

# Concentration Dependence on Viscosity of Oligourethane Diols

SYED HASEEBUDDIN, K. V. S. N. RAJU, M. YASEEN

Organic Coatings and Polymers Division, Indian Institute of Chemical Technology, HYDERABAD—500 007, India

Received 3 October 1996; accepted 10 April 1997

**ABSTRACT:** To obtain viscosity suitable for application, relatively low molecular weight polymers, i.e., oligomers, are used in the formulation of high solids coatings. To support this requirement, the concentration dependence of the viscosity of synthesized oligourethane diols in different solvents was analyzed using Erickson's models. By regression analysis, it was found that the correlation coefficients are fairly good and the plots of the residuals are more random. The weight intrinsic viscosity,  $[\eta_w]$ , composed of the oligomer component,  $O_{[\eta]w}$ , and the oligomer-solvent interaction component,  $I_{[\eta]w}$ , was calculated from the intercept of the plot of  $1/\ln \eta_r$  vs.  $1/w_0$ . The parameter  $I_{[\eta]w}$ , related to the solvent molar volume and the distance between the oligomer and solvent partial cohesion parameter coordinates, indicates the degree of interaction between the oligomer and solvent. The partial cohesion parameters of the oligomers obtained by the group-contribution method were used for calculating the interaction component of oligourethane diols. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **66**: 1343–1351, 1997

## INTRODUCTION

The present-day regulatory restrictions on the emission of solvents have forced industry to concentrate efforts on the development of promising formulations of high solids coatings. Usually, a combination of low molecular weight polymers (oligomers) and reactive solvents is used to achieve a suitable application viscosity with a minimum solvent content. The solvent-oligomer interaction has a significant effect on the flow behavior of high solids. The high solids coating formulations containing oligomers differ from conventional binders. Because their molecular weights are below the critical molecular weight, their properties are influenced by solvent type and content. In high solids formulations, the addition of a small amount of solvent serves the function of

plasticization while solvent-oligomer interaction reduces the  $T_g$  more than that observed in the case of high molecular weight polymers. The effective lowering of viscosity by a solvent can be considered in terms of the efficiency of the solvent-oligomer interaction over the oligomer-oligomer interaction as well as the reduction in  $T_g$ .

Solvents which interact with polymer segments are effective in reducing viscosity, in comparison to those which are nonfunctional or having the least interaction. In concentrated solutions, the entanglement of polymer chains contributes to the viscosity. However, the interaction of the solvent with the polymer causes facile slippage at entanglement points, consequently reducing the viscosity.

Knowledge concerning parameters which control the viscosity of multicomponent high solids facilitates the efficient use of reactive solvents. The models suggested by Erickson<sup>1</sup> provide information about the interaction parameters of solvent-oligomer systems. In an exhaustive review on design considerations of high solids formula-

Correspondence to: M. Yaseen.  
IICT Communication No. 3696.

tions, Hill and Wicks<sup>2</sup> described various aspects of the flow behavior of high solids. They also reported on the findings of Burrell<sup>3</sup> that hydrogen-bond-acceptor solvents reduced the viscosity of hydroxy functional oligomers more rapidly than did non-hydrogen-bond-acceptor solvents.

Wicks and Fitzgerald<sup>4</sup> tested Erickson's equation as a model for viscosity dependence on the concentration of oligomeric butyl methacrylate and oligomeric methyl methacrylate in *m*-xylene. They found by regression analysis moderately high correlation factors ( $r^2 > 0.96$ ) and the plots of residuals vs.  $w_0$  showed curvature. On modifying Erickson's equation by adding a second term to the denominator, they got higher correlation factors ( $r^2 > 0.999$ ) with more random scattering of residuals. Bauer and Briggs<sup>5</sup> used Erickson's equation to calculate the reduction in viscosity of a resin during the initial stages of curing and found a subsequent viscosity increase dependent on the viscosity and molecular weight relationship.

With structural similarity of the solute and solvent, the molecular chains uncoil to a great extent and provide a larger surface area to accommodate more solids in a solvent. These characteristics are better defined in terms of a partial cohesion parameter,  $\delta_H$  (contribution due to hydrogen bonding) of the two components. The ability of a system to eliminate oligomer-oligomer linkage is greater for hydrogen-bond-acceptor solvents, which tends to compensate for their lower  $\delta_H$ .

McKay et al.<sup>6,7</sup> found that methyl ethyl ketone (MEK) was the most effective among numerous common solvents tested for the viscosity reduction of hydroxyl bearing high solids oligomers. Sherwin et al.<sup>8</sup> reported that  $\Delta\delta$  has only a minor effect on the intrinsic viscosity and on the relative viscosity of concentrated solutions when concentration is expressed in terms of the volume fraction. According to Erickson,<sup>1</sup>  $[\eta]_w$  depends, in part, on the  $\Delta\delta$  between the oligomer and solvent. Oligomer segments interact mainly with the solvent and the oligomer molecules adopt an extended conformation when the cohesion parameters of the oligomer and solvent do not differ much from each other (i.e.,  $\Delta\delta \rightarrow 0$ ). With increase in the  $\Delta\delta$  oligomer, segments first interact intramolecularly and then intermolecularly, which favors more compact conformation, finally resulting in a cluster formation.

In this study, the viscosity vs. concentration data of oligomer-solvent systems were analyzed

with the help of semiempirical Erickson's models to derive various parameters and to estimate the suitability of solvents for oligourethane diols. The difference in the three-dimensional cohesion parameters of the oligomer and solvent,  $\Delta\delta$ , was calculated by using Hoy's method<sup>9</sup> to estimate the solvent-oligomer interaction component,  $I_{[\eta]w}$ . The effectiveness of various parameters was also examined.

## EXPERIMENTAL

### Preparation of Oligourethane Diols

Seven oligourethane diols were synthesized by reacting the diols with polyisocyanates 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 the IR band at  $2250\text{ cm}^{-1}$ . Molecular weight data were obtained from a Shimadzu CR4A Chrotopac GPC unit using Waters (100 Å) columns. The details of the oligomers and their molecular weights and polydispersities are given in Table I.

### Procedure

Solutions having a different weight fraction of the resin were prepared in a solvent and stored in a room conditioned at  $25 \pm 2^\circ\text{C}$  for at least 24 h before conducting viscosity measurements at  $25 \pm 0.1^\circ\text{C}$  by using a Haake-Rotovisco RV-12 Searl-type rotational viscometer (Gebrüder Haake, Germany) with an M-500 measuring head and an NV sensor system and double-gap sensor, at different shear rates. The apparent viscosity was calculated as described in the viscometer manual.

The viscosity determination was conducted at shear rates ranging from 170 to  $2770\text{ s}^{-1}$ . However, the apparent viscosity data of oligomer solutions (40, 45, 50, 55, 60, and 80% concentration) in propanol, butanol, 2-ethoxyethanol, MIBK, and cyclohexanone determined at a shear rate of  $1385\text{ s}^{-1}$  were used for analyzing the results using Erickson's models. The reason for selecting data at a  $1385\text{ s}^{-1}$  shear rate is because it has been reported<sup>10</sup> that the rheological property data at  $1370\text{ s}^{-1}$  are found to give good correlation with brushability and film buildup. For the sake of convenience, a set of apparent viscosity vs. concentra-

**Table I** Molecular Weights and Polydispersity of Oligourethane Diols

Oligomer Code No.	Diol	Diisocyanate	$M_w$	$M_n$	$M_w/M_n$
I	1,2-Propanediol	TDI	1142	1038	1.10
II	1,2-Ethanediol	TDI	1175	1020	1.15
III	1,3-Butanediol	TDI	984	751	1.31
IV	1,2-Propanediol	IPDI	1135	1010	1.12
V	1,2-Ethanediol	IPDI	1107	987	1.12
VI	1,4-Butanediol	IPDI	1115	1015	1.10
VII	1,3-Butanediol	IPDI	1125	1035	1.08

TDI: toluenediisocyanate; IPDI: isophoronediiisocyanate.

tion data for one oligomer in different solvents is illustrated in Figure 1.

**RESULTS**

**Expressions Used for Analyzing the Results**

The following semiempirical linear relationship suggested by Erickson<sup>1</sup> for analyzing the viscosity data as a function of the weight fraction of the oligomer was used:

$$\frac{w_0}{\ln \eta_r} = \frac{1}{[\eta]_w} + k_2 w_0 \quad (1)$$

or

$$\frac{1}{\ln \eta_r} = \frac{1}{[\eta]_w w_0} + k_2 \quad (2)$$

where  $\eta_r$  is the relative viscosity;  $w_0$ , the weight

fraction of the oligomer;  $[\eta]_w$ , the weight intrinsic viscosity; and  $k_2$ , a constant.

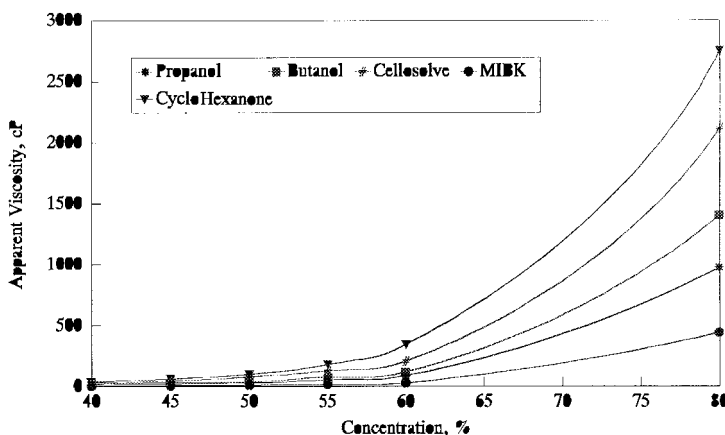
The slope of the plot which represents  $1/[\eta]_w$  was used to calculate the weight intrinsic viscosity of the oligomer with respect to a particular solvent.  $[\eta]_w$  is assumed to be composed of contributions due to the oligomer component,  $O_{[\eta]w}$ , and the solvent-oligomer interaction component,  $I_{[\eta]w}$ :

$$[\eta]_w = I_{[\eta]w} + O_{[\eta]w} \quad (3)$$

The component  $I_{[\eta]w}$  is expressed in terms of a Gaussian function<sup>1</sup>:

$$I_{[\eta]w} = \text{function of } V_s^{1/2}(\Delta\delta) \quad (4)$$

where  $V_s$  is the molar volume of the solvent, and  $\Delta\delta$ , a component of three-dimensional cohesion parameters of solvent and solute, is defined below<sup>9</sup>:



**Figure 1** Diisocyanate apparent viscosity versus concentration of oligourethane diol in propanol, butanol, cellosolve, MIBK and cyclohexanone.

**Table II** Values of Weight Intrinsic, Intrinsic Viscosities, and  $k_2$  Obtained from Eq. (1)

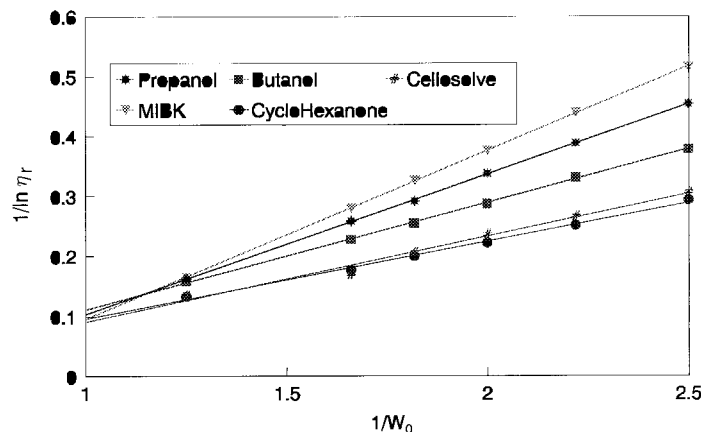
Oligomer Code no.	Solvent	$1/[\eta]_w$ Slope	$[\eta]_w$	$[\eta]$ (dL/g)	$k_2$ Intercept at $w_0 \rightarrow 1$
I	Propanol	0.241	4.144	0.515	0.100
	Butanol	0.225	4.444	0.549	0.102
	Cellosolve	0.171	5.833	0.628	0.100
	MIBK	0.244	4.100	0.512	0.090
	Cyclohexanone	0.128	7.777	0.822	0.100
II	Propanol	0.260	3.846	0.478	0.118
	MIBK	0.240	4.166	0.520	0.110
III	Propanol	0.240	4.166	0.518	0.110
	Butanol	0.213	4.688	0.579	0.113
	Cellosolve	0.250	4.000	0.431	0.110
	MIBK	0.273	3.667	0.458	0.100
	Cyclohexanone	0.152	6.562	0.694	0.108
IV	Propanol	0.234	4.275	0.532	0.102
	Butanol	0.200	5.000	0.617	0.104
	Cellosolve	0.137	7.273	0.783	0.101
	MIBK	0.295	3.387	0.423	0.091
	Cyclohexanone	0.125	8.000	0.846	0.100
V	Propanol	0.264	3.788	0.471	0.114
	Butanol	0.246	4.065	0.502	0.116
	Cellosolve	0.171	5.833	0.628	0.113
	MIBK	0.231	4.321	0.539	0.102
	Cyclohexanone	0.140	7.143	0.755	0.110
VI	Propanol	0.200	5.000	0.622	0.124
	Butanol	0.136	7.331	0.905	0.125
	Cellosolve	0.143	7.000	0.753	0.120
	MIBK	0.189	5.274	0.658	0.109
	Cyclohexanone	0.118	8.437	0.892	0.120
VII	Propanol	0.250	4.000	0.497	0.112
	Butanol	0.184	5.435	0.671	0.114
	Cellosolve	0.170	5.882	0.633	0.112
	MIBK	0.225	4.444	0.555	0.100
	Cyclohexanone	0.139	7.206	0.762	0.111

$$\Delta\delta = [(\delta_{Do} - \delta_{Ds})^2 + (\delta_{Po} - \delta_{Ps})^2 + (\delta_{Ho} - \delta_{Hs})^2]^{1/2} \quad (5)$$

Here, the cohesion parameters,  $\delta_D$ ,  $\delta_P$ , and  $\delta_H$ , depend on dispersion forces, on polar forces, and on hydrogen-bonding effects and other donor-acceptor interactions,<sup>6</sup> respectively. The subscripts "o" and "s" represent the oligomer and solvent, respectively. The three-dimensional cohesion parameters of the oligomers were calculated by using the group contribution method of Hoy et al.<sup>9,11-15</sup>

### Analysis of Practical Viscosity Data

The concentration of the oligomer solution was expressed in terms of the weight fraction,  $w_0$ . The relative viscosity,  $\eta_r$ , was calculated by dividing the apparent viscosity of solution by the viscosity of solvent. The data of  $1/\ln \eta_r$  as a function of  $1/w_0$  were plotted and the values of the slope ( $1/[\eta]_w$ ) and the intercept  $k_2$  at  $w_0 \rightarrow 1$  derived from the individual plots are reported in Table II. A set of representative plots of  $1/\ln \eta_r$  vs.  $1/w_0$  is presented in Figure 2. The plot is extrapolated to  $w_0 \rightarrow$



**Figure 2** A representative plot of  $1/\ln \eta_r$  versus  $1/W_0$ .

1, the limiting 100% concentration of oligomer in a solution. The value of intercept  $k_2$  at  $w_0 \rightarrow 1$  was used for calculating the viscosity of the oligomer with respect to a solvent. An example for the calculation of the viscosity of the oligomer code no. 1 with respect to propanol is presented here.

The plot of  $1/\ln \eta_r$  vs.  $1/w_0$  in Figure 2 intercepts the  $y$ -axis at  $1/\ln \eta_r$ ,  $k_2 \simeq 0.1$  at a limiting value  $1/w_0 = 1$  on the  $x$ -axis when  $w_0 \rightarrow 1$ , i.e., the concentration of the oligomer is almost 100% in the solution with respect to a particular solvent:

Step 1:  $1/\ln \eta_r = 0.1$ , or  $\ln \eta_r = 10$ , or  $\eta_r = 22026$ .

Step 2:

$$\eta_r = \frac{\text{Viscosity of 100\% solution of oligomer}}{\text{Viscosity of solvent}}$$

The viscosity of propanol<sup>9</sup> (solvent) is 1.89 cP at 25°C. Hence, the viscosity of a 100% solution of the oligomer with respect to propanol is

Step 3: Viscosity of 100% oligomer solution,  $\eta_0$   
 $= \eta_r \times \text{viscosity of solvent, } \eta_s$ :

$$\eta_0 = \eta_r \times \eta_s = 22026 \times 1.89 = 41630 \text{ cP}$$

The data of the viscosity of the oligomer at 100% solids with respect to a solvent derived from the intercept at  $w_0 \rightarrow 1$  are reported in Table III. The cohesion parameters  $\delta_D$ ,  $\delta_P$ ,  $\delta_H$ , and  $\delta_{\text{Total}}$  of the oligomers calculated by using Hoy's method are reported in Table IV. The reported partial and total cohesion parameters of solvents are listed in

Table V. The values of  $\Delta\delta$  calculated by using the difference between cohesion parameters of the oligomer and solvent as per eq. (5), the reported value of  $V_s^{1/2}$  of solvents, the values of  $I_{[\eta]w}$ , the solvent-oligomer interaction component derived from eq. (4), and  $[\eta]_w$  are reported in Table VI.

## DISCUSSION

### Apparent Viscosity

In general, the ability of a fluid to resist flow is specifically defined in terms of the coefficient of viscosity or apparent viscosity. The solvent power of a liquid is closely associated with the viscosity data: The greater the solvent power, the lower the viscosity of its solution.

The apparent viscosity of a concentrated oligomer solution was found to be influenced more by the type of solvent rather than by the viscosity of the solvent. For example, the difference in the apparent viscosity of 50% oligomer solutions in cyclohexanone and in other solvents is not very significant, whereas the viscosity of solutions which contain 80% oligomer and 20% cyclohexanone is much higher compared to other solutions having the same concentration (Fig. 1).

According to Erickson's equation,  $[\eta]_w$  is low for systems having lower  $\eta_r$ . Since the viscosity of MIBK is low, the relative viscosity,  $\eta_r$ , of the oligomer solution in it is likely to be of a lower order, especially in the case of dilute solutions. However, in concentrated solutions, the solvent content decreases with the oligomer content; consequently,

**Table III Viscosity of 100% Oligomer Concentration with Respect to Individual solvents Derived from the Intercept of the Plot of Eq. (1) at Weight Fraction  $w_0 \rightarrow 1$**

Oligomer Code No.	Solvent	$k_2$ Intercept at $w_0 \rightarrow 1$	Viscosity (cP)
I	Propanol	0.100	41630
	Butanol	0.102	45442
	Cellosolve	0.100	40749
	MIBK	0.090	37838
	Cyclohexanone	0.100	39647
II	Propanol	0.188	9056
	Butanol	0.120	10442
	MIBK	0.106	7072
III	Propanol	0.110	16770
	Butanol	0.113	17498
	Cellosolve	0.110	16417
	MIBK	0.100	15276
	Cyclohexanone	0.109	17363
IV	Propanol	0.102	34217
	Butanol	0.104	37634
	Cellosolve	0.101	36908
	MIBK	0.091	33489
	Cyclohexanone	0.101	35910
V	Propanol	0.114	12192
	Butanol	0.116	13918
	Cellosolve	0.113	12897
	MIBK	0.102	10238
	Cyclohexanone	0.112	13580
VI	Propanol	0.124	6009
	Butanol	0.125	7482
	Cellosolve	0.121	7184
	MIBK	0.109	5455
	Cyclohexanone	0.121	6990
VII	Propanol	0.112	14260
	Butanol	0.114	16191
	Cellosolve	0.111	15126
	MIBK	0.100	12456
	Cyclohexanone	0.110	15974

the  $\eta_r$  of the solution is not influenced much by the solvent viscosity.

#### Limiting Viscosities, $[\eta]_w$ and $[\eta]$

The effectiveness of a solvent in reducing the viscosity of oligomers can be analyzed in terms of  $[\eta]_w$ , the weight intrinsic viscosity. It is observed that the values of  $[\eta]_w$  for the oligomer solution in propanol and MIBK are relatively of a lower

order and do not differ much from each other (Table II). In other words, both the solvents are equally good in reducing the viscosity of the oligomer solutions. The high values of  $[\eta]_w$  for an oligomer solution in cyclohexanone indicate that cyclohexanone is not so effective in reducing the viscosity of the oligomer solutions.

The data of  $[\eta]_w$  and  $[\eta]$  values of oligomers in various solvents show a gradual increase from propanol to cellosolve and MIBK to cyclohexanone. This may be due to better interaction of oligomer segments with solvents which have an extended conformation of oligomer molecules in propanol compared to cellosolve and similarly with MIBK compared to cyclohexanone. This extended conformation causes an increase in  $[\eta]_w$  which produces an increase in  $[\eta]$ . Toussaint and Szigetvari reported<sup>16</sup> that the best reducing viscosity power solvents for solutions of hydroxylated oligomers are ketones.

Based on the hydrogen-bonding cohesion parameters, ( $\delta_H$ ) propanol (alcohols), being a hydrogen-bond donor and acceptor, may be expected to replace oligomer-oligomer hydrogen bonds effectively, but it is observed that MIBK reduces the oligomer solution viscosity more effectively than does propanol, despite a much lower  $\delta_H$ . The effectiveness of MIBK (being a proton acceptor only) in reducing the viscosity could be due to its greater ability in eliminating oligomer-oligomer linkage. This was explained by Hill and Wicks<sup>2</sup> in that solvents that can accept, but not donate, hydrogen bonds may be more effective in replacing oligomer-oligomer interactions than are solvents that can donate and accept hydrogen bonds.

#### Limiting Viscosity of 100% Oligomer Solution, $[\eta]_0$

Details about the estimation of  $\eta_0$  from the intercept ( $1/\ln \eta_r$ ) at  $w_0 \rightarrow 1$  were explained in the Results section. The viscosity data of the 100% oligomer do differ from each other with respect to individual solvents; however, the difference is within estimation limits (Table IV). This outcome of Erickson's equation could be utilized in determining the viscosity of oligomers which are usually viscous. The reproducible viscosity data of highly viscous polymers/oligomers (100% solids) could only be obtained by using precise and sophisticated rotational or plate viscometry. The use of Erickson's equation in the present study provides a method in which the viscosity data of a polymer solution obtained by using a simple ro-

**Table IV Partial and Total Cohesion Parameter Values of Oligomers Calculated by Hoy's Method<sup>9</sup>**

Oligomer Code No.	Cohesion Parameters in MPa <sup>1/2</sup>			
	$\delta_D$	$\delta_P$	$\delta_H$	$\delta_{Total}$
I	26.777	15.021	15.374	34.34
II	28.775	16.196	17.579	37.41
III	25.877	14.405	14.318	25.88
IV	23.849	12.231	13.612	30.06
V	25.533	13.366	15.552	32.75
VI	23.907	11.905	13.544	29.94
VII	23.374	11.743	12.953	29.19

tational viscometer can be used for the estimation of the viscosity of highly viscous polymers/oligomers. Wicks et al.<sup>17</sup> also calculated the viscosity of solvent-free oligomers by setting  $w_0 \rightarrow 1$  and found that the viscosity of solvent-free oligomer increased with molecular weight.

#### Interaction Component, $I_{[\eta]w}$

The large difference between partial cohesion parameters of MIBK and oligomers results in a relatively high value of  $\Delta\delta$ . The imperfect match between  $\delta$  values of oligomers and solvents results in compact conformations of oligomer segments and low viscosity for oligomer-solvent systems having relatively high  $\Delta\delta$  values.

The interaction component of oligomer and solvent,  $I_{[\eta]w}$ , a function of  $\Delta\delta$  and the molar volume [eq. (4)], is found to be of greater magnitude in the case of MIBK compared to  $I_{[\eta]w}$  values with respect to other solvents. The high value of  $I_{[\eta]w}$  for oligomers in MIBK indicates that the interaction of MIBK with an oligomer is not so good, whereas MIBK, being a proton acceptor, is effective in reducing the viscosity of oligomers because

of its ability to eliminate the oligomer-oligomer linkage.

The low values of  $I_{[\eta]w}$  for oligomer-propanol systems indicate that propanol has a relatively better interaction with the oligomer. It has been reported that, when  $I_{[\eta]w}$  is low, the optimum association between the solvent and oligomer results in a large hydrodynamic volume and radius of gyration.<sup>1</sup> The high magnitude of  $I_{[\eta]w}$  results in weakening of the solvent-oligomer linkages and more intraoligomer segment-to-segment contact occurs. At a limiting high  $I_{[\eta]w}$  value, the solution attains the  $\theta$ -state and may tend to separate into two phases. Mangaraj et al.<sup>18</sup> also reported that the  $[\eta]$  of polymer solutions in solvents of similar structure decreases with respect to the increase in  $V_s^{1/2}(\delta_p - \delta_s)$ . The large difference between  $\delta_p$  and  $\delta_s$  may lead to incompatibility between solute and solvent. Wicks et al.<sup>17</sup> also claimed the indication of the  $\theta$ -condition with decrease in the  $[\eta]$  of the polymer solution.

#### CONCLUSIONS

The concentration dependence of oligomer solutions is observed to follow Erickson's semiempiri-

**Table V Reported Partial and Total Cohesion Parameters of Solvents<sup>15</sup>**

Solvent	Cohesion Parameters in MPa <sup>1/2</sup>			
	$\delta_D$	$\delta_P$	$\delta_H$	$\delta_{Total}$
Propanol	15.9	6.8	17.4	24.5
Butanol	16.0	5.7	15.8	23.3
Cellosolve	16.1	9.2	14.3	24.3
MIBK	15.3	6.1	4.1	17.5
Cyclohexanone	19.7	8.4	5.1	20.2

**Table VI** Values of  $\Delta\delta$ ,  $V_s^{1/2}$ ,  $I_{[\eta]w}$ , and  $[\eta]_w$ 

Oligomer Code No.	Solvent	$\Delta\delta$ (cal/cc) <sup>1/2</sup>	$V_s^{1/2}$ (cc/mol) <sup>1/2</sup>	$I_{[\eta]w}$	$[\eta]_w$
I	Propanol	6.63	8.78	58.23	4.14
	Butanol	6.96	9.56	66.65	4.44
	Cellosolve	5.97	9.84	58.71	5.83
	MIBK	8.99	11.17	100.48	4.10
	Cyclohexanone	6.90	9.92	68.44	7.77
II	Propanol	7.79	8.78	67.33	3.84
	Butanol	8.13	9.56	77.74	4.65
	Cellosolve	7.25	9.84	71.38	—
	MIBK	10.54	11.17	117.81	4.16
	Cyclohexanone	8.45	9.92	83.81	—
III	Propanol	6.31	8.78	54.57	4.17
	Butanol	6.45	9.56	61.76	4.69
	Cellosolve	5.41	9.84	53.26	4.00
	MIBK	8.25	11.17	92.26	3.67
	Cyclohexanone	6.17	9.92	61.17	6.56
IV	Propanol	5.05	8.78	43.70	4.27
	Butanol	5.10	9.56	48.82	5.00
	Cellosolve	4.08	9.84	40.15	7.27
	MIBK	6.93	11.17	77.47	3.38
	Cyclohexanone	4.99	9.92	49.53	8.00
V	Propanol	5.77	8.78	49.86	3.79
	Butanol	5.98	9.56	57.26	4.06
	Cellosolve	5.08	9.84	49.95	5.83
	MIBK	8.30	11.17	92.80	4.32
	Cyclohexanone	6.33	9.92	62.83	7.14
VI	Propanol	5.01	8.78	43.29	5.00
	Butanol	5.03	9.56	48.16	7.33
	Cellosolve	4.05	9.84	39.89	7.00
	MIBK	6.86	11.17	76.66	5.27
	Cyclohexanone	4.92	9.92	48.79	8.44
VII	Propanol	4.90	8.78	42.38	4.00
	Butanol	4.86	9.56	46.52	5.43
	Cellosolve	3.82	9.84	37.62	5.88
	MIBK	6.47	11.17	72.34	4.44
	Cyclohexanone	4.54	9.92	45.05	7.21

cal models. The parameters like solvent viscosity,  $[\eta]_w$ , hydrogen-bonding cohesion parameters, and the difference in the three-dimensional cohesion parameter of the solute and solvent are found to be interrelated to the effectiveness of a solvent in reducing the viscosity of the oligomer solution. The solvent free viscosity of the oligomer,  $\eta_0$ , estimated from the plot of  $1/\ln \eta_r$  vs.  $1/w_0$ , is influenced by the quality of the solvent but not greatly. The solvent-oligomer interaction component, a function of  $V_s^{1/2} \Delta\delta$ , indicates the extent of interaction between the solvent and oligomer.

## REFERENCES

1. J. R. Erickson, *J. Coat. Technol.*, **48**(620), 58 (1976).
2. L. W. Hill and Z. W. Wicks, Jr., *Prog. Org. Coat.*, **10**, 55 (1982).
3. H. Burrell, Personal communication to L. W. Hill.
4. Z. W. Wicks, Jr. and L. G. Fitzgerald, *J. Coat. Technol.*, **57**(730), 45 (1985).
5. D. R. Bauer and L. M. Briggs, *J. Coat. Technol.*, **56**(716), 87 (1984).
6. G. L. McKay, Technical Report AFML-TR-79-4041,



- Air Force Materials Lab, Wright-Patterson AFB, OH, 1979.
7. J. M. Butler, R. E. Wolf, C. J. Ray, and G. L. McKay, ACS Symposium Series 132, American Chemical Society, Washington, DC, 1980, p. 132.
  8. M. A. Sherwin, J. V. Koleske, and R. A. Taller, *J. Coat. Technol.*, **53**(683), 35 (1981).
  9. D. W. Van Krevelen, *Properties of Polymers, Their Correlation with Chemical Structure, Their Numerical Estimation and Prediction from Additive Group Contributions*, Elsevier, Amsterdam, 1990.
  10. N. Sarkar and R. H. Lalk, *J. Paint Technol.*, **46**(590), 29 (1974).
  11. H. H. Nijhuis, M. H. V. Mulder, and C. A. Smolders, *J. Appl. Polym. Sci.*, **47**, 2232 (1993).
  12. D. M. Koenhen and C. A. Smolders, *J. Appl. Polym. Sci.*, **19**, 1163 (1975).
  13. T. Matsuura, P. Blais, and S. Sourirajan, *J. Appl. Polym. Sci.*, **20**, 1515 (1976).
  14. K. L. Hoy, *J. Paint Technol.*, **42**, 76 (1970).
  15. C. M. Hansen, *Ind. Eng. Chem. Prod. Res. Dev.*, **8**, 2 (1969).
  16. A. Toussaint and I. Szigetvari, *J. Coat. Technol.*, **59**(750), 49 (1987).
  17. Z. W. Wicks, G. F. Jacobs, I. C. Lin, E. H. Urutti, and L. G. Fitzgerald, *J. Coat. Technol.*, **57**(725), 51 (1985).
  18. D. Mangaraj, S. Patra, and P. C. Roy, *Makromol. Chem.*, **67**, 75 (1963).