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Volumetric Properties of 1-Alkanols at Temperatures in the Range 298–348 K and Pressures up to 40 MPa

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Molar volumes, thermal expansion coefficients, and isothermal compressibilities of six higher 1-alkanols (1-hexanol, 1-octanol, 1-decanol, 1-dodecanol, 1-tetradecanol, and 1-hexadecanol) have been determined at temperatures from 298 to 348 K and pressures up to 40 MPa. The density measurements were performed using a vibrating densitometer with an uncertainty of ±0.06%. The relationship between the properties and the structures of these alkanols is discussed in terms of the carbon-chain lengths.

KEY WORDS: decanol; density; dodecanol; hexadecanol; hexanol; high pressure; isothermal compressibility; octanol; Tait equation; tetradecanol; thermal expansion coefficient.

1. INTRODUCTION

The relationship between the thermodynamic properties of liquids in a homologous series and their chain lengths is of interest and many researchers [1–4] have tried to correlate them based on the group-contribution or corresponding-state theories. In the case of molar volume, the interests of the researchers have been concentrated upon some unbranched and branched alkanes or aromatic hydrocarbons, and none of them has touched on the higher alcohols. The purpose of this work is to provide the accurate *P–V–T* data for 1-hexanol ($C_6H_{13}OH$), 1-octanol ($C_8H_{17}OH$), 1-decanol ($C_{10}H_{21}OH$), 1-dodecanol ($C_{12}H_{25}OH$), 1-tetradecanol ($C_{14}H_{29}OH$), and 1-hexadecanol ($C_{16}H_{33}OH$) and to correlate their molar volumes with their carbon numbers.

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2. EXPERIMENTAL

2.1. Measurements at Atmospheric Pressure

Densities at atmospheric pressure were measured at 11 temperatures from 298 to 348 K at an interval of 5 K using a glass pycnometer calibrated against pure water.

2.2. Measurements Under High Pressures

2.2.1. Apparatus and Procedure

High-pressure densities were measured at 298, 323, and 348 K using a vibrating densitometer. A schematic diagram of the high-pressure apparatus is given in Fig. 1. The apparatus consists of a stainless-steel oscillating U-shaped tube, A, and a driving and frequency counting unit, B (Anton-Paar DMA 512), connected with a pressure supplying system. Pressure generated by a hydraulic oil pump, P, is transmitted to a sample liquid filled in the U-tube through a mercury separator, M. The U-tube housed in a brass vessel is regulated thermostatically within ±10 mK with an external water circulator. Temperature and pressure were determined by a thermistor, T (Takara D641), within ±10mK and a digitized Bourdon gauge, G (Heise 901B), within ±20 kPa, respectively. The vibrating period (reciprocal of the frequency), temperature, and pressure measured are all digitized and recorded by a microcomputer, C.

Through the valve, V_2, a sample was introduced into the U-tube previously evacuated. After thermal equilibration, the data were taken at nominal pressures spaced 5 MPa.

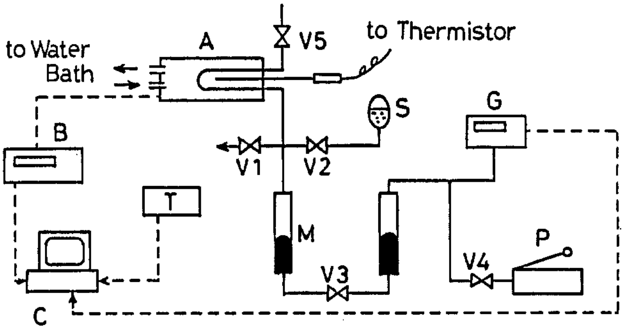

Fig. 1. Schematic diagram of experimental apparatus. (A, B) Vibrating densitometer (Paar DMA 512); (G) digitized Bourdon gauge; (C) microcomputer; (S) sample holder; (M) mercury separator; (T) thermistor; (P) oil pump; (V1–V5) valves.

2.2.2. *Calibration*

The measuring principle of vibrating densitometer is based on the change of the natural frequency of a U-tube when filled with different liquids. Using the simple relationship between the liquid density and the natural frequency of the tube, the sample density ρ_s can be determined by the following equation:

$$\rho_s = K(\tau_s^2 - \tau_{H_2O}^2) + \rho_{H_2O} \tag{1}$$

where τ_s and τ_{H_2O} are the periods when the sample liquid and pure water are filled, respectively, ρ_{H_2O} is the water density, and K is the cell constant calibrated with different standard fluids of known density. In the first step of the calibration, the cell constant at atmospheric pressure K_0 was determined, using degassed pure water and dried air at each temperature. And in the second step, the pressure dependence of the cell constant was determined with pure water H_2O [5] and heavy water D_2O [6], whose high-pressure densities are well known. As the result of this calibration procedure, it was found that the cell constant decreases monotonously with increasing pressure at any temperature. At the highest pressure, 40 MPa, the decrease in K was about 0.3%, which was equivalent to 6 $kg \cdot m^{-3}$ in density and should not be negligible.

2.3. Materials

The sample materials were obtained from Tokyo Chemical Industry Co., Ltd., with guaranteed purities more than 99% except 1-octanol (97%). These samples have been used after degasification without any further purification.

2.4. Uncertainty

Judging from the precision of our temperature and pressure control and the purity of the sample materials, the estimated uncertainties in the densities obtained at atmospheric pressure and under high pressures should be within ±0.04 and ±0.06%, respectively.

3. RESULTS AND DISCUSSION

3.1. Density at Atmospheric Pressure

The densities obtained at atmospheric pressure are given in Table I, together with some literature values at 298 and 348 K. As shown in this

Table I. Densities of 1-Alkanols at Atmospheric Pressure in kg·m^{-3}

Temp. (K)	$C_6H_{13}OH$ [102.18][a]	$C_8H_{17}OH$ [130.23]	$C_{10}H_{21}OH$ [158.29]	$C_{12}H_{25}OH$ [186.34]	$C_{14}H_{29}OH$ [214.39]	$C_{16}H_{33}OH$ [242.45]
298.15	815.5	822.8	826.6	829.6		
303.15	812.0	819.3	823.2	826.3		
308.15	808.3	815.7	819.7	822.9		
313.15	804.6	812.1	816.3	819.5	822.3	
318.15	800.9	808.5	812.8	816.1	818.8	
323.15	797.2	804.9	809.3	812.6	815.5	
328.15	793.4	801.3	805.9	809.1	812.0	814.3
333.15	789.6	797.5	802.3	805.6	808.6	810.8
338.15	785.7	793.8	798.7	802.1	805.2	807.3
343.15	781.8	790.0	795.1	798.6	801.6	803.9
348.15	778.0	786.2	791.4	795.0	798.1	800.3
298.15	815.65[b]	822.60[b]	826.23[b]	829.95[b]		
(lit.)	815.9[c]	822.2[c]	826.5[c]	830.4[c]		
	815.89[d]	821.77[d]	826.70[e]			
	816.2[f]	822.3[f]	826.3[f]	830.8[f]		
333.15	794.05[b]	797.58[b]	802.03[b]	806.06[b]		
(lit.)	791.4[c]	795.4[c]	802.0[c]	806.7[c]		
	790.3[f]	797.0[f]	801.7[f]	806.3[f]	808.1[f]	811.6[f]

[a] [Molar mass]: calculated with standard atomic weights (IUPAC 1987).
[b] From Ref. 9.
[c] From Ref. 11.
[d] From Ref. 8.
[e] From Ref. 7.
[f] From Ref. 10.

table, the density decreases monotonously with increasing temperature for each alkanol. In the comparison with the literature values, the present results agree with the data of Benson and his co-workers [7, 8] and Diaz Pena and Trardajos [9] within the mutual uncertainties at any temperature. The most probable values presented by Wilhoit and Zwolinski [10] and Rossini et al. [11] show some systematic discrepancies from our data. But their temperature coefficients of the molar volumes $(\partial V/\partial T)_P$ are similar to ours.

On the assumption that the thermal expansion coefficient can be given in powers of the temperature,

$$\alpha = (1/V)(\partial V/\partial T)_P = (\partial \ln V/\partial T) = \alpha_1 + \alpha_2 T + \alpha_3 T^2 + \cdots \qquad (2)$$

the following equation has been adopted to represent the present data:

$$V_0 = A_1 \exp(A_2 T + A_3 T^2) \qquad (3)$$

Table II. Coefficients in Eqs. (4), (5), and (6)

a_{11}	a_{12}	$10^4 a_{21}$	$10^3 a_{22}$	$10^4 a_{23}$	$10^7 a_{31}$	$10^6 a_{32}$
26.499	13.747	4.7692	−2.6802	9.20	4.594	5.523

where V_0 is the molar volume at atmospheric pressure in $cm^3 \cdot mol^{-1}$ and T is the temperature in K. In the first step, A_1, A_2, and A_3 were determined as the parameters of a least-squares fitting. As the parameter A_1 corresponds to the hypothetical liquid molar volume at 0 K, where no free volume can be expected, it is rational to consider that A_1 increases linearly with the carbon number C_n of 1-alkanol. After confirming this linearlity by a graphical plot, this relationship was represented by the following equation:

$$A_1 = a_{11} + a_{12} C_n \tag{4}$$

where a_{11} and a_{12} are the parameters. In the second step, the parameters A_2 and A_3 were redetermined using the smoothed A_1 values calculated by Eq. (4). The graphical plots of new A_2 and A_3 against the carbon number suggested that they can be correlated satisfactorily with the carbon number by the following equations:

$$A_2 = a_{21} + a_{22}/C_n + a_{23}/C_n^2 \tag{5}$$

$$A_3 = a_{31} + a_{32}/C_n \tag{6}$$

where a_{21} to a_{32} are also empirical fitting parameters and given in Table II. The average and the maximum deviations of the experimental data from Eq. (3) are given in Table III. All the maximum deviations are within the uncertainty of our data except that of 1-octanol, whose purity is a little inferior to that of other 1-alkanols.

Table III. Average and Maximum Deviations of Experimental Data from Eq. (3)

	$C_6H_{13}OH$	$C_8H_{17}OH$	$C_{10}H_{21}OH$	$C_{12}H_{25}OH$	$C_{14}H_{29}OH$	$C_{16}H_{33}OH$
Max. (%)	0.019	0.059	0.023	0.040	0.011	0.025
Ave. (%)	0.012	0.035	0.013	0.034	0.007	0.020

Table IV. Densities of 1-Alkanols Under High Pressures

298.15 K		323.15 K		348.15 K	
Press. (MPa)	Density ($kg \cdot m^{-3}$)	Press. (MPa)	Density ($kg \cdot m^{-3}$)	Press. (MPa)	Density ($kg \cdot m^{-3}$)
		[$C_6H_{13}OH$]			
0.10	815.7	0.10	797.3	0.10	777.9
4.80	818.7	5.30	801.2	5.18	782.4
10.00	822.1	9.70	804.3	9.80	786.3
15.15	825.3	15.25	808.1	15.00	790.3
20.15	828.2	20.40	811.6	20.00	794.0
23.16	829.9	22.95	813.2	23.90	796.5
28.22	832.9	28.95	817.1	29.45	800.5
31.00	834.3	34.80	820.6	40.02	807.6
35.20	836.7	38.90	823.0	30.40	801.1
40.00	839.4	30.60	818.1	19.70	793.6
30.40	834.0	20.20	811.5	10.30	786.5
16.40	826.0	10.40	804.9	0.15	777.9
6.20	819.7	0.20	797.3		
0.20	815.8				
		[$C_8H_{17}OH$]			
0.10	822.3	0.10	804.6	0.10	786.2
5.15	825.4	4.94	808.0	5.30	790.3
10.10	828.4	10.15	811.5	14.77	797.3
15.20	831.3	15.15	814.7	20.22	801.2
20.35	834.2	20.25	817.9	22.95	803.0
23.35	835.8	23.70	819.9	29.35	807.2
29.20	839.0	29.40	823.3	34.62	810.4
34.65	841.7	34.75	826.4	40.03	813.9
39.35	844.1	40.18	829.5	30.05	807.5
30.40	839.6	29.95	823.7	19.97	800.9
20.20	834.1	20.15	817.9	9.68	793.6
10.80	828.8	10.30	811.6	0.15	786.1
		0.20	804.6		
		[$C_{10}H_{21}OH$]			
0.10	826.8	0.10	809.4	0.10	791.5
1.00	827.3	2.02	810.8	1.25	792.4
4.80	829.6	5.35	813.0	5.10	795.3
10.20	832.7	10.00	816.0	10.23	799.1
14.80	835.3	14.80	818.9	14.58	802.0
19.45	837.8	18.85	821.3	18.90	804.9
22.95	839.6	26.90	826.0	24.40	808.3
27.80	842.1	31.90	828.8	29.50	811.6
32.80	844.7	26.15	831.2	35.00	815.0
37.30	846.9	40.00	833.2	40.20	818.1
40.20	848.3				

Table IV. (*Continued*)

323.15 K		348.15 K	
Press. (MPa)	Density ($kg \cdot m^{-3}$)	Press. (MPa)	Density ($kg \cdot m^{-3}$)
	[$C_{12}H_{25}OH$]		
0.10	812.9	0.10	795.2
2.45	814.4	0.85	795.8
5.60	816.4	5.45	799.2
10.35	819.4	10.20	802.5
23.25	826.9	14.85	805.6
28.45	829.9	20.85	809.4
28.30	829.8	27.90	813.8
33.85	832.8	26.95	813.2
37.40	834.7	32.75	816.6
40.00	836.1	37.23	819.3
4.15	815.6	39.70	820.7
1.43	813.8		
	[$C_{14}H_{29}OH$]		
0.10	815.5	0.10	798.0
0.55	815.7	5.30	801.8
1.80	816.5	10.20	805.1
5.15	818.6	14.80	808.1
10.30	821.8	19.80	811.2
15.40	824.8	22.55	812.9
19.95	827.4	28.15	816.2
22.60	828.8	32.80	819.0
28.60	832.1	32.25	818.6
32.70	834.4	35.60	820.5
36.40	836.6	39.65	822.9
39.40	837.9	2.05	799.4
	[$C_{16}H_{33}OH$]		
		0.10	800.2
		0.30	800.3
		4.10	802.9
		8.20	805.8
		12.10	808.4
		16.25	811.0
		21.20	814.0
		25.95	816.7
		30.35	819.3
		35.05	822.0
		40.10	824.9

3.2. Density Under High Pressures

Densities obtained under high pressures are given in Table IV. Pressure effects on the densities at 348 K are typically shown in Fig. 2. The molar volume isotherms were represented by the Tait equation,

$$V = V_0\{1 - C\ln[(B+P)/(B+P_0)]\} \tag{7}$$

where V_0 is the molar volume at atmospheric pressure P_0 and P is the pressure in MPa. The smoothed values calculated by Eq. (3) were adopted as V_0. The optimum values of B and C are given in Table V. As is shown in this table, the parameter C is almost independent of both temperature and sample materials within the uncertainty of the present measurements. Thus b values for B are redetermined using the average value of C:

$$C = 0.09195 \tag{8}$$

In order to represent the parameter B as functions of temperature and carbon number C_n, after testing several different forms of correlation equations, the following equation has been chosen:

$$B = (b_1 + b_2/T) + (b_3 + b_4/T)/C_n + (b_5 + b_6/T)/C_n^2 \tag{9}$$

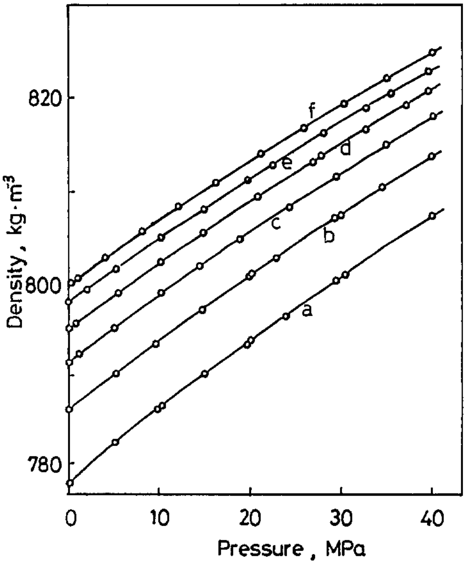

Fig. 2. Densities of 1-alkanols at 348.15 K as a function of pressure. (a) $C_6H_{13}OH$; (b) $C_8H_{17}OH$; (c) $C_{10}H_{21}OH$; (d) $C_{12}H_{25}OH$; (e) $C_{14}H_{29}OH$; (f) $C_{16}H_{33}OH$.

Table V. Optimum Coefficients of the Tait Equation

	Temp. (K)	B (MPa)	C (−)	Ave. dev. (%)	Max. dev. (%)
$C_6H_{13}OH$	298.15	119.72	0.09784	0.005	0.012
	323.15	96.98	0.09314	0.004	0.009
	348.15	76.15	0.08676	0.012	0.021
$C_8H_{17}OH$	298.15	118.95	0.09065	0.003	0.005
	323.15	104.54	0.09221	0.005	0.008
	348.15	89.47	0.09220	0.005	0.011
$C_{10}H_{21}OH$	298.15	122.37	0.08958	0.003	0.007
	323.15	108.94	0.09143	0.005	0.010
	348.15	89.11	0.08729	0.008	0.017
$C_{12}H_{25}OH$	323.15	116.20	0.09395	0.004	0.008
	348.15	95.10	0.08902	0.004	0.008
$C_{14}H_{29}OH$	323.15	127.39	0.09959	0.002	0.004
	348.15	101.56	0.09164	0.004	0.011
$C_{16}H_{33}OH$	348.15	104.71	0.09222	0.005	0.010

Table VI. Coefficients in Eq. (9)

b_1	$10^{-4}b_2$	$10^{-2}b_3$	$10^{-5}b_4$	$10^{-3}b_5$	$10^{-5}b_6$
−40.15	5.698	−8.087	1.633	2.735	−7.69

Table VII. Deviations of Experimental Data from the Generalized Tait Equation in %

	298.15 K		323.15 K		348.15 K	
	Ave.	Max.	Ave.	Max.	Ave.	Max.
$C_6H_{13}OH$	0.006	0.020	0.004	0.0011	0.012	0.025
$C_8H_{17}OH$	0.003	0.007	0.006	0.016	0.005	0.012
$C_{10}H_{21}OH$	0.005	0.011	0.005	0.014	0.009	0.023
$C_{12}H_{25}OH$			0.004	0.007	0.005	0.011
$C_{14}H_{29}OH$			0.004	0.010	0.004	0.011
$C_{16}H_{33}OH$					0.005	0.010

The coefficients b_1 to b_6 are given in Table VI. The average and maximum deviations of the experimental molar volume from those calculated are given in Table VII. As this procedure shows very little effect on both the average and the maximum deviations, our smoothing operation has been done satisfactorily. Furthermore, the volumetric properties of other 1-alkanols could be predicted by the interpolation or extrapolation of the present correlation against the carbon number.

3.3. Temperature and Pressure Effects on Density

The thermal expansion coefficients α and isothermal compressibilities β at various temperatures and pressures can be calculated by the following equations with the aid of parameters shown in Tables II and VI.

$$\alpha = (A_2 + 2A_3 T) + \left[1 - C \ln \frac{B+P}{B+P_0}\right]^{-1} \frac{C(P-P_0)}{(B+P)(B+P_0)} \frac{\partial B}{\partial T} \qquad (10)$$

$$\frac{\partial B}{\partial T} = -(b_2 + b_4/C_n + b_6/C_n^2)/T^2 \qquad (10a)$$

$$\beta = \left(1 - C \ln \frac{B+P}{B+P_0}\right)^{-1} \frac{C}{B+P} \qquad (11)$$

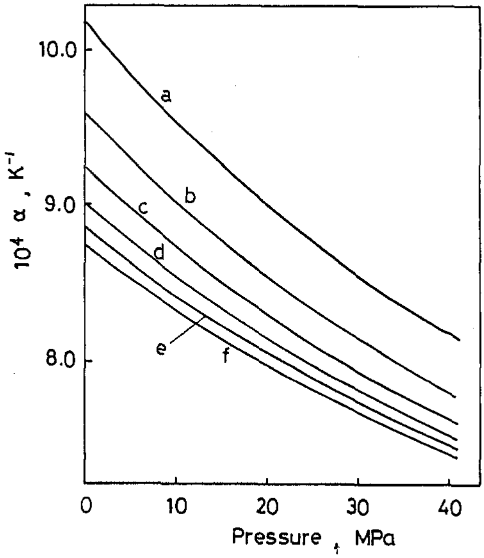

Fig. 3. Thermal expansion coefficients of 1-alkanols at 348.15 K as a function of pressure. (a) $C_6H_{13}OH$; (b) $C_8H_{17}OH$; (c) $C_{10}H_{21}OH$; (d) $C_{12}H_{25}OH$; (e) $C_{14}H_{29}OH$; (f) $C_{16}H_{33}OH$.

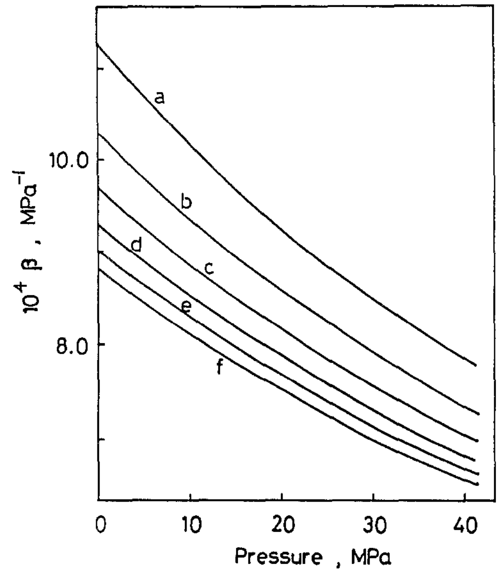

Fig. 4. Isothermal compressibilities of 1-alkanols at 348.15 K as a function of pressure. (a) $C_6H_{13}OH$; (b) $C_8H_{17}OH$; (c) $C_{10}H_{21}OH$; (d) $C_{12}H_{25}OH$; (e) $C_{14}H_{29}OH$; (f) $C_{16}H_{33}OH$.

Table VIII. Thermal Expansion Coefficients and Isothermal Compressibilities of 1-Alkanols at 298 K and Atmospheric Pressure

	$10^4\alpha$ (K^{-1})			$10^4\beta$ (MPa^{-1})		
	This work	Ref. 10[a]	Ref. 13	This work	Ref. 12	Ref. 9
C_4H_9OH	9.62	9.14	9.32	9.62	9.41	9.24
$C_5H_{11}OH$	9.10[b]	8.69		8.75[b]	8.83	8.84
$C_6H_{13}OH$	8.79	8.69	8.46	8.22	8.24	8.36
$C_7H_{15}OH$	8.57[b]	8.78		7.86[b]	7.78	8.00
$C_8H_{17}OH$	8.42	8.28	8.28	7.61	7.64	7.77
$C_9H_{19}OH$	8.30[b]	7.88		7.42[b]	7.45	7.52
$C_{10}H_{21}OH$	8.21	8.19		7.27		7.33
$C_{11}H_{23}OH$	8.14[b]	8.13		7.15[b]		7.23
$C_{12}H_{25}OH$	8.08[b]	8.25		7.05[b]		7.09

[a] Values calculated using Eq. (3).

[b] Interpolated or extrapolated values by Eq. (11).

The thermal expansion coefficients and isothermal compressibilities at 348 K are typically shown in Figs. 3 and 4, respectively. Both of them decrease monotonously with increasing pressure. In Table VIII the thermal expansion coefficients and isothermal compressibilities at 298 K calculated by Eqs. (10) and (11) are compared with those from the literature, including some interpolated and extrapolated values (1-butanol, 1-pentanol, 1-heptanol, 1-nonanol, and 1-undecanol). Some of our thermal expansion coefficients and those calculated from Ref. 10 are in fairly good agreement, in spite of their systematical discrepancies in density. But the comparison is difficult in general because of their poor consistency against the carbon number. The disagreement of the values given by Schmittecker [13] with ours is also beyond our comprehension. Meanwhile our isothermal compressibilities showed an excellent agreement with the values given by Sahli et al. [12]. The values of Diaz Pena and Trardajos [9] are a little higher than ours but they are still within combined uncertainties of the measurements.

4. CONCLUSION

Accurate experimental densities of six 1-alkanols (1-hexanol, 1-octanol, 1-decanol, 1-dodecanol, 1-tetradecanol, and 1-hexadecanol) are presented at temperatures from 298 to 348 K and pressures up to 40 MPa. The thermal expansion coefficients and isothermal compressibilities are determined using the presented correlation, which made it possible to represent the experimental densities as a function of temperature, pressure, and carbon number. This work would present the important information on the thermophysical properties of higher alcohols including the viscosity, whose measurements are now in progress under high pressures.

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