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Viscosity *B* Coefficients and Activation Parameters of Viscous Flow for Hexanedioic Acid in Aqueous Dextran Solution

Yun Zhang, Tong-Chun Bai,* and Ji-Qing Xie

Department of Chemistry and Chemical Engineering, Suzhou University, Suzhou, 215123, China

Viscosity and density data for the ternary solution of hexanedioic acid + dextran 40000 + water at the temperatures (293.15, 298.15, 303.15, 308.15, and 313.15) K have been measured. On the basis of the Eyring and Feakins equation, the viscosity *B* coefficients and the activation parameters for viscous flow of the solution have been evaluated. The effect of temperature and the dextran concentration on these parameters has been discussed. With an increase in the dextran concentration, the activation free energy of viscous flow first decreases and then increases. Dextran improves the hydrophobic property of hexanedioic acid. However, the interaction between dextran and hexanedioic acid makes the flowability of the ternary solution decrease.

Introduction

The effective components of drugs are mainly hydrophobic organic compounds, and many of them show a rather low solubility and dissolution rate in water. Therefore, the dissolution enhancement of these compounds is an important task in pharmaceutical technology because it leads to better bioavailability and to more efficient application. A broad variety of solubilization methods have been developed, including the application of polymer surfactants and dispersants.[1,2] For example, dextran is commonly used as a blood plasma substitute, and it is now widely under investigation as a polymeric carrier in novel drug delivery systems.[3,4] However, introducing a polymer into water often causes change in the viscosity of the medium.

Drug diffusion rate in aqueous dispersions of polymer is basically governed by the restrictive effect of the polymer on drug mobility, whether due to a reduction in free volume or an increase in medium viscosity. Systems of this type generally show an inverse relationship between release rate and viscosity of the type predicted by the Stokes−Einstein equation, so that medium viscosity has been widely used as a routine predictor of a resistance to diffusion.[5] The macroviscosity of aqueous dispersions of polymer at some concentrations is related to drug diffusion coefficients using

$$D/D_0 = \eta_0/\eta \tag{1}$$

where η and η_0 are the viscosities of the polymer solution and of the medium without polymer, respectively. D and D_0 are diffusion coefficients for the drugs in the presence and absence of polymer, respectively.

Drug diffusion is not only related to the properties of the medium but also related to the structure and properties of the drug molecule itself and to the interaction between solute and solvents. Inspecting eq 1, it is difficult to discover the connection between viscosity and the intrinsic properties of the drug itself. Therefore, it is necessary to select a suitable parameter to express the relationship between them.

In this paper, we use the theory of activation parameters of viscous flow to express the relationship between the diffusion capacity and the viscous parameters of the medium. Viscosities of a solution composed of hexanedioic acid, a hydrophobic model compound, and dextran 40000 aqueous solution were measured at temperatures of (293.15, 298.15, 303.15, 308.15, and 313.15) K. Viscosity *B* coefficients and activation parameters of viscous flow for hexanedioic acid in aqueous dextran solution were evaluated. The effect of temperature and the dextran concentration on these parameters were also evaluated.

Activation Parameters of Viscous Flow

The measurement of the viscosities of solutions formed the basis of the studies of solute−solvent interactions. Jones and Dole[6] showed that the viscosities of dilute solutions of strong electrolytes could be represented as

$$\eta_{13}/\eta_1 = \eta_r = 1 + A\sqrt{c_3} + Bc_3 \tag{2}$$

where η_{13} and η_1 are the viscosities of the solution and solvent, respectively, and c_3 is the solute concentration. The *A* coefficient takes account of ion−ion interactions and can be calculated theoretically from the physical parameters of the solvent and the limiting ionic equivalent conductances using the Falkenhagen and Vernon equation as described by Saha and Das.[7] The *B* coefficient reflects the effects of solute−solvent interactions on the solution viscosity. For a nonassociated nonelectrolyte, solute 3, dissolved in binary solvents 1 + 2 with fixed concentration, the viscosities of dilute solutions can be represented as

$$\eta_{123}/\eta_{12} = \eta_r = 1 + Bc_3 \tag{3}$$

where the symbols have the obvious meanings.

Viscosity *B* coefficients are important for a number of reasons.[8] Their application in two research areas is interesting. First, *B* coefficients are known to provide information concerning the solvation of the solutes and their effects on the structure of the solvent in the near environment of the solute molecules. Second, since some activation parameters of viscous flow can be obtained from *B* coefficients,[9] it is possible to analyze the viscous properties on the basis of enthalpy and entropy terms. The values of *B* coefficients have been measured for a wide range of electrolytes in aqueous solutions, as well as in mixed

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* Corresponding author. E-mail: tcbai@suda.edu.cn.

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Table 1. Densities ρ/g·cm^{-3} of Dextran (2) + Water (1) and Hexanedioic Acid (3) + Water (1) Binary Solutions

m_2	ρ/g·cm^{-3}				
mol·kg^{-1}	293.15 K	298.15 K	303.15 K	308.15 K	313.15 K
			Dextran + Water		
0	0.99820	0.99704	0.99564	0.99404	0.99221
0.00574	0.99856	0.99741	0.99604	0.99440	0.99258
0.01239	0.99897	0.99781	0.99637	0.99478	0.99294
0.01493	0.99913	0.99796	0.99649	0.99489	0.99309
0.02006	0.99945	0.99825	0.99678	0.99521	0.99335
0.02523	0.99977	0.99860	0.99715	0.99555	0.99370
0.02837	0.99997	0.99876	0.99728	0.99570	0.99386
0.03404	1.00032	0.99914	0.99768	0.99606	0.99422
0.03536	1.00040	0.99927	0.99775	0.99625	0.99433
0.03935	1.00065	0.99950	0.99804	0.99643	0.99454
0.04602	1.00106	0.99989	0.99846	0.99681	0.99496
0.04985	1.00130	1.00006	0.99859	0.99699	0.99518
0.05843	1.00183	1.00064	0.99919	0.99755	0.99566
0.07208	1.00268	1.00145	0.99999	0.99831	0.99644

m_3	ρ/g·cm^{-3}	m_3	ρ/g·cm^{-3}			
mol·kg^{-1}	293.15 K	mol·kg^{-1}	298.15 K	303.15 K	308.15 K	313.15 K
			Hexanedioic Acid + Water			
0	0.99820	0	0.99704	0.99564	0.99404	0.99221
0.00708	0.99848	0.01287	0.99749	0.99607	0.99441	0.99254
0.01399	0.99872	0.01540	0.99752	0.99608	0.99445	0.99258
0.02122	0.99901	0.02570	0.99783	0.99656	0.99479	0.99289
0.02857	0.99920	0.02702	0.99791	0.99651	0.99489	0.99301
0.05669	1.00016	0.03133	0.99811	0.99664	0.99496	0.99319
0.08401	1.00095	0.03789	0.99827	0.99683	0.99517	0.99329
0.1125	1.00181	0.04282	0.99842	0.99699	0.99534	0.99345
0.1430	1.00278	0.05544	0.99881	0.99738	0.99571	0.99389
		0.06825	0.99920	0.99772	0.99607	0.99421
		0.06989	0.99921	0.99773	0.99609	0.99421
		0.08417	0.99971	0.99828	0.99655	0.99466
		0.09767	1.00015	0.99874	0.99695	0.99503
		0.1088	1.00049	0.99901	0.99725	0.99533
		0.1136	1.00066	0.99910	0.99747	0.99547
		0.1266	1.00101	0.99956	0.99779	0.99588
		0.1377	1.00133	0.99993	0.99816	0.99619

organic−aqueous solvents.[8−10] Data are available for molecules, such as amino acids and amides, in aqueous organic mixed solvent systems.[11−14] However, there are fewer reports on the data of hydrophobic solutes in solutions containing dextran.

Eyring and co-workers[15] proposed this equation

$$\eta_1 = (hN_A/V_{m1})\exp(\Delta G_{m1}^{0\neq}/RT) \tag{4}$$

to calculate the molar Gibbs free energy of activation ($\Delta G_{m1}^{0\neq}$) for the viscous flow of a pure solvent 1 in terms of its viscosity (η_1) and molar volume (V_{m1}). In eq 4, N_A and h are Avogadro's number and Planck's constant. For a solution containing a solute (3) dissolved in pure liquid (1), they proposed this equation[13]

$$\eta_{13} = (hN_A/V_{m13})\exp(\Delta G_{m13}^{\neq}/RT) \tag{5}$$

to define a common or average molar Gibbs energy of activation ($\Delta G_{m13}^{\neq}$). In eq 5, V_{m13} is the molar volume of the solution 1 + 3. For a nonassociated nonelectrolyte, solute 3, dissolved in binary solvents 1 + 2 with fixed concentration, and as $c_3 \rightarrow 0$, from eq 3 we have

$$\ln \eta_r = \ln(\eta_{123}/\eta_{12}) = Bc_3 = \ln(V_{m12}/V_{m123}) + (\Delta G_{m123}^{\neq} - \Delta G_{m12}^{\neq})/RT \tag{6}$$

where

$$\Delta G_{m123}^{\neq} = (1 - x_3)\Delta G_{m12}^{\neq} + x_3\Delta G_{m3}^{\neq} \tag{7}$$

$$V_{m123} = (1 - x_3)V_{m12} + x_3\bar{V}_3^{\infty} \tag{8}$$

In eqs 7 and 8, $\Delta G_{m12}^{\neq}$ is the average molar free energy of activation for binary solvent 1 + 2. $\Delta G_{m3}^{\neq}$ is the contribution to the free energy per mole of solute 3. $\bar{V}_3^{\infty}$ and V_{m12} are the partial molar volume of solute 3 at infinite dilution and the average molar volume of binary solvent 1 + 2, respectively. On considering the connection between x_3 and c_3, as $x_3 \rightarrow 0$, we have

$$x_3 = M_{12}c_3/\rho_{12} \tag{9}$$

where M_{12} and ρ_{12} are the average molar mass and density for binary solvent 1 + 2, respectively. Combination of eqs 6 to 9 gives

$$B = (V_{m12} - \bar{V}_3^{\infty}) + (V_{m12}/RT)(\Delta G_{m3}^{\neq} - \Delta G_{m12}^{\neq}) \tag{10}$$

For the mixed solvent 1 + 2, the average activation free energy ($\Delta G_{m12}^{\neq}$) can be calculated from their viscosity (η_{12}) via a variant of eq 5. The value of $\Delta G_{m3}^{\neq}$ can be calculated from eq 10. When solute 3 dissolves in pure solvent 1, we have $V_{m12} = V_{m1}^0$ and $\Delta G_{m12}^{\neq} = \Delta G_{m1}^{0\neq}$, respectively.

If B is known at various temperatures, we can calculate the solute molar activation enthalpy ($\Delta H_{mi}^{\neq}$) from

$$\Delta H_{m3}^{\neq} = [\partial(\Delta G_{m3}^{\neq}/T)/\partial(1/T)]_p \tag{11}$$

and the solute molar activation entropy ($\Delta S_{mi}^{\neq}$) from

$$\Delta S_{m3}^{\neq} = (\Delta H_{m3}^{\neq} - \Delta G_{m3}^{\neq})/T \tag{12}$$

Table 2. Viscosities $\eta/10^{-3}$ Pa·s of Dextran (2) + Water (1) and Hexanedioic Acid (3) + Water (1) Binary Solutions

m_2 / mol·kg^{-1}	$\eta/10^{-3}$ Pa·s 293.15 K	298.15 K	303.15 K	308.15 K	313.15 K
			Dextran + Water		
0	1.002	0.8904	0.7975	0.7194	0.6529
0.00574	1.018	0.9033	0.8122	0.7304	0.6631
0.01239	1.036	0.9216	0.8235	0.7422	0.6731
0.01493	1.043	0.9292	0.8301	0.7477	0.6768
0.02006	1.057	0.9409	0.8385	0.7563	0.6849
0.02523	1.072	0.9537	0.8517	0.7676	0.6959
0.02837	1.080	0.9591	0.8561	0.7723	0.6992
0.03404	1.096	0.9757	0.8718	0.7860	0.7116
0.03536	1.100	0.9800	0.8736	0.7868	0.7128
0.03935	1.111	0.9890	0.8820	0.7945	0.7223
0.04602	1.129	1.004	0.8990	0.8110	0.7318
0.04985	1.139	1.015	0.9053	0.8173	0.7395
0.05843	1.163	1.043	0.9305	0.8372	0.7564
0.07208	1.201	1.069	0.9617	0.8651	0.7824

m_3 / mol·kg^{-1}	$\eta/10^{-3}$ Pa·s 293.15 K	m_3 / mol·kg^{-1}	$\eta/10^{-3}$ Pa·s 298.15 K	303.15 K	308.15 K	313.15 K
			Hexanedioic Acid + Water			
0	1.002	0	0.8904	0.7975	0.7194	0.6530
0.00708	1.006	0.01540	0.8959	0.8022	0.7229	0.6559
0.01399	1.008	0.02570	0.8985	0.8060	0.7255	0.6585
0.02122	1.010	0.03133	0.9017	0.8073	0.7275	0.6600
0.02857	1.014	0.03789	0.9028	0.8085	0.7285	0.6612
0.05669	1.023	0.04550	0.9050	0.8116	0.7309	0.6625
0.08401	1.035	0.05256	0.9074	0.8134	0.7323	0.6639
0.1125	1.047	0.05776	0.9102	0.8148	0.7334	0.6643
0.1430	1.060	0.06453	0.9122	0.8157	0.7353	0.6663
		0.06989	0.9136	0.8172	0.7362	0.6674
		0.08956	0.9197	0.8233	0.7406	0.6708
		0.1136	0.9285	0.8297	0.7457	0.6754

In the opinion of Feakins et al.,[13] there are two contributions to $\Delta G_{m3}^{\neq}$. The first one is thought of as the Gibbs energy of interaction of the solute with a hypothetical transition state of viscous flow for the solvent. The effect of the solute on the Gibbs energy of activation of viscous flow for the solvent molecule is, in fact, the difference between the solvation energies of solute 3 in the ground-state solvent 1 and in the transition-state solvent 1′ or Gibbs energy of transfer, $\Delta G_{m3}^{\neq}(1-1')$. The second contribution to $\Delta G_{m3}^{\neq}$ comes from the movement of the solute through its own viscous transition state, $\Delta G_{m3}^{\neq}(3-3')$, thus

$$\Delta G_{m3}^{\neq} = \Delta G_{m3}^{\neq}(1-1') + \Delta G_{m3}^{\neq}(3-3') \qquad (13)$$

In order to estimate $\Delta G_{m3}^{\neq}(3-3')$ and then to obtain $\Delta G_{m3}^{\neq}(1-1')$, Feakins et al.[13] proposed a simple method. The Gibbs energies of activation for the conductivity of alkali−metal ions in water are in a narrow range (14−16 kJ·mol^{-1}) and close to the Gibbs energy of activation for the self-diffusion of water (14 kJ·mol^{-1}). The Gibbs energy of activation for the diffusion of *tert*-butyl alcohol (TBA) in water is also close to these values (16 kJ·mol^{-1}). This suggests a common mechanism for their movement. Feakins et al.[13] proposed that in estimating $\Delta G_{m3}^{\neq}(3-3')$ for molecules, its value is close to the Gibbs energy of activation for viscous flow of the solvent ($\Delta G_{m1}^{0\neq}$). We shall therefore use this value as a common value for all $\Delta G_{m3}^{\neq}(3-3')$. Thus the values of $\Delta G_{m3}^{\neq}(1-1')$ may be obtained from

$$\Delta G_{m3}^{\neq}(1-1') = \Delta G_{m3}^{\neq} - \Delta G_{m1}^{0\neq} \qquad (14)$$

On considering the solute diffusion in binary solvents 1 + 2 and in pure solvent 1, $\Delta G_{m3}^{\neq}(12-12')$ and $\Delta G_{m3}^{\neq}(1-1')$ might be well approximated by the corresponding activation free energy of diffusion of solute 3, respectively. Their value is affected by some parameters such as *B* coefficients, medium volume, and solute size. Among them, the *B* coefficient is a characteristic parameter of solute−solvent interaction.

Experimental Section

Materials. Dextran was used as received from the Shanghai Chemical Reagent Inc. Its purity was of reagent grade. Hexanedioic acid, analytical grade also from the Shanghai Chemical Reagent Inc. was purified by recrystallization from acetone solvent and then dried under vacuum at 393.15 K over 10 h.[16] Both reagents were then stored over P_2O_5 in a desiccator before use. Water was obtained by distilling deionized water from alkaline $KMnO_4$ solution to remove any organic matter.

Density and Viscosity Measurement. Mixtures of the desired compositions were prepared by mixing accurately weighed quantities of the material, using a TG328B balance with a precision of ± 0.1 mg. Densities were measured with an Anton Paar DMA 602 vibrating-tube densimeter. The temperature of the cell was controlled by circulation of water from a water bath with the temperature within ± 0.01 K. The densimeter was calibrated by using degassed water and dry air as calibration substances. The estimated error of density measurement is within ± 0.00002 g·cm^{-3}. The kinematic viscosities (ν) were measured by means of a suspended level Ubbelohde viscometer. The efflux time of the fluid was measured with a digital stopwatch to ± 0.01 s. The viscometer was kept in a water thermostat controlled to ± 0.01 K. The kinematic viscosity (ν) and the dynamic viscosity (η) are given by the following equations:

$$\nu = Lt - K/t \qquad (15)$$

$$\eta = \nu\rho \qquad (16)$$

where *t* is the efflux time of the fluid, ρ is the density of solution, and *L* and *K* are the characteristic constants of the viscometer.

Table 3. Densities ρ/g·cm^{-3} of the Hexanedioic Acid (3) + Dextran (2) + Water (1) Ternary Solutions

m_3	ρ/g·cm^{-3}				
mol·kg^{-1}	293.15 K	298.15 K	303.15 K	308.15 K	313.15 K
			$m_2 = 0.01239$		
0	0.99898	0.99781	0.99637	0.99478	0.99294
0.01429	0.99941	0.99829	0.99689	0.99530	0.99344
0.02803	0.99985	0.99873	0.99733	0.99568	0.99385
0.05552	1.00070	0.99956	0.99816	0.99651	0.99458
0.08367	1.00161	1.00043	0.99898	0.99732	0.99542
0.1120	1.00245	1.00122	0.99980	0.99808	0.99617
0.1403	1.00331	1.00211	1.00066	0.99896	0.99697
			$m_2 = 0.02523$		
0	0.99989	0.99860	0.99715	0.99555	0.99370
0.01452	1.00032	0.99915	0.99775	0.99604	0.99413
0.02827	1.00077	0.99953	0.99812	0.99648	0.99446
0.05554	1.00160	1.00040	0.99917	0.99728	0.99535
0.08311	1.00234	1.00110	0.99961	0.99789	0.99594
0.1118	1.00325	1.00196	1.00055	0.99873	0.99683
0.1401	1.00416	1.00290	1.00138	0.99973	0.99767
			$m_2 = 0.03404$		
0	1.00048	0.99914	0.99768	0.99608	0.99422
0.01426	1.00091	0.99974	0.99830	0.99665	0.99464
0.02768	1.00135	1.00021	0.99875	0.99709	0.99503
0.05571	1.00226	1.00109	0.99957	0.99794	0.99584
0.08353	1.00311	1.00194	1.00047	0.99859	0.99665
0.1122	1.00401	1.00283	1.00127	0.99960	0.99739
0.1405	1.00489	1.00360	1.00212	1.00041	0.99827

Table 4. Viscosities $\eta/10^{-3}$ Pa·s of the Hexanedioic Acid (3) + Dextran (2) + Water (1) Ternary Solutions

m_3	$\eta/10^{-3}$ Pa·s				
mol·kg^{-1}	293.15 K	298.15 K	303.15 K	308.15 K	313.15 K
			$m_2 = 0.01239$		
0	1.028	0.9216	0.8236	0.7423	0.6731
0.01274	1.034	0.9263	0.8276	0.7452	0.6753
0.03351	1.046	0.9355	0.8351	0.7519	0.6817
0.05493	1.050	0.9395	0.8387	0.7552	0.6835
0.07510	1.058	0.9456	0.8438	0.7599	0.6870
0.09599	1.067	0.9532	0.8487	0.7637	0.6912
0.1212	1.076	0.9611	0.8571	0.7705	0.6965
0.1421	1.084	0.9677	0.8624	0.7750	0.7006
			$m_2 = 0.02523$		
0	1.064	0.9532	0.8518	0.7676	0.6959
0.01456	1.070	0.9569	0.8552	0.7698	0.6987
0.02734	1.074	0.9616	0.8582	0.7731	0.7011
0.05777	1.088	0.9712	0.8668	0.7807	0.7086
0.07434	1.096	0.9784	0.8733	0.7863	0.7131
0.09656	1.105	0.9848	0.8796	0.7916	0.7170
0.1208	1.112	0.9942	0.8868	0.7970	0.7228
0.1412	1.119	1.001	0.8927	0.8019	0.7266
			$m_2 = 0.03404$		
0	1.096	0.9758	0.8719	0.7861	0.7116
0.01444	1.102	0.9818	0.8775	0.7903	0.7162
0.03519	1.111	0.9901	0.8851	0.7972	0.7215
0.05559	1.120	0.9971	0.8922	0.8023	0.7273
0.07555	1.128	1.006	0.8992	0.8089	0.7319
0.09725	1.137	1.014	0.9066	0.8155	0.7363
0.1183	1.145	1.021	0.9127	0.8219	0.7419
0.1393	1.155	1.029	0.9199	0.8275	0.7478

The values of the constants *L* and *K* were determined by using the density and viscosity values of water and benzene from the literature.[17] Two viscometers were used in the experiments. Experiments were performed at least in six replicates for each composition at each temperature, and the results were averaged. The estimated relative standard deviation of replicates for η was ± 0.1 %.

Results and Discussion

B Coefficients of Viscous Flow. The densities and viscosities of the binary solutions of dextran 40000 (2) + water (1) and hexanedioic acid (3) + water (1) are measured and provided in Tables 1 and 2, respectively. The densities and viscosities of ternary solutions of hexanedioic acid (3) + dextran (2) + water (1) with three fixed dextran concentrations are provided in Tables 3 and 4, respectively. Since the ionization constants K_1 and K_2 for hexanedioic acid are 3.71 × 10^{-5} and 3.87 × 10^{-6} at 298.15 K,[17] and the experimental concentration c_3 is less than 0.2 mol·dm^{-3}, the ionization process of hexanedioic acid and the contribution of the *A* coefficients to η_r were assumed to be negligible. The correlation of η_{123} with c_3 follows a linear relationship with a standard deviation less than 0.002, that is, they follow eq 3. Here we treat (1) + (2) as a solvent and hexanedioic acid as a nonelectrolyte solute. The *B* coefficients

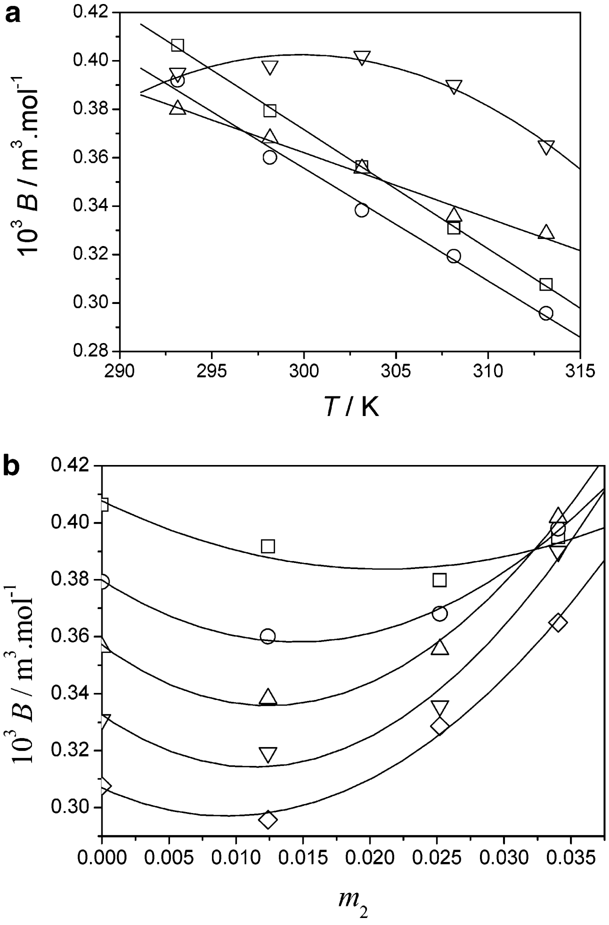

Figure 1. (a) *B* coefficients of hexanedioic acid in aqueous dextran solution: the effect of temperature for m_2 = □, 0; ○, 0.01239 mol·kg^{-1}; △, 0.02523 mol·kg^{-1}; and ▽, 0.03404 mol·kg^{-1}. (b) *B* coefficients of hexanedioic acid in aqueous dextran solution: the effect of dextran concentration at *T* = □, 293.15 K; ○, 298.15 K; △, 303.15 K; ▽, 308.15 K, and ◇, 313.15 K.

Table 5. Values of *B* Coefficients (10^{-3} m^3·mol^{-1}) for Hexanedioic Acid Dissolved in Aqueous Dextran Solution and Data for Dextran Dissolved in Water

	$B/10^{-3}$ m^3·mol^{-1}				
	hexanedioic acid in aqueous dextran solution				dextran in water
T	m_2/mol·kg^{-1}				
K	0	0.01239	0.02523	0.03404	
293.15	0.406	0.392	0.380	0.395	0.0278
298.15	0.379	0.360	0.368	0.398	0.0286
303.15	0.356	0.338	0.356	0.402	0.0286
308.15	0.331	0.319	0.336	0.390	0.0285
313.15	0.308	0.296	0.329	0.365	0.0279

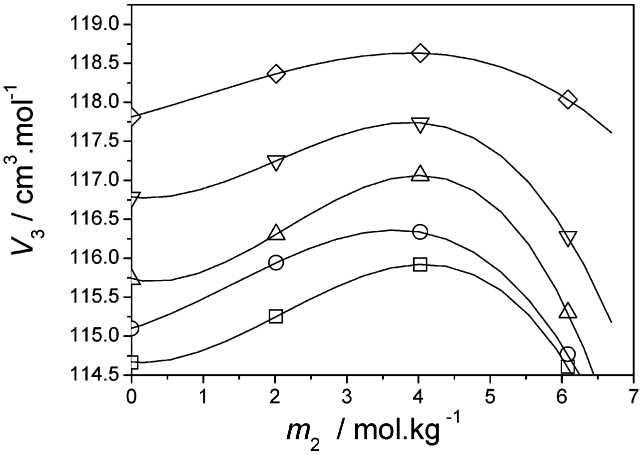

Figure 2. Partial molar volumes $\bar{V}_3^\infty$ at infinite dilution for hexanedioic acid in aqueous dextran solution at T = □, 293.15 K; ○, 298.15 K; △, 303.15 K; ▽, 308.15 K; and ◇, 313.15 K.

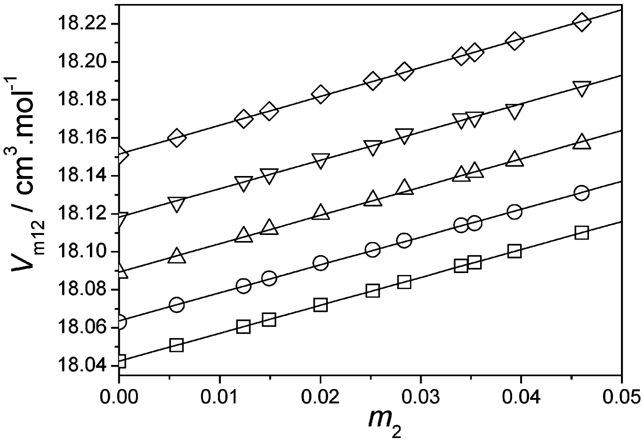

Figure 3. Average molar volumes V_{m12} of aqueous dextran solution at T = □, 293.15 K; ○, 298.15 K; △, 303.15 K; ▽, 308.15 K; and ◇, 313.15 K.

Table 6. Partial Molar Volumes at Infinite Dilution $\bar{V}_3^\infty$/cm^3·mol^{-1} of Hexanedioic Acid in Aqueous Dextran Solution

T	$\bar{V}_3^\infty$/cm^3·mol^{-1}			
	m_2/mol·kg^{-1}			
K	0	0.01239	0.02523	0.03404
293.15	114.66	115.25	115.92	114.61
298.15	115.10	115.94	116.34	114.77
303.15	115.73	116.31	117.06	115.31
308.15	116.78	117.25	117.74	116.28
313.15	117.81	118.37	118.63	118.04

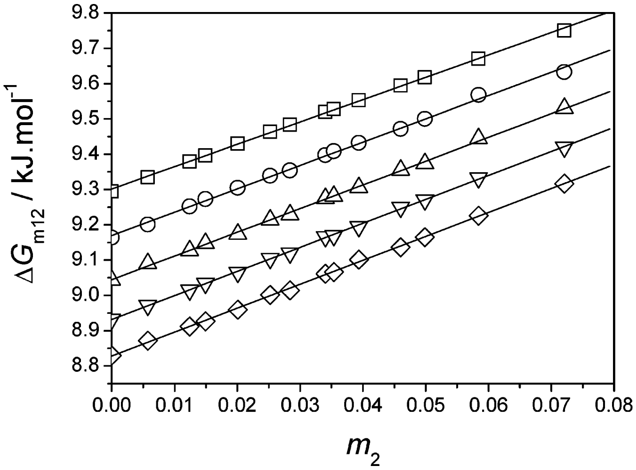

Figure 4. Average activation free energy of viscous flow, $\Delta G_{m12}^{\neq}$, for dextran + water solution at T = □, 293.15 K; ○, 298.15 K; △, 303.15 K; ▽, 308.15 K; and ◇, 313.15 K.

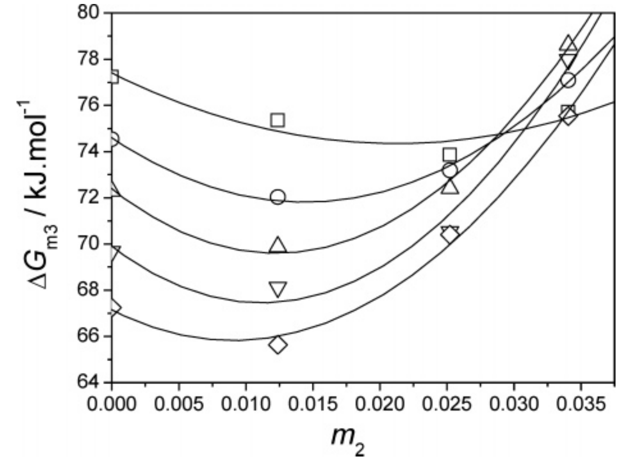

Figure 5. Values of $\Delta G_{m3}^{\neq}$ as a function dextran concentration m$_2$ at T = □, 293.15 K; ○, 298.15 K; △, 303.15 K; ▽, 308.15 K; and ◇, 313.15 K.

are determined by a least-squares regression method and are listed in Table 5.

Figure 1, panels a and b, shows the effect of temperature and dextran concentration on *B* coefficients, respectively. The viscosity *B* coefficient originally introduced as an empirical term has been found to depend upon solute−solvent interactions and on the relative size of the solute and solvent molecules. Larger and positive *B* values indicate a structure-making action (hydrophobic and hydrogen bonding actions) of solute on solvents. Wang et al.[11] studied the *B* coefficients of some amino acids in aqueous urea solution at several temperatures. Their results indicated that the *B* coefficient could be considered as a contribution from particular groups of the solute. The values of d*B*/d*T* for groups can provide direct evidence regarding their structure making or breaking effect in solution. The values of d*B*/d*T* are positive for hydrophilic structural breaking groups. For a hydrophobic structure-making group, the value of d*B*/d*T* is negative. In Figure 1a, the *B* coefficient decreases with an increase in temperature, and the d*B*/d*T* is negative. This is an indication that the hydrophilic groups make less contribution the hydrophobic groups. The d*B*/d*T* is less negative with an increase in the dextran concentration. This means that, with the increase in the concentration of dextran, the hydrophobic character of hexanedioic acid is decreased. For m_2 = 0.03404 mol·kg^{-1}, the slope of d*B*/d*T* approaches the horizontal. This means the structure-making effect of hexanedioic acid is diminished by the addition of more dextran.

In discussing the properties of the polymer, the molecular weight is indispensable. In molar concentration conversion, we use the monomer unit mass as the molecular weight. In the case of dextran, the monomer unit mass is 162.053 g·mol^{-1}. The *B* coefficients of dextran in water (0.0278 to 0.0286 dm^3·mol^{-1}) are much lower than the data of hexanedioic acid in dextran + water binary solvents (0.406 to 0.296 dm^3·mol^{-1}), and the slope of d*B*/d*T* is approximately horizontal. The lower *B* coefficient is an indication of a weak effect on viscosity. In Figure 1b, the effect of dextran concentration on the *B* coefficient of hexanedioic acid is shown. In the experimental concentration range, *B* coefficients decrease first and then increase with an increasing concentration of dextran. In the section before the minimum point, dextran impairs the hydrophobic property of the acid and causes *B* to decrease. However in the second section after the minimum point, with an increase in the dextran concentration, *B* increases. A possible explanation is that the interaction

Table 7. Activation Parameters of Viscous Flow of $\Delta G_{m3}^{\neq}$, $\Delta H_{m3}^{\neq}$, and $\Delta S_{m3}^{\neq}$

	293.15 K	298.15K	303.15 K	308.15 K	313.15 K	
m_2/mol·kg^{-1}			$\Delta G_{m3}^{\neq}$/kJ·mol^{-1}			$\Delta H_{m3}^{\neq}$/kJ·mol^{-1}
0	77.2	74.5	72.3	69.7	67.2	223
0.01239	75.4	72.0	69.9	68.1	65.6	212
0.02523	73.9	73.2	72.4	70.5	70.4	130
0.03404	75.7	77.1	78.6	78.0	75.5	71.8
m_2/mol·kg^{-1}			$\Delta S_{m3}^{\neq}$/kJ·mol^{-1}·K^{-1}			
0	0.497	0.498	0.497	0.497	0.497	
0.01239	0.467	0.471	0.470	0.468	0.468	
0.02523	0.192	0.191	0.190	0.193	0.191	
0.03404	−0.0133	−0.0176	−0.0224	−0.0200	−0.0119	

between acid and dextran substitutes for the interaction between acid and water. This substitution increases the viscosity.

Volumetric Properties of Solution. To evaluate the activation parameters of viscous flow, the volumetric properties of solute and solvent are necessary. The density of hexanedioic acid (3) + dextran (2) + water (1) solution is a linear function of m_3:

$$\rho_{123} = \rho_{12} + \alpha m_3 \tag{17}$$

The partial molar volume of solute 3 at infinite dilution ($\bar{V}_3^{\infty}$) may be estimated by

$$\bar{V}_3^{\infty} = M_3/\rho_{12} - 1000\alpha/\rho_{12}^{\ 2} \tag{18}$$

where m_3 is the molality of hexanedioic acid in solution (mol·kg^{-1}); ρ_{123} and ρ_{12} represent the densities of the solution (1 + 2 + 3) and (1 + 2), respectively; and M_3 is the molecular weight of component 3. The value of α is determined from eq 17 by a least-squares regression method. The data for $\bar{V}_3^{\infty}$ are listed in Table 6. The effect of the dextran concentration on $\bar{V}_3^{\infty}$ is shown in Figure 2.

For a solution of dextran (2) + water (1), its average molar volume is expressed by V_{m12}, which is necessary in calculations of the activation thermodynamic parameters of viscous flow. Figure 3 shows the effect of m_2 on V_{m12}.

Activation Parameters of Viscous Flow. For the binary solvent 1 + 2, the average activation free energy ($\Delta G_{m12}^{\neq}$) was calculated from their viscosities (η_{12}) via a variant of eq 5. The value of $\Delta G_{m1}^{0\neq}$ was calculated from eq 4 using η_1. The values of $\Delta G_{m12}^{\neq}$ are shown in Figure 4. Linear curves of $\Delta G_{m12}^{\neq}$ versus m_2 are found. The value of $\Delta G_{m3}^{\neq}$, when solute 3 dissolves in binary solvents 1 + 2, was calculated by eq 10. The effect of the dextran concentration on $\Delta G_{m3}^{\neq}$ is shown in Figure 5. The data of $\Delta G_{m3}^{\neq}$ are given in Table 7.

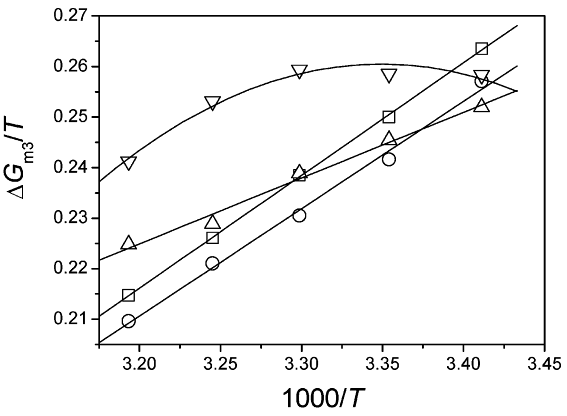

Figure 6. Values of $\Delta G_{m3}^{\neq}/T$ change with 1000/T at m_2 = □, 0; ○, 0.01239 mol·kg^{-1}; △, 0.02523 mol·kg^{-1}; and ▽, 0.03404 mol·kg^{-1}.

For the dextran + water solvent, $\Delta H_{m12}^{\neq}$ and $\Delta S_{m12}^{\neq}$ were calculated from $\Delta G_{m12}^{\neq}$ by using eqs 11 and 12. $\Delta G_{m12}^{\neq}$ are linear functions of temperature, and $\Delta H_{m12}^{\neq}$ may be considered as a constant. The value of $\Delta H_{m3}^{\neq}$ and $\Delta S_{m3}^{\neq}$ were calculated from $\Delta G_{m3}^{\neq}$ by the same method. The curves of ($\Delta G_{m3}^{\neq}/T$) versus (1000/T) are shown in Figure 6. In view of the narrow temperature range and the limitation of experimental accuracy, it is not sufficient to consider the relationship between $\Delta H_{m3}^{\neq}$ and T on the basis of these experimental data. However, in order to continue our theoretical analysis on viscous flow, the curves were considered as approximately linear. Therefore, $\Delta H_{m3}^{\neq}$ may be considered to be approximately constant within the temperature region. The $\Delta H_{m3}^{\neq}$ and $\Delta S_{m3}^{\neq}$ data are given in Table 7. The effect of the dextran concentration on the activation parameters $T\Delta S_{m3}^{\neq}$, $\Delta H_{m3}^{\neq}$, $T\Delta S_{m12}^{\neq}$, and $\Delta H_{m12}^{\neq}$ is shown in Figure 7. Because the temperature effect on $\Delta S_{m3}^{\neq}$ and $\Delta S_{m12}^{\neq}$ is much weaker, the data at 298.15 K are shown for comparison.

It can be observed from Figure 7 that $\Delta H_{m3}^{\neq} > T\Delta S_{m3}^{\neq} > \Delta H_{m12}^{\neq} > T\Delta S_{m12}^{\neq}$. The value of $\Delta H_{m12}^{\neq}$ and $T\Delta S_{m12}^{\neq}$ change little with an increase in m_2. The values of $\Delta H_{m3}^{\neq}$ and $\Delta S_{m3}^{\neq}$ decrease with an increase in m_2. At m_2 = 0.03404 mol·kg^{-1}, $T\Delta S_{m3}^{\neq}$ is close to $T\Delta S_{m12}^{\neq}$. The activation enthalpy of $\Delta H_{m3}^{\neq}$ decreases with increasing m_2. This indicates that the relative movement of hexanedioic acid in aqueous dextran solution becomes easier.

The value of $\Delta S_{m12}^{\neq}$ is associated with a structural change of the solvent in the bulk zone, from a ground to a transition state. A small value of $\Delta S_{m12}^{\neq}$ reveals that the structural change and the disordered state in this transition process can be neglected. The value of $\Delta S_{m3}^{\neq}$ is associated with the structural change in the solvation shell of solute 3, from a ground to a

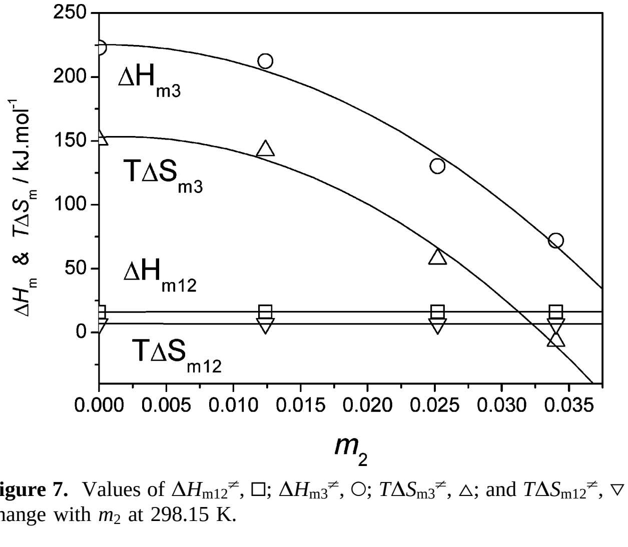

Figure 7. Values of $\Delta H_{m12}^{\neq}$, □; $\Delta H_{m3}^{\neq}$, ○; $T\Delta S_{m3}^{\neq}$, △; and $T\Delta S_{m12}^{\neq}$, ▽ change with m_2 at 298.15 K.

Table 8. Activation Free Energy of $\Delta G_{m3}^{\neq}(12-12')$/kJ·mol^{-1}

m_2	$\Delta G_{m3}^{\neq}(12-12')$/kJ·mol^{-1}				
mol·kg^{-1}	293.15 K	298.15 K	303.15 K	308.15 K	313.15 K
0	68.0	65.4	63.3	60.7	58.4
0.01239	66.0	62.8	60.8	59.1	56.7
0.02523	64.4	63.8	63.2	61.4	61.4
0.03404	66.2	67.7	69.4	68.8	66.5

transition state. A large positive value of $\Delta S_{m3}^{\neq}$ is an indication that the structure in the solvation shell in the transition state is of a lesser order than the shell in the ground state. With an increase in m_2, $\Delta S_{m3}^{\neq}$ decreases, and the order of the solvation shell in the transition state increases. This makes the movement of hexanedioic acid difficult. The effect of $\Delta S_{m3}^{\neq}$ is opposite to the effect of $\Delta H_{m3}^{\neq}$. Because $\Delta H_{m3}^{\neq} > T\Delta S_{m3}^{\neq}$, the final effect is determined by the enthalpy term.

Activation Free Energy of Diffusion for Hexanedioic Acid in Dextran Aqueous Solution. The values of $\Delta G_{m3}^{\neq}(12-12')$, the difference between the solvation Gibbs free energies of solute 3 in the ground state of viscous flow for solvent $(1 + 2)$ and in the transition state for solvent $(1 + 2)'$ can be calculated from eq 14. The data of $\Delta G_{m3}^{\neq}(12-12')$ are given in Table 8. $\Delta G_{m3}^{\neq}(12-12')$ initially decreased and then increased with an increase in the dextran concentration.

For hydrophobic solutes, their value of $\Delta G_{m3}^{\neq}$ is greater than $\Delta G_{m12}^{\neq}$; that is, $\Delta G_{m3}^{\neq}(12-12') > 0$. This had already been demonstrated experimentally.[11,13] Values of $\Delta G_{m3}^{\neq}(12-12')$ in Table 8 are all positive. This indicates that hexanedioic acid behaves as a hydrophobic structure maker. This conclusion is consistent with the results deduced from the values of B and dB/dT. The physical meaning of $\Delta G_{m3}^{\neq}(12-12') > 0$ is that, in aqueous solution, the interactions between solute and solvent molecules in the ground state of viscous flow are stronger than those in the transition state. Thus, the solute solvation in the transition state is unfavorable in free energy terms. With an increase in the dextran concentration, the decrease in $\Delta G_{m3}^{\neq}(12-12')$ reveals that the solute solvation state has improved and that its hydrophobic property is improved. However, after a minimum value, $\Delta G_{m3}^{\neq}(12-12')$ increases. Following the increase in $\Delta G_{m3}^{\neq}(12-12')$, the flowability of solute will be decreased.

Conclusion

From the data of the viscosity of a solution, parameters of viscous B coefficients, activation parameters of viscous flow [$\Delta G_{m3}^{\neq}$, $\Delta H_{m3}^{\neq}$, $\Delta S_{m3}^{\neq}$, and $\Delta G_{m3}^{\neq}(12-12')$] are obtained. The effect of temperature and dextran concentration on the viscous parameters was discussed. In dextran aqueous solution, hexanedioic acid behaves as a hydrophobic structure maker. In our experimental region, B, $\Delta G_{m3}^{\neq}$, and $\Delta G_{m3}^{\neq}(12-12')$ first decreased and then increased with an increase in the dextran concentration. This is an indication that with the addition of dextran into solution, the hydrophobic property of hexanedioic acid is improved. However, with the further addition of dextran into solution, the interaction between hexanedioic acid and dextran makes the flowability of the solution difficult.

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