111.3413	4.3521
12	3.155	75.5868	80.5767	4.9899

\* Temperature of solution

\*\* Weight of empty jar and cap

\*\*\* Weight of jar, cap and solution

\*\*\*\* Weight of solution

Table 2 shows the weight of the solution for each of the twelve solutions prepared. The weight was calculated by using the following formula:

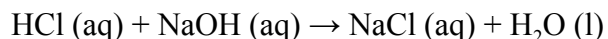
$$W(g) = W_2(g) - W_1(g) \text{ (Eq. 1)}$$

**Table 3: Volume Titrated for 12 Solutions**

Set #	Initial Buret Reading (mL)	Final Buret Reading (mL)	Volume Titrated (mL)
1	1.21	9.61	8.40
2	0.51	29.11	28.60
3	1.09	39.95	38.86
4	0.68	49.79	55.43
	1.40	7.72	
5	0.43	49.10	62.50
	1.82	15.65	
6	0.29	50.00	90.65
	0.25	41.19	
7	1.03	49.65	48.62
8	1.80	31.45	29.65
9	1.19	14.69	13.50
10	0.90	22.98	22.08
11	0.62	15.75	15.13
12	0.15	19.59	19.44

For each aliquot pipetted into an erlenmeyer flask, it was titrated with NaOH solution with the respective volume titrated tabulated in Table 3. For each of sets 4, 5, and 6, the volume titrated was exceeded 50 mL because the volume of the aliquot in the Erlenmeyer flask was too large; therefore, more NaOH solution was needed to reach the endpoint. The volume titrated was calculated using the following equation:

$$\text{Volume titrated (mL)} = \text{Final buret reading (mL)} - \text{Initial buret reading (mL)} \text{ (Eq. 2)}$$



The reaction shown above was the neutralization reaction between HCl (unknown concentration) and NaOH (known concentration). The concentration of NaOH was given as  $0.1000 \pm 0.0005 \text{ N}$ , where N stands for normality concentration. In this case, [NaOH] in M was the same,  $0.1000 \pm 0.0005 \text{ M}$ . Based on the stoichiometry, 1 mole of HCl reacts with 1 mole of NaOH to form 1 mole of NaCl and 1 mole of  $\text{H}_2\text{O}$ . From the volume titrated, in Table 3, the number of moles of NaOH was easily obtained by doing the following:

$$M = \frac{\text{number of moles (mol)}}{\text{volume (L)}}, \text{ Number of moles titrated (mol)} = [\text{NaOH}] M \times \text{Volume titrated (L)} \quad (\text{Eq. 3})$$

By the 1:1 mole ratio, the number of moles of HCl present in the flask was the same as the number of moles of NaOH titrated. From here, the mass of HCl was found by using the formula listed below. The molality of HCl was computed by finding the mass of solvent (kg). Since the mass of HCl was obtained, the mass of solvent was easily calculated, as shown below.

$$\text{Mass of HCl (g)} = \text{Moles of HCl (mol)} \times 36.46 \frac{\text{g}}{\text{mol}} \quad (\text{Eq. 4})$$

$$\text{Mass of solvent (kg)} = \text{Mass of solution (kg)} - \text{Mass of HCl (kg)} \quad (\text{Eq. 5})$$

**Table 4: The Mass of Solvent in the Flask**

Set #	Mole of NaOH (mol)	Mole of HCl (mol)	Mass of HCl (g)	Mass of solvent (g)
1	0.00010	0.00010	0.0036	0.0035
2	0.00020	0.00020	0.0073	0.0071
3	0.00030	0.00030	0.0109	0.0106
4	0.00040	0.00040	0.0146	0.0142
5	0.00050	0.00050	0.0182	0.0177
6	0.00060	0.00060	0.0219	0.0213
7	0.00070	0.00070	0.0255	0.0248
8	0.00080	0.00080	0.0292	0.0284
9	0.00090	0.00090	0.0328	0.0319
10	0.00100	0.00100	0.0365	0.0355
11	0.00110	0.00110	0.0401	0.0390
12	0.00120	0.00120	0.0438	0.0426



**Table 5:  $\Delta T_F$  and Molality for 12 Solutions**

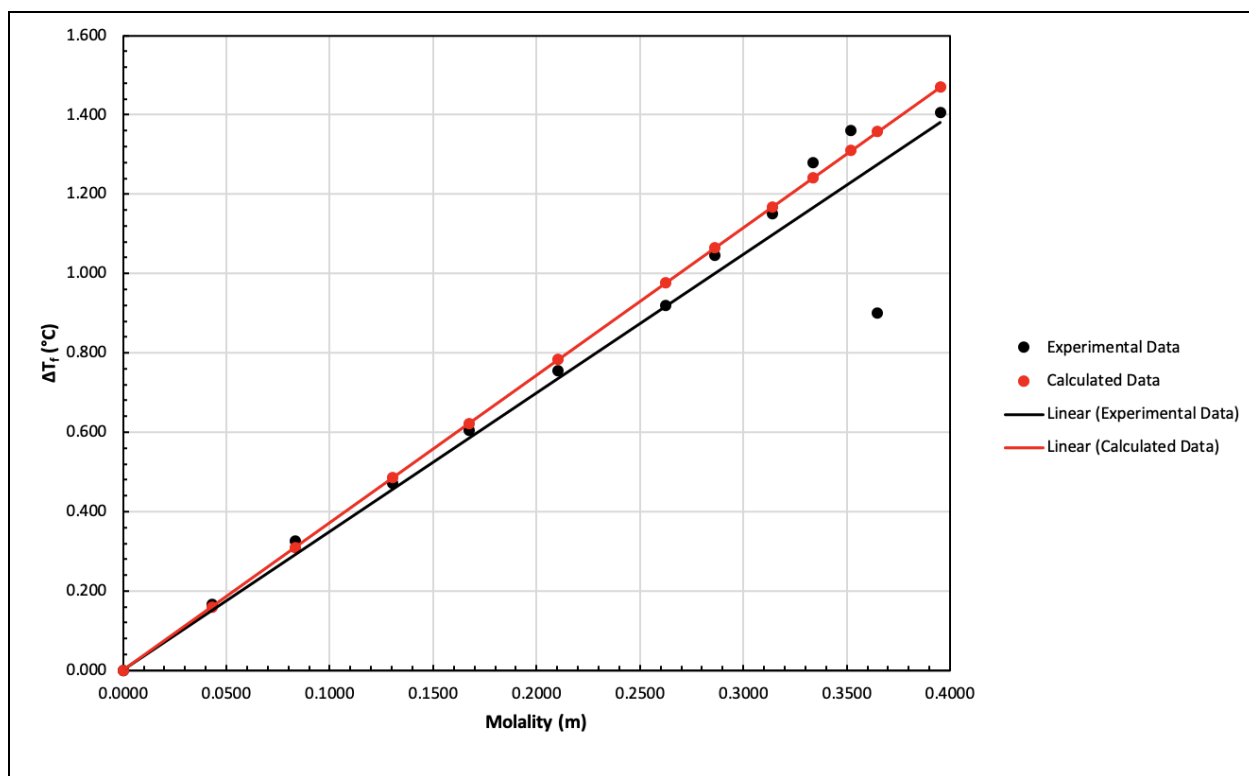
Set #	Molality (m)	$\Delta T_{f, \text{exp}} (^{\circ}\text{C})$	$\Delta T_{F, \text{calc}} (^{\circ}\text{C})$
1	0.0430	0.166	0.160
2	0.0834	0.325	0.310
3	0.1304	0.471	0.485
4	0.1672	0.605	0.622
5	0.2106	0.755	0.783
6	0.3648	0.902	1.357
7	0.2625	0.920	0.976
8	0.2864	1.046	1.065
9	0.3141	1.151	1.168
10	0.3339	1.281	1.242
11	0.3521	1.361	1.310
12	0.3952	1.406	1.470

$$\text{Molality (m)} = \frac{\text{Moles of HCl (mol)}}{\text{Mass of solvent (kg)}} \text{ (Eq. 6)}$$

$$\Delta T_{F, \text{exp}} (^{\circ}\text{C}) = T_{F, \text{solution}} (^{\circ}\text{C}) - T_{F, \text{distilled water}} (^{\circ}\text{C}) \text{ (Eq. 7)}$$

$$\Delta T_{F, \text{calc}} (^{\circ}\text{C}) = vK_F m \text{ (Eq. 8)}$$

Table 4 summarizes the data calculated by using equations 3, 4 and 5 for each solution. By using the mass of solvent (kg), the molality of HCl was calculated by using equation 6.  $\Delta T_{F, \text{exp}}$  and  $\Delta T_{F, \text{calc}}$  are the freezing point depression of the solutions obtained from experiment and through calculation, by using Eq. 7 and 8 respectively. In Eq. 7,  $T_{F, \text{distilled water}}$  is the average freezing point of distilled water obtained earlier (tabulated in Table 1). The parameters  $v$ ,  $K_F$ , and  $m$  in Eq. 8 are the number of moles of ions produced per mole of HCl (2 moles), the freezing point depression constant ( $1.860 \frac{^{\circ}\text{C}}{\text{molal}}$ ), and the molality of HCl, respectively. The freezing point depression for both, experimental and theoretical, with their respective molality, were tabulated in Table 5.



**Figure 1: Graph of  $\Delta T_f$  versus molality for 12 solutions**

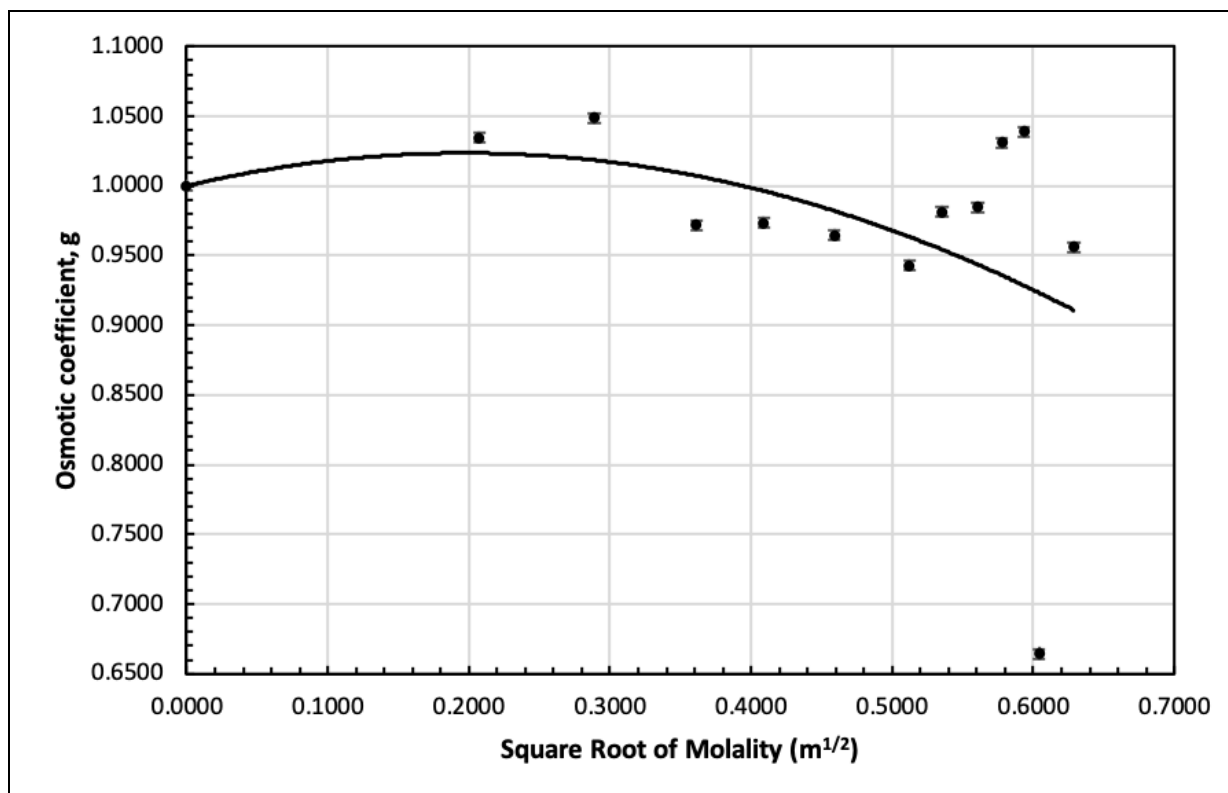
As can be seen from figure 1, the data points for each set (experimental and calculated) were fitted with linear trendlines. The freezing point depression for both the calculated and experimental data shows a linear relationship with the molality (of HCl), within the molality range of HCl used in the experiment. The two trend lines almost overlap with each other, indicating that the experimental data obtained were almost accurate and precise as predicted theoretically by Eq. 8.

One of the points obtained experimentally ( $m = 0.3648$  m,  $\Delta T_{f, \text{exp}} = 0.902$  °C) seemed to deviate away from the general trend. It was suspected to be an outlier; however, after running a Q-test, it was determined that it was not an outlier and should remain in the analysis.

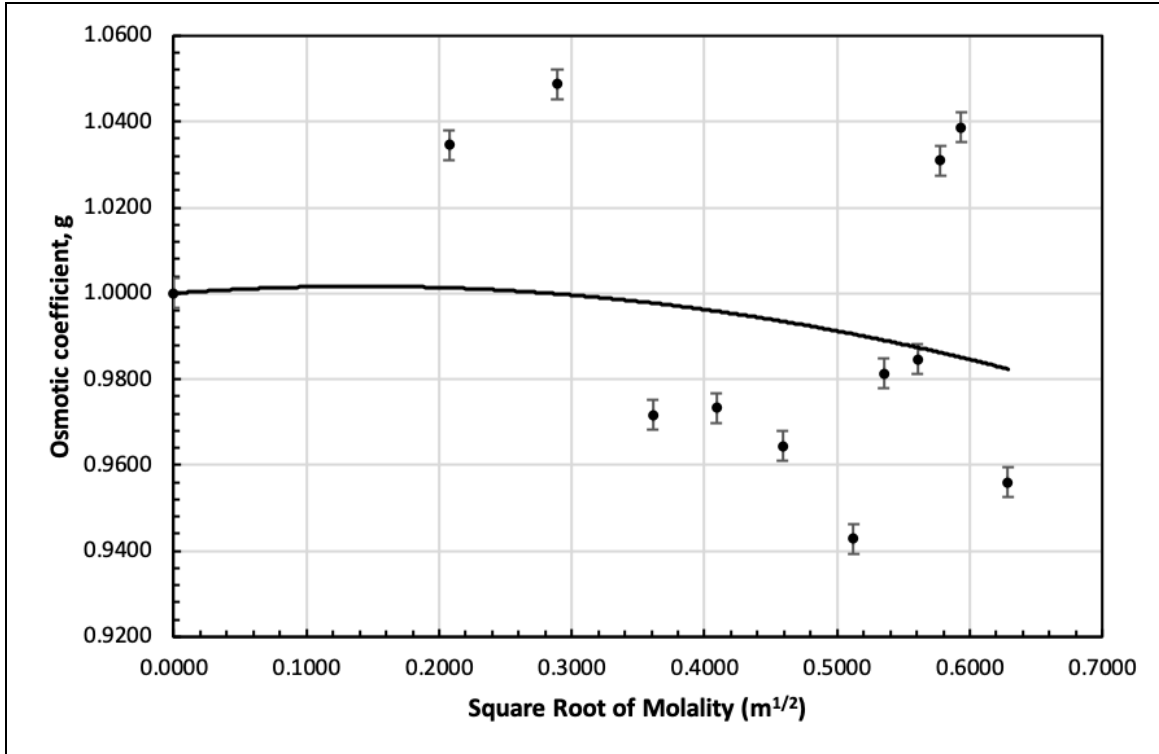
**Table 6: Osmotic Coefficient for Each Solution**

Set #	Square Root of Molality ( $m^{0.5}$ )	$g^*$	Uncertainty in $g$
1	0.2074	1.0346	0.00346
2	0.2889	1.0487	0.00346
3	0.3612	0.9716	0.00346
4	0.4089	0.9734	0.00346
5	0.4589	0.9645	0.00346
6	0.6040	0.6643	0.00346
7	0.5123	0.9428	0.00346
8	0.5352	0.9813	0.00346
9	0.5604	0.9847	0.00346
10	0.5778	1.0309	0.00346
11	0.5934	1.0387	0.00346
12	0.6286	0.9560	0.00346

\* Osmotic coefficient



**Figure 2a: Graph of  $g$  versus  $m^{0.5}$  for 12 Solutions with Uncertainty (with outlier)**



**Figure 2b: Graph of  $g$  versus  $m^{0.5}$  for 12 Solutions with Uncertainty (without outlier)**

$$g = \frac{\Delta T_{F,exp}}{vK_F m}, v = 2, K_F = 1.860 \frac{^{\circ}C}{molal} \text{ (Eq. 9)}$$

The osmotic coefficient,  $g$ , of HCl was determined by using Eq. 9 above and tabulated in Table 6. The data point highlighted in yellow was assumed to be an outlier in the experiment as it did not follow the general behavior of the plot, as shown in Figure 2a. The Q-test was conducted on the data point and it was found to be an outlier. Consequently, the outlier was removed in Figure 2b (and retained in Figure 2a). This outlier may be due to experimental error.

By referring to Figure 2b, the data points were fitted by using a second-degree polynomial fit line. The intercept was set to 1.0 and the equation of the line of best fit is as shown below:

$$g = -0.08117m + 0.02302m^{0.5} + 1.0 \text{ (Eq. 10)}$$

The intercept was set to 1.0 in order to determine how the experimental data deviated from the ideal electrolyte solution ( $g = 1$ ). As can be seen from Figure 2b, all of the data points were above/below  $g = 1$  for all values of  $m^{0.5}$  used in this experiment. The fitted line was concave downwards as the experimental data were not perfect and deviated from the ideal electrolyte solution. This is due to experimental error, such as lack of experience in getting higher precision in measurements. Close-to-perfect results are when the fitted line is linear through  $g = 1$ ; in which for this case, it was not.

Since the thermometer had an uncertainty of  $\pm 0.002\text{ }^{\circ}\text{C}$ ,  $g$  has the same uncertainty as it is a function of temperature. The uncertainty was derived as follows:

$$T_{F, \text{distilled water}} \pm u_{T1} \text{ }^{\circ}\text{C} = \frac{(T_{F1, DI \text{ water}} \pm 0.002 \text{ }^{\circ}\text{C}) + (T_{F2, DI \text{ water}} \pm 0.002 \text{ }^{\circ}\text{C})}{2}$$

$$u_{T1} = \pm \sqrt{0.002^2 + 0.002^2} \text{ }^{\circ}\text{C}$$

$$\Delta T_{F, \text{exp}} \pm u_{T2} \text{ }^{\circ}\text{C} = (T_{F, \text{solution}} \pm 0.002 \text{ }^{\circ}\text{C}) - (T_{F, \text{distilled water}} \pm u_{T1} \text{ }^{\circ}\text{C})$$

$$u_{T2} = \pm \sqrt{u_{T1}^2 + 0.002^2} \text{ }^{\circ}\text{C}$$

$$g \pm u_g = \frac{\Delta T_{F, \text{exp}} \pm u_{T2}}{vK_F m}, \text{ assuming } m \text{ had no } u_m$$

$$u_g = u_{T2} \text{ (Eq. 11)}$$

From Eq. 11, the uncertainty of the osmotic coefficient is equal to the uncertainty in the freezing point depression of the solution. All of the uncertainties tabulated in Table 6 are less than 1%, which was as expected. Furthermore, the error bars in Figure 2b were plotted by using the uncertainty computed,  $u_g$ .

The trendline function passing through the data points in Figure 2b was also obtained by using the Multiple Linear Regression (MLR) function in excel. In general, the function of osmotic coefficient is as shown below:

$$g = 1 + am^{0.5} + bm \text{ (Eq. 12)}$$

Could be rearranged to:

$$1 - g = -am^{0.5} - bm \text{ (Eq. 13)}$$

(1 - g) : dependent variable  
 $m^{0.5}$  and  $m$ : independent variables

**Table 7: The Coefficients of Equation 12 and the Respective Uncertainties from MLR**

<b>a</b>	<b>u<sub>a</sub></b>	<b>b</b>	<b>u<sub>b</sub></b>
0.023	0.130	-0.081	0.242

$$g = 1 + (0.023 \pm 0.130) m^{0.5} + (-0.081 \pm 0.242) m \text{ (Eq. 14)}$$

As tabulated in Table 7, the  $g$  function was re-written as in Eq. 13. By comparing Eq. 14 and Eq. 10, it can be seen that they both have the same coefficients, with Eq. 14 including the uncertainties generated from MLR. Consequently, from Eq. 12, the activity coefficient,  $\gamma$ , was derived as shown below:

$$\begin{aligned} \ln \gamma &= g - 1 + \int_0^m \frac{g-1}{m} dm \\ \ln \gamma &= 1 + am^{0.5} + bm - 1 + \int_0^m \frac{1 + am^{0.5} + bm - 1}{m} dm \\ \ln \gamma &= am^{0.5} + bm + \int_0^m \left( \frac{a}{m^{0.5}} + b \right) dm \\ \ln \gamma &= am^{0.5} + bm + [2am^{0.5} + bm]_0^m \\ \ln \gamma &= am^{0.5} + bm + 2am^{0.5} + bm \\ \ln \gamma &= 3am^{0.5} + 2bm \text{ (Eq. 15)} \\ a &= 0.02302, b = -0.08117 \text{ (from Eq. 10)} \end{aligned}$$

Equation 15 was then transformed to  $\log_{10} \gamma$ , as shown in Eq. 16 below. Two other equations, known as the Debye-Hückel Limiting Law (DHLL) (Eq. 17) and Davies (Eq. 18) equations, could also be used to find  $\gamma$  of HCl in the solutions. These three equations are as shown below:

$$\begin{aligned} \log_{10} \gamma_i &= \frac{\ln \gamma_i}{\ln 10} \text{ (Eq. 16)} \\ \log_{10} \gamma_i &= -0.491 \sqrt{I} \text{ (Eq. 17) }^{[2]} \\ \log_{10} \gamma_i &= -0.491 Z_i^2 \left( \frac{\sqrt{I}}{1 + \sqrt{I}} - 0.30I \right) \text{ (Eq. 18) }^{[1]} \\ \text{i: HCl species, I: ionic strength, Z: charge of ion i} \end{aligned}$$

**Table 8: Values of  $\log_{10} \gamma$  From 3 Different Equations for 12 Solutions**

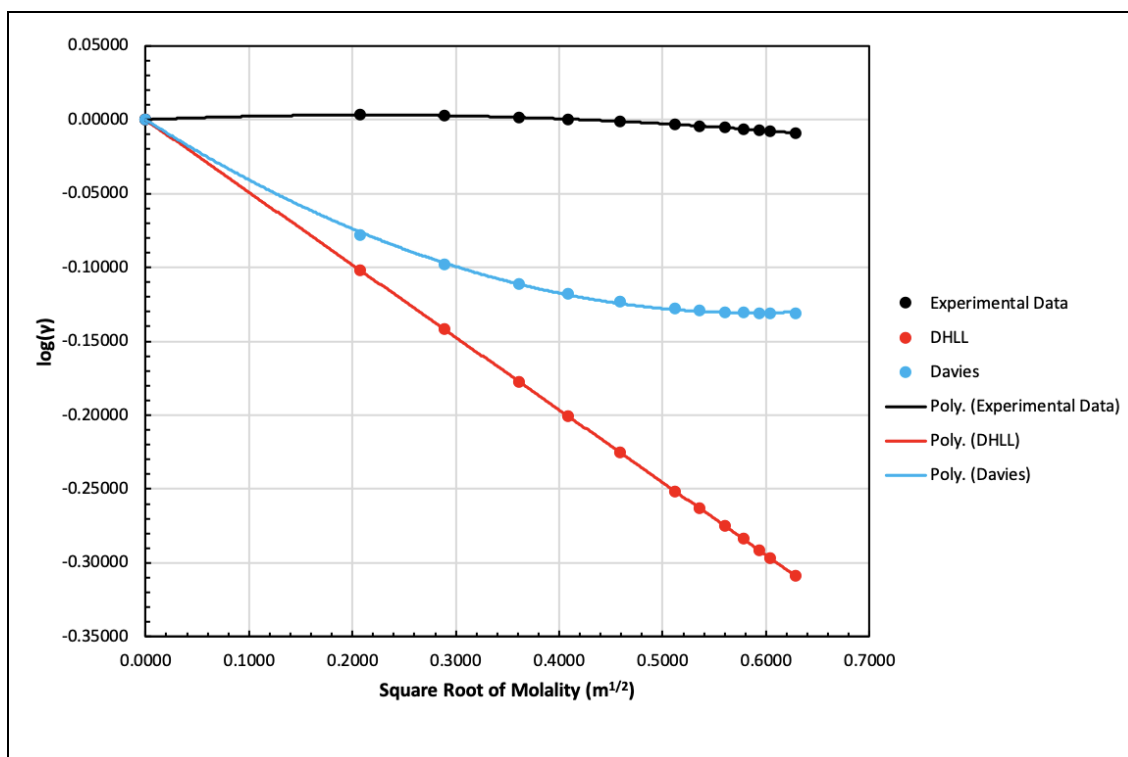
Set #	Molality (m)	Square Root of Molality ( $m^{1/2}$ )	$\ln \gamma$	$\log \gamma$ *	$\log \gamma$ **	$\log \gamma$ ***
1	0.0430	0.2074	0.0073	0.00319	-0.10182	-0.07800
2	0.0834	0.2889	0.0064	0.00278	-0.14183	-0.09775
3	0.1304	0.3612	0.0038	0.00164	-0.17734	-0.11107
4	0.1672	0.4089	0.0011	0.00047	-0.20079	-0.11788
5	0.2106	0.4589	-0.0025	-0.00108	-0.22531	-0.12342
6	0.3648	0.6040	-0.0175	-0.00761	-0.29655	-0.13115
7	0.2625	0.5123	-0.0072	-0.00314	-0.25155	-0.12767
8	0.2864	0.5352	-0.0095	-0.00414	-0.26277	-0.12898
9	0.3141	0.5604	-0.0123	-0.00534	-0.27517	-0.13008
10	0.3339	0.5778	-0.0143	-0.00621	-0.28372	-0.13063
11	0.3521	0.5934	-0.0162	-0.00703	-0.29135	-0.13099
12	0.3952	0.6286	-0.0207	-0.00901	-0.30867	-0.13131

\* Eq. 16

\*\* Eq. 17

\*\*\* Eq. 18

The logarithmic of  $\gamma$  from all three equations was calculated and tabulated in Table 8. The ionic strength,  $I$ , of HCl is the same as its molality. Hence,  $I$  in Eq. 17 and 18 could be substituted directly with  $m$ . Meanwhile,  $Z$  of HCl is 1.



**Figure 3: Graph of  $\log_{10} \gamma$  Versus  $m^{0.5}$  From All Three Equations for 12 solutions**

As illustrated in Figure 3, for all three equations used to determine  $\log_{10} \gamma$  as a function of the square root of the molality, it can be seen that, as the square root of the molality increases,  $\gamma$  ( $10^{\log_{10} \gamma}$ ) decreases. This is expected since more concentrated solutions have lower  $\gamma$ . The more the ions that are dissociated in solution, the higher the ionic strength and therefore, the lower  $\gamma$ .

The trendline delineating the experimental data shows that over the range  $m^{0.5}$  values,  $\log_{10} \gamma$  takes on values equal to/around zero. This translates to  $\gamma$  values equal to/around 1 ( $\log_{10} \gamma = 0$ ,  $\gamma = 1$ ). As for the data plotted using Eq. 17 and 18,  $\gamma$  values obtained were less than 1 which is as predicted. As mentioned earlier, there were some experimental errors in terms of getting higher precision measurements when recording the data. The value of  $0.20 m^{0.5}$  is considered to be concentrated enough for the solution to have a  $\gamma$  value of less than 1; however, the experimental data did not support such predictions. There were flaws in this experiment making the analysis fully relied on the theoretical values, obtained from Eq. 17 and 18 only.

Davies equation is applicable to a wide range of  $I$  unlike the DHLL equation<sup>[4]</sup>; however, it is still limited to certain concentrations. Based on lecture notes presented by Professor James. W. Murray from the University of Washington<sup>[3]</sup>, the Davies equation is appropriate for  $I$  values of less than 0.5 M, while the DHLL equation is only suitable for  $I$  values of less than  $10^{-2.3} \approx 0.005$  M. Hence, the Davies equation correctly models the behavior of the twelve solutions, as each of them had an  $I$  value of less than 0.5 ( $I=m$  for HCl), unlike the DHLL, since all of the  $m$  values obtained experimentally were more than 0.04 m.



## CONCLUSIONS

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The freezing point depression displayed a positive linear relationship with the molality, which was in close agreement with its theoretical, calculated counterpart. Furthermore, these experimental results were further supported by the calculated values for the osmotic coefficient which remained close to one for each data point. In other words, there was relatively minimal deviation from ideality. As for the two equations that were used to model the activity coefficient of the solution as function of the square of the molality, neither of them provided a good fit to the experimental data. This could be due to the associated experimental error, with the Davies equation providing a better theoretical representation of the data points.

## REFERENCES

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<sup>[3]</sup> Murray, J. W. Chapter 6 Activity Scales and Activity Corrections.

<sup>[4]</sup> Pardue, H. L. *Chemical equilibria: exact equations and spreadsheet programs to solve them*; CRC press, Taylor & Francis group.: Boca Raton.