

THE STUDY OF MISCIBILITY IN THE REPLACEMENT OF AK-225 IN  
INDUSTRIAL CLEANING APPLICATIONS

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A Thesis

Presented to

The Faculty of the Department of Chemistry  
Sam Houston State University

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In Partial Fulfillment

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Master of Science

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by

James E. Huskey

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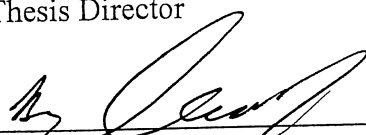
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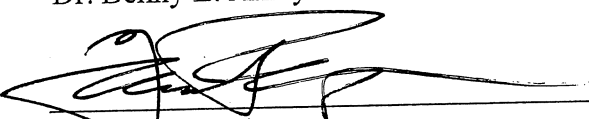
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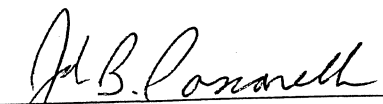
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## **DEDICATION**

I would like to dedicate this thesis to my father, James Ethel Huskey. He had more patience than any man I have ever known. My father was a mechanic, ex-racecar driver, amazing father, and a great man. He worked hard his whole life to provide for my mother and me. When I was in high school, my father asked that I get a college education. This is something that I had always wanted to do, but it was never the right time. Years later I was able to go back to college where I earned my Bachelor of Science in Chemistry. My father was there the day I graduated and he was a very proud man. He encouraged me when I started graduate school. My father passed away half way through finishing a Master of Science in Chemistry. I would like to thank my father for teaching me to think, work hard, and never give up.

## ABSTRACT

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As ozone-depleting solvents are being phased out, the demand for solvent replacements in industrial cleaning applications grows. Asahiklin® AK-225, a widely-used industrial cleaning solvent, was a replacement for a previously banned solvent but now has a phase-out date of January 2015. One way to replace a solvent or solvent blend is to locate a solvent or blend with similar solvation abilities as characterized by solubility parameters. The Hansen solubility parameters (HSPs) have proven themselves able to predict blend solvation character but not blend miscibility. The Godfrey miscibility index (M-number) is a miscibility ranking of over 400 solvents. To date, there has not been a thorough exploration of the relationship between the HSPs and Godfrey's M-numbers. A statistical modeling approach to predicting the miscibility of blend components will be studied, and the connection of Godfrey's M-numbers to the HSPs will be presented in a quantitative structure property relationship (QSPR) between HSPs and Godfrey's M-numbers. The QSPR model will enable solvent blend miscibility to be estimated using an HSP database of over 10,000 solvents and help predict solvent blend miscibility without the requirement of costly trial and error benchwork.

**KEY WORDS:** solvent replacement, solubility parameters, solvent blend, miscibility, quantitative structure property relationship, AK-225, QSPR

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# CHAPTER I

## INTRODUCTION

For many years industry used solvents like CFC-113 and 1,1,1-trichloroethane for precision cleaning. These solvents are great for removing a soil from a surface. In industry, cleaning is concerned with safety, surface, soil, solvent, and savings. The safety concerns range from flammability to ozone depletion. The surface must not be damaged, deformed, or rusted by the cleaning process. The solvent should target the soil, which means the solvent and soil must mix spontaneously. The solvent must be affordable and must satisfy all of the above criteria.

An ideal solvent should have a low surface tension and low viscosity to be able to penetrate between the soil and the surface. This is shown by the wetting index ( $w$ ), which is calculated by

$$w = \frac{1000\rho}{\gamma\eta} \quad (1)$$

where  $\rho$  is the density,  $\gamma$  is the surface tension, and  $\eta$  is the viscosity.<sup>1</sup> A high wetting index will allow solvent to go into crevices. The solvent should also have minimal non-volatile residue (NVR) so rinsing is not required.

Many of the substances that fit into the category are chlorofluorocarbons (CFCs). These CFCs are great for cleaning due to their low surface tension, heat of vaporization, and viscosity. They are highly volatile and inert, so they do not react with the surface being cleaned. Some of the bad qualities of these solvents are that they persist in the upper atmosphere and deplete the ozone layer. Sometimes the CFCs are so persistent

they can exist in the upper atmosphere for over a hundred years.<sup>2</sup> So their use has been restricted or banned in industrial cleaning.

### **Ozone-depleting Substances**

Ozone is naturally produced and destroyed in the upper atmosphere. The CFCs that enter the atmosphere undergo photodecomposition, which releases a chlorine atom. The chlorine atom acts as a catalyst in its reactions with ozone.<sup>2</sup> This process is very detrimental to the ozone layer so other cleaning solvents began to replace CFCs. These solvents are ranked on their ozone depletion potential (ODP) which is calculated from

$$ODP = \frac{\text{Global } \Delta O_3 \text{ caused by substance}}{\text{Global } \Delta O_3 \text{ caused by CFC - 11}} \quad (2)$$

where each substance is compared to CFC-11, which is trichlorofluoromethane.<sup>3</sup> This ODP compares the amount of ozone the substance will destroy over its lifetime relative to the amount of ozone that would have been destroyed by an equal mass of CFC-11.

While hydrochlorofluorocarbons (HCFCs) were used to replace some of the chlorofluorocarbons, they too are now on the list to be banned. The *Montreal Protocol on Substances that Deplete the Ozone Layer* is an agreement of nations to reduce the amount of ozone-depleting substances (ODS) in production and consumption and went into effect in 1989.<sup>4</sup> The goal of the Montreal Protocol is to assist in replenishing the ozone-layer through reduction of ODS worldwide. To date there are 197 parties involved in the Montreal Protocol.<sup>4</sup> To assist companies in the transition of selecting new solvents, the United States has the Significant New Alternatives Policy (SNAP) and is required by the Environmental Protection Agency to produce a list of acceptable and unacceptable replacements for ODS that are being phased out under the Federal Clean Air Act.<sup>5</sup>

As regulations and restrictions tighten on industry for their solvent of choice for cleaning, their need for replacement solvents is ever increasing. One widely used industrial cleaning solvent is Asahiklin® AK-225 and has a phase out date of January 2015.<sup>5</sup> To be prepared for the phase out industry needs methods to find a suitable replacement for their solvent of choice, as AK-225 was a replacement for the previously banned CFC-113, and HCFC-141b.<sup>5</sup> AK-225 is a mixture of two isomers, HCFC-225ca (3,3-dichloro-1,1,1,2,2-pentafluoropropane) and HCFC-225cb (1,2-dichloro-1,1,2,2,3-pentafluoropropane).

### Solubility Parameters

One way to find a solvent replacement is to locate a solvent or solvent blend with similar properties and one set of properties used in industry for solvent selection are solubility parameters. Solubility parameters are derived from the Gibbs energy of mixing equation.

$$\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix} \quad (3)$$

Spontaneous mixing requires a negative Gibbs energy of mixing which is favored by the positive entropy of mixing ( $\Delta S_{mix}$ ). It is the enthalpy of mixing ( $\Delta H_{mix}$ ) that will typically prevent spontaneous mixing from occurring. The enthalpy of mixing can be related to the cohesive energy density of the individual components.<sup>6</sup>

$$\Delta H_{mix} = \phi_1\phi_2V_{total}(\delta_{T,1} - \delta_{T,2})^2 \text{ where } \delta_T \equiv \sqrt{\frac{\Delta H_{vap}}{V_m}} \quad (4)$$

The Hildebrand solubility parameter ( $\delta_T$ ) is the square root of the energy of vaporization ( $\Delta H_{vap}$ ) divided by the molar volume ( $V_m$ ). The  $\phi_1$  and  $\phi_2$  in eq 4 are the volume ratios of the individual components. Equation 4 shows that the closer the

solubility parameter of one component is to the other component the enthalpy of mixing comes closer to zero, ensuring spontaneous mixing.<sup>7</sup> If the solubility parameters are too far apart, then spontaneous mixing will not occur.

Hildebrand's work involved only hydrocarbons, so problems developed when predicting the mixing behavior of polar molecules. The Hildebrand solubility parameter is a single number and does not take into account the polar or hydrogen bonding association between molecules. A quick example of where the Hildebrand solubility parameters fail is ethanol (26.5) and nitromethane (25.3), they have similar  $\delta_T$  values, but only ethanol is water soluble.<sup>8</sup>

Hansen separated Hildebrand's solubility parameter into three individual parts to account for dispersion ( $\delta_D$ ), polarity ( $\delta_P$ ), and hydrogen bonding ability ( $\delta_H$ ).<sup>8</sup>

$$\delta_T^2 = \delta_D^2 + \delta_P^2 + \delta_H^2 \quad (5)$$

These ( $\delta_D$ ,  $\delta_P$ , and  $\delta_H$ ) are known as the Hansen solubility parameters (HSPs). In the 1960s, Hansen used polymer swelling experiments to compile a self-consistent table of HSP values, which has grown to over 10,000 substances.<sup>8</sup> Since then, Hansen and others have explored other ways to determine the various HSP values.<sup>9, 10</sup>

Small, Hoy, van Krevelen, and others have developed group contribution methods to compute the solubility parameters.<sup>11</sup> The group contribution (GC) method is a QSPR that uses the number and type of chemical structure elements as input to compute the HSP values. The HSPiP software has the van Krevelen, Hoy, Stefanis-Panayiotou, and Yamamoto methods.<sup>12</sup> The software takes the Simplified Molecular-Input Line-Entry System (SMILES) structure as input.<sup>13</sup>

The dispersion ( $\delta_D$ ), polarity ( $\delta_P$ ), and hydrogen bonding ability ( $\delta_H$ ) can also be calculated using various physical properties of the solvent. The polar and dispersion terms, in  $\text{MPa}^{1/2}$ , can be calculated from knowing the dipole moment ( $\mu$ ) in Debye, molar volume ( $V_m$ ) in  $\text{cm}^3/\text{mol}$ , and index of refraction ( $RI$ ) as shown in eq. 6 and 7.<sup>12</sup>

$$\delta_P = \frac{36.1 \times \mu}{V_m^{0.5}} \quad (6)$$

$$\delta_D = \frac{(RI - 0.784)}{0.0395} \quad (7)$$

There is not an agreed-upon method to determine the hydrogen bonding term. The  $\delta_H$  is frequently determined by the difference once the other terms are measured or computed from the Hildebrand parameter as shown in eq 8.

$$\delta_H^2 = \delta_T^2 - \delta_D^2 - \delta_P^2 \quad (8)$$

Another major strength the Hansen solubility parameters have over the Hildebrand parameter is the ability to visualize the components of cohesion in 3D space (Figure 1). For a solvent to interact with another, it should be within the Hansen sphere ( $R_0$ ) of the other solvent. The Hansen sphere is a volume calculated area utilizing empirical data and represents the interaction radius in which solvents, and the trajectory of solvent blends, will interact with the soil of interest.<sup>8</sup> The method to empirically determine the Hansen sphere is explained in Hansen Solubility Parameters: A User's Handbook.<sup>8</sup>

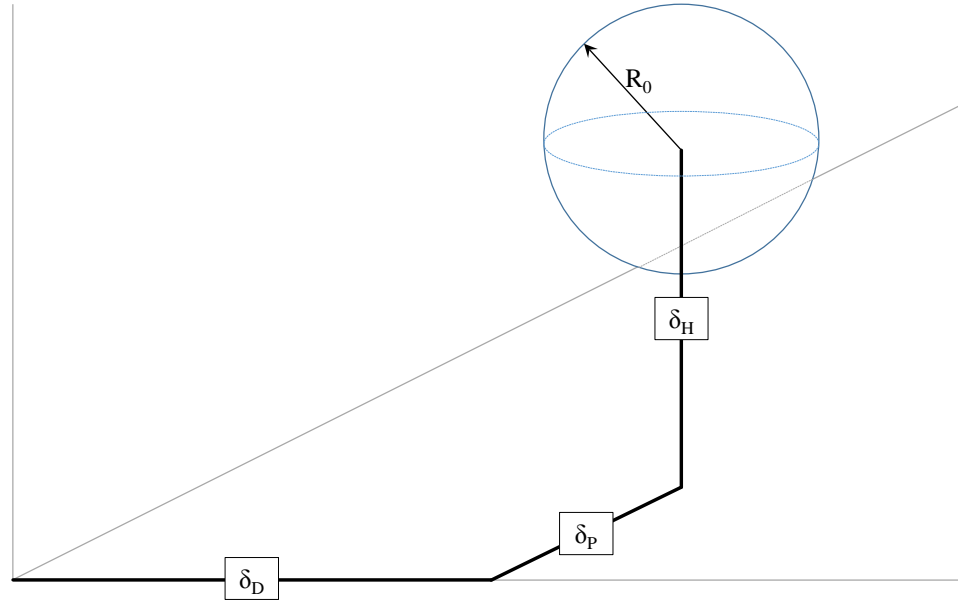


Figure 1. Example of HSP 3D space with Hansen sphere.

If one solvent cannot match the HSPs of a soil targeted for removal, then a solvent blend can be utilized. The HSPs of a solvent blend can be calculated by the volume-fraction-weighted sum of each term. The sum of the volume-weighted-fraction for the dispersion term is shown in eq 9 and the same format is used for the polarity and H-bonding terms. By preparing a solvent blend, one can obtain desired  $\delta_D$ ,  $\delta_P$ , and  $\delta_H$  values within the Hansen sphere of the soil to ensure spontaneous mixing. It is simple to search for blends using eq 9 and the Hansen distance ( $R_a$ ) to the HSPs of the soil as shown in eq 10. However, this is a tedious task to go through every possible combination of solvent blends to match the HSPs of the soil.

$$\delta_D = \sum_i \phi_i \delta_{D,i} \quad (9)$$

$$R_a = \sqrt{(2\delta_{D,blend} - 2\delta_{D,soil})^2 + (\delta_{P,blend} - \delta_{P,soil})^2 + (\delta_{H,blend} - \delta_{H,soil})^2} \quad (10)$$

In 2008, Dr. Brian Loft Associate Professor of Mathematics at Sam Houston State University was contracted to provide an algorithm using Mathematica (Wolfram Inc.) that can predict two-, three-, and four-solvent blends to target or match a soil's  $\delta_D$ ,  $\delta_P$ , and  $\delta_H$  values. While the current algorithm can predict solvent blends to match the values, it cannot predict if the paired solvents will be sufficiently miscible to form a single homogeneous phase. Thus, the top ranked solvent blends must be tested for miscibility before they can be applied to the soil to test for solvency. This results in a waste of solvents and time.

### **Godfrey's Miscibility Numbers**

Hildebrand and Scott reported a miscibility limit of  $(\delta_{T,1} - \delta_{T,2}) = 3.4 \text{ MPa}^{1/2}$ .<sup>6</sup> Godfrey found many exceptions to this rule of thumb.<sup>14</sup> An exception is shown in Table 1. Godfrey meticulously tested pair-wise miscibility of 31 solvents at many concentrations and temperatures. These became Godfrey's standards and were arranged in order of increasing lipophilicity (1 to 31). Godfrey then compared these standards to many other solvents and created a Miscibility Index (M) Number for over 400 solvents. Godfrey stated that a pair of solvents with  $\Delta M < 15$  are miscible in all concentrations at 25 ° C.<sup>14</sup>

Table 1

*Problem with Hildebrand and Scott Rule of Thumb*

Solvent	$\delta_T/MPa^{1/2}$	$\Delta\delta_T$	Miscible
hexadecane	8.0	0.4	No
benzonitrile	8.4		
isoprene	7.5	7.0	Yes
methanol	14.5		

Godfrey also assigned some solvents a dual M-number to compensate for some of the observations he witnessed where miscibility was not predicted by the  $\Delta M < 15$  rule. The dual M-number helped accommodate the miscibility outliers in some of the tested solvents. If Godfrey assigned a solvent with a dual M-number the lower number restricted the miscibility range on the higher end of the scale while the higher number restricted the miscibility range on the lower end of the scale.

To help visualize the purpose of a dual M-number consider the values for nitromethane (10, 19) on a number line (Figure 2). The lower number, 10, restricts the upper miscibility limits to 25 and the upper number 19 restricts the lower miscibility limit to 4 giving a miscibility range of 4 to 25. If nitromethane had the single M-number value of 15, utilizing a  $\Delta M \pm 15$ , nitromethane would have a miscibility range of 0-30. The purpose of the dual M-number is to further restrict the outer miscibility limits of the solvent closer than the  $\Delta M \pm 15$  range. If nitromethane was assigned the M-number 14.5, the  $\Delta M$  would be  $\pm 11$  and it would follow the same constraints as the assigned dual M-number.



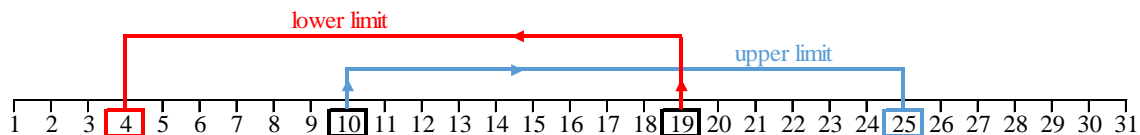


Figure 2. Example of upper and lower miscibility limits for dual M-numbers.

### Miscibility Modeling

While Godfrey empirically tested different solvent concentrations, testing every possible combination would have been impractical. If Godfrey tested each pairing at one concentration he would have performed over 82,000 experiments. Godfrey states a wide enough range of concentrations were tested, so at four concentrations he would have performed over 330,000 tests. This amount of testing is impractical. Instead, Godfrey compared the solvents to the 31 standards in order to effectively perform the miscibility testing. By designing the experiment in such a way Godfrey saved a lot of time without sacrificing the integrity of the experiment. To expand Godfrey's list of solvents, a miscibility model, based on the solubility parameters of Godfrey's solvents as a training set, can be used to assign other solvents an M-number. The modeling can be performed in MiniTab with a Quantitative Structure Property Relationship (QSPR). An example of two different ways a QSPR can be performed is a stepwise and best subsets regression. The stepwise method will add and remove factors until a final model is selected. The best subsets method will try every combination of factors and will give many models from which the user must make a final selection.

### Figures of Merit

To assist in determining the appropriate model to be used in predicting solvent miscibility, certain standards or figures of merit must be utilized. Dr. Ananda Manage, Associate Professor of Statistics at Sam Houston State University, was consulted to

explain the many numerical figures of merit and to assist in the selection of the most reasonable QSPR.

The coefficient of determination ( $R^2$ ) is used to show how well the model fits the data.<sup>15</sup> The value of  $R^2$  is the proportion of the variation that is accounted for by the model and is always between 0 and 1. The higher the value of  $R^2$  the more effective the model. The value of  $R^2$  increases as more factors are added to the model, so an adjusted  $R^2$  should also be utilized.<sup>15</sup> The adjusted  $R^2$  takes into account the number of factors in the model and reduces the  $R^2$  accordingly.

Another consideration is the  $p$ -value which determines if coefficients of the factors given in the linear regression equation between the predictor and the response are significant.<sup>15</sup> The  $p$ -value is the probability that a given coefficient of a factor is caused by noise. In this work if the  $p$ -value is greater than 0.05, the coefficient is deemed insignificant statistically. The confidence is  $1-p$ , or 95%.

If factors are correlated with each other, problems can occur by influencing the model. The variance inflation factor (VIF) is used to determine if the factors are influencing each other in the model.<sup>15</sup> The values of the VIF are greater than 1 and the rule of thumb is to have a VIF below 10.<sup>16,17</sup> Some have a stricter VIF requirement of 1 to 5 and 1 to 4 to ensure minimal multicollinearity.<sup>18, 19</sup>

If the best subset method is used in Minitab, it is imperative to know which model to select. The Mallows'  $C_p$  assists in not overfitting the data and is a good starting point on the path to selecting a good model.<sup>15</sup> The value of the Mallows'  $C_p$  should be close to the number of factors in the model.<sup>15</sup> Since the best subsets method does not provide the

$p$  or VIF values, regressions of each equation must be performed until an equation that meets all the set requirements are met.

## CHAPTER II

### EXPERIMENTAL

Godfrey's solvent list was used as the QSPR training set, but the list contained many out-dated common names (like amyl alcohol). The National Institute of Standards and Technology Chemistry WebBook (NIST) database number 69 and The PubChem Project were utilized to find current International Union of Pure and Applied Chemistry (IUPAC) names and Chemical Abstract Service Registry (CAS) numbers. The CAS number was searched in the Hansen Solubility Parameters in Practice (HSPiP) software<sup>12</sup> to determine the  $\delta_D$ ,  $\delta_P$ ,  $\delta_H$ , and  $V_m$  values. The solvent list in Godfrey's ChemTech article was used because the list from Perry's Chemical Engineer's Handbook had at least one error. An example of an incorrect entry is 1,1,2-trichloro-2,2,2-trifluoroethane, where Godfrey's article listed 1,1,1-trichloro-2,2,2-trifluoroethane. The solvent 1,1,2-trichloro-2,2,2-trifluoroethane listed in Perry's is a mistake because the name implied one carbon was bonded to five atoms. Godfrey's list was correlated to NIST and HSPiP twice to help find any possible transcription errors.

An effective method for obtaining the CAS number was to search for the Godfrey solvent name in the NIST WebBook. Sometimes PubChem was needed to find a match, then structures were compared to NIST. The CAS number was entered in HSPiP to obtain the  $\delta_D$ ,  $\delta_P$ ,  $\delta_H$ , and  $V_m$  values. Of the 31 standards Godfrey utilized, 30 were retrieved through NIST/HSPiP. The HSPs for Godfrey's 31<sup>st</sup> standard, petrolatum, were given by Dr. Steven Abbott of the HSPiP Team in a personal correspondence.<sup>20</sup> Of the 407 Godfrey solvents, 344 were matched with the appropriate  $\delta_D$ ,  $\delta_P$ ,  $\delta_H$ , and  $V_m$  values, and this formed the training set for the QSPR.

The  $\delta_D$ ,  $\delta_P$ ,  $\delta_H$ , and  $V_m$  were entered into MicroSoft Excel and formulas were used to determine the energy of vaporization, Hildebrand parameter, dipole moment, and index of refraction for each solvent (eqs 4-7). Once these results were calculated, several trial QSPRs were computed to model Godfrey's M-numbers.

In the cases where a solvent had a dual M-number, the average of the dual numbers was used. There was no justification to use anything other than the average M-number for the dual M-number solvents to constrain the outer miscibility limits without changing the  $\Delta M$  value. So for nitromethane, an M-number of 14.5 was assigned as explained in Figure 2. This would give the dual M-number solvents a larger miscibility range than Godfrey intended, but for ease of calculation it was a reasonable option.

In Excel, the relationship to the Hildebrand parameter was tested with  $\delta_T$  as the X-Input and M as the Y-Input in Excel's regression tool.

$$M_{calc} = a + b\delta_T \quad (11)$$

In Excel, the relationship to the Hansen solubility parameters ( $\delta_D$ ,  $\delta_P$ , and  $\delta_H$ ) was tested as the X-Input and M as the Y-Input.

$$M_{calc} = a + b\delta_D + c\delta_P + d\delta_H \quad (12)$$

The values were then imported into Minitab 16 and a multitude of regressions were performed to decide on an equation that can be used to quickly determine if two solvents were miscible. The best subsets regression tool in Minitab16 was used to search through all the possible combinations of x-input factors given in Eq 12.

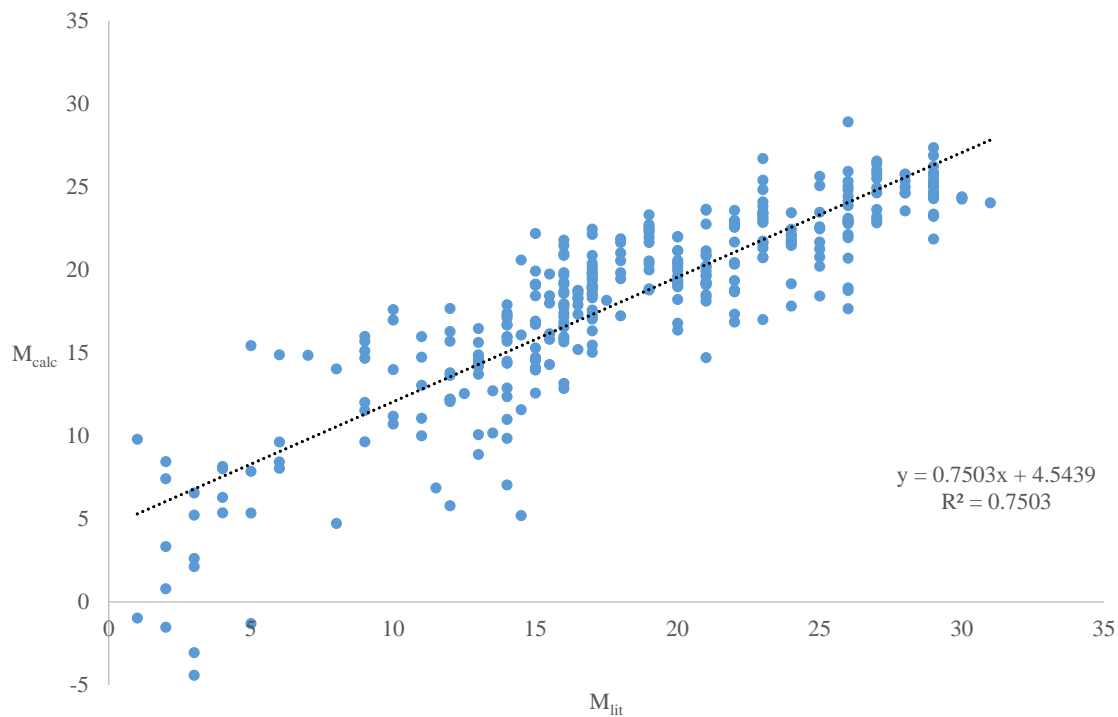
$$M_{calc} = a + b\delta_T + c\delta_D + d\delta_P + e\delta_H + fV_m + g\mu + h(\Delta H_{vap}) \quad (13)$$

## CHAPTER III

### RESULTS

A performance chart compares the QSPR output to the training set values. In a perfect model the QSPR output would match the training set values yielding a performance plot where the data lies on a line with a slope of one and the intercept zero with no scatter ( $R^2 = 1$ ). The performance plot of several trial QSPRs are given for comparison and discussion. They range from simple one-factor designs to the most complicated seven-factor design.

The one-factor Hildebrand solubility parameter regression compares Godfrey's M-numbers to the Hildebrand solubility parameter. The performance plot of this model showing the calculated M-number against the literature M-number is Figure 3.



*Figure 3.* Performance plot of the one-factor Hildebrand regression  $M_{\text{calc}}=47.2-1.41\delta_T$ .

A linear regression was performed comparing the three factor Hansen solubility parameters to Godfrey's  $M$ -numbers. The performance plot is shown in Figure 4.

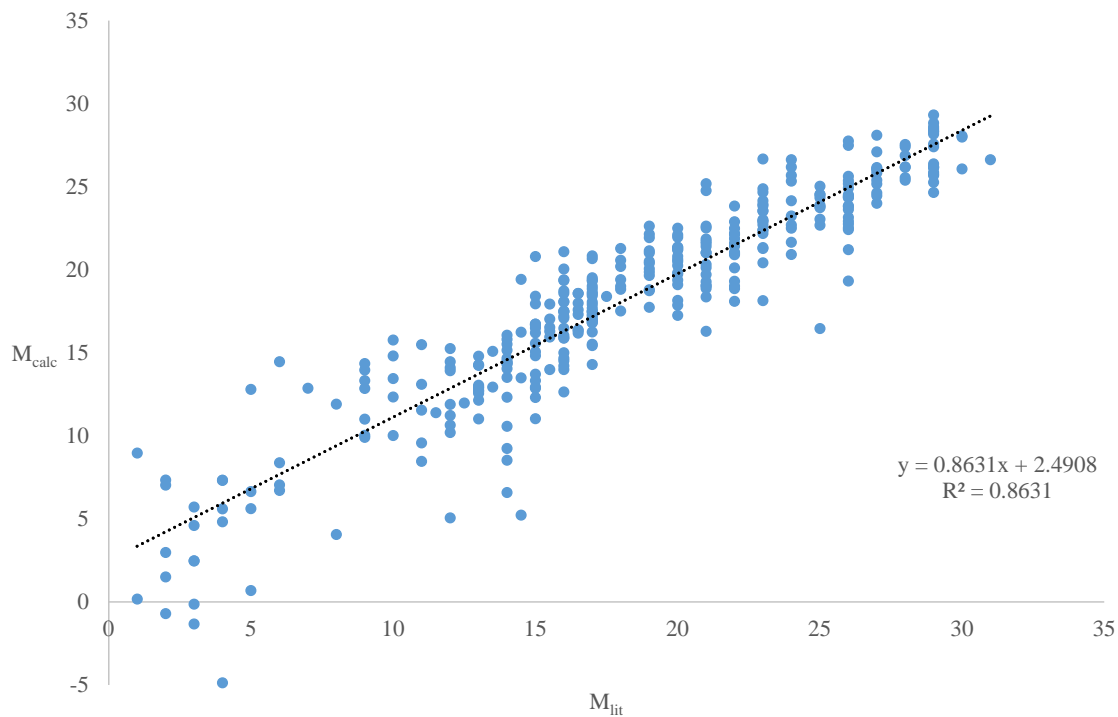


Figure 4. Performance plot of M-number to Hansen solubility parameters  $M_{calc}=37.8-0.600\delta_D-0.536\delta_P-0.776\delta_H$ .

The figures of merit for the Hansen solubility parameters to M-number regression performed in Minitab is shown in Table 2.

Table 2

*Figures of Merit for Hansen Solubility Parameters Regression*

Predictor	Coefficient	<i>p</i> -value	VIF
Constant	37.8	0.000	
$\delta_D$	-0.600	0.000	1.050
$\delta_P$	-0.536	0.000	1.388
$\delta_H$	-0.776	0.000	1.380



A best subsets was performed in Minitab to help determine the most reasonable QSPR. The regression analysis forced the elimination of refractive index as a factor because it was correlated too directly with  $\delta_D$ . Table 3 shows the results from the best subset performed.

Table 3

*Best Subset Equations in Increasing Number of Factors*

Vars	R <sup>2</sup>	adj R <sup>2</sup>	C <sub>p</sub>	$\sigma$	$\delta_T$	$\delta_D$	$\delta_P$	$\delta_H$	$V_m$	$\mu$	$\Delta H_{vap}$
1	75.0	75.0	398.0	3.39	X						
1	73.3	73.2	450.7	3.51				X			
1	52.5	52.3	1065.4	4.67			X				
2	84.9	84.8	107.7	2.64			X	X			
2	83.5	83.4	150.3	2.76				X		X	
2	81.0	80.9	222.9	2.96	X			X			
3	87.3	87.2	38.9	2.42				X	X	X	
3	86.3	86.2	68.6	2.52		X	X	X			
3	86.1	86.0	73.5	2.53				X		X	X
4	88.3	88.2	11.4	2.33		X		X		X	X
4	88.2	88.1	14.7	2.34		X		X	X	X	
4	87.5	87.3	36.9	2.41	X	X	X	X			
5	88.5	88.3	8.7	2.32	X	X		X	X	X	
5	88.4	88.2	11.0	2.32	X	X		X		X	X
5	88.4	88.2	12.0	2.33	X	X	X	X	X		
6	88.6	88.4	6.3	2.30	X	X	X	X	X	X	
6	88.6	88.4	7.6	2.31	X	X	X	X	X		X
6	88.5	88.3	9.4	2.31	X	X		X	X	X	X
7	88.6	88.4	8.0	2.31	X	X	X	X	X	X	X

Further regressions were carried out on the most promising models from Table 3 to determine the corresponding  $p$ -values and VIF. A regression using all seven factors was performed as shown in Table 4.

Table 4

*The Seven Factor Model of Best Subset*

Predictor	Coefficient	$p$ -value	VIF
Constant	32.1	0.000	
$\delta_T$	0.644	0.008	65.17
$\delta_D$	-0.992	0.000	3.678
$\delta_P$	-0.459	0.065	85.43
$\delta_H$	-0.996	0.000	13.53
$V_m$	0.0229	0.011	20.04
$\mu$	-0.979	0.202	54.64
$\Delta H_{vap}$	-0.0000184	0.567	35.99

The regression for the top six factor equation was performed as shown in Table 5.

Table 5

*Second Regression of Best Subset with Six Factors*

Predictor	Coefficient	<i>p</i> -value	VIF
Constant	33.5	0.000	
$\delta_T$	0.538	0.001	27.25
$\delta_D$	-0.973	0.000	3.55
$\delta_P$	-0.355	0.036	39.730
$\delta_H$	-0.987	0.000	12.96
$V_m$	0.0181	0.000	2.672
$\mu$	-1.32	0.006	21.25

## CHAPTER IV

### DISCUSSION

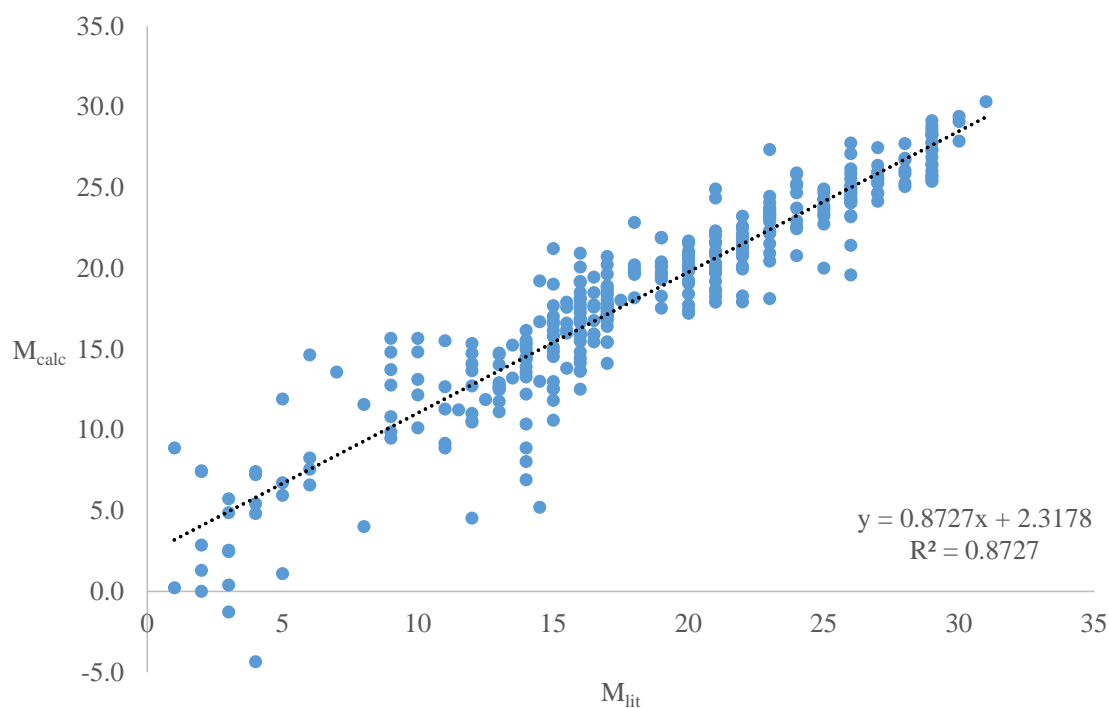
Multiple QSPRs were evaluated to determine which had the most rational support. The first regression performed was the simplest model which only had one factor, the Hildebrand solubility parameter. This regression was first performed because Godfrey had issues with the miscibility rule of thumb that utilized the Hildebrand solubility parameter and a miscibility limit of  $3.4 \text{ MPa}^{1/2}$  between two solvents. The regression showed an  $R^2$  value of 75.0%, which is not bad for a rule of thumb. The example used by Godfrey where the rule of thumb failed was shown in Table 1. Godfrey's M-numbers for hexadecane (15, 19) and benzonitrile (30) have a  $\Delta M$  of 15, which he later stated that sometimes there are near misses with miscibility.

Since the Hildebrand parameter was separated into three parts to account for dispersion, polarity, and hydrogen bonding ability, the next regression performed was  $M_{\text{lit}}$  versus the Hansen solubility parameters. This regression was performed in MS Excel. The  $R^2$  of the HSP regression model was 86.3%. The increase in  $R^2$  is expected because more factors were introduced into the model. This is a better  $R^2$  than the single parameter Hildebrand model, but a more thorough search for relevant factors was performed in Minitab (Table 2).

The  $p$ -values for the coefficients in the HSP were 0.000 for each factor, showing that random noise was not a significant part of any coefficient. Since the HSP regression had more than one factor, the VIF was analyzed. The highest value was 1.380 showing minimal multicollinearity in the model. Overall the Hansen solubility parameters model was a better choice than the Hildebrand model.

Dr. Steven Abbott, of the Hansen Team, hinted that molar volume plays a significant role in miscibility but could not expand further because of proprietary concerns with his HSPiP software. So, a regression was performed on  $M_{lit}$  versus the Hansen solubility parameters and molar volume (eq 14). With the addition of molar volume the model increased the  $R^2$  to 87.3% (Figure 5).

$$M_{calc} = 35.1 - 0.557\delta_D - 0.495\delta_P - 0.750\delta_H + 0.0117V_m \quad (14)$$



*Figure 5.* Performance plot of the QSPR of Hansen solubility parameters and molar volume  $M_{calc}=35.1-0.557\delta_D-0.495\delta_P-0.750\delta_H+0.0117V_m$ .

The addition of  $V_m$  improved  $R^2$  by 1%, this model is shown in Table 6. The  $p$ -values are all 0.000, and the highest VIF is 1.470, this is within the desired limits.

Table 6

*Regression of Hansen Solubility Parameters in Addition to Molar Volume*

Predictor	Coefficient	<i>p</i> -value	VIF
Constant	35.1	0.000	
$\delta_D$	-0.557	0.000	1.058
$\delta_P$	-0.495	0.000	1.470
$\delta_H$	-0.750	0.000	1.433
$V_m$	0.0117	0.000	1.211

To further explore different models, the best subsets tool in Minitab was used. Table 3 shows the results of the best subsets tool. A best subsets analysis uses all of the factors in every possible combination. The table is ranked in order based on the number of factors used then highest  $R^2$  for each set, starting with lowest number of factors and increasing to using all factors. For this experiment, Minitab showed the best set of three for each number of increasing factors. The best subset function does not provide the *p*-value or the VIF, so separate regressions must be performed to determine the values that assist in selecting a model.

When sorting through the multitude of equations given by the best subset table the goal is to find the simplest model with the best performance, significant *p*-values (<0.05), low VIF, and appropriate Mallows  $C_p$ . Starting with the model utilizing all of the factors (Table 4) the  $R^2$  is 88.6 and the adjusted  $R^2$  is 88.4, which is better than both the Hildebrand and Hansen regression models. As with the Hansen model, there is more than one factor, so further figures of merit needed to be checked. The Mallows'  $C_p$  of the seven factor model is 8.0, which is acceptably close to the number of factors. The highest

$p$ -value in the model is 0.567, which is above the 0.05 significance level. The VIF for the seven factor model is very high for each factor except  $\delta_D$  showing that there is multicollinearity in the model. Based on these results, the seven factor model is not a good model.

The next model in the best subsets is the first model with six factors. The  $R^2$  and adjusted  $R^2$  of the model is the same as the seven factor model, 88.6% and 88.4% respectively. The Mallows'  $C_p$  of the model is 6.3 where there are six factors, so the value of the Mallows'  $C_p$  is great. The  $p$ -values of the coefficients are all below the 0.05 limit. The VIF values are lower than the seven factor model but only two factors,  $\delta_D$  and  $V_m$ , are below 10. This model had the best Mallows'  $C_p$  value to number of factors, good  $p$ -values but the VIF was above the limit of 10 and showing that there was multicollinearity in the model. From the results of the six factor model, this model's VIF does not meet the requirements.

Based on the Mallows'  $C_p$  and using the last model as a starting point, attempting to remove the multicollinearity components from the model one at a time was the next step. By knowing that  $\delta_P$  and  $\mu$  are correlated (eq 6), determining which needed to be removed was resolved by the highest VIF values, in this case  $\delta_P$ . The results of the new regression (Table 7) reduced the VIF to where four of the five factors in the model were within acceptable limits of multicollinearity.

Table 7

*Regression of Best Subsets with Best Mallows' Cp with Removal of  $\delta_P$* 

Predictor	Coefficient	<i>p</i> -value	VIF
Constant	32.5	0.000	
$\delta_T$	0.294	0.005	12.16
$\delta_D$	-0.735	0.000	2.012
$\delta_H$	-0.879	0.000	6.876
<i>V<sub>m</sub></i>	0.0231	0.000	1.271
$\mu$	-2.26	0.000	2.802

From the results in Table 7 the next factor removed was the  $\delta_T$  due having the highest VIF. This is understandable, because it was derived from the Hansen solubility parameters (eq 5). The *p* and VIF values were within the required limits as shown in Table 8. The final equation (eq 15) with the best figures of merit and only four factors utilizes Hansen's dispersion and hydrogen bonding terms, molar volume and dipole moment. As Dr. Abbott hinted, molar volume plays a part with miscibility.

To see how the model performs against Godfrey's standards, the assigned M-numbers were plotted in a performance plot as shown in Figure 6. The model has an R<sup>2</sup> of 96.6% with respect to Godfrey's 31 standards. The QSPR modeled Godfrey's empirical work very well. The same model was applied to the 344 solvents that were the training set, as shown in a performance plot in Figure 7. The model had an R<sup>2</sup> of 88.2%, an adjusted R<sup>2</sup> of 88.1% when taking the training set into account.

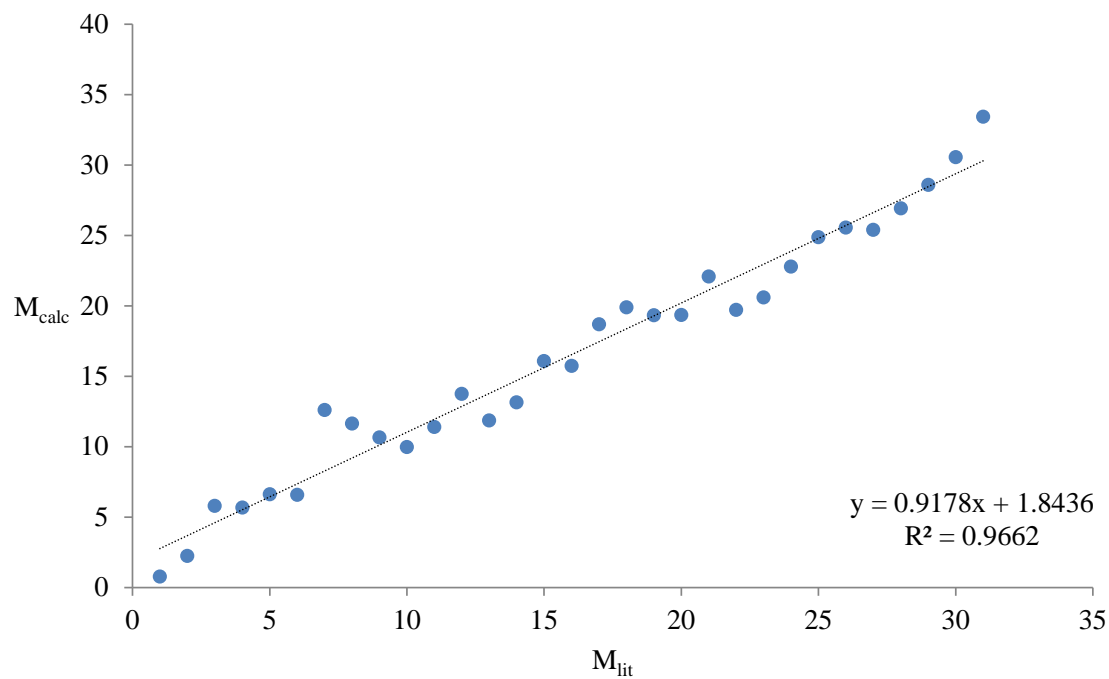


Table 8

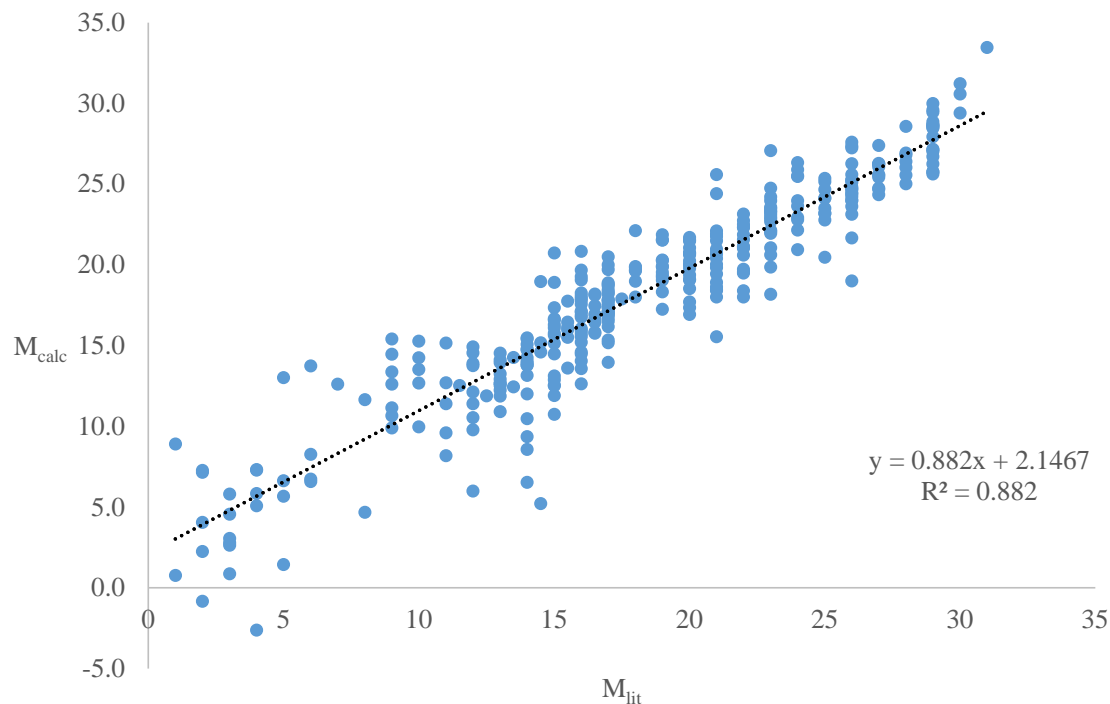
*Regression of Best Subsets with Lowest Mallows'  $C_p$  with Removal of  $\delta_P$  and  $\delta_T$*

Predictor	Coefficient	$p$ -value	VIF
Constant	32.9	0.000	
$\delta_D$	-0.484	0.000	1.073
$\delta_H$	-0.741	0.000	1.430
$V_m$	0.0211	0.000	1.145
$\mu$	-1.90	0.000	1.294

$$M_{calc} = 32.9 - 0.484\delta_D - 0.741\delta_H + 0.0212V_m - 1.90\mu \quad (15)$$



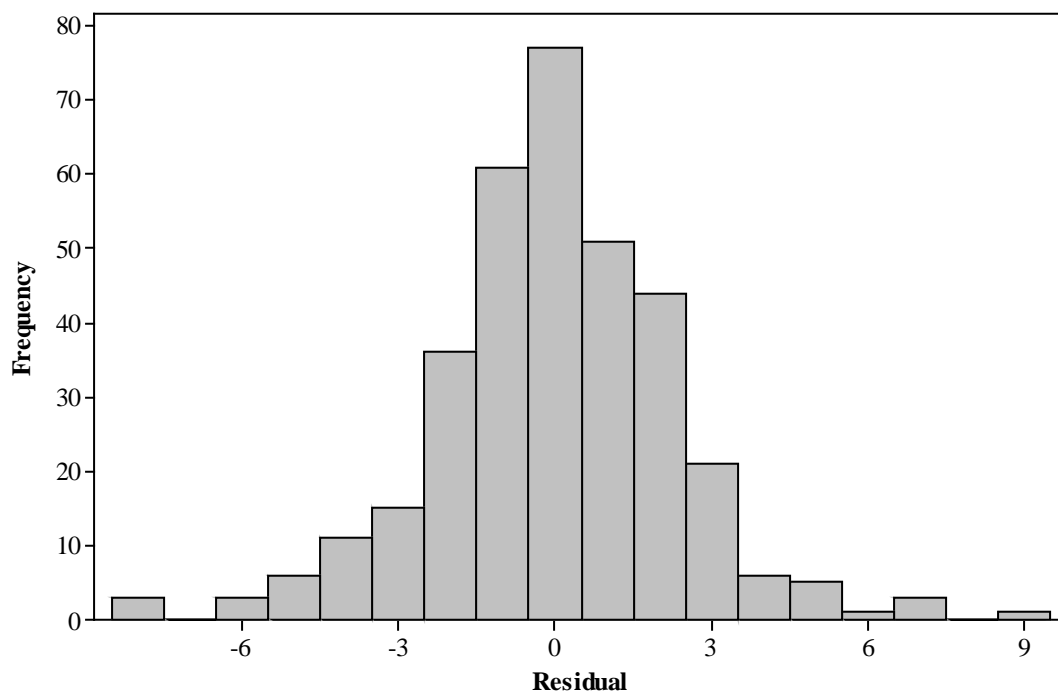
*Figure 6. Performance plot of the QSPR of modified best subset with Godfrey's standards  $M_{cal}=32.9-0.484\delta_D-0.741\delta_H+0.0211V_m-1.90\mu$ .*



*Figure 7.* Performance plot of the QSPR of M-number of modified best subset  $M_{cal}=32.9-0.484\delta_D-0.741\delta_H+0.0211V_m-1.90\mu$ .

While an  $R^2$  of 88.2% is sufficient, the  $\delta_P$  and  $\delta_D$  calculations from HSPiP could prevent the model from predicting with higher accuracy. HSPiP derives  $\delta_P$  in a QSPR with an  $R^2$  of 82.0% and  $\delta_D$  in a separate QSPR with an  $R^2$  of 84.1%. This could potentially limit the accuracy of the model due to the noise from those HSPiP calculations. From looking at the histogram of residuals (Figure 8) and determining which solvents were not modeled as accurately as others a residual versus fit plot was created. The solvents were labeled if they were predicted with a difference of  $\pm 5.0$  from the literature value. The residual versus fit plot in Figure 9 was color-coded based on if the solvent was an alcohol, amine, or alcohol and amine. When the graph was color-coded it became apparent that the amines are calculated higher than the empirical M-number data and the alcohols are calculated lower than the empirical M-number data.

This follows Godfrey's statement that wrong predictions may be expected when predicting miscibility for ethers, amines, or hydroxylic solvents, due to their hydrogen bonding ability.



*Figure 8.* Histogram showing residuals and frequency of the calculated M-number.

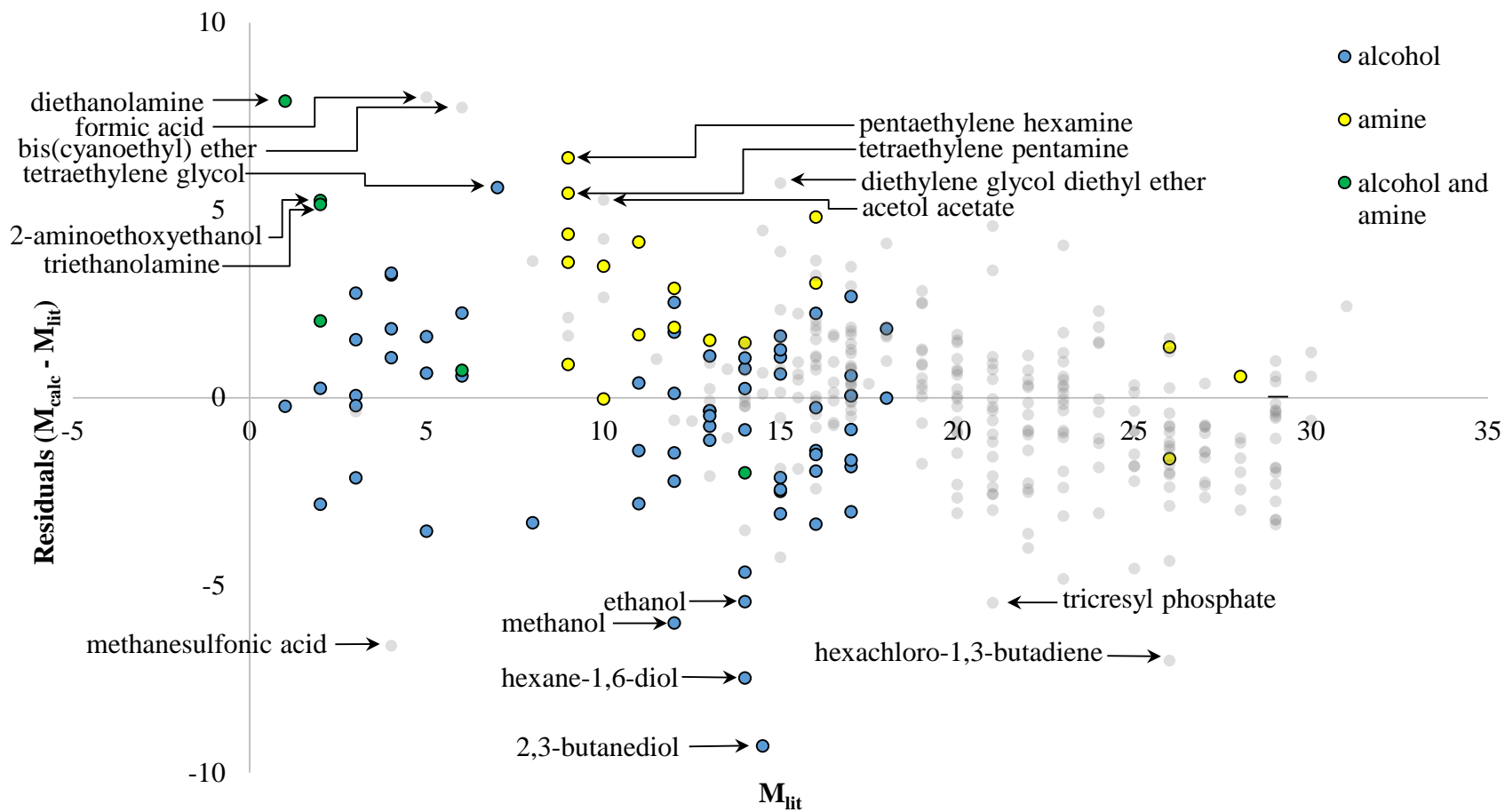


Figure 9. Residuals of  $M_{lit}$  value for final model.

To delve further into miscibility, Table 9 shows Godfrey's standards with their respective  $\delta_T$ ,  $\delta_D$ ,  $\delta_P$ ,  $\delta_H$ , and  $V_m$  values that were color coded based on the value of each column. A trend becomes apparent, as  $M_{lit}$  increases,  $\delta_T$  decreases. As stated earlier, Godfrey assigned the standards M-numbers in order of increasing lipophilicity. As expected with Godfrey's standards, this trend in increasing lipophilicity shows a decrease in the hydrogen bonding ability.

Table 9

*Godfrey's Standards with their Hildebrand, HSP, and Molar Volume Values*

Godfrey's Standards	$M_{lit}$	$\delta_T$	$\delta_D$	$\delta_P$	$\delta_H$	$V_m$
glycerol	1	34.2	17.4	11.3	27.2	73.4
ethylene glycol	2	33.0	17.0	11.0	26.0	55.9
1,4-butanediol	3	28.9	16.6	11.0	20.9	88.9
2,2'-thiodiethanol	4	29.2	17.9	9.8	20.9	103.3
diethylene glycol	5	27.9	16.6	12.0	19.0	95.3
triethylene glycol	6	27.5	16.0	12.5	18.6	134.2
tetraethylene glycol	7	23.0	16.7	9.1	12.9	171.2
methoxyacetic acid	8	23.6	15.9	8.6	15.1	82.4
dimethyl sulfoxide	9	26.7	18.4	16.4	10.2	71.3
N-formylmorpholine	10	25.9	18.6	13.3	12.2	99.9
furfuryl alcohol	11	24.3	17.4	7.6	15.1	87.1
2-(2-methoxyethoxy) ethanol	12	22.0	16.2	7.8	12.6	118.2
2-methoxyethanol	13	23.4	16.0	8.2	15.0	79.3
2-ethoxyethanol	14	22.4	15.9	7.2	14.0	97.5
2-(2-butoxyethoxy) ethanol	15	20.4	16.0	7.0	10.6	170.4
2-butoxyethanol	16	20.8	16.0	5.1	12.3	131.8
p-dioxane	17	19.8	17.5	1.8	9.0	85.7
3-pentanone	18	18.2	15.8	7.6	4.7	106.4
1,1,2,2-tetrachloroethane	19	20.2	18.8	5.1	5.3	105.8
1,2-dichloroethane	20	19.9	18.0	7.4	4.1	79.4
chlorobenzene	21	19.6	19.0	4.3	2.0	102.1
1,2-dibromobutane	22	19.1	17.3	6.2	5.1	122.5
1-bromobutane	23	18.4	16.3	7.9	3.2	109.3
1-bromo-3-methylbutane	24	16.9	16.0	4.0	3.6	126.3
sec-amylbenzene	25	17.8	17.5	1.6	2.8	172.2
4-vinylcyclohexene	26	17.1	17.0	1.6	1.2	129.9
1-methylcyclohexene	27	16.7	16.6	0.8	2.0	117.5
cyclohexane	28	16.8	16.8	0.0	0.2	108.9
heptane	29	15.3	15.3	0.0	0.0	147.0
tetradecane	30	16.2	16.2	0.0	0.0	261.3
petrolatum	31	16.5	16.4	0.7	1.2	482.8

The relative effect of each factor on the miscibility limit of  $\Delta M=15$  was explored by coding or normalizing each factor. The method to derive the coded factors was accomplished by subtracting  $M_{calc1}$  from  $M_{calc2}$  and simplifying (eqs 16 and 17).

$$M_{calc1} - M_{calc2} = a + b\delta_{D1} + c\delta_{P1} + d\delta_{H1} + eV_{m1} - a - b\delta_{D2} - c\delta_{P2} - d\delta_{H2} - eV_{m2} \quad (16)$$

$$M_{calc1} - M_{calc2} = b(\delta_{D1} - \delta_{D2}) + c(\delta_{P1} - \delta_{P2}) + d(\delta_{H1} - \delta_{H2}) + e(V_{m1} - V_{m2}) \quad (17)$$

Each coefficient of the equation was multiplied by that factor's maximum and the terms were divided by the factor's maximum (eq 18).

$$M_{calc1} - M_{calc2} = b\delta_{D\max} \left( \frac{\delta_{D1} - \delta_{D2}}{\delta_{D\max}} \right) + c\delta_{P\max} \left( \frac{\delta_{P1} - \delta_{P2}}{\delta_{P\max}} \right) + d\delta_{H\max} \left( \frac{\delta_{H1} - \delta_{H2}}{\delta_{H\max}} \right) + eV_{m\max} \left( \frac{V_{m1} - V_{m2}}{V_{m\max}} \right) \quad (18)$$

The values for each coefficient from eq 14 and maximums from Table 9 were inserted into eq 18, then coefficients for the coded factors were obtained (eq 19).

$$M_{calc1} - M_{calc2} = -10.6 \left( \frac{\delta_{D1} - \delta_{D2}}{\delta_{D\max}} \right) - 8.12 \left( \frac{\delta_{P1} - \delta_{P2}}{\delta_{P\max}} \right) - 20.4 \left( \frac{\delta_{H1} - \delta_{H2}}{\delta_{H\max}} \right) + 5.65 \left( \frac{V_{m1} - V_{m2}}{V_{m\max}} \right) \quad (19)$$

The largest coefficient in eq 19 is the  $\delta_H$  parameter. This implies that the hydrogen bonding ability of a solvent has the largest role in miscibility, followed by dispersion, polarity, and lastly molar volume.

## CHAPTER V

### CONCLUSION

This research set out to develop a method of replacing AK-225 as an industrial cleaning solvent with a solvent blend and has expanded to developing a methodical way to replace cleaning solvents based on a solvent blend's solvation abilities. This used the Hansen solubility parameters and Godfrey's empirical Miscibility Number Index where a relationship was found through a Quantitative Structure Property Relationship. The findings were two equations that could be utilized by an end user that has knowledge of, and access to, the Hansen solubility parameters.

The first equation only used Hansen solubility parameters and molar volume, which are given in the HSPiP software. If the solvent is not in the HSPiP database, HSPiP can calculate the  $\delta_D$ ,  $\delta_P$ ,  $\delta_H$ , and  $V_m$  values based on group contribution methods by entering the SMILES code. Equation 20 can simply be used in Excel to assign M-numbers to any solvent.

$$M_{calc} = 35.1 - 0.557\delta_D - 0.495\delta_P - 0.750\delta_H + 0.0117V_m \quad (20)$$

The second equation uses Hansen's dispersion and hydrogen bonding terms, molar volume, and dipole moment. The dipole moment can be derived from eq 6 so an extra calculation is required when calculating M-numbers. The extra step of calculations can be entered into Excel if the user chooses as shown in eq 21.

$$M_{calc} = 32.9 - 0.484\delta_D - 0.741\delta_H + 0.0212V_m - 1.90 \left( \frac{\delta_P \sqrt{V_m}}{36.1} \right) \quad (21)$$

Either of the above equations can be used to predict miscibility. Equation 20 has one less calculation, whereas eq 21 has an  $R^2$  one percent higher. The difference in  $R^2$  is



minimal between the two models. The top blend predictions will still need to be taken to the bench to be tested for solvency performance. The model will alleviate some of the miscibility testing in solvent blending where predictions are based on HSPs.

Using the algorithm from Mathematica for the binary solvent blends in addition to the miscibility eq 21, a set of proposed blend predictions were calculated. Appendix B lists the possible solvent blends that could replace AK-225 based on HSPs. The list is ranked according to the  $R_a$  distance using eq 10. The blends with a high  $\Delta M$  were left in Appendix B to help show which predicted blends this model can remove.

While this research only covers the miscibility and solvation aspect of solvent replacement, ongoing research involving low-boiling azeotropes is currently being performed to work in conjunction with this project in the Williams' lab. The ultimate goal of this ongoing program of research is to find a low-boiling azeotrope to replace ozone depleting solvents.

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## APPENDIX A

### TRAINING SET SHOWING THE DIFFERENCE BETWEEN $M_{\text{CALC}}$ AND $M_{\text{AVG}}$

Solvents	M	M'	$M_{\text{avg}}$	$M_{\text{calc}}$	$M_{\text{calc}} - M_{\text{avg}}$	Solvents	M	M'	$M_{\text{avg}}$	$M_{\text{calc}}$	$M_{\text{calc}} - M_{\text{avg}}$
diethanolamine	1		1	8.9	7.9	1,5-pentanediol	3		3	4.6	1.6
glycerol	1		1	0.8	-0.2	2-butene-1,4-diol	3		3	2.8	-0.2
1,2,6-hexanetriol	2		2	-0.8	-2.8	formamide	3		3	2.6	-0.4
2-aminoethoxyethanol	2		2	7.3	5.3	glycerol carbonate	3		3	0.9	-2.1
ethanolamine	2		2	4.0	2.0	1,2-propanediol, 3-chloro-	4		4	5.1	1.1
ethylene glycol	2		2	2.3	0.3	1,3-butanediol	4		4	7.3	3.3
triethanolamine	2		2	7.2	5.2	methanesulfonic acid	4		4	-2.6	-6.6
1,3-propanediol (trimethyleneglycol)	3		3	3.1	0.1	propylene glycol	4		4	5.8	1.8
1,4-butanediol	3		3	5.8	2.8	thiodiethylenglycol	4		4	7.3	3.3

Solvents	M	M'	M <sub>avg</sub>	M <sub>calc</sub>	$\frac{M_{calc}-M_{avg}}{M_{avg}}$
2,5-hexanediol	5		5	5.7	0.7
diethylene glycol	5		5	6.6	1.6
ethanesulfonic acid	5		5	1.4	-3.6
formic acid	5		5	13.0	8.0
1,2-butanediol	6		6	8.3	2.3
1-amino-2-propanol	6		6	6.7	0.7
ethylene carbonate	6	17	11.5	12.5	1.0
bis(cyanoethyl) ether	6		6	13.7	7.7
triethylene glycol	6		6	6.6	0.6
tetraethylene glycol	7		7	12.6	5.6
adiponitrile	8	19	13.5	14.3	0.8
methyl cyanoacetate	8	17	12.5	11.9	-0.6

Solvents	M	M'	M <sub>avg</sub>	M <sub>calc</sub>	$\frac{M_{calc}-M_{avg}}{M_{avg}}$
acetol	8		8	4.7	-3.3
methoxyacetic acid	8		8	11.6	3.6
propylene carbonate	9	17	13	13.2	0.2
sulfolane (tetramethylene sulfone)	9	17	13	10.9	-2.1
diethylenetriamine	9		9	12.6	3.6
dimethyl sulfoxide (DMSO)	9		9	10.7	1.7
ethylenediamine	9		9	9.9	0.9
pentaethylene hexamine	9		9	15.4	6.4
propanamide	9		9	11.1	2.1
tetraethylenepentamine	9		9	14.5	5.5
triethylene tetramine	9		9	13.4	4.4

Solvents	M	M'	M <sub>avg</sub>	M <sub>calc</sub>	$\frac{M_{calc}-M_{avg}}{M_{avg}}$
methyl sulfolane	10	17	13.5	12.4	-1.1
2-pyrrolidone	10		10	13.5	3.5
nitromethane	10	19	14.5	14.6	0.1
N-formylmorpholine	10		10	10.0	0.0
acetol acetate	10		10	15.3	5.3
trimethylphosphate	10		10	14.2	4.2
4-butyrolactone (GBL)	10		10	12.7	2.7
1,1,2,2-tetrabromoethane	11	19	15	15.1	0.1
3-methoxypropionitrile	11	17	14	13.8	-0.2
furfural	11	17	14	14.7	0.7
glycerol triacetate	11	19	15	18.9	3.9
dipropylene glycol	11		11	8.2	-2.8
2-chloroethanol	11		11	9.6	-1.4

Solvents	M	M'	M <sub>avg</sub>	M <sub>calc</sub>	$\frac{M_{calc}-M_{avg}}{M_{avg}}$
furfuryl alcohol	11		11	11.4	0.4
methylethanolamine	11		11	12.7	1.7
N-acetylmorpholine	11		11	15.2	4.2
1,3-dichloro-2-propanol	12		12	10.5	-1.5
2,3-butanediol	12	17	14.5	5.2	-9.3
2,5-hexanedione	12	17	14.5	19.0	4.5
acetic anhydride	12	19	15.5	13.6	-1.9
pentane-2,4-dione	12	18	15	17.3	2.3
diethyl sulfate	12	21	16.5	16.6	0.1
dimethyl maleate	12	19	15.5	15.5	0.0
dimethyl phthalate	12	19	15.5	16.4	0.9
dipropyl sulfone	12	17	14.5	15.2	0.7
ethylene glycol diacetate	12	19	15.5	17.7	2.2
2-hydroxyethyl methacrylate	12		12	9.8	-2.2

Solvents	M	M'	M <sub>avg</sub>	M <sub>calc</sub>	M <sub>calc</sub> - M <sub>avg</sub>
phenyl acetonitrile	12	19	15.5	16.1	0.6
aniline	12		12	13.9	1.9
diethylene glycol monomethyl ether	12		12	13.8	1.8
dimethyl formamide (DMF)	12		12	11.4	-0.6
ethylene glycol mono benzyl ether	12		12	14.5	2.5
methanol	12		12	6.0	-6.0
N-aminoethyl piperazine	12		12	14.9	2.9
tripropylene glycol	12		12	12.1	0.1
1,2-epoxy-3-phenoxypropane	13	19	16	17.9	1.9
diethyl phthalate	13	20	16.5	18.1	1.6
ethyl acetoacetate (keto)	13	19	16	17.1	1.1

Solvents	M	M'	M <sub>avg</sub>	M <sub>calc</sub>	M <sub>calc</sub> - M <sub>avg</sub>
2-allyloxyethanol	13		13	12.2	-0.8
methyl chloroacetate	13	19	16	16.7	0.7
nitroethane	13	20	16.5	16.4	-0.1
propionitrile	13	17	15	16.6	1.6
propylene glycol monophenyl ether	13	17	15	15.6	0.6
benzyl alcohol	13		13	12.7	-0.3
dichloroacetic acid	13		13	12.9	-0.1
ethylene glycol monomethyl ether	13		13	11.9	-1.1
ethylthioethanol	13		13	12.7	-0.3
N,N-dimethyl acetamide	13		13	13.9	0.9
N-methyl-2-pyrrolidone (NMP)	13		13	14.5	1.5
tetrahydrofurfuryl alcohol	13		13	12.5	-0.5



Solvents	M	M'	M <sub>avg</sub>	M <sub>calc</sub>	$\frac{M_{calc}-M_{avg}}$
triethylene glycol monomethyl ether	13		13	14.1	1.1
acetonitrile	14	18	16	15.2	-0.8
acrylonitrile	14	18	16	16.0	0.0
butyronitrile	14	19	16.5	17.5	1.0
diethyl oxalate	14	20	17	16.5	-0.5
dimethyl carbonate	14	19	16.5	15.8	-0.7
epichlorohydrin	14	19	16.5	16.9	0.4
ethylene glycol monomethyl ether acetate	14	17	15.5	16.0	0.5
methyl formate	14	19	16.5	15.8	-0.7
nitrobenzene	14	20	17	17.4	0.4
3-methoxy butanol	14		14	14.8	0.8
4-methyl cyclohexanol (mix)	14		14	14.2	0.2
acetic acid	14		14	13.9	-0.1

Solvents	M	M'	M <sub>avg</sub>	M <sub>calc</sub>	$\frac{M_{calc}-M_{avg}}$
allyl alcohol	14		14	9.3	-4.7
diacetone alcohol	14		14	15.1	1.1
dimethyl ethanolamine	14		14	12.0	-2.0
ethanol	14		14	8.6	-5.4
ethyl lactate	14		14	14.0	0.0
ethylene glycol monoethyl ether	14		14	13.1	-0.9
hexylene glycol	14		14	6.5	-7.5
morpholine	14		14	15.5	1.5
N,N-diethyl acetamide	14		14	15.4	1.4
propylene chlorohydrin	14		14	10.5	-3.5
triethylphosphate	14		14	13.8	-0.2

Solvents	M	M'	M <sub>avg</sub>	M <sub>calc</sub>	$\frac{M_{calc}-M_{avg}}{M_{avg}}$
1-butanol	15		15	12.5	-2.5
2-nitropropane	15	20	17.5	17.9	0.4
acetone	15	17	16	17.1	1.1
acetophenone	15	18	16.5	18.2	1.7
benzaldehyde	15	19	17	17.8	0.8
benzotrile	15	19	17	17.1	0.1
benzyl benzoate	15	21	18	19.7	1.7
di-(2-methoxyethyl) ether	15	17	16	19.7	3.7
1-propanol	15		15	10.7	-4.3
ethyl formate	15	19	17	16.9	-0.1
ethylene glycol monoethyl ether acetate	15	19	17	17.3	0.3
ethylene glycol monoisobutyl ether	15	17	16	18.3	2.3
methacrylonitrile	15	19	17	18.4	1.4
methyl acetate	15	17	16	18.1	2.1

Solvents	M	M'	M <sub>avg</sub>	M <sub>calc</sub>	$\frac{M_{calc}-M_{avg}}{M_{avg}}$
2-propanol	15		15	11.9	-3.1
paraldehyde	15	19	17	20.5	3.5
3-methyl allyl alcohol	15		15	12.5	-2.5
styrene oxide (phenyl oxirane)	15	19	17	17.8	0.8
diethylene glycol diethyl ether	15		15	20.7	5.7
diethylene glycol monobutyl ether	15		15	16.1	1.1
dipropylene glycol methyl ether	15		15	16.6	1.6
hexamethyl phosphoramidate	15		15	13.1	-1.9
isobutyl alcohol	15		15	12.9	-2.1
propionic acid	15		15	15.8	0.8
propylene glycol monoethyl ether	15		15	16.3	1.3

Solvents	M	M'	M <sub>avg</sub>	M <sub>calc</sub>	$\frac{M_{calc}-M_{avg}}$
tetramethylurea	15		15	14.5	-0.5
2,5-dimethylpyrazine	16		16	15.6	-0.4
2-butanol	16		16	13.6	-2.4
2-chlorophenol	16		16	12.6	-3.4
2-methyl-2-butanol	16		16	14.6	-1.4
2-methylpyridine	16		16	17.8	1.8
4-ethyl morpholine	16		16	19.1	3.1
butyric acid	16		16	15.9	-0.1
cyclohexanecarboxylic acid	16		16	19.3	3.3
cyclohexanol	16		16	14.5	-1.5
ethylene glycol monobutyl ether	16		16	15.7	-0.3

Solvents	M	M'	M <sub>avg</sub>	M <sub>calc</sub>	$\frac{M_{calc}-M_{avg}}$
N,N'-dimethylpiperazine	16		16	20.8	4.8
pyridine	16		16	16.9	0.9
t-butyl alcohol	16		16	14.0	-2.0
trimethyl borate	16		16	17.6	1.6
1,4-dioxane	17		17	18.7	1.7
1-heptanol	17		17	16.2	-0.8
1-hexanol	17		17	15.2	-1.8
1-nonanol	17		17	17.4	0.4
1-octanol	17		17	16.9	-0.1
1-pentanol	17		17	14.0	-3.0
2,5-dihydrofuran	17		17	18.9	1.9

Solvents	M	M'	M <sub>avg</sub>	M <sub>calc</sub>	$\frac{M_{calc}-M_{avg}}$
2-ethyl-1-butanol	17		17	15.3	-1.7
2-ethyl-hexanol	17		17	17.6	0.6
2-octanol	17		17	17.1	0.1
cyclohexanone	17		17	18.2	1.2
dimethyl cellosolve	17		17	20.0	3.0
hexanoic acid	17		17	16.7	-0.3
methyl ethyl ketone (MEK)	17		17	18.8	1.8
methyl isobutyl carbinol	17		17	17.1	0.1
nonyl phenol	17		17	19.7	2.7
propylene oxide	17		17	18.3	1.3
tetrahydrofuran (THF)	17		17	17.9	0.9

Solvents	M	M'	M <sub>avg</sub>	M <sub>calc</sub>	$\frac{M_{calc}-M_{avg}}$
1-decanol	18		18	18.0	0.0
diethyl ketone	18		18	19.9	1.9
dodecanol	18		18	19.8	1.8
isophorone	18		18	19.0	1.0
mesityl oxide	18		18	19.6	1.6
tri-n-butyl phosphate	18		18	22.1	4.1
1,1,2,2-tetrachloroethane	19		19	19.3	0.3
1,1,2-trichloroethane	19		19	18.3	-0.7
1,2-dibromoethylene	19		19	21.8	2.8
1-propen-2-ol, acetate	19		19	19.9	0.9
butyl formate	19		19	17.2	-1.8

Solvents	M	M'	M <sub>avg</sub>	M <sub>calc</sub>	$\frac{M_{calc}-M_{avg}}$
chloroform	19		19	20.3	1.3
diethyl adipate	19		19	19.0	0.0
ethyl acetate	19		19	19.2	0.2
isopropyl acetate	19		19	19.5	0.5
methyl isoamyl ketone	19		19	21.5	2.5
methyl isobutyl ketone (MIBK)	19		19	21.5	2.5
methylal (dimethoxy methane)	19		19	20.3	1.3
n-propyl acetate	19		19	19.9	0.9
1,1-dichloroethane	20		20	20.7	0.7
1,2,3-trichloropropane	20		20	17.3	-2.7
1,2-dichloroethylene (cis)	20		20	20.2	0.2

Solvents	M	M'	M <sub>avg</sub>	M <sub>calc</sub>	$\frac{M_{calc}-M_{avg}}$
1,2-dichloropropane	20		20	20.7	0.7
1,3-dichloro propane	20		20	19.8	-0.2
1,4-dichlorobutane	20		20	20.0	0.0
anisole	20		20	19.1	-0.9
di-(2-chloroethyl) ether	20		20	16.9	-3.1
ethylene dichloride	20		20	19.4	-0.6
fluorobenzene	20		20	21.5	1.5
furan	20		20	21.5	1.5
methyl methacrylate	20		20	20.0	0.0
methylene dichloride (dichloromethane)	20		20	17.7	-2.3
o-chlorotoluene	20		20	21.7	1.7

Solvents	M	M'	M <sub>avg</sub>	M <sub>calc</sub>	$\frac{M_{calc}-M_{avg}}$
phenetole (ethyl phenyl ether)	20		20	21.0	1.0
thiophene	20		20	18.5	-1.5
trichloroethylene	20		20	20.6	0.6
vinyl acetate	20		20	19.1	-0.9
1,2-dibromopropane	21		21	18.4	-2.6
1,4-dibromobutane	21		21	20.7	-0.3
1-fluoronaphthalene	21		21	21.8	0.8
benzene	21		21	24.4	3.4
bromobenzene	21		21	19.8	-1.2
butyric anhydride	21		21	18.4	-2.6
chlorobenzene	21		21	22.1	1.1

Solvents	M	M'	M <sub>avg</sub>	M <sub>calc</sub>	$\frac{M_{calc}-M_{avg}}$
dichloroethylene (trans)	21		21	20.4	-0.6
diethyl carbonate	21		21	21.9	0.9
diphenylmethane	21		21	25.6	4.6
ethyl benzoate	21		21	18.9	-2.1
ethyl bromide	21		21	21.0	0.0
ethyl propionate	21		21	20.8	-0.2
ethyl trichloroacetate	21		21	19.4	-1.6
isobutyl acetate	21		21	21.5	0.5
methyl iodide	21		21	18.6	-2.4
o-dichlorobenzene	21		21	20.0	-1.0
tetramethylene sulfide	21		21	18.0	-3.0

Solvents	M	M'	M <sub>avg</sub>	M <sub>calc</sub>	$\frac{M_{calc}-M_{avg}}$
tricresyl phosphate	21		21	15.5	-5.5
1,1,1-trichloroethane	22		22	23.1	1.1
1,2-dibromobutane	22		22	19.7	-2.3
1-chloronaphthalene	22		22	21.0	-1.0
1-methyl naphthalene	22		22	22.3	0.3
2-octanone	22		22	22.3	0.3
diallyl ether	22		22	21.5	-0.5
dibutyl maleate	22		22	19.6	-2.4
dibutyl phthalate	22		22	19.5	-2.5
dimethyl sebacate	22		22	22.5	0.5
ethyl butyl ketone	22		22	21.9	-0.1

Solvents	M	M'	M <sub>avg</sub>	M <sub>calc</sub>	$\frac{M_{calc}-M_{avg}}$
ethyl butyrate	22		22	21.1	-0.9
ethyl iodide	22		22	18.4	-3.6
iodobenzene	22		22	18.0	-4.0
n-butyl acetate	22		22	21.1	-0.9
styrene	22		22	22.7	0.7
vinyl butyrate	22		22	20.6	-1.4
1,1-diethoxy ethane	23		23	23.6	0.6
1-bromobutane	23		23	20.6	-2.4
1-chlorobutane	23		23	22.8	-0.2
2,4-dimethyl-3-pentanone	23		23	21.9	-1.1
diethyl ether	23		23	23.1	0.1

Solvents	M	M'	M <sub>avg</sub>	M <sub>calc</sub>	$\frac{M_{calc}-M_{avg}}$
diethylene glycol dibutyl ether	23		23	23.3	0.3
di-isobutyl ketone	23		23	23.3	0.3
dipropyl ketone	23		23	19.8	-3.2
ethyl capronate	23		23	22.1	-0.9
isobutyl isobutyrate	23		23	23.0	0.0
isopropyl chloride (2-chloro propane)	23		23	22.1	-0.9
m-xylene	23		23	24.7	1.7
n-butyl methacrylate	23		23	21.0	-2.0
o-xylene	23		23	24.0	1.0
phenyl acetate	23		23	18.2	-4.8
tetraethylorthosilicate	23		23	27.1	4.1

Solvents	M	M'	M <sub>avg</sub>	M <sub>calc</sub>	$\frac{M_{calc}-M_{avg}}$
toluene	23		23	24.2	1.2
triethoxymethane	23		23	22.7	-0.3
$\alpha$ -methyl styrene	23		23	23.5	0.5
1,2,4-trichlorobenzene	24		24	20.9	-3.1
1-bromo-3-methylbutane	24		24	22.8	-1.2
1-bromohexane	24		24	22.1	-1.9
carbon tetrachloride	24		24	25.9	1.9
diethylhexyl phthalate (dioctyl phthalate)	24		24	23.6	-0.4
ethyl benzene	24		24	25.5	1.5
isopropyl benzene (cumene)	24		24	25.5	1.5
mesitylene	24		24	26.3	2.3



Solvents	M	M'	M <sub>avg</sub>	M <sub>calc</sub>	$\frac{M_{calc}-M_{avg}}$
p-xylene	24		24	24.0	0.0
tetrahydronaphthalene	24		24	22.9	-1.1
1,3-pentadiene (trans)	25		25	23.5	-1.5
1-phenyl-3-methylbutane	25		25	25.1	0.1
castor oil	25		25	20.4	-4.6
cyclohexane, bromo-	25		25	22.8	-2.2
diisopropylbenzene	25		25	25.3	0.3
ethylene glycol dibutyl ether	25		25	23.2	-1.8
isoprene (2-methyl-1,3-butadiene)	25		25	24.1	-0.9
p-cymene	25		25	24.1	-0.9
tetrachloroethylene	25		25	23.2	-1.8

Solvents	M	M'	M <sub>avg</sub>	M <sub>calc</sub>	$\frac{M_{calc}-M_{avg}}$
triethylbenzene	25		25	24.6	-0.4
1-bromooctane	26		26	24.0	-2.0
2-methyl-2-butene	26		26	24.8	-1.2
butyl oleate	26		26	26.3	0.3
carbon disulfide	26		26	24.0	-2.0
cyclohexene	26		26	24.7	-1.3
dibutyl sulfide	26		26	25.3	-0.7
dicyclopentadiene	26		26	24.6	-1.4
diethoxydimethylsilane	26		26	27.6	1.6
di-n-butyl ether	26		26	24.4	-1.6
di-n-decyl phthalate	26		26	25.6	-0.4

Solvents	M	M'	M <sub>avg</sub>	M <sub>calc</sub>	$\frac{M_{calc}-M_{avg}}$
di-n-pentyl ether	26		26	25.1	-0.9
dipentene (DL-limonene)	26		26	23.6	-2.4
diphenyl ether	26		26	21.6	-4.4
hexachloro-1,3-butadiene	26		26	19.0	-7.0
isopropyl ether	26		26	24.2	-1.8
methyl oleate	26		26	25.2	-0.8
octadecanoic acid, methyl ester	26		26	27.2	1.2
octyl mercaptan	26		26	23.1	-2.9
triethylamine	26		26	27.4	1.4
tripropylamine	26		26	24.4	-1.6

Solvents	M	M'	M <sub>avg</sub>	M <sub>calc</sub>	$\frac{M_{calc}-M_{avg}}$
1,1,2-trichloro trifluoroethane (Freon113)	27		27	27.4	0.4
1-bromodecane	27		27	24.7	-2.3
1-bromododecane	27		27	26.1	-0.9
1-hexene	27		27	25.6	-1.4
1-methylcyclohexene	27		27	25.4	-1.6
2,4,4-trimethyl-1-pentene	27		27	26.3	-0.7
2,4,4-trimethyl-2-pentene	27		27	26.2	-0.8
2-methyl-1-butene	27		27	26.2	-0.8
4-methyl-cis-2-pentene	27		27	24.7	-2.3
cis-2-octene	27		27	25.5	-1.5

Solvents	M	M'	M <sub>avg</sub>	M <sub>calc</sub>	$\frac{M_{calc}-M_{avg}}$
cyclooctene	27		27	24.3	-2.7
1-heptene	28		28	26.0	-2.0
1-octene	28		28	26.4	-1.6
4-methyl-1-pentene	28		28	25.0	-3.0
cyclohexane	28		28	26.9	-1.1
methyl cyclopentane	28		28	26.8	-1.2
trans-2-octene	28		28	25.5	-2.5
tributylamine	28		28	28.6	0.6
1-bromotetradecane	29		29	26.7	-2.3
1-decene	29		29	27.0	-2.0
1-dodecene	29		29	27.1	-1.9

Solvents	M	M'	M <sub>avg</sub>	M <sub>calc</sub>	$\frac{M_{calc}-M_{avg}}$
1-hexadecene	29		29	28.5	-0.5
1-tetradecene	29		29	28.7	-0.3
2,2,4-trimethylpentane	29		29	29.6	0.6
2-methylpentane	29		29	25.7	-3.3
3-methylpentane	29		29	25.7	-3.3
bicyclohexyl	29		29	28.6	-0.4
cyclooctane	29		29	25.6	-3.4
decane	29		29	29.4	0.4
dodecane	29		29	30.0	1.0
heptane	29		29	28.6	-0.4
hexane	29		29	28.5	-0.5

Solvents	M	M'	M <sub>avg</sub>	M <sub>calc</sub>	$\frac{M_{\text{calc}} - M_{\text{avg}}}{M_{\text{avg}}}$
methyl cyclohexane	29		29	27.1	-1.9
naphtha	29		29	26.2	-2.8
octane	29		29	28.8	-0.2
tetramethylsilane	29		29	27.9	-1.1

Solvents	M	M'	M <sub>avg</sub>	M <sub>calc</sub>	$\frac{M_{\text{calc}} - M_{\text{avg}}}{M_{\text{avg}}}$
1-octadecene	30		30	29.4	-0.6
hexadecane	30		30	31.2	1.2
n-tetradecane	30		30	30.6	0.6
petrolatum	31		31	33.4	2.4

## APPENDIX B

### POSSIBLE SOLVENT BLENDS TO REPLACE AK-225

R <sub>a</sub>	Volume 1	Solvent 1	M <sub>calc</sub>	Volume 2	Solvent 2	M <sub>calc</sub>	ΔM
0.094	0.2	ethyl benzene	25.2	0.8	HFE-8200	27.2	2.0
0.098	0.2	acetonitrile	13.7	0.8	HFE-7300	29.8	16.1
0.189	0.2	ethyl benzene	25.2	0.8	HFE-7000	26.6	1.4
0.194	0.9	HFE-7100	27.5	0.1	propylene carbonate	12.9	14.6
0.220	0.2	1,2-dichloro- 3,3,3-trifluoro propane	22.0	0.8	HFE-7100	27.5	5.5
0.241	0.8	HFE-8200	27.2	0.2	Solvesso 100	25.1	2.1

$R_a$	Volume 1	Solvent 1	$M_{calc}$	Volume 2	Solvent 2	$M_{calc}$	$\Delta M$
0.268	0.2	acetonitrile	13.7	0.8	aliphatic hydrocarbons	28.4	14.8
0.291	0.3	cyclohexane	26.8	0.7	HFE-7000	26.6	0.2
0.301	0.8	HFE-7000	26.6	0.2	Solvesso 100	25.1	1.5
0.315	0.8	HFE-8200	27.2	0.2	toluene	24.1	3.2
0.383	0.3	cyclohexane	26.8	0.7	HFE-8200	27.2	0.4
0.389	0.9	HFE-7100	27.5	0.1	dichloroethylene (trans)	20.3	7.2
0.401	0.3	1,1-dimethyl cyclohexane	25.0	0.7	HFE-8200	27.2	2.2

$R_a$	Volume 1	Solvent 1	$M_{calc}$	Volume 2	Solvent 2	$M_{calc}$	$\Delta M$
0.410	0.2	1,2-dichloro- 3,3,3-trifluoro propane	22.0	0.8	HFE-7500	28.4	6.4
0.413	0.6	perfluorohexane (PFC 5060)	30.7	0.4	dichloroethylene (trans)	20.3	10.3
0.435	0.8	HFE-7000	26.6	0.2	toluene	24.1	2.6
0.435	0.5	1,2-dichloro- 3,3,3-trifluoro propane	22.0	0.5	perfluorohexane (PFC 5060)	30.7	8.7
0.442	0.7	HFE-7000	26.6	0.3	methyl cyclohexane	26.9	0.2

$R_a$	Volume 1	Solvent 1	$M_{calc}$	Volume 2	Solvent 2	$M_{calc}$	$\Delta M$
0.460	0.2	aromatic hydrocarbons	23.5	0.8	HFE-8200	27.2	3.8
0.490	0.8	HFE-8200	27.2	0.2	o-xylene	23.7	3.5
0.496	0.3	1,1-dimethyl cyclohexane	25.0	0.7	HFE-7000	26.6	1.6



## VITA

James E. Huskey was born in Texas City, Texas in July 1973 to James and Betty Huskey. He graduated from Texas City High School in 1991. In 1996 James joined the United States Marine Corps. Upon returning to civilian life, James started working for the City of Texas City - Public Works Street and Bridge division. After ten years of working in road construction, James felt the need to attend college.

James attended Sam Houston State University for an undergraduate degree in forensic chemistry, began taking more chemistry electives, and joined Dr. Darren Williams' research group for three semesters where he became interested in solubility parameters and contact angle of surfaces. James changed his major to chemistry and obtained a Bachelor of Science in Chemistry. He enjoyed chemistry and decided to work toward a Master of Science in Chemistry, which he obtained in May 2014. While at Sam Houston State University, James Huskey presented twice at the Texas Academy of Science.

James Huskey's focus in graduate school was in computational chemistry and solubility parameters. He also worked at the Texas Research Institute for Environmental Studies analytical lab to expand his knowledge in chemistry.