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pVT Data of Liquid 1-, 2-, and 3-Pentanol from 10 to 200 MPa and from 233 to 433 K

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Molar volumes of 1-, 2-, and 3-pentanol have been determined using a piston−cylinder apparatus. All isotherms are well described by the modified Tait equation $(V_0 - V)/V_0 = A \ln\{(B + p)/(B + p_0)\}$, with a temperature-independent parameter A, while B proved to increase monotonically with falling temperature. The quality of the fits suggests that the results can be extrapolated reliably by the Tait equation to pressures and temperatures beyond the range covered by our experiments (10−200 MPa, 233−433 K).

Introduction

In the course of an investigation of the molecular mobility of a series of hydrogen-bonded liquids, we measured the self-diffusion coefficients of the three pentanols over a wide range of temperature and pressure (*1*). For a meaningful interpretation of the data, however, the densities of the liquids under study are needed.

Since published *pVT* data for the pentanols cover only a very limited range of pressure and temperature, we decided to determine the densities for all three pentaols at temperatures between 230 and 433 K at pressures up to 200 MPa.

Experimental Section

Substances. 1- and 2-pentanol were obtained from Aldrich (Steinheim, FRG); 3-pentanol was purchased from E. Merck (Darmstadt, FRG). All substances were of the highest available purity (>99%). In order to remove residual moisture the substances were stored over 3 Å molecular sieves.

Apparatus. Densities were measured in a cylinder and piston type *pVT* cell, which is shown in Figure 1. The cylinder and piston are manufactured from a highly austenitic steel (RGT 100, Deutsche Edelstahlwerke, Witten, Germany). The bore of the cylinder has a diameter of 22.0 mm. The outer diameter is 70.0 mm. The maximum cell content is 110 cm^3. The movable piston and the front and back stamps, which close the bore, are sealed with O-rings. For the low temperature measurements ($T < T_{\mathrm{amb}}$) the O-rings employed were made from silicone, while for higher temperatures Viton was used (all O-rings were obtained from Busak & Shamben, Stuttgart, Germany). The low temperature, high pressure limit of the measurements was set by the embrittlement of the silicone. The cell is a modification of a design proposed by Francesconi et al. (*2*).

Thermostating of the cell is achieved by pumping silicone oil through a jacket around the cylinder. The temperature of the oil was kept constant to ±0.1 K by a commercial temperature controller (Haake N3, Haake, Berlin, FRG).

The temperature inside the sample volume is measured with a metal-sheathed chromel/alumel thermocouple (Philips GmbH, Kassel, Germany) which was soldered into a high pressure plug and led into the vessel through a 6 mm o.d. high pressure line. The thermocouple and display unit (W. Scholl, Siegen, Germany) were calibrated in a stirred liquid bath to ±0.2 K.

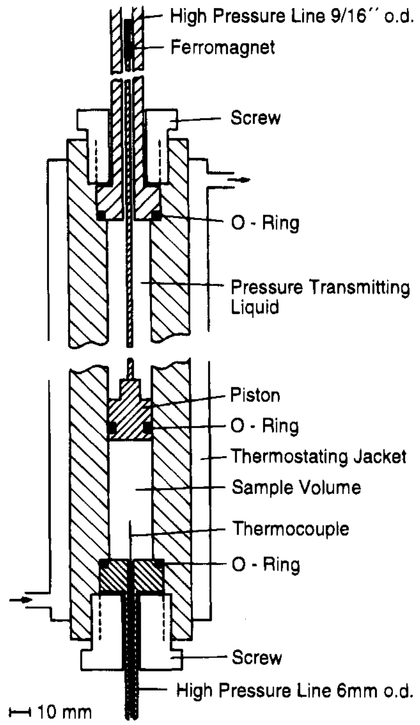

Figure 1. *pVT* cell used for the measurements.

To avoid a temperature gradient over the sample volume, it had to be stirred with an 8 mm ϕ steel ball by tipping the whole cylinder. The maximum uncertainty in the temperature is estimated to be smaller than ±0.3 K. This includes the effect of small temperature inhomogeneities over the sample volume.

The pressure was determined with two precision Bourdon gauges (Heise, New Haven, CT) with ranges of 100 and 400 MPa, respectively. It was measured in the pressure liquid circle, and hence the measured values had to be corrected for the friction of the piston. This was done by moving the piston forward and backward to a defined position and determining the pressure difference. This correction was applied to the pressures given below. The accuracy of the pressure data is judged to ±0.2 MPa below 100 MPa and ±1 MPa above 100 MPa.

The position of the piston could be determined to ±0.05 mm by detecting the magnetic field of a ferromagnet which is connected to the piston by a rigid steel rod.

Calibration. The sample volume was calibrated with the known *pVT* data for methane (*3*) and checked with *pVT* data for methanol (*4*); cf. Figure 2. The calibration with

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Table 1. Experimental Densities ϱ of 1-Pentanol

	ϱ/(kg·m^{-3})							
p/MPa	228.8 K	250.9 K	283.5 K	313.2 K	343.0 K	373.4 K	403.3 K	433.0 K
10	866.3	850.2	825.7	805.7	783.2	758.6	732.5	703.4
20	871.3	855.5	832.3	812.3	790.9	767.7	743.0	716.5
30	876.5	860.9	838.4	819.0	798.4	776.2	753.1	728.1
40	880.2	866.3	844.2	825.2	805.5	784.1	761.8	738.2
50				831.1	812.1	791.5		
60		875.8	854.7	836.9	818.2	798.2	777.4	756.0
80		884.8	864.3	847.6	829.1	810.4	791.0	771.1
100		892.8	873.5	856.6	839.7	821.7	803.3	784.5
120		900.5	881.6	865.5	848.5	831.8	814.2	796.4
140			889.6	873.4	857.5	840.8	824.1	806.8
160			896.9	880.8	865.7	849.7	833.6	816.8
180			904.4	888.4	873.4	858.1	842.3	826.2
200			911.2	895.3	880.8	864.0	850.6	835.1

Table 2. Experimental Densities ϱ of 2-Pentanol

	ϱ/(kg·m^{-3})							
p/MPa	234.0 K	249.3 K	283.4 K	313.2 K	342.9 K	373.4 K	403.2 K	433.0 K
10	859.2	847.7	822.3	799.1	774.4	745.6	715.1	680.6
20	864.3	853.0	828.9	806.8	783.1	755.9	727.9	696.9
30	869.5	858.4	835.3	814.1	791.1	765.3	739.3	710.3
40	874.4	863.9	840.8	820.8	798.7	774.2	749.4	722.0
50				826.9	805.8	782.3	758.8	732.5
60		873.6	852.0	832.9	812.4	789.7	766.9	741.9
80		882.5	861.5	844.0	818.4	802.8	781.9	758.5
100		890.8	870.5	853.6	824.3	814.8	795.1	773.0
120		898.9	879.0	863.3	835.1	825.8	806.8	785.9
140			886.6	871.4	844.6	835.7	817.6	797.4
160			893.9	879.5	854.0	844.5	827.4	808.0
180			901.3	886.8	862.4	853.2	836.7	817.6
200			908.1	894.2	870.7	861.7	845.2	825.1

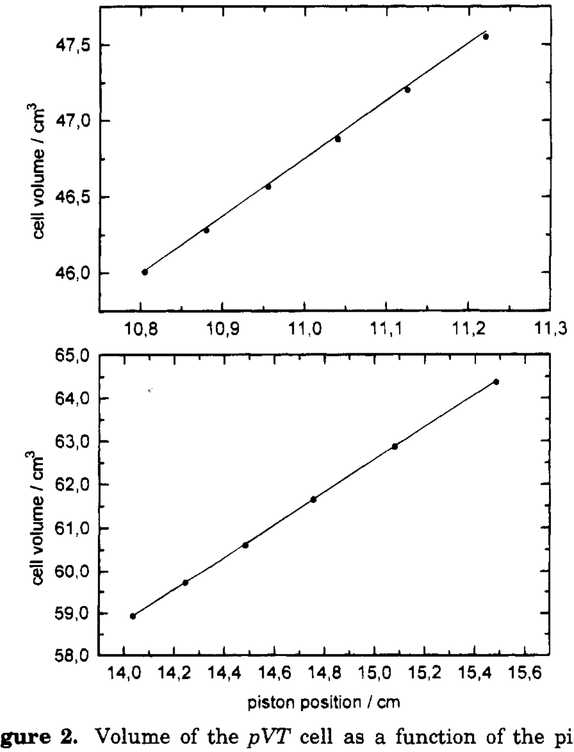

Figure 2. Volume of the *pVT* cell as a function of the piston position: line, as obtained from a fit to our methane calibration measurements; squares, results of test measurements with methanol, calculated with the densities of Goodwin (*4*); a, top, 237.9 K; b, bottom, 432.9 K.

methane data was done over the whole temperature and pressure range. Temperature and pressure effects on the steel cylinder and the steel rod are thus included in the calibration.

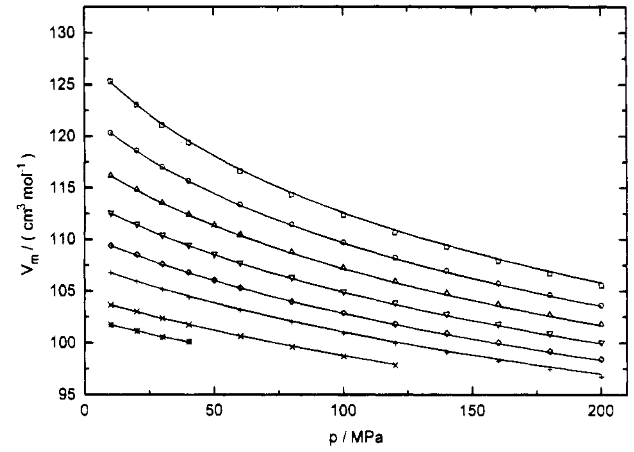

Figure 3. Experimental points of the molar volume of 1-pentanol: (O) 433.0 K, (O) 403.3 K, (△) 373.4 K, (▽) 343.0 K, (◇) 313.2 K, (+) 283.5 K, (×) 250.9 K, (*) 228.8 K. The lines result from fitting the modified Tait equation (eq 1) to the experimental results.

Filling Procedure. Before filling, the sample volume was evacuated by a vacuum pump to 10^{-1} Pa. The liquids were injected into the sample volume through a high pressure valve at the front of the cell. For this procedure, a syringe and a modified needle with a high pressure adapter were used. The amount of the injected substance was determined to ±0.001 g by weighing the syringe with an analytical balance before and after filling. The amount of substance used in the experiments ranged from 37.7 to 43.4 g. The accuracy of the mass determinations is estimated to be smaller than ±0.05% including the loss of substance during the filling procedure.

Accuracy. The results of both calibrations agree within ±0.2%. The overall accuracy of our results, which includes

Table 3. Experimental Densities ϱ of 3-Pentanol

p/MPa	ϱ/(kg·m^{-3}) 233.6 K	250.6 K	283.6 K	313.3 K	343.1 K	373.4 K	403.3 K	433.1 K
10	873.4	861.3	836.2	812.2	782.8	756.4	725.5	691.9
20	878.2	867.1	842.7	819.5	791.5	766.9	738.0	707.8
30	882.8	872.2	848.6	826.3	799.5	776.4	749.2	721.3
40	887.8	877.1	854.2	832.6	807.0	785.0	759.3	733.2
60	896.4	886.2	864.4	844.4	820.7	800.2	776.6	753.1
80		894.9	874.4	854.9	832.4	813.4	791.5	769.4
100		902.6	883.3	864.4	843.0	825.3	804.4	783.8
120		910.0	891.1	873.3	852.5	836.0	816.1	796.5
140			898.3	881.4	861.8	845.8	826.6	807.3
160			905.7	889.2	870.1	854.5	836.4	818.5
180			912.5	896.9	878.2	863.1	845.6	828.2
200			919.0	903.9	886.4	871.2	854.0	837.5

Table 4. Fit Parameter (with Standard Deviations) for the Modified Tait Equation (Eqs 1 and 2)

1-Pentanol								
p_o = 10 MPa, A = 0.10151 ± 3.2%, b_0 = 380.9 MPa ± 7.7%, b_1 = −1.18 MPa·K^{-1} ± 15.5%, b_2 = 9.21 × 10^{-4} MPa·K^{-2} ± 30.4%								
T/K	228.8	250.9	283.5	313.2	343.0	373.4	403.3	433.0
V_o/(cm^3·mol^{-1})	101.76	103.67	106.76	109.41	112.56	116.20	120.34	125.31
2-Pentanol								
p_o = 10 MPa, A = 0.09912 ± 4.4%, b_0 = 383.2 MPa ± 2.8%, b_1 = −1.24 MPa·K^{-1} ± 5.5%, b_2 = 9.795 × 10^{-4} MPa·K^{-2} ± 10.2%								
T/K	234.0	249.3	283.4	313.2	342.9	373.4	403.2	433.0
V_o/(cm^3·mol^{-1})	102.60	103.99	107.20	110.31	113.84	118.23	123.26	129.52
3-Pentanol								
p_o = 10 MPa, A = 0.09779 ± 3.8%, b_0 = 428.6 MPa ± 2.4%, b_1 = −1.45 MPa·K^{-1} ± 4.4%, b_2 = 12.2 × 10^{-4} MPa·K^{-2} ± 8.2%								
T/K	233.6	250.6	283.6	313.3	343.1	373.4	403.3	433.1
V_o/(cm^3·mol^{-1})	100.93	102.35	105.42	108.53	112.61	116.55	121.50	127.40

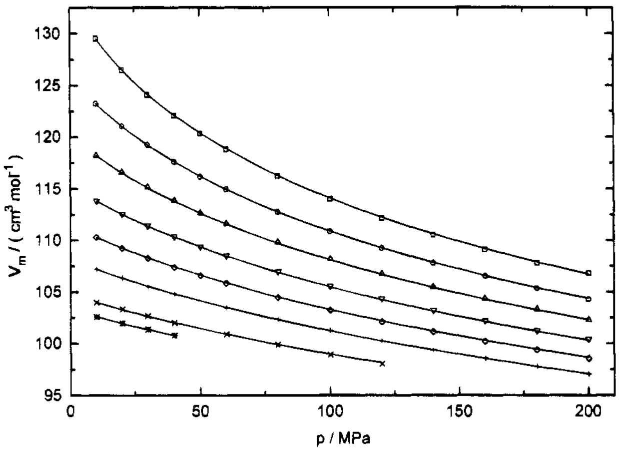

Figure 4. Experimental points of the molar volume of 2-pentanol: (□) 433.0 K, (○) 403.2 K, (△) 373.4 K, (▽) 342.9 K, (◇) 313.2 K, (+) 283.4 K, (×) 249.3 K, (*) 234.0K. The lines result from fitting the modified Tait equation (eq 1) to the experimental results.

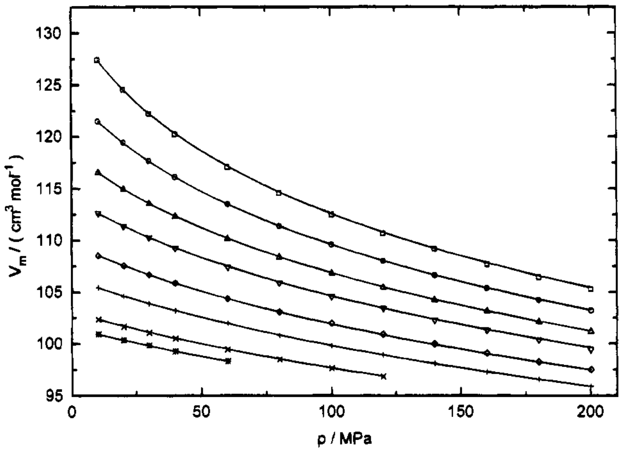

Figure 5. Experimental points of the molar volume fo 3-pentanol: (□) 433.1 K, (○) 403.3 K, (△) 373.4 K, (▽) 343.1 K, (◇) 313.3 K, (+) 283.6 K, (×) 250.6, (*) 233.6 K. The lines result from fitting the modified Tait equation (eq 1) to the experimental results.

the uncertainty in the pressure, temperature, and volumetric measurements and weighing is estimated to ±0.4% in the pressure range up to 100 MPa and ±0.6% above 100 MPa.

Discussion

Comparison with Literature Values. A number of studies (for recent results cf. refs 5−9) give densities for 1-pentanol. Except for the data of Sahli et al. (*8*), which extend to 7 MPa, and the results of Garg et al. (*6*) (10 MPa), all results are reported for vapor pressure only. Within the combined experimental errors, our data agree well with these values and do not show systematic deviations.

When extrapolated to vapor pressure, our results for 2-pentanol are in agreement with the values given by Riggio et al. (*5*).

Our results for 3-pentanol agree well with the data of Sahli et al. (*8*), when one of the data sets is extrapolated to reach the range covered by the other group.

The experimentally determined densities of the three substances are given in Tables 1−3. As can be seen from Figures 3−5, all isotherms can be well described by the modified Tait equation

$$\frac{V_o - V}{V_o} = A \ln\left(\frac{B + p}{B + p_o}\right) \qquad (1)$$

For each isotherm, the experimental points at the lowest pressure investigated (10 MPa) were taken for p_o and V_o. The A parameter proved to be independent of temperature, but different for each substance (all fit parameters are compiled in Table 4). B decreases monotonically with rising temperature and can be represented by the following empirical equation:

$$B(T) = b_0 + b_1T + b_2T^2 \qquad (2)$$

All experimental points can be described with eq 1 to within ±0.5%. The quality of the fits suggests that the modified Tait equation can be used to extrapolate the data to higher pressures as well as higher and lower temperatures with good confidence. A comparison with literature values also showed agreement at vapor pressure.

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