EXPERIMENTAL STUDY OF ISOBARIC SPECIFIC HEAT OF HIGHER ALCOHOLS AT HIGH PRESSURES

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Results of measurements of isobaric specific heat of n-octyl and n-nonyl alcohols and n-hexane are presented.

Study of the dependence of thermophysical properties of aliphatic alcohols on temperature and pressure is important in connection with the ever wider use of these substances in technological processes.

The goal of the present study, which is a continuation of [1], is an experimental investigation of isobaric specific heat (c_p) of two representatives of the normal alcohols, n-octyl and n-nonyl, at high pressures and various temperatures.

The experiments were performed with impulsive regular regime equipment to determine the isobaric volume specific heat of the liquids. A description of the equipment and measurement methods are presented in [1, 2].

Values of c'_p of n-octyl and n-nonyl alcohols were measured at temperatures of 303.1-523.15°K and pressures of 0.1-50 MPa. In addition c'_p of n-hexane was measured at the same state parameters, as a control, in order to confirm the reliability of the data obtained for the alcohols, since the specific heat of n-hexane at high pressures has been studied quite thoroughly [3-7].

The n-octyl and n-nonyl alcohols and the n-hexane used in the experiments were of the "Ch" purity grade, with purities of 99.6, 99.4, and 99.8%, respectively, with the following characteristics:

$$\rho_4^{20} = 825{,}8\,\text{kg/m}^3;\quad n_D = 1{,}4288;\quad T_b = 468{,}43\,\text{K};\quad T_f = 258{,}15\,\text{K};$$

$$\rho_4^{20} = 827{,}8\,\text{kg/m}^3;\quad n_D = 1{,}4336;\quad T_b = 486{,}65\,\text{K};\quad T_f = 268{,}15\,\text{K};$$

$$\rho_4^{20} = 659{,}5\,\text{kg/m}^3;\quad n_D = 1{,}3747;\quad T_b = 341{,}89\,\text{K};\quad T_f = 177{,}83\,\text{K}.$$

The experimental data on isobaric specific heat of the alcohols at high pressure were obtained for the first time.

The experiments were carried out along isotherms, with temperature steps of ~25°K. On all the isotherms c'_p was measured at pressure values of 0.1, 2.5, 5.0, 10.0, 20.0, 30.0, 40.0, 50.0 MPa.

Isobaric (volume) specific heat c'_p values were calculated with the following computation equation derived in [2]:

$$c'_p = \frac{1}{V\left(1 + \dfrac{2\delta}{3R_1} + \dfrac{2\delta'}{3l}\right)}\left[\frac{W(1-K)}{b} - M_b c_b\right], \tag{1}$$

where $K = W_{loss}/W$.

The experiments revealed that the value of K was not dependent on pressure, and that it was desirable to determine the temperature dependence K = f(T) by control measurements on one isobar for well-studied substances. Water and benzol can be recommended for this purpose, since experimental data on c_p and c'_p for these liquids are most reliable.

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TABLE 1. Isobaric Mass $c_p \cdot 10^{-3}$, J/(kg•K) and Volume $c'_p \cdot 10^{-3}$, J/(m³•K) Specific Heats of n-Hexane

T, K	P, MPa									
	0,1		2,5		5,0		10		20	
	c_p	c'_p	c_p	c'_p	c_p	c'_p	c_p	c'_p	c_p	c'_p
308,35	2,356	1520,8	2,3498	1525,0	2,337	1528,0	2,325	1535,2	2,318	1550,9
333,15	2,485	1543,2	2,464	1540,0	2,45	1546,8	2,437	1555,2	2,43	1575,9
366,15	—	—	2,660	1561,4	2,648	1573,0	2,632	1585,9	2,611	1610,8
397,95	—	—	2,803	1564,1	2,790	1576,4	2,777	1596,8	2,758	1636,0
423,05	—	—	2,933	1550,1	2,914	1564,6	2,893	1591,2	2,873	1648,1
447,15	—	—	3,083	1526,1	3,053	1544,7	3,016	1582,0	2,987	1655,0
473,65	—	—	3,35	1490,8	3,262	1515,08	3,166	1562,4	3,10	1646,1
496,65	—	—	—	—	3,563	1478,8	3,317	1537,4	3,185	1630,0
519,15	—	—	—	—	4,029	1438,6	3,481	1505,3	3,251	1601,0

T, K	P, MPa					
	30		40		50	
	c_p	c'_p	c_p	c'_p	c_p	c'_p
308,35	2,312	1567,6	2,306	1583,9	2,299	1599,3
333,15	2,422	1594,7	2,416	1615,0	2,408	1632,6
366,15	2,598	1635,5	2,585	1658,2	2,574	1678,0
397,95	2,733	1661,7	2,71	1684,3	2,688	1703,9
423,05	2,852	1682,7	2,827	1707,5	2,80	1731,8
447,15	2,96	1694,6	2,93	1722,8	2,90	1747,3
473,65	3,06	1693,7	3,022	1727,1	2,984	1751,6
496,65	3,14	1684,6	3,088	1716,9	3,038	1742,0
519,15	3,19	1657,0	3,122	1692,0	3,06	1713,6

TABLE 2. Isobaric Mass $c_p \cdot 10^{-3}$, J/(kg•K) and Volume $c'_p \cdot 10^{-3}$, J/(m³•K) Specific Heats of n-Octyl Alcohol

T, K	P, MPa							
	0,1		2,5		5,0		10	
	c_p	c'_p	c_p	c'_p	c_p	c'_p	c_p	c'_p
303,2	2,53	2064,2	2,527	2065,0	2,524	2066,1	2,52	2069,9
323,65	2,637	2113,6	2,633	2114,8	2,629	2116,4	2,625	2120,8
350,45	2,779	2173,2	2,775	2175,6	2,77	2177,2	2,763	2181,4
371,55	2,896	2216,0	2,889	2218,2	2,882	2220,3	2,873	2224,6
400,15	3,052	2263,0	3,043	2265,1	3,032	2268,2	3,019	2274,6
422,65	3,182	2297,4	3,168	2298,4	3,153	2300,4	3,135	2307,3
448,65	3,347	2326,0	3,315	2325,2	3,296	2329,0	3,273	2336,5
476,60	—	—	3,476	2352,0	3,456	2353,5	3,42	2363,2
499,65	—	—	3,626	2364,3	3,595	2368,1	3,55	2377,3
523,15	—	—	3,792	2374,0	3,76	2380,1	3,704	2393,3

T, K	P, MPa							
	20		30		40		50	
	c_p	c'_p	c_p	c'_p	c_p	c'_p	c_p	c'_p
303,2	2,516	2080,2	2,512	2089,0	2,508	2097,2	2,505	2105,5
323,65	2,62	2132,7	2,615	2143,0	2,61	2153,3	2,606	2163,0
350,45	2,755	2195,0	2,748	2209,4	2,741	2220,2	2,735	2231,8
371,55	2,863	2239,4	2,854	2255,2	2,846	2268,3	2,839	2281,1
400,15	3,006	2291,7	2,994	2309,0	2,983	2325,6	2,974	2341,1
422,65	3,115	2326,0	3,10	2345,1	3,088	2364,3	3,078	2381,5
448,65	3,245	2357,0	3,225	2380,1	3,212	2401,8	3,20	2421,9
476,60	3,385	2388,1	3,360	2413,8	3,34	2435,6	3,325	2461,8
499,65	3,51	2407,8	3,477	2436,7	3,455	2461,9	3,435	2490,0
523,15	3,638	2423,0	3,595	2452,0	3,57	2482,8	3,55	2515,1

On the basis of the experimental data obtained for c'_p the isobaric (mass) specific heat c_p was calculated, for which step a knowledge of the density of the materials studied is required. Density values for n-ocyl and n-nonyl alcohols and n-hexane were taken from [8-10]. Results of the c_p and c'_p measurements are presented in Tables 1-3.

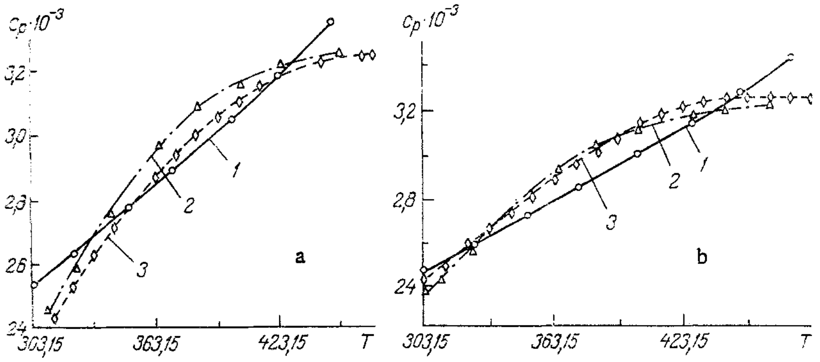

Fig. 1. Comparison of isobaric specific heat data for n-octyl (a) and n-nonyl (b) alcohols at atmospheric pressure: a: 1) present data; 2) [13]; 3)[11]; b: 1) present data; 2: [13]; 3) [12].

TABLE 3. Isobaric Mass $c_p \cdot 10^{-3}$, J/(kg•K) and Volume $c'_p \cdot 10^{-3}$, J/(m^3•K) Specific Heats of n-Octyl Alcohol

T, K	P, MPa							
	0,1		2,5		5		10	
	c_p	c'_p	c_p	c'_p	c_p	c'_p	c_p	c'_p
303,1	2,470	2029,8	2,467	2031,1	2,463	2032,0	2,46	2035,9
325,95	2,594	2094,3	2,59	2095,3	2,585	2096,5	2,58	2099,6
351,35	2,730	2155,7	2,723	2156,6	2,716	2157,6	2,709	2160,4
374,15	2,854	2206,0	2,848	2208,4	2,84	2211,0	2,833	2215,4
401,55	2,995	2252,0	2,986	2254,4	2,979	2258,0	2,968	2261,3
427,65	3,132	2287,01	3,117	2288,9	3,108	2292,1	3,094	2297,3
450,05	3,263	2312,0	3,245	2313,9	3,228	2316,0	3,205	2321,2
474,15	3,42	2340,9	3,385	2337,3	3,362	2339,1	3,33	2344,4
498,45	—	—	3,541	2354,6	3,51	2359,0	3,467	2365,9
522,45	—	—	3,713	2367,0	3,663	2373,1	3,605	2381,1

T, K	P, MPa							
	20		30		40		50	
	c_p	c'_p	c_p	c'_p	c_p	c'_p	c_p	c'_p
303,1	2,456	2045,8	2,452	2054	2,448	2062,7	2,445	2072,1
325,95	2,574	2110,2	2,568	2119,0	2,564	2128,1	2,56	2137,6
351,35	2,703	2173,2	2,698	2185,4	2,693	2195,1	2,688	2205,5
374,15	2,825	2227,1	2,817	2242,3	2,811	2254,4	2,805	2265,5
401,55	2,955	2278,0	2,947	2295,1	2,941	2310,2	2,935	2327,4
427,65	3,077	2315,0	3,068	2337,8	3,062	2356,2	3,058	2375,0
450,05	3,182	2341,4	3,171	2365,6	3,162	2387,0	3,158	2410,0
474,15	3,3	2369,0	3,281	2393,5	3,272	2419,8	3,267	2445,1
498,45	3,423	2392,0	3,399	2420,0	3,385	2449,0	3,379	2477,1
522,45	3,545	2411,8	3,516	2443,5	3,50	2475,0	3,492	2505,0

The data obtained for c_p of n-hexane were compared to the results of [3-7]. In [3-5] the isobaric specific heat of n-hexane was studied by the flow adiabatic calorimeter method with a closed circulation system at pressures of 0.1-60 MPa and temperatures from 293.15 to 624.3°K. Comparison of experimental data on c_p of n-hexane with available values at atmospheric pressure [3, 4] revealed that the data of [3, 4] are low in value by a maximum of 1.7%. Comparison at high temperatures and pressures showed that the results of [4, 5] are low by an average of 3.0%, and in individual cases — at 40.0 MPa pressure and 447.15°K temperature — the divergence reaches 5.2%.

In [6] the isobaric specific heat of n-hexane was measured by the Tian—Calvet method (relative variant) at the single temperature of 298.15°K and pressures from 0.098 to 147 MPa. Considering that our measurements of n-hexane c_p commenced from 308.35°K, for comparison purposes the data was extrapolated to a temperature of 298.15°K. The divergence of the data of [6] comprised 2.0% at atmospheric pressure, increasing to 6.0% at high (50.0 MPa) pressure.

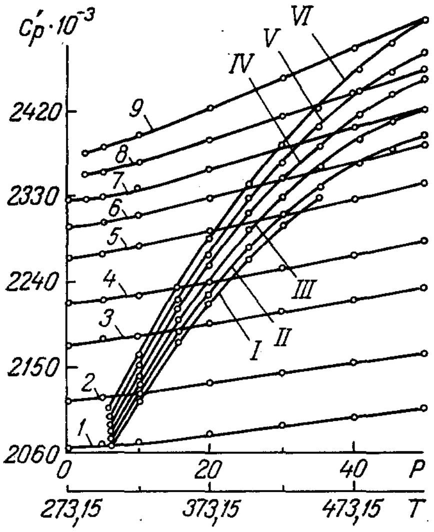

Fig. 2. Volume isobaric specific heat of n-octyl alcohol vs temperature and pressure: 1) T = 303.2°K; 2) 323.65; 3) 350.45; 4) 371.55; 5) 400.15; 6) 422.65; 7) 448.65; 8) 476.60; 9) 523.15°K; I) P = 0.1 MPa; II) 10.0; III) 20; IV) 30; V) 40; VI) 50.

Hadden [7] proposed a generalized equation for calculation of isobaric specific heat of liquid n-alkanes from the fusion temperture to the boiling point at atmospheric pressure. The calculated values of n-hexane c_p computed with Hadden's expression were compared to the present experimental data, and a maximum divergence of no more than 2.6% was found.

Thus, the divergence of data available in the literature from the present data at low pressures lies in the range 2.0-2.5%, which is essentially within the limits of experimental uncertainty for determination of c_p of liquids.

There have been only a limited number of studies of isobaric specific heat of n-ocyl and n-nonyl alcohols, providing data only at atmospheric pressure [11-13]. Temperature intervals for study of c_p comprise: in [11] for n-ocyl 313.15-468.15°K, in [12] for n-nonyl 303.15-483.15°K, and in [13] for n-octyl 310.67-452.29°K and for n-nonyl 304.17-464.24°K. Results of a comparison of the present experimental data at atmospheric pressure with data of [11-13] for c_p of n-octyl and n-nonyl alcohols are shown in Fig. 1, whence it is evident that the maximum deviations of the data of [11, 13] for n-octyl alcohol are 6.4 and 4.3%, respectively, while for n-nonyl alcohol the divergences from the data of [12, 13] do not exceed 5.3 and 4.7%, respectively.

Since data on isobaric specific heat of n-octyl and n-nonyl alcohols at high pressures have been obtained for the first time in the present study, it is impossible to compare them to other values.

To better clarify the dependence $c'_p = f(P, T)$ for n-octyl alcohol we present the data graphically in Fig. 2. It is evident that with increase in temperature and growth in pressure c'_p increases. A similar pattern was also found for n-nonyl alcohol.

To generalize the c_p data obtained the $c_p - \rho$ relationship proposed in [14] for liquid toluol (5.0, 10.0, 20.0, 30.0 MPa isobars) was used. For the spirits studied a slight layering over isobars was observed, especially noticable at pressures above 30.0 MPa.

The dependence can be expressed in the form of interpolation equations

$$c_p = 10^3 \sum_{i=1}^{n} A_i \left(\frac{\rho}{100}\right)^{i-1}. \tag{2}$$

To approximate Eq. (2) in polynomial form and determine the optimum value of n by the method of least squares a FORTRAN program for the ES-1022 computer was developed. The program permitted determination of the polynomial coefficients to the sixth degree with subsequent calculation of mean square deviations from smoothed curves. As a result the optimal degree of the polynomial was determined, corresponding to minimum mean square deviation. In the present case for Eq. (2) n = 2, i.e., a rectilinear dependence was obtained for all isobars of the alcohols studied. Values of the coefficients of Eq. (2) are presented in Table 4.

To consider the effect of layering over isobars in the coefficients A_1 and A_2 in Eq. (2) we introduce a parameter P:

TABLE 4. Coefficients of Eq. (2)

Substance	Coefficient	P, MPa							
		0,1	2,5	5	10	20	30	40	50
n-Octyl alcohol	A_1	8,048005	7,899964	7,935562	8,031140	8,256345	8,518218	8,774221	9,126382
	A_2	—0,674715	—0,654662	—0,658120	—0,668019	—0,691199	—0,718792	—0,745770	—0,784318
n-Nonyl alcohol	A_1	8,107812	7,939711	8,011864	8,079167	8,299903	8,648950	8,966676	9,246096
	A_2	—0,682409	—0,659655	—0,667634	—0,674199	—0,696774	—0,735472	—0,770027	—0,799280

TABLE 5. Coefficients of Eqs. (3), (4)

Substance	Coefficient					
	B_1	B_2	B_3	C_1	C_2	C_3
n-Octyl alcohol	7,9382437	0,0091516	0,0002968	—0,6608405	—0,0006917	—0,00003613
n-Nonyl alcohol	7,9810253	0,0117329	0,0002898	—0,6662371	—0,0010287	—0,00003497

$$A_1 = \sum_{j=1}^{m} B_j \cdot P^{j-1}, \tag{3}$$

$$A_2 = \sum_{\varepsilon=1}^{k} C_\varepsilon \cdot P^{\varepsilon-1}. \tag{4}$$

The method described above was used to determine the optimal degree of polynomials (3) and (4): $m = k = 3$ and the values of the coefficients B_j, C_ε, which are presented in Table 5.

Equations (2)-(4) can be used for interpolation and extrapolation of c_p data for the alcohols studied.

NOTATION

c'_p, volume specific heat, J/(m³•K); c_p, isobaric specific heat, J/(kg•K); ρ, density of material in ampul, kg/m³; $b = \Delta t/\Delta\tau$, heating rate at given temperature, K/sec; W, internal-heater power, W; W_{loss}, correction for the thermal power losses, W; $M_b c_b$, total ballast heat capacity of ampul, J/K; δ, δ', thicknesses of annular and plane end liquid layers, m; R_1, l, ampul radius and length, m; T, thermodynamic temperature, °K; P, pressure, MPa; T_f, T_b, fusion and boiling points of substance, °K; n_D, index of refraction; A_i, B_j, C_ε, equation constants; n, m, k, degrees of polynomials.

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VISCOELASTIC PROPERTIES OF THERMOTROPIC LIQUID CRYSTAL POLYMERS FROM ANALYSIS OF DYNAMICAL CHARACTERISTICS

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The rheological properties of liquid-crystal polymers with side-chain mesogenic groups are studied by means of small-amplitude periodic deformations in the mesophase and in the isotropic melt.

Thermotropic liquid-crystal polymers have been studied intensively in recent years in connection with their structure and behavior [1]. Therefore it is important to be able to describe their behavior in the different physical states, in particular, the viscous fluid state. The rheological approach to the study of the physical-chemical and physical-mechanical properties of liquid-crystal polymers is very fruitful and highly informative, since the viscoelastic parameters depend strongly on the structure and phase-aggregate state of the system.

Examination of the literature shows that in the majority of papers devoted to discussions of the rheological properties of liquid-crystal systems, only the viscous characteristics of the systems are considered. This is true both for thermotropic linear polymer systems [1, 2] as well as for polymers with a comblike structure [3]. However it is well known that the most complete rheological behavior of a system reflects its viscoelastic characteristics, which have not been studied extensively for liquid-crystal polymers, and have been limited to only a few systems [4-7].

The rheological behavior of liquid-crystal polymers with lateral mesogenic groups connected directly to the principal chains is of significant interest, for the following reasons. First, in polymers systems of this type the principal chain actively participates in the formation of the liquid-crystal phase, and hence the mesophases of these systems are true polymers. In addition, the macromolecules of these polymers are characterized by low equilibrium and high kinetic rigidity of the principal chain [8]. Finally polymers of this type have a layered structure which develops reversibly with increasing temperature [9, 10]. The features of the layered ordering depend on the structure of the monomeric unit and affect the thermodynamic, relaxational, and other properties of the polymers. In particular, for the series poly-n-methacryloiloxyphenyl ether n-H-alkyloxybenzoic acid (PMB-n), the methods of differential scanning calorimetry and linear thermodilatometry show that the parameters of the

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