

# Solution Behavior of Urethane Acrylate Anionomer Synthesized with Dimethylolpropionic Acid: Viscosity Prediction Through Rheological Equation of State

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**ABSTRACT:** Urethane acrylate anionomer was synthesized incorporating dimethylolpropionic acid (DMPA) on the molecular backbone as a water-soluble oligomer. The solution behavior of the urethane acrylate anionomer was examined by viscosities as a function of the shear rate, temperature, and anionomer fraction. The logarithmic viscosities of the urethane acrylate anionomer solution followed well the Arrhenius equation and showed a linear relationship with the fraction and reciprocal temperature. So, it was possible to predict the viscosity of the urethane acrylate anionomer solution as functions of the fraction and reciprocal temperature, based on the rheological equation of state. The viscosities obtained from the equation of state successfully coincided with the results of the experiments. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 69: 1079–1088, 1998

**Key words:** urethane acrylate anionomer; solution behavior; reciprocal temperature; fraction; rheological equation of state

## INTRODUCTION

Recently, ultraviolet (UV) curing technology has rapidly expanded into numerous commercial applications, including binders for magnetic media, vehicles for inks, and coatings for vinyl floor tiles, optical fibers, paper, and so on.<sup>1,2</sup> A wide range of acrylate monomers and oligomers, that is, poly(ester acrylate), epoxy acrylate, urethane acrylate, and so on, is available to meet the various application requirements. In particular, urethane acrylates have gained wide industrial interest because they impart the toughness, abrasion resistance, and elastomeric properties inherent to polyurethane acrylate to the coating.<sup>3–5</sup> However, in the course of curing, they need an organic solvent or diluent to reduce the viscosity. In many

cases, the high fraction of volatile organic compounds (VOCs) and a reactive diluent having a vinyl group were used, resulting in serious pollution problems and the diminution of coating properties of raw materials. So, in the present stage, research is being performed with the viewpoint of dispersing or solubilizing UV-curable materials in order to solve the problems of VOCs and diluents. Many studies have been introduced concerning water-dispersible and UV-curable materials to solve the problems of VOCs.<sup>4–6</sup> However, few studies have been performed concerning water-soluble and UV-curable materials.

The ultimate goal of this study was to synthesize a water-soluble urethane acrylate anionomer by incorporating dimethylolpropionic acid (DMPA) on the molecular backbone as an anionic group and to predict the viscosity of an urethane acrylate anionomer solution as a function of fraction and reciprocal temperature based on the rheological equation of state.

In all applications of water-soluble polymers, the viscosity is an important factor to be consid-

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ered for material handling and compound preparation, because the viscosity in the course of curing affects several operation controls such as the reaction kinetics, final temperature, and agitation controls. Therefore, in this study, experimental and theoretical studies for the behavior of urethane acrylate anionomer solutions were performed. The rheological equation of state was used to predict the viscosity of the anionomer solutions and compared with the experimental data.

## EXPERIMENTAL

### Reagents

Isophorone diisocyanate (IPDI, Junsei Chemical Co., Japan) was vacuum-distilled before use. Poly-(tetramethylene glycol) (PTMG,  $\overline{M}_w = 1000$  g mol<sup>-1</sup>, Hyosung BASF, Korea), dimethylolpropionic acid (DMPA, Aldrich Chemical Co., USA), triethylamine (Kanto Chemical Co., Inc., Japan), and dibutyltindilaurate were used as received. The inhibitor in 2-hydroxyethyl methacrylate (2-HEMA) was removed through a removing column (Aldrich Chemical Co.) and stored at 5°C. *N,N*-Dimethylacetamide (DMAc) was used as a solvent of DMPA and a viscosity reducer after degassing at room temperature for 48 h.

### Synthesis of Urethane Acrylate Anionomer

For the synthesis of the DMPA-incorporated urethane acrylate anionomer (DUAA), the reaction was carried out in a four-necked glass reactor equipped with a stirrer, a reflux condenser, thermocouples, and a nitrogen gas inlet system. In the first step, IPDI was poured into the glass reactor and nitrogen gas was inlet for 10 min to eliminate the residual moisture. After dissolving 1 wt % of dibutyltindilaurate, DMPA dissolved in DMAc was dropped into the reactor slowly at room temperature and the reaction temperature was increased to 80°C so that 2 mol of IPDI was reacted with 1 mol of DMPA, resulting in the molecular structure having a carboxylic acid group in the middle and isocyanates on the end sides. In this stage, care must be taken to control the molar ratio of the reaction, so as not to increase the molecular weight. This temperature was maintained for 4 h to retain an acceptable rate of reaction. The change of the NCO value during the reaction was determined using a dibutylamine back-titra-

tion method to determine the end point of the reaction.<sup>7</sup>

In the second step, 0.5 mol of PTMG was added slowly into the reactor to incorporate the soft segment into the molecular backbone using the same method as of the first step and reacted for 4 h at 80°C. In the last step, after dissolving 1 wt % dibutyltindilaurate into the reactor, 2 mol of 2-HEMA was reacted to the residual NCO group at 45°C for 12 h, which introduces a reactive vinyl group in the molecular ends. The reaction end point was determined by the disappearance of the NCO stretching peak (2270 cm<sup>-1</sup>) through IR spectroscopy.

To purify DMAc, unreacted 2-HEMA, and DMPA, the reaction mixture was precipitated from the water and filtered several times to give a crude product. The crude product was dried *in vacuo*. The carboxylic acid group of DUAA was ionized with an appropriate amount of triethylamine at room temperature for 1 h. The reaction procedure and molecular structure of DUAA are shown in Scheme 1.

### Preparation of Urethane Acrylate Ionomer Solution

Ten grams of DUAA was placed in a 100 mL beaker and stirred vigorously with a mechanical stirrer and deionized water was dropped continuously. With the amount of deionized water, the fraction of DUAA in water was controlled.

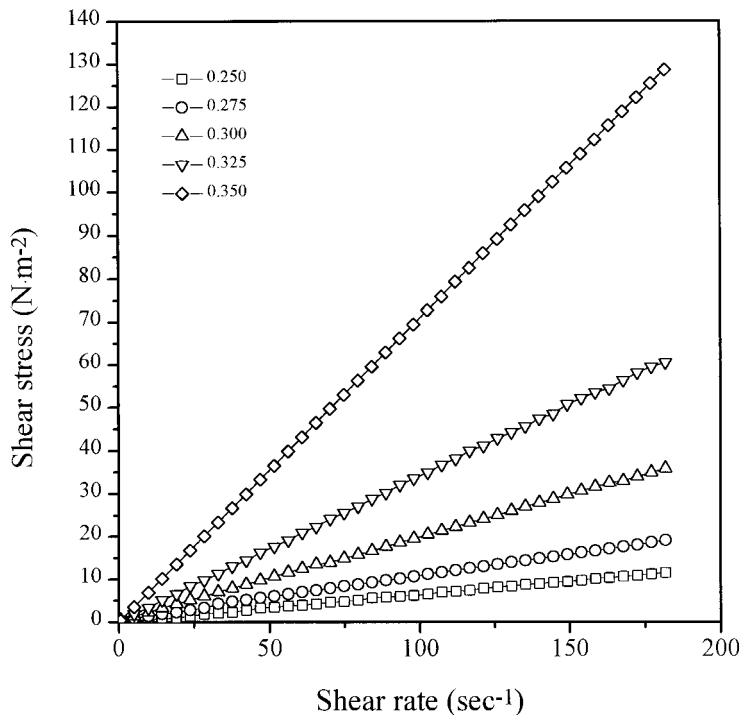
### Measurements

Molecular weight distributions of DUAA were measured by a Model 410 GPC equipped with Styragel HR 1–4 columns from Waters Associates at 25°C. The flow rate of the carrier solvent, THF, was 0.5 mL min<sup>-1</sup>. The average molecular weights of DUAA were calculated on the basis of the molecular weight versus retention volume curve of monodisperse polystyrene standards and were  $\overline{M}_w = 10,572$  g mol<sup>-1</sup> and  $\overline{M}_n = 7,997$  g mol<sup>-1</sup>. The index of polydispersity (IP) was 1.32.

The 200 MHz <sup>1</sup>H-NMR spectra were recorded with a Varian Gemini spectrometer, and the <sup>13</sup>C-NMR spectra were obtained on solutions in CDCl<sub>3</sub> using a JEOL GX400 spectrometer operating at 100 MHz for carbon. Chemical shifts were calculated relative to CDCl<sub>3</sub>: 77.0 ppm.

The viscosity of the DUAA solution was measured with a Brookfield synchroelectric viscometer, Model RVRH. The temperature of the solution was varied from 10 to 50°C with an accuracy of





**Figure 2** Shear stress versus shear rate for DUAA in solutions of different fractions at the temperature of 30°C.

such results, it was reasonable to expect that the urethane acrylate molecule designed was synthesized.

#### Solution Behavior as a Function of DUAA Fraction and Temperature

The viscosity of a polymer solution including a water-soluble polymer depends on the following factors: temperature,<sup>8-11</sup> polymer fraction,<sup>12-15</sup> polymer molecular weight, and polymer miscibility.<sup>16-18</sup> Especially, in a coating formulation, the polymer fraction and temperature are major factors to be considered in viscosity control. In this study, therefore, the viscosity behavior for the water-soluble urethane acrylate anionomer (DUAA) solution was studied with respect to the fraction, which is proper for the coating formulation together with the temperature and predicted on the basis of the rheological equation of state.

Figure 2 shows the shear stress versus shear rate for the DUAA solution with the fraction of DUAA at the temperature of 30°C. All the curves in Figure 2 are linear, indicating that the shear stress of the DUAA solution was shear rate-independent below the resin fraction of 0.35. Figure 3 shows the shear stress versus shear rate for the DUAA solution with the temperature at the

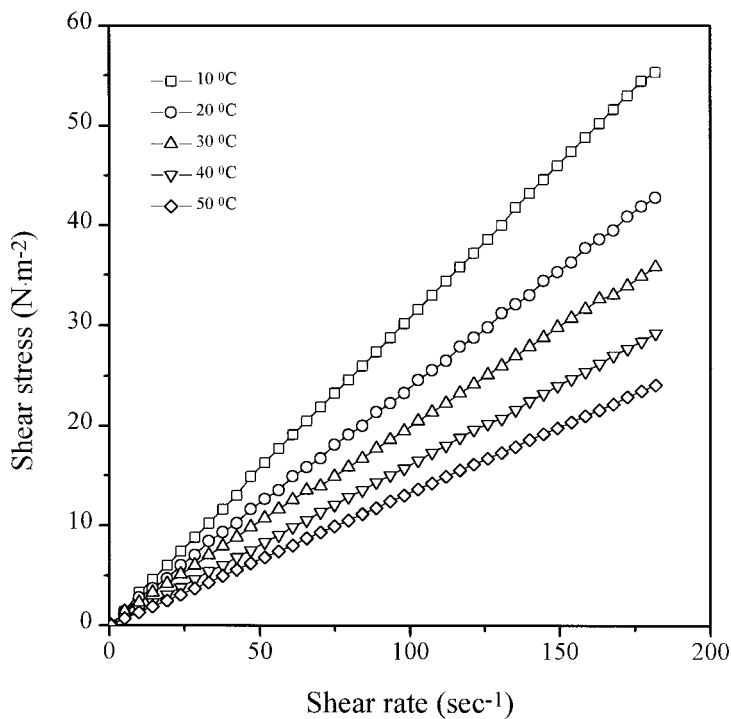
DUAA fraction of 0.30. Similarly, all the curves of Figure 3 are linear, representing that the shear stress was also shear rate-independent within a given temperature range. The viscosities were measured below the temperature of 50°C, because the vinyl groups of the DUAA molecular ends polymerized in the course of measuring the viscosities.

The viscosity of the DUAA solution of different DUAA fractions is shown as a function of temperature in Figure 4. The viscosity of the DUAA solution with temperature was correlated using the Arrhenius equation:

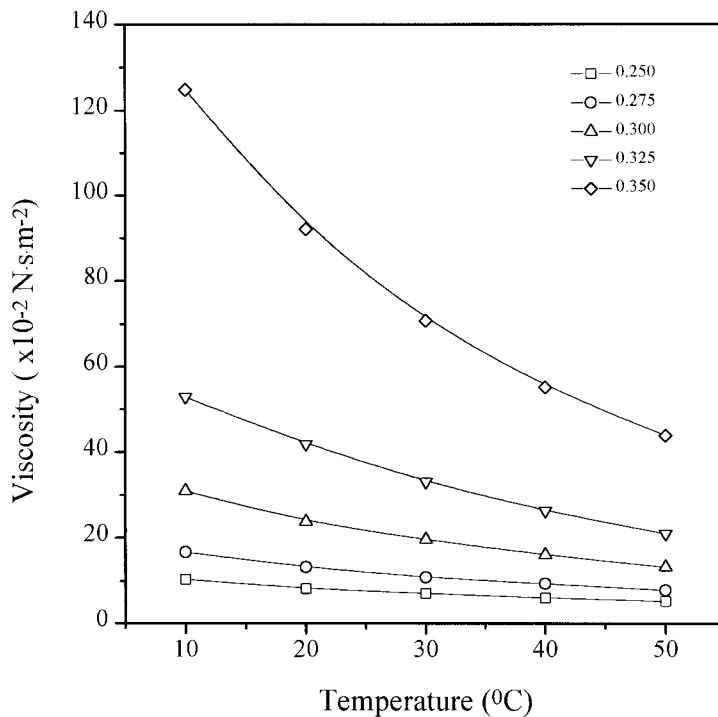
$$\eta_0 = \eta_\infty e^{E/RT} \quad (1)$$

$$\ln \eta_0 = \ln \eta_\infty + E/RT \quad (2)$$

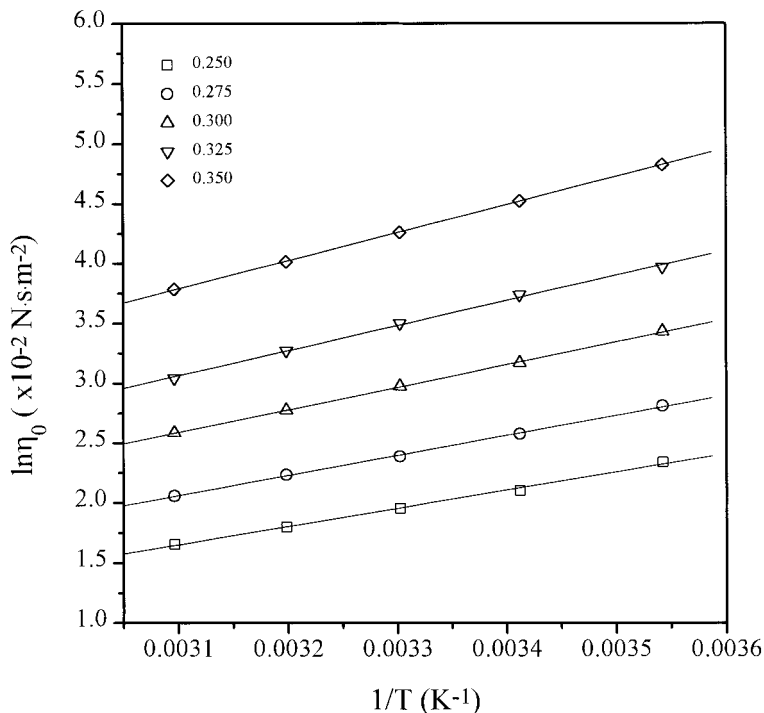
where  $\eta_0$  is the solution viscosity;  $\eta_\infty$ , the infinite viscosity;  $E$ , the activation energy of the solution;  $R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ ; and  $T$ , the temperature in K. Therefore, the results of Figure 4 were rearranged as the logarithmic viscosity versus the reciprocal of temperature and are shown in Figure 5. The viscosity points were regressed linearly, showing that the DUAA solution viscosity followed well the Arrhenius equation for given compositions. The slope of the line represents the acti-



**Figure 3** Shear stress versus shear rate for DUAA solutions of different temperatures at the DUAA fraction of 0.30.

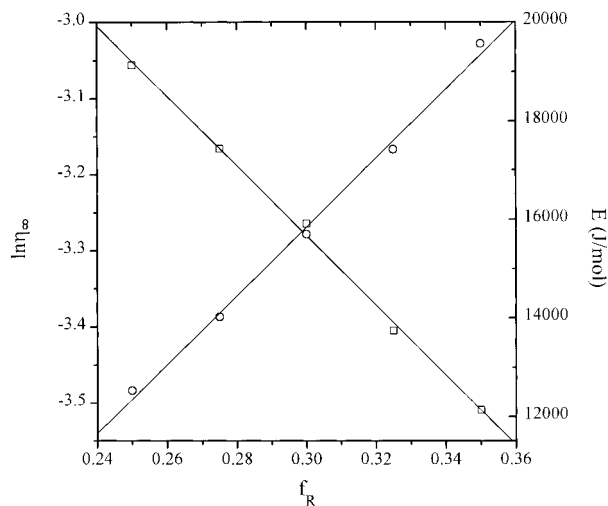


**Figure 4** Viscosity of DUAA solution of different DUAA fractions as a function of temperature.



**Figure 5** Logarithmic viscosity versus reciprocal temperature.

vation energy and the Y-axis intercept shows the logarithmic of infinite viscosity,  $\ln \eta_\infty$ . The  $\ln \eta_\infty$  and the activation energy for the DUAA solution are shown with the fraction of DUAA,  $f_R$ , in Figure 6. We could obtain the result of the increasing activation energy and decreasing  $\ln \eta_\infty$  with the fraction of DUAA. This reflected that the molecular interactions had an effect on the viscosity behavior of the DUAA solution.<sup>13-15</sup> It was of inter-



**Figure 6** DUAA fraction versus the logarithmic viscosity and the activation energy (J/mol): (—○—) activation energy; (—□—)  $\ln \eta_\infty$ .

est to note that the activation energy and  $\ln \eta_\infty$  showed a linear relationship with the fraction for a given fraction region. This suggested that intramolecular and intermolecular interactions coexist. The intermolecular interaction induced by the hydrogen bond and the hydrophobic attraction of polyethers can raise the viscosity of the DUAA solution while intramolecular interaction generated by the Coulombic force of the ionic groups incorporated (polyelectrolyte effect) can collapse the coil, lowering the viscosity. However, in our study, we could find that above the fraction of 0.35 the activation energy and  $\ln \eta_\infty$  deviated from the linear relationship, which means that the DUAA chains interact intermolecularly radially to form species with a larger hydrodynamic volume, resulting in a sharp viscosity increase.<sup>12</sup>

**Consideration of Rheological Equation of State**

From the linear relationship of  $\ln \eta_\infty$  and the activation energy with the fraction of DUAA in solution,  $\ln \eta_\infty$ , the activation energy could be empirically expressed as a function of the fraction. Therefore, it was possible to depict the following:

$$E = E_1 + E_2 f_R \tag{3}$$

$$\ln \eta_\infty = a_1 + a_2 f_R \tag{4}$$

where  $E_1$  is the extrapolated activation energy;  $E_2$ , the slope of Figure 6;  $a_1$ , the extrapolated infinite viscosity; and  $a_2$ , the slope of Figure 6. Substituting eq. (3) and (4) into eq. (1), one could obtain

$$\begin{aligned}\eta_0 &= e^{(a_1+a_2f_R)}e^{(E_1+E_2f_R)/RT} \\ &= e^{(a_1+E_1/RT)}e^{(a_2+E_2/RT)f_R}\end{aligned}\quad (5)$$

Therefore, the following functional relationship was possible:

$$\eta_0 = f(f_R, 1/T) \quad (6)$$

That is, the viscosity of the urethane acrylate anionomer solution could be expressed as functions of the fraction and reciprocal temperature.

Taking the mutual log of both sides of eq. (5) gave

$$\ln \eta_0 = a_1 + E_1/RT + (a_2 + E_2/RT)f_R \quad (7)$$

The derivative  $[\partial \ln \eta_0 / \partial (1/T)]_{f_R}$  at a fixed fraction has the form

$$[\partial \ln \eta_0 / \partial (1/T)]_{f_R} = (E_1 + E_2f_R)/R \quad (8)$$

The derivative  $[\partial \ln \eta_0 / \partial f_R]_{1/T}$  at a fixed temperature has the form

$$[\partial \ln \eta_0 / \partial f_R]_{1/T} = a_2 + E_2/RT \quad (9)$$

The thermodynamic criterion for eq. (7) shows

$$\begin{aligned}\partial^2 \ln \eta_0 / \partial (1/T) \partial f_R &= \partial^2 \ln \eta_0 / \partial f_R \partial (1/T) \\ &= E_2/R\end{aligned}\quad (10)$$

To verify that eq. (7) is the thermodynamic equation of state, the derivatives,  $J$  and  $D$ , for the DUAA solution must be determined experimentally:

$$J = \partial^2 \ln \eta_0 / \partial (1/T) \partial f_R \quad (11)$$

$$D = \partial^2 \ln \eta_0 / \partial f_R \partial (1/T) \quad (12)$$

### Viscosity Prediction Through Rheological Equation of State

To verify that eq. (7) is the rheological equation of state,  $J$  and  $D$  could be obtained by the following procedure: The slopes in Figure 5 represent  $(E_1 + E_2f_R)/R$ . Therefore, the values of  $(E_1 + E_2f_R)/R$  at different  $f_R$  could be determined and plotted

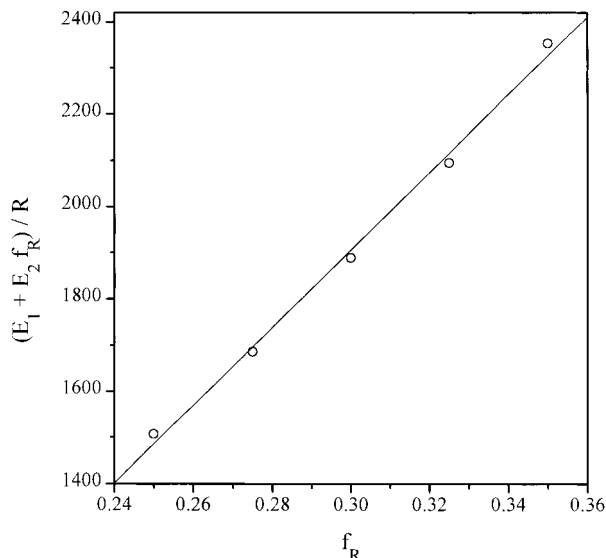


Figure 7 DUAA fraction versus  $(E_1 + E_2f_R)/R$ .

against  $f_R$  in Figure 7. The slope in Figure 7 corresponds to the  $J$  of eq. (11). The  $J$  obtained had the value of 8407.030.

The logarithmic viscosity versus the DUAA fraction is shown for different temperatures in Figure 8, resulting in that the logarithmic viscosity is linear-regressed. From the slope in Figure 8, the values of  $a_2 + E_2/RT$  were determined and plotted against the reciprocal temperature in Figure 9. The slope in Figure 9 corresponds to the  $D$  of eq. (12). The  $D$  obtained had the value of 8423.530.

The negligible difference between  $J$  and  $D$  could be obtained, indicating that eq. (7) satisfied the thermodynamic criterion. This result suggested that the DUAA solution followed well the thermodynamic equation of state, and the rheological equation of state, eq. (7), was the state functions of the fraction and temperature.

By taking the average value of  $J$  and  $D$ , 8415.280 could be obtained. The constants of  $E_1/R$  in eq. (8) and  $a_2$  in eq. (9) could be calculated using the results in Figures 7 and 9. The  $E_1/R$  and  $a_2$  calculated were  $-618,818$  and  $-4.893$ , respectively. Also, the value of  $a_1$  in eq. (7) could be calculated using the value of  $E_1/R$  and  $a_2$ , and  $a_1$  showed the value of  $-1.812$ . From the constants of  $E_1/R$ ,  $a_2$ , and  $a_1$ , eq. (7) could be expressed again as the following:

$$\begin{aligned}\ln \eta_0 &= -1.812 - 618.818/T \\ &\quad + (-4.893 + 8415.280/T)f_R\end{aligned}\quad (13)$$

The logarithmic viscosities measured were

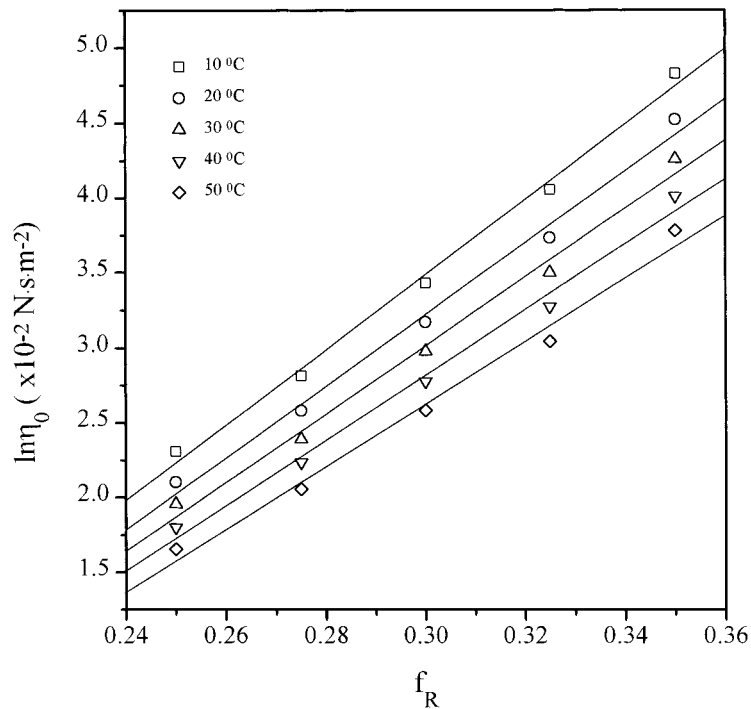


Figure 8 Logarithmic viscosity versus DUAA fraction.

compared with the logarithmic viscosities calculated from eq. (13) as functions of the DUAA fraction and reciprocal temperature in Figure 10. Also, the data fitted are listed in Table I. The experimental error was within the maximum of 6.117%. The viscosities calculated from the rheological equation of state of eq. (13) showed good correspondence to the viscosities measured. From this result, the rheological equation of state could

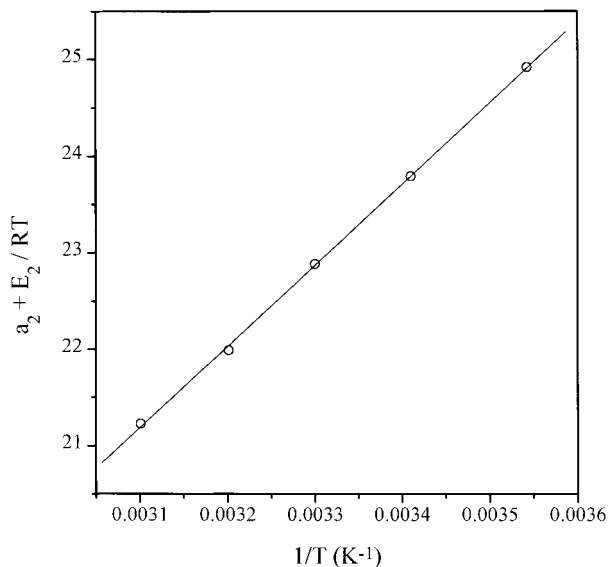


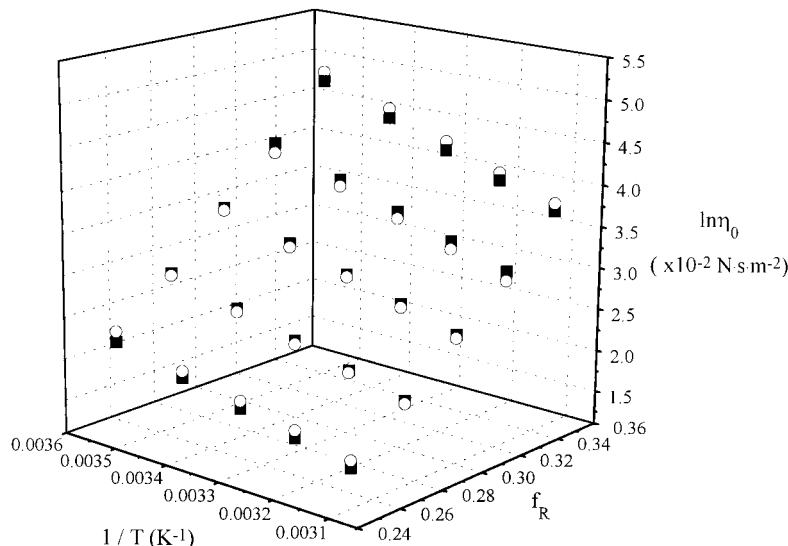
Figure 9  $1/T$  versus  $a_2 + E_2/RT$ .

be used for predicting the viscosities of the DUAA solution successfully.

In the DUAA viscosity behavior, it is notable that the viscosity of the DUAA aqueous solution was predicted within the fraction range where the coating formulation is applicable. This viscosity prediction was possible because the  $\ln \eta_\infty$  and the activation energy showed a linear relationship with the fraction of DUAA.

In general, it has been known that ionomers in aqueous media show unique behaviors: a polyelectrolyte effect and an intermolecular interaction.<sup>13–15,19</sup> Lundberg and Makowski<sup>13</sup> and Hara and Wu<sup>14</sup> showed that at low concentration there was a viscosity increase, which was interpreted by the intramolecular repulsion between fixed ions in the polymer chain. However, at high concentration, the viscosity behavior was dominated by an intermolecular interaction, resulting in a sharp viscosity increase. The viscosity behavior of the ionomers is also influenced by the ion content, molecular weight of the polymer, hydrophobicity of the polymer chain, and the temperature.<sup>19</sup> Especially, as the molecular weight and hydrophobicity of the ionomers increased, the intermolecular interaction has the trend to be more enhanced. At the present stage, the viscosity prediction of the aqueous ionomer solution is difficult, because of these many interaction parameters.





**Figure 10** Logarithmic viscosity versus DUAA fraction and reciprocal temperature: (—○—) measured value; (—■—) calculated value from eq. (13).

The DUAA prepared in this study is a hydrophobically modified ionomer. However, it should be noted that the molecular weight of DUAA is considerably low, of about 10,000 g mol<sup>-1</sup>, sug-

gesting that the intermolecular interaction resulting in the viscosity increase can be diminished by this low molecular weight of DUAA. Therefore, even though DUAA had a hydrophobic segment

**Table I** Comparison of ln η₀ Measured with ln η₀ Calculated

$f_R$	$1/T$ (K <sup>-1</sup> )	ln η₀ (Experimental)	ln η₀ (Theoretical)	Error %
0.250	0.00353	2.342	2.207	6.117
0.250	0.00341	2.103	2.029	3.647
0.250	0.00330	1.954	1.865	4.772
0.250	0.00319	1.801	1.702	5.817
0.250	0.00310	1.655	1.568	5.548
0.275	0.00353	2.815	2.827	0.424
0.275	0.00341	2.580	2.624	1.677
0.275	0.00330	2.389	2.437	1.970
0.275	0.00319	2.234	2.251	0.755
0.275	0.00310	2.057	2.098	1.954
0.300	0.00353	3.431	3.447	0.464
0.300	0.00341	3.170	3.219	1.522
0.300	0.00330	2.974	3.009	1.163
0.300	0.00319	2.775	2.799	0.857
0.300	0.00310	2.584	2.628	1.674
0.325	0.00353	3.969	4.068	2.434
0.325	0.00341	3.734	3.814	2.098
0.325	0.00330	3.497	3.581	2.346
0.325	0.00319	3.272	3.348	2.270
0.325	0.00310	3.043	3.158	3.642
0.350	0.00353	4.828	4.688	2.986
0.350	0.00341	4.523	4.409	2.586
0.350	0.00330	4.260	4.153	2.576
0.350	0.00319	4.011	3.897	2.925
0.350	0.00310	3.782	3.688	2.549

in its molecular backbone, it did not show a shear viscosity increase in the broad fraction range (from 0.25 to 0.35).

## CONCLUSIONS

The logarithmic viscosities of a DMPA-incorporated urethane acrylate anionomer (DUAA) synthesized as a water-soluble urethane acrylate showed a linear relationship with the fraction of DUAA and the reciprocal temperature. By using the functional relationship between the logarithmic viscosity and the fraction and reciprocal temperature, a rheological equation of state could be proposed. The rheological equation of state agreed well with experiment, in comparison to the value calculated with the value of that measured and could be used for predicting the viscosities of the DUAA solution successfully.

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