# Temperature Dependence of the Thermophysical Properties of 1-Chlorohexane, 1-Iodohexane, 1-Iodoheptane, and 1-Chlorononane at Saturation Condition

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The speed of sound $u$, density $\rho$, and specific heat capacity at constant pressure $C_P$ for liquid 1-chlorohexane, 1-iodohexane, 1-iodoheptane, and 1-chlorononane were measured as a function of temperature along the saturation line between (293.15 and 373.15) K. The experimental results were used to calculate various thermophysical properties such as the isobaric thermal expansion coefficient $\alpha_P$, the isentropic compressibility $k_S$, the isothermal compressibility $k_T$, the specific heat capacity at constant volume $C_V$, the ratio of $C_P$ to $C_V$, the temperature coefficient of pressure at constant volume $(\partial P/\partial T)_V$, and the internal pressure $P_i$.

## Introduction

Thermodynamic properties of nonelectrolyte liquids are of profound importance in various fields related to the petrochemical industry and technology. In contrast to the $n$-alkanes, which have been studied comprehensively, their halogen-substituted analogues are less well understood. This could be related to the high chemical activity and relative thermal instability of certain haloalkanes. Presently, the sphere of application of haloalkanes is wide, including raw material for synthesis of alkanes and alkenes, solvents, anesthetics, insecticides, bactericidal preparations, and so forth.[1]

A literature search indicated the availability of only a few thermodynamic properties for 1-chlorohexane, 1-iodohexane, 1-iodoheptane, and 1-chlorononane. Enthalpies of vaporization $\Delta_{vap}H°$ of 1-chlorohexane in the temperature range from (298 to 368) K have been studied by Majer and Svoboda,[2] and heat capacities at constant pressure of 1-chlorohexane, 1-iodohexane, and 1-iodoheptane at 298.15 K and 308.15 K have been studied by Shehatta.[3] The Antoine equation parameters of 1-chlorohexane in the temperature range from (288 to 408.7) K and 1-chlorononane in the temperature range from (342.2 to 477.9) K have been reported by Kemme and Kreps;[4] corresponding parameters for 1-iodohexane in the temperature range from (293 to 453) K and 1-iodoheptane in the temperature range from (298 to 477) K are given in Potekhin's reference book.[5] There is sufficient information on the temperatures of boiling for the investigated liquids.[2,6−9] A value of the critical temperature is known only for 1-chlorohexane ($T_c$ = 594.6 K).[2] Abramzon's reference book[12] provides data on surface tension for 1-iodoheptane from (293.15 to 373.15) K and for 1-chlorohexane, 1-iodohexane, and 1-chlorononane from (283.15 to 373.15) K, respectively. The speed of sound values of 1-chlorohexane and 1-iodohexane were reported by us in a previous paper.[10]

For this reason, we present here an experimental study of the thermodynamic properties of 1-chlorohexane, 1-iodohexane, 1-iodoheptane, and 1-chlorononane at saturation condition. These data are of interest because of the effect on the molecular interactions of chlorine and the iodine substitution in $n$-alkanes.

## Experimental Section

***Materials.*** The material used in this study, 1-chlorohexane and 1-iodohexane (mole fraction > 0.99) and 1-iodoheptane and 1-chlorononane (mole fraction > 0.98), was supplied by Sigma-Aldrich Ltd. All reagents were used after purification by fractional distillation. All chemicals were partially degassed and dried over Fluka type 0.4 nm molecular sieves. The purity of the products was checked by gas chromatography (GC). We obtained GC purity data of (99.3, 99.4, 98.8, and 98.4) mol % for 1-chlorohexane, 1-iodohexane, 1-iodoheptane, and 1-chlorononane, respectively.

***Measurements.*** The ultrasonic speed was measured along the saturation line with our pulse-phase echo ultrasonic device, with a precision of $\pm 1$ m·s$^{-1}$. The details of the method and technique used to determine speed of sound have been described previously.[10] The speed of sound was measured at 2 and 5 MHz. Dispersion was not observed. The speed of sound measuring cell was thermostated with a temperature stability of $\pm 10^{-2}$ K.

The specific heat capacity at constant pressure $C_P$ was determined by a method of continuous heating with the help of a differential scanning modified Calvet type calorimeter IT-CP-400 (Russia). The general principles of operation of this type of calorimeter have been discussed in detail.[16,17] For a Calvet type calorimeter, the specific heat capacity of liquid can be calculated with the relation

$$C_{Px} = C_{Pr}\frac{Q_x - Q_0}{Q_r - Q_0}\frac{m_r}{m_x} + \Delta C \qquad (1)$$

where $C_{Px}$ is the specific heat capacity of the researched liquid, $C_{Pr}$ is the specific heat capacity of the reference liquid, $m_x$ is the mass of the sample liquid, $m_r$ is the mass of the reference liquid, $Q_0$ is the quantity of heat transferring into the empty measuring cell, $Q_x$ is the quantity of heat transferred into the measuring cell filled with the

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**Table 1. Comparison of Densities and Specific Heat Capacity at Constant Pressure for Saturated Liquid 1-Chlorohexane, 1-Iodohexane, and 1-Iodoheptane at Different Temperatures**

| $\rho$/(kg·m$^{-3}$) this work | $\rho$/(kg·m$^{-3}$) literature (ref) | $C_P$/(J·kg$^{-1}$·K$^{-1}$) this work | $C_P$/(J·kg$^{-1}$·K$^{-1}$) literature (ref) |
|---|---|---|---|
| | 1-Chlorohexane, $T$ = 293.15 K | | |
| 878.52 | 878.30 (7) | | |
| | 879.0 (14) | | |
| | 1-Chlorohexane, $T$ = 298.15 K | | |
| 873.75 | 873.54 (7) | 1694 | 1792 (3) |
| | 874.5 (14) | | |
| | 873.43 (15) | | |
| | 1-Chlorohexane, $T$ = 308.15 K | | |
| | | 1720 | 1826 (3) |
| | 1-Iodohexane, $T$ = 298.15 K | | |
| 1430.50 | | 1027 | 1028 (3) |
| | 1-Iodohexane, $T$ = 308.15 K | | |
| 1417.13 | | 1041 | 1041 (3) |
| | 1-Iodoheptane, $T$ = 298.15 K | | |
| 1371.93 | | 1105 | 1114 (3) |
| | 1-Iodoheptane, $T$ = 308.15 K | | |
| 1359.91 | | 1124 | 1132 (3) |

sample liquid, and $Q_r$ is the quantity of heat transferred into the measuring cell filled with the reference liquid.

The value $\Delta C$ takes into account the difference between the enthalpy of vaporization for the sample and the reference liquids. However, even for precision measurements, the value $\Delta C$ can be neglected.

In the measurement method for heat capacity, it was reasoned that the quantity of heat is always proportional to the heating time for the value of the temperature steps $\theta_i$ set up by flowmeter. In this case, eq 1 becomes

$$C_{Px} = C_{Pr}\frac{\tau_x - \tau_0}{\tau_r - \tau_0}\frac{m_r}{m_x} \tag{2}$$

where $\tau_0$, $\tau_r$, and $\tau_x$ are the heating times for the temperature steps ($\theta_0$, $\theta_r$, and $\theta_x$) of the empty cell, the cell filled with the reference liquid, and the cell filled with the sample liquid, respectively.

The calorimeter was calibrated with benzene, octane, and hexane. The uncertainty of the $C_P$ measurements was estimated to be 3% over the entire temperature range. Densities were measured with an Ostwald−Sprengel type pycnometer, with a capacity of about 50 cm$^3$. The uncertainty of the density measurements was estimated to be $\pm 3 \times 10^{-5}$ g·cm$^{-3}$. Experimental values of density and specific heat capacity at constant pressure for the 1-chlorohexane, 1-iodohexane, and 1-iodoheptane were compared with those found in the literature, and they were found to be in fairly good agreement (with the exception of specific heat capacity data for 1-chlorohexane), as shown in Table 1.

## Results and Discussion

The densities, speed of sound, and specific heat capacity at constant pressure of the sample liquids are given in Table 2 from (293.15 to 373.15) K, respectively. These data were fitted by the method of least squares with the following equation:

$$Y = \sum_{i=0}^{n} A_i (T/\mathrm{K})^i \tag{3}$$

where $Y$ denotes $\rho$/kg·m$^{-3}$, $u$/m·s$^{-1}$, or $C_P$/J·kg$^{-1}$·K$^{-1}$, $T$ is the absolute temperature, and $A_i$ are the adjustable parameters. The resulting coefficients $A_i$ are listed in Table 3 along with the standard deviation $\sigma$, defined by

$$\sigma = [\sum_{i=1}^{n}(Y_{obs} - Y_{cal})^2/(n - p)]^{1/2} \tag{4}$$

where $Y_{obs}$ and $Y_{cal}$ are the observed and calculated quantities as defined earlier, $n$ is the total number of experimental points, and $p$ is the number of parameters.

**Table 2. Measured Densities, Speed of Sound, and Specific Heat Capacity at Constant Pressure for Saturated Liquid 1-Chlorohexane, 1-Iodohexane, 1-Iodoheptane, and 1-Chlorononane from (293.15 to 373.15) K**

| $T$/K | $\rho$/kg·m$^3$ | $u$/m·s$^{-1}$ | $C_P$/J·kg$^{-1}$·K$^{-1}$ | $\rho$/kg·m$^3$ | $u$/m·s$^{-1}$ | $C_P$/J·kg$^{-1}$·K$^{-1}$ |
|---|---|---|---|---|---|---|
| | 1-Chlorohexane | | | 1-Iodohexane | | |
| 293.15 | 878.52 | 1219.1 | 1680 | 1437.18 | 1045.5 | 1021 |
| 298.15 | 873.75 | 1200.1 | 1694 | 1430.50 | 1031.3 | 1027 |
| 303.15 | 868.98 | 1181.9 | 1707 | 1423.82 | 1017.2 | 1034 |
| 308.15 | 864.21 | 1166.2 | 1720 | 1417.13 | 1003.2 | 1041 |
| 313.15 | 859.44 | 1140.7 | 1732 | 1410.44 | 989.2 | 1049 |
| 318.15 | 854.67 | 1128.1 | 1745 | 1403.74 | 975.4 | 1057 |
| 323.15 | 849.90 | 1106.0 | 1758 | 1397.04 | 961.6 | 1065 |
| 328.15 | 845.12 | 1087.0 | 1771 | 1390.33 | 947.9 | 1071 |
| 333.15 | 840.35 | 1068.8 | 1783 | 1383.61 | 934.2 | 1075 |
| 338.15 | 835.58 | 1050.2 | 1796 | 1376.89 | 920.7 | 1080 |
| 343.15 | 830.81 | 1031.7 | 1807 | 1370.17 | 907.2 | 1084 |
| 348.15 | 826.04 | 1013.3 | 1816 | 1364.44 | 893.8 | 1090 |
| 353.15 | 821.27 | 995.0 | 1832 | 1356.70 | 880.5 | 1097 |
| 358.15 | 816.50 | 976.9 | 1844 | 1349.96 | 867.3 | 1105 |
| 363.15 | 811.73 | 958.9 | 1856 | 1343.21 | 854.1 | 1113 |
| 368.15 | 806.96 | 940.6 | 1868 | 1336.46 | 841.0 | 1120 |
| 373.15 | 802.19 | 922.9 | 1879 | 1329.70 | 828.0 | 1126 |
| | 1-Iodoheptane | | | 1-Chlorononane | | |
| 293.15 | 1377.90 | 1079.0 | 1092 | 871.36 | 1297.2 | 1809 |
| 298.15 | 1371.93 | 1064.5 | 1105 | 867.35 | 1278.2 | 1822 |
| 303.15 | 1365.93 | 1050.2 | 1116 | 863.32 | 1259.5 | 1835 |
| 308.15 | 1359.91 | 1035.9 | 1124 | 859.28 | 1240.9 | 1848 |
| 313.15 | 1353.87 | 1021.6 | 1133 | 855.23 | 1222.5 | 1861 |
| 318.15 | 1347.80 | 1007.4 | 1141 | 851.15 | 1204.3 | 1874 |
| 323.15 | 1341.71 | 993.3 | 1150 | 847.07 | 1186.3 | 1888 |
| 328.15 | 1335.59 | 979.2 | 1158 | 842.96 | 1168.4 | 1902 |
| 333.15 | 1329.45 | 965.2 | 1165 | 838.85 | 1150.7 | 1915 |
| 338.15 | 1323.29 | 951.3 | 1172 | 834.71 | 1133.2 | 1929 |
| 343.15 | 1317.10 | 937.4 | 1180 | 830.57 | 1115.9 | 1942 |
| 348.15 | 1310.89 | 923.6 | 1185 | 826.40 | 1098.8 | 1956 |
| 353.15 | 1304.65 | 909.8 | 1194 | 822.22 | 1081.9 | 1970 |
| 358.15 | 1298.39 | 896.1 | 1200 | 818.03 | 1065.1 | 1984 |
| 363.15 | 1292.11 | 882.5 | 1208 | 813.82 | 1048.5 | 1998 |
| 368.15 | 1285.80 | 869.0 | 1215 | 809.60 | 1032.2 | 2012 |
| 373.15 | 1279.47 | 855.4 | 1223 | 805.36 | 1015.9 | 2026 |

**Table 3. Coefficients $A_i$ of the Least-Squares Fit by Equation 3 for Densities, Speed of Sound, and Specific Heat Capacity at Constant Pressure for 1-Chlorohexane, 1-Iodohexane, 1-Iodoheptane, and 1-Chlorononane from 293.15 K to 373.15 K and Standard Deviation $\sigma$**

| property | $A_0$ | $A_1$ | $A_2$ | $\sigma(Y)$ |
|---|---|---|---|---|
| | | 1-Chlorohexane | | |
| $\rho$/kg·m$^{-3}$ | $1.158 \times 10^3$ | −0.955 | $1.806 \times 10^{-6}$ | $8.831 \times 10^{-3}$ |
| $C_P$/J·kg$^{-1}$·K$^{-1}$ | 767.336 | 3.615 | $-1.703 \times 10^{-3}$ | 2.852 |
| $u$/m·s$^{-1}$ | $2.458 \times 10^3$ | −4.621 | $1.356 \times 10^{-3}$ | 0.148 |
| | | 1-Iodohexane | | |
| $\rho$/kg·m$^{-3}$ | $1.81 \times 10^3$ | −1.218 | $-1.861 \times 10^{-4}$ | 0.566 |
| $C_P$/J·kg$^{-1}$·K$^{-1}$ | 553.759 | 1.839 | $-8.308 \times 10^{-4}$ | 8.001 |
| $u$/m·s$^{-1}$ | $2.014 \times 10^3$ | −3.762 | $1.566 \times 10^{-3}$ | 0.084 |
| | | 1-Iodoheptane | | |
| $\rho$/kg·m$^{-3}$ | $1.686 \times 10^3$ | −0.911 | $-4.795 \times 10^{-4}$ | $7.270 \times 10^{-3}$ |
| $C_P$/J·kg$^{-1}$·K$^{-1}$ | 159.079 | 4.470 | $-4.355 \times 10^{-3}$ | 5.149 |
| $u$/m·s$^{-1}$ | $2.034 \times 10^3$ | −3.624 | $1.246 \times 10^{-3}$ | 0.112 |
| | | 1-Chlorononane | | |
| $\rho$/kg·m$^{-3}$ | $1.080 \times 10^3$ | −0.622 | $-3.040 \times 10^{-4}$ | 0.012 |
| $C_P$/J·kg$^{-1}$·K$^{-1}$ | $1.186 \times 10^3$ | 1.661 | $1.584 \times 10^{-3}$ | 0.862 |
| $u$/m·s$^{-1}$ | $2.727 \times 10^3$ | −5.946 | $3.647 \times 10^{-3}$ | 0.113 |

**Table 4. Calculated Isobaric Thermal Expansion Coefficient, Isentropic Compressibilities, Isothermal Compressibilities, Specific Heat Capacity at Constant Volume, the Ratio of $C_P$ to $C_V$, Temperature Coefficient of Pressure at Constant Volume and Internal Pressure for Saturated Liquid 1-Chlorohexane, 1-Iodohexane, 1-Iodoheptane and 1-Chlorononane from 293.15 K to 373.15 K**

| $T$/K | $\alpha_P \times 10^3$/K$^{-1}$ | $C_V$/J·kg$^{-1}$·K$^{-1}$ | $k_S \times 10^{10}$/Pa$^{-1}$ | $k_T \times 10^{10}$/Pa$^{-1}$ | $\gamma = C_P/C_V$ | $(\mathrm{d}P/\mathrm{d}T)_V$/bar·K$^{-1}$ | $P_i$/bar |
|---|---|---|---|---|---|---|---|
| | | | 1-Chlorohexane | | | | |
| 293.15 | 1.086 | 1287 | 7.659 | 10.00 | 1.3058 | 10.861 | 3182 |
| 298.15 | 1.092 | 1301 | 7.947 | 10.35 | 1.3024 | 10.553 | 3145 |
| 303.15 | 1.098 | 1314 | 8.238 | 10.70 | 1.2992 | 10.261 | 3109 |
| 308.15 | 1.104 | 1326 | 8.508 | 11.04 | 1.2971 | 10.006 | 3082 |
| 313.15 | 1.111 | 1343 | 8.942 | 11.54 | 1.2899 | 9.627 | 3013 |
| 318.15 | 1.117 | 1354 | 9.194 | 11.85 | 1.2891 | 9.421 | 2996 |
| 323.15 | 1.123 | 1370 | 9.619 | 12.35 | 1.2835 | 9.096 | 2938 |
| 328.15 | 1.129 | 1384 | 10.014 | 12.81 | 1.2793 | 8.816 | 2892 |
| 333.15 | 1.136 | 1398 | 10.417 | 13.29 | 1.2754 | 8.550 | 2847 |
| 338.15 | 1.142 | 1413 | 10.851 | 13.80 | 1.2710 | 8.283 | 2799 |
| 343.15 | 1.149 | 1427 | 11.308 | 14.32 | 1.2668 | 8.022 | 2751 |
| 348.15 | 1.156 | 1442 | 11.790 | 14.88 | 1.2664 | 7.766 | 2703 |
| 353.15 | 1.163 | 1456 | 12.299 | 15.47 | 1.2580 | 7.515 | 2653 |
| 358.15 | 1.170 | 1471 | 12.833 | 16.09 | 1.2536 | 7.271 | 2603 |
| 363.15 | 1.177 | 1486 | 13.398 | 16.74 | 1.2492 | 7.032 | 2553 |
| 368.15 | 1.184 | 1501 | 14.007 | 17.43 | 1.2446 | 6.794 | 2500 |
| 373.15 | 1.192 | 1516 | 14.636 | 18.15 | 1.2401 | 6.566 | 2449 |
| | | | 1-Iodohexane | | | | |
| 293.15 | 0.929 | 803 | 6.365 | 8.09 | 1.2708 | 11.481 | 3364 |
| 298.15 | 0.934 | 809 | 6.572 | 8.34 | 1.2693 | 11.191 | 3335 |
| 303.15 | 0.939 | 816 | 6.787 | 8.60 | 1.2673 | 10.921 | 3309 |
| 308.15 | 0.944 | 822 | 7.011 | 8.88 | 1.2658 | 10.639 | 3277 |
| 313.15 | 0.949 | 830 | 7.245 | 9.15 | 1.2634 | 10.370 | 3246 |
| 318.15 | 0.955 | 838 | 7.487 | 9.44 | 1.2611 | 10.110 | 3215 |
| 323.15 | 0.960 | 846 | 7.741 | 9.74 | 1.2587 | 9.854 | 3183 |
| 328.15 | 0.966 | 852 | 8.005 | 10.06 | 1.2566 | 9.599 | 3148 |
| 333.15 | 0.971 | 856 | 8.281 | 10.39 | 1.2550 | 9.343 | 3111 |
| 338.15 | 0.977 | 862 | 8.567 | 10.74 | 1.2532 | 9.097 | 3075 |
| 343.15 | 0.982 | 866 | 8.867 | 11.10 | 1.2514 | 8.852 | 3036 |
| 348.15 | 0.988 | 873 | 9.180 | 11.47 | 1.2490 | 8.615 | 2998 |
| 353.15 | 0.994 | 880 | 9.507 | 11.85 | 1.2464 | 8.385 | 2960 |
| 358.15 | 0.999 | 888 | 9.847 | 12.25 | 1.2435 | 8.162 | 2922 |
| 363.15 | 1.005 | 897 | 10.205 | 12.66 | 1.2406 | 7.941 | 2883 |
| 368.15 | 1.011 | 904 | 10.579 | 13.10 | 1.2378 | 7.723 | 2842 |
| 373.15 | 1.017 | 911 | 10.969 | 13.55 | 1.2352 | 7.509 | 2801 |
| | | | 1-Iodoheptane | | | | |
| 293.15 | 0.865 | 887 | 6.234 | 7.67 | 1.2311 | 11.274 | 3303 |
| 298.15 | 0.872 | 901 | 6.431 | 7.89 | 1.2270 | 11.056 | 3295 |
| 303.15 | 0.880 | 908 | 6.638 | 8.16 | 1.2295 | 10.779 | 3266 |
| 308.15 | 0.887 | 914 | 6.853 | 8.43 | 1.2300 | 10.525 | 3242 |
| 313.15 | 0.894 | 921 | 7.077 | 8.71 | 1.2300 | 10.277 | 3217 |
| 318.15 | 0.902 | 928 | 7.309 | 8.99 | 1.2300 | 10.035 | 3191 |
| 323.15 | 0.909 | 936 | 7.554 | 9.29 | 1.2291 | 9.800 | 3165 |
| 328.15 | 0.918 | 943 | 7.807 | 9.59 | 1.2289 | 9.564 | 3137 |
| 333.15 | 0.925 | 949 | 8.074 | 9.91 | 1.2279 | 9.335 | 3108 |
| 338.15 | 0.933 | 955 | 8.350 | 10.25 | 1.2275 | 9.106 | 3078 |
| 343.15 | 0.941 | 962 | 8.640 | 10.60 | 1.2265 | 8.884 | 3047 |
| 348.15 | 0.949 | 967 | 8.943 | 10.96 | 1.2258 | 8.663 | 3015 |
| 353.15 | 0.958 | 975 | 9.260 | 11.34 | 1.2246 | 8.446 | 2981 |
| 358.15 | 0.966 | 981 | 9.589 | 11.73 | 1.2235 | 8.234 | 2948 |
| 363.15 | 0.974 | 989 | 9.935 | 12.14 | 1.2222 | 8.025 | 2913 |
| 368.15 | 0.983 | 995 | 10.296 | 12.57 | 1.2210 | 7.819 | 2877 |
| 373.15 | 0.992 | 1003 | 10.679 | 13.02 | 1.2194 | 7.615 | 2840 |
| | | | 1-Chlorononane | | | | |
| 293.15 | 0.919 | 1474 | 6.820 | 8.39 | 1.2276 | 10.947 | 3207 |
| 298.15 | 0.927 | 1481 | 7.057 | 8.69 | 1.2298 | 10.658 | 3176 |
| 303.15 | 0.935 | 1493 | 7.302 | 8.98 | 1.2288 | 10.402 | 3152 |
| 308.15 | 0.943 | 1504 | 7.558 | 9.29 | 1.2285 | 10.142 | 3124 |
| 313.15 | 0.951 | 1517 | 7.824 | 9.61 | 1.2267 | 9.896 | 3097 |
| 318.15 | 0.959 | 1528 | 8.101 | 9.94 | 1.2264 | 9.644 | 3067 |
| 323.15 | 0.967 | 1541 | 8.389 | 10.28 | 1.2249 | 9.406 | 3038 |
| 328.15 | 0.975 | 1554 | 8.690 | 10.64 | 1.2240 | 9.166 | 3006 |
| 333.15 | 0.984 | 1566 | 9.003 | 11.01 | 1.2229 | 8.932 | 2974 |
| 338.15 | 0.992 | 1579 | 9.329 | 11.40 | 1.2216 | 8.706 | 2943 |
| 343.15 | 1.001 | 1591 | 9.669 | 11.79 | 1.2204 | 8.482 | 2909 |
| 348.15 | 1.009 | 1604 | 10.022 | 12.22 | 1.2190 | 8.264 | 2876 |
| 353.15 | 1.018 | 1617 | 10.391 | 12.65 | 1.2176 | 8.050 | 2842 |
| 358.15 | 1.027 | 1631 | 10.776 | 13.11 | 1.2161 | 7.839 | 2806 |
| 363.15 | 1.036 | 1645 | 11.177 | 13.58 | 1.2145 | 7.631 | 2770 |
| 368.15 | 1.046 | 1659 | 11.593 | 14.07 | 1.2130 | 7.432 | 2735 |
| 373.15 | 1.055 | 1672 | 12.031 | 14.57 | 1.2116 | 7.239 | 2700 |

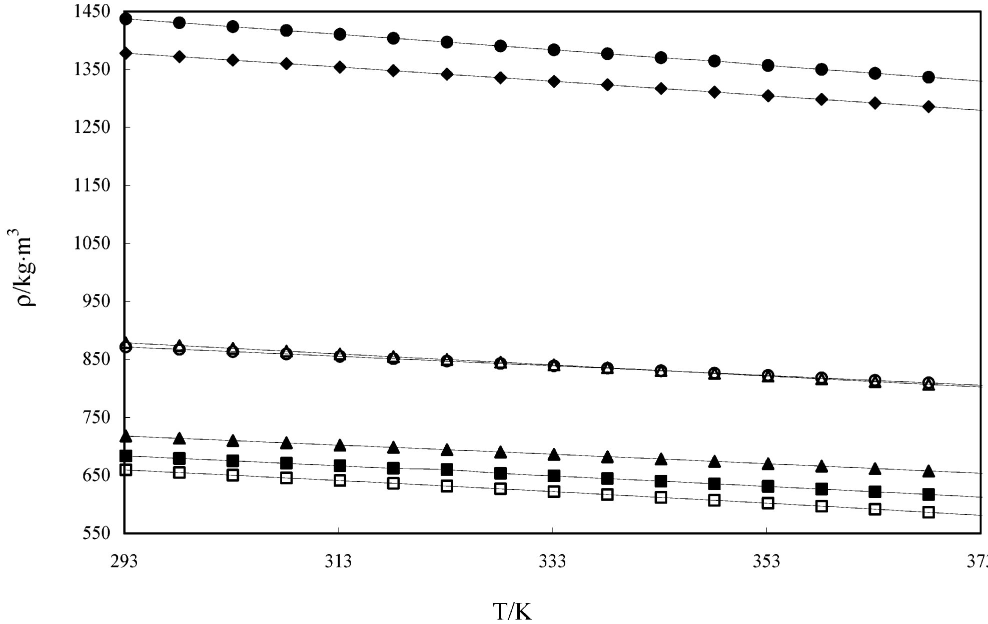


**Figure 1.** Densities $\rho$ as a function of temperature from (293.15 to 373.15) K: □, hexane; ■, heptane; ▲, nonane; ○, 1-chlorononane; △, 1-chlorohexane; ◆, 1-iodoheptane; ●, 1-iodohexane.

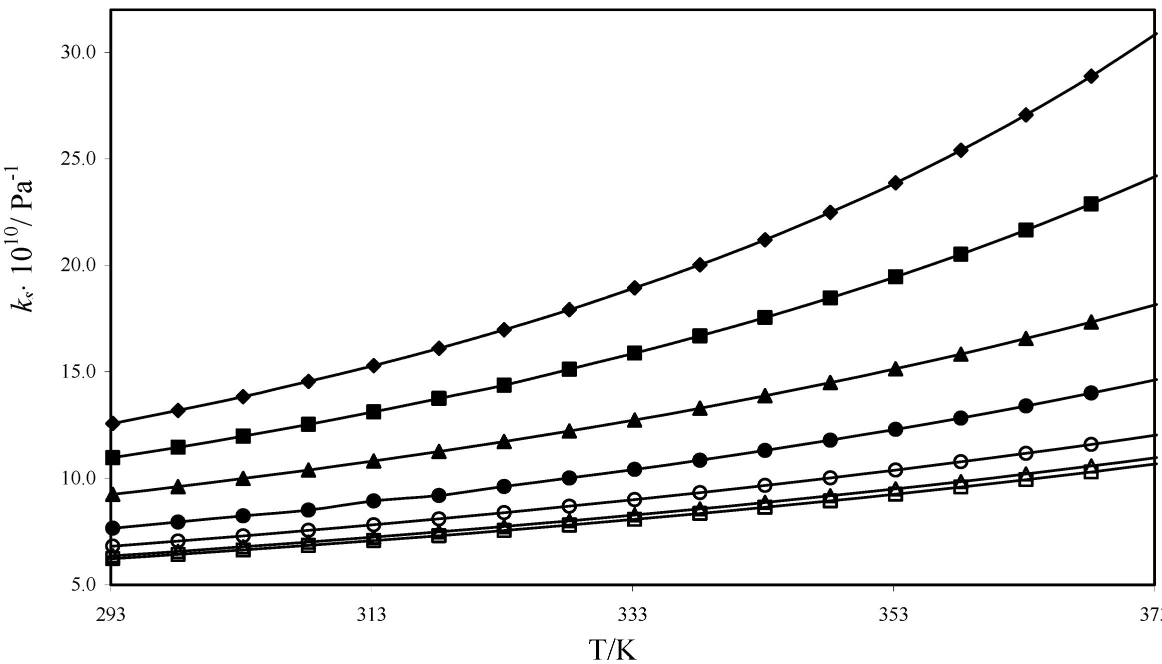


**Figure 2.** Isentropic compressibilities $k_S$ as a function of temperature from (293.15 to 373.15) K: ◆, hexane; ■, heptane; ▲, nonane; ○, 1-chlorononane; ●, 1-chlorohexane; □, 1-iodoheptane; △, 1-iodohexane.

Isentropic compressibilities $k_S$ of the measuring liquids were calculated from the Laplace equation,

$$k_S = \frac{1}{\rho u^2} \tag{5}$$

where $u$ is the sound velocity and $\rho$ is the density of the measuring liquids. The isobaric thermal expansion coefficient

$$\alpha_P = -\frac{1}{\rho}\left(\frac{\partial P}{\partial T}\right)_P \tag{6}$$

was calculated from numerical differentiation of the density fitting equation. Calculations of the values (see Table 4) of isothermal compressibilities $k_T$, specific heat capacity at constant volume $C_V$, $\gamma$ (which is the ratio of $C_P$ to $C_V$), temperature coefficient of pressure at constant volume $(\partial P/\partial T)_V$, and internal pressure $P_i$ were carried out with the following system of equations:

$$\gamma = 1 + \frac{u^2 \alpha_P{}^2 T}{C_P} \tag{7}$$

$$\gamma = \frac{k_T}{k_S} = \frac{C_P}{C_V} \tag{8}$$

$$k_T = k_S + \frac{\alpha_P{}^2 T}{\rho C_P} \tag{9}$$

$$\left(\frac{\mathrm{d}P}{\mathrm{d}T}\right)_V = \frac{\alpha_P}{k_T} \tag{10}$$

$$P_\mathrm{i} = \left(\frac{\mathrm{d}E}{\mathrm{d}V}\right)_T = T\left(\frac{\mathrm{d}P}{\mathrm{d}T}\right)_V - P \tag{11}$$

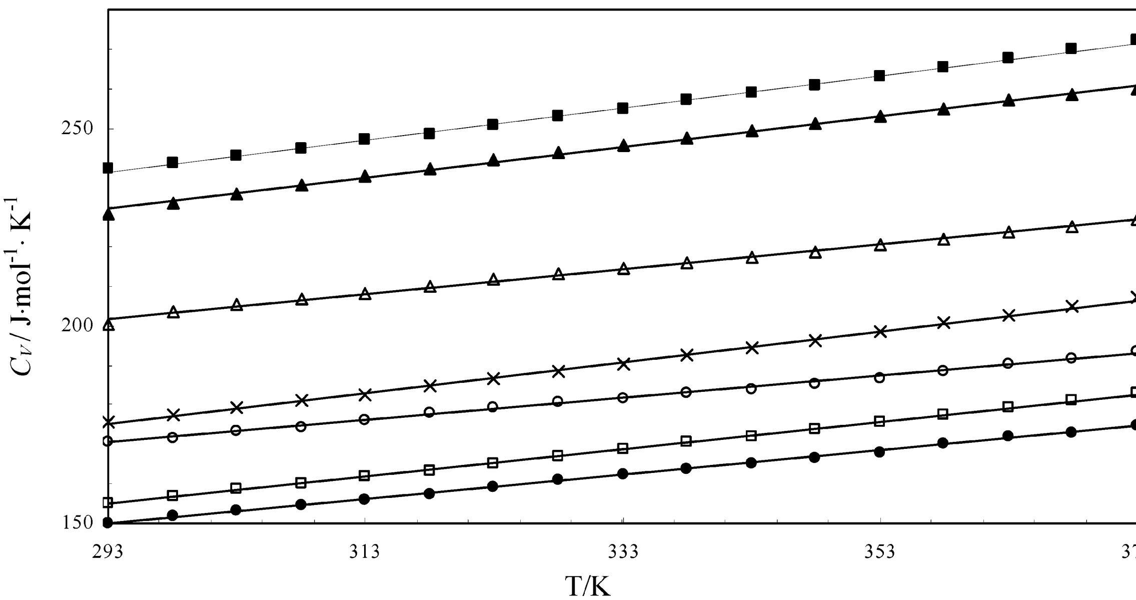


**Figure 3.** Molar heat capacity at constant volume as a function of temperature from (293.15 to 373.15) K: ●, hexane; ×, heptane; ▲, nonane; ■, 1-chlorononane; □, 1-chlorohexane; △, 1-iodoheptane; ○, 1-iodohexane.

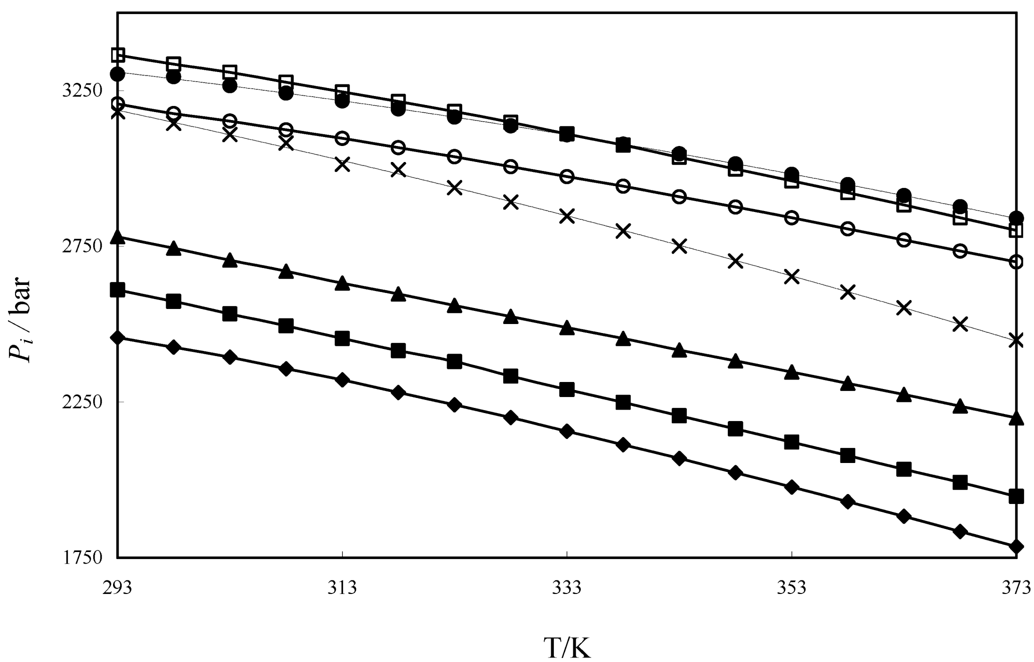


**Figure 4.** Internal pressure $P_i$ as a function of temperature from (293.15 to 373.15) K: ◆, hexane; ■, heptane; ▲, nonane; ○, 1-chlorononane; ×, 1-chlorohexane; ●, 1-iodoheptane; □, 1-iodohexane.

The accuracies of calculated values of $k_S$, $k_T$, $\alpha_P$, $C_V$, $\gamma$, $(\partial P/\partial T)_V$, and $P_i$ were (0.1 to 0.2)% for isentropic compressibilities, (1 to 2)% for isothermal compressibilities, 1% for the isobaric thermal expansion coefficient, 3% for specific heat capacity at constant volume, 1% for the ratio of $C_P$ to $C_V$, and 1% for the temperature coefficient of pressure at constant volume and for internal pressure.

The density, isentropic compressibilities, molar heat capacity at constant volume, and internal pressure of the investigated liquids and their *n*-alkane analogues from (293.15 to 373.15) K are shown in Figures 1−4, respectively. The densities for hexane, heptane, and nonane presented in Figure 1 are taken from Vargaftik's reference book.[11] Values of isentropic compressibilities, molar heat capacity at constant volume, and internal pressure for hexane, heptane, and nonane that are presented in Figures 2−4 are taken from Neruchev's article.[13] As can be seen from Figure 1, the densities of haloalkanes far exceed the densities of *n*-alkanes corresponding to them. The density of iodoalkanes is almost twice that of *n*-alkanes corresponding to them.

The isentropic compressibility carries more information on intensity of intermolecular interaction in liquid. A larger intensity of intermolecular interaction corresponds to a lower isentropic compressibility. As can be seen from Figure 2, the isentropic compressibility of haloalkanes is less than the isentropic compressibility of *n*-alkanes corresponding to them. Substitution of the chlorine atom by

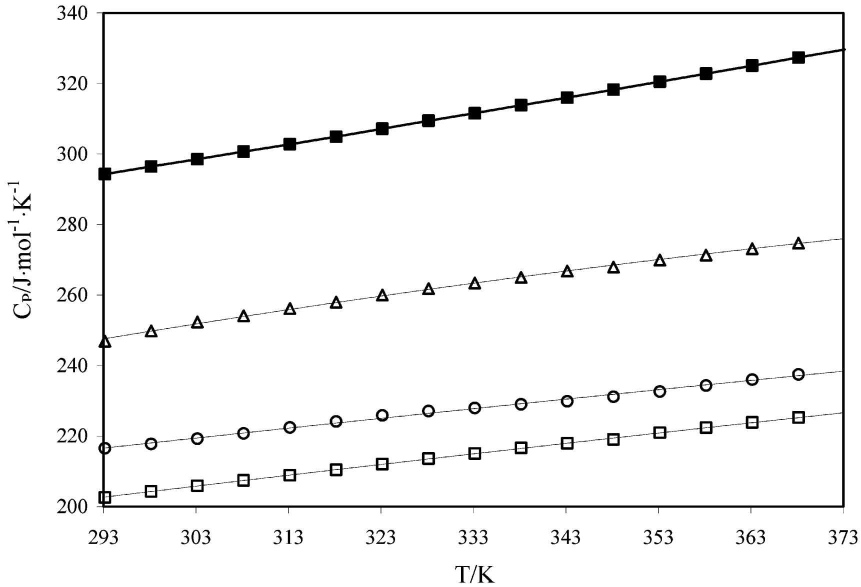


**Figure 5.** Molar heat capacity at constant pressure as a function of temperature from (293.15 to 373.15) K: ■, 1-chlorononane; □, 1-chlorohexane; △, 1-iodoheptane; ○, 1-iodohexane.

iodine in haloalkanes increases the intensity of intermolecular interactions. From Figure 2, it follows that with an increase in temperature, intensity of intermolecular interaction decreases for the liquids in this study.

An elementary analysis of the behavior of molar heat capacity at constant volume for the liquids studied results (Figure 3) in the following conclusion. The difference between a molecule of *n*-alkane and a molecule of haloalkane consists of substitution of an atom of hydrogen (H) with a heavier atom of a halogen (G). Thus the distinction of their molar heat capacity at constant volume will depend on the value of the amplitude of oscillations of atoms in C−H and C−G bonds. We think that the contribution of the C−G bond to the thermal capacity $C_V$ is more than the contribution of the C−H bond because of the appreciable difference between the atomic masses of hydrogen and the halogens. Therefore, we expected to see a higher value of molar heat capacity at constant volume for haloalkanes than for their corresponding alkanes and their temperature dependences should be similar. The dependences of the thermal capacities $C_V$ presented in Figure 3 on temperature for the researched liquids confirmed our assumptions.

Some essential information on the intensity of intermolecular interaction may be obtained from internal pressure data for liquids (Figure 4). As can be seen from Figure 4, the internal pressure of haloalkanes is more than that in *n*-alkanes where intermolecular interactions are less.

In Figure 5, results of measurements of the molar heat capacity for the investigated liquids are shown. As can be seen from Figure 5, the molar heat capacity of the researched liquids in the range of temperatures under study grows practically linearly with increasing temperature.

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