THERMODYNAMIC PROPERTIES OF HEPTANOL-1 AT ATMOSPHERIC PRESSURE

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Polynomial expressions are used to generalize data from the literature on density and isobaric specific heat of liquid heptanol-1 in the temperature interval 239.15-449.45°K. Isochoric specific heat and adiabatic and isothermal compressibilities are calculated.

A list of the main studies of density of liquid heptanol-1 at atmospheric pressure and on the saturation curve is presented in Table 1. In the majority of those studies density was measured at only one or two points, or only over a narrow temperature range. The widest studies of density were carried out in [4, 11]. In the low-temperature range there is only one experimental point [7], obtained at the fusion temperature. It should be noted that this temperature differs markedly from the fusion temperature recommended in the standard reviews [17, 18]. In the high-parameter range ($T = 273.15$-575.07°K and $P = 10.86$-491.4 bar) density was studied in [19]. The alcohol used was 99.43% pure with 0.089% water. The accuracy of the measurements was estimated at 0.1%. Only one analytical generalization of the available data [17] exists, encompassing the temperature range 273-413°K and based on experimental data accumulated before 1967. A preliminary analysis of the original density values used therein reveals that the majority agree with each other within limits of 0.1-0.3%, which exceeds the net uncertainty of the data compared. This is apparently due to inaccuracies of the experimental methods employed and the presence of unconsidered water and other impurities in the alcohols studied. Moreover, for $T < 273$ and $T > 373$°K (see Table 1) reliable data for processing are almost absent, so that for the present study density values here were taken from those based on the previously noted observation of [14] that in the homological series of N-alcohols at $T = 298$-333°K, beginning with the third member, propanol-1, there is a clearly expressed functional dependence of density of members of the series taken at identical temperatures upon number of carbon atoms in the molecule (methanol and ethanol, the first two members of the series, do not follow this rule). Calculations performed for the alcohols C_3-C_6, C_8, C_{10}, C_{12} using the results of [20-25] and the precise measurements of [26] showed that this dependence is satisfied with an error of no more than 0.1% over a wide temperature interval (233-453°K). This fact allows us to define or refine alcohol densities within the homologic series ($3 < n_C < 12$) to the required accuracy in cases where experimental data are absent or of low accuracy.

In Fig. 1 the function $\rho = f(n_C)$, depicted as a family of continuous curves, is passed through points taken from the results of [20-26] at identical temperature. There are no points for the alcohols C_7, C_9, and C_{11} on the graph because of the few reliable data available. The density values of heptanol-1 were taken from the graph at the points of intersection of the curves (isotherms) with a vertical line corresponding to $n_C = 7$. Since at $T < 258$°K the alcohols with $n_C \geqq 8$ are in the solid state, while at $T > 430$°K those with $n_C \leqq 6$ are gaseous, the density of liquid heptanol-1 at these temperatures was determined by graphical extrapolation of the curves with $n_C = 7$. To increase calculation accuracy the extrapolated density values were corrected with consideration of the temperature dependence of ρ of N-alcohols at atmospheric pressure. We estimate that the uncertainty of the calculation does not exceed 0.1%. This is also indicated by comparison at $T = 273$-333°K with the most reliable data of [2, 3, 5, 6, 9, 14-16]. The divergence lies within the limits ±(0.05-0.08%).

In the final processing, data from all the studies presented in Table 1 were used, with density values at 273-424°K obtained by graphic extrapolation of measurements of [19] to atmospheric pressure and results of a calculation for $T = 243$-448°K, based on use of the function $\rho = f(n_C)$.

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TABLE 1. Experimental Studies of Density of Liquid Heptanol-1

Reference	No. of points	Temp. range	Uncertainty, %
[1]	8	295—358	—
[2]	6	298—342	—
[3]	11	273—308	—
[4]	10	273—413	—
[5]	2	273,15; 298,15	—
[6]	1	298,15	0,01
[7]	1	237,65	0,1
[8]	5	293—373	0,1
[9]	1	273,15	0,01
[10]	7	293—343	0,1
[11]*	23	273—633	0,1
[12]	9	283—363	0,02
[13]	3	285—313	0,1
[14]	4	298—333	—
[15]	1	303,15	—
[16]	5	278—318	$2 \cdot 10^{-3}$ kg/m^3

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*Measurements on saturation curve.

TABLE 2. Calculated Thermodynamic Properties of Heptanol-1

T	ρ	c_P	c_V	$\beta_S \cdot 10^5$	$\beta_T \cdot 10^5$
239,15	0,8598	2,010	1,691	49,8	59,1
243,15	0,8570	2,022	1,705	50,8	60,3
253,15	0,8500	2,066	1,751	53,6	63,3
263,15	0,8431	2,120	1,804	56,7	66,6
273,15	0,8362	2,181	1,862	60,0	70,2
283,15	0,8292	2,246	1,924	63,5	74,2
293,15	0,8223	2,319	1,990	67,3	78,5
298,15	0,8188	2,359	2,025	69,4	80,8
303,15	0,8152	2,400	2,062	71,5	83,2
313,15	0,8081	2,489	2,141	76,0	88,4
323,15	0,8008	2,586	2,225	80,9	94,0
333,15	0,7934	2,687	2,313	86,2	100,2
343,15	0,7858	2,790	2,402	92,1	107,0
353,15	0,7780	2,891	2,485	98,5	114,5
363,15	0,7701	2,984	2,562	105,5	122,9
373,15	0,7619	3,066	2,627	113,3	132,3
383,15	0,7535	3,135	2,678	122,0	142,7
393,15	0,7448	3,189	2,716	131,6	154,5
403,15	0,7359	3,229	2,739	142,4	167,8
413,15	0,7268	3,256	2,752	154,7	183,0
423,15	0,7174	3,275	2,759	168,7	200,2
433,15	0,7078	3,290	2,763	184,7	220,0
443,15	0,6979	3,304	2,770	203,4	242,7
449,45	0,6916	3,313	2,775	217,0	259,0

An interpolation equation for inverse density was sought in the form

$$y = \sum_{i=0}^{n} a_i (T/1000)^i , \tag{1}$$

where y is ρ^{-1}. The coefficients a_i in Eq. (1) for ρ^{-1} have the following values: $a_0 = 0.816383829$, $a_1 = 2.4371056$, $a_2 = -6.20417089$, $a_3 = 8.6733857$.

These values were determined by the method of least squares using double precision arithmetic.

The divergence of the calculated density values from the original experimental ones is shown in Fig. 2. Also shown for comparison are deviations from the results of the generalization performed in [17]. As is evident from the figure, the divergence of the calculation from the reliable data of [2, 3, 5, 9, 13-16, 19] does not exceed ±0.1% practically everywhere in the comparison region. The values of [4] and the results of generalization [17] which rely thereon are low by 0.05-0.36 and 0.01-0.23% (at 303-413°K) respectively. The agreement with the data of [11] at T ≧ 313°K is within limits of ±0.10%. The divergence with the results of calculation by the method described above (not shown in the figure) are within limits of ±0.05%.

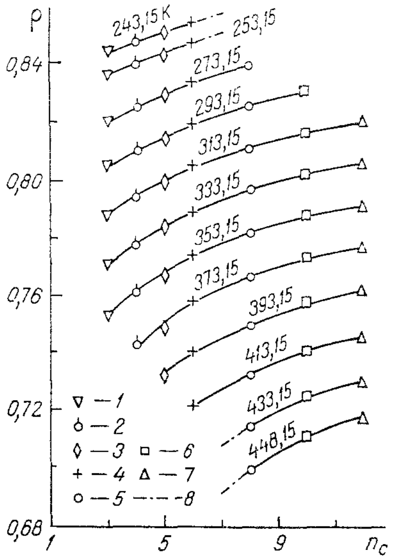

Fig. 1. Density vs number of carbon atoms in alcohol molecule: 1) data of [20]; 2) [21]; 3) [22]; 4) [23]; 5) [24]; 6) [25]; 7) [26]; 8) extrapolation.

Fig. 2. Comparison of calculated density values with data of other authors ($\delta\rho = (\rho[i] - \rho) \cdot 100/\rho$, %; i, reference); 1) [1]; 2) [2]; 3) [3]; 4) [4]; 5) [5]; 6) [6]; 7) [8]; 8) [9]; 9) [10]; 10) [11]; 11) [12]; 12) [13]; 13) [17]; 14) [14]; 15) [19]; 16) [15]; 17) [16].

With consideration of the character of the deviations the uncertainty of the recommended density values of Table 2 can be estimated at 0.1% over the entire temperature interval studied, i.e., from the normal fusion point (T = 239.15°K [17]) to the boiling point (T = 449.45°K [17]).

Specific heat Cp in the liquid phase was studied in [27] at temperatures of 303-443°K, at 240-300°K in [28], and 323-448°K in [29], with uncertainties of 0.9, 0.6-1, and 2.5%, respectively. In [29] measurement results were presented analytically in the form of a third degree polynomial in temperature. The original data agree with each other within the limits of experimental error. The most reliable are those of [27].

By statistical processing of these data, coefficients a_i were calculated in Eq. (1) for Cp: $a_0 = 799.498606$, $a_1 = -17181.7621$, $a_2 = 156977.667$, $a_3 = -788072.498$, $a_4 = 2346237.20$, $a_5 = -4139270.92$, $a_6 = 4005483.18$, $a_7 = -1640234.79$.

Equation (1) with coefficients for Cp describes the original data with a divergence not exceeding the experimental uncertainty, and is applicable in the temperature interval 239-449°K. The possible error of the recommended C_p values in Table 2 can be estimated at 1%.

It should be noted that the approximation of C_P data was performed with consideration of the unique temperature dependence of this property. In view of the absence of experimental specific heat values at node points such values were determined by graphoanalytical extrapolation of the data of [27, 28].

The interpolation equations obtained for inverse density and isobaric specific heat, as well as speed of sound [30], were used to calculate isochoric specific heat and adiabatic and isothermal compressibilities by the method presented in [31] (Table 2). There is practically no information on C_V and β_T in the literature. Comparison of calculated β_T values with the experimental data of [14] at temperatures of 298-333°K and data of [32] at 293.15 and 298.15°K indicates that the latter are low in value by average amounts of 1 and 4% respectively.

NOTATION

T, absolute temperature, °K; P, pressure, MPa; ρ, density, g/cm³; C_V and C_P, isochoric and isobaric specific heats, kJ/(kg·K); β_S and β_T, adiabatic and isothermal compressibilities, 1/MPa; n_C, number of carbon atoms per molecule.

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THERMAL DIFFUSIVITY OF CARBON DIOXIDE IN THE CRITICAL REGION

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An analysis and comparison of CO_2 thermal diffusivity measurements in the critical region performed in [1] and [2] is presented.

In [1] the present authors presented results of measurement of thermal diffusivity of CO_2 in the critical region. The measurements were performed with a polarization shift interferometer.

The results obtained in [2] with the aid of a holographic interferometer were presented in the form of tables and graphs in the coordinates $a-\rho$ and compared to our data. In constructing the graph $a = f(\rho)$ in [1] density values taken from [3] were used, these agreeing satisfactorily with the data used in [2].

Becker and Grigull graphed our results in the coordinates $a-\rho$, using density values obtained from the equation of state of Meyer-Pittroff et al. [4], obtaining a distorted graph with intersecting isotherms (Fig. 1). This was the basis for the conclusion that the data of [1] were evidently distorted by the effect of convection. In support of this conclusion it was noted that a polarization shift interferometer is less sensitive than the holographic one used in [2], so that in the process of measuring thermal diffusivity the authors of [1] had created temperature differentials between the foil and CO_2 under study an order of magnitude, or in some cases, two orders of magnitude, larger than in the experiments of [2].

The latter is in fact true. In [1] $\Delta T \approx 0.03$°K, while in [2] ΔT varied from approximately 0.3°K far from the critical point to 0.0001°K near the point. Nevertheless, it can be said with assurance that our results were not distorted by convection effects. Firstly, in the thermal diffusivity measurements visual monitoring of the interference pattern was carried out continually. Second, the method used for processing the interferograms permitted error-free detection of the commencement of convection. With molecular heat transfer the graph $(2x)^2 = f(\tau)$ which was constructed by decoding the interferograms is linear in character, beginning to curve when convection develops.

The distortion of the graph obtained by Becker and Grigull in processing our results can be explained in the following manner.

The Meyer-Pittroff equation does not describe the state of a material in the critical region sufficiently well. This statmeent is supported by the fact that in [2] isotherms in the coordinates $\lambda-\rho$ using density values obtained with this equation have a double "hump" at densities close to critical, not corresponding to the real character of the change in λ with ρ.

Naturally, use of an undoubtedly inaccurate equation of state cannot serve as a criterion for evaluating the correctness of experimental data. A direct comparison of the results of [1] and [2] would be of interest. Figure 2 shows isotherms $a = f(\rho)$ for the data of [2] (dashed lines) and [1] (solid lines). Density values obtained by Zenger [5, 6] were used for both sets of graphs. There is good qualitative agreement on all isotherms. On the descending portions of the isotherms over a wide pressure range and on the critical isochor the results also agree well quantitatively. On the lower portion of the descending branch and the rising branches there is some layering. However, in the critical region, where measurement becomes more complex, and the measurement uncertainty increases significantly, such divergence of the rsults can be regarded as completely acceptable.

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