Oxygenated Gasoline Additives: Saturated Heat Capacities between (277 and 355) K

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The saturated heat capacities of oxygenated gasoline additives methyl *tert*-butyl ether (MTBE), ethyl *tert*-butyl ether (ETBE), diisopropyl ether (DIPE), and *tert*-amyl methyl ether (TAME) in the temperature range of 277.15 K to some degrees below their normal boiling temperatures have been measured. A Micro DSC II from Setaram (France) with batch cells designed in our laboratory and the "scanning method" were used to perform the measurements. The estimated uncertainty of the saturated heat capacities was better than 0.3%. In the literature, there exist $c_{\mathrm{sat}}(T)$ data for some of the liquids studied. Agreement with our measurements is within the range of the experimental uncertainties. At each temperature, the saturated heat capacity of liquid MTBE is smaller than those of ETBE, DIPE, and TAME, and the corresponding c_{sat} values of these three liquids are similar. This behavior can be related with the surface fraction of the ether group in each molecule.

Introduction

In the past decades, a group of chemicals commonly known as "oxygenates" have been used as fuel additives in motor gasoline. Most oxygenates used in gasolines are either alcohols (ethyl alcohol (EtOH), *tert*-butyl alcohol (TBA)) or ethers (methyl *tert*-butyl ether (MTBE), ethyl *tert*-butyl ether (ETBE), diisopropyl ether (DIPE), *tert*-amyl methyl ether (TAME)) and contain 1 to 6 carbons. Alcohols have been used since the 1930s, and MTBE was first used at low levels in commercial gasolines in Italy in 1973 and in the U.S. in 1979 to replace lead as an octane enhancer (helps prevent the engine from "knocking"). Initially, the oxygenates were added to hydrocarbon fractions that were slightly modified unleaded gasoline fractions, and these were known as "oxygenated" gasolines. In 1995, the hydrocarbon fraction was significantly modified, and these gasolines are called "reformulated gasolines" (RFGs).

The environmentally friendly oxygenate compounds function in various ways. First, they have high blending octane and so can replace high-octane aromatics in the fuel. These aromatics are responsible for exhaust emissions of large amounts of CO and hydrocarbons. The presence of oxygen helps gasoline burn more completely, reducing harmful tailpipe emissions from motor vehicles. The use of RFG compared to conventional gasoline has resulted in important reductions in smog-forming pollutants (volatile organic compounds and nitrogen oxides) and toxics (such as benzene).

Owing to the increasing practical interest in these oxygenated fuel additives, an exact knowledge of their physical properties is of great importance. In this work, accurate saturated heat capacities were determined for the following four ethers: MTBE, ETBE, DIPE, and TAME in the temperature range (277 to 355) K.

Experimental Section

Apparatus. To measure the molar saturated heat capacities, a differential heat-flux calorimeter Micro DSC II from Setaram (France) was used. The basic design of this apparatus is similar to that of a standard Calvet calorimeter,[1] but with the exception that the temperature is set by Peltier elements with an internal liquid (undecane) loop which flows around the calorimeter block. An additional external water circulation circuit is needed to provide or remove heat from the thermoelectric elements. This arrangement produces accurate temperature control, excellent thermal homogeneity, and low inertia, factors which account for its very good baseline stability. By application of two symmetrical semiconducting heat-flow meters, sensitivity is increased to about 106 μV·mW^{-1}, which is double that of the thermopile detectors in the standard Calvet calorimeter. The assembly is set in an inert atmosphere of dry nitrogen.

The experimental calorimetric "batch" vessels used have been designed in our laboratory 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 internal vessel volume is approximately 1 cm^3. The features of these vessels have been described elsewhere.[2]

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 Pt-1000 probe embedded in a stainless steel block of the same geometry as the vessels. This process has been carried out at different scanning rates, from 0 K·min^{-1} (isothermal mode) to 0.2 K·min^{-1}, and the corrections were smoothed with a polynomial equation, the coefficients of which have been introduced in the software of the apparatus. We estimate the final uncertainty of the temperature to be ±0.03 K for the scanning mode.

To carry out the caloric calibration at each temperature, the Setaram vessels were specially designed to produce electrical heating of an already known power in the socket

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Table 1. Experimental Molar Saturated Heat Capacities, c_{sat}, at Different Temperatures

T/K	$c_{sat}/(J \cdot K^{-1} \cdot mol^{-1})$	T/K	$c_{sat}/(J \cdot K^{-1} \cdot mol^{-1})$	T/K	$c_{sat}/(J \cdot K^{-1} \cdot mol^{-1})$	T/K	$c_{sat}/(J \cdot K^{-1} \cdot mol^{-1})$
Methyl *tert*-Butyl Ether (MTBE)		Ethyl *tert*-Butyl Ether (ETBE)		Diisopropyl Ether (DIPE)		*tert*-Amyl Methyl Ether (TAME)	
277.15	180.9	277.14	211.4	277.17	207.7	279.16	206.8
279.15	181.4	281.17	213.3	279.16	208.5	281.15	207.7
281.16	182.3	283.15	214.2	281.15	209.4	283.16	208.5
283.15	183.1	285.16	215.2	283.14	210.4	285.16	209.3
285.15	183.8	287.15	216.0	285.16	211.3	287.16	210.2
287.14	184.4	289.16	216.9	287.16	212.2	289.16	211.0
289.16	185.3	291.14	217.7	289.15	213.1	291.17	211.7
291.15	186.0	293.14	218.5	291.17	214.0	293.15	212.5
293.16	186.8	295.15	219.3	293.15	214.8	295.15	213.5
295.15	187.7	297.14	220.1	295.16	215.5	297.16	214.5
297.14	188.3	299.15	220.9	297.16	216.3	299.16	215.3
299.14	189.0	301.14	221.7	299.16	217.2	301.14	216.1
301.16	189.7	303.16	222.6	301.16	218.0	303.14	216.9
303.16	190.4	305.14	223.3	303.15	218.7	305.15	217.8
305.15	191.1	307.15	224.2	305.14	219.5	307.15	218.3
307.15	191.8	309.14	225.3	307.14	220.3	309.15	219.1
309.16	192.6	311.15	225.9	309.16	221.0	311.16	220.1
311.16	193.2	313.14	226.7	311.15	222.0	313.16	220.6
313.15	193.9	315.16	227.6	313.15	222.7	315.13	221.3
315.15	194.6	317.14	228.6	315.15	223.6	317.13	222.1
317.14	195.2	319.15	229.5	317.17	224.4	319.14	222.8
319.16	196.0	321.14	230.1	319.16	225.1	321.14	223.5
321.15	196.5	323.15	231.0	321.15	225.9	323.14	224.5
323.15	197.3	325.14	231.7	323.14	226.7	325.15	225.0
325.15	198.0	327.16	232.6	325.14	227.4	327.16	225.7
		329.15	233.3	327.13	228.3	329.16	226.7
		331.16	234.2	329.16	229.0	331.17	227.4
		333.15	235.1	331.15	229.9	333.13	228.1
		335.16	235.9	333.15	230.5	335.14	228.9
		338.16	237.1	335.14	231.4	337.14	229.7
		339.14	237.4	337.14	232.2	339.15	230.4
		341.15	238.1			341.16	231.0
						343.17	231.9
						345.14	232.6
						347.14	233.5
						349.15	234.3
						351.15	234.9
						353.16	235.7
						355.14	236.4

of the measuring heat-flow meter with the EJ2 constant power source (Setaram). Taking into account the incertitude of this calibration method, those of the experimental procedure (scanning mode), and the purity of the materials used, we consider that the uncertainty of our molar saturated heat capacity measurements is better than 0.3%.

Experimental Procedure. The "scanning or continuous method" was used to measure the saturated heat capacity of the ethers with the differential scanning calorimeter. This method is based on the relation between the heat flow rate $\dot{Q}$, which is proportional to the measured calorimetric signal, the overall heat capacity of the sample (liquid and vapor) inside the sample cell, c_t, which corresponds to saturation conditions in batch cells, and the scanning rate β:

$$\dot{Q} = c_t(T)\beta \tag{1}$$

The experimental procedure consists of three steps in which the reference cell is always filled with a liquid (dodecane in this work): (a) The heat flow rate of the baseline is determined with an empty sample cell, which we term $\dot{Q}[\text{empty, C}_{12}]$. (b) A calibration liquid (water) of well-known heat capacity[3] is put into the sample cell. The corresponding heat flow rate is termed $\dot{Q}[\text{water, C}_{12}]$. (c) The calibration liquid is replaced by the sample liquid, and the heat flow rate obtained is termed $\dot{Q}[\text{sample, C}_{12}]$.

By successively applying eq 1 to each of the above steps, we obtain the following ratio for the overall heat capacity of the sample:

$$(c_t)_{\text{Sample}} = \frac{m_{\text{Water}}}{m_{\text{Sample}}}(c_t)_{\text{Water}} \frac{\dot{Q}[\text{sample, C}_{12}] - \dot{Q}[\text{empty, C}_{12}]}{\dot{Q}[\text{water, C}_{12}] - \dot{Q}[\text{empty, C}_{12}]} \tag{2}$$

where m_{Water} and m_{Sample} denote the water and sample mass, respectively, and $(c_t)_{\text{Water}}$ denotes the specific heat capacity of water inside the cell (liquid and vapor).

The scanning rate does not appear in eq 2, but in practice the one chosen must be fast enough to avoid very long experiments and slow enough to prevent excessive thermal delay between the programmed and the real heating or cooling rates, with the subsequent disturbance of the quasi-steady-state condition in the cells. A scanning rate of 0.15 $K \cdot min^{-1}$ has been selected in our experiments. The scanning method allows a large temperature range to be covered in one run. This gives a continuous heat capacity–temperature curve.

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, c_t, 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 heat capacity in order to obtain the value of c_{sat}[2] 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 condensation

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

liquid	a_0	a_1	a_2	a_3	s (J·K^{-1}·mol^{-1})
MTBE	26.718	0.7243	−0.000 608 2		0.08
ETBE	96.591	0.4156			0.13
DIPE	−382.91	4.951	−0.014 34	0.000 015 04	0.08
TAME	−261.16	3.695	−0.010 07	0.000 010 18	0.12

heat during measurement. The heat of condensation is obtained from the literature.[3−5] Although corrections are 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 isobaric heat capacity, c_p, and that at the saturation curve, c_{sat}, are less than the experimental uncertainty.

Materials. MTBE (Fluka AG, puriss p.a.; ≥99.5 mol %), ETBE (Fluka AG, purum; ≥97 mol %), DIPE (Fluka AG, puriss p.a.; ≥99 mol %), and TAME (Fluka AG, purum; ≥97 mol %) were used without further purification. Prior to measurements, the liquids were stored over Fluka molecular sieve type 4 Å to reduce any traces of water.

Experimental Results and Discussion

Experimental values of the saturated heat capacities as a function of temperature of MTBE, ETBE, DIPE, and TAME in the temperature range 277.15 K to some degrees below their normal boiling temperatures are presented in Table 1. The reported values correspond to the average of two consecutive experimental determinations, one heating and the other cooling. For each pure liquid, a polynomial function of the type

$$c_{sat}/(\mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}) = a_0 + a_1 T/\mathrm{K} + a_2 (T/\mathrm{K})^2 + a_3 (T/\mathrm{K})^3 \quad (3)$$

was used to correlate the experimental values of c_{sat} according to temperature, application being made of the method of least squares with all points weighted equally. The number of coefficients used in eq 3 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 2.

Graphical representations of the percentage deviations of our measurements of saturated heat capacities, c_{sat}, of pure liquids with respect to the smoothing of eq 3 with coefficients of Table 2 as a function of temperature are given in Figure 1 for MTBE, Figure 2 for ETBE, Figure 3 for DIPE, and Figure 4 for TAME.

In the literature monograph,[6,7] $c_{sat}(T)$ data exist for some of the liquids studied in this paper, and we can compare our measurements with these. For liquid MTBE, one very old measurement[8] at 298.1 K and one data set[9] in the range (168.3 to 308.4) K, which is used to evaluate a polynomial regression with an overall error of 0.3% assigned by the monograph evaluators, are reported. In Figure 1, a representation is given by dashes of the percentage deviation of the polynomial regression with respect to the smoothing of eq 3 for comparison. We can observe an increasing deviation with temperature between the regression and our measurements. Nevertheless, we must consider that the literature measurements have been obtained with a low-temperature adiabatic batch calorimeter in a continuous run from 11.5 K, where the MTBE is crystal, to 308.4 K and that only the last 9 points of a total of 200 partly cover the temperature interval of our data. Moreover, the error intervals of the two sets of measurements overlap except for the three points at the end. These considerations give us confidence about our data.

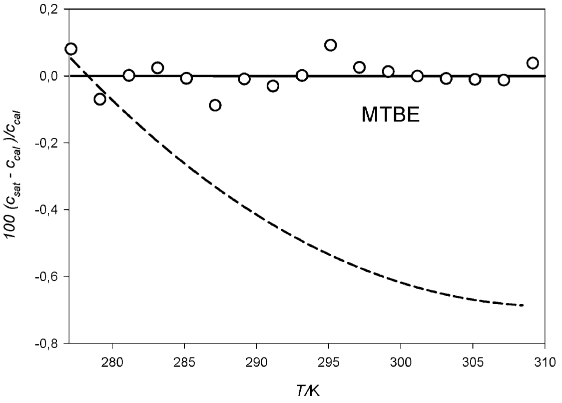

Figure 1. Percentage deviations of the saturated heat capacities of MTBE with respect to the smoothing of eq 3 with the coefficients of Table 2 as a function of temperature: ○, experimental data. The dashed line corresponds to literature values (ref 6).

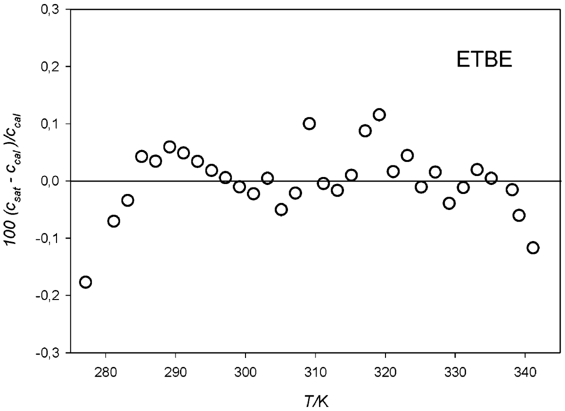

Figure 2. Percentage deviations of the saturated heat capacities of ETBE with respect to the smoothing of eq 3 with the coefficients of Table 2 as a function of temperature: ○, experimental data.

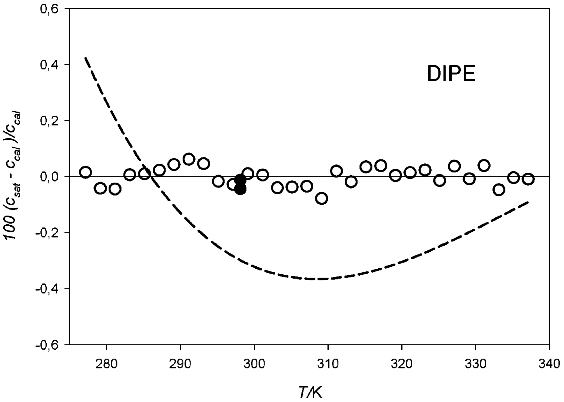

Figure 3. Percentage deviations of the saturated heat capacities of DIPE with respect to the smoothing of eq 3 with the coefficients of Table 2 as a function of temperature: ○, experimental data; ●, literature data (refs 12−14). The dashed line corresponds to literature values (refs 6 and 7).

As far as we know, there is only in the literature[8] one poor quality measurement of c_p at 298.15 K for the liquid ETBE, which was rejected in the critical analysis of the monograph.[6,7] For liquid TAME, we have found two c_p data at 298.15 K. The first one, taken from the same reference as for the ETBE, is also not acceptable for comparison, and another,[10] obtained with a differential scanning calorimeter, was measured as auxiliary data for heat of combustion

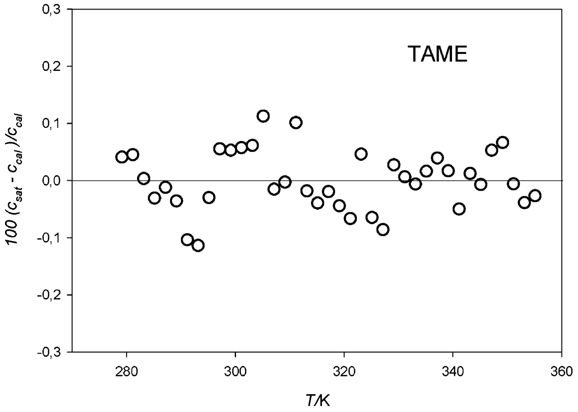

Figure 4. Percentage deviations of the saturated heat capacities of TAME with respect to the smoothing of eq 3 with the coefficients of Table 2 as a function of temperature: ○, experimental data.

Table 3. Saturated Heat Capacities of MTBE, ETBE, DIPE, and TAME at 298.15 and Their Ether Surface Fractions, α_O

liquid	$c_{sat}/(J{\cdot}K^{-1}{\cdot}mol^{-1})$	α_O
MTBE	188.6	0.0661
ETBE	220.5	0.0575
DIPE	217.1	0.0587
TAME	215.2	0.0575

determination. The differences between the second value in relation to the first and to ours are so large (greater than 35%) that we are certain that it is wrong. Recently, saturated heat capacities of TAME have been measured[17] with a differential scanning calorimeter in a broad temperature range with an uncertainty of 1%. The agreement with our values is very good and within that experimental uncertainty.

With respect to liquid DIPE, we have found one poor quality isobaric heat capacity set of data[11] in the interval 194.5 to 293.1 K and some single data[12−14] at 298.15 K. None of these have been considered in the final analysis of the monograph.[6,7] Nevertheless, these last three data are represented in Figure 3 and show very good agreement with our data. In the same figure, we have represented also the percentage deviations of the polynomial regression with respect to the smoothing of eq 3 proposed by the above-mentioned monograph, which have been evaluated with the set of data[15] measured in the same laboratory as for MTBE. In this case, there is a close agreement within the experimental uncertainties between the literature values and the measurements in this work in the whole temperature interval.

At each temperature, the saturated heat capacity of liquid MTBE is smaller than those of the other ethers and the corresponding c_{sat} values of these three liquids are similar. As an example, in Table 3 we present the saturated heat capacities of each ether at 298.15 K calculated using eq 3 with the coefficients of Table 2. This behavior can be related with the surface fraction of the ether group in each type of molecule. In fact, using the Bondi method,[16] we have calculated the surface fractions of the ether group, α_O, for the four ether molecules studied, and these are indicated in Table 3. It can be observed that a higher value of α_O corresponds to a smaller value of the saturated heat capacity, which is the case of MTBE, and similar values of the surface fraction correspond to comparable values of the saturated heat capacities as occurs with ETBE, DIPE, and TAME.

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