

GROUP CONTRIBUTION MODELING OF PHYSICAL
PROPERTIES DURING URETHANE REACTION

A Thesis presented to
The Faculty of the Graduate School
At the University of Missouri-Columbia

In Partial Fulfillment
Of the Requirements for the Degree
Master of Science in Chemical Engineering

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MAY 2014

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GROUP CONTRIBUTION MODELING OF
PHYSICAL PROPERTIES DURING URETHANE REACTION

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ACKNOWLEDGEMENTS

First and foremost, I would like to thank the members of my committee: Professors. Galen Suppes, Paul Chan and Fu-hung Hsieh. I would also like to express my sincere gratitude to my advisor Professor Galen Suppes for continuous support of my MS study and research, for his patience, motivation, enthusiasm and immense knowledge. His guidance helped me in all the time of research and writing of this thesis. I could not have imagined having a better advisor and mentor for my MS study.

I would like to extend my gratefulness to the members in our polyol group: Yusheng Zhao, Lu Shen, Rima Ghoreishi, Harith H. Al-Moameri, Huaqi Wang and Yingyue Li, for all the stimulating discussions and fun in the last two years we shared together. Also I thank other members in our laboratory: Ali Teekei, Michael Gordon, Ramsey Hilton and Donald Dornbusch.

Last, but not the least, I would like to acknowledge my family: my parents Zhuqin Huang and Zheng Fu, for giving birth to me at the first place and supporting me spiritually throughout my life.

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GROUP CONTRIBUTION MODELING OF PHYSICAL PROPERTIES DURING URETHANE REACTION

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ABSTRACT

The work of this thesis is part of a larger effort to develop a computer-based simulation package to assist in understanding urethane-forming thermoset polymerizations and to assist in developing improved formulations. One of the challenges of simulating polymerization is the prediction of the large number of products and intermediates formed during polymerization reactions. The goal of this work is to estimate the viscosities of urethane-forming reactions; accurate viscosity information is critical as an intermediate step to predict how successful a foam formulation would be and to ultimately estimate the final physical properties of the foam.

Based on experimental viscosity data collected from single materials and binary system mixtures, a group contribution method was introduced to estimate viscosities of a range of polyol oligomers and urethane polymers at temperatures from 25 to 150°C. Use of mixture rules then extends the estimation method to multi-component reacting systems. Mixture viscosity data were used to determine the Gibbs free energy (G) in the Grundberg-Nissan equation which can be used to estimate mixture viscosities with

correction for some non-idealities. The resulting model is able to accurately predict mixture viscosities based on binary interaction.

Chapter 2 summarizes the group contribution equations, methodology, and experimental data used to verify the method. Chapter 3 summarizes the Chapter 2 group contribution method along with a method developed for heat capacities and presents them in a textbook format with a focus on common features of the group contribution approaches and examples on how to use the methods.

Chapter 1. Introduction

Group contribution approaches have found utility in engineering applications for predicting molecular and mixture properties ranging from physical properties to phase behavior. The value of the approach resides in there being far fewer molecular “groups” than molecules, and so, a database of less than two dozen common molecular groups can be used to predict the properties of thousands of molecules and an infinite variation of mixtures.

For reacting polymer systems, the use of group contribution approaches can be particularly useful because the molecular composition is often known with less certainty than the composition of the groups. To that end, for reacting polymer systems the use of group contribution methods provides a viable approach where the attempt to use molecular properties would be futile.

This chapter presents a brief summary of this thesis project.

Chapter 2 presents original research on group contribution modeling and original experimental data taken on molecules specific to viscosity modeling of urethane systems. A group contribution based model is introduced to accurately predict both pure and mixture viscosities including applications during urethane reactions. It is well known that mixture viscosities can be related to the polymerization extents of reaction. Although some formulation-specific empirical correlations can be used to quantify those correlations, a more-fundamental approach is required for some more-diverse applications. Based on previous work in our polyol group, this research is on the use of a group contribution method to simulate the viscosity of typical urethane foaming reactions.

Chapter 3 summarizes some group contribution approaches to estimate multiple chemical properties in the urethane reaction process. A MATLAB program model based on the simultaneous solution of several group contribution models was developed. This chapter presents viscosity and heat capacity estimation methods as part of the output generated by the model. Experiments of different recipes were conducted to verify and fix those simulation parameters in the urethane reaction process. The goal of this work is to optimize the viscosity simulation and extend its versatility to estimate heat capacity profiles and aqueous solubility profiles. The contents of this chapter are part of the requirements for a CH ENG 8001 topics course with copyright granted for use in a book on thermoset polymerization substantially resulting from that course.

Chapter 4 suggests possible future work and cognition in doing research. More sophisticated functional contribution group approaches may be required to distinguish between different combinations of structures that can occur in some of the more-complex polymer structures. The attaining of a mature cognition in the MS study requires more than coursework and performing of laboratory experiments; it requires a persistent and systematic hard work that proceeds to higher orders of learning that include evaluation and scrutiny of results. In addition, a proper way to master and apply is an indispensable condition to gain knowledge. As a chemical engineering, just-in-time learning is definitely important and is a reasonable approach to efficiently acquire new knowledge.

Chapter 2. Group Contribution Modeling of Viscosity during Urethane Reaction

2.1 Introduction

It is known that the viscosities of mixtures undergoing polymerization can be correlated with the polymerization extents of reaction. Formulation-specific empirical correlations can be used to quantify these correlations; however, for the more-diverse applications of quantifying extents of reaction for entire categories of reactions, a more-fundamental approach is required. This paper is on the use of a group-contribution approach to model the viscosities of typical urethane-forming mixtures.

Zhao et al [1, 2] have initiated a fundamentally-based model for urethane-forming reactions based on the simultaneous solution of over a dozen ordinary differential equations that describe reactions and energy balances. Concentration and temperature profiles can be accurately modeled, and in many applications performances can be accurately extrapolated to (predictively) simulate performances of new formulations[3, 4] as a tool in new formulation development.

The extension of the modeling to include viscosity profiles is a critical step toward the broader objective of being able to simulate urethane foam-forming processes. The proper timing of viscosity increase with eventual setting of the resin is critical for the stabilizing of the gas cells/bubbles that convert a resin to a foam.

The main variables that influence mixture viscosities are temperature, mole fractions of the components, and the viscosities of the pure components. During thermoset polymerization, the system contains reaction intermediates and products with a wide

range of molecular weights and structures. For such a system it would be an overwhelming task to measure viscosities of all intermediates toward the purpose of estimating mixture viscosities during reaction. However, a group contribution approach to viscosity modeling provides a viable approach to estimate the viscosities of intermediates and the mixtures of these intermediates.

Group contribution models are particularly appropriate for polymerizing systems because of limited number of different “groups” that are present due to the limited number of different monomers used in any formulation—typically two to four monomers for a urethane formulation.

Estimation methods for liquid viscosity often employ structure-sensitive parameters which are valid only for certain homologous series or are found from group contributions.[5] For many urethane recipes the materials have complex structures and are outside the range of existing data or empirical equations for estimating liquid viscosity. And so, the work of this paper was undertaken to build upon existing methods and make them more accurate for urethane systems.

Orrick and Erbar[5] proposed a method for estimating liquid viscosity from the structure of molecule starting with the equation 1 reliance on temperature, density, and molecular weight.

$$\ln\left[\frac{\eta_L}{\rho_L M}\right] = A + \left(\frac{B}{T}\right) \quad (1)$$

where η_L is liquid viscosity in cP, ρ_L is the density at 20°C in g/cm³, M is molecular weight and T is absolute temperature in K.

The parameters A and B are estimated using group contribution according to equations (2) and (3).

$$A = \sum n_i A_i \quad (2)$$

$$B = \sum n_i B_i \quad (3)$$

where n_i is the number of groups for each chemical structure, A_i and B_i are the group contributions to A and B respectively.

Values of group contribution parameters A_i and B_i based on the Orrick and Erbar Equation were obtained after testing 188 organic liquids with an average deviation of 15% [5]. Jhunjhunwala et al. [6] provided methods to increase the accuracy with which the pure component viscosities could be used to estimate mixture viscosities.

Jhunjhunwala et al. [6] presented an Enskog-Thorne based model for estimating viscosities of simple liquid mixtures and reported very good agreement with experimental data in the case of argon-krypton system. Application of the significant liquid structure theory to the binary mixtures of carbontetrachloride with acetone, benzene, chloroform and cyclohexane and acetone with benzene by Singh and Sinha [7] provided estimated viscosities in good agreement with the experimental values. Dizechi and Marschall [8] obtained a modified version of McAllister's equation for liquid mixtures with the temperature dependence. The equation correlates the viscosity data of 41 binary and 6 ternary mixtures as well. A survey of several equations for the estimation of liquid mixture viscosities by Irving [9] revealed only a few that do not contain the adjustable parameters. However, these equations were found to be applicable primarily to the components of similar nature with comparable viscosities. From a later study on the

evaluation of various mixing rules[10], Irving recommended the one-constant Grunberg-Nissan[11] model for liquid mixtures.

Based on these pure viscosities the Grunberg-Nissan method can be used to estimate mixture viscosities. The calculation of the low-temperature liquid viscosity for a multi-component system using this approach is summarized by equation 4:

$$\ln\eta_m = \sum_i x_i \ln\eta_i + \frac{1}{2} \sum_{i \neq j} \sum x_i x_j G_{ij} \quad (4)$$

where η_m is the viscosity of the mixture, η_i is the viscosity of component i , x_i is the mole fraction of component i in the mixture and G_{ij} is the Gibbs free energy which depends on temperature as well as the composition, and $G_{ii} = 0$.

The Isdale et al. Method[12] was used to estimate the Gibbs free energy G_{ij} at 298 K

1. For a binary of i and j , select i by following the priority rule below. (j then becomes the second component.)
 - a. i = an alcohol, if present
 - b. i = an acid, if present
 - c. i = the component with the most carbon atoms
 - d. i = the component with the most hydrogen atoms
 - e. i = the component with the most $-CH_3$ groups

$G_{ij} = 0$ if none of these rules establish a priority.
2. Once the decision has been made which component is i and which is j , calculate $\sum \Delta$ for i and j from the group contribution equation 5.

Δ is a parameter that describes the energy property of materials based on group contributions. The subtraction result of two components shows the excess Gibbs energy. In this way it is easier and more efficient to know some chemical properties of some components and their mixtures. And also this predictable method provides very sufficiently good estimation for materials with known structures.

$$\Delta = \sum n_k \Delta_k \quad (5)$$

where n_k is the number of groups in i or j for each chemical structure.

3. Determine the parameter W from equation 6. (If either i or j contains atoms other than carbon and hydrogen, set $W = 0$ and go to the 4th step.) Let the number of

carbon atoms in i be N_i and that j be N_j . W is the correction parameter of energy between i and j .

$$W = \frac{(0.3161)(N_i - N_j)^2}{N_i + N_j} - (0.1188)(N_i - N_j) \quad (6)$$

4. Calculate G_{ij} from equation 7.

$$G_{ij} = \Delta_i - \Delta_j + W \quad (7)$$

G_{ij} is sometimes a function of temperature. However, existing data suggest that, for alkane-alkane solutions or for mixtures of an associated component with an unassociated one, G_{ij} is independent of temperature. However, for mixture of nonassociated components (but not of only alkanes) or for mixtures of associating compounds, G_{ij} is a mild function of temperature. And Isdale et al.[12] suggest for these latter two cases where as summarized by equation 8:

$$G_{ij}(T) = 1 - [1 - G_{ij}(298)] \frac{573 - T}{275} \quad (8)$$

where T is in kelvins.

2.2 Experimental Methods

2.2.1 Experimental Design

Viscosities were measured for a series of polyols, isocyanates, reaction intermediates, and mixtures as consistent with rigid urethane recipes and of molecular weights ranging from 266 to 730. Single component and binary mixture viscosities were measured under shear at temperatures from 20 to 80°C. A Cole-Parmer® Basic Viscometer and a Precision® 280 Series Water Bath were used to measure viscosities at a spin rate of 2.5 to 100 rpm with spindles of L1 to L4 which depends on viscosity range.

2.2.2 Mixture Preparation and Data Collection

The following steps were used to measure viscosities:

1. Pre-weighed polyols or isocyanate were added into a transparent bottle with lid. For mixtures they were well mixed and kept still for a day to degas.
2. Samples were taken into a water bath at the designed temperature for 20 min to ensure it at the steady state.
3. The spindle was then placed in the container and allowed to equilibrate to the temperature for 5 minutes.
4. Viscosity was measured for 5 minutes each time. Measurements at different temperatures were attained by using the water bath.

Binary systems were evaluated at mole fractions of 0 to 1 with a step change of 0.2.

A high speed mixer was taken into use to ensure a perfect mixture. Since bubbles in liquid will have a great impact on viscosity measurement, a long stewing time was needed.

Since isocyanate would react with all polyols in the designed recipe, mono-functional alcohol was introduced to totally react with isocyanate moieties before measuring viscosities in binary mixtures with polyols. This approach allowed mixtures to be evaluated having the same groups as the isocyanate.

Figure 1 shows the experimental data for viscosities of Poly G76-635 and a viscosity standard under the same condition of 20°C. From this comparison result it can be concluded that the viscosity measured by the COLE-PARMAR viscometer is able to reliably measure the viscosities of the polyols being studied. The standard is D1000 from Paragon Scientific Ltd. with a designated viscosity of 1477 cP at 20°C, and the instrument was calibrated to read 1460 cP. With ordering of molecules due to laminar shear the viscosity attains a steady value after about two minutes, and that is the value used to fit group contribution parameters.

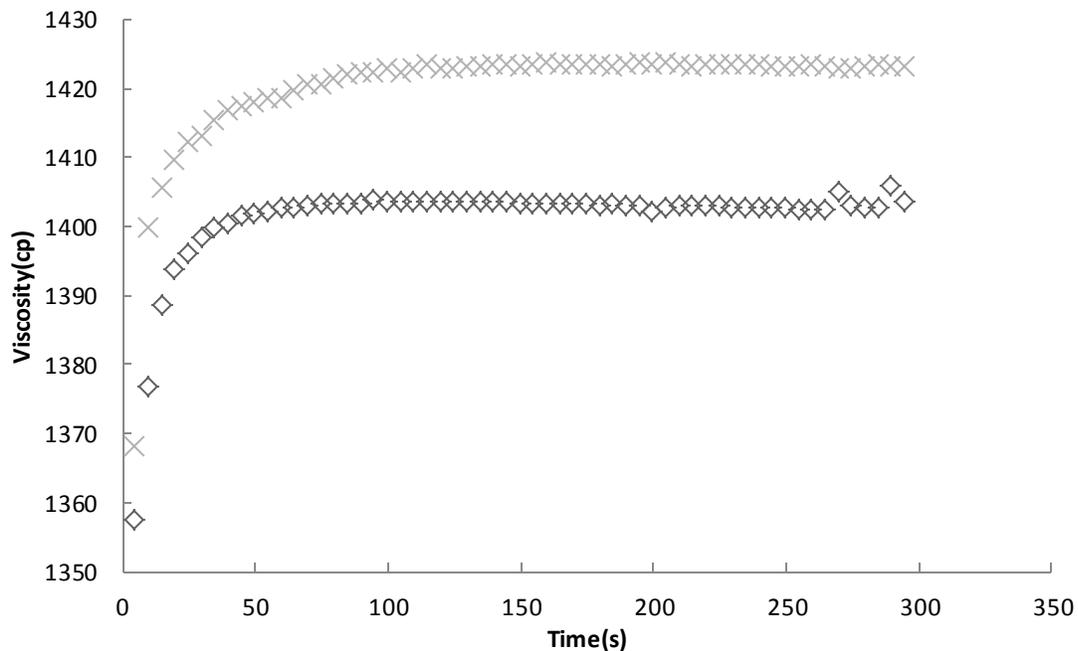


Figure 1. Viscosity of Poly G76-635 & Viscosity Standard at 20°C. Symbol “x” represents experimental data of viscosity standard D1000; symbol “◇” represents experimental data of Poly G76-635.

Example physical properties and values of viscosity as reported in the literature are provided in Table 1 for the polyols and RUBINATE M (Standard Polymeric Methylene Diphenyl Diisocyanate) of this study. Up to a 30% deviation is noted which can be attributed to a number of factors such as slight variations in oligomer molecular weight and the impact that aging can have on some materials (especially water-sensitive PMDI). The results section reports the viscosities over a range of temperatures, mixture viscosities, and modeling both in terms of mixture parameters and group contribution correlations.

Table 1. Pure material information on viscosity, density and molecular weight. [13] [14]

Component	Exp. Viscosity (cP, 25°C)	Lit. Viscosity (cP, 25°C)	MW (Lit.)	MW (Model)	Density (g/cm ³ , 25°C)	Ref.
Voranol 360	3054	3600	728	730	1.09	[15]
Poly G76-635	950	930	265	266	1.08	[16]
Jeffol R-315x	2153	Not available--	534	540	1.07	[1]
Voranol 490	7075	5500	460	456	1.109	[17]
Rubinate M	376	190	340	338	1.23	[18]

2.3 Results and Discussion

Table 2 summarizes data collected on the viscosities as measured for the materials of Table 1 at temperatures from 20 to 80°C. Viscosity measurements were repeated four times under the same condition with the average values being reported. Average errors for the four repeated experimental data are presented in the last column.

Table 2. Experimental data of viscosities of pure components under the impact of temperature.

Voranol 360				
T(°C) Designed	T(°C) Real	Average Viscosity(cP)	Model Viscosity(cP)	Average Error (%)
20	20	4294	5220	20.28
30	29.9	2115	2114	-0.379
40	39.9	697.3	906.8	29.89
50	49.8	464.9	409.9	-11.69
60	59.5	169.5	194.4	14.55
70	69.7	103.1	96.26	-7.093
80	79.6	73.2	49.61	-31.35
Poly G76-635				
T(°C) Designed	T(°C) Real	Average Viscosity(cP)	Model Viscosity(cP)	Average Error (%)
20	20.8	1360	1181	-13.19
30	29.9	724.3	595.7	-17.75
40	39.6	301.7	313.9	4.054
50	49.8	149.2	172.1	15.34
60	59.5	74.40	97.83	31.51
70	69.7	44.66	57.47	28.73
80	79.2	32.15	34.79	8.301
Jeffol R-315x				
T(°C) Designed	T(°C) Real	Average Viscosity(cP)	Model Viscosity(cP)	Average Error (%)
20	20	2988	2973	-0.516
30	29.9	1365	1425	4.402
40	39.5	668.4	716.3	7.252
50	49.8	289.7	375.7	29.69
60	59.6	159.4	204.8	28.49
70	69.6	88.54	115.7	30.70
80	79.5	67.75	67.47	-0.147
Voranol 490				
T(°C) Designed	T(°C) Real	Average Viscosity(cP)	Model Viscosity(cP)	Average Error (%)
20	20.4	11329	11284	-0.401
30	29.9	4645	4785	3.014
40	39.8	2038	2143	5.189
50	49.6	861.5	1009	17.12
60	59.8	379.6	497	30.93

70	69.7	190.2	255.1	34.14
80	79.7	136.2	136	-0.105
Rubinate M				
T(°C) Designed	T(°C) Real	Average Viscosity(cP)	Model Viscosity(cP)	Average Error (%)
20	20.0	465.1	465.4	0.074
30	30.0	189.6	254.4	34.21
40	39.9	102.8	144.6	40.56
50	49.7	56.14	85.05	51.50
60	60.0	37.41	51.66	38.11
70	70.0	28.74	32.31	12.42
80	80.0	20.73	20.75	0.083

Group contribution parameters of A_i and B_i [5] were adjusted to minimize the error for the model estimates. Optimized values of A_i and B_i are reported in Table 3 and are compared to values as previously reported in literature. The viscosities follow anticipated trends with a steady decrease in viscosity with increasing temperature (see Figure 2). The data fit the Orrick and Erbar[5] Equation (Equation 1) with good correlation.

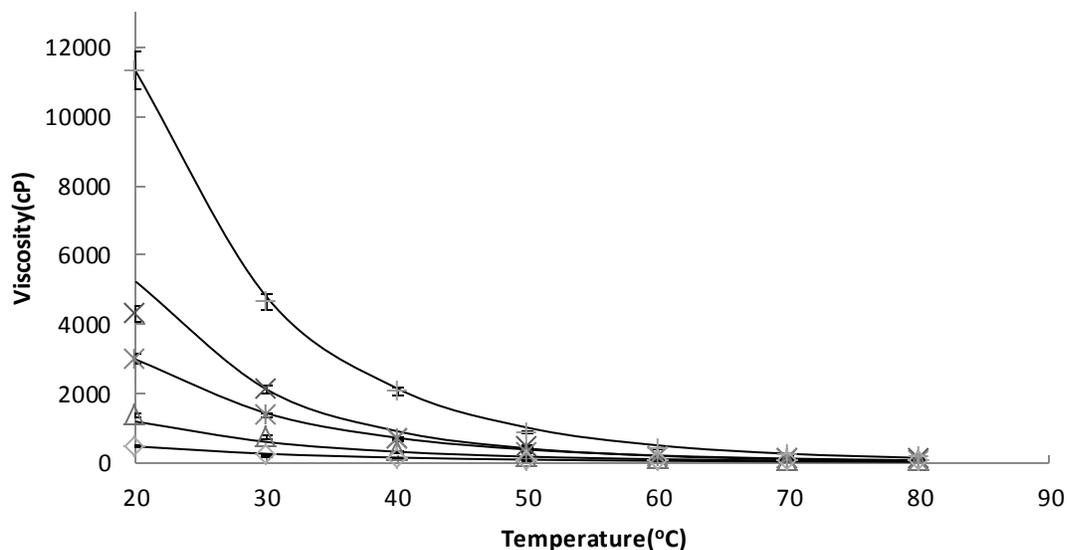


Figure 2. Temperature impact on all pure components. Symbol “+” represents experimental data of Voranol 490, symbol “x” represents Jeffol Voranol 360 case, symbol “Ж” represents Jeffol R-315x case, symbol “Δ” represent Poly G76-635 case and symbol “◇” represent Rubinate M case. These solid lines represent modeling results for each single material respectively.

The process used to optimize the group contribution parameters of Table 3 included retaining of literature values for most groups and limiting the variation of the Carbon Atoms term to less than about 10% of what was previously reported. This was done because previous compilations included a wider range of hydrocarbon materials. Revising of parameters was limited to those that were prevalent in the polyol and isocyanate monomers. The Carbon Atoms are only those carbon atoms not accounted for by other groups.

The ether group with inclusion of carbons, C-O-C, was introduced rather than the using only the ether group’s oxygen, -O-. This is because the impact of the ether group’s oxygen on viscosity extends to the neighboring carbon groups; these carbons behaved differently than those lumped into the Carbon Atoms term. Attempts to optimize with the

-O- ether group designation resulted in the need to significantly revise the Carbon Atoms' parameter values which did not extrapolate well.

Table 3. Orrick and Erbar Group Contributions for A and B in Equation (2) and (3).[19]

Groups	$A_i(\text{Lit.})$	$A_i(\text{Revised})$	$B_i(\text{Lit.})$	$B_i(\text{Revised})$
Carbon Atoms (n excluding those present in the group shown below)	$-(6.95+0.21n)$	$-(6.53+0.21n)$	$275+99n$	$263+88n$
-CH<	-0.15	--	35	--
>C<	-1.20	--	400	--
Double bond	0.24	--	-90	--
Five Membered Ring	0.10	--	32	--
Six Membered Ring	-0.45	--	250	--
Aromatic Ring	0	--	20	--
Ortho Substitution	-0.12	--	100	--
Meta Substitution	0.05	--	-34	--
Para Substitution	-0.01	--	-5	--
Chlorine	-0.61	--	220	--
Bromine	-1.25	--	365	--
Iodine	-1.75	--	400	--
-OH	-3.00	-2.14	1600	1218
-COO-	-1.00	--	420	--
-O-	-0.38	--	140	--
-C=O-	-0.50	--	350	--
-COOH	-0.90	--	770	--
-N=C=O	--	-4.83	--	2176
C-O-C	--	-0.73	--	210
Sugar Ring	--	0.83	--	-1408

Table 4. Numbers of groups in each single component and calculated molecular weight.

Groups	MW_i	Voranol 360	Poly G76-635	Jeffol R-315x	Voranol 490	Rubinate M	EG	DEG	TEG	n- Penpane	n- Decane	n- Dodecane
C	12*	9	6	13	5	1	2	4	6	5	10	12
Aromatic Ring	78					2						
Ortho Substitution	--					2						
-OH	17	5	3	3	6		2	2	2			
-O-	16							1	2			
-N=C=O	42					2						
C-O-C	40*	9	3	7	4	2						
Sugar Ring	81	1			1	2						
	MW	730	266	540	456	338	62	106	150	72	142	180
	C : O	7:3	2:1	27:10	2:1	19:4	2:2	4:3	6:4	--	--	--
	A	-25.40	-19.34	-20.71	-22.87	-18.09	-11.22	-11.95	-12.68	-7.56	-8.59	-9.00
	B	7885	6076	6526	7616	5362	2875	3085	3294	702	1141	1316

*The value 12 or 40 of molecular weight of carbon atom here excludes the attached hydrogen atoms, but in the total molecular weight (MW) those hydrogen atoms are included.

Table 4 contains an extended list of compounds for which model values of viscosity are compared to either newly-collected data or data reported in literature. This table summarizes the A_i and B_i parameters used to represent the molecules, provides the molecular weights as estimated by the sum of the parameters, and provides the C:O ratio as estimated by the sum of the parameters. For the oligomers the molecular weights are within about 3% of reported values and the C:O ratios are consistent with the monomers used to make the oligomers.

Excess Gibbs energies, G_{ij} , for several chemical structures for at 25°C from the Isdale et al. method were summarized in Table.5. These values were used to calculate the binary interaction terms as reported in Table 6 using Equation7 at 25°C. Equation 8 was used to estimate values of the binary interaction parameters at different temperatures and as reported in Table 7.

Table 5. Values of group contributions for G_{ij} at 25°C.[12]

Groups	Δ_i	Remarks
-CH ₃	-0.100	
>CH ₂	0.096	
>CH-	0.204	
>C<	0.433	
Benzene ring	0.766	
Substitutions: Ortho	0.174	
Meta	—	
Para	0.154	
Cyclohexane ring	0.416	
-OH	0.887	Methanol
	-0.023	Ethanol
	-0.443	Higher aliphatic alcohols
>C=O	1.046	Ketones
-Cl	$0.653-0.161N_{cl}$	
-Br	-0.116	
-COOH		Acid with:
	$-0.411+0.06074N_c$	Nonassociated liquid
	1.130	Ketones
	0.167	Formic acid with ketones
-O-*	-0.327	Assumption
-N=C=O*	-1.252	Assumption
Sugar Ring*	1.684	Assumption
Urethane Group*		
-N(H)-C(O)-*	-1.671	Assumption

N_{cl} = number of chlorine atoms in the molecule

N_c = total number of carbon atoms in the binary set

*Values not from literature reference. Values optimized from this work.

Table 6. Parameters in the G_{ij} for all binary systems.

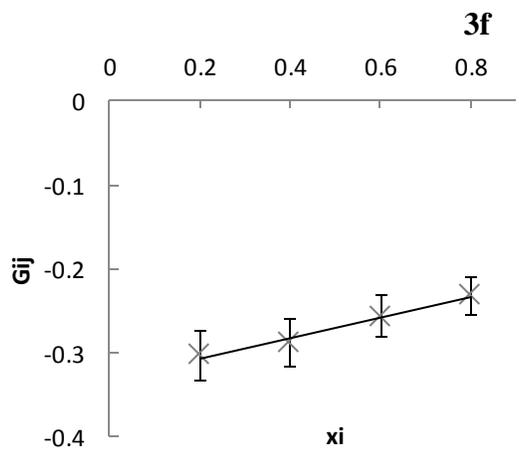
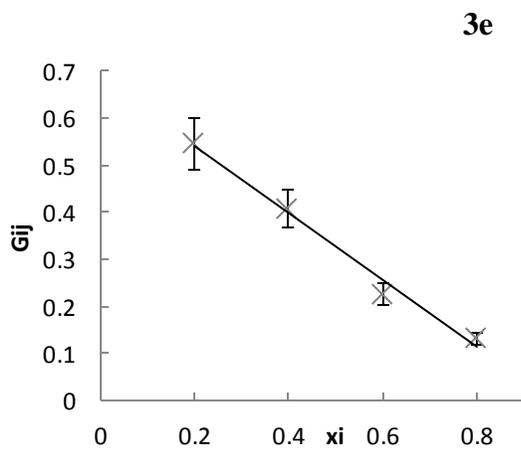
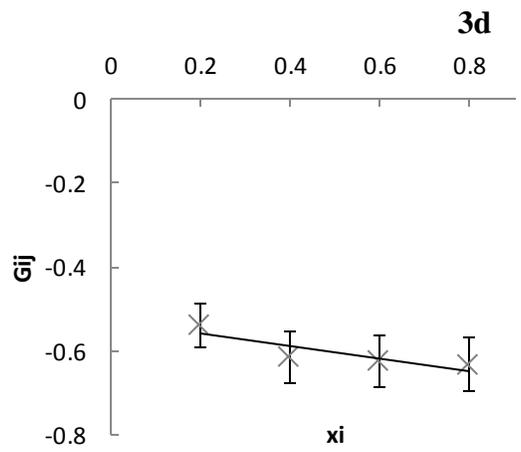
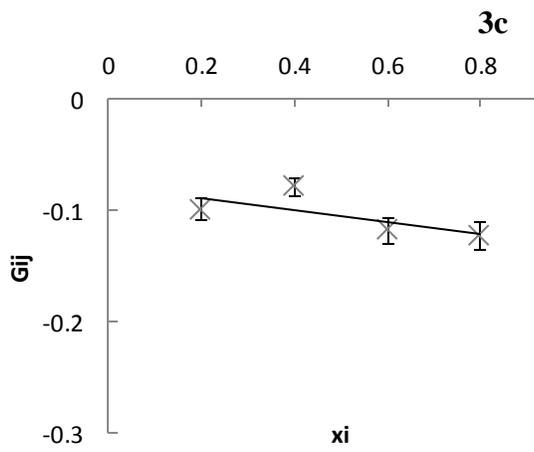
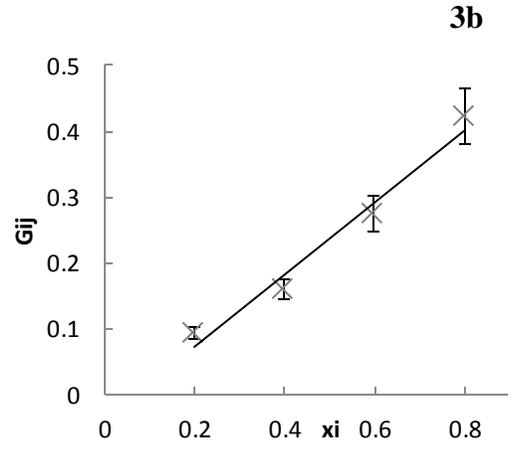
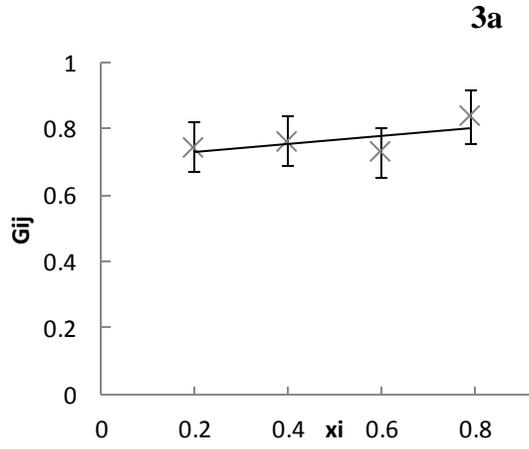
Binary System ($i + j$)	$\sum \Delta_i n_i$	$\sum \Delta_j n_j$	W	G_{ij} (298K)
Voranol 360 + Poly G76-635	-1.388	-1.227	0	-0.161
Jeffol R-315x + Poly G76-635	-1.535	-1.227	0	-0.309
Voranol 360 + Jeffol R-315x	-1.388	-1.535	0	0.147
Voranol 360 + Voranol 490	-1.388	-1.087	0	-0.301
Voranol 490 + Poly G76-635	-1.087	-1.227	0	0.140
Jeffol R-315x + Voranol 490	-1.535	-1.087	0	-0.448
Voranol 360 + Rubinate M	-1.388	-0.590	0	-0.798
Poly G76-635 + Rubinate M	-1.227	-0.590	0	-0.637
Jeffol R-315x + Rubinate M	-1.535	-0.590	0	-0.945
Voranol 490 + Rubinate M	-1.087	-0.590	0	-0.497

Table 7. Values of G_{ij} at different temperatures from Equation 8.

G_{ij}					
Binary System ($i+j$)	Voranol 360 Poly G76-635	Jeffol R-315x Poly G76-635	Voranol 360 Jeffol R-315x	Voranol 360 Voranol 490	Voranol 490 Poly G76-635
Temp.(°C)					
20	-0.182	-0.333	0.132	-0.325	0.124
30	-0.140	-0.285	0.163	-0.277	0.155
40	-0.098	-0.237	0.194	-0.230	0.187
50	-0.056	-0.190	0.225	-0.183	0.218
60	-0.014	-0.142	0.256	-0.135	0.249
70	0.029	-0.095	0.287	-0.088	0.280
80	0.071	-0.047	0.318	-0.041	0.312

G_{ij}					
Binary System ($i+j$)	Jeffol R-315x Voranol 490	Voranol 360 Rubinate M	Poly G76-635 Rubinate M	Jeffol R-315x Rubinate M	Voranol 490 Rubinate M
Temp.(°C)					
20	-0.475	-0.831	-0.666	-0.981	-0.524
30	-0.422	-0.765	-0.607	-0.910	-0.470
40	-0.369	-0.700	-0.547	-0.839	-0.415
50	-0.317	-0.635	-0.488	-0.769	-0.361
60	-0.264	-0.569	-0.428	-0.698	-0.307
70	-0.211	-0.504	-0.369	-0.627	-0.252
80	-0.159	-0.438	-0.309	-0.556	-0.198

The model values of G_{ij} (lines) superimposed over the experimental data in Figure 3. Experimental values of G_{ij} were determined by recalculating equation 4 using these experimental mixture viscosity data gained at different mole fractions. As can be seen by the plots, modeling G_{ij} as a linear function of mole fraction falls within the standard deviations of the data. Only the Voranol 360/Poly G76-635, Jeffol R-315x/Poly G76-635 and Voranol 360/Rubinate M systems exhibited positive deviations in the mixtures. These positive deviations are likely due to the components i in the binary systems are likely to be the solvent than the other one which means their solubility is greater.



3g

3h

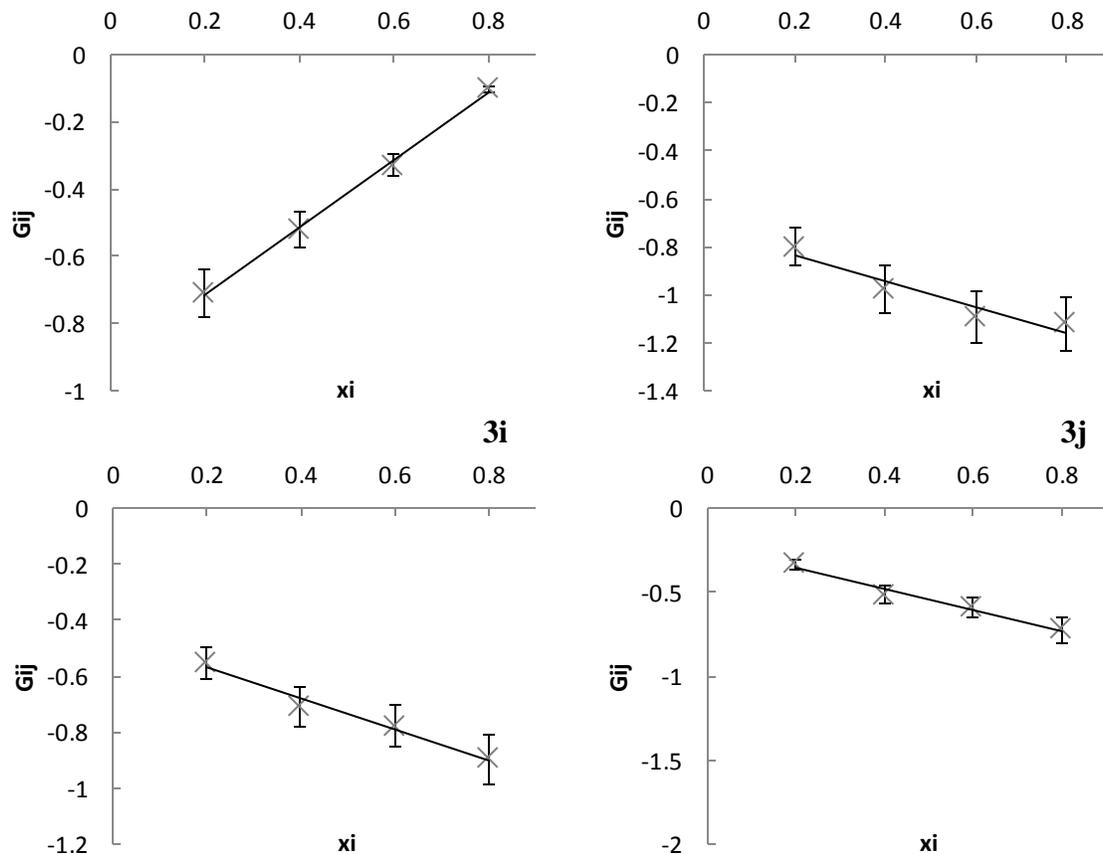
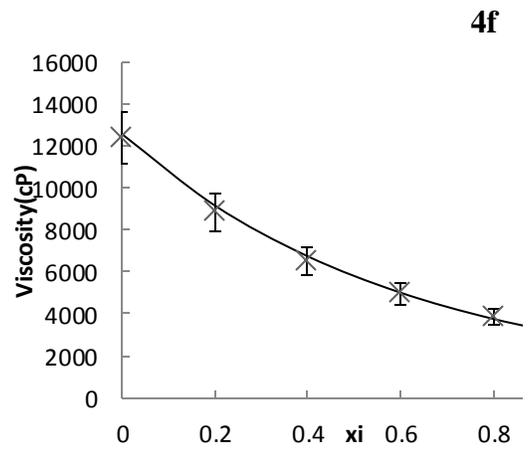
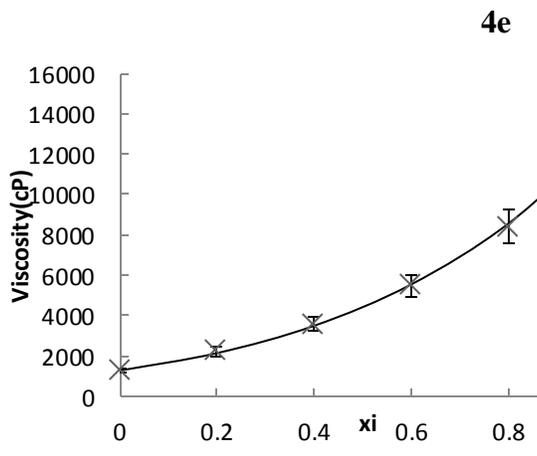
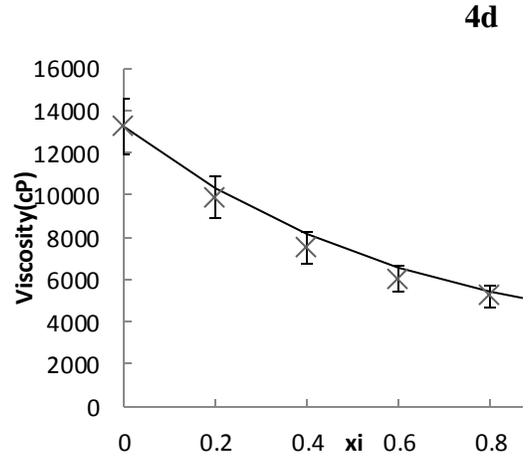
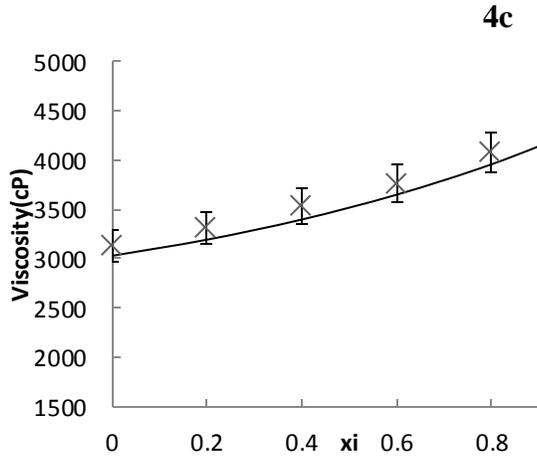
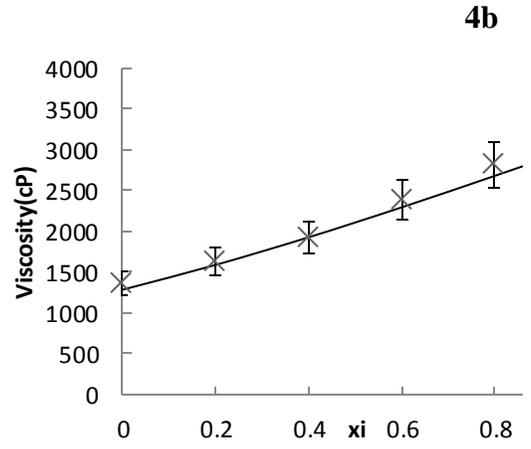
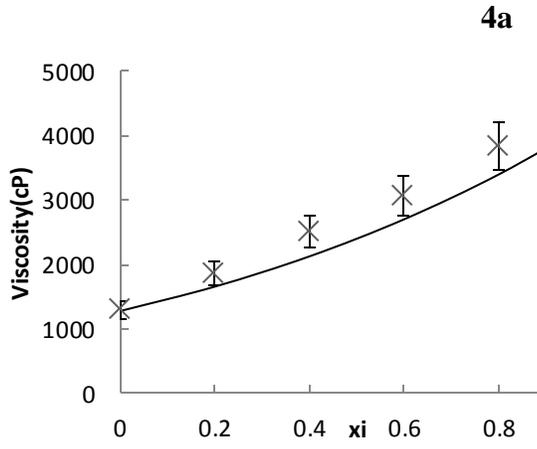
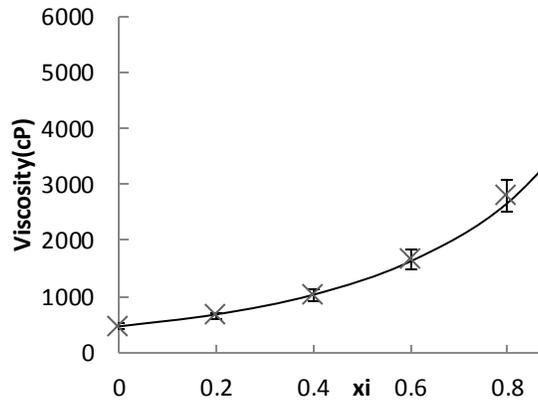


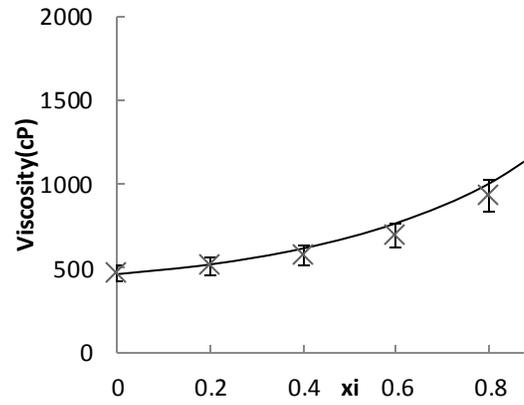
Figure 3. Impact of mole fraction on G_{ij} at 20°C for the following binary systems: a) Voranol 360 + Poly G76-635, b) Jeffol R-315x + Poly G76-635, c) Voranol 360 + Jeffol R-315x, d) Voranol 360 + Voranol 490, e) Voranol 490 + Poly G76-635, f) Jeffol R-315x + Voranol 490, g) Voranol 360 + Rubinate M, h) Poly G76-635 + Rubinate M, i) Jeffol R-315x + Rubinate M, j) Voranol 490 + Rubinate M.

Estimates of mixture viscosities using the linear model approximations for the binary interaction parameters, G_{ij} , are provided by Figure 4. The model fits are within the standard deviations of the data. All the concave-down curves are likely due to that the components with low viscosity are more soluble than the other ones.





4i



4j

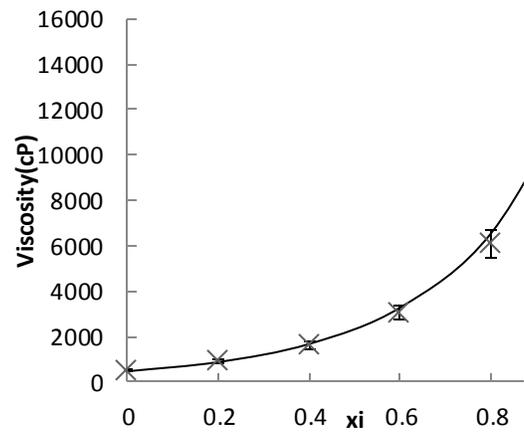
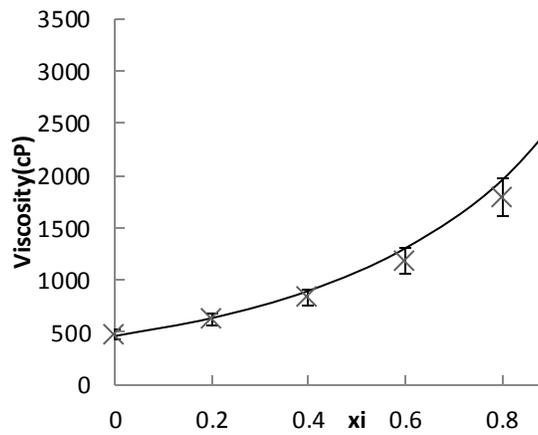
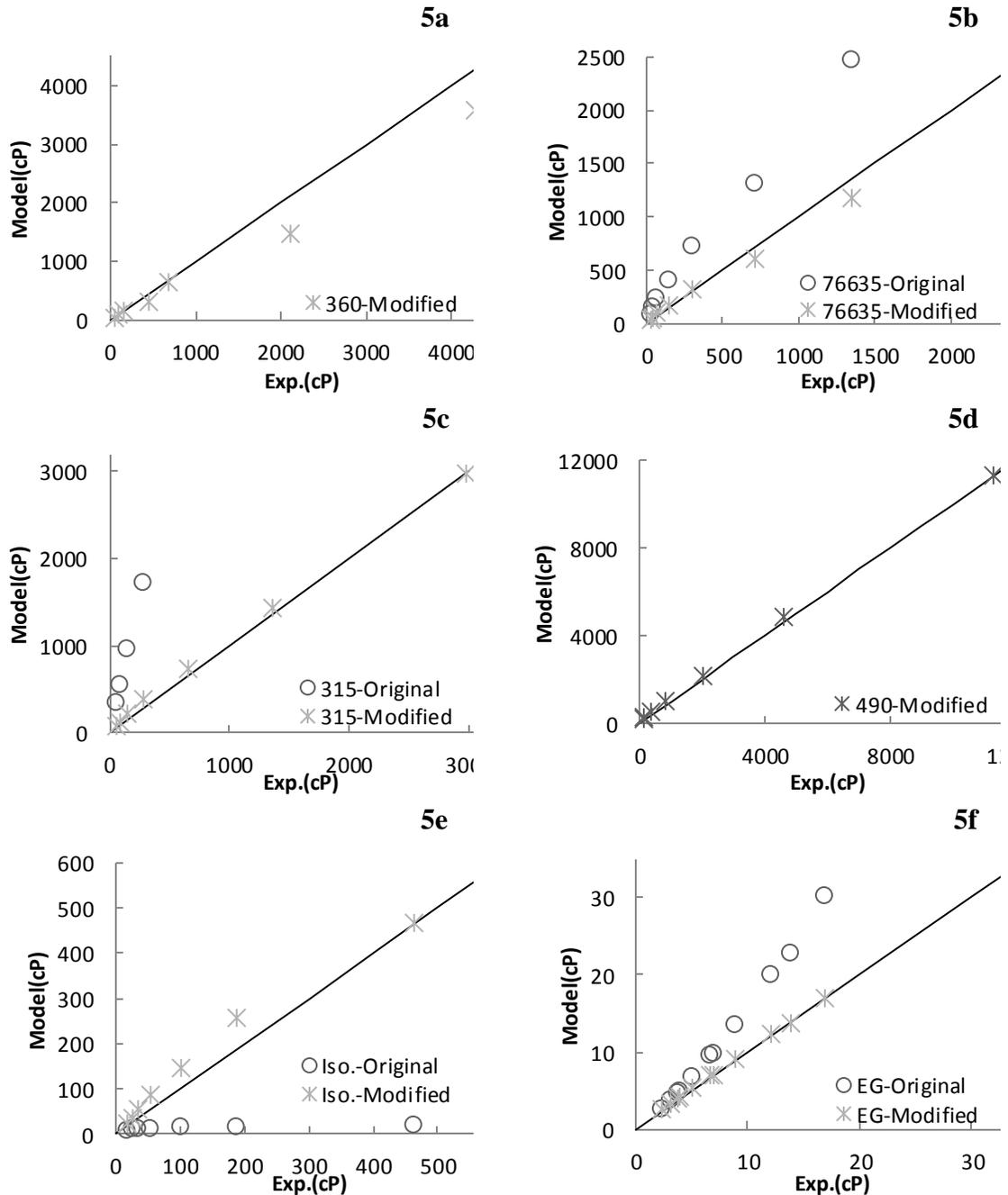


Figure 4. Impact of mole fraction on mixture viscosity at 20°C for the following binary systems: a) Voranol 360 + Poly G76-635, b) Jeffol R-315x + Poly G76-635, c) Voranol 360 + Jeffol R-315x, d) Voranol 360 + Voranol 490, e) Voranol 490 + Poly G76-635, f) Jeffol R-315x + Voranol 490, g) Voranol 360 + Rubinate M, h) Poly G76-635 + Rubinate M, i) Jeffol R-315x + Rubinate M, j) Voranol 490 + Rubinate M.

The images of Figure 5 compare the experimental values of viscosity to those predicted by the group contribution approach before and after modification based on data of this paper. The modified values consistently provided a better fit to the data. For Voranol 360 and Voranol 490, the fit to the original parameters were not included as their deviation was so significant that the presentation was not of value.



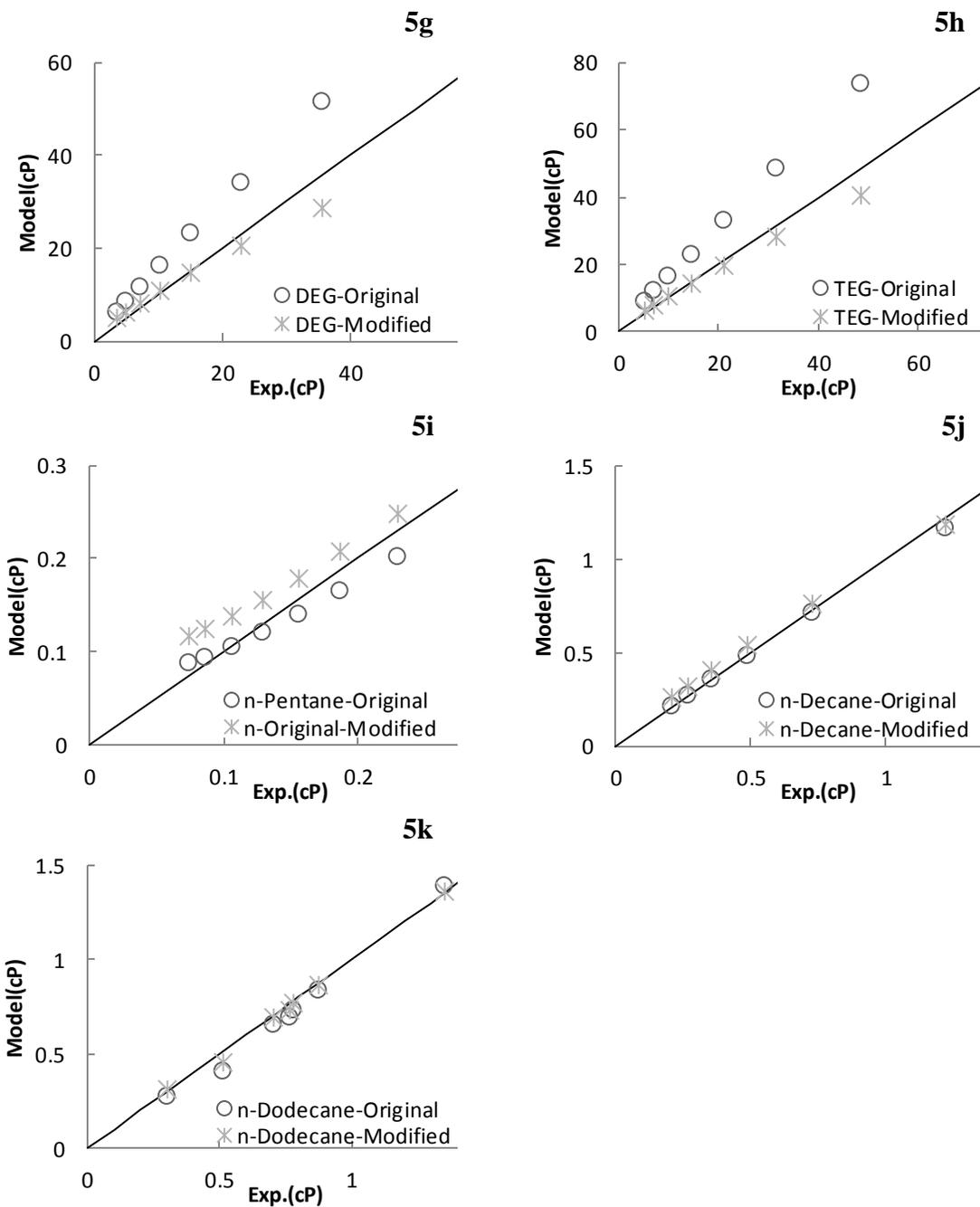


Figure 5. Comparison of original Orrick and Erbar Group Contributions method with revised ones for the following single materials: a) Voranol 360, b) Poly G76-635, c) Jeffol R-315x, d) Voranol 490, e) Rubinate M, f) Ethylene Glycol, g) Diethylene Glycol, h) Triethylene Glycol, i) n-Pentane, j) n-Decane, k) n-Dodecane. The circle markers represent the original model viscosities; the star ones represent the revised mixture model viscosities. The x axis exhibits experimental viscosity data and y axis exhibits modeling data.

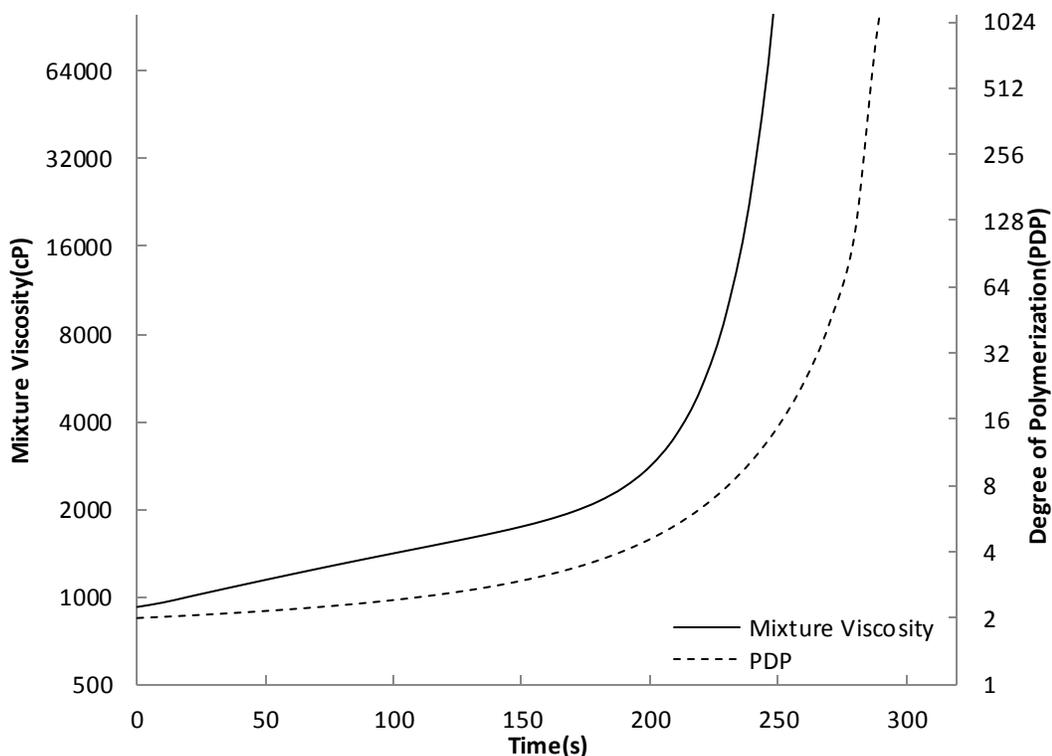


Figure 6. Sample plot for reacting system. The solid line represents the mixture viscosity change during reaction. The dash line represents the degree of polymerization change during reaction. This is a standard sample gel recipe with three polyols (Voranol 360, Poly G76-635 and Jeffol R-315x) and isocyanate also with both Cat5 and Cat8. Both y axes are in logarithmic form.

Using the group contribution approach, viscosities can be calculated for the sequence of oligomers and polymers formed in urethane polymerization reactions. But more efficiently, a reacting system can be considered as a mixture of monomers and a polymer where the polymer is characterized as having an average degree of polymerization and comprised of the monomers that reacted to form the polymer. Based on the viscosities characterizing each component, mixture rules can then be used to calculate the mixture viscosity. Figure 6 provides example profiles for degrees of polymerization and viscosity for the system of Zhao and Suppes[20].

As described in the introduction, this viscosity information is needed for more-ambitious modeling efforts intended to simulate foam formation including the estimation

of physical properties for successful formation of foam as well as the collapse of unsuccessful formulations. In addition, viscosity profiles of reacting gels can be used to back-calculate extents of reaction, reactivity, and even the functionality of monomers. The functionality of monomers can then be used to estimate molecular weights of monomers with a rigor directly related to how the molecules react. A case can be made that monomer characterization that is directly linked to how the monomer behaves in a reacting system is one of the most valuable characterizations that can be made.

The example provided by Figure 6 is based on the use of an average degree of polymerization. As the polydispersity of a reacting system increases so does the error of representing the system by a single degree of polymerization. To this end, it must be noted that this approach is an entry point to a methodology that is less than perfect and comprehensive at this entry point, but is capable of evolving.

2.4 Conclusion

The group contribution approach of Orrick and Erbar for estimating viscosities was modified to include the addition of three and adjustment of three group contribution parameters based on viscosity data collected for several monomers used to form urethanes. The following are concluded:

- The updated predicted performance based on revised group contribution parameters shows a good agreement with the experimental data with model fits within the data's standard deviations.
- The Isdale et al. estimates for excess Gibbs energies, G_{ij} , worked well without modification.
- Addition excess Gibbs energies were estimated for groups specific to the urethane system and not previously reported.
- For mixtures, the mixture's excess Gibbs energies were linear with composition within the standard deviation of the data.

The use of group contribution estimates for viscosity can be particularly useful when simulating polymerization reactions. Useful applications also include using polymer reactivity to estimate extents of reaction and monomer properties, such as functionality, that have a high impact on degree of polymerization.

Chapter 3. Group Contribution Methods Application in Physical Properties

3.1 Introduction

3.1.1 Introduction

Basic Physical properties of the components and their mixtures substantially empower scientists and engineers to practice their professions. However, it is expensive to gain these data via experimental measurements. Even in instances when such data has been previously obtained by other researchers, the time and expense to locate and implement these data can be overwhelming. A predictive method – the group contribution method - is sufficiently accurate for many applications. At the very least, such methods can provide good base case calculations that can be used to make informed decisions.

A group contribution method is used to predict properties of pure components and mixtures by using group or atom properties. In this method, only a few dozens or hundreds of groups instead of thousands or millions of compounds have to be known which dramatically reduces needed data.

The simplest method using group contribution to determine component properties is to sum up all the group contributions. Researchers like Joback and Reid[21], Lydersen[22], Ambrose[23], Klincewicz and Reid[24], Lyman et al.[25] and Horvath[26] have made nice contributions in this additive group contribution method. In this method, properties are assumed to be linear with the number of groups with different groups

having different impacts on the properties. This approach assumes no interactions between the groups and does not account for the possibility of different combinations of the groups within molecules (ie different isomers). Although this method can quickly estimate component properties, it only works well in a limited range and could lead to significant errors outside the limitation.

To overcome these limitations and difficulties of some more complex estimation technique, simple methods are proposed which consider the contributions of interactions between bonding groups instead of the contributions of simple groups, which allow the distinction of a large number of isomers.

Usually, the group contribution method is used to predict chemical properties of a single material, such as viscosity, heat capacity and other thermodynamics. Orrick and Erbar[27] proposed a temperature dependent method to accurately estimate pure viscosity when molecular weight and density are known. For molar heat capacity of an organic liquid component, Missenard[28] developed a functional group method for estimation in the -25°C to 100°C range. Klopman[29] proposed a very stable and accurate model to predict aqueous solubility, which covers every class of organic chemicals and a wide applicability.

In the polyurethane industry, group contribution methods can have an increasingly important role in the understanding and design of chemical processes. Viscosity, heat capacity, and solubility methods would have the most utility for applications on the urethane-forming reactions. This work includes comparisons of experimental and modeling data for molecules of specific interest to the urethane industry.

Typically, liquid viscosity decreases with temperature in a non-linear relation and is not significantly dependent on pressures. However, some experimental data suggest that high pressures do change the liquid viscosities. Such pressures are far greater than those encountered with most commercial processes. Due to practical purposes, influences of pressure do not take into consideration where in most cases liquids are remaining at atmosphere pressure. The methods presented here on viscosity, heat capacity, and solubility do not consider the impact of pressure.

3.1.2 Molecular Groups and Their Contributions

Values of group contributions of viscosity, molar heat capacity and thermodynamics are presented in Table 8. While the groups are not comprehensive of common organic chemistries, they are can be used to describe the components of most polyurethane foaming recipes.

Table 8. Values of group contributions in Eq (1), (5), (6).

Groups	Viscosity		Heat Capacity		Solubility
	A	B	a	b	C
Carbon Atoms ¹	$-(6.53+0.21n)^*$	$263+88n^*$			
-CH ₃			0.09	39.2	-0.4169
>CH ₂			0.037	27.25	-0.5199
-CH<	-0.15	35	0.041	23.75	-0.3057
>C<	-1.20	400	0.066	8.414	-0.1616
Aromatic Ring	0	20	0.287	160.01	-2.8266
Ortho	-0.12	100	0	0	0
Substitution					
Meta Substitution	0.05	-34	0	0	0
Para Substitution	-0.01	-5	0	0	0
-OH	-2.14*	1218*	0.364	34.5	1.0910
-O-	-0.38	140	0.017	39.25	0.4452
-N=C=O	-4.83	2176	1.195	230.295	-0.3555
C-O-C	-0.73	210			

Sugar Ring	0.42	-1408	0	368.9	-1.0833
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1: n excluding those present in the group shown below

In the viscosity column, the numbers with * are modified specific to data from components of urethane systems as compared to data collected by others for other systems. In addition, some groups shown in Table 8 have not been previously characterized, such as $-N=C=O$, $C-O-C$ and sugar ring.

In Figures 7, 8, and 9 both 2D and 3D molecular structures are shown. In the 3D molecular structures, each color represents a specific molecule, such as the red represents oxygen atom and the white is hydrogen atom in figure 8. The following example provides calculations for these molecules.

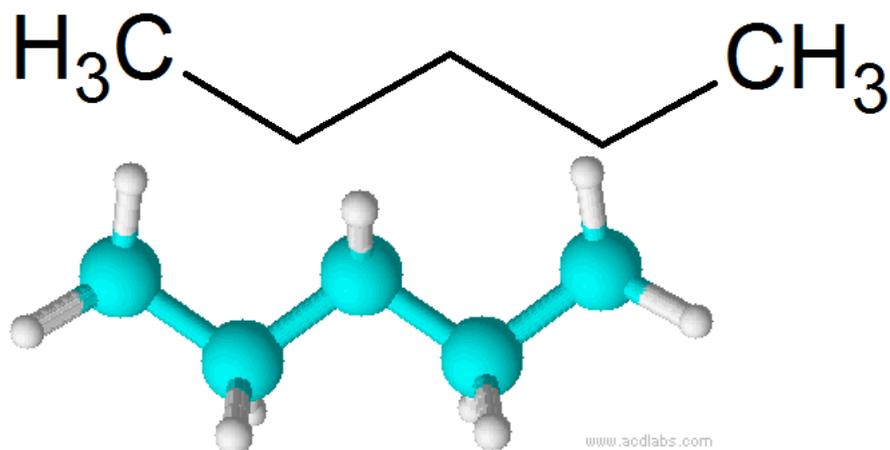


Figure 7. Example polymer structures of n-pentane generated by Gaussian computer program. White bonds represent atoms of hydrogen; blue bonds represent atoms of carbon.

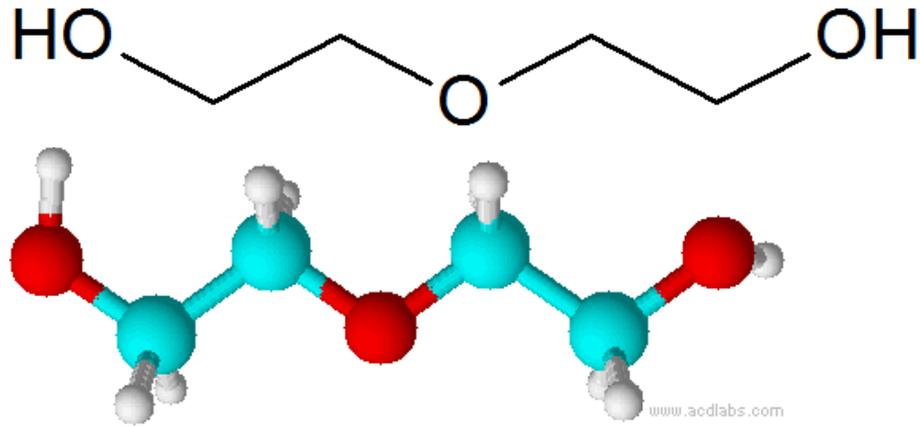


Figure 8. Example polymer structures of Diethylene Glycol. White bonds represent atoms of hydrogen; blue bonds represent atoms of carbon; Red bonds represent atoms of oxygen.

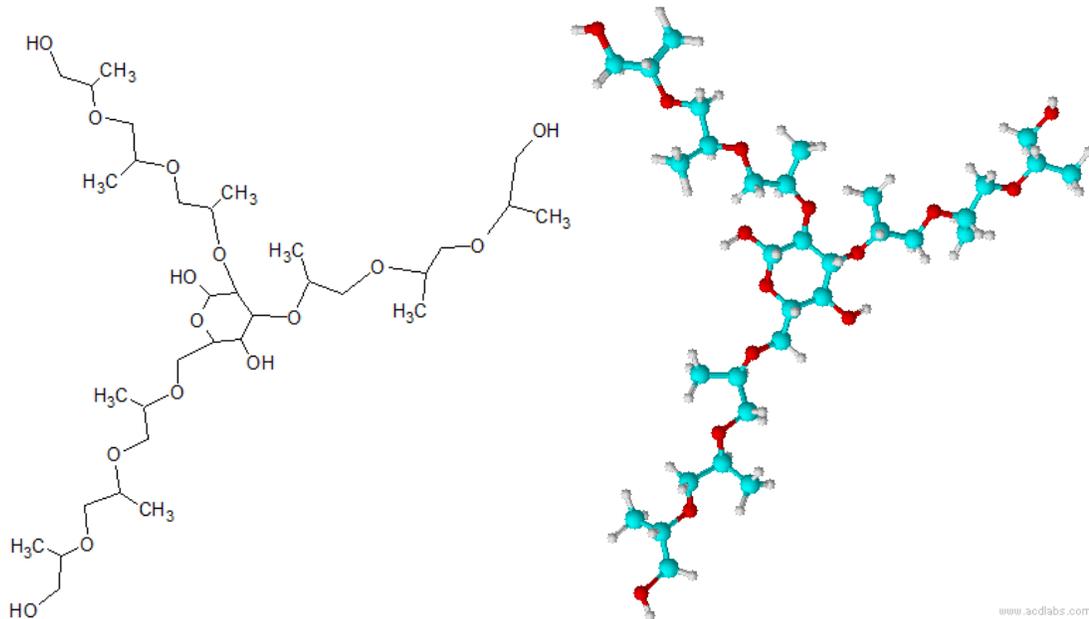


Figure 9. Example polymer structures of Voranol 360. White bonds represent atoms of hydrogen; blue bonds represent atoms of carbon; Red bonds represent atoms of oxygen.

Example Calculation

The following is an example calculation of the heat capacity and viscosity (25°C) for diethylene glycol (see Figure 2):

For diethylene glycol, $\text{HO}(\text{CH}_2)_2\text{O}(\text{CH}_2)_2\text{OH}$, $n=2$, the number of $-\text{OH}$ is 2, $-\text{C}-\text{O}-\text{C}-$ is 1. From Table 8, viscosity,

$$A = -6.53 - (0.21)(2) - (2.14)(2) - (0.73)(1) = -11.96$$

$$B = 263 + (88)(2) + (1218)(2) + (210)(1) = 3085$$

From Dow Chemical Properties[30], at 20°C, $\rho = 1.118 \text{ g/cm}^3$, molecular weight is 106.12. Then, with Eq. (1),

$$\ln \left[\frac{\eta_i}{(1.118)(106.12)} \right] = 11.96 + \left(\frac{3079}{T} \right)$$

At 25°C, where T=298K, the pure viscosity of diethylene glycol,

$$\eta_i = \mathbf{23.77 \text{ cP}}$$

For heat capacity of diethylene glycol at 25°C, there are 2 of >CH₂, 2 of -OH and 1 of -O-. From Table 1, heat capacity,

$$Cp = [(0.037)(2) + (0.052)(2) + (0.426)(1)]T + [(27.25)(2) + (33.105)(2) + (2.236)(1)]$$

At 25°C, the heat capacity of diethylene glycol,

$$\mathbf{Cp = 138.05J/(mol \cdot K) = 1.301J/(g \cdot K)}$$

The algorithm of Figure 10 summarizes the approach to calculate liquid viscosities either based on the known molecular structure of a molecule or the repeat units known to be in the polymer. If those components in the mixture react to each other, especially in some reactions that have polymer as the product, the viscosity of the polymer can be calculated by the steps by the right column of the algorithm.

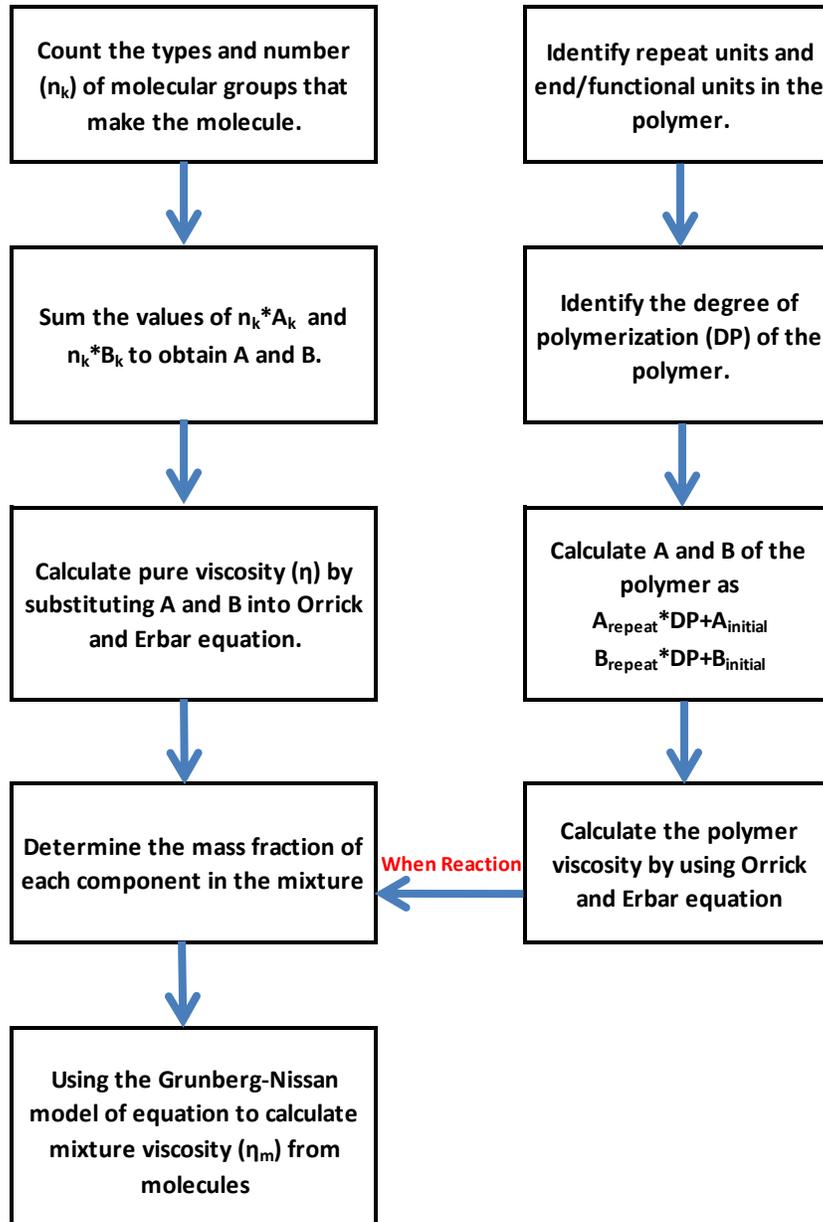


Figure 10. Algorithm 1 summary of group contribution approach mixtures viscosity.

For this algorithm, it is important to get the exact number of groups in molecules. The total contribution of a group in a molecule should be multiplied by its number in this molecule. Mass fraction instead of mole fraction is been used in the mixing rule due to large molecules have greater impact on properties than smaller molecules.

3.2 Different methods showing how to combine groups to form molecules

3.2.1 Viscosity - Orrick and Erbar Method

A group contribution methodology proposed by Orrick and Erbar[27] to estimate pure liquid viscosity is provided by equation 9,

$$\ln \left[\frac{\eta_i}{\rho M} \right] = A + \left(\frac{B}{T} \right) \quad (9)$$

where η is liquid viscosity in cP, ρ is the density at 20°C in g/cm³, M is molecular weight and T is absolute temperature in K, both A and B are group contributions.

The parameters A and B are estimated using group contribution according to equations (10) and (11).

$$A = \sum n_k A_k \quad (10)$$

$$B = \sum n_k B_k \quad (11)$$

where n_k is the number of groups of chemical structure type k , A_k and B_k are the group contributions to A and B respectively.

For liquids whose freezing point is above 20°C, the density of this liquid at its melting point should be used. Values of A and B were obtained after 188 organic liquids test by Orrick and Erbar, with an average deviation of 15%. However, some compounds containing sulfur did not correlate; further study is needed to extend this limitation. Table 8 shows values of A and B in Orrick and Erbar method except as indicated.

3.2.2 Mixture Viscosity - Grunberg-Nissan Model

With pure-component viscosities in hand, the Grunberg-Nissan[31] method can be used to estimate mixture viscosities. The calculation of the low-temperature liquid viscosity for a multi-component system using this approach is summarized by equation (12):

$$\ln\eta_m = \sum_i x_i \ln\eta_i + \frac{1}{2} \sum_{i \neq j} \sum x_i x_j G_{ij} \ln\eta_m \quad (12)$$

where η_m is the viscosity of the mixture in cP, η_i is the viscosity of component i in cP, x_i is the mass fraction of component i in the mixture.

An overall root mean square deviation for the mixtures is 1.6% based on more 2000 experimental mixture data points by Isdale[32].

3.2.3 Heat Capacity - Missenard Method

The Missenard[28] method can be used to estimate heat capacities in a temperature range from -25°C to 100°C. In this method, equation 13 is used to estimate heat capacity of pure-component liquids. Values of some contribution groups a & b are given in Table 8.

$$C_p = \sum_i n_i a_i \cdot T + \sum_i n_i b_i \quad (13)$$

Here, n_i is the number of group of type i , T is the temperature in °C, both a_i and b_i are values of group contributions of group of type i and the C_p here is the molar heat capacity in J/(mol·°C).

In this method, heat capacity is estimated as a linear function of temperature. The Missenard method should not be used for any molecules with double bonds (>C=C<). In

addition, this method is not applicable at reduced temperatures greater than 0.75 (ie, the method is valid for liquids where $T_r < 0.75$).

3.2.4 Solubility - Klopman Method

A reliable and generally applicable aqueous solubility estimation method for organic compounds based on group contribution approach has been developed by Klopman[29]. The aqueous solubility can be calculated by the following equation (14).

$$\log S = C_0 + \sum_{i=1}^N n_i C_i \quad (14)$$

where S is the aqueous solubility in mol/m^3 and C_0 is a constant. In this model, $C_0 = 3.7253$, n_i is the number of groups of type i and C_i is the value of contribution groups of type i in the molecule.

In this method, the effect of interactions between groups is negligible. 483 compounds were studied in this system with a standard deviation of 0.526 in log units. The advantage of this method is its simplicity and wide applicability. However, because of the neglecting of interactions, the effect of interactions between polar functional groups in the aqueous solubility estimation is not explicitly shown in the molecule.

3.3 Simulation of Polymerization

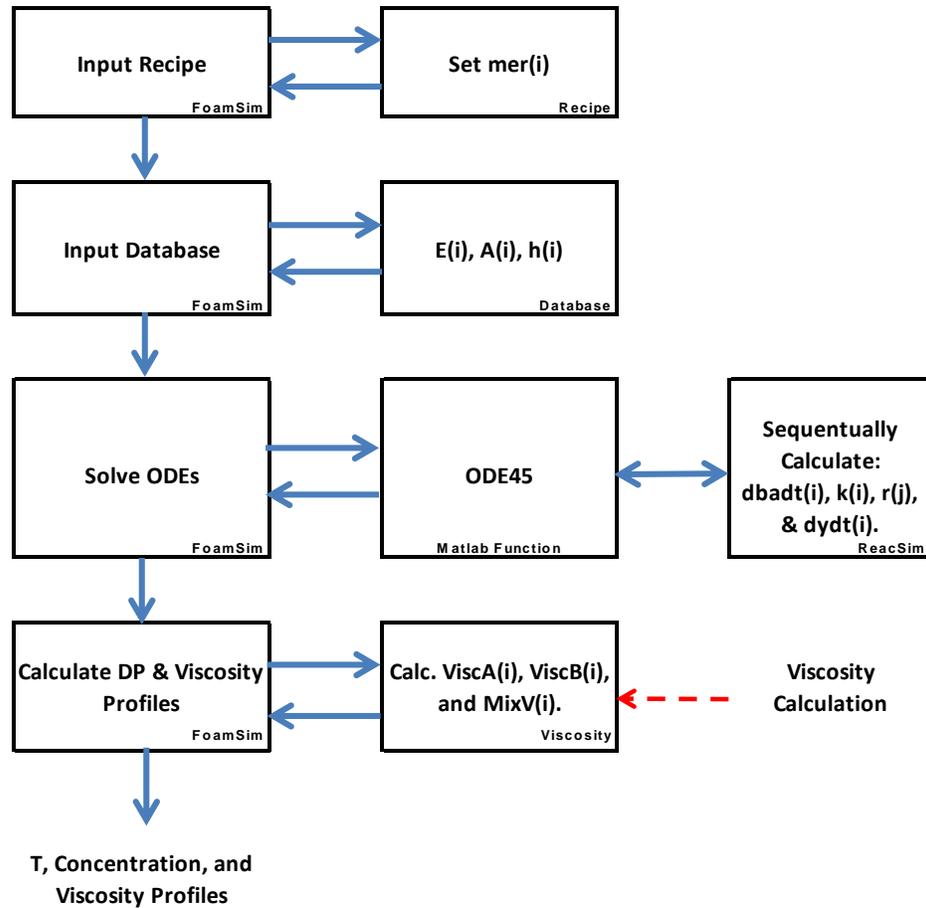


Figure 11. Algorithm 2 summary of group contribution program approach.

During the simulation of urethane-forming processes, heat capacities must be calculated during the reaction simulation. The values of the heat capacities can be impacted by the extent of reaction and the heat capacities are needed to estimate changes in temperature that impact reaction rates.

To a first approximation, reaction rates are assumed to be independent of viscosity. Under this assumption, the viscosity profile (viscosity as a function of temperature) can

be calculated after reaction simulation is used to provide concentration and temperature profiles.

The algorithm of Figure 11 illustrates how the addition of viscosity calculations is added to a simulation program that provides concentration and temperature profiles. For the first step in the Recipe function reactant information should be modified as the recipe. In the second step, based on the input recipe modify kinetic parameters like A, E and h in the Database function. In the fourth step, modify the number of groups of both reactant and polymer molecule in the mixture as well as the excess Gibbs free energy. Both degree of polymerization and viscosity are then calculated through the use of a function called upon as one of the last steps in the procedure.

Table 9. MATLAB Simulation code.

```
clear;clc;close all;
global mer NW0 NCO2 E A h vapH TCPP L6900 cat catsum T0 H0 NBp0 NBS0
NBt0 cp U Uf Toluene ptot Ant_const kmass MWba NBA dp pdp vapHba NBet0
gm g

Recipe
Database

[t,c]=ode45(@ReacSim,[0:10:1000],[mer(4,1);mer(4,2);mer(4,3);mer(4,4);m
er(4,5);mer(4,6);mer(4,7);mer(4,8);mer(4,9);mer(4,10);NBet0;mer(4,1)*m
er(5,1);NBp0;NBS0;NBt0;0;NW0;0;NCO2;0;0;0;0;0;T0;H0;NBA(1);NBA(2);NBA(3)]
);

pdpn=((c(1,1)+c(1,2)+c(1,3)+c(1,4))-(c(:,1)+c(:,2)+c(:,3)+c(:,4)));
pdpd=(c(:,21));
for i=1:101
    pdp(i)=pdpn(i)/pdpd(i);
end
figure
plot(t,pdp)

Viscosity(t,c);

function Viscosity(t,c)
global mer NW0 NCO2 E A h vapH TCPP L6900 cat catsum inert rouinert T0
H0 NBp0 NBS0 NBt0 cp U Uf Toluene ptot Ant_const kmass MWba NBA dp pdp
vapHba NBet0 g gm

MWpro=318.*pdp(:)+421;
```

```

Denpro=1.116;
%1      2      3      4      5      6      7      8      9      10     11     12
AGC=[-0.21 -0.15 -1.20 0 -0.12 0.05 -0.01 -2.14 -0.38 -4.83 -0.73
0.42]; %values of group contributions A of some groups
%carbon -CH< >C< AR Ortho Meta Para -OH -O- -N=C=O C-O-C
SugarRing
BGC=[88 35 400 20 100 -34 -5 1218 140 2176 210 -1408]; %values of group
contributions A of some groups
%iso G76 V360 R315x
Ac=[(-6.53+AGC(1)*1)+AGC(4)*2+AGC(5)*2+AGC(10)*2+AGC(11)*2 (-
6.53+AGC(1)*6)+AGC(8)*3+AGC(11)*3 (-
6.53+AGC(1)*12)+AGC(8)*5+AGC(11)*9+AGC(12)*1 (-
6.53+AGC(1)*13)+AGC(8)*3+AGC(11)*7]; %%Total values of group
contribution to A
Acpro=-0.9.*pdp(:)-21.43; %Total values of polymer group contribution
to A
Bc=[(263+BGC(1)*1)+BGC(4)*2+BGC(5)*2+BGC(10)*2+BGC(11)*2
(263+BGC(1)*6)+BGC(8)*3+BGC(11)*3
(263+BGC(1)*12)+BGC(8)*5+BGC(11)*9+BGC(12)*1
(263+BGC(1)*13)+BGC(8)*3+BGC(11)*7]; %Total values of group
contribution to B
Bcpro=500.*pdp(:)+7085; %Total values of polymer group contribution to
B

W=0; %parameter in Isdale et.al Method
del=[-1.388 -1.227 -1.535 -1.087 -0.590]; %Values of delta
delpro=-8.*pdp(:);
Gij=[del(1)-del(2)+W del(3)-del(2)+W del(1)-del(3)+W del(1)-del(4)+W
del(4)-del(2)+W del(3)-del(4)+W del(1)-del(5)+W del(2)-del(5)+W del(3)-
del(5)+W del(4)-del(5)+W ]; %%Gibbs free energy at 298K
% 360+635 315+635 360+315 360+490 490+635
315+490
% 360+ISO 635+ISO 315+iso 490+iso 360+pro
635+pro
% 315+pro 490+pro iso+pro
Gijpro=[del(1)-delpro+W del(2)-delpro+W del(3)-delpro+W del(4)-delpro+W
del(5)-delpro+W];
% iso M5020 V360 R315x polymer

g=[mer(10,1)*mer(3,1)*exp(Ac(1)+Bc(1)./c(:,24))
mer(10,2)*mer(3,2)*exp(Ac(2)+Bc(2)./c(:,24))
mer(10,3)*mer(3,3)*exp(Ac(3)+Bc(3)./c(:,24))
mer(10,4)*mer(3,4)*exp(Ac(4)+Bc(4)./c(:,24))
Denpro.*MWpro.*exp(Acpro+Bcpro./c(:,24))]; %% calculate viscosity at
T(K) in cP
Gija=[0 0 0 0 0 0 0 0 0 0 0 0 0 0 0]; %Gibbs free energy at T(K)
% 360+635 315+635 360+315 360+490 490+635
315+490
% 360+ISO 635+ISO 315+iso 490+iso 360+pro
635+pro
% 315+pro 490+pro iso+pro
x1=((c(:,1)*mer(3,1))./(c(:,1)*mer(3,1)+c(:,2)*mer(3,2)+c(:,3)*mer(3,3)
+c(:,4)*mer(3,4)+c(:,21).*MWpro)); % mass fraction of isocyanate
x2=((c(:,2)*mer(3,2))./(c(:,1)*mer(3,1)+c(:,2)*mer(3,2)+c(:,3)*mer(3,3)
+c(:,4)*mer(3,4)+c(:,21).*MWpro)); % mass fraction of M5020
x3=((c(:,3)*mer(3,3))./(c(:,1)*mer(3,1)+c(:,2)*mer(3,2)+c(:,3)*mer(3,3)

```

```

+c(:,4)*mer(3,4)+c(:,21).*MWpro)); % mass fraction of Voranol 360
x4=(c(:,4)*mer(3,4))./(c(:,1)*mer(3,1)+c(:,2)*mer(3,2)+c(:,3)*mer(3,3)
+c(:,4)*mer(3,4)+c(:,21).*MWpro)); % mass fraction of R-315x
x5=(c(:,21).*MWpro)./(c(:,1)*mer(3,1)+c(:,2)*mer(3,2)+c(:,3)*mer(3,3)+
c(:,4)*mer(3,4)+c(:,21).*MWpro)); % mass fraction of polymer
gm=exp(x1.*log(g(:,1))+x2.*log(g(:,2))+x3.*log(g(:,3))+x4.*log(g(:,4))+
x5.*log(g(:,5))); %mixture viscosity in cP
%+0.5*x2.*x3.*Gij1a(:)+0.5*x2.*x4.*Gij2a(:)+0.5*x3.*x4.*Gij3a(:)+0.5*x1
.*x3.*Gij7a(:)+0.5*x1.*x2.*Gij8a(:)+0.5*x1.*x4.*Gij9a(:)+0.5*x3.*x5.*Gi
j11a(:)+0.5*x2.*x5.*Gij12a(:)+0.5*x4.*x5.*Gij13a(:)+0.5*x1.*x5.*Gij15a(
:));
[t,gm(:)];
figure
plot(t,gm(:))
axis([0,600,0,100000])
title('viscosity vs. time')

```

3.4 Simulation Output and Discussion

Example viscosity profiles generated by the simulation are shown in Figures 12, 13, and 14. Figures 12 and 13 present mixture viscosity versus time of Voranol 360 and Voranol 490. In the first 300 seconds mixture viscosities increase slowly because, at the onset of polymerization, the polymer generate in a slow rate and viscosity increases due to polymerization are offset by increases in temperature. After this initial time, temperature reaches to a high level which allows reaction rate to be much higher that mixture viscosity increases rapidly.

Figure 14 shows viscosity versus temperature of Diethylene Glycol. Viscosity follows anticipated trends with a steady decrease with increasing temperature. This is a system with one single material where no reaction takes place.

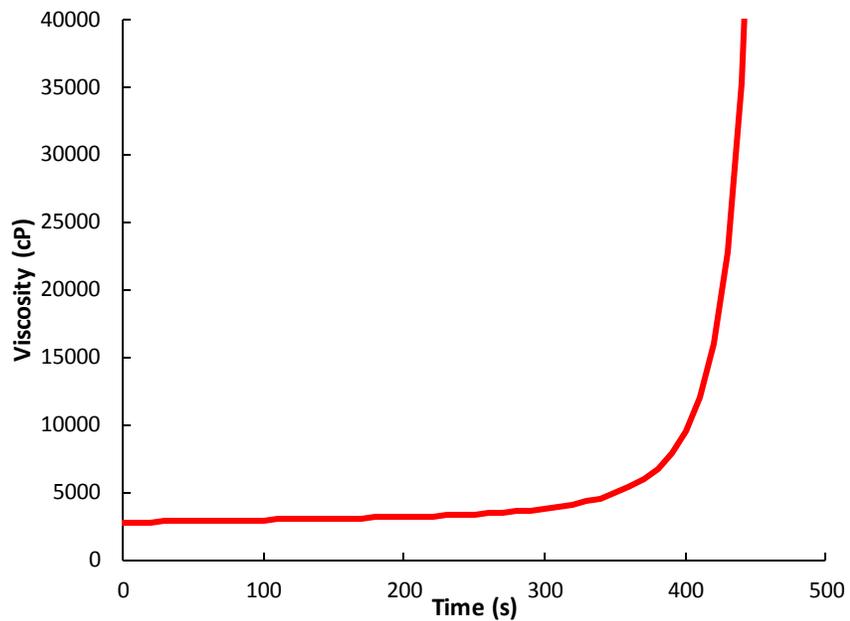


Figure 12. Example viscosity simulation output of a standard recipe of isocyanate with Voranol 360.

In this reaction process, in the first 350 seconds mixture viscosity remains at a steady value where the decrease of pure viscosity and the increase of mixture viscosity stay balanced. After that time mixture viscosity increases sharply where reactants are all done the only donation to the mixture is the polymer. As the degree of polymerization goes to infinite the mixture viscosity goes to infinite.

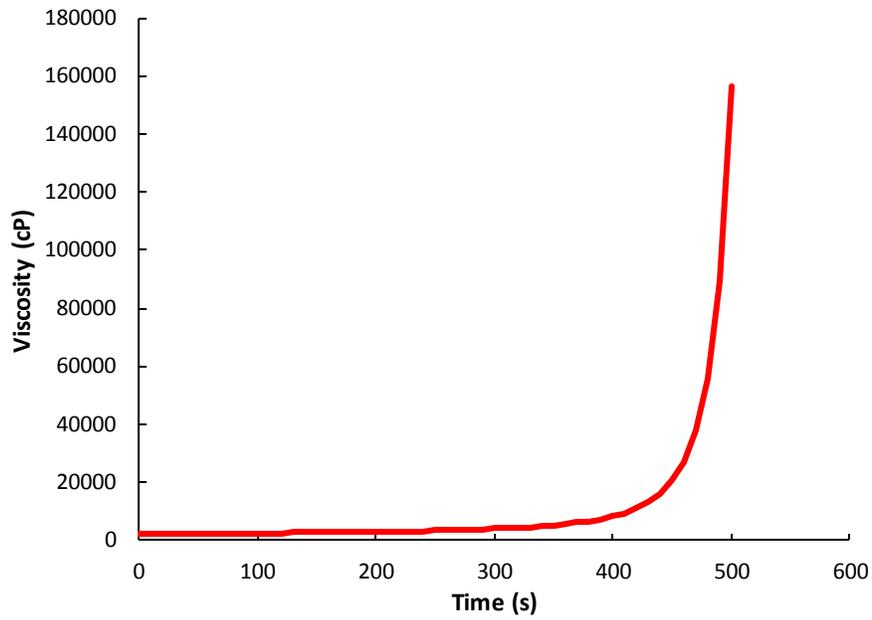


Figure 13. Example viscosity simulation output of a standard recipe of isocyanate with Voranol 490.

The mixture viscosity of reaction between isocyanate with Voranol 490 drops a little bit within the first 100 seconds. Then before approximately 420 seconds the viscosity of the mixture increases at a low speed to about 1500cP. The mixture viscosity increase very quickly to infinity after that.

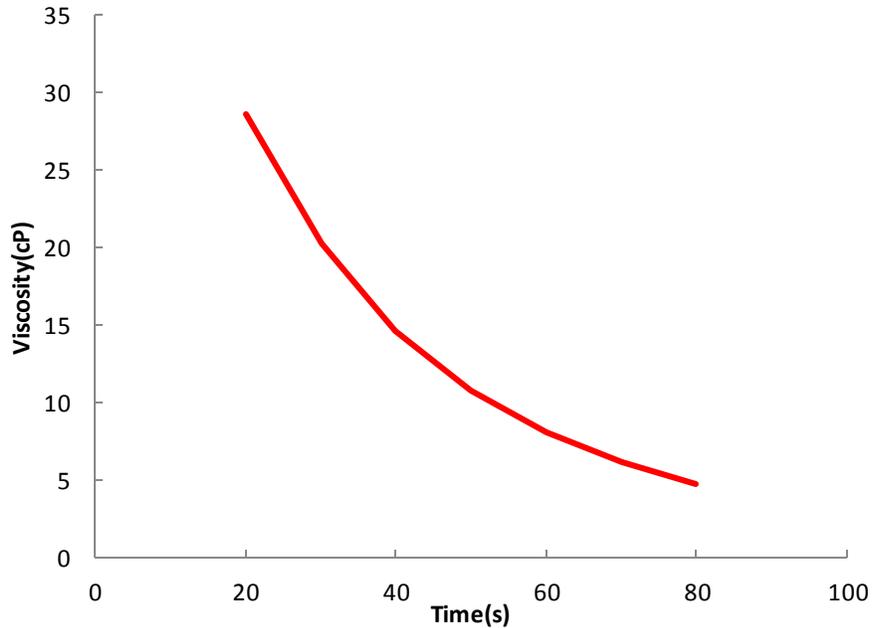


Figure 14. Example simulation output of Diethylene Glycol.

This is a nonreactive pure viscosity simulation as a function of temperature. The model result follows a steady decrease trends between controlled temperature range.

3.5 Experimental Studies and Verification of Model

3.5.1 Viscosity

A Cole-Parmer® Basic Viscometer and a Precision® 280 Series Water Bath were used to measure viscosities at a spin rate of 2.5 to 100 rpm with spindles of L1 to L3 which depends on viscosity range.

The following steps were used to measure viscosities:

1. Pre-weighed components were added into a transparent bottle with lid. For mixtures they were well mixed and kept still for a day to degas.
2. Samples were taken into a water bath at the designed temperature for 20 min to ensure it at the steady state.
3. The spindle was then placed in the container and allowed to equilibrate to the temperature for 5 minutes.

4. Viscosity was measured for 5 minutes each time. Measurements at different temperatures were attained by using the water bath.

This approach was used to measure gel viscosity for reactions for comparison to the simulation output.

3.5.2 Heat Capacity [33]

Differential Scanning Calorimeter (DSC) analyses were conducted over a temperature range from 15°C to 130°C, using the liquid nitrogen cooling accessory (TA Instruments) to achieve subambient temperatures. During the measurements, the DSC cell was purged with dry nitrogen at the rate of 50ml/min. The linear heating or cooling rate was 20°C/min. Sample analysis included two calibration steps followed by sample analysis. Sample sizes ranged from 9.00 to 17.00 mg.

1. The blank pan test, two empty pans, the specimen and reference pan were positioned in the DSC chamber. The DSC chamber was heated from 15°C to 130°C, holding at 130°C for 5 min and subsequently cooled from 130°C back to 15°C.
2. A sapphire standard was placed into the same reference pan using the same heating/cooling cycle as step 1.
3. The sample was placed into the empty specimen pan. Two consecutive cycles were performed where the sample was heated from 15°C to 130°C, held at 130°C for 5 min, and cooled to 15°C. The value of heat capacity was determined from the second heating curve to avoid any water traced in the system. Only data from 25 to 120°C were used to avoid transient effects at the maximum/minimum cycle temperatures.

3.5.3 Simulation Output vs. Experimental Data

The model values of viscosity (lines) are superimposed over the experimental data in Figures 15, 16, and 17. Figures 15 and 16 compare experimental and simulated viscosities during reaction.

Figure 17 presents pure viscosity change with temperature. All data fit the model with good correlation.

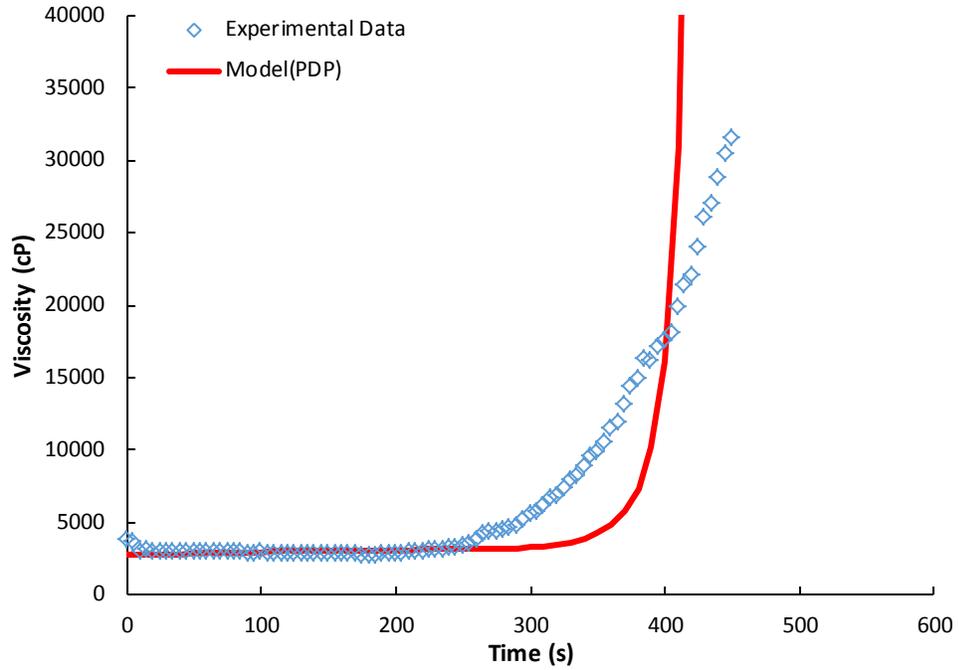


Figure 15. Experimental data with superimposition of model of a recipe of isocyanate with Voranol 360.

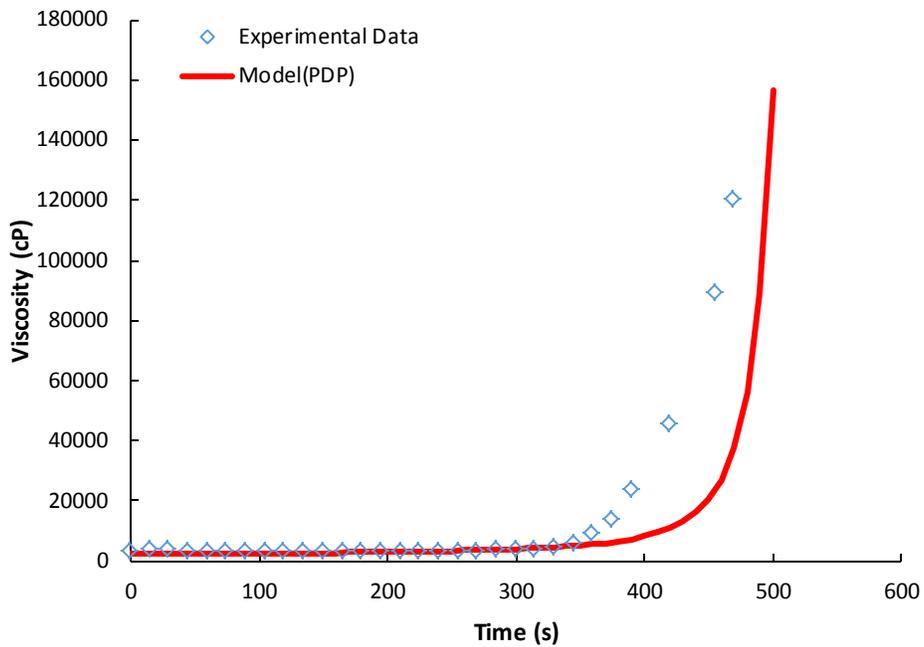


Figure 16. Experimental data with superimposition of model of a recipe of isocyanate with Voranol 490.

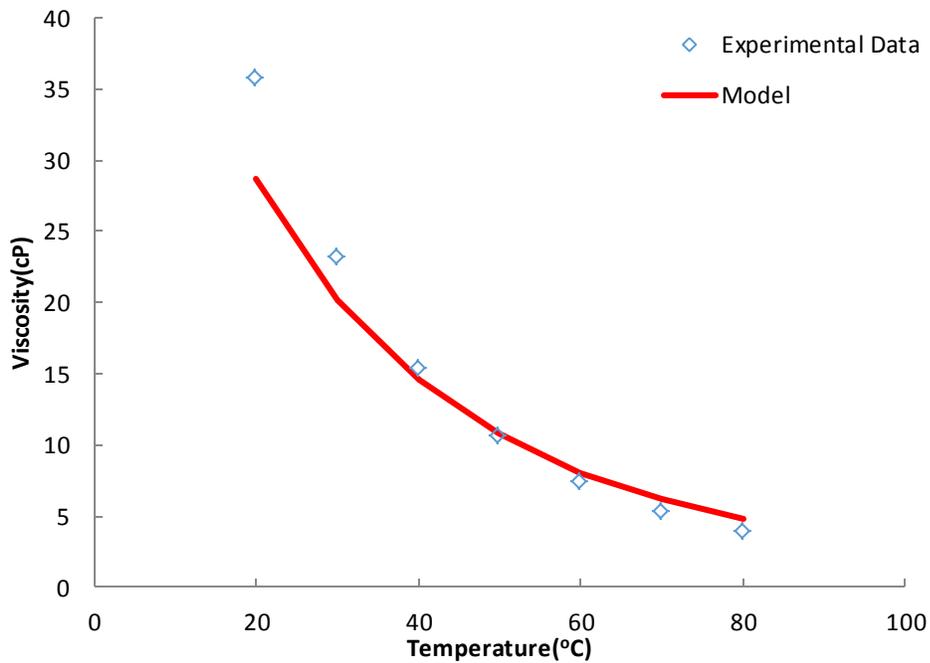


Figure 17. Experimental data with superimposition of model of Diethylene Glycol at different temperature.

Chapter 4. Future Research and Recommendations

A group contribution model for liquid viscosity of organic compounds has been developed. The model requires the functional group characterization of the molecule and application of the correlation to mixtures of model compounds. The basic, linear, models developed do a good job of characterizing important phenomena of interest. The success of a basic model can be attributed to the dramatic increases in viscosity that occur during reaction and as the extent of reaction reaches that critical extent of reaction that leads to thermoset formation (infinite viscosity).

The following can be successfully detected by this model:

- An accurate estimation of pure viscosity as a function of time where temperature is less than 160°C.
- Mixture viscosity in both reactive and nonreactive polyurethane systems can be precisely determined.
- A proper timing of viscosity change with eventual setting of the resin.

Future studies should include suitable groups for representing complex molecules and more experimental data of organic liquid mixtures for improvement of accuracy and wide-ranging applicability. Also, interaction parameters need to be modified to include. Such improvements could lead to detection of or discriminating of the following phenomena:

- A wider applicable temperature range of pure and mixture viscosity are obtained to allow dig into more areas.
- Difference among isomers where polyfunctional, polar or nonpolar, different ring substituents can be determined.
- Materials with more structural groups that are not shown before can be easily and accurately generated.

- Impact of other additives like catalyst and surfactant on the mixture viscosity of polyurethane mixtures will be included to ensure to find properties of polyurethane and proper use for them.

In addition, aqueous solubility experimental data are needed from systematic experiments to verify and correct some of those group contribution parameters. Interaction correction should be included in the model to show interactions between groups like some polar functional groups.

It is particularly meaningful and useful to use the group contribution approach to estimate chemical properties in the polyurethane process. This kind of methods is easy to use and results in accurate predictions. Increasing useful applications have been taken into use to evaluate extends of reactions and monomer or polymer properties.

Bibliography

1. Zhao, Y., et al., *Modeling reaction kinetics of rigid polyurethane foaming process*. J. Appl. Polym. Sci., 2013. **130**(Copyright (C) 2013 American Chemical Society (ACS). All Rights Reserved.): p. 1131-1138.
2. Shen, L., et al., *Density modeling of polyurethane box foam*. Polym. Eng. Sci., (Copyright (C) 2013 American Chemical Society (ACS). All Rights Reserved.): p. Ahead of Print.
3. Tu, Y.C., G.J. Suppes, and F.H. Hsieh, *Water-blown rigid and flexible polyurethane foams containing epoxidized soybean oil triglycerides*. Journal of Applied Polymer Science, 2008. **109**(1): p. 537-544.
4. Tu, Y.C., et al., *Physical properties of water-blown rigid polyurethane foams containing epoxidized soybean oil in different isocyanate indices*. Journal of Applied Polymer Science, 2009. **114**(5): p. 2577-2583.
5. Reid, R.C., J.M. Prausnitz, and B.E. Poling, *The Properties of Gases and Liquid*. 4th ed. 1987, New York: McGraw-Hill. 456-457.
6. Jhunjhunwala, N., et al., *The shear viscosity of simple fluid mixtures*. Physica, 1969. **41**(3): p. 536-540.
7. Singh, P.P. and C.P. Sinha, *Application of significant liquid structure theory to the mixture viscosity of apolar-apolar and polar-polar binary liquid system*. Ind. J. Chem. Section A: Inorganic, Physical, Theoretical & Analytical, 1978. **16A**(3): p. 821-825.
8. Dizechi, M. and E. Marschall, *Correlation for viscosity data of liquid mixtures*. Industrial and Engineering Chemistry Process Design and Development, 1982. **21**(2): p. 282-289.
9. Irving, J.B., *Viscosity of binary liquid mixtures: a survey of mixture equations*. 1977.
10. Irving, J.B., *Viscosities of binary liquid mixtures: the effectiveness of mixture equations*. 1977.
11. Grunberg, L. and A.H. Nissan, *Mixture law for viscosity*. Nature, 1949. **164**(4175): p. 799-800.
12. Isdale, J.D., J.C. MacGillivray, and G. Gartwright, *Prediction of Viscosity of Organic Liquid Mixtures by a Group Contribution Method*, in *Nalt. Eng. Lab. Rept.* 1985: East Kilbride, Glasgow, Scotland.

13. Dow, *Dow Polyurethanes - Functionality, OH Number, and Equivalent Weight Definitions*. 2010.
14. HuntsmanCo., *Adhesives Coatings and Elastomers Polyurethanes Product Line*. 2010.
15. DowPlastics, *Voranol 360-Polyether Polyol*. 2001.
16. Arch Chemicals, I., *Performance Chemicals Typical Polyol Properties*. 2007.
17. DowPlastics, *Voranol 490-Polyether Polyol*. 2001.
18. HuntsmanCo., *Rubinate® M MDI*. 2010.
19. Orrick, C. and J.H. Erbar, *Privae Communication to Reid. R.C., Praunitz, J.M., and Poling, B.E.* 1974.
20. Zhao, Y., et al., *Modeling reaction kinetics of rigid polyurethane foaming process*. Journal of Applied Polymer Science, 2013. **130**(2): p. 1131-1138.
21. Joback, K.G., R. C. Reid, *Estimation of Pure-Component Properties from Group-Contributions*. Chem. Eng. Comm., 1987. **57**: p. 233.
22. Lydersen, A.L., *Estimation of Critical Properties of Organic Compounds*. Univ. Cool. Exp. Stn., Rept., Madison, WI, April, 1955.
23. Ambrose, D., *Correlation and Estimation of Vapor-Liquid Critical Properties: I. Critical Temperatures of Organic Compounds*. Nat. Physical Lab., Teddington, UK, NPL Rep. Chem., 1978: p. 92.
24. Klinecicz, K.M. and R.C. Reid, *ESTIMATION OF CRITICAL PROPERTIES WITH GROUP CONTRIBUTION METHODS*. AIChE Journal, 1984. **30**(1): p. 137-142.
25. Lyman, W.J., W. F. Reehl and D. H. Rosenblatt, *Handbook of Chemical Property Estimation Methods*. American Chemical Soc., Washington, DC, 1990.
26. Horvath, A.L., *Molecular Design*. Elsevier, Amsterdam, 1992.
27. Orrick, C., J.H. Erbar, *private communication*. 1974.
28. Missenard, F.A., 1965. **260**: p. 5521.
29. Klopman, G., S. Wang, and D.M. Balthasar, *Estimation of aqueous solubility of organic molecules by the group contribution approach. Application to the study of biodegradation*. Journal of Chemical Information and Computer Sciences, 1992. **32**(5): p. 474-482.
30. Dow, *Dow Ethylene Glycols*.

31. Grunberg, L. and A.H. Nissan, *Mixture law for viscosity [21]*. Nature, 1949. **164**(4175): p. 799-800.
32. Isdale, J.D., *Symp. Transp. Prop. Fluids and Fluid Mixtures*. Natl. Eng. Lab., East Kilbride, Glasgow, Scotland, 1979.
33. Shen, L., *Heat Capacity of Polyols and Isocyanate in Polyurethane(PU) Foams by Group Contribution Method*. Journal of Applied Polymer Science, 2013. NA: p. NA.