DENSITY OF ISOAMYL AND HEPTYL ALCOHOLS AT VARIOUS TEMPERATURES AND PRESSURES

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UDC 547.265:547.267:532.14

The hydrostatic weighing method is used to determine the density of isoamyl alcohol at T = 273.15-587.37°K and the density of heptyl alcohol at T = 273.15-575.07°K at pressures of 10.86-491.4 bar. An equation of state is presented.

Using the hydrostatic weighing method described previously [1], the densities of isoamyl and heptyl alcohols were determined over the temperature ranges 273.15-587.37°K and 273.15-575.07°K for pressures of 10.86-491.4 bar. The impurity content of the isoamyl alcohol used was 3.28%, with 3.14% being optically active amyl alcohol. The heptyl alcohol was 99.43% pure, containing 0.089% water. Pressure in the measurement vessel was generated and measured by a class 0.05 type MP-600 piston manometer.

Experimental temperature was maintained with a VRT-2 temperature regulator and Chromel–Alumel thermocouple, and measured by a platinum resistance thermometer and class 0.002 type R 363-2 potentiometer.

The uncertainty of the experimental data obtained does not exceed 0.1%, with the exception of the first two data points for amyl alcohol on the 587°K isotherm, where the uncertainties are 0.3 and 0.2%, respectively.

The experimental values of the alcohols' densities are presented in Table 1. The p, ρ, T data obtained for both alcohols were approximated by an equation of the form

$$p=\sum_{i=1}^{r}\sum_{j=0}^{s_i} b_{ij}\omega^i \frac{1}{\tau^j}\ (\text{bar}), \tag{1}$$

where

$$\omega=\rho/\rho_{cr},\quad \tau=T/T_{cr}.$$

The coefficients of Eq. (1) were calculated by the least-squares method in two stages. Initially calculations were performed with all points being given the same weight. In the second stage the equation thus obtained was used to calculate $(\partial p/\partial \rho)_T$. Then each point was assigned a weight $1/(\partial p/\partial \rho)_T^2$ and the coefficients of Eq. (1) were recalculated. Fisher's criterion was used to determine the number of terms in the equation of state.

The values of the critical parameters appearing in Eq. (1) were taken from data in the literature as follows: for isoamyl alcohol ρ_{cr} = 270 kg/m³ and T_{cr} = 579.5°K; for heptyl alcohol ρ_{cr} = 270 kg/m³ and T_{cr} = 633.15°K. The coefficients of Eq. (1) for isoamyl alcohol are:

$$\begin{array}{ll}
b_{10}=5582,468862, & b_{31}=218,5261725,\\
b_{11}=-23802,2149, & b_{32}=260,7375389,\\
b_{12}=42082,36055, & b_{33}=-49,02813695,\\
b_{13}=-39085.00174, & b_{40}=312,8490607,\\
b_{14}=20212.76065, & b_{50}=-45.06740077,\\
b_{15}=-5479.205455, & b_{51}=-168.9662867,\\
b_{16}=-609.4535298, & b_{60}=17.98707567,\\
b_{20}=902.8232039, & b_{61}=46.5528324,\\
b_{21}=-966.1503255, & b_{70}=-2.511029452,\\
b_{30}=-605.8680059, & b_{71}=-3.117753252.
\end{array}$$

For heptyl alcohol:

State Nitrogen Industry Institute, Moscow. Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 40, No. 2, pp. 313-318, February, 1981. Original article submitted February 2, 1980.

 0022-0841/81/4002-0194$07.50

TABLE 1. Densities of Isoamyl and Heptyl Alcohols

T, K	p, bar	ρ, kg/m^3	T, K	p, bar	ρ, kg/m^3
		Isoamyl alcohol			
273,15	10,84	824,4	329,69	148,10	793,1
273,15	20,65	825,1	329,69	197,20	796,9
273,15	50,06	827,0	329,70	295,30	803,9
273,15	74,57	828,7	329,71	393,30	810,1
273,15	99,09	830,1	329,72	491,40	816,2
273,15	148,10	833,0	386,78	10,84	733,0
273,15	197,20	836,0	386,79	20,65	734,6
273,15	295,20	841,5	386,80	50,07	738,2
273,15	393,30	846,7	386,83	74,58	741,1
273,15	491,40	851,3	386,84	99,10	743,8
292,32	10,84	810,3	386,85	148,10	749,1
292,30	20,65	811,0	386,87	197,20	754,5
292,33	50,07	812,8	386,90	295,30	763,1
292,35	74,57	814,9	386,86	393,30	771,8
292,38	99,09	816,5	386,83	491,40	779,0
292,40	148,10	819,5	426,45	10,86	692,0
292,43	197,20	822,6	426,51	20,67	693,7
292,47	295,30	828,7	426,51	50,07	698,8
292,50	393,30	834,2	426,54	74,58	702,8
292,52	491,40	839,2	426,56	99,10	706,8
329,64	10,84	781,7	426,58	148,10	713,7
329,65	20,65	782,7	426,52	197,20	720,4
329,66	50,07	785,1	426,56	295,30	731,8
329,67	74,58	787,3	426,62	393,30	742,0
329,68	99,10	789,3	426,63	491,40	750,5
455,79	10,86	656,9	524,24	393,30	661,4
455,84	20,67	659,1	524,25	491,40	675,3
455,89	50,09	666,0	551,09	25,58	484,5
455,91	74,60	671,1	551,12	30,48	493,7
455,89	99,12	676,2	551,13	50,10	518,5
455,88	148,10	685,1	551,13	74,60	538,8
455,87	197,20	692,8	551,12	99,12	554,2
455,78	295,80	706,7	551,13	148,10	576,3
455,77	393,30	718,2	551,13	197,20	593,9
455,72	491,40	728,5	551,10	295,30	619,8
488,74	10,86	609,7	551,04	393,30	638,9
488,76	20,67	613,4	551,03	491,40	654,7
488,78	50,09	623,6	574,01	35,39	386,5
488,81	74,60	631,1	574,14	40,29	424,3
488,80	99,12	638,0	574,17	50,10	455,6
488,79	148,20	649,7	574,19	74,61	493,9
488,78	197,20	659,9	574,21	99,13	516,3
488,77	295,30	676,7	574,23	148,20	546,6
488,74	393,30	691,1	574,23	197,20	567,3
488,73	491,40	703,0	574,22	295,30	597,7
524,34	20,68	551,0	574,21	393,30	620,0
524,32	30,47	557,8	574,18	491,40	637,4
524,31	50,09	569,9	585,90	35,44	122,0
524,30	74,60	582,1	587,06	40,33	170,9
524,28	99,12	592,5	587,18	45,20	350,7
524,28	148,20	609,3	587,23	50,11	395,7
524,25	197,20	623,1	587,26	74,61	462,8
524,23	295,30	644,4	587,29	99,13	492,6
587,35	148,20	528,2			
587,37	197,20	552,3			
587,34	295,30	585,3			
		Heptyl alcohol			
273,15	10,87	837,5	322,77	74,61	806,8
273,15	20,68	837,9	322,78	99,12	808,6
273,15	50,10	839,6	322,79	148,20	811,7
273,15	74,61	841,1	322,80	197,20	815,1
273,15	99,13	842,5	322,81	295,20	821,0
273,15	148,20	844,8	322,82	393,30	826,4
273,15	197,20	847,2	322,83	491,40	831,8
273,15	295,30	852,5	374,13	10,87	763,5
273,15	393,30	856,7	374,12	20,68	764,4
273,15	491,40	861,5	374,05	50,10	767,3
289,43	10,87	825,9	374,11	74,61	769,3
289,44	20,68	826,5	374,06	99,13	771,8
289,21	50,09	828,5	374,08	148,20	775,9
289,22	74,60	830,1	374,09	197,20	780,2
289,25	99,12	831,5	374,15	295,20	787,4
289,30	148,20	834,3	374,20	393,30	793,8

TABLE 1 (Continued)

T, K	p, bar	ρ, kg/m³	T, K	p, bar	ρ, kg/m³
		Heptyl alcohol			
289,33	197,20	836,9	374,29	491,40	800,2
289,37	295,30	842,1	424,30	10,87	719,4
289,40	393,30	846,9	424,31	20,68	721,2
289,43	491,40	851,6	424,25	50,10	725,5
322,74	10,87	802,3	424,29	74,61	727,9
322,75	20,68	803,0	424,33	99,13	731,1
322,76	50,10	805,0	424,36	148,20	736,6
424,43	197,20	742,2	575,03	50,10	554,7
424,44	295,20	751,5	575,02	74,61	567,9
424,47	395,30	759,9	575,02	99,13	578,9
424,49	491,40	768,0	575,01	148,20	596,7
475,00	10,88	666,7	575,02	197,20	610,5
474,93	20,69	669,5	574,98	295,30	632,9
474,93	50,10	675,8	574,95	393,30	650,9
474,88	74,61	680,6	574,92	491,40	665,1
474,90	99,13	684,4			
474,92	148,20	692,3			
474,87	197,20	699,6			
474,88	295,30	712,6			
474,92	393,30	723,4			
474,99	491,40	733,3			
524,01	10,87	607,3			
523,99	20,68	611,4			
524,02	50,10	621,3			
524,00	74,61	628,9			
523,99	99,13	634,9			
523,95	148,20	647,0			
523,98	197,20	657,0			
523,93	295,30	673,5			
523,85	393,30	687,4			
523,87	491,40	699,0			
575,07	15,78	528,7			
575,02	20,69	533,4			

TABLE 2. Densities of Isoamyl and Heptyl Alcohols at Equal Temperatures and Pressures, kg/m³

T, °K	p, bar									
	10	20	50	75	100	150	200	300	400	500
					Isoamyl alcohol					
273,15	824,4	825,0	827,0	828,6	830,2	833,3	836,2	841,7	846,9	851,7
280	819,4	820,1	822,2	823,9	825,5	828,6	831,6	837,3	842,6	847,5
290	811,9	812,6	814,8	816,5	818,2	821,5	824,7	830,6	836,1	841,3
300	804,2	805,0	807,3	809,1	810,9	814,4	817,7	823,9	829,6	835,0
310	796,6	797,4	799,8	801,7	803,6	807,3	810,7	817,2	823,2	828,8
320	789,0	789,8	792,3	794,4	796,4	800,2	803,8	810,6	816,8	822,6
330	781,3	782,2	784,9	787,0	789,1	793,1	796,9	804,0	810,5	816,5
340	773,4	774,4	777,2	779,5	781,7	785,9	789,9	797,3	804,1	810,3
350	765,4	766,4	769,4	771,8	774,1	778,6	782,8	790,5	797,6	804,1
360	757,1	758,2	761,4	763,9	766,3	771,0	775,4	783,5	790,9	797,7
370	748,4	749,6	753,0	755,7	758,3	763,2	767,9	776,4	784,1	791,1
380	739,4	740,7	744,3	747,2	749,9	755,2	760,1	769,0	777,1	784,5
390	730,0	731,4	735,2	738,3	741,3	746,8	752,0	761,5	769,9	777,6
400	720,2	721,6	725,8	729,1	732,3	738,2	743,7	753,7	762,6	770,6
410	709,9	711,5	716,0	719,6	723,0	729,3	735,2	745,7	755,0	763,4
420	699,2	700,9	705,8	709,7	713,4	720,2	726,4	737,6	747,4	756,2
430	687,9	689,8	695,2	699,4	703,4	710,7	717,4	729,2	739,6	748,8
440	676,2	678,3	684,2	688,8	693,1	701,0	708,2	720,8	731,6	741,3
450	663,8	666,2	672,8	677,8	682,5	691,1	698,8	712,1	723,6	733,7
460	650,9	653,5	660,9	666,5	671,6	680,9	689,2	703,4	715,5	726,1
470	637,2	640,2	648,5	654,7	660,4	670,5	679,4	694,6	707,3	718,5
480	622,7	626,2	635,6	642,5	648,8	659,9	669,4	685,6	699,1	710,8
490	607,2	611,3	622,1	629,9	636,9	649,0	659,3	676,6	690,8	703,1
500	—	595,4	608,0	616,8	624,6	637,9	649,1	667,5	682,6	695,4
510	—	578,1	593,0	603,1	611,9	626,5	638,7	658,4	674,3	687,7
520	—	559,0	577,1	588,9	598,7	614,9	628,1	649,2	665,9	680,0
530	—	—	560,1	573,9	585,1	603,1	617,5	640,0	657,6	672,3
540	—	—	541,5	558,0	570,9	591,0	606,7	630,7	649,3	664,7
550	—	—	520,9	541,1	556,1	578,7	595,7	621,5	641,0	657,1
560	—	—	497,3	522,9	540,6	566,0	584,6	612,1	632,8	649,5
570	—	—	469,2	503,1	524,2	553,0	573,4	602,8	624,5	641,9
580	—	—	432,5	481,1	506,9	539,6	561,9	593,4	616,3	634,4
585	—	—	408,2	469,1	497,8	532,8	556,2	588,7	612,1	630,7

TABLE 2 (Continued)

T, K	p, bar									
	10	20	50	75	100	150	200	300	400	500
					Heptyl alcohol					
273,15	837,3	837,9	839,6	841,0	842,4	845,0	847,6	852,6	857,3	861,7
280	832,6	833,2	835,0	836,4	837,8	840,6	843,2	848,3	853,1	857,6
290	825,6	826,2	828,0	829,5	831,0	833,9	836,7	841,9	846,9	851,6
300	818,4	819,1	821,0	822,6	824,2	827,2	830,1	835,6	840,7	845,5
310	811,3	812,0	814,0	815,7	817,3	820,5	823,5	829,2	834,6	839,6
320	804,1	804,9	807,0	808,8	810,5	813,8	816,9	822,9	828,5	833,7
330	796,9	797,7	800,0	801,8	803,6	807,1	810,4	816,6	822,4	827,8
340	789,6	790,4	792,8	794,8	796,6	800,3	803,7	810,2	816,3	821,9
350	782,2	783,0	785,6	787,6	789,6	793,4	797,0	803,8	810,1	815,9
360	774,5	775,4	778,1	780,3	782,4	786,4	790,2	797,3	803,8	809,9
370	766,7	767,6	770,5	772,7	775,0	779,2	783,2	790,6	797,4	803,7
380	758,6	759,6	762,6	765,0	767,4	771,8	776,0	783,8	790,9	797,4
390	750,2	751,3	754,5	757,1	759,6	764,3	768,7	776,9	784,3	791,1
400	741,6	742,7	746,2	748,9	751,5	756,5	761,2	769,8	777,5	784,6
410	732,6	733,9	737,6	740,5	743,3	748,6	753,5	762,6	770,7	778,0
420	723,4	724,8	728,7	731,9	734,8	740,5	745,7	755,2	763,7	771,4
430	713,9	715,4	719,6	723,0	726,2	732,2	737,7	747,7	756,6	764,6
440	704,1	705,7	710,3	713,9	717,3	723,7	729,6	740,2	749,5	757,8
450	693,9	695,7	700,7	704,6	708,2	715,1	721,3	732,5	742,3	751,0
460	683,5	685,4	690,8	695,0	699,0	706,3	713,0	724,8	735,0	744,1
470	672,6	674,7	680,7	685,3	689,5	697,4	704,5	716,9	727,7	737,2
480	661,5	663,8	670,3	675,3	679,9	688,4	695,9	709,1	720,4	730,3
490	649,9	652,5	659,6	665,1	670,1	679,2	687,2	701,2	713,0	723,4
500	637,9	640,8	648,7	654,7	660,1	669,9	678,5	693,3	705,7	716,5
510	625,4	628,7	637,5	644,0	650,0	660,5	669,7	685,3	698,4	709,7
520	612,4	616,1	625,9	633,1	639,6	651,0	660,8	677,4	691,1	702,9
530	—	603,0	614,0	622,0	629,1	641,4	651,9	669,4	683,8	696,1
540	—	589,2	601,8	610,6	618,4	631,7	643,0	661,5	676,6	689,4
550	—	574,7	589,1	598,9	607,5	621,9	634,0	653,6	669,4	682,7
560	—	559,1	575,9	586,9	596,4	612,1	625,0	645,7	662,3	676,1
570	—	542,1	562,0	574,6	585,0	602,1	615,9	637,9	655,2	669,6

$$
\begin{aligned}
b_{10} &= 2924.859224, & b_{31} &= 3528.313611,\\
b_{20} &= -3086.462337, & b_{32} &= -4138.945295,\\
b_{21} &= -6763.820069, & b_{33} &= 2105.215218,\\
b_{22} &= -6467.646571, & b_{34} &= -494.8092873,\\
b_{23} &= -2520.915495, & b_{35} &= 42.81367913,\\
b_{24} &= 358.959955, & b_{40} &= -1413.758322,\\
b_{30} &= 3046.116958, & b_{50} &= 199.9077443.
\end{aligned}
$$

The calculated density values deviate from experiment by not more than 0.1%. Equation (1) was then used to calculate densities of isoamyl and heptyl alcohols for equal temperature and pressure values (Table 2).

Apaev, Lipovetskii, and Gylmanov [2] used the hydrostatic weighing method to obtain p, ρ, T data for isoamyl alcohol at T = 280-570°K and p = 1-800 bar, and described these data by an equation of state to an accuracy of ±0.12%. A comparison with the results of the present study shows that the divergence of individual points reaches ≈1.8%. It is possible that this may be due to the use of industrial grade isoamyl alcohol containing 15% optically active amyl alcohol in [2].

This is the first time that density data have been obtained for heptyl alcohol under pressure.

NOTATION

p, pressure, bar; T, temperature, °K; b_{ij}, coefficients of equation of state; ω, dimensionless density; τ, dimensionless temperature; ρ, liquid density, kg/m³; ρ_{cr}, critical density, kg/m³; T_{cr}, critical temperature, °K.

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EXPERIMENTAL INVESTIGATION AND DEVELOPMENT OF A METHOD FOR COMPUTING THE THERMOPHYSICAL PROPERTIES OF HYDROCARBONS AND PETROLEUM PRODUCTS

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UDC 536.7:541.122.3

The results of comprehensive experimental investigations of the thermophysical properties of n-hexane and cyclohexane and the thermoconductivity of liquid petroleum products are presented.

The thermophysical properties (specific volumes v, isobaric heat capacity C_p, and dynamic viscosity η) of n-hexane and cyclohexane were studied from the triple point to their transition points, including the liquid, vapor, two phase, critical, and supercritical regions. The C_6H_{14} specimen, after additional purification, contained 99.93% of the principal component (mixture: 2- and 3-methylpentane 0.047%, methylcyclohexane 0.023%); the C_6H_{12} specimen contained 99.90% of the principal component (mixture: cycloparafin and its derivatives 0.06%, aromatic hydrocarbons 0.04%). We monitored the purity of the specimens studied by periodic sampling for different values of the parameters p and t while making sample tests followed by a determination of their relative density ρ_4^{20} and index of refraction n_d^{20} and analysis on the Tsvet-4.69 and Khrom-4 chromatographs.

The upper temperature limits for measurements of the properties of n-hexane (350°C) and cyclohexane (425°C) are determined by the thermostability of these substances in piezometers, calorimeters, and viscosimeters, made of chrome-nickel steels. The parameters (p and t) corresponding to the transition points of hydrocarbons were established in experiments measuring v. For C_6H_{14}, beginning with 325°C, and for C_6H_{12} beginning with 375°C, samples were extracted at different pressures in the piezometers, which were subjected to special physicochemical tests, including fractional distillation in a capillary column (d = 0.25 mm, l = 50 mm) followed by chromatographic analysis. It was established that in C_6H_{14} there are no transitions for $t \leqslant 350$°C and in C_6H_{12}, for $t \leqslant 425$°C and p > 11 MPa.

In view of the fact that the measurements of v, C_p, and η for cyclohexane at low temperatures and high pressures were carried out near its melting curve, special tests were made in order to determine the melting pressure p_{melt} in the temperature range 9.9-42.9°C. p_{melt} was measured with the use of the falling body method [1, 2] and the capillary method [3], used in viscosimetry. The melting curve was approached from the solid phase side. The values of p_{melt}, obtained with two experiments, agree within 0.2-0.3%. The experimental values of p_{melt} for cyclohexane were approximated by the equation

$$p_{melt} = -10.8918 + 1.65297t + 0.0037149t^2. \quad (1)$$

The mean-square deviation of the computed values of p_{melt} from the experimental values constitutes 0.15%, and the maximum error in determining p_{melt} is 3%. Equation (1) encompasses the temperature range from 6.554 to 43°C. The value p_{melt} = 0.1013 MPa at t = 6.554°C was taken from the data in [4].

The saturated vapor pressure for C_6H_{14} and C_6H_{12} was studied by the piezometer method at constant volume [5] in the temperature ranges 100-234.7°C and 110-281°C, in which there is

M. D. Millionshchikov Petroleum Institute, Grozny. Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 40, No. 2, pp. 319-331, February, 1981. Original article submitted October 5, 1979.

 0022-0841/81/4002-0198$07.50