

Eyring Functions of Activation for the Viscous Flow of Some Higher Alcohols in Cyclohexane Solutions

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Summary. The viscosities of solutions of 1-octanol, 1-nonanol, and 1-decanol in cyclohexane up to concentrations of $1.56 \text{ mol} \cdot \text{kg}^{-1}$ were determined in the temperature range from 293.15 to 333.15 K. Applying Eyring's transition state theory, the Eyring functions of activation for the viscous flow of binary mixtures, *i.e.* the molar Gibbs free energy, entropy, and enthalpy were estimated. The correlation coefficients β_Y ($Y = G, H, \text{ or } S$) were derived and used to discuss the initial effect of the solute on the activation parameters for the viscous flow. From the partial molar thermodynamic functions of activation and the partial molar volumetric data of solute and solvent at infinite dilution, the viscosity coefficient B was determined. For the interpretation of the experimental data, the Unified Interaction Parameter Formalism was used.

Keywords. Alcohol; Cyclohexane; Eyring functions of activation for viscous flow; Viscosity coefficient.

Eyringsche Aktivierungsfunktionen der Viskosität einiger höherer Alkohole in Cyclohexan

Zusammenfassung. Die Viskositäten von Lösungen von 1-Octanol, 1-Nonanol und 1-Decanol in Cyclohexan wurden im Temperaturbereich von 293.15 bis 333.15 K bis zu Konzentrationen von $1.56 \text{ mol} \cdot \text{kg}^{-1}$ bestimmt. Anwendung der Eyringschen Theorie des Übergangszustandes erlaubte die Abschätzung der Eyringschen Aktivierungsfunktionen für das viskose Fließen binärer Mischungen, d.h. der molaren Größen Gibbsche Energie, Entropie und Enthalpie. Anhand der Korrelationskoeffizienten β_Y ($Y = G, H \text{ oder } S$) wird der Effekt des gelösten Stoffes auf die Aktivierungsparameter diskutiert. Aus den partiellen molaren thermodynamischen Aktivierungsfunktionen des viskosen Flusses und den partiellen molaren volumetrischen Daten von Lösungsmittel und gelöstem Stoff bei unendlicher Verdünnung wurde der Viskositätskoeffizient B bestimmt. Zur Interpretation der Daten wurde der *Unified Interaction Parameter-Formalismus* angewandt.

Introduction

In mixtures of alcohols with cyclohexane the alcohol molecules are strongly associated through hydrogen bonds [1]. In the dilution process, extensive

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dissociation of hydrogen bonded alkanol associates takes place [2–4]. The degree and extent of self-association as well as the dissociation of the alcohol molecules depend on solute, solvent, and temperature [5]. Thus, the process of such interactions may be followed *via* changes in the thermodynamic, spectroscopic, transport, and dielectric properties.

The purpose of this work is to describe the transport properties of some 1-alkanol solutions in cyclohexane. The viscosity of these solutions was determined and interpreted on the basis of the viscosity coefficients and by rate process theory. Some *Eyring* functions of viscous flow for the investigated systems were obtained with the aim of demonstrating the effect of solute on the solute-solvent and solute-solute interactions.

Results and Discussion

The viscosity data of the systems investigated, given in Table 1, were interpreted on the basis of the theory of rate processes [6]. The molar *Gibbs* free energy of activation for viscous flow of the solution, $\Delta^\# \bar{G}_{1,2}$ ($\text{J} \cdot \text{mol}^{-1}$), was calculated according to Eq. (1) where $\eta_{1,2}$ ($\text{kg} \cdot \text{m}^{-1} \cdot \text{s}^{-1}$) is the dynamic viscosity of solutions, R is the gas constant, h is *Planck's* constant, $\bar{V}_{1,2}$ ($\text{m}^3 \cdot \text{mol}^{-1}$) is the volume of one mole of solution, and $\bar{V}_{1,2} = V_{1,2}/(n_1 + n_2)$, n_1 and n_2 being the means the number of moles of solvent and solute, respectively. For the investigated systems, the volumetric data were taken from Ref. [7].

$$\Delta^\# \bar{G}_{1,2} = RT \ln \left(\frac{V_{1,2} \eta_{1,2}}{hN} \right) \quad (1)$$

In the present investigation it was found that the dependence of the molar *Gibbs* free energy of activation for the viscous flow of the solution on the mole fraction of the solute, x_2 , could with reasonable accuracy be described by

$$\Delta^\# \bar{G}_{1,2} = \Delta^\# G_1^0 + \beta_G x_2 \quad (2)$$

where $\Delta^\# G_1^0$ is the activation parameter for the viscous flow of pure solvent and β_G is a coefficient which depends on solute, solvent, and temperature. The values of $\Delta^\# G_1^0$ and β_G at a definite temperature were determined *via* Eq. (2) by the method of least squares. In the calculations, the values of $\Delta^\# G_1^0$ do not differ by more than 0.15% from the molar *Gibbs* free energy of activation for the viscous flow for the pure solvent, *i.e.* cyclohexane, calculated from its viscosity and density. The values of β_G in the investigated temperature range are presented in Table 2. In Fig. 1, as an example the dependence of $\Delta^\# \bar{G}_{1,2}$ on the mole fraction of 1-nonanol is shown. The lines in Fig. 1 are the $\Delta^\# \bar{G}_{1,2}$ values calculated by Eq. (2) using the corresponding values for β_G .

The values of the coefficients β_s were obtained from the derivative $\beta_s = -(\delta\beta_G/\delta T)_p$ [8]. For the systems investigated, the temperature dependence of β_G can be expressed by the second degree polynomial

$$\beta_G = c_0 + c_1(T - T_0) + c_2(T - T_0)^2 \quad (3)$$

where c_0 , c_1 , and c_2 are regression coefficients whose values, obtained by the least squares method, are given in Table 3. At 298 K, the value of the coefficient β_s is

Table 1. Viscosities of 1-octanol, 1-nonanol, and 1-decanol solutions in cyclohexane and viscosity of pure cyclohexane as a function of temperature

m (mol · kg ⁻¹)	$10^3 \times \eta$ (kg · m ⁻¹ · s ⁻¹)					
	T (K)	293.15	298.15	303.15	313.15	323.15
	1-octanol					
0.0457	0972	0.892	0.823	0.703	0.610	0.535
0.1153	0.976	0.893	0.825	0.705	0.610	0.536
0.1940	0.986	0.902	0.829	0.709	0.611	0.536
0.3287	1.006	0.916	0.843	0.718	0.619	0.539
0.5632	1.045	0.954	0.875	0.737	0.635	0.553
0.7166	1.070	0.977	0.896	0.756	0.647	0.563
0.9161	1.109	1.011	0.923	0.780	0.665	0.576
1.1785	1.157	1.051	0.958	0.808	0.692	0.595
1.5284	1.216	1.109	1.009	0.852	0.721	0.620
	1-nonanol					
0.0458	0.977	0.895	0.824	0.707	0.611	0.535
0.1155	0.982	0.899	0.826	0.708	0.612	0.536
0.1946	0.994	0.910	0.835	0.713	0.613	0.536
0.3302	1.020	0.933	0.856	0.727	0.624	0.544
0.5675	1.074	0.982	0.899	0.758	0.646	0.562
0.7233	1.110	1.012	0.926	0.780	0.667	0.577
0.9269	1.157	1.053	0.960	0.809	0.691	0.594
1.1964	1.220	1.107	1.008	0.849	0.721	0.619
1.5585	1.294	1.169	1.062	0.884	0.744	0.638
	1-decanol					
0.0458	0.976	0.896	0.825	0.704	0.611	0.534
0.1156	0.989	0.907	0.835	0.709	0.615	0.537
0.1949	1.008	0.920	0.843	0.716	0.619	0.540
0.3314	1.036	0.948	0.869	0.737	0.629	0.548
0.5713	1.108	1.009	0.923	0.779	0.665	0.573
0.7298	1.155	1.052	0.961	0.807	0.688	0.593
0.9380	1.217	1.106	1.011	0.844	0.717	0.615
1.2154	1.296	1.175	1.070	0.892	0.755	0.646
1.5919	1.407	1.274	1.156	0.960	0.810	0.688
	cyclohexane					
	0.972	0.892	0.822	0.703	0.609	0.534

Table 2. Values of coefficients β_G for the investigated 1-alkanols in cyclohexane solutions

Solute T (K)	β_G (kJ · mol ⁻¹)					
	293.15	298.15	303.15	313.15	323.15	333.15
1-octanol	6.1 ± 0.1	6.0 ± 0.2	5.8 ± 0.2	5.6 ± 0.2	5.2 ± 0.2	4.8 ± 0.2
1-nonanol	7.7 ± 0.1	7.5 ± 0.1	7.3 ± 0.1	7.0 ± 0.2	6.6 ± 0.2	6.2 ± 0.2
1-decanol	9.6 ± 0.1	9.5 ± 0.1	9.4 ± 0.2	9.0 ± 0.2	8.6 ± 0.2	8.1 ± 0.2

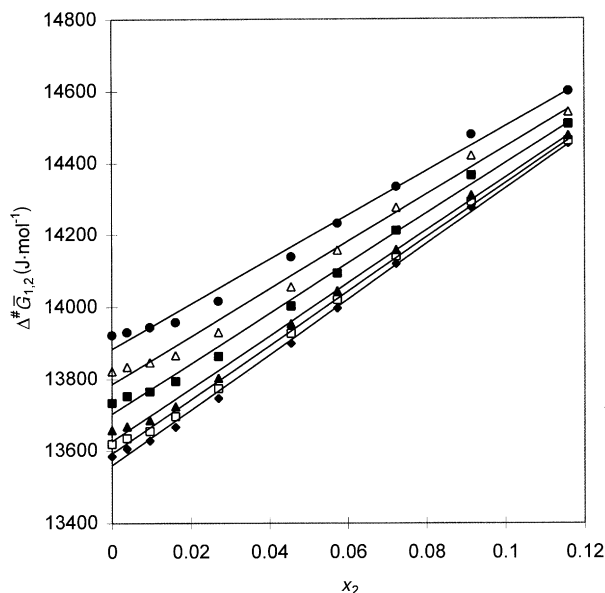


Fig. 1. Dependence of the molar *Gibbs* free energy of activation for the viscous flow of a solution of 1-nonanol in cyclohexane, $\Delta^{\#}\bar{G}_{1,2}$, on the mole fraction of the solute, x_2 , at \blacklozenge , 293.15 K; \square , 298.15 K; \blacktriangle , 303.15 K; \blacksquare , 313.15 K; \triangle , 323.15 K; \bullet , 333.15 K

equal to $-c_1$. The values of β_H were calculated from the *Gibbs-Helmholtz* relation (Eq. (4)).

$$\beta_H = \beta_G + T \beta_s \quad (4)$$

The values of β_H are given in Table 3. From Tables 2 and 3 it can be seen that the coefficients β_G , β_s , and β_H are positive which indicates an initial increase of the activation parameter of the viscous flow of the investigated solutions with concentration. β_G and β_H increase with increasing alkyl residue in the alcohol molecule. The highest value of β_s is found for 1-nonanol, the lowest value for 1-octanol (Table 3).

The coefficient β_Y may be considered as the difference between the partial molar parameter of activation for the viscous flow of a solute at infinite dilution, $\Delta^{\#}\bar{Y}_{2,0}$, and the respective molar quantity of the pure solvent [8]. The $\Delta^{\#}\bar{Y}_{2,0}$ values were calculated by Eq. (5) and are given in Table 4.

$$\Delta^{\#}\bar{Y}_{2,0} = \Delta^{\#}Y_1^0 + \beta_Y \quad (Y = G, H, \text{ or } S) \quad (5)$$

Table 3. Values of regression coefficients in Eq. (3) with standard error of the regression analysis, s , values of coefficient β_H for 1-alkanols in cyclohexane solutions at 298.15 K

Solute	c_0 ($\text{J} \cdot \text{mol}^{-1}$)	$-c_1$ ($\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$)	$-c_2$ ($\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-2}$)	s	β_H ($\text{kJ} \cdot \text{mol}^{-1}$)
1-octanol	6008 ± 10	21.7 ± 1.6	0.34 ± 0.055	19	12.5 ± 0.2
1-nonanol	7518 ± 2	35.8 ± 0.3	0.007 ± 0.01	4	18.2 ± 0.1
1-decanol	9522 ± 4	29.3 ± 0.6	0.30 ± 0.02	7	18.3 ± 0.1

Table 4. Partial molar parameters of activation for the viscous flow of the investigated 1-alkanols in cyclohexane at 298.15 K

Solute	$\Delta^{\#}\bar{G}_{2,0}$ (kJ · mol ⁻¹)	$\Delta^{\#}\bar{S}_{2,0}$ (Jmol ⁻¹ · K ⁻¹)	$\Delta^{\#}\bar{H}_{2,0}$ (kJ · mol ⁻¹)
1-octanol	19.6 ± 0.2	14.7 ± 1.6	24.0 ± 0.2
1-nonanol	21.1 ± 0.1	28.8 ± 0.3	29.7 ± 0.1
1-decanol	23.1 ± 0.1	22.3 ± 0.6	29.8 ± 0.1

The values of $\Delta^{\#}Y_1^0$ used at 298.15 K are: $\Delta^{\#}G_1^0 = 13.6$ kJ · mol⁻¹, $\Delta^{\#}S_1^0 = -7.0$ J · mol⁻¹ · K⁻¹ (obtained from the linear dependence of $\Delta^{\#}G_1^0$ in the temperature interval from 293.15 K to 333.15 K), and $\Delta^{\#}H_1^0 = 11.5$ kJ · mol⁻¹; the values of $\Delta^{\#}G_1^0$ at a definite temperature were calculated from the experimental values for viscosity and density of pure cyclohexane

From Table 4 it can be seen that the values of $\Delta^{\#}\bar{G}_{2,0}$, $\Delta^{\#}\bar{S}_{2,0}$, and $\Delta^{\#}\bar{H}_{2,0}$ are positive. According to the transition state theory of viscosity, the value of $\Delta^{\#}\bar{G}_{2,0}$ depends on the difference in the solute-solvent interactions in the ground and transition state and does not represent any contribution in the changes of solvent-solvent interactions caused by the molecule of the solute. At infinite dilution, when dissociation of self-associated alcohol molecules is complete, the dispersion forces and dipole-induced dipole forces between alcohol and cyclohexane molecules persist. As may be seen from Table 4, the value of $\Delta^{\#}\bar{G}_{2,0}$ almost linearly increases with the number of methylene groups in the alcohol molecule. It is known from the literature that the dipole moment of the hydroxyl group in an alcohol molecule is practically independent of the alkyl chain length [9]. Therefore, dipole-induced dipole forces between alcohol and cyclohexane molecules are constant for the investigated systems, and the observed increase of $\Delta^{\#}\bar{G}_{2,0}$ can be ascribed to stronger dispersion forces as the chain length increases. On the other hand, the values of $\Delta^{\#}\bar{H}_{2,0}$ and $\Delta^{\#}\bar{S}_{2,0}$ describe not only the changes in the solute-solvent interactions, but also the changes of solvent-solvent interactions. The changes in the solute-solvent interactions are indicated as the breaking or as the formation of solute-solvent bonds in the transition state, which is related to a decrease or an increase of order. The positive values of $\Delta^{\#}\bar{S}_{2,0}$ could mean that for the investigated systems in the formation of the transition state bond-breaking along with a decrease in order occurs. This phenomenon is associated with the fact that $\Delta^{\#}\bar{G}_{1,2} > \Delta^{\#}G_1^0$. Although this inequality is not so drastic it may be anticipated that for these systems the solute-solvent bonds are relatively stronger than the solvent-solvent bonds, indicating a less favourable transition state in the presence of the solute.

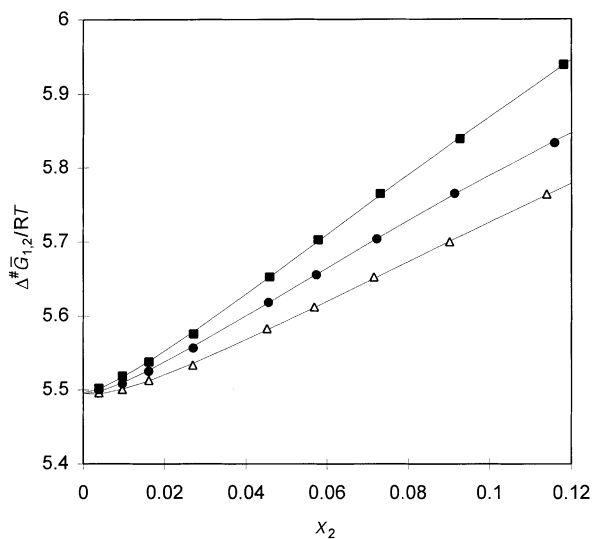
The experimental data were also interpreted applying the Unified Interaction Parameter Formalism (UIPF, [10]) leading to the following relation:

$$\frac{\Delta^{\#}\bar{G}_{1,2}}{RT} = a + bx_2 + cx_2^2 + (1 - x_2)\ln(1 - x_2) + x_2\ln(x_2) \quad (6)$$

a , b , and c are regression coefficients whose values together with the standard error of regression analysis (s) in the temperature range studied are given in Table 5. Thus, at infinite dilution, as $x_2 \rightarrow 0$, $\lim_{x_2 \rightarrow 0}(\Delta^{\#}\bar{G}_{1,2}/RT) = (\Delta^{\#}G_1^0/RT) \equiv a$. In Fig. 2 the dependence of $\Delta^{\#}\bar{G}_{1,2}/RT$ against x_2 for the investigated alcohols at 298.15 K is shown.

Table 5. Values of regression coefficients in Eq. (6) with standard error of the estimate, s , for 1-alkanols in cyclohexane solutions

	293.15 K	298.15 K	303.15 K	313.15 K	323.15 K	333.15 K
1-octanol						
a	5.576 ± 0.001	5.495 ± 0.001	5.421 ± 0.001	5.281 ± 0.002	5.150 ± 0.002	5.034 ± 0.001
b	6.46 ± 0.04	6.30 ± 0.06	6.15 ± 0.05	5.71 ± 0.07	5.55 ± 0.06	5.33 ± 0.05
$-c$	8.2 ± 0.3	7.3 ± 0.5	7.1 ± 0.4	4.5 ± 0.6	4.9 ± 0.6	4.8 ± 0.4
s	1×10^{-3}	2×10^{-3}	2×10^{-3}	2×10^{-3}	2×10^{-3}	1×10^{-3}
1-nonanol						
a	5.576 ± 0.001	5.495 ± 0.001	5.417 ± 0.001	5.277 ± 0.003	5.144 ± 0.005	5.026 ± 0.004
b	7.26 ± 0.06	7.23 ± 0.06	7.10 ± 0.07	6.71 ± 0.09	6.55 ± 0.21	6.21 ± 0.17
$-c$	9.6 ± 0.5	10.3 ± 0.5	10.3 ± 0.5	9.1 ± 1.1	9.4 ± 1.8	8.7 ± 1.5
s	2×10^{-3}	2×10^{-3}	2×10^{-3}	4×10^{-3}	6×10^{-3}	4×10^{-3}
1-decanol						
a	5.575 ± 0.001	5.496 ± 0.001	5.419 ± 0.002	5.275 ± 0.002	5.147 ± 0.003	5.029 ± 0.002
b	8.07 ± 0.07	7.89 ± 0.07	7.76 ± 0.10	7.42 ± 0.06	6.96 ± 0.13	6.61 ± 0.11
$-c$	9.6 ± 0.5	9.0 ± 0.5	8.9 ± 0.8	8.1 ± 0.5	6.4 ± 1.1	5.7 ± 0.9
s	2×10^{-3}	2×10^{-3}	3×10^{-3}	2×10^{-3}	4×10^{-3}	1×10^{-3}

**Fig. 2.** Dependence of $\Delta^{\#}\bar{G}_{1,2}/RT$ on the mole fraction of the solute, x_2 , at 298.15 K; 1-octanol; ●, 1-nonanol; ■, 1-decanol

The relative viscosity of non-electrolyte solutions, η_r , can be interpreted as

$$\eta_r = \frac{\eta_{1,2}}{\eta_1} = 1 + Bm + Dm^2 \quad (7)$$

where m is the molality of the solution ($\text{mol} \cdot \text{kg}^{-1}$) and η_1 is the viscosity of the solvent. The coefficients B and D are empirical constants which characterize the effect of the size and shape of the solute molecules. The viscosity coefficient B is

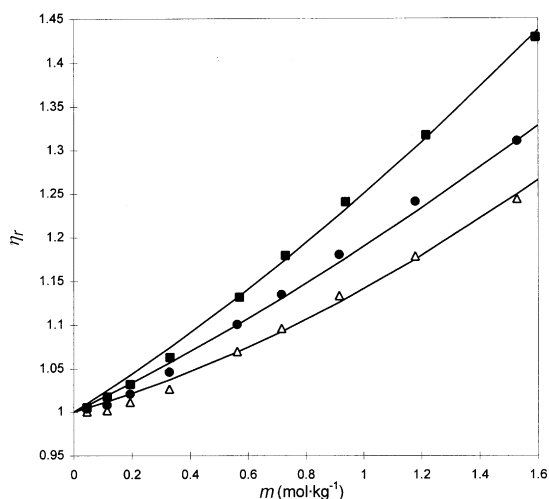


Fig. 3. Dependence of relative viscosity on concentration at 298.15 K; Δ , 1-octanol; \bullet , 1-nonanol; \blacksquare , 1-decanol

considered to reflect mainly the effect of the solute-solvent interactions on viscous flow, whereas the viscosity coefficient D is related to the solute-solute as well as to the solute-solvent interactions. Figure 3 presents the concentration dependence of relative viscosity for the investigated alcohols at 298.15 K.

Considering *Eyring's* theory of rate processes applied to viscous flow, the relation for viscosity coefficient B is given by Ref. [8]

$$B = d_1(V_1^0 - \bar{V}_{2,0}) + \frac{\beta_G M_1}{RT} \quad (8)$$

where $V_1^0 = M_1/d_1$ is the molar volume of the solvent and $\bar{V}_{2,0}$ is the partial molar volume of solute given in Ref. [7]. Eq. (8) shows that the viscosity coefficient B also includes, besides partial molar volumes, the contributions of changes of the partial molar *Gibbs* free energy of activation for the viscous flow of solvent and solute. Since for the investigated systems $V_1^0 < \bar{V}_{2,0}$, the first term in Eq. (8) gives a negative contribution to the viscosity coefficient B , whereas the second term, due to $\Delta^\# \bar{G}_{2,0} > \Delta^\# G_1^0$, affords a positive contribution to coefficient B . The values of viscosity B coefficient calculated by Eq. (8) at 298.15 K amount to 0.163 kg · mol⁻¹ for 1-octanol, 0.200 kg · mol⁻¹ for 1-nonanol, and 0.258 kg · mol⁻¹ for 1-decanol. Considering the values of coefficient B and assuming that it is related only to solute-solvent interactions, we can conclude that each additional methylene group in the 1-alkanol molecule increases the intensity of solute-solvent interactions in the solution.

Experimental

Materials

1-Octanol, 1-decanol (Fluka A.G.), and 1-nonanol (American Enzymes Ltd.) were purified by distillation under reduced pressure and stored over 4 Å molecular sieves in a well-closed container.

Cyclohexane (Merck) was shaken first with a mixture of concentrated nitric and sulfuric acid (1:4) and then with distilled water. Purified cyclohexane was distilled and stored over 4 Å molecular sieves. From the purified 1-alkanol and cyclohexane, a stock solution was prepared; the other solutions were prepared by further dilution.

Viscosity measurements

The dynamic viscosity $\eta_{1,2}$ ($\text{kg} \cdot \text{m}^{-1} \cdot \text{s}^{-1}$) of the solutions was determined with a *Cannon-Fenske* viscometer. The dynamic viscosity was estimated by means of the following equation [11]:

$$\eta_{1,2} = C d_{1,2} t - \frac{E d_{1,2}}{t^2} \quad (9)$$

where t is the measured flow time, C and E are instrumental constants, and $d_{1,2}$ is the density of the solution. The density values of the investigated systems were taken from Ref. [7]. The instrumental constants C and E were evaluated with water in the temperature range from 293.15 to 333.15 K in 5 K steps using the corresponding values for the viscosity and density of water from Ref. [12]. The value for C amounts to $(2.89 \pm 0.003) \times 10^{-9} \text{ m}^2 \cdot \text{s}^{-2}$, that for E to $(1.7074 \pm 0.2) \times 10^{-5} \text{ m}^2 \cdot \text{s}$. Flow times for each solution were obtained in five parallel determinations which agreed within $\pm 0.05\%$. The temperature of the bath was controlled to 0.05 K. The estimated error in viscosity determination was not greater than 0.2%.

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