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Saturated Heat Capacities of Some Linear and Branched Alkylbenzenes between (332 and 401) K

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The saturated heat capacities of some linear alkylbenzenes (ethylbenzene, propylbenzene, butylbenzene, hexylbenzene, 1-phenylheptane, and 1-phenylhexadecane) and branched alkylbenzenes (*m*-xylene, cumene, (1-methylpropyl)benzene, (1,1-dimethylethyl)benzene, and (2-methylpropyl)benzene) in the temperature range from (332.15 to 401.15) K have been measured. A Calvet calorimeter C80D from Setaram (France) with batch cells modified from the standard vessels of Setaram, along with the "step by step method", has been used to perform the measurements. The estimated uncertainty of the saturated heat capacities was better than 0.5 % for the substances with higher purity and of the order of 1 % for the others. In the literature there exists $c_{\mathrm{sat}}(T)$ data for some of the liquids studied. Agreement with our measurements is within the range of the experimental uncertainties.

Introduction

Alkylbenzenes, which are among one of the first synthetic lubricants ever developed, have been used for lubricant purposes. With the elimination of chlorine in new refrigerants, lubricity and solubility of existing lubricants were diminished. However, some small systems, such as air conditioners, vending machines, and home refrigerators where the lubricant will return to the compressor despite poor solubility, have continued to use alkylbenzene lubricants. Mixtures of alkylbenzenes are also used as secondary thermal fluids in indirect heat pump and refrigeration systems to transport heat from the object to be cooled to the evaporator.[1]

These liquids must possess good thermophysical properties.[2] One of the most important properties with respect to such applications is the heat capacity that is needed for designing equipments and making calculations of the processes in which they are involved. As a sequel and complement of a previous paper,[3] we present here measurements of the saturated heat capacity as a function of temperature of some linear and branched alkylbenzenes, with a temperature range from (332.15 to 401.15) K. Linear alkylbenzenes studied are ethylbenzene, propylbenzene, butylbenzene, hexylbenzene, 1-phenylheptane, and 1-phenylhexadecane while branched alkylbenzenes studied are *m*-xylene, cumene, (1-methylpropyl)benzene, (1,1-dimethylethyl)benzene, and (2-methylpropyl)benzene. These branched alkylbenzenes have been selected because they are isomers of some of the linear alkylbenzenes. In this way, the influence of the molecular structures of the liquids on their heat capacities can be analyzed.

Experimental Section

Apparatus. To measure the saturated heat capacities, a differential heat-flux calorimeter C80D from Setaram (France) was used. The basic design of this apparatus is similar to that of a standard Calvet calorimeter.[4] The main differences lie in an essentially lighter calorimeter block and a lower response time.

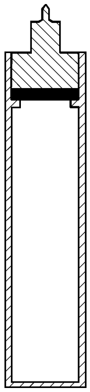

Figure 1. Experimental vessel.

The experimental calorimetric "batch" cells used have been modified from the original standard vessels of Setaram in such a way to avoid any leak so that the mass of the sample (and reference) can be considered constant throughout the measurement. The design is shown in Figure 1. A hermetic seal has been obtained by means of a Teflon disk 0.5 mm thick set on the vessel's fill hole and made tight by the lid. The height of the body cell is 80 mm, and it has an internal diameter of 15 mm. The internal vessels volume is approximately 8 cm^3.

The temperature is measured in the calorimetric block, which contains the two vessels, but it does not correspond to the true temperature of the measured sample. The necessary temperature calibration has been undertaken by means of a calibrated 2804A Hewlett-Packard thermometer with the quartz probe embedded in a stainless steel block of the same geometry as the vessels. We estimate the final uncertainty of the temperature to be better than ± 0.1 K.

To carry out the caloric calibration at each temperature, the Setaram vessels were specially designed to produce the electrical

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Table 1. Experimental Molar Saturated Heat Capacities ($C_{\mathrm{sat,m}}$) at Different Temperatures of Linear Alkylbenzenes

	$C_{\mathrm{sat,m}}/(\mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}})$					
T/K	ethylbenzene	propylbenzene	butylbenzene	hexylbenzene	1-phenylheptane	1-phenylhexadecane
332.2	198.7	227.4	259.1	323.1	353.6	640.0
342.1	202.4	231.4	263.0	328.8	359.6	651.3
354.9	205.9	235.8	267.8	334.1	364.9	662.0
361.8	210.2	240.1	272.9	340.1	371.5	671.9
371.6	213.6	244.6	277.6	347.9	377.2	683.3
381.5	218.0	249.3	283.9	353.8	384.3	695.3
391.4	221.7	252.0	288.0	359.1	389.9	710.0
401.3			293.9	366.1	396.5	721.1

Table 2. Experimental Molar Saturated Heat Capacities ($C_{\mathrm{sat,m}}$) at Different Temperatures of Branched Alkylbenzenes

	$C_{\mathrm{sat,m}}/(\mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}})$				
T/K	*m*-xylene	cumene	(1-methylpropyl)benzene	(1,1-dimethylethyl)benzene	(2-methylpropyl)benzene
332.2	193.6	229.1	258.5	259.0	259.1
342.1	197.6	234.2	262.6	263.1	263.5
354.9	201.7	238.5	267.9	268.3	268.8
361.8	205.7	242.5	272.5	272.7	273.9
371.6	209.4	246.7	277.5	278.4	278.6
381.5	213.6	251.1	282.4	283.0	283.0
391.4	217.4	255.2	287.3	288.8	289.1
401.3	221.7	259.5	292.1	293.5	293.8

heating of an already known power in the socket of the measuring heat flowmeter with the EJ2 constant power source (Setaram). Taking into account the uncertainty of this calibration method, those of the experimental procedure (step-by-step mode), and the purity of the materials used, we consider that the uncertainty of our molar saturated heat capacity measurements is better than 0.5 % for the purer substances and of the order of 1 % for the others.

Experimental Procedure. The "step-by-step method" has been used to measure the saturated heat capacities of the liquids studied. This method consists of waiting till the temperature of the calorimetric block settles at a constant plateau temperature. The actual heat capacity measurement is performed during a temperature increase $\Delta T \approx 2$ K centered across the plateau temperature. The heat flow rate is then recorded and integrated as a function of time to give directly the difference in heat transferred to the cells during heating, which is termed Q. Three steps are needed: one with the sample cell empty, Q[empty, C_{12}], another with this cell filled with the reference liquid decane, Q[decane, C_{12}], and the last involving decane replaced by the sample liquid Q[sample, C_{12}]. As indicated, the reference cell of the calorimeter is in all cases filled with dodecane. Considering that the overall molar heat capacity of the sample, $(C_{\mathrm{t,m}})_{\mathrm{sample}}$, inside the cell is nearly constant across the interval ΔT, it could be expressed as

$$(C_{\mathrm{t,m}})_{\mathrm{sample}} = \frac{n_{\mathrm{decane}}}{n_{\mathrm{sample}}} \frac{\int_{\Delta T} (C_{\mathrm{t,m}})_{\mathrm{decane}}\,\mathrm{d}T}{\Delta T} \frac{Q[\mathrm{sample, C_{12}}] - Q[\mathrm{empty, C_{12}}]}{Q[\mathrm{decane, C_{12}}] - Q[\mathrm{empty, C_{12}}]} \quad (1)$$

where n_{decane} and n_{sample} denote the decane and sample mole numbers, respectively, and $(C_{\mathrm{t,m}})_{\mathrm{decane}}$ is the molar heat capacity of decane inside the cell (liquid and vapor), which has been taken from the literature.[9,10]

In our "batch" cells, the liquid fills most of the inner space and is in equilibrium with its vapor. The overall heat capacity of such a two-phase system consists of the contribution from the saturation heat capacities of the liquid and vapor and further reflects the heat evolved during condensation inside the sample cell. Therefore, only a few small corrections have to be applied to the overall molar heat capacity in order to obtain the value of $C_{\mathrm{sat,m}}$ in the liquid phase. The first one corresponds to the heat capacity of the substance in the vapor phase, which can be calculated if we assume ideal behavior in the vapor phase. The second correction term provides the contribution of vaporization heat during measurement. The enthalpy of vaporization was obtained from the literature.[5−7] Although corrections were very small and in many cases negligible, we have applied them to all the heat capacity measurements presented in this paper. Furthermore, for the liquids studied in this work, the differences between molar isobaric heat capacity ($C_{\mathrm{p,m}}$) and at the saturation curve ($C_{\mathrm{sat,m}}$) are less than the experimental uncertainty.

Materials. The materials listed include the supplier and their mole fraction purity: ethylbenzene (Fluka AG, puriss p.a.; ≥ 99 %), propylbenzene (Fluka AG, puriss; ≥ 99 %), butylbenzene (Fluka AG, purum; ≥ 99 %), hexylbenzene (Fluka AG, purum; ≥ 97 %), 1-phenylheptane (Fluka AG, puriss; ≥ 99 %), 1-phenylhexadecane (Fluka AG, purum; ≥ 97 %), *m*-xylene (Fluka AG, puriss p.a.; ≥ 99 %), cumene (Fluka AG, purum; ≥ 98 %), (1-methylpropyl)benzene (Fluka AG, purum; ≥ 99 %), (1,1-dimethylethyl)benzene (Fluka AG, purum; ≥ 97 %), and (2-methylpropyl)benzene (Fluka AG, purum; ≥ 99 %) were used without further purification. Prior to measurements, the liquids were stored over molecular sieve type 4 Å from Fluka to remove any traces of water.

Results and Discussion

Experimental values of the molar saturated heat capacities as a function of temperature of liquids *n*-alkylbenzenes studied (ethylbenzene, propylbenzene, butylbenzene, hexylbenzene, 1-phenylheptane, and 1-phenylhexadecane) are presented in Table 1 and of the corresponding alkylbenzenes isomers (*m*-xylene, cumene, (1-methylpropyl)benzene, (1,1-dimethylethyl)benzene, and (2-methylpropyl)benzene) are presented in Table 2. These measurements complete another series made in a lower temperature range from (288 to 348) K that have been obtained in our laboratory and that have been published elsewhere[3]. For each pure liquid, a polynomial function of the type

$$C_{\mathrm{sat,m}}/(\mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}) = a_0 + a_1 T/\mathrm{K} + a_2 (T/\mathrm{K})^2 \quad (2)$$

was used to correlate the two series of experimental values of $C_{\mathrm{sat,m}}$ according to temperature with the method of least squares with all points weighted equally. The number of coefficients

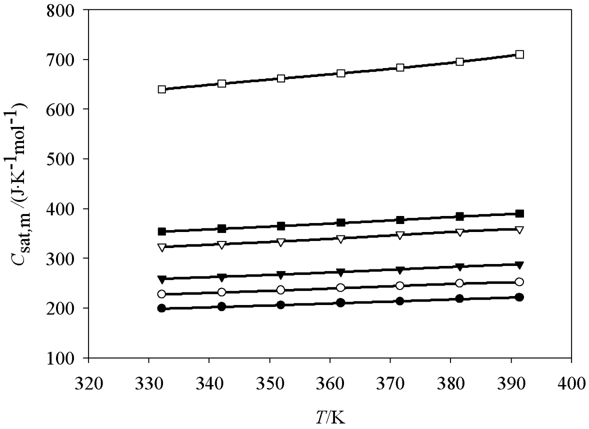


Figure 2. Saturated molar heat capacities of linear alkylbenzenes: ●, ethylbenzene; ○, propylbenzene; ▼, butylbenzene; ▽, hexylbenzene; ■, 1-phenylheptane; □, 1-phenylhexadecane. Full curves represent the smoothing of eq 2 with the coefficients of Table 3.

Table 3. Parameters a_i of Equation 2 and Standard Deviations. s

liquid	a_0	a_1	a_2	s (J·K^{-1}·mol^{-1})
ethylbenzene	110.73	0.1461	0.000352	0.4
propylbenzene	103.34	0.3514	0.0000753	0.7
butylbenzene	120.92	0.3288	0.000253	0.5
hexylbenzene	201.64	0.1337	0.000690	0.8
1-phenylheptane	188.44	0.3912	0.000316	0.6
1-phenylhexadecane	628.23	−0.9255	0.00289	0.8
m-xylene	118.40	0.08452	0.000431	0.3
cumene	104.54	0.3223	0.000161	0.3
(1-methylpropyl)benzene	131.74	0.2978	0.000254	0.6
(1,1-dimethylethyl)-benzene	116.87	0.3523	0.000219	0.4
(2-methylpropyl)benzene	123.29	0.3328	0.000229	0.4

used in eq 2 for each fit was determined by applying an F-test. The coefficients (a_i) together with the standard deviations (s) obtained in the regression are shown in Table 3. The polynomial correlation functions are then valid in a wide range of temperature from (288 to 401) K.

Graphical representation of our measurements of molar saturated heat capacities ($C_{\mathrm{sat,m}}$) of pure liquids as a function of temperature are given in Figure 2 for linear alkylbenzenes. We have also represented the values (full line) given by eq 2 with the coefficients of Table 3. For each temperature studied, $C_{\mathrm{sat,m}}$ increases linearly as the alkyl chain length increases. This behavior is similar to that obtained by Finke et al.[8] for the saturated heat capacities of a series of alkylcyclohexanes.

In the literature few $C_{\mathrm{sat,m}}(T)$ data exist for the liquids ethylbenzene, propylbenzene, butylbenzene, *m*-xylene, cumene, and (1-methylpropyl)benzene, and we can compare our measurements with these. All the data relating to the existing heat capacities of organic and inorganic liquid compounds have been collected and critically assessed in the monographs of Zábranský et al.[9,10] Graphical representations of the percentage deviations of all our measurements of saturated heat capacities ($C_{\mathrm{sat,m}}$) of the studied pure liquids with respect to the smoothing of eq 2 with coefficients of Table 3 as a function of temperature are given in Figure 3 for linear alkylbenzenes and in Figure 4 for branched alkylbenzenes. We observe that the two series of measurements corresponding to our previous paper[3] (full symbols) and this paper (open symbols) overlap in an interval of temperature within the uncertainties assigned to each calorimeter used.

We have also represented by dashes the polynomial regressions calculated in the monograph using selected data sets for comparison. For liquid ethylbenzene, the regression is valid in the interval (178.1 to 393.0) K with an uncertainty of 1 % and is in accordance with our measurements except for temperatures greater than 360 K.This discrepancy is not relevant because the majority of the selected data for the regression corresponds to the lower temperatures of the interval. Furthermore, some single data[11,12] at 298.15 K show very good agreement with our data. In the case of propylbenzene, an excellent agreement is observed; nevertheless, liquid butylbenzene shows a deviation between the regression and our measurements. Curiously both regressions have been evaluated with the data of only one paper[13] dedicated to the study of low-temperature properties of these substances in the interval (12 to 370) K with an overall error of 0.3 % for the liquid heat capacity assigned by the monograph evaluators. Nevertheless, we must take into account that the main part of the data correspond to heat capacities on both metastable and stable crystals from 12 K to the melting points and only a scarce number of measurements correspond to the liquid state. Moreover, the error intervals of the literature data and of our sets of measurements overlap except for three points. All these considerations give us confidence about our

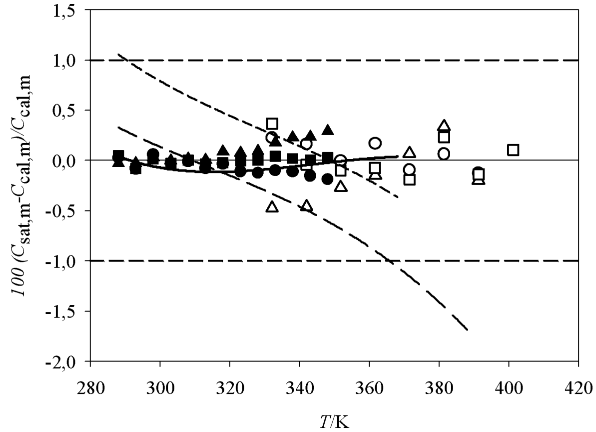


Figure 3. Percentage deviations of the saturated heat capacities of linear alkylbenzenes with respect of the smoothing of eq 2 with the coefficients of Table 3 as a function of the temperature: ●, ethylbenzene (ref 3); ▲, propylbenzene (ref 3); ■, butylbenzene (ref 3); ○, ethylbenzene; △, propylbenzene; □, butylbenzene. The lines correspond to the literature values (refs 9 and 10): long dashed lines, ethylbenzene; solid lines, propylbenzene; short dashed lines, butylbenzene.

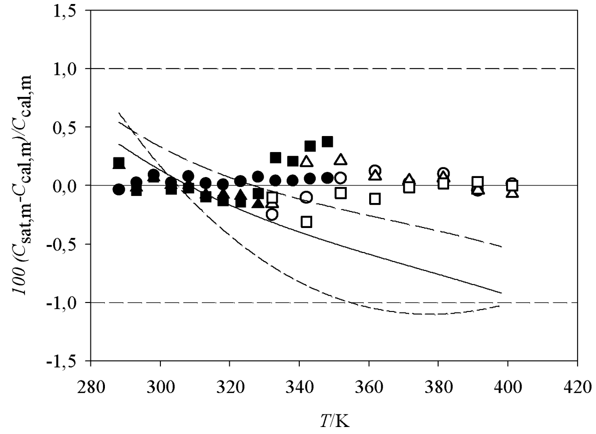


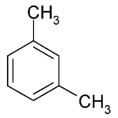
Figure 4. Percentage deviations of the saturated heat capacities of branched alkylbenzenes with respect of the smoothing of eq 2 with the coefficients of Table 3 as a function of the temperature: ●, *m*-xylene (ref 3); ▲, cumene (ref 3); ■, 1-methylpropyl)benzene (ref 3); ○, *m*-xylene; △, cumene; □, 1-methylpropyl)benzene. The lines correspond to the literature values (refs 9 and 10): long dashed lines, *m*-xylene; solid lines, cumene; short dashed lines, 1-methylpropyl)benzene.

data for the liquids propylbenzene and butylbenzene, which extend the temperature range consider in the literature.

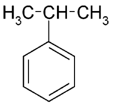
For liquids *m*-xylene and cumene, the calculated regressions have uncertainties of 0.5 % and 1 %, respectively, according to the monograph. From Figure 4, we observe an agreement with our measurements within those uncertainties. In the case of liquid (1-methylpropyl)benzene, only nine points have been selected to evaluate the regression in the interval (293.7 to 429.6) K with an uncertainty of 1 %. We can observe from Figure 4 an increasing deviation with temperature between the regression and our measurements, which can be due probably to the small number of data used for the regression.

As far as we know, there are no experimental data in the literature for comparison for the liquids hexylbenzene, 1-phenylheptane, 1-phenylhexadecane, (1,1-dimethylethyl)benzene, and (2-methylpropyl)benzene for the temperatures studied in this paper.

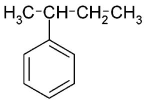
It is worth comparing the saturated heat capacities of ethylbenzene, propylbenzene, and butylbenzene with those of their isomers. The $C_{\mathrm{sat,m}}$ of ethylbenzene and isomer *m*-xylene:

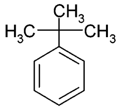


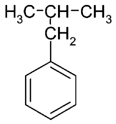
of propylbenzene and isomer cumene:



and of butylbenzene and its isomers (1-methylpropyl)benzene, (1,1-dimethylethyl)benzene, and (2-methylpropyl)benzene:







have been represented in Figure 5 for comparison. We have also represented the values (full line) given by eq 2 with the coefficients of Table 3.

It can be observed in Figure 5 that, in the case of ethylbenzene, the saturated heat capacity of this compound is higher than that of its isomer *m*-xylene. Propylbenzene has a saturated heat capacity, which is slightly smaller than of the isomer cumene at each temperature. From the same figure, we deduce that the saturated heat capacities of butylbenzene and those of its three isomers studied are also very similar. This behavior can be related to the structures of the molecules. In our previous paper,[3] we concluded that the heat capacity of this type of systems is sensitive to differences in shape and size of the molecules. The new heat capacity data measured at higher temperatures confirm again this analysis. Especially as regards *m*-xylene, where two alkyl groups are connected separately to the benzene ring, the saturated heat capacity differs appreciably from that of ethylbenzene. Nevertheless, the values of $C_{\mathrm{sat,m}}$ for linear and branched alkylbenzenes approach each other as the size of the alkyl chains increases. This is the case with propylbenzene and isomer cumene and butylbenzene and the three isomers.

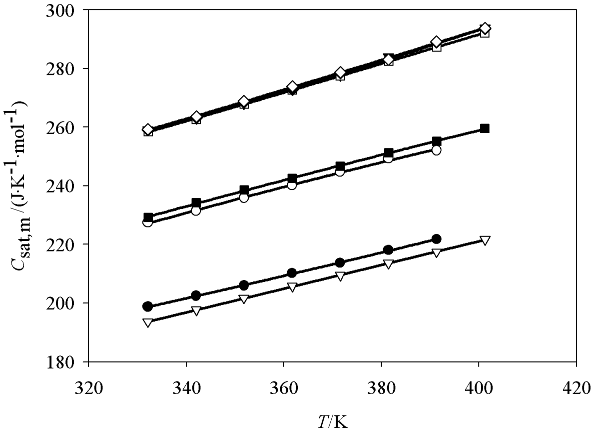


Figure 5. Saturated molar heat capacities of linear and branched alkylbenzene:. ●, ethylbenzene; ○, propylbenzene; ▼, butylbenzene; ▽, *m*-xylene; ■, cumene; □, (1-methylpropyl)benzene; ◆, (1,1-dimethylethyl)benzene; ◇, (2-methylpropyl)benzene. Full curves represent the smoothing of eq 2 with the coefficients of Table 3.

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