

# Temperature Dependence of Viscosity of Polyurethane Polyol Solutions: Application of Rheological Models\*

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## SYNOPSIS

Polyurethane polyols were synthesized by reacting the diols with polyisocyanates. Viscosity of their 50% (w/w) solutions in various solvents has been determined at different temperatures by using Haake RotoVisco RV12 Rotational Viscometer. The temperature dependence of viscosity data was solved by Levenberg Marquardt's algorithm by using nonlinear regression models based on WLF, Vogel, and Arrhenius equations. The  $T_g$  values obtained from WLF and Vogel equation are comparable to each other and these equations can be satisfactorily used for the analysis of temperature dependence of viscosity data of oligomer solutions. The residuals are random and the absolute average percentage error in analyzing the viscosity data by these equations is minimum. The values of constants in WLF equation are found to be system dependent and adjustable parameters. The predicted  $\ln \eta$  values obtained from WLF and Vogel equations fit well with the plots of experimental  $\ln \eta$  values as a function of temperature. © 1996 John Wiley & Sons, Inc.

## INTRODUCTION

The need to reduce the solvent content of coatings as per federal regulations and air pollution control has led to the development of newer formulations of high solids coatings. These coatings are frequently based on similar type of resins used in conventional systems, but the molecular weight of the resinous part is considerably reduced. Such resinous products can be used as reactive diluents and plasticizers in the coating formulations.<sup>1,2</sup> The low molecular weight of the resin helps to achieve application viscosity at high solids content. The physical and mathematical aspects of flow associated with free volume concept<sup>3,4</sup> of high solids has been discussed by Wicks in his Mattiello Memorial Lecture.

Polyols form the basic components of high solid coatings formulations and their design traditionally involves a compromise concerning their molecular weights. Takahashi<sup>5</sup> has summarized the recent advances in high solids coatings while Hill et al.<sup>6</sup> have

reviewed the importance of basic principles in formulating high solids coatings. Blank<sup>2,7</sup> reports that oligomeric  $\beta$ -hydroxyalkyl urethane polyols may find application as resin intermediates, modifiers, and crosslinkers for water-borne and high solids coatings. Gardon<sup>8</sup> prepared polyurethane polyols and claimed that their melamine-cured product may find application as high solids coating for automobiles.

Wicks et al.<sup>9</sup> have determined the temperature dependence of viscosity of oligomeric butylmethacrylate (OBMA) in *m*-xylene and found to follow Williams-Landel-Ferry (WLF) type of equations over a wide range of concentrations. They claim that the WLF equation provides a better model of viscosity as a function of temperature than a Arrhenius type expression for a wide range of oligomers. They point out that the viscosity of oligomer solutions depends upon oligomer, solvent viscosity, oligomer solution  $T_g$ , solvent-oligomer interaction, temperature, and concentration.

The approach to expressing the effect of free volume on viscosity has led to the derivation of relationships commonly known as WLF type equations. They are used widely for interpreting the flow behavior of polymer melts<sup>10</sup> and the dependence of viscosity of oligomer solution on temperature. One form of WLF equation is given below:

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$$\ln \eta = \ln \eta_{T_g} - [A(T - T_g)] /$$

$$[B + (T - T_g)] - \ln(\rho_g T_g / \rho T) \quad (1)$$

where  $\eta$  is the viscosity,  $\eta_{T_g}$  is the viscosity at  $T_g$ ,  $T_g$  is the solution glass transition temperature,  $A$  and  $B$  are constants, and  $\rho$  and  $\rho_g$  are densities at  $T$  and  $T_g$ .

Originally  $A$  and  $B$  were thought to be universal constants ( $A = 17.44$  and  $B = 51.6$ ), but later work by the same authors<sup>10</sup> and others<sup>11,12</sup> has shown that  $A$  and  $B$  are material specific. Nielson<sup>13</sup> has simplified this equation by using the universal constants  $A$  and  $B$  and setting  $\eta_{T_g} \cong 10^{13}$  P for any polymer and neglecting the small term, temperature  $\times$  density product. The result of these simplifications with  $T = 298$  K is

$$\log \eta = 13 - [17.44(298 - T_g)] / [51.6 + (298 - T_g)] \quad (2)$$

Hill and Kozlowski<sup>14</sup> have applied this equation to viscosity-temperature data for several oligomer solutions. They calculated the  $T_g$  of the oligomer solution from the above equation and found that the calculated values of  $T_g$  were constant for high solids polyester resins and three melamine formaldehyde resins, whereas, the  $T_g$  values were not constant for the solutions of high solids acrylic and conventional acrylic resins. It was suggested that high molecular weight might permit coil formation. Blank<sup>1</sup> reports that although these constants ( $A$  and  $B$ ) are not truly universal, they can be used for oligomers with some modifications. He found good correlation of the above WLF equation with the experimental data of polyurethane polyols over a temperature range of between 25 and 120°C.

Wicks et al.<sup>9</sup> have tested the WLF equation by treating the universal constants as adjustable parameters but keeping the other simplifications of Hill the same. They have used the following equation (referred to as Model 1 in Results):

$$\ln \eta = 34.5 - [A(T - T_g)] / [B + (T - T_g)] \quad (3)$$

They found that nonlinear regression analysis gives high correlation coefficients for viscosity dependence on temperature of OBMA solution in *m*-xylene over a wide range of temperatures.

The following form of the Vogel equation<sup>12,15</sup> is

widely used to describe temperature dependence of viscosity (referred to as Model 2 in Results):

$$\ln \eta = \ln C + D / (T - T_g) \quad (4)$$

The Modified form of the Vogel equation<sup>12</sup> seems to be attractive since it appears to combine the concept of an activation energy for flow with a free volume effect:

$$\ln \eta = \ln C + E_v / RT + D / (T - T_g) \quad (5)$$

Wicks et al.<sup>9</sup> reported the following equation (referred to as Model 3 in Results), which they derived by making suitable substitution in eq. (5):

$$\begin{aligned} \ln \eta = & \ln \eta_{T_g} \\ & + (E_v / R)(1/T - 1/T_g) \\ & - A(T - T_g) / [B + (T - T_g)] \\ & - \ln(\rho_g T_g / \rho T) \quad (6) \end{aligned}$$

It has been reported that the modified form of the Vogel equation gives a better fit for the viscosity-temperature data.<sup>9,12</sup>

Sherwin et al.,<sup>16</sup> Porter and Johnson,<sup>17</sup> and Patton<sup>18</sup> report that following Arrhenius equation (referred to as Model 4 in Results) follows well the temperature dependence of viscosity of resin solutions and oligomers:

$$\ln \eta = \ln F + (E_v / RT) \quad (7)$$

Wicks et al.<sup>9</sup> report that the temperature dependence of viscosity of oligomer solutions does not follow the Arrhenius equation. They found correlation coefficients of the order of 0.96 or higher for the solutions of OBMA in *m*-xylene and the plots of residuals were a definite curved pattern and concluded that the Arrhenius equation was not a satisfactory model for the solutions of oligomers.

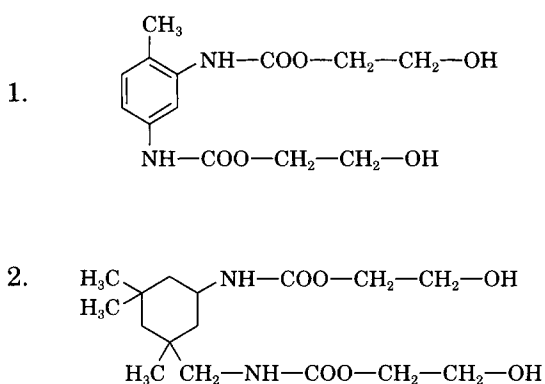
In this study a competitive evaluation of four rheological models that are represented by eqs. (3), (4), (6), and (7) has been done by statistical analysis of the data of temperature dependence of viscosity of polyurethane polyols in different solvents.

## EXPERIMENTAL

Various polyurethane polyols (PU-POs) have been synthesized by reacting the diols with polyisocyan-

ates in a 2-L round-bottom flask equipped with stirrer, thermocouple, nitrogen purge, sample port, and condenser. Complete reaction of isocyanate was confirmed by loss of IR band at  $2250\text{ cm}^{-1}$ . Molecular weight data were obtained from GPC unit of SHIMADZU C-R4A Chromopac by using Waters (100 Å) columns. Samples were dissolved in tetrahydrofuran (THF) at approximately 0.1 g/10 mL concentration. A 1 mL/min flow rate with THF as the mobile phase was used. The columns were calibrated using Aldrich polyethyleneglycol standards. The details of these polyols and their properties are given in Table I.

The general structural formulas of PU-PO are given below:



## Procedure

A solution was prepared by dissolving a certain amount of the resin in a solvent. The homogeneous polyol solution was passed through a closed fritted-glass-filtering unit to make it free from any suspending particles or undissolved material. The

weight fraction of the polyol in the solution was estimated after filtration. The solution was diluted to 50% solid content and stored in a room conditioned at  $25 \pm 1^\circ\text{C}$  for at least 24 h before conducting viscosity measurements at 25, 35, 45, and  $55^\circ\text{C}$ . A Haake Rotovisco RV-12 Searl-type rotational viscometer with M-500 measuring head and NV sensor system (double gap sensor) at different shear rates was used. The apparent viscosity and the shear rate data were calculated by using the methods given in the manual<sup>19,20</sup> supplied along with the viscometer. For the sake of convenience the viscosity data at shear rate  $1385\text{ sec}^{-1}$  have been reported here and analyzed for the applicability of various rheological models.

The practical viscosity data of 50% concentration of polyol at different temperatures show the usual trend like decrease in viscosity with increase in temperature (Table II). In most of the polyols it has been observed that the viscosity of polyols decreases relatively more sharply from 25 to  $35^\circ\text{C}$  and the decrease is not so sharp from 35 to  $45^\circ\text{C}$  and 45 to  $55^\circ\text{C}$ . The viscosity of the oligomer solution in a solvent is a function of interaction between solute and solvent. The degree of interaction does change with the increase/decrease in temperature of the system. A solvent that has good solvency power for a polymer at ambient temperature may not have the same with the change in temperature of the solution.

## Evaluation of Rheological Models

The nonlinear regression analysis of four rheological models (1, 2, 3, and 4) represented by eqs. (3), (4), (6), and (7) was solved by using Levenberg Mar-

**Table I** Molecular Weights and Polydispersity of Polyurethane Polyols

S. No.	Diol	Diisocyanate	$M_w$	$M_n$	$M_w/M_n$
I	1,4-Butanediol	TDI <sup>a</sup>	1187	992	1.19
II	1,2-Propanediol	TDI	1142	1038	1.10
III	Ethyleneglycol	TDI	1175	1020	1.15
IV	1,3-Butanediol	TDI	984	751	1.31
V	1,2-Propanediol	IPDI <sup>b</sup>	1135	1010	1.12
VI	Ethyleneglycol	IPDI	1107	987	1.12
VII	1,4-Butanediol	IPDI	1115	1015	1.10
VIII	1,3-Butanediol	IPDI	1125	1035	1.08

<sup>a</sup> Toluene diisocyanate.

<sup>b</sup> Isophoronediiisocyanate.

**Table II Viscosity of 50% Polyurethane Polyol Solutions at Different Temperatures**

PU-PO	Solvent	Viscosity (cP)			
		Temperatures (°K)			
		298	308	318	328
II	Propanol	38.55	23.13	16.71	14.14
	Butanol	42.41	25.70	20.13	14.14
	MIBK	37.27	24.42	16.70	14.14
III	Propanol	39.89	26.35	21.84	17.35
IV	Propanol	30.20	19.92	14.35	11.35
	Butanol	40.70	25.49	18.42	13.92
	MIBK	21.20	14.14	11.14	9.34
V	Propanol	34.70	21.20	14.99	11.14
	Butanol	39.84	21.85	14.56	11.56
	MIBK	19.70	12.85	9.64	8.35
VI	Propanol	29.56	19.28	13.71	10.71
	Butanol	36.63	22.49	15.42	12.21
VII	Propanol	50.12	34.06	21.85	16.06
	Butanol	19.70	11.78	8.57	5.99
	MIBK	37.27	22.49	16.06	13.92
VIII	Propanol	28.91	18.63	13.92	10.49
	Butanol	28.27	20.50	14.35	10.92
	MIBK	11.99	8.14	—	7.92

PU-PO III is not soluble in butanol and MIBK and PU-PO VI is not soluble in MIBK.

quardt's algorithm.<sup>21</sup> The details about the estimation of various parameters using this algorithm are described elsewhere.<sup>22</sup>

## RESULTS AND DISCUSSION

The data of molecular weight and polydispersity index of polyurethane polyol reported in Table I show that the polyols have their molecular weight in the range of 984 to 1175 and the polydispersity index (1.082, 1.31) indicates that most of the polyols have narrow molecular weight distribution. Their chemical structure varies with the substitution of diol moiety as indicated in the general formulas of polyurethane polyol. Depending on their molecular weight and chemical structure  $T_g$  values of these polyols do differ from each other with respect to solvents. However, this aspect has not been studied in detail because the main objective of this work was to evaluate the application of rheological models to the viscosity dependence on temperature.

The WLF eq. (1) simplified to eq. (3) in which  $A$  and  $B$  were originally considered to be universal constants was tested by using the viscosity data of polyurethane polyol solutions at different temperatures in various solvents.

The practical observations indicate that the values of universal constants  $A$  and  $B$  suggested by Nielson<sup>13</sup> do not hold for all types of polymer solutions. The values of parameters  $A$  and  $B$  are found to be system dependent and support the observations reported by Wicks et al.<sup>9</sup> The values of  $A$  and  $B$  obtained by computing the viscosity data in the WLF equation, model (1), show that the value of parameter  $A$  varies in the range of 32.4 to 35.6

**Table III Values of Various Parameters, Obtained from WLF Equation, Model (1)**

PU-PO	Solvent	$A$	$B$	$T_g$ (°K)	Abs. Avg. % Error
II	Propanol	34.25	6.93	236.7	1.096
	Butanol	33.28	3.06	258.6	0.786
	MIBK	32.98	2.05	267.1	0.806
III	Propanol	32.57	1.86	265.5	0.706
IV	Propanol	34.00	5.03	244.2	0.146
	Butanol	33.96	5.51	244.4	0.199
	MIBK	33.14	1.65	267.4	0.128
V	Propanol	34.34	6.05	243.2	0.025
	Butanol	33.38	2.46	268.5	0.343
	MIBK	33.20	1.44	271.1	0.429
VI	Propanol	34.24	5.65	241.7	0.148
	Butanol	33.69	3.80	256.0	0.333
VII	Propanol	34.67	9.16	230.1	0.811
	Butanol	35.67	8.86	230.5	0.924
	MIBK	32.71	1.39	274.5	0.542
VIII	Propanol	34.36	6.23	237.7	0.405
	Butanol	33.55	3.35	254.3	0.831
	MIBK	32.44	0.01	296.9	0.000

whereas there is wide variation in the values of parameter  $B$ , i.e., 0.01 to 8.86 (Table III). Based on these results parameter  $A$  can be considered a universal constant with a numerical figure of 34, which is just double the value of  $A$  assigned by others.

The fairly low absolute average percentage error (Abs. avg. % error) indicates that the analysis of viscosity data by using the WLF equation, model (1), produces good results.

The high solids polyesters data reported by Hill and Kozlowski<sup>14</sup> were also tested by using eq. (3). The average absolute percent errors are low with random residuals. The values of  $A$  and  $B$  have minimum variation up to 80% concentration, which is of interest with respect to high solids coatings.

Wicks et al.<sup>9</sup> report that Vogels' equation, model (2), has been used to describe the temperature dependence of viscosity and call it an advantage to fit in viscosity data relatively better. The constants  $C$  and  $D$  in this equation have not been assigned any specific significance and the value of  $T_g$  is the main outcome. The regression analysis of practical data obtained by using this equation are reported in Table IV. The values of  $C$  and  $D$  for a PU-PO do not show a significant relation with respect to the three solvents or the polyols used in this study. However, the values of  $T_g$  obtained by the use of the Vogel equation, model (2) are more or less equal to those obtained from the WLF equation model (1). The comparison of  $T_g$  values obtained by the use of these two equations, models (1) and (2), indicates no significant difference among them. The absolute av-

erage percentage errors is also found to be of lower order.

The modified form of the Vogel equation, model (3), is said to give an improvement in fit of data.<sup>9</sup> In this model the last term, i.e.,  $\ln(\rho_g T_g / \rho T)$  has not been considered in the analysis because its influence in the output data is expected to be negligible. The values of constants  $A$  and  $B$  obtained by using a modified form of the Vogel equation, model (3), are not concurrent and they are given in Table V. In the case of formulation PU-PO VI and VII the values of  $A$  are negative and the values of  $B$  are also negative for PU-POs II, III, IV, V, and VIII. The nature of the values of  $A$  and  $B$  is so scattered that it is difficult to establish any relationship between the value of these constants and the quality of solvent used for the determination. The values of  $E_v$  obtained for various PU-PO formulations in different solvents also do not provide information that could be used in establishing the compatibility of the polyol with the solvent. The  $T_g$  values for various PU-POs obtained by the use of this equation, model (3), are also almost half of the values of  $T_g$  obtained from the WLF equation, model (1), and the Vogel equation, model (2). Moreover, the  $T_g$  values also do not indicate a relationship with the quality of solvent used for the viscosity determination. The absolute average percentage error is also found to be relatively higher in the case of this equation.

Wicks et al.<sup>9</sup> claimed that model (3) might be found attractive since it appeared to combine the concept of an activation energy with a free volume

**Table IV Values of Various Parameters, Obtained from Vogel Equation, Model (2)**

PU-PO	Solvent	$C$	$D$	$T_g$ (°K)	Abs. Avg. % Error
II	Propanol	1.37	226.91	231.6	1.101
	Butanol	3.40	102.02	255.5	0.791
	MIBK	4.92	67.69	265.0	0.804
III	Propanol	6.88	60.68	263.6	0.706
IV	Propanol	1.65	171.04	239.2	0.151
	Butanol	1.71	187.31	238.8	0.199
	MIBK	4.79	39.36	271.4	0.084
V	Propanol	1.13	208.04	237.2	0.204
	Butanol	3.04	82.17	266.1	0.344
	MIBK	3.64	47.87	269.7	0.429
VI	Propanol	1.30	193.59	236.0	0.155
	Butanol	2.24	128.03	252.2	0.333
VII	Butanol	0.31	316.09	221.7	0.930
	MIBK	5.97	45.71	273.1	0.543
VIII	Propanol	1.15	214.25	231.5	0.402
	MIBK	7.81	0.46	296.9	0.000

**Table V Values of Various Parameters, Obtained from Modified Form of Vogel Equation, Model (3)**

PU-PO	Solvent	A	B	$E_v$	$T_g$ (°K)	Abs. Avg. % Error
II	Propanol	7.87	-394	18730	139	1.057
	Butanol	34.49	-934	17910	131	1.156
	MIBK	0.01	-241	78970	90	0.000
III	Propanol	8.50	-439	16430	129	0.901
IV	Propanol	2.32	-344	13240	119	0.000
	Butanol	18.98	-596	19290	138	0.310
	MIBK	24.14	-532	23660	147	0.273
V	Propanol	60.11	-1019	23680	146	0.305
	Butanol	3.00	14	7891	96	2.725
	MIBK	2.58	8	5529	72	2.551
VI	Propanol	-226.27	1324	32950	151	0.054
	Butanol	-6.29	426	8363	89	1.747
VII	Propanol	-4.95	348	8525	91	0.627
	Butanol	2.30	28	7368	88	1.255
	MIBK	-392.62	712	83710	187	0.161
VIII	Propanol	2.38	12	6390	81	1.000
	MIBK	3.61	-381	13620	119	0.985

effect. However, the results reported in Table V indicate that it is difficult to derive concrete information from the viscosity data analyzed by using a modified form of the Vogel equation, model (3).

The Arrhenius equation, model (4), is said to provide temperature dependence of resin and oligomer solutions with low residuals and satisfactory values of parameters. The significance of the constant  $F$  in this equation is supposed to be similar to the constant  $A$  in WLF equation, model (1), and  $C$  in Vogel equation, model (2). The values of this constant vary from 0.000047 to 0.192 irrespective to the solvent used for PU-POs II-VIII. The values of  $A$  derived by using WLF equation, model (1), vary within a narrow range of 32.4-35.6 whereas the values of  $F$  obtained from Arrhenius equation, model (4) differs in fairly wide dimensions. Hence the term  $F$  in Arrhenius equation may not be considered to be equivalent to the term  $A$  in WLF equation, model (1). The values of  $E_v$  derived from this equation indicate that a relatively low energy of activation is required for PU-PO solution in MIBK compared to that of PU-PO solutions in alcohols. The PU-PO solution in propanol has relatively low  $E_v$  compared to its solution in butanol. The average absolute percentage error is also found to be higher compared to that observed in the case of the WLF equation, model (1), and the Vogel equation, model (2).

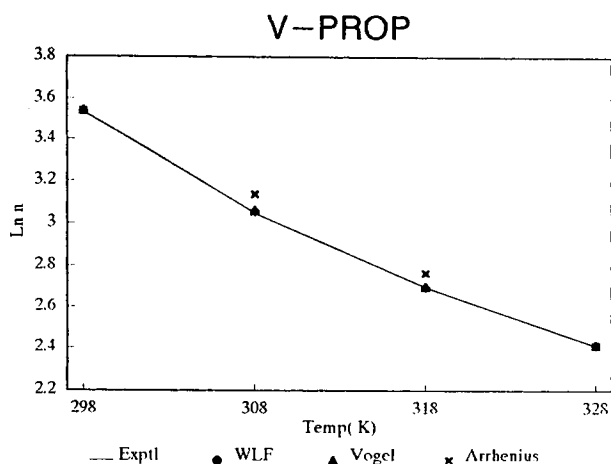
The data reported in Table VI indicate that the applicability of the Arrhenius equation, model (4) to the temperature dependence of viscosity reported in this paper is not convincing.

The data reported in Tables III, IV, V, and VI for PU-PO V in propanol, butanol, and MIBK have been used for calculating the predicted values of  $\ln \eta$  at temperatures 298, 308, 318, and 328 K. For the sake of comparison the predicted values of  $\ln \eta$  are plotted along with experimental values of  $\ln \eta$ , in Figures 1, 2, and 3.

The regression output also provide parameters like standard error, correlation coefficient, and

**Table VI Values of Various Parameters, Obtained from Arrhenius Equation, Model (4)**

PU-PO	Solvent	$F \times 10^3$	$E_v$	Abs. Avg. % Error
II	Propanol	0.84	6312	1.613
	Butanol	0.36	6886	1.227
	MIBK	0.71	6410	1.818
III	Propanol	5.00	5319	1.271
IV	Propanol	0.63	6353	1.243
	Butanol	0.34	6896	1.137
	MIBK	3.0	5257	1.894
V	Propanol	0.14	7310	1.255
	Butanol	0.05	8031	2.734
	MIBK	1.00	5588	2.546
VI	Propanol	0.41	6592	1.239
	Butanol	0.19	7157	1.781
VII	Propanol	0.16	7493	0.628
	Butanol	0.05	7561	1.268
	MIBK	0.66	6428	2.687
VIII	Propanol	0.49	6484	0.991
	Butanol	0.76	6232	0.437
	MIBK	192	2389	7.470



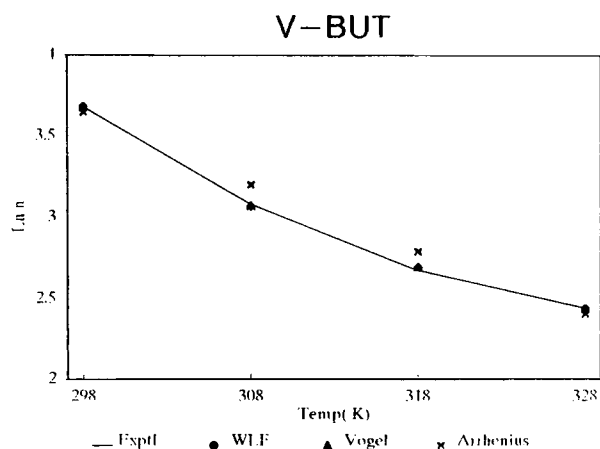
**Figure 1**  $\ln \eta$  of PU-PO in propanol at different temperatures, calculated and measured data points.

X-coefficient, however, they have not been reported here. The values of correlation coefficient are high (0.999) in all cases and standard error are less than 0.1.

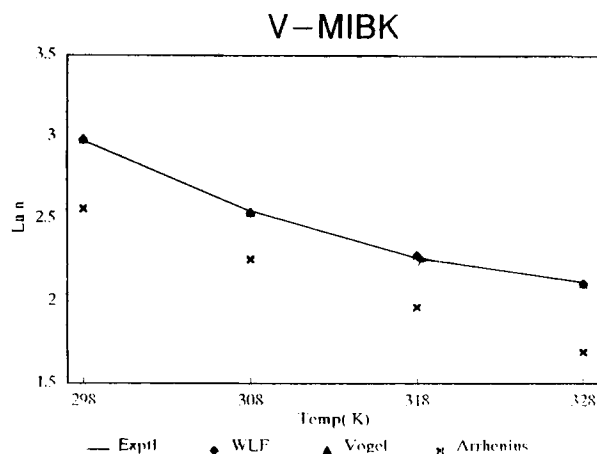
The plots in Figures 1, 2, and 3 show a good fit of calculated  $\ln \eta$  obtained by using the WLF equation, model (1), and the Vogel equation, model (2), with experimental  $\ln \eta$ , whereas the calculated  $\ln \eta$  obtained from Arrhenius equation, model (4), does not fit so well.

### Significance of $T_g$ in High Solids Coatings

Weight fraction of the resin as well as its molecular weight have a profound effect on solution viscosity and it increases with the increase in them. This aspect has been dealt in detail by Hill et al.<sup>6</sup> by taking



**Figure 2**  $\ln \eta$  of PU-PO in butanol at different temperatures, calculated and measured data points.



**Figure 3**  $\ln \eta$  of PU-PO in MIBK at different temperatures, calculated and measured data points.

the free volume concept into consideration. The data reported in Tables III & IV indicate variation in  $T_g$  values of a polyol with respect to a solvent. The  $T_g$  of the resin is influenced by solvent-oligomer interaction. Resin-solvent interaction involves forces such as hydrogen bonding, dipole-dipole interaction, and dispersion effect. Solvents that behave only as hydrogen bond acceptors rather than hydrogen bond acceptors and donors efficiently eliminate oligomer-oligomer interaction and thereby give rise to a decrease in viscosity. The results reported here suggests that solvent selection should be made on the basis of its efficiency in reducing viscosity.<sup>23</sup>

### CONCLUSIONS

The observations in this study indicate that  $T_g$  values obtained from the WLF equation, model (1), and the Vogel equation, model (2), are comparable to each other and these models can be used satisfactorily for the analysis of the temperature dependence of viscosity of oligomer solutions.

Equation (3), model (1), has been used wherein the values of  $A$  and  $B$  are found to be adjustable parameters and other simplifications being the same as in eq. (2).

The temperature dependence of viscosity data of polyurethane polyols has been found to obey eq. (3), model (1), and the absolute average percent error for all the polyols in different solvents is minimum.

The data are found to fit very well in eq. (3), model (1), and not in eq. (2), as the values of parameters  $A$  and  $B$  are fixed in numerical terms in this equation.

The residuals are random and constants  $A$  and  $B$  are found to be system dependent. The value of  $A$  is almost constant for a particular resin in different solvents, whereas the variation in the value of  $B$  with solvents indicates its dependence on the quality of the solvent.

The plots of predicted  $\ln \eta$  obtained from models (1) and (2) are found to fit well with the experimental  $\ln \eta$  versus temperature plot.

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