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HEAT CAPACITY OF LIQUID ORGANIC COMPOUNDS: EXPERIMENTAL DETERMINATION AND METHOD OF GROUP APPROXIMATION OF ITS TEMPERATURE DEPENDENCE

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The article describes the experimental method and presents results of the investigation of the heat capacity of liquid n-alcohols and esters. It examines the method of group approximation of the temperature dependence on the example of n-alkanes and n-alkenes.

A calorimetric device was designed and made at the research institute VNIIFTRI. This device makes it possible rapidly and with sufficient accuracy to determine the heat capacity of small quantities (up to 12 cm^3) of both liquids and solids in the temperature interval 40-350°C. The device has the following main component units: an adiabatic calorimeter, a vacuum system, an automatic system of maintaining adiabatic conditions, and a potentiometric measuring console.

The adiabatic calorimeter is schematically illustrated in Fig. 1. The calorimetric cup 1 is made of two thin-walled copper tubes, each of which has a bottom of the same material soldered to it. Fixedly mounted between the tubes is a heater assembled on a mica frame and insulated on each side by mica plates. On top the cup is covered by a lid and suspended inside the massive block 3 by steel braces.

Block 3 is an adiabatic shell consisting of a thick-walled copper cylinder and massive bottom and lid with sliding fit. Heaters are situated on the outer surface of the cylinder, the bottom, and the lid. A differential Chromel—Constantan thermocouple is provided for registering possible temperature gradients between the upper, central, and lower parts of the block. The junctions of this thermocouple are situated in special holes and fixed with a heat-resisting paste (Fig. 1 does not show the position of this thermocouple). Block 3 is mounted inside furnace 4 on thin stainless-steel tubes 7. Furnace 4 is made of a thick-

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TABLE 1. Coefficients of the Equation Expressing the Dependence of Molar Heat Capacity (J/mole·°K) of Alcohols on the Temperature

Substance	Coeff. of equation			σ	Temp. intervals, °C
	A	B	$C\cdot 10^2$		
n-Heptanol	214,298	1,7618	—0,4575	2,43	50—180
n-Octanol	252,623	1,7670	—0,4581	3,46	40—195
n-Decanol	317,790	1,7410	—0,3499	4,42	50—130
	431,048	0,6027	—0,1317	4,04	130—230
n-Tridecanol	391,867	2,6319	—0,7826	2,74	50—150
	661,379	—0,5633	0,1598	2,44	150—280
n-Tetradecanol	393,373	2,9705	—0,8483	7,13	60—140
	499,044	1,6728	—0,4584	6,82	140—190
	746,313	—0,9838	0,2560	5,55	190—300
n-Octadecanol	588,698	2,3814	—0,6614	5,24	80—140
	770,719	0,1735	0,0045	4,52	140—240
	746,285	0,02991	0,1062	5,93	240—350

walled copper cylinder onto whose outer surface a heater is wound. The cylinder is mounted on flange 8; on top it is covered by a lid.

The adiabatic conditions in the calorimeter are maintained by highly accurate temperature regulators (ART-3 and VRT-3). The sensors are two differential Chromel—Constantan thermopiles 9, 10. One of them, 9, ensures equal temperature of the calorimetric cup 1 and the block 3. The other, 10, is instrumental in maintaining a constant temperature difference between furnace 4 and the block. The temperature of the calorimeter is measured by the platinum resistance thermometer 11 mounted in a recess of the copper block.

The calorimetric system is situated inside vacuum jackets made up of the two stainless-steel cylinders 5, 6. All copper parts of the calorimeter are silver-plated.

In investigations of the heat capacity of liquids, the thin-walled calorimetric ampoule 2 is used. It is made of steel brand 1Kh18N9T, has itself low heat capacity, can withstand excess pressure of 0.2 MPa, and has an overall volume of 17 cm^3. The investigated liquid is poured into it through a shut-off device to 2/3 of its total volume. The ampoule fits with a sliding fit into the calorimetric cup 1.

During the certification tests of the device, optimum operating conditions were selected, the deviations of the experimental points from the smoothed curve and the reproducibility

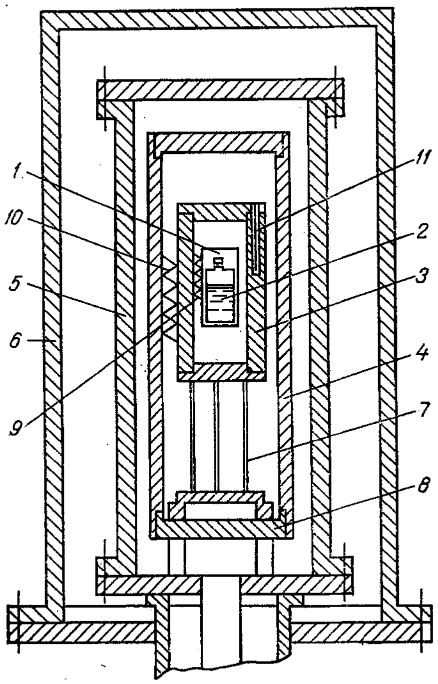

Fig. 1. Adiabatic calorimeter with continuous heat supply.

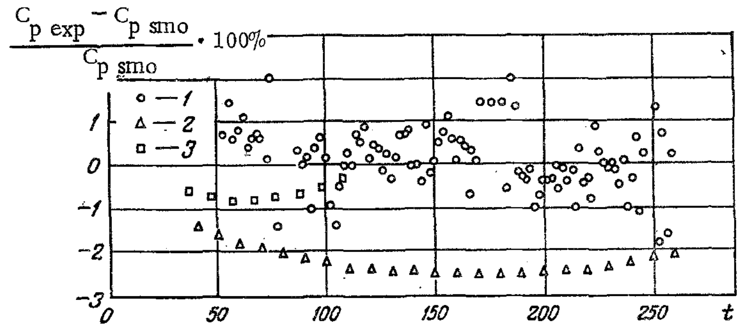

Fig. 2. Deviation of the experimental points on heat capacity from the smoothed curve $(C_{p\ exp} - C_{p\ smo})/(C_{p\ smo}) \cdot 100\%$: 1) our data on diphenyl ether; 2) literature data on diphenyl ether; 3) literature data on n-heptane; t, °C.

of the results and systematic errors due to various factors were evaluated. The temperature dependence of the heat capacity of the empty calorimeter was obtained from two series of measurements carried out at the beginning and at the end of the investigations. Both sets of these experimental data were processed jointly and represented by a polynomial of second degree for the temperature interval 40-350°C. The rms deviation of the experimental points from the smoothed curve does not exceed 0.6%.

The standard samples in calibrating the device were n-heptane and diphenyl ether because for them reliable data on heat capacity are known in a broad temperature interval [1, 2]. The purity of these substances was determined by the cryometric method on a device "KASKAD-01" [3]. It was established that the purity of n-heptane was 99.92 and of diphenyl ether 99.95 mole %.

Since the calorimetric ampoule for liquid samples withstands an excess pressure of 0.2 MPa (2 atm) and is filled with the investigated liquid at atmospheric pressure, the upper limit of the measurements is confined for any substance to a temperature close to the normal boiling point. The heat capacity of n-heptane was therefore investigated in the temperature interval 40-110°C, and the heat capacity of diphenyl ether in the interval 40-260°C.

Calibration of the device with the standard samples showed that the scatter of the extremal points around the smoothed curves does not exceed 2%. Figure 2 shows the deviations of the experimental data from the smoothed values of heat capacity for diphenyl ether. The results of our measurements were compared with the literature data on the heat capacity of heptane [1] and diphenyl ether [2] (Fig. 2). The values obtained by us are larger than those in the literature. For n-heptane this difference is about 0.8%, for diphenyl ether it is 2.6%. This discrepancy in the results is due to a systematic error, apparently caused by the differences in the conditions of heat exchange in an empty and a filled calorimeter.

n-Heptanol, n-octanol, and n-decanol were purified by the following method. One liter of alcohol was agitated with 50 ml concentrated sulfuric acid in a separating funnel. The acid layer was separated, the alcohol was washed with aqueous solution of NaOH, then with water up to neutral reaction, and dried with calcined Na_2SO_4. The dry alcohol was distilled

TABLE 2. Coefficients of the Approximating Polynomials for the Heat Capacity (J/mole·°K) of Butyl Acetate and Butyl Butyrate

Temp. interval, °C	T_0, °C	M	A_0	A_1	A_2	A_3	σ
			Butyl acetate				
—77,12—6,85	—43,15	100	209,33	12,45	16,68	—6,95	0,45
6,85—9,7	46,85	100	229,84	32,50	7,81	—20,41	0,41
27—126	66,85	100	241,93	37,98	—3,42	—	0,99
			Butyl butyrate				
—91,57—6,85	—43,15	100	262,51	16,21	17,57	—4,25	0,44
6,85—97	46,85	100	289,70	40,20	5,21	—5,14	0,36
37—166	96,85	100	314,99	47,7	—2,59	—	2,28

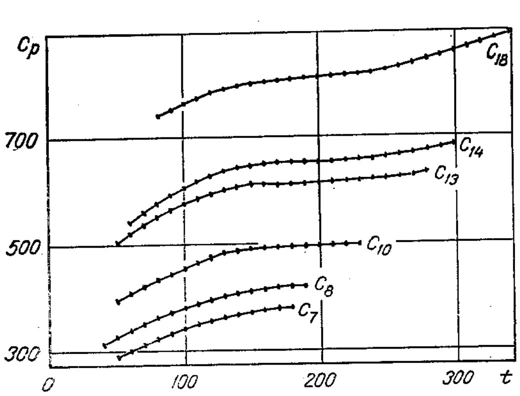

Fig. 3

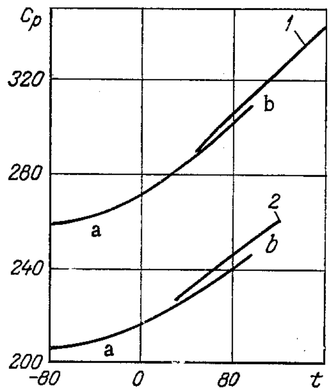

Fig. 4

Fig. 3. Dependence of the heat capacity of n-alcohols on the temperature: C_7) heptanol; C_8) octanol; C_{10}) decanol; C_{13}) tridecanol; C_{14}) tetradecanol; C_{18}) octadecanol.

Fig. 4. Dependence of the heat capacity of esters on the temperature: 1) butyl butyrate; 2) butyl acetate; (a, b — data obtained on low-temperature and high-temperature devices, respectively).

in vacuum and twice purified in a rectification column at atmospheric pressure. The n-tridecanol was purified by repeated recrystallization from the melt. The n-tetradecanol was only distilled in vacuum. The n-octadecanol was twice recrystallized from benzene and dried in vacuum at 80°C. Butyl butyrate was purified by threefold distillation in a vacuum rectification column. Butyl acetate brand "chemically pure for chromatography" was not subjected to supplementary purification.

The purity of the alcohol samples was determined by the cryometric method and was (mole %): for n-heptanol 99.2; n-octanol 99.6; n-tetradecanol 99.2; octadecanol 99.8. The purities of butyl acetate and of butyl butyrate were determined by the calorimetric method and were 99.62 and 99.41 mole %, respectively.

The heat capacity of alcohols was investigated in the interval from 40-50°C (or from the melting points) to the normal boiling points. The dependence of the heat capacity of alcohols on the temperature is of a complex nature (Fig. 3). At first the smoothed curves rise fairly steeply, but with increasing temperature the derivative dC_p/dt decreases monotonically, and sections of the curves appear where the heat capacity changes only slightly. With all the investigated alcohols the beginning of such a section lies in the region of 150-160°C.

With higher alcohols (C_{13}, C_{14}, C_{18}) the decrease of the derivative is maintained approximately up to 220 or 230°C. Above this temperature the rate of increase of heat capacity increases again. Thus in the entire measured temperature interval the curves are S-shaped, with the point of inflection around 220-230°C.

For lower alcohols (C_7, C_8, C_{10}) the curves of heat capacity end near the point of inflection because their normal boiling points are relatively low. It may be assumed that at higher temperatures the course of the heat capacity of lower alcohols is similar to that of the higher alcohols.

So far it has not been established why the dependence of the heat capacity of liquid alcohols on the temperature is so complex. It seems that it is caused by the contribution of a component, due to the association of molecules, to the normal heat capacity of alcohols.

Since the curve of molar heat capacity vs. temperature cannot always be satisfactorily described by a single simple equation, it was divided into sections for some alcohols. The experimental data for the sections were processed by the least-squares method according to the equation $C_p = A + Bt + Ct^2$. The results of the processing are presented in Table 1.

The heat capacity of liquid ethers in the temperature interval from room temperature to the normal boiling point was investigated by the above-described method, and in the

TABLE 3. Results of Individual and Joint Processing of the Heat Capacity of Liquid n-Alkanes and n-Alkenes by Eqs. (1) and (3)

Substance	No. of points	Individual processing			Joint processing σ, %
		coeff. of Eq. (1)		σ, %	
		a	*b*		
Pentane	20	0,038097	0,89834	0,11	0,83
Hexane	24	0,058901	1,0219	0,23	0,97
Heptane	25	0,035645	0,98564	0,46	0,48
Octane	17	0,12086	1,3430	0,08	0,64
Nonane	19	0,18060	1,7070	0,20	0,47
Decane	17	0,24659	1,1769	0,05	0,65
Undecane	12	0,14783	1,6890	0,07	0,16
Dodecane	11	0,25237	1,6482	0,07	0,38
Tridecane	8	0,80768	3,3771	0,08	0,25
Tetradecane	7	0,48994	—1,1274	0,06	0,38
Pentadecane	7	0,30342	1,5357	0,04	0,27
Hexadecane	9	0,34203	2,0566	0,03	0,15
Heptadecane	11	0,31805	1,5078	0,32	1,24
Octadecane	11	0,44183	0,91928	0,09	0,87
1-Pentene	24	—0,15090	1,0145	0,23	0,75
1-Hexene	23	—0,072177	1,1519	0,33	1,13
1-Heptene	22	—0,35702	2,8067	1,70	1,86
1-Octene	20	—0,19163	1,9975	0,73	0,76
1-Decene	17	—0,11933	2,0327	1,10	2,76
1-Undecene	12	—0,20183	3,3300	0,60	0,72
1-Dodecene	11	—0,12644	3,6902	0,33	0,42
1-Hexadecene	14	0,13857	4,3150	0,07	0,31

interval between the melting point and 100°C on an adiabatic vacuum calorimetric device by the method described in [4]. The experimental data were smoothed by the least-squares method by cross-linked polynomials of the type

$$C_p = \sum_{i=0}^{k} A_i \left(\frac{t - t_0}{M} \right)^i$$

by a method described in [5]. The results of the processing are presented in Table 2.

The dependence of the heat capacity of butyl butyrate and of butyl acetate on the temperature is presented in Fig. 4.

The discrepancy in the heat capacity of esters obtained by different methods at temperatures below 100°C may be due to the above-mentioned systematic error of the high-temperature device.

As a result of fractional melting, the melting points and triple points of the esters were determined; they were -77.12 ± 0.4 and -77.03 ± 0.03°C for butyl acetate and -91.57 ± 0.03 and -91.47 ± 0.02°C for butyl butyrate, respectively.

The above method of approximating the temperature dependence of the heat capacity by polynomials of second, third, or higher degree of the temperature is widely used. This method, as well as other methods dealt with in the literature (see, e.g., [6]), have a grave shortcoming: according to the approximating nonlinear equations it is impossible to extrapolate the heat capacity to temperatures lying outside the interval of experimental data. This shortcoming can be eliminated by finding a method of linearizing the dependence of the heat capacity of the liquid on the temperature. For this purpose, an expression of the following type was suggested:

$$\left(\frac{C_p^{\mathrm{T}}}{C_p^{\mathrm{mp}}} - 1 \right) \Big/ \left(\frac{T - T_{\mathrm{mp}}}{T_{\mathrm{cr}} - T_{\mathrm{mp}}} \right) = a + b \left(\frac{T - T_{\mathrm{mp}}}{T_{\mathrm{cr}} - T_{\mathrm{mp}}} \right), \qquad (1)$$

in which a and b are linear regression coefficients.

With Eq. (1) by the least-squares method we approximated the experimental values of heat capacity, available in the literature, on the saturation line of liquid normal hydrocarbons from C_5 to C_{18} and of normal olefins from C_5 to C_{16} in the interval of values of the arguments 0-0.8. The results of such processing are presented in Table 3 in the column "Individual processing." The error of the approximation was calculated by the equation

$$\Delta = \sqrt{\Sigma\left(\frac{C_{p\,\mathrm{exp}} - C_{p\,\mathrm{theo}}}{C_{p\,\mathrm{theo}}}\right)^2 \Big/ n} \cdot 100. \qquad (2)$$

In the analysis of the results we found a linear dependence of the coefficients of Eq. (1) for the chain of molecules for each homological series, in consequence of which Eq. (1) can be represented in the more general form

$$\left(\frac{C_p^T}{C_p^{\mathrm{mp}}} - 1\right) \Big/ \left(\frac{T - T_{\mathrm{mp}}}{T_{\mathrm{cr}} - T_{\mathrm{mp}}}\right) = a_0 + a_1 N + (b_0 + b_1 N)\left(\frac{T - T_{\mathrm{mp}}}{T_{\mathrm{cr}} - T_{\mathrm{mp}}}\right). \qquad (3)$$

The coefficients of Eq. (3) were found in the joint processing of the experimental data of all compounds of each homological series. For n-alkanes they were: $a_0 = -0.047324$, $a_1 = 0.022489$, $b_0 = 0.005402$ and $b_1 = 0.11940$; and for n-alkenes $a_0 = -0.35712$, $a_1 = 0.025789$, $b_0 = 0.00829$ and $b_1 = 0.23767$. The error of joint processing, calculated by Eq. (2), is also shown in Table 3.

Thus the above-explained method makes it possible to calculate with good accuracy the heat capacity of all the compounds of the homological series in the entire region of their liquid state when the amount of experimental data is limited. The method unfortunately cannot be used for liquid normal alcohols because of the complex temperature dependence of their heat capacity.

NOTATION

C_p, heat capacity at constant pressure; T, t, Kelvin and Celsius temperatures, respectively; t_0, point of recording of the temperature in the approximation range; M, scale factor; A, B, C, A_0, A_1, A_2, A_3, a, b, a_0, a_1, b_0, b_1, coefficients in equations; T_{mp}, melting point; T_{cr}, critical temperature; C_p^T and C_p^{mp}, heat capacity at temperatures T and T_{mp}, respectively; C_p exp, C_p smo, C_p theo, experimental, smoothed, and calculated values of heat capacity, respectively; K, power of the polynomial; n, number of experimental points; N, number of carbon atoms in a compound; σ, rms deviation; Δ, error of the approximation.

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