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# Enthalpies of Mixing of Water and Alkoxyethanols

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# ENTHALPIES OF MIXING OF WATER AND ALKOXYETHANOLS

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Patricia D. Witherspoon, Ph.D.  
Dean of the Graduate School

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By

John Enriquez

2010

## **Dedication**

This thesis is dedicated to my parents, Miguel Enriquez and Manuela R. Enriquez, for all of their unconditional love, support and understanding throughout my seemingly long educational career.

I also dedicate my thesis to my late brother Mike Enriquez Jr. It's been so long, that I honestly don't know what to write. I will say this, thank you for watch over me. I knew that was you.

# ENTHALPIES OF MIXING OF WATER AND ALKOXYETHANOLS

By

JOHN ENRIQUEZ

THESIS

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## Abstract

Alkoxyethanols [ $C_mH_{2m+1} \cdot (OC_2H_4) \cdot OH$ ] (conveniently abbreviated to  $C_mE_1$ ) are a subgroup of the alkyl poly(ethylene glycol) mono-ethers. They are small relatives of a large number of non-ionic detergents. The thermodynamic properties of their mixing in water have been shown to be good sources of information about the interactions of both hydrophilic and hydrophobic groups with water. These alkoxyethanols, or glycol ethers, are the ether derivatives of ethylene glycol where one hydroxyl functional group is substituted for an alkoxy functional group. Our group has already published results for aqueous excess properties of 2-Methoxyethanol ( $C_1E_1$ ), 2-Ethoxyethanol ( $C_2E_1$ ) and 2-Butoxyethanol ( $C_4E_1$ ),<sup>1,2</sup> three more alkoxyethanols will be added to a list of calorimetric data, being collected, for these small alkoxyethanols<sup>3</sup>. The three amphiphiles used in this experiment are 2-Propoxyethanol ( $C_3E_1$ ), 2-Isopropoxyethanol ( $i-C_3E_1$ ) and 2-Isobutoxyethanol ( $i-C_4E_1$ ). Since limited thermodynamic information exists for these three liquids, supplemental data was needed. Excess enthalpy data collected for 2-Propoxyethanol ( $C_3E_1$ ) and 2-Isopropoxyethanol ( $i-C_3E_1$ ) were obtained with no problems. Data collected for 2-Isobutoxyethanol ( $i-C_4E_1$ ) revealed some serious discrepancies from literature values.

## Table of Contents

Acknowledgements.....	v
Abstract.....	vi
Table of Contents.....	vii
List of Tables.....	ix
List of Figures.....	x
Chapter 1: Introduction.....	1
1.1 Alkoxyethanols.....	1
1.2 Background on Previous Work and Research.....	3
1.3 Alkoxyethanol Aggregation/Micelle Behavior.....	4
1.4 Thermodynamic Mixing Quantities ( $\Delta_{\text{mix}}G$ , $\Delta_{\text{mix}}S$ , $\Delta_{\text{mix}}H$ , and $\Delta_{\text{mix}}V$ ).....	5
Chapter 2: Experimental Procedures (Chemicals, Instrumentation and Thermogram).....	7
2.1 Chemical Reagents.....	7
2.2 Equipment and Materials.....	7
2.3 Protocol for Determining Enthalpies of Mixing of Alkoxyethanols with Water.....	9
2.4 Producing a Thermogram/Thermograph.....	11
Chapter 3: Results and Discussion.....	16
3.1 Experimental Data Collected.....	16
3.2 Data Interpretation.....	17
3.3 Enthalpies of Mixing for other Alkoxyethanol-Water Mixtures ( $C_mE_1$ ), $m \leq 2$ .....	19
3.4 Further Reading.....	19
Chapter 4: Conclusions.....	21
References.....	22



Appendix.....	23
Curriculum Vita.....	29

### **List of Tables (Appendix I)**

Table 1: Mole Fraction and Excess Enthalpy Data (2-Propoxyethanol) for Fig. 3.1.1.....	23
Table 2: Mole Fraction and Excess Enthalpy Data (2-Isopropoxyethanol), Fig. 3.1.1.....	23
Table 3: Mole Fraction & Excess Enthalpy Data for 2-Isopropoxyethanol, See ref. 15.....	24

### **List of Tables (Appendix II)**

Table 1: Mole Fraction & Excess Enthalpy Data for (2-Butoxyethanol), Fig. 3.1.2.....	25
Table 2: Mole Fraction & Excess Enthalpy Data for (2-Isobutoxyethanol), Fig. 3.1.2.....	25
Table 3: Mole Fraction & Excess Enthalpy Data for 2-Isobutoxyethanol, Fig. 3.1.2 & Ref. 16..	25

### **List of Tables (Appendix III)**

Table 1: Excess Molar Volume (2-PE) & (2-IPE).....	27
Table 2: Excess Molar Volume (2-BE) & (2-IBE).....	27
Table 3: Isentropic Compressibility (2-BE) & (2-IBE).....	28

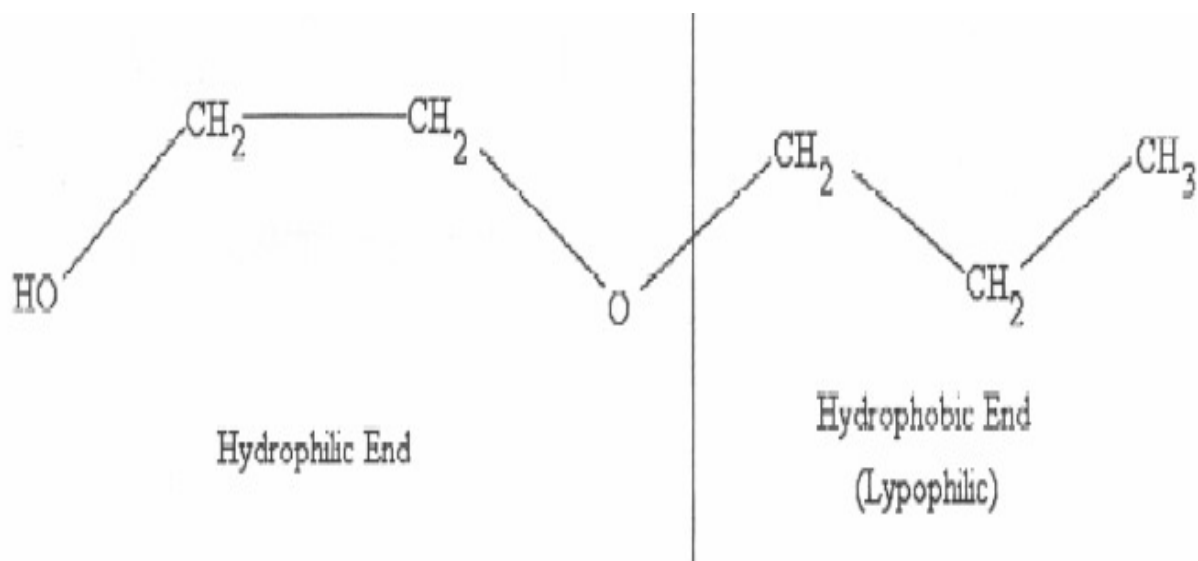
## List of Figures

Figure 1.1.1: Amphiphile Example (2-Propoxyethanol).....	2
Figure 1.1.2: Structures of three Alkoxyethanols.....	2
Figure 2.2.1: PARR 1455 Solution Calorimeter.....	8
Figure 2.2.2: Glass Cell Sample.....	8
Figure 2.2.3: Internal Diagram (Side View) of Parr 6755, Analog to Parr 1455.....	9
Figure 2.4.1: Time/Temperature Sheet Example.....	11
Figure 2.4.2: Thermograph Example.....	12
Figure 2.4.3: Pre & Post Drift Equations & Mid-Point of Reaction Temp. Rise.....	14
Figure 2.4.4: Thermograph with Corrected Temperature Values.....	15
Figure 3.1.1: Enthalpy of Mixing for (2-PE) & (2-IPE).....	16
Figure 3.1.2: Enthalpy of Mixing for (2-BE) & (2-IBE).....	17

## Chapter 1: Introduction

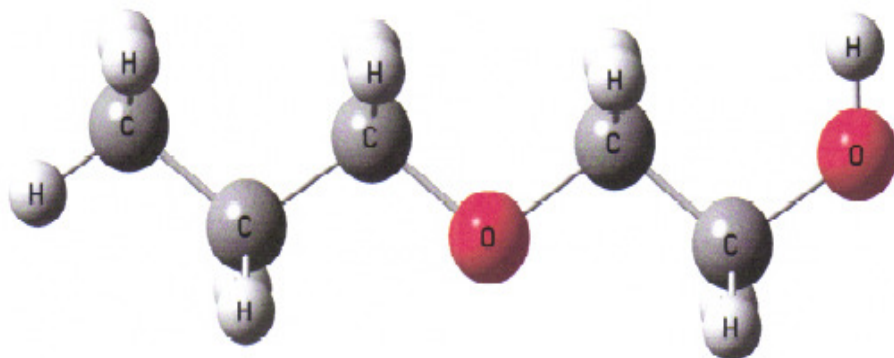
### 1.1: Alkoxyethanols

Since alkoxyethanol molecules are part of the family of alkyl poly(ethylene glycol) mono-ethers  $[C_mH_{2m+1} \cdot (OC_2H_4)_n \cdot OH]$ , they are model compounds for a range of patterns of amphiphile aggregation such as micelles, bilayers and vesicles. The smaller alkoxyethanols ( $C_1$  thru  $C_6$ ) have found extensive industrial applications as solvents. They are also known by their trade name as cellosolves. These cellosolves have distinct properties and have been used as solvents for cellulose compounds, resins, oils, greases, dyes, paints, and many other materials<sup>4</sup>. To gain a deeper understanding of the role of alkoxyethanols, we study the thermodynamic properties of their aqueous mixtures. Alkoxyethanols are derivatives of ethylene glycol  $[HO-CH_2CH_2-OH]$  where one alcohol functional group  $[-OH]$  has been substituted by the alkoxy group  $[R-O-]$ ; where R can be any alkyl functional group. For example, inserting the propyl chain to the alkoxy group  $[C_3H_7-O-]$ , it now becomes 2-Propoxyethanol,  $[C_3H_7-O-CH_2CH_2-OH]$  and the butyl chain  $[C_4H_9-O-]$  becomes 2-Butoxyethanol  $[C_4H_9-O-CH_2CH_2-OH]$ . It is this combination of the ether and alcohol group which gives this molecule its non-ionic detergent amphiphilic characteristic. Typically, amphiphilic molecules contain a hydrophilic polar head attached to a long hydrophobic (lipophilic) tail. In the alkoxyethanol molecule, the alcohol group at the end of the ethane chain represents the hydrophilic polar head  $[-CH_2CH_2-OH]$  where hydrogen bonding occurs. The alkyl group  $[R-]$  is the hydrophobic (lipophilic) tail end. Figure 1.1.1 indicates the different locations of an amphiphilic molecule using 2-Propoxyethanol as an example. Figure 1.1.2 shows the three dimensional structures for all three alkoxyethanols used in this work.

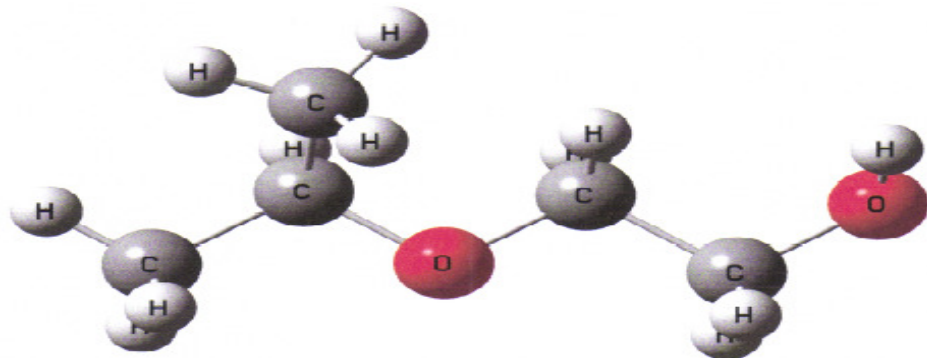


**Figure 1.1.1: Amphiphile Example (2-Propoxyethanol)**

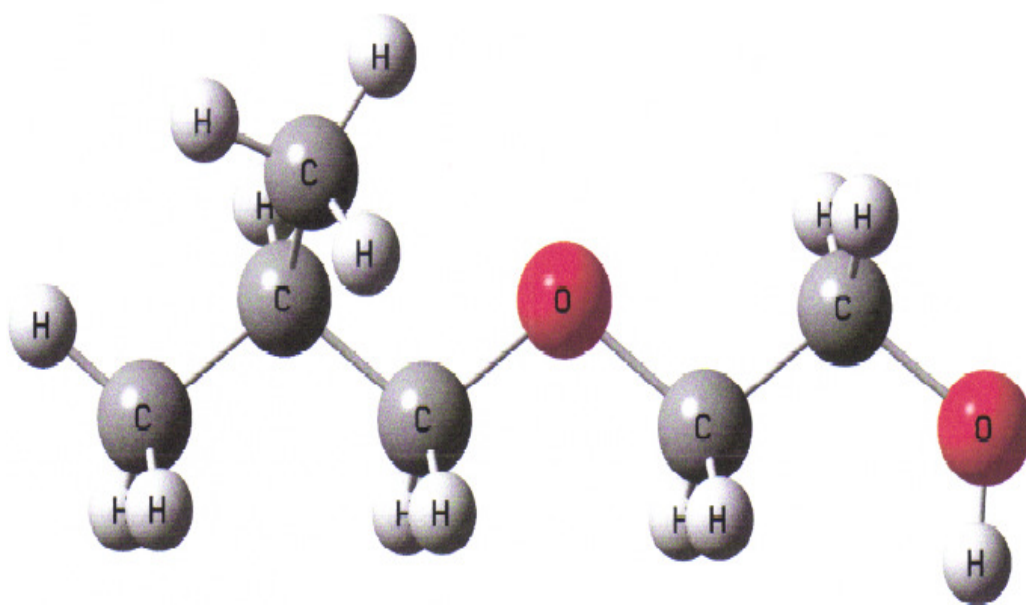
**Figure 1.1.2: Structures for the Ethylene Glycol Mono-Alkyl Ethers**



**2-Propoxyethanol ( $C_3E_1$ )**



**2-Isopropoxyethanol ( $i-C_3E_1$ )**



## 2-Isobutoxyethanol (*i*-C<sub>4</sub>E<sub>1</sub>)

### 1.2: Background of Previous Work/Research

Previous research into these cellosolves has involved their potential toxic effects on people as well as on the environment<sup>4,5</sup>. Previous work done by our group has used both calorimetric and volumetric research in order to compile specific solution thermodynamic data for a few alkoxyethanol-water systems. This includes data for excess molar volumes ( $\Delta V_m^E$ ), isobaric expansivities ( $\Delta E_m$ ), excess molar enthalpy ( $\Delta H_m^E$ ), excess molar heat capacities ( $\Delta C_p^E$ ) and the excess isentropic compressibility ( $\Delta K_S^E$ )<sup>3</sup>. This investigation studied the excess molar enthalpy ( $\Delta H_m^E$ ), which is identical to the enthalpy of mixing ( $\Delta_{\text{mix}}H$ ), between 2-Propoxyethanol (C<sub>3</sub>E<sub>1</sub>), 2-Isopropoxyethanol (*i*-C<sub>3</sub>E<sub>1</sub>) and 2-Isobutoxyethanol (*i*-C<sub>4</sub>E<sub>1</sub>) and water using the full composition mole fraction range. Using these calorimetric findings should not only add to the thermodynamic data; it will also provide good information on how these three compounds interact in an aqueous environment.

### 1.3: Alkoxyethanol Aggregation/Micelle Behavior.

In general, most organic liquids are not soluble in water due to the fact that the hydrocarbon moieties cannot form hydrogen bonds with water. To overcome this action, the organic solvent would need to have both hydrophilic and hydrophobic properties. The term used for organic solvents with these two properties is called amphiphilic molecules. This component affects the water surface tension allowing for the compound to become soluble in water. With this change in solubility, interactions between water and the amphiphile will now come into play. There are three possible intermolecular interactions that the amphiphile and water may encounter, solute-solute, solvent-solvent and solute-solvent. For this research, the solute-solvent interaction was important in determining the mixing parameters between the two liquids; the alkoxyethanol was the solute and water the solvent.

It has been determined that amphiphiles with six or more carbon atoms and greater than three oxyethylene components, ( $C_mE_n$ ), have been classified as detergents and can form micelles<sup>6</sup>. A micelle is an organized cluster which is composed of many individual amphiphiles. In the work presented here, all three alkoxyethanols have less than six carbon atoms in their alkyl structure, so it will be safe to say that all three will aggregate, or cluster, if and when certain conditions are met. Keep in mind, when stable micelles form all of the hydrophilic alkyl groups are isolated from their water environment forming an oily core. When smaller amphiphiles cluster, their alkyl groups are not totally isolated while some alkyl groups remain in contact with water. At low concentrations there is strong evidence of clathrate formation<sup>7,8</sup>.

#### 1.4 Thermodynamic Mixing Quantities ( $\Delta_{\text{mix}}G$ , $\Delta_{\text{mix}}S$ , $\Delta_{\text{mix}}H$ , and $\Delta_{\text{mix}}V$ ).

For any physical or chemical change that takes place under constant temperature and pressure, the driving potential is the Gibbs Energy ( $G$ ). From the ideal gas equation, one can derive an expression for the molar ideal Gibbs energy of mixing for two ideal gases (A & B),

$$\Delta_{\text{mix}}G_m (\text{ideal}) = RT \cdot [X_A (\ln X_A) + X_B (\ln X_B)] \quad (1)$$

The symbol  $X_A$  represents the mole fraction for component A and  $X_B$  is the mole fraction for component B. The ideal Gibbs energy of mixing for two liquids is identical to that for ideal gases. This is consistent with Raoult's Law. Equation (1) carries with it implications regarding the entropy change, the volume change, and the enthalpy change which accompanies the mixing process. To find the entropy of mixing,  $\Delta_{\text{mix}}S_m (\text{ideal})$ , the partial derivative of  $\Delta_{\text{mix}}G_m$  with respect to temperature is calculated from equation (1).

$$\Delta_{\text{mix}}S_m = - (\partial \Delta_{\text{mix}}G_m / \partial T)_P \quad (2)$$

$$\Delta_{\text{mix}}S_m (\text{ideal}) = -R \cdot [X_A (\ln X_A) + X_B (\ln X_B)] \quad (3)$$

As for the volume, the partial derivative of  $\Delta_{\text{mix}}G_m$  with respect to pressure is calculated from equation (1).

$$\Delta_{\text{mix}}V = - (\partial \Delta_{\text{mix}}G_m / \partial P)_T \quad (4)$$

Since  $\Delta_{\text{mix}}G$  is independent of pressure in equation (1), the  $\Delta_{\text{mix}}V (\text{ideal})$  equals zero.

$$\Delta_{\text{mix}}V (\text{ideal}) = 0 \quad (5)$$

Now, using equation (1) and (3), at constant temperature and pressure, along with equation (6),

$$\Delta_{\text{mix}}G = \Delta_{\text{mix}}H - T\Delta_{\text{mix}}S \quad (6)$$

the enthalpy of mixing can now be calculated by rearranging equation (6) to find  $\Delta_{\text{mix}}H (\text{ideal})$ .

$$\Delta_{\text{mix}}H (\text{ideal}) = T\Delta_{\text{mix}}S (\text{ideal}) + \Delta_{\text{mix}}G (\text{ideal}) \quad (7)$$



Substituting equation (3), for  $\Delta_{\text{mix}}S$  (ideal), and equation (1), for  $\Delta_{\text{mix}}G$  (ideal), will show that  $\Delta_{\text{mix}}H$  (ideal) equals zero.

$$\Delta_{\text{mix}}H \text{ (ideal)} = 0 \text{ (8)}$$

No heat is evolved when two pure liquids are mixed to form an ideal solution.

Since thermodynamic properties of mixtures between two liquids are usually expressed in terms of excess functions, the mixing quantities can be calculated from the excess functions. For example,

$$\Delta_{\text{mix}}G = G^E + \Delta_{\text{mix}}G \text{ (ideal)} \text{ (9)}$$

$$\Delta_{\text{mix}}S = S^E + \Delta_{\text{mix}}S \text{ (ideal)} \text{ (10)}$$

$$\Delta_{\text{mix}}H = H^E + \Delta_{\text{mix}}H \text{ (ideal)} \text{ (11)}$$

For this research, our excess molar quantity  $Q^E$  is defined by the equation

$$Q^E = Q_{\text{mix}} \text{ (experimental)} - Q_{\text{mix}} \text{ (ideal)} \text{ (12)}$$

therefore  $H^E = \Delta_{\text{mix}}H$  (experimental).

## **Chapter 2: Experimental Procedures (Chemicals, Instrumentation and Thermogram)**

### **2.1: Chemical Reagents**

Three alkoxyethanols were used in this experiment. The organic reagents of 2-Isopropoxyethanol (purity > 99% by GC) and 2-Isobutoxyethanol (purity 98% min. by GC) were obtained from TCI-America and used without any further purification. The 2-Propoxyethanol (purity assay 99%) was supplied from Aldrich Chemicals and was also used, as is, without further purification. While using these chemical reagents, caution was used to limit any atmospheric moisture or other contaminants from coming in contact with the pure liquids by keeping all bottles closed between experiments and sealing the bottles when not in use. Also, for these experiments, Millipore Grade purified water was used as the solvent. Millipore grade water is prepared by passing distilled water through an osmosis membrane removing any water-soluble contaminants, which may interfere with the tests. The conductivity of the water was measured at  $4.4 \text{ M}\Omega \cdot \text{cm}$ . For consistency purposes, the Millipore water bottle was treated as the chemical reagents were in limiting its exposure to atmospheric moisture and other contaminants by keeping the bottle closed between experiments and sealed when not being used.

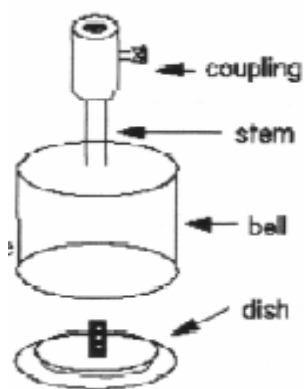
### **2.2: Equipment and Materials**

The instrument used to determine the excess molar enthalpies/heats of mixing ( $\Delta_{\text{mix}}H$ ) was the Parr Instruments 1455 Solution Calorimeter which was used at room temperature and under atmospheric pressure conditions (See Fig. 2.2.1).

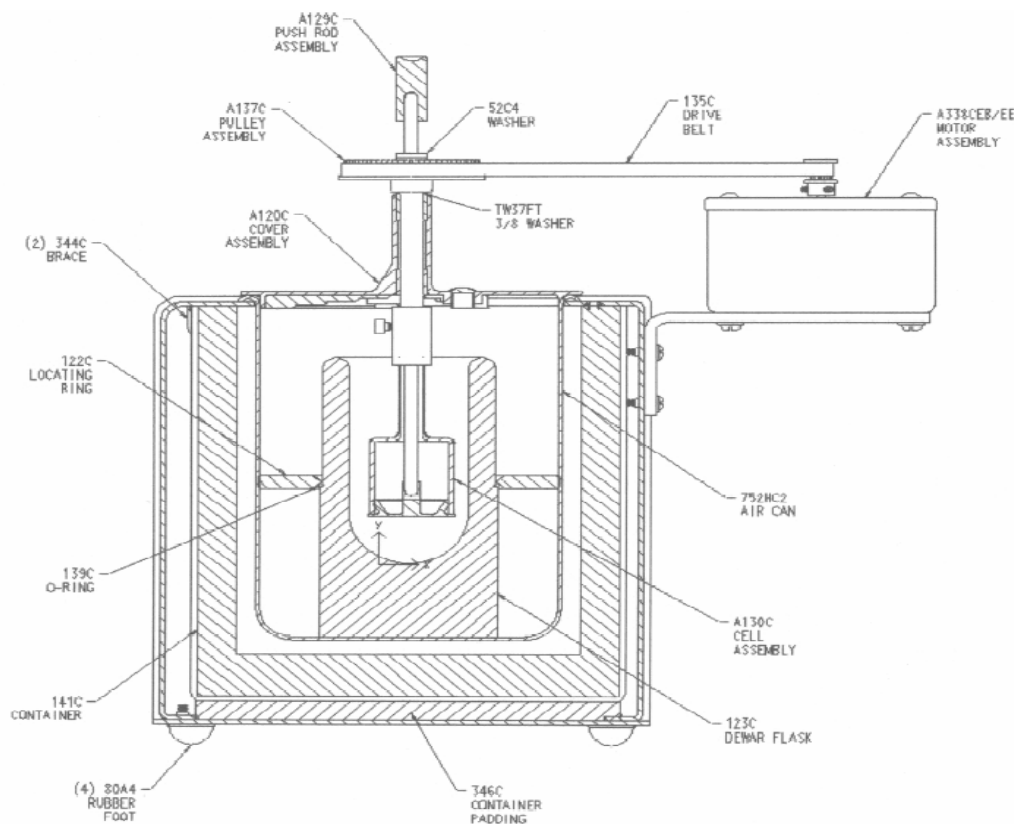


**Figure 2.2.1: Parr 1455 Solution Calorimeter**

The standard parts that make up the 1455 calorimeter are as follows, the Glass-like Dewar Vessel, a small Sample Glass Rotating Cell w/ a Teflon sample dish and a Thermistor Probe for temperature readings, as well as a small motor for stirring the mixture (See Fig. 2.2.2) & (See Fig. 2.2.3)<sup>9,10,11</sup>.



**Figure 2.2.2 Glass Sample Cell**



**Figure 2.2.3: Internal Diagram (Side View) of Parr 6755, Analog to Parr 1455.**

Since the heat capacity of the calorimeter will be used to calculate final enthalpy changes, calibration of the calorimeter was performed using the standardization guidelines provided in the Parr 1455 Solution Calorimeter Operating Instruction Manual. The calibration procedure calls for reacting 0.5 grams of (Tris[hydroxymethyl]aminomethane) with 100 milliliters of 0.1M HCl. Carefully following these instructions, the heat capacity ( $C_p$ ) was determined to be 101.25 J/°C for the empty calorimeter.

### **2.3: Protocol for Determining Enthalpies of Mixing of Alkoxyethanols with Water.**

According to operating instructions, the Dewar should be filled with a volume between 90 mL and 120 mL. The sample cell can hold up to 20 mL of liquid sample. Using these parameters, calculations were made to determine the volumes needed to produce 90 mL of an alkoxyethanol/water mixture, in the Dewar, when specific mole fractions of the solute were

needed. Two protocols were used for the enthalpy determinations, the first method is as follows. When no alkoxyethanol/water mixture was needed in the Dewar, it was simply filled with 90 mL of the solvent, water in this case. With these calculations complete, experimental data can now be collected. An empty clean dry Dewar was weighed on a Scientech<sup>®</sup> Analytical Balance,  $W(D)$ . The established volume of water was added to the Dewar and then reweighed. This weight equals to the weight of the Dewar plus the weight of the water. Subtraction of the two numbers will now give the weight of the water,  $W(W)$ . To the water in the Dewar, the established volume of the alkoxyethanol is added to the Dewar where weight increases. Again, subtraction of these two values will give the weight of the alkoxyethanol,  $W(C_mE_1)$ . The second method for enthalpy determinations is to calculate an alkoxyethanol/water mixture inside the Dewar. This is done in order to obtain excess molar enthalpy data slightly beyond the allowable volumes in the Dewar and in the sample cell. The first thing done is to choose an appropriate alkoxyethanol mole fraction starting point. Doing this will also give the mole fraction starting point for water. From here, calculations are performed to determine the approximate masses for each one, using their individual molecular weights. With this complete, the corresponding volumes are measured from their calculated masses using the density for the pure liquids and then adjusting these values to 90 milliliters; the starting volume for the Dewar cell. As was done in the first method, the weights for water and the alkoxyethanol are taken and recorded for the Dewar and sample cell. I now have the weights for both the alkoxyethanol and the water inside the Dewar. These masses are converted to units of moles and then converted to mole fractions for the alkoxyethanol and water. These starting point mole fractions are important for the reason that data interpolation will be used to calculate the excess molar enthalpy at those specific mole fraction points which will then be added to the final excess molar enthalpy calculations. The

next step is to add the prescribed volume amount of the alkoxyethanol to the sample cell and determine its weight. From here, the calorimeter can now be loaded to begin the experiment in order to collect data for production of a thermogram/thermograph.

#### 2.4: Producing a Thermogram/Thermograph.

One accessory the Parr 1455 Calorimeter makes use of is a dot matrix printer for thermogram charts (Parr Instruments 1755). Because this printer was not available, a slight modification was used to produce a thermograph. Since the calorimeter thermister measured temperature readings every ten seconds, while displaying them on the instrument panel, a time/temperature sheet was carefully used to manually record the solution mixture temperature. Below is a truncated time/temperature sheet example of a mixture of 2-Isobutoxyethanol and water (See Fig. 2.4.1).

Time Seconds	Temperature Celsius	Time Seconds	Temperature Celsius
0	25.11211	410	25.6597
10	25.20254	420	25.82727
20	25.22637	430	25.85704
30	25.23591	440	25.86437
40	25.2418	450	25.86755
50	25.24537	460	25.8692
60	25.24847	470	25.87041
70	25.2505	480	25.87125
80	25.25203	490	25.87211
90	25.25297	500	25.87292
100	25.25362	510	25.87352
110	25.25404	520	25.87421
120	25.25429	530	25.87482
130	25.25409	540	25.87546
140	25.25431	550	25.87615
150	25.25431	560	25.87689
160	25.25421	570	25.87749
170	25.25416	580	25.87813
180	25.25431	590	25.87877
190	25.25429	600	25.87938
200	25.25434	610	25.88012

Figure 2.4.1: Time/Temperature Sheet Example

With these temperatures now manually recorded, they are now entered into an excel spreadsheet program where a thermograph is plotted. This thermograph plots puts time on the x-axis and the temperature on the y-axis (See Fig. 2.4.2).

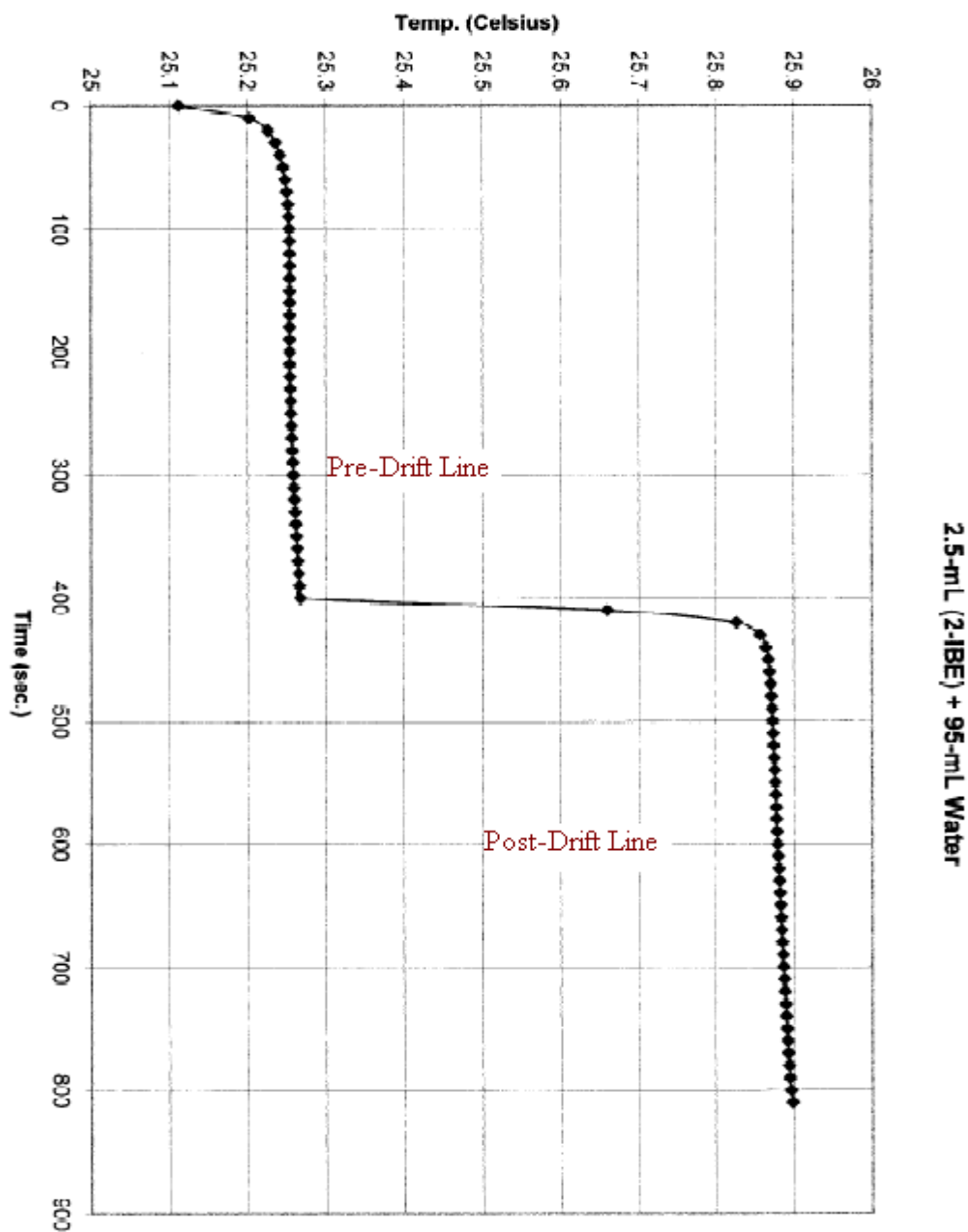


Figure 2.4.2: Thermograph Example

Now with the thermograph plotted, interpretation, of the graphical data, is done in order to determine the overall net temperature change ( $\Delta T = T_f - T_i$ ) and the temperature of the mixture ( $T_{\text{mix}}$ ) for the reaction between the two solutions. Before computing this change in temperature, a line is drawn over the pre-drift points and extended out pass the point where the sample cell was opened to start the reaction. A similar line is drawn over the post-drift line and extended backwards to a point just before the sample cell was opened. Noticing that the pre-drift and the post-drift lines are approximately linear, the method of least squares is employed to find the best straight line through the pre-drift and post-drift points<sup>12</sup>. These two, separate, equations will then be used to determine the final and initial temperature of the mixture (See Fig. 2.4.3). The pre-drift line equation used was  $y = 8.8545 \times 10^{-5}(x) + 25.2318$  with a correlation coefficient ( $R^2$ ) value of 0.99876 and the post-drift line equation used was  $y = 7.7324 \times 10^{-5}(x) + 25.8333$  with a correlation coefficient ( $R^2$ ) value of 0.99591. Using the time/temperature spreadsheet, the median value is used to locate the point in the middle of the reaction rise. Using this median point, a vertical line is drawn and the distance, R, is measured using a centimeter straight edge. Do not confuse this distance R with the symbol used for the correlation coefficient. This measured distance is then multiplied by 0.63 to find the point which is 63% above the start of the reaction rise. Specific mathematical calculations and derivations on how this value is worked out can be found in literature<sup>13</sup>. With this new 0.63R distance, the zero end of the ruler is placed on the pre-drift line and moved along the extrapolated line to the new vertical position of the temperature rise. A second vertical line is drawn between the pre-drift and post-drift line. This line will now be used to estimate the change in temperature as well as the temperature of the mixture (See Fig. 2.4.4).



280	25.0647	Product			
290	25.0651	xy	x-squared		
300	25.06537	7519.6110	90000	Sum of x:	3850
310	25.06582	7770.4042	96100	Sum of y:	275.7459
320	25.06632	8021.2224	102400	Sum of xy:	96511.5923
330	25.06681	8272.0473	108900	Sum of x-sq.:	1358500
340	25.06736	8522.9024	115600	n-Variable:	11
350	25.0679	8773.7650	122500	C-Variable:	11000
360	25.0683	9024.5880	129600	Slope (m):	4.7936E-05
370	25.0687	9275.4190	136900	Intercept (b):	25.051
380	25.06927	9526.3226	144400	<b>Mid Point:</b>	25.4148
390	25.06976	9777.2064	152100	Pre-Drift Line Equation: $y = mx + b$	
400	<b>25.07026</b>	10028.1040	160000		
410	<b>25.2816</b>				
420	<b>25.39331</b>				
430	<b>25.41034</b>				
440	<b>25.41481</b>	Center Point of the Reaction			
450	<b>25.41699</b>				
460	<b>25.41843</b>				
470	<b>25.41939</b>				
480	<b>25.42033</b>	Product			
490	25.42097	xy	x-squared		
500	25.42169	12710.8450	250000	Sum of x:	20960
510	25.42241	12965.4291	260100	Sum of y:	813.8017
520	25.423	13219.9600	270400	Sum of xy:	533057.7823
530	25.423	13474.1900	280900	Sum of x-sq.:	14001600
540	25.42426	13729.1004	291600	n-Variable:	32
550	25.42471	13983.5905	302500	C-Variable:	272800
560	25.42525	14238.1400	313600	Slope (m):	6.4768E-05
570	25.4257	14492.6490	324900	Intercept (b):	25.3889
580	25.42642	14747.3236	336400		
590	25.42708	15001.9772	348100	Post-Drift Line Equation	
600	25.42751	15256.5060	360000		

**Figure 2.4.3: Pre & Post Drift Equations & Mid-Point of Reaction Temp. Rise.**

# 2.5-mL (2-IBE) + 95-mL Water

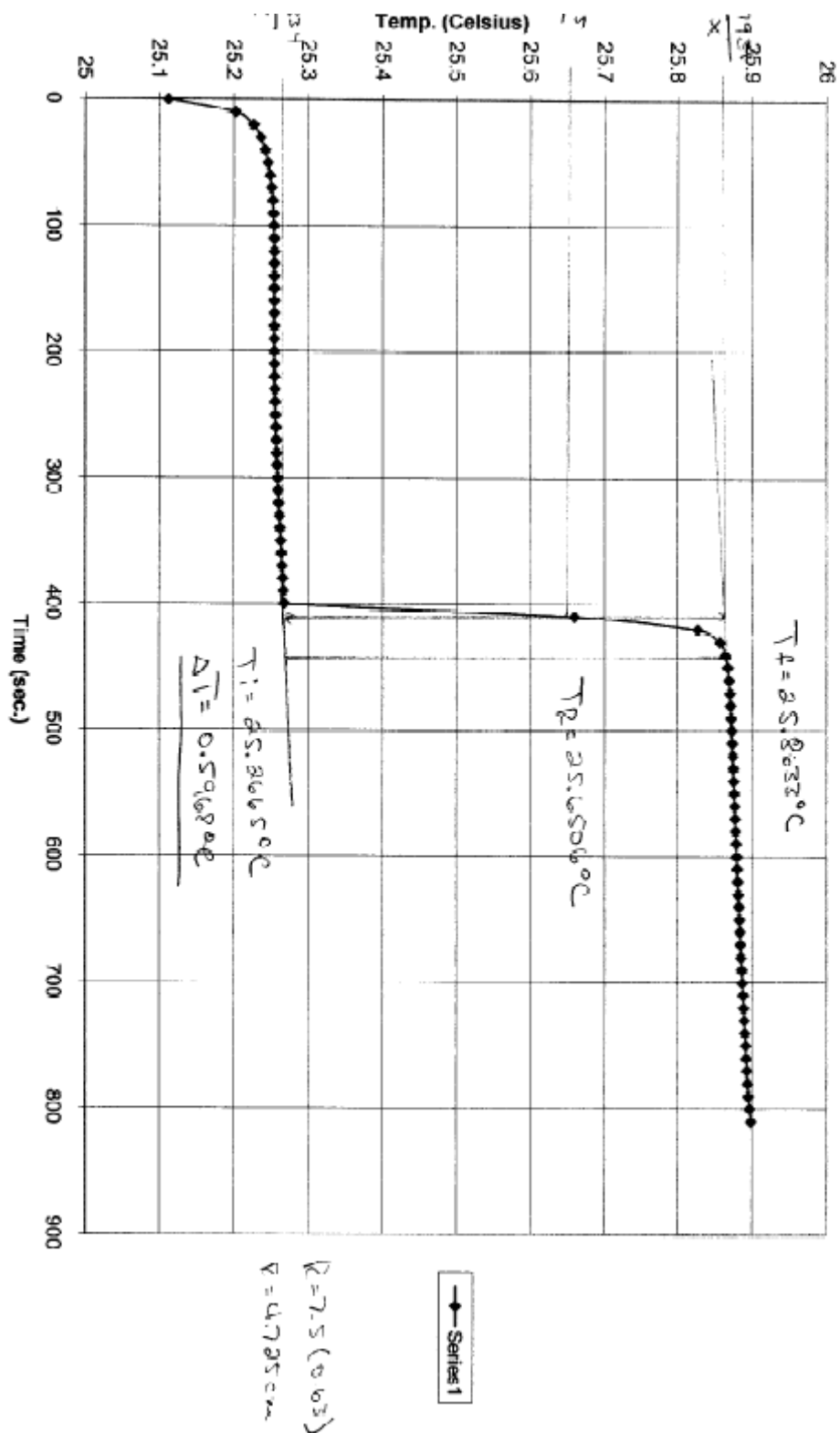


Figure 2.4.4: Thermograph with Corrected Temperature Values

## Chapter 3: Results and Discussions

### 3.1 Experimental Data Collected:

See figures 3.1.1 and 3.1.2 for calorimetric data collected for 2-Propoxyethanol, 2-Isopropoxyethanol and 2-Isobutoxyethanol. See appendix I for numerical mole fraction and excess molar enthalpy data.

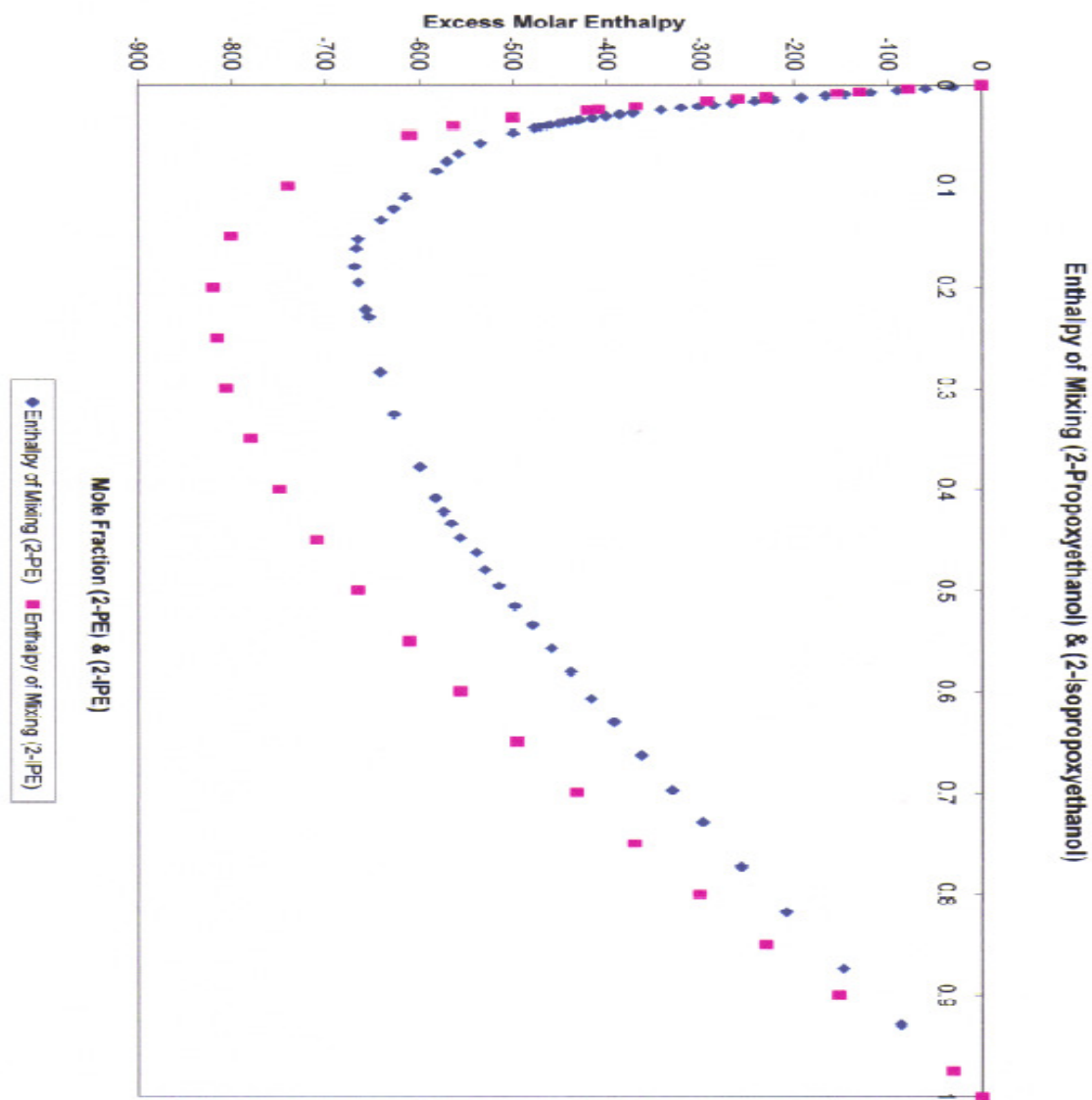
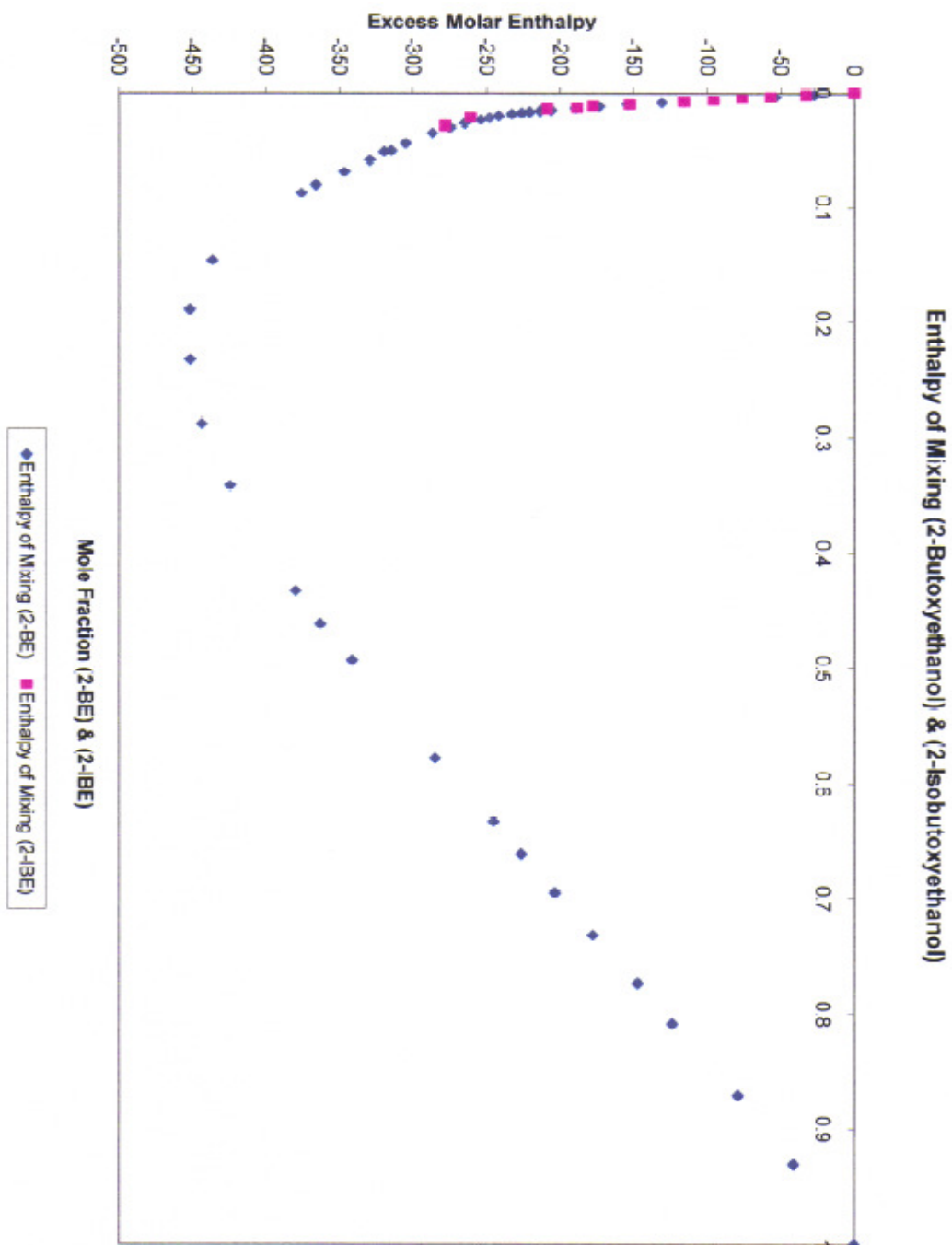


Figure 3.1.1: Enthalpy of Mixing for (2-PE) & (2-IPE)



**Figure 3.1.2: Enthalpy of Mixing for (2-BE) & (2-IBE)**

### 3.2 Data Interpretation:

From viewing the full mole fraction composition range for 2-Propoxyethanol (2-PE), blue dots, in figure 3.1.1, the excess molar enthalpy, or ( $\Delta_{\text{mix}}H$ ), indicates a value of  $-667.0 \text{ J}\cdot\text{mol}^{-1}$  at

a mole fraction just under 0.18. The work done in order to determine the enthalpy of mixing for this solvent began with work, from our group, to determine the excess molar enthalpy at the water rich end and then at the solute rich end. This analysis was successful in finding the excess molar enthalpies in these two regions, but it left a gap, in the graph, near the middle of the mole fraction range<sup>14</sup>. With this mole fraction gap now filled and the composition range complete, the ( $\Delta_{\text{mix}}H$ ) was analytically determined to be  $-668.6 \text{ J}\cdot\text{mol}^{-1}$  at a mole fraction near 0.18. On the same figure 3.1.1 graph, the data collected for 2-Isopropoxyethanol (2-IPE), purple dots, was placed. The excess molar enthalpy indicates a value of  $-819.8 \text{ J}\cdot\text{mol}^{-1}$  at a mole fraction of 0.2. This result is in good agreement with a recorded value of  $-820.0 \text{ J}\cdot\text{mol}^{-1}$  at a mole fraction of 0.2 from work done by one other group investigating 2-Isopropoxyethanol<sup>15</sup>. By putting both 2-Propoxyethanol and 2-Isopropoxyethanol on the same graph, one can observe that the mixing enthalpy is significantly more exothermic for 2-Isopropoxyethanol. This is possible due to the formation of stronger hydrogen bonds at the ether region as well as at the alcohol end. Excess molar volumes and compressibility's are also more negative for 2-Isopropoxyethanol than 2-Propoxyethanol (Appendix III, Table 1). However, there is very little difference between those properties for 2-Butoxyethanol and 2-Isobutoxyethanol (Appendix III, Table 2 & 3). In figure 3.1.2, the full mole fraction range for 2-Butoxyethanol is seen along with limited data points for 2-Isobutoxyethanol. From the data points obtained by our group, the excess molar enthalpy for 2-BE was determined to be  $-451.5 \text{ J}\cdot\text{mol}^{-1}$  at a mole fraction just below 0.19. Experiments to determine the excess molar enthalpy of 2-Isobutoxyethanol began in order to corroborate findings from another group which published excess molar enthalpy data for (2-IBE)<sup>16</sup>. My first experimental run into determining the excess molar enthalpy ended with inconclusive results. A second experimental run was made which ended with similar results as the first test. After

discussions with my graduate research professor, it was decided that he would look into the data from all 2-Isobutoxyethanol experiments as well as data from the published article. One solubility property, for aqueous 2-Isobutoxyethanol, is a lower critical solution temperature (LCST) at 300.15 K (27 °C)<sup>17</sup>. Since measurements for the PARR 1455 solution calorimeter are read at room temperature, it became evident that solution demixing was coming into play between water and 2-IBE<sup>18</sup>. A third experiment was planned but never performed due to events beyond our control. Construction began on the south end of the physical science building which affected the ambient temperature in our laboratory (22 °C) even with the building cooling system running. A temperature reading taken around this same time indicated a laboratory room temperature just above 301.15 K (28 °C); well above the lower critical solution temperature for 2-IBE. For this reason, no further experiments, with the 2-IBE, were performed. The usable data collected was in the small 2-IBE mole fraction range. The excess molar enthalpy points collected were placed on the same graph with the 2-BE. The findings here show that at small mole fractions, 2-Butoxyethanol and 2-Isobutoxyethanol have similar excess molar enthalpies.

### **3.3: Enthalpies of Mixing for other Alkoxyethanol-Water Mixtures ( $C_mE_1$ ), $m \leq 2$ .**

From the excess molar enthalpy data for aqueous 2-Methoxyethanol ( $C_1E_1$ ), the enthalpy of mixing was determined to be  $-1355.19 \text{ J}\cdot\text{mol}^{-1}$  at a mole fraction close to 0.25. Also, using the excess molar enthalpy data for aqueous 2-Ethoxyethanol ( $C_2E_1$ ), the enthalpy of mixing was determined to be  $-1143.83 \text{ J}\cdot\text{mol}^{-1}$  at a mole fraction of 0.2<sup>[1,2]</sup>.

### **3.4: Further Reading.**

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## **Chapter 4: Conclusions**

The main goal for this research was to provide supplemental enthalpy of mixing data for the limited values that exist for 2-Propoxy, 2-Isopropoxy and 2-Isobutoxyethanol. The results obtained for 2-Propoxyethanol and 2-Isopropoxyethanol were in good agreement. This could not be said for 2-Isobutoxyethanol. The literature data shows enthalpies of mixing for the full mole fraction range at 25 °C. Experiments done in this laboratory, slightly below that temperature, do not correspond with the published literature possibly due to demixing in their experiment.



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# **APPENDIX I: 2-Propoxyethanol & 2-Isopropoxyethanol**

Mole Frac. 2-PE	Excess Molar Enthalpy	Mole Frac. 2-PE	Excess Molar Enthalpy	Mole Frac. 2-PE	Excess Molar Enthalpy
0	0	0.03691	-445.5	0.37819	-599.3
0.00183	-31.1	0.03786	-450.8	0.40881	-582.6
0.00356	-60	0.03923	-459.8	0.42221	-573.8
0.00539	-90.2	0.03997	-463.7	0.434	-565.5
0.00721	-118.5	0.04138	-471	0.44791	-556.1
0.00905	-145.8	0.04254	-476.8	0.46201	-538.8
0.01044	-166.4	0.04765	-499.6	0.47959	-529.8
0.01223	-192.3	0.05791	-534.5	0.49526	-515
0.01441	-222.1	0.06832	-557.5	0.51555	-498.1
0.01597	-241.8	0.0756	-570.2	0.53428	-479.2
0.01794	-266.7	0.08551	-581.3	0.55674	-459
0.01953	-285.6	0.11131	-614.7	0.5805	-438.2
0.02094	-302	0.1229	-627	0.60719	-416.5
0.02249	-320.5	0.13372	-640.3	0.63038	-392.4
0.02454	-341.9	0.15285	-664.8	0.66328	-363.2
0.02762	-371.8	0.1622	-666.7	0.69754	-330.5
0.02907	-386	0.17988	-668.6	0.72908	-297.5
0.03079	-400.7	0.19552	-664.4	0.77298	-256.6
0.03271	-415	0.2221	-656.8	0.81808	-208.7
0.03444	-428.7	0.22964	-653.2	0.87339	-147.7
0.03482	-430.9	0.28425	-641.2	0.92892	-86.3
0.03565	-437.6	0.32595	-626.7	1	0

**Table 1: Mole Fraction and Excess Enthalpy Data (2-Propoxyethanol) for Fig. 3.1.1.**

Mole Frac. 2-IPE	Excess Molar Enthalpy	Mole Frac. 2-IPE	Excess Molar Enthalpy	Mole Frac. 2-IPE	Excess Molar Enthalpy
0	0	0.03228	-500.2	0.45	-709.2
0.00395	-78.8	0.03996	-563.2	0.5	-665.2
0.00694	-130.2	0.05	-609.6	0.55	-610.9
0.00806	-154.1	0.05	-611.8	0.6	-556.2
0.0121	-230	0.1	-740.2	0.65	-496.2
0.01381	-260.1	0.15	-800.8	0.7	-432.2
0.01609	-292.8	0.2	-819.8	0.75	-370.8
0.02094	-369	0.25	-815.6	0.8	-301.2
0.02427	-409	0.3	-806	0.85	-230.8
0.025	-419.3	0.35	-779.8	0.9	-152.7
0.025	-420	0.4	-749.6	0.975	-30.9
				1	0

**Table 2: Mole Fraction and Excess Enthalpy Data (2-Isopropoxyethanol), Fig. 3.1.1.**

$x^b$	$H^E$	$x$	$H^E$	$x$	$H^E$	$x$	$H^E$
0.02500	-418.3	0.20000	-819.7	0.50000	-665.3	0.79999	-301.4
0.02500	-420.0	0.25000	-815.0	0.54997	-609.1	0.85000	-231.1
0.05000	-603.2	0.30000	-808.9	0.59999	-556.7	0.89999	-152.5
0.05000	-610.9	0.35000	-778.5	0.64999	-496.5	0.97500	-25.8
0.10000	-740.9	0.39999	-751.4	0.70000	-431.2		
0.15000	-799.9	0.44998	-707.1	0.74998	-371.8		

**Table 3: Mole Fraction & Excess Enthalpy Data for 2-Isopropoxyethanol, See ref. 15.**

Appendix I contains the recorded data for 2-Propoxyethanol and 2-Isopropoxyethanol. Appendix I, table 1, contains values obtained from work done by Michelle Peck and M. I. Davis; 2-PE mole fractions from  $0.0 \rightarrow 0.03997$  and  $0.40881 \rightarrow 1$ <sup>[14]</sup>. Work and data for the mole fraction gap between these two numbers were completed by John Enriquez and M. I. Davis. Appendix I, table 2, shows the full mole fraction range for 2-Isopropoxyethanol and how it supports the only published data for this solvent<sup>[15]</sup>, see appendix I, table 3. It can now be said that the enthalpy of mixing ( $\Delta_{\text{mix}}H$ ), for these cellosolves, are now complete.

## APPENDIX II: 2-Butoxyethanol & 2-Isobutoxyethanol

Mole Frac.	Excess	Mole Frac.	Excess	Mole Frac.	Excess
2-BE	Molar Enthalpy	2-BE	Molar Enthalpy	2-BE	Molar Enthalpy
0	0	0.0231	-263.8	0.2876	-443.2
0.0017	-27.3	0.0264	-264.8	0.341	-424.2
0.0034	-53.8	0.0299	-274.8	0.4327	-379.6
0.0085	-130.8	0.0348	-286.6	0.4615	-362.8
0.0102	-154	0.044	-304.8	0.493	-341.2
0.0118	-173.5	0.05	-314.5	0.5782	-284.8
0.0133	-189.6	0.051	-319.5	0.633	-245.1
0.015	-205.9	0.0586	-329.2	0.6612	-226.2
0.0159	-213.6	0.0685	-346.5	0.6948	-203.4
0.0167	-220.6	0.0799	-365.8	0.7313	-177.8
0.0175	-225.9	0.087	-375.6	0.7737	-147.2
0.0184	-232.6	0.1455	-436.2	0.8085	-123.7
0.02	-241.8	0.1881	-451.5	0.8709	-79
0.0216	-248	0.2318	-451.2	0.931	-41.4
				1	0

Table 1: Mole Fraction and Excess Enthalpy Data (2-Butoxyethanol), Fig 3.1.2.

Mole Frac.	Excess
2-IBE	Molar Enthalpy
0	0
0.00203	-32.75
0.00356	-56.78
0.00491	-76.34
0.00636	-95.71
0.00769	-115.87
0.00988	-152.64
0.01135	-177.66
0.01278	-188.55
0.01387	-208.73
0.02123	-261.02
0.02809	-278.08

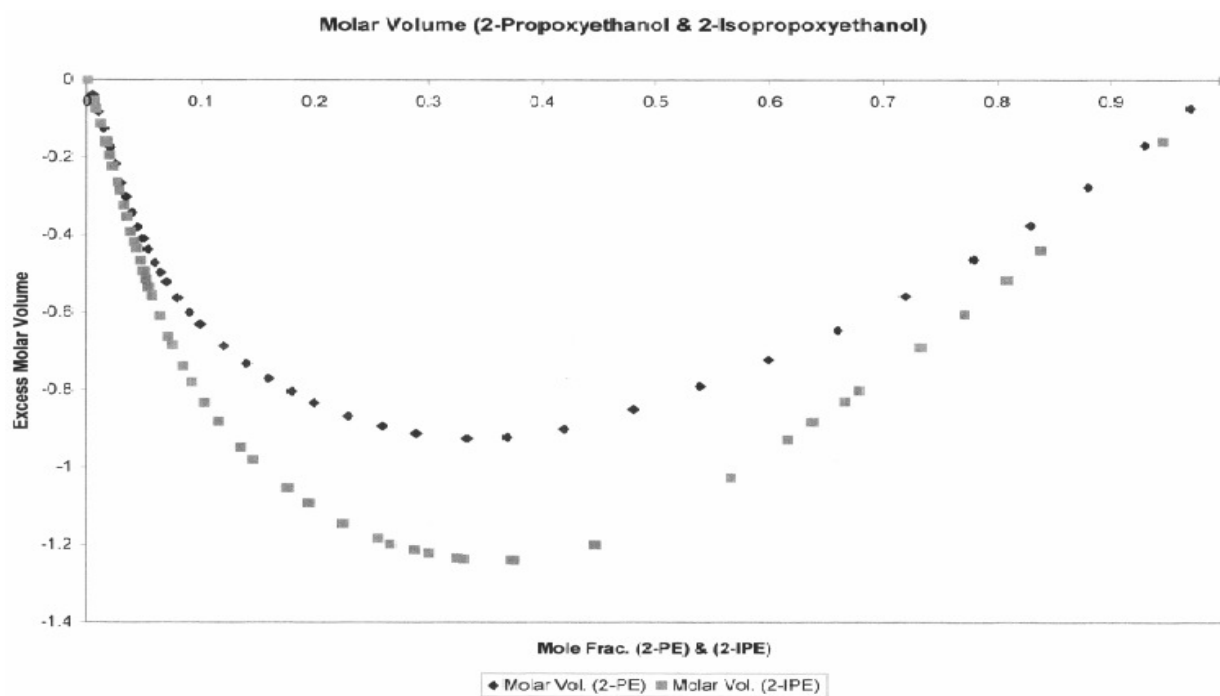
Table 2: Mole Fraction and Excess Enthalpy Data (2-Isobutoxyethanol), Fig. 3.1.2.

Mole Fraction	Excess Molar	Mole Fraction	Excess Molar	Mole Fraction	Excess Molar
2-Isobutoxy	Enthalpy	2-Isobutoxy	Enthalpy	2-Isobutoxy	Enthalpy
0.01	-127.6	0.17	-260.4	0.35	-250
0.02	-156.3	0.18	-261.4	0.37499	-246
0.03	-172.5	0.19	-262.5	0.39999	-245
0.04	-187.8	0.2	-263.9	0.39999	-239.7
0.05	-199.3	0.2	-265.2	0.42499	-235.2
0.06	-209.5	0.21	-264	0.44999	-226.7
0.07	-221	0.22001	-264.8	0.47498	-220.6
0.08	-232.5	0.23	-265	0.49998	-218.7
0.09	-242.5	0.24	-264.2	0.49998	-214.7
0.1	-250.9	0.25	-263.3	0.54998	-200.4
0.1	-250.3	0.26	-258.4	0.59997	-182.6
0.11	-255.3	0.26999	-257.4	0.59997	-182.4
0.12	-260.1	0.28	-257.6	0.69999	-135.9
0.13	-261.6	0.29	-257.1	0.69999	-134.9
0.14	-256.5	0.30001	-256.2	0.79998	-77.5
0.15	-258.4	0.30001	-262	0.79998	-76.9
0.15999	-259.6	0.325	-253.2	0.9	-29.8
				0.9	-28.5

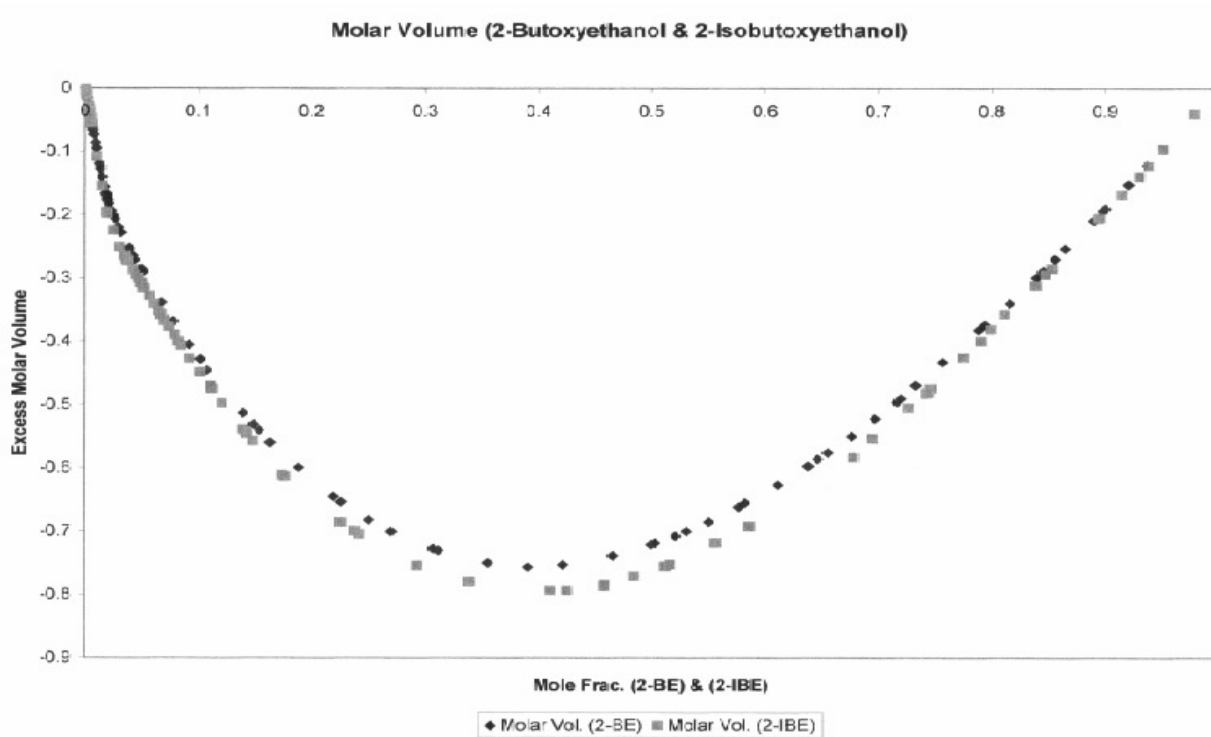
Table 3: Mole Fraction & Excess Enthalpy Data for (2-Isobutoxyethanol), Fig. 3.1.2 & Ref. 16.

Appendix II contains the full mole fraction range for 2-Butoxyethanol with a partial listing for 2-Isobutoxyethanol and mole fraction range from 2-Isobutoxyethanol literature. Appendix II, table 1, shows the full mole fraction range from work done by our group<sup>[1]</sup>. Appendix II, tables 2 and 3 contain were to be used for mole fraction comparison. Unfortunately, due to building construction and aqueous 2-Isobutoxyethanol demixing near 25 °C, the excess molar enthalpy ( $\Delta H^E$ ) could not be determined.

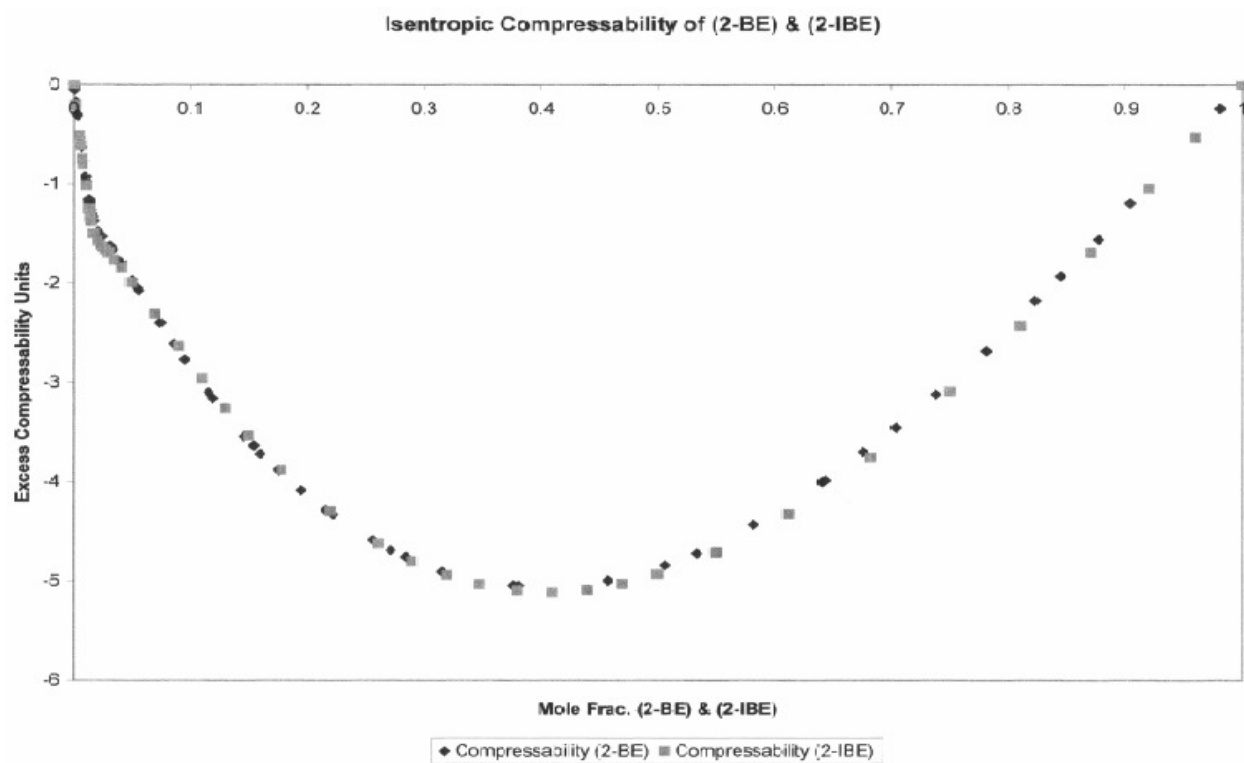
### APPENDIX III: Excess Molar Volumes and Compressibility Graphs



**Table 1: Excess Molar Volume (2-PE) & (2-IPE).**



**Table 2: Excess Molar Volume (2-BE) & (2-IBE).**



**Table 3: Isentropic Compressibility (2-BE) & (2-IBE).**

## **Curriculum Vita**

In March of 1968, John Enriquez was born in El Paso, TX. He is the son of Miguel Enriquez and Manuela R. Enriquez. While working full-time at a local medical supply company (A&M Medical Rental and Supplies), he enrolled at the El Paso Community College in the spring of 1994, as a part-time student, taking evening classes. While a student there, he was given the opportunity to research with chemistry professor, Dr. Jawad Mahmoud during the summer months of 1997 and 1998. This research was part of the El Paso Community College's, Biology Department, Bridges to the Future Program. The research John performed, in 1997, was to determine copper metal binding to peat moss in aqueous solutions. The following summer, research continued. This time, determinations were made to investigate chromium metal binding to alfalfa plants in aqueous solutions. In May 1998, John graduate from the El Paso Community College with an Associates Degree in Science, Chemistry. In August of this same year, John transferred to the University of Texas El Paso where he pursued his bachelor's degree in science. Finally, in May of 2003, John graduated with his Bachelor's Degree in Science, Chemistry. In August 2006, after taking some time off, John enrolled in the Graduate School at the University of Texas El Paso to pursue a Master of Science degree in physical chemistry under the direction of Dr. Michael I. Davis, professor of physical chemistry. He successfully defended his Master thesis on July 22, 2010.

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