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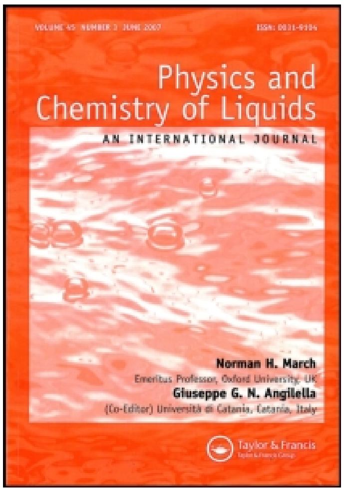

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DENSITY AND VISCOSITY OF 1-ALKANOLS

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(Received 9 June 2004)

Densities and viscosities have been measured for twelve 1-alkanols from methanol to 1-dodecanol at temperatures ranging from 303.15 to 323.15 K. Molar volumes, V_m, have been calculated from the density data, which have been found to follow the additive equation, $V_m = V_{CH_3} + nV_{CH_2} + V_{OH}$, where n is the number of CH_2 groups. V_m have been plotted against n, showing an excellent linear relationship. The average values of V_{CH_2} at 303.15 K and 323.15 K have been determined from the slopes of this equation. The viscosities have been found to increase almost exponentially with the number of carbon atoms at different temperatures. The thermodynamic activation parameters, free energy, $\Delta G^{\neq}$, enthalpy, $\Delta H^{\neq}$, and entropy, $\Delta S^{\neq}$ for viscous flow have been plotted against the number of C atoms – all have been found to increase with the chain length of 1-alkanols.

Keywords: 1-alkanols; Density; Molar volumes; Viscosity; Thermodynamic activation parameters for viscous flow

1. INTRODUCTION

There are scattered reports on the densities and viscosities of different 1-alkanols in the literature. The data were obtained as a prerequisite for studying the properties of solutions of 1-alkanols formed by other components. Only a very few studies were devoted to investigate the properties of pure 1-alkanols. However, to mention a few, Matsuo *et al.* [1] carried out a systematic study on viscosity for six 1-alkanols from 1-hexanol to 1-hexadecanol with an even number of carbon atoms in the temperature range, 298–348 K. Liew *et al.* [2] also reported a systematic investigation on the densities of 1-alkanols from 1-hexanol to 1-octadecanol over a large temperature range, 288.15–353.15 K, again with an even number of C atoms. In an effort to make a comprehensive study we measured densities and viscosities and calculated the related properties, such as molar volumes and thermodynamic activation parameters for viscous flow for twelve 1-alkanols starting from methanol to 1-dodecanol in the temperature range of 303.15–323.15 K. Earlier a similar study was made by us on 1-bromoalkanes [3].

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TABLE I Density, $\rho \times 10^{-3}$ (kg m^{-3}), of 1-alkanols at different temperatures

1-alkanols	*Temperatures* (K)				
	303.15	*308.15*	*313.15*	*318.15*	*323.15*
Methanol	0.7822				
	0.78199^{a}	0.7774	0.7731	0.7681	0.7632
	0.7820^{b}	0.7769^{c}	0.7726^{c}		
	0.7816^{c}				
Ethanol	0.7807				
	0.7806^{c}	0.7769	0.7721		
	0.78069^{d}	0.7762^{c}	0.77183^{d}	0.7684	0.7639
	0.7808^{e}		0.7726^{b}		
	0.7810^{b}				
1-Propanol	0.7962	0.7922	0.7879		
	0.7956^{b}	0.7916^{f}	0.7874^{b}	0.7842	0.7797
	0.79584^{d}		0.78747^{c}		
			0.7876^{f}		
1-Butanol	0.8021		0.7943		
	0.80194^{d}	0.7983	0.79405^{d}	0.7908	0.7865
	0.8019^{e}	0.7981^{f}	0.7943^{f}		0.7852^{g}
	0.8024^{g}		0.7947^{g}		
1-Pentanol			0.7998		
	0.8073	0.8036	0.79987^{d}	0.7962	0.7925
	0.80736^{d}	0.8036^{h}	0.7999^{f}		0.7905^{g}
	0.8072		0.7997^{g}		
1-Hexanol	0.8120		0.8049		
	0.8115^{g}	0.8085	0.8043^{g}	0.8012	0.7976
	0.81144^{h}	0.80781^{h}	0.80417^{h}	0.80051^{h}	0.7953^{g}
1-Heptanol	0.8153	0.8118	0.8083		
	0.81530^{d}	0.81161^{h}	0.80897^{d}	0.8048	0.8014
	0.8153^{g}		0.8082^{g}	0.80443^{h}	0.7994^{g}
	0.81519^{h}		0.80803^{h}		
1-Octanol	0.8179		0.8109		
	0.81831^{d}	0.8144	0.81188^{d}	0.8074	0.8042
	0.8182^{e}	0.8149^{f}	0.8115^{f}	0.80755^{h}	0.8023^{g}
	0.8181^{g}	0.81458^{h}	0.8111^{g}		
	0.81808^{h}		0.81109^{h}		
1-Nonanol	0.8209	0.8174	0.8139	0.8102	0.8067
	0.82066^{h}	0.8176^{c}	0.8143^{c}	0.81026^{h}	
		0.81723^{h}	0.81379^{h}		
1-Decanol	0.8226		0.8158		
	0.82288^{d}	0.8192	0.81606^{d}	0.8122	0.8086
	0.8231^{e}	0.8200^{f}	0.8167^{f}	0.81249^{h}	
	0.82269^{h}	0.81928^{h}	0.81612^{h}		
1-Undecanol	0.8246	0.8212	0.8177	0.8141	0.8106
		0.8223^{f}	0.8191^{f}		
1-Dodecanol	0.8274	0.8240	0.8207	0.8174	0.8141

[a]Ref. [13]; [b]Ref. [15]; [c]Ref. [16]; [d]Ref. [10]; [e]Ref. [12]; [f]Ref. [11]; [g]Ref. [14]; [h]Ref. [9].

2. EXPERIMENTAL

Chemicals used in the present study are 1-alkanols from methanol to 1-dodecanol. The following alkanols were supplied by Aldrich with quoted purities: methanol (99.9%), 1-propanol (99.5 +%), 1-butanol (99.8%), 1-pentanol (99 + %), 1-hexanol (98 %), 1-heptanol (98+%), 1-octanol (99 + %) and 1-dodecanol (98%). E. Merck supplied

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the following chemicals with the quoted purities: ethanol (>99%), 1-nonanol (>98%), 1-decanol (>99%) and 1-undecanol (>98%). All these chemicals were used without further treatment, except that these were kept over molecular sieves (4 A) for at least three weeks prior to their use.

The density was measured by using a 25 mL specific gravity bottle and a 10 mL bicapillary pycnometer previously calibrated by redistilled water. Ostwald U-tube viscometers (British Standard Institution) with sufficiently long efflux time were used, so that, no kinetic energy correction was necessary in the viscosity measurement. The time of flow was recorded by an electronic timer reading up to ±0.01 s. An analytical balance of accuracy ± 0.0001 g was used in the density measurement. Temperature was controlled by a thermostatic water bath with a fluctuation of ±0.05 K. The average uncertainties in density and viscosity measurements were estimated to be less than $0.25\,\mathrm{kg\,m^{-3}}$ and $6 \times 10^{-7}\,\mathrm{kg\,m^{-1}\,s^{-1}}$, respectively.

3. RESULTS AND DISCUSSION

Densities of 1-alkanols from methanol to 1-dodecanol are shown in Table I at temperatures ranging from 303.15–323.15 K. In Fig. 1 the values have been plotted against the number of carbon atoms at different temperatures. The densities increase, almost in a regular fashion with the chain length for all temperatures, from C_3–C_{12} alkanols. However, methanol and ethanol deviate significantly from this trend. It is to be noted that methanol has a higher density than ethanol at lower temperatures. The same observation was made by other researchers. The densities of alkanols, especially lower alkanols, are quite prevalent in literature. Some of them are quoted in Table

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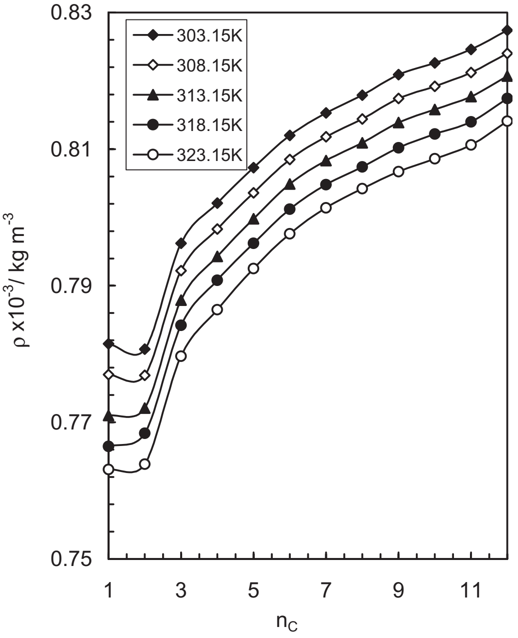

FIGURE 1 Densities of 1-alkanols against the number of C atoms, n_C.

I, showing generally good agreement with our values. The densities and viscosities of higher 1-alkanols are rather scarce, more so with alkanols with odd carbon number. The higher densities of methanol indicate that methanol forms an efficient packing in its pure state, which may be ascribed to its cyclic dimers as observed by spectroscopic studies [4,5]. The rate of decrease of density of methanol with temperature is found to be larger than that of all other alkanols, indicating that the dimers formed by methanol are probably much less stable thermally.

Molar volumes, V_m, of alkanols at different temperatures have been calculated by dividing molar mass, M_w, by density ρ, i.e., $V_m = M_w/\rho$. The V_m data are listed in Table II and represented in Fig. 2 at temperatures 303.15 and 323.15 K. The molar

TABLE II Molar volume, $V_m \times 10^6$ ($m^3 mol^{-1}$), of 1-alkanols at different temperatures

1-alkanols	*303.15 K*		*308.15 K*	*313.15 K*	*318.15 K*	*323.15 K*
	M_w/ρ	*Using Eq. (2)*	M_w/ρ			
Methanol	40.998	42.465	41.236	41.556	41.800	41.987
Ethanol	59.011	59.115	59.300	59.668	59.956	60.309
1-Propanol	75.484	75.765	75.865	76.279	76.639	77.081
1-Butanol	92.407	92.415	92.847	93.315	93.728	94.240
1-Pentanol	109.191	109.065	109.694	110.215	110.713	111.230
1-Hexanol	125.837	125.715	126.382	126.947	127.534	128.109
1-Heptanol	142.524	142.365	143.139	143.759	144.384	144.996
1-Octanol	159.225	159.015	159.909	160.599	161.296	161.937
1-Nonanol	175.734	175.665	176.486	177.245	178.055	178.827
1-Decanol	192.427	192.315	193.225	194.030	194.890	195.758
1-Undecanol	208.962	208.965	209.827	210.725	211.683	212.571
1-Dodecanol	225.212	225.615	226.141	227.050	227.967	228.891

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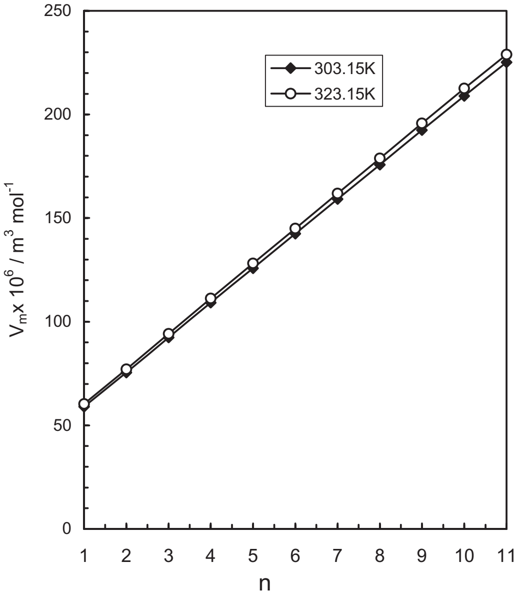

FIGURE 2 Molar volumes of 1-alkanols as a function of number of CH_2 groups, *n*.

volumes have been found to follow a linear equation of the form:

$$V_m = a + bn \tag{1}$$

where a is the sum of the volumes, V_{CH_3} and V_{OH} due to CH_3 and OH, respectively, b is the molar volume of CH_2, V_{CH_2}, and n is the number of CH_2 groups. So, Eq. (1) can be written as,

$$V_m = V_{CH_3} + nV_{CH_2} + V_{OH} \tag{2}$$

The V_{CH_3} and V_{OH} are assumed to be practically constant for all alkanols at a particular temperature. The average V_{CH_2} can be determined from the slope of the linear variation of V_m as a function of n (number of CH_2 groups). At 303.15 K the value of V_{CH_2} has been found to be $16.65\,\mathrm{cm^3\,mol^{-1}}$ by the least squares method with an extremely high correlation coefficient (>0.9999), which is very close to the value, $16.64\,\mathrm{cm^3\,mol^{-1}}$, as determined in our earlier study on 1-bromoalkanes [3]. Using the density data obtained by Liew *et al.* [5] for C_6, C_8, C_{10} and C_{12} 1-alkanols at 303.15 K, a value for V_{CH_2} has been calculated to be $16.62\,\mathrm{cm^3\,mol^{-1}}$, which is also very close to our V_{CH_2} value. At 323.15 K, V_{CH_2} has been found to be $16.895\,\mathrm{cm^3\,mol^{-1}}$.

To find V_{CH_3}, the molar volumes of different *n*-alkanes (*n*-hexane to *n*-undecane) were calculated by using their density values taken from the literature [6–8]. The molar volumes of these hydrocarbons show excellent linear relationship with n, following Eq. (1), the intercept now being equal to $2V_{CH_3}$, from which V_{CH_3} is calculated. The V_{CH_3} has been found to be $33.82\,\mathrm{cm^3\,mol^{-1}}$ at 303.15 K. Using the values of V_{CH_2} and V_{CH_3} so obtained and the molar volumes of all the alkanols except methanol, the average value of V_{OH} has been calculated to be $8.644\,\mathrm{cm^3\,mol^{-1}}$ at 303.15 K. Now, putting the values of V_{CH_3}, V_{CH_2} and V_{OH} in Eq. (2), the V_m have been calculated at 303.15 K. The calculated V_m and those obtained directly by (M_w/ρ) are shown in Table II. The agreement between the two sets of values is found to be generally very good, except for methanol.

Viscosities of 1-alkanols at different temperatures are listed in Table III and plotted in Fig. 3 against the number of C atoms, n_C. The values increase almost exponentially with the number of C atoms. The thermodynamic activation parameters for viscous flow have been calculated using Eyring equation [17],

$$\eta = \frac{hN}{V_m} e^{\Delta G^{\neq}/RT} \tag{3}$$

where, the symbols have their usual significance.
$\Delta G^{\neq}$ is related to enthalpy, $\Delta H^{\neq}$, and entropy, $\Delta S^{\neq}$, by the following equation,

$$\Delta G^{\neq} = \Delta H^{\neq} - T\Delta S^{\neq} \tag{4}$$

By substitution of Eq. (4) into Eq. (3) and rearrangement, we can write,

$$\ln\left(\frac{\eta V_{\mathrm{m}}}{hN}\right) = \frac{\Delta H^{\neq}}{RT} - \frac{\Delta S^{\neq}}{R} \tag{5}$$

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TABLE III Viscosity, $\eta \times 10^4$ (kg m^{-1} s^{-1}), of 1-alkanols at different temperatures

1-alkanols	*Temperature* (K)				
	303.15	*308.15*	*313.15*	*318.15*	*323.15*
Methanol	5.133				
	5.14^{a}	4.798	4.504	4.216	3.975
	5.14^{b}	4.80^{b}	4.48^{a}		
Ethanol	9.93				
	9.930^{c}		8.27		
	9.95^{d}	9.13	8.291^{c}	7.58	6.99
	9.86^{a}	8.81^{b}	8.23^{a}		
	9.65^{b}				
1-Propanol	17.03	15.26	13.66		
	17.843^{c}	15.46^{e}	13.970^{c}	12.45	11.21
			13.85^{c}		
1-Butanol	22.37		17.64		
	22.853^{c}	19.77	18.170^{c}	15.75	14.06
	22.76^{d}	20.17^{e}	17.93^{e}		13.93^{f}
	22.61^{f}		17.65^{f}		
1-Pentanol			23.069		
	30.083	25.436	23.443^{c}		18.087
	28.315^{d}	26.52^{e}	23.33^{e}	20.419	17.65^{f}
	30.56^{f}		23.61^{f}		
1-Hexanol	39.161		29.460		
	39.1^{g}	33.795	29.4^{g}	25.772	22.644
	38.61^{f}	33.8^{g}	29.36^{f}	26.0^{g}	22.48^{f}
1-Heptanol	50.716		37.386		
	50.3^{g}	43.451	37.6^{a}	32.42	28.299
	47.853^{c}	42.5^{g}	35.786^{b}	32.3^{a}	27.41^{f}
	50.35^{f}		36.71^{f}		
1-Octanol	64.221		46.4455		
	63.6^{a}	54.353	46.5^{g}	39.984	34.543
	61.023^{b}	53.8^{a}	44.132^{c}	39.6^{g}	33.61^{f}
	61.00^{d}	54.58^{c}	46.46^{e}		
	62.56^{f}		45.84^{f}		
1-Nonanol	79.098	66.372	56.267		41.069
	78.6^{g}	66.6^{g}	55.9^{g}	47.919	
		67.41^{e}	57.07^{e}	48.1^{g}	
1-Decanol	96.759		67.922		
	95.7^{g}	80.712	67.4^{g}	57.542	
	88.347^{c}	78.3^{g}	69.555^{c}	57.4^{g}	48.947
	93.42^{d}	81.74^{e}	68.41^{e}		
1-Undecanol	116.008	96.080	80.317	67.595	57.506
		93.80^{e}	78.37^{e}		
1-Dodecanol	135.12	111.58	92.71	77.48	65.11
	130.8^{h}	108.4^{h}	90.2^{h}	75.7^{h}	64.5^{h}

[a]Ref. [15]; [b]Ref. [16]; [c]Ref. [10]; [d]Ref. [12]; [e]Ref. [11]; [f]Ref. [14]; [g]Ref. [9]; [h]Ref. [1].

The plots of $\ln(\eta V_m/hN)$ against $1/T$ yield excellent straight lines as shown in Fig. 4. In practice, the slopes and intercepts of these lines were determined by least squares method, which gave $\Delta H^{\neq}$ and $\Delta S^{\neq}$, respectively. By substituting these values in Eq. (4), $\Delta G^{\neq}$ values have been calculated at different temperatures, which are shown in Table IV. The $\Delta H^{\neq}$ and $\Delta S^{\neq}$ are also listed in Table IV. Figure 5 shows the plots of $\Delta G^{\neq}$ at 303.15 and 323.15 K. Figure 6 shows the plots of $\Delta H^{\neq}$ and $\Delta S^{\neq}$

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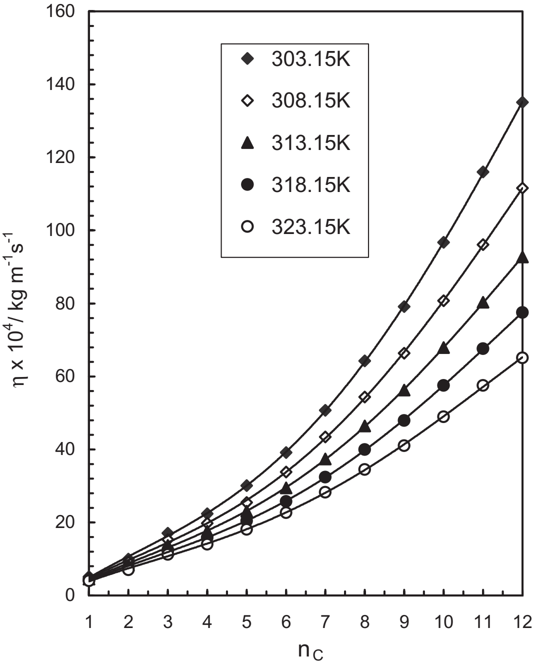

FIGURE 3 Viscosities of 1-alkanols against the number of C atoms, n_C.

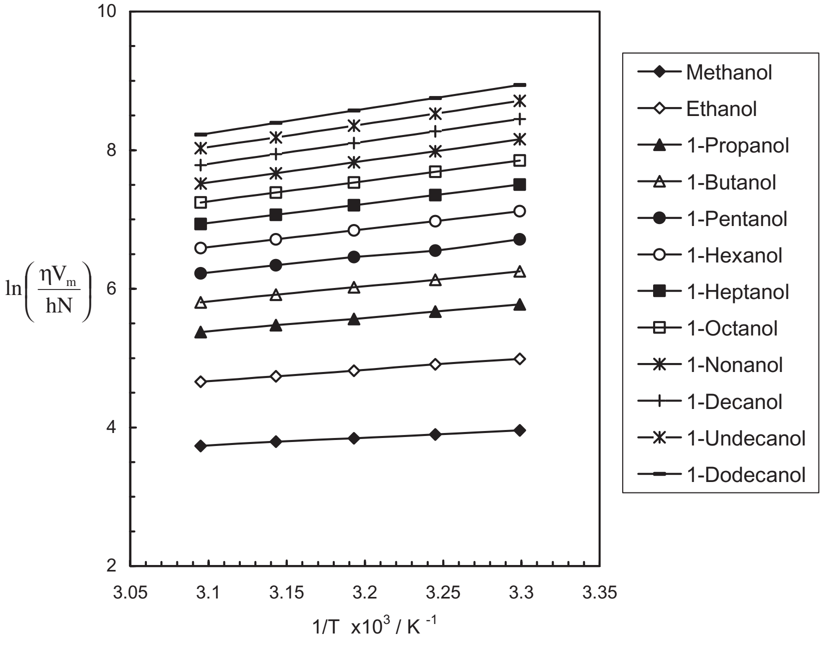

FIGURE 4 Plot of $\ln(\eta V_m/hN)$ against $1/T$ for 1-alkanols.

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TABLE IV Free energy of activation, $\Delta G^{\neq}$ (at different temperatures), enthalpy, $\Delta H^{\neq}$, and entropy, $\Delta S^{\neq}$, of activation for viscous flow of 1-alkanols

1-alkanols	$\Delta G^{\neq}$ (kJ mol^{-1})					$\Delta H^{\neq}$ (kJ mol^{-1})	$\Delta S^{\neq}$ (J mol^{-1})
	303.15 K	*308.15 K*	*313.15 K*	*318.15 K*	*323.15 K*		
Methanol	9.992	10.001	10.009	10.019	10.028	9.438	−1.825
Ethanol	12.582	12.565	12.549	12.532	12.516	13.583	3.302
1-Propanol	14.553	14.527	14.502	14.476	14.451	16.096	5.091
1-Butanol	15.752	15.714	15.676	15.638	15.601	18.041	7.553
1-Pentanol	16.884	16.842	16.800	16.758	16.717	19.416	8.351
1-Hexanol	17.938	17.878	17.818	17.759	17.700	21.538	11.877
1-Heptanol	18.905	18.835	18.767	18.698	18.629	23.084	13.788
1-Octanol	19.776	19.698	19.619	19.541	19.463	24.522	15.654
1-Nonanol	20.551	20.462	20.373	20.284	20.195	25.955	17.825
1-Decanol	21.289	21.194	21.099	21.005	20.911	27.022	18.913
1-Undecanol	21.951	21.852	21.754	21.656	21.558	27.901	19.628
1-Dodecanol	22.531	22.423	22.315	22.207	22.099	29.074	21.581

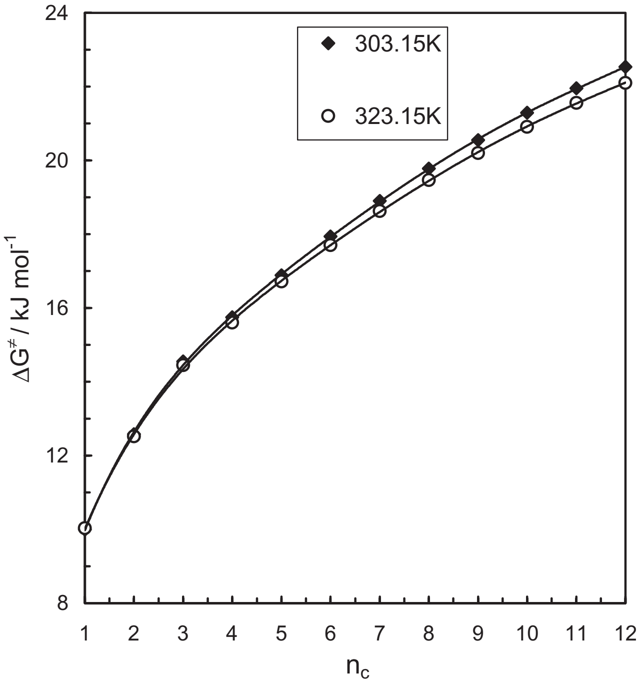

FIGURE 5 Free energy of activation for viscous flow, $\Delta G^{\neq}$, at 303.15 K and 323.15 K for 1-alkanols as a function of number of C atoms, n_C.

against n_C. All these quantities have been found to increase with the number of C atoms. The $\Delta S^{\neq}$ have been found to be positive for all alkanols, except methanol – which has a small negative value. The negative value for methanol is attributed possibly to its cyclic structures, which can align more easily along the direction of flow in the activation process, resulting in a somewhat ordered orientation. This causes the entropy

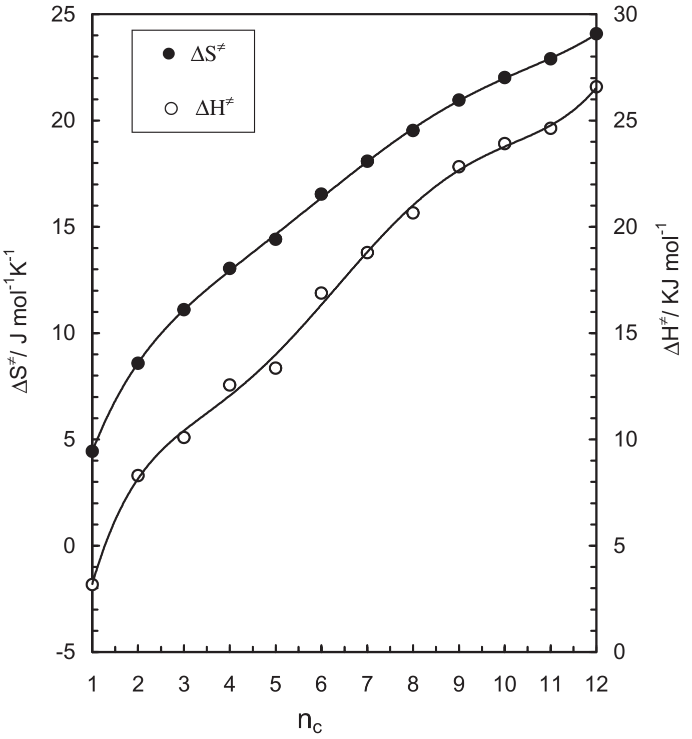

FIGURE 6 Enthalpy, $\Delta H^{\neq}$, and entropy, $\Delta S^{\neq}$, of activation for viscous flow for 1- alkanols as a function of number of C atoms, n_C.

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to decrease and hence the negative $\Delta S^{\neq}$. The positive $\Delta S^{\neq}$ for all other alkanols indicates that, probably rupturing of hydrogen bonds formed through OH groups of alkanols in the activation process for viscous flow occurs, resulting in the structural disorder.

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