New Batch Cells Adapted To Measure Saturated Heat Capacities of Liquids

R. Páramo,[†] M. Zouine,[‡] and C. Casanova*,[†]

Department Termodinámica y Física Aplicada, Universidad de Valladolid, 47005 Valladolid, Spain, and Department des Sciences de Base, École National d'Agriculture, Université de Meknès, Meknès, Maroc

New "batch" cells adapted to measure saturated heat capacities with a Micro DSC II (Setaram) microcalorimeter designed to avoid any leakage during measurement are described. Using the "scanning" and "step-by-step" methods, the heat capacities of pure organic liquids—hexane, heptane, decane, dodecane, cyclohexane, toluene, methanol, and 1-butanol—in the temperature range (5 to 75) °C were determined. In addition, the excess heat capacities of several binary liquid mixtures—(benzene + cyclohexane) and (2,5,8,11-tetraoxadodecane + dodecane)—with the step-by-step procedure were measured. A very close agreement with literature values better than 1% indicates that the apparatus and technique are suitable for heat capacity measurements on volatile liquids.

Introduction

Heat capacity is one of the more valuable thermophysical quantities to be considered when studying pure liquids and liquid mixtures. Accurate values are needed in many areas of physics, chemistry, and chemical engineering for establishing energy balances, obtaining entropy and enthalpy values, or studying phase transitions. Moreover, ascertainment of the heat capacity of liquids as a function of temperature is a source of important information concerning their molecular structure and is essential for checking the efficiency of estimation models used in industry.

To obtain direct and accurate heat capacity measurements, a suitable calorimeter must be used. The adiabatic calorimeter is the most important and accurate tool for heat capacity determination over a wide range of temperatures. However, other approaches to heat capacity measurement have been developed which are less costly, faster, and easier to use. This is the case of the Picker differential flow calorimeter, which has been extensively used to determine heat capacities of liquids but which has the shortcoming of having a limited operating range of temperature. Another possibility is the calculation of heat capacity from heating or cooling curves obtained with a differential scanning calorimeter (DSC). This method has become widespread, but most of these instruments lack the resolution needed for the precise determination of liquid heat capacity values.

Setaram Micro DSC instruments offer a very high sensitivity which enables highly precise measurements of liquid heat capacities over a wide temperature range. Another advantage with respect to other calorimeters is the small sample size required for the operation.

In this work, new "batch" cells adapted to measure saturated heat capacities with a Micro DSC II microcalorimeter designed to avoid any leakage during measurement are presented. By means of the "scanning" and "step-by-step" methods, heat capacities of several pure organic liquids and the excess heat capacities of several binary liquid mixtures at different temperatures were measured. The results agree well with those of the literature.

Experimental Section

Apparatus. To measure the molar saturated heat capacities, a Setaram Micro DSC II microcalorimeter was used. The basic design of this apparatus is similar to that of a standard Calvet calorimeter,[1] but with the further 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 required 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 applying two symmetrical semiconducting heat flow meters, sensitivity is increased to about 106 μV/mW, 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 vessels provided by Setaram to measure heat capacities of liquids with this calorimeter are of the open type, fitted with two tubes welded to the body. The sample and reference liquids enter their corresponding vessels via one of the tubes so as to avoid any vapor phase. The calorimetric signal obtained in the scanning or step-by-step method is then proportional to the heat capacity per unit volume of the sample liquid (C_pV^{-1}). Therefore, to obtain the heat capacity, it is necessary to measure the density of the liquid at the same temperature.

If this last condition cannot be fulfilled, the Setaram closed "batch" vessels can be used. This alternative method makes it possible for the specific heat capacity to be obtained (density is not required), as long as there are no leaks and the mass of the sample (and reference) is constant throughout the measurement. The vessel is made fluid-tight by an elastomer seal, able to stand a maximum internal pressure of 20 bar, according to Setaram. From our experience, these types of vessels always leak when the temperature is changed. This even occurs in the case

---

* To whom correspondence should be addressed. E-mail: casanova@termo.uva.es. Fax: (34) 983 42 31 36.

[†] Universidad de Valladolid.

[‡] Université de Meknès.

10.1021/je0155103 CCC: $22.00

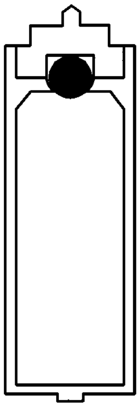

Figure 1. New experimental vessel suitable for saturated liquid heat capacity measurements using a Micro DSC (Setaram) microcalorimeter.

of not very volatile liquids; hence, it is not possible to obtain the necessary accuracy in heat capacity measurements. Furthermore, the elastomer seal may be affected by the organic solvents. For this reason, the vessels were modified. The new design is shown in Figure 1. A hermetic seal has been obtained by means of a stainless steel sphere set on the vessel's fill hole and made tight by the lid. The height of the body cell is 27 mm, and it has an external diameter of 9 mm. The internal cell volume is approximately 1 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. For this reason, the microcalorimeter requires a temperature calibration procedure which 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 (isothermal mode) to 0.2 K/min, and the corrections have been 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 ±0.01 K for the isothermal mode and ±0.03 K for the scanning mode.

In this type of calorimeter, the output signal recorded is proportional to the total heat flow rate. Therefore, a calorimetric calibration must be performed to determine the proportionality coefficient between those two magnitudes at each temperature. To carry out this calibration, the Setaram vessels specially designed to produce electrical heating of a known power with the EJ2 constant power source (Setaram) were used. Taking into account the uncertainty of this calibration method and that of the best experimental procedure (isothermal mode), we consider that the uncertainty of our molar heat capacity measurements is better than 0.05 $J \cdot K^{-1} \cdot mol^{-1}$.

Experimental Procedure. Two experimental procedures can be used to measure heat capacity with a differential scanning calorimeter: the scanning or continuous method and the step-by-step or discontinuous method. Determinations with the first method are both easy and very fast. The second method requires lengthy experiments but is able to produce more accurate measurements. In this work both methods to determine the saturated heat capacities of the same organic liquids were used and subsequently the results have been compared.

The scanning method principle 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:

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

This method 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 with an empty sample cell, which is termed $\dot{Q}[\text{empty},C_{12}]$, is determined.

(b) A calibration liquid (water) of a recognized heat capacity 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, the following ratio for the overall heat capacity of the sample is obtained:

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

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 consequent disturbance of the quasi-steady-state condition in the cells. A scanning rate of 0.15 $K \cdot min^{-1}$ has been selected in all the experiments.

The step-by-step 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 or decrease $\Delta T \approx 1$ 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 or cooling, which is termed Q. As in the previous method, three steps are needed: one with the sample cell empty, $Q[\text{empty},C_{12}]$, another with this cell filled with water, $Q[\text{water},C_{12}]$, and the last involving water replaced by the sample liquid, $Q[\text{sample},C_{12}]$. As indicated, the reference cell is in all cases filled with dodecane. Considering that the overall heat capacity of the sample, $(c_t)_{\text{sample}}$, inside the cell is nearly constant across the interval ΔT, it could be expressed as

$$(c_t)_{\text{sample}} = \frac{m_{\text{water}}}{m_{\text{sample}}}\left[\int_{\Delta T}(c_t)_{\text{water}}\,dT\right]\frac{Q[\text{sample},C_{12}] - Q[\text{empty},C_{12}]}{Q[\text{water},C_{12}] - Q[\text{empty},C_{12}]} \tag{3}$$

Corrections. The saturation heat capacity, c_{sat}, can be obtained from the calorimetric determinations of the overall heat capacity of a sample inside a "batch" cell, c_t, given by eq 2 or 3. Only a few small corrections have to be applied in order to obtain the value of c_{sat}, provided that the temperature in not very close to the critical one. Furthermore, for liquids, it is not necessary to make any distinction below $\sim 0.9T_{\text{nb}}$, where T_{nb} is the normal boiling temperature, between the isobaric heat capacity at the saturation curve, c_p, and c_{sat}, as the differences are less than the experimental uncertainty, which is the case in our measurements.

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 absorbed or evolved during vaporization or condensation inside the sample cell. The relationship between the measured c_t and c_{sat} can be obtained as follows.

The entropy of the two-phase equilibrium system, S_t, can be written as

$$S_t = n^l s^l + n^g s^g \tag{4}$$

where s^l and s^g are the molar entropies of the coexisting phases and n^l and n^g are the amounts of substance in the liquid and vapor phases, respectively. As the cells are hermetically sealed, the total amount of substance, $(n^l + n^g)$, can be considered to be constant throughout the experiment.

Considering the expression of heat capacity according to entropy, $C_x = T(\partial S/\partial T)$, and by taking the temperature derivative of eq 4, the overall heat capacity of the substance inside the sample cell is obtained:

$$C_t = n^l c^l_{sat} + n^g c^g_{sat} + \Delta_{vap}H\left(\frac{\partial n^g}{\partial T}\right)_{sat} \tag{5}$$

where c^l_{sat} and c^g_{sat} are the saturation heat capacities in the liquid and vapor phases, respectively, and $\Delta_{vap}H$ is the enthalpy of vaporization (or condensation) of the sample.

From eq 5 the correction terms which must be applied to the experimental measurement C_t to obtain the saturated heat capacity in the liquid phase, c^t_{sat}, can be easily inferred. First, the second term on the right-hand side of eq 5, $n^g c^g_{sat}$, which corresponds to the heat capacity of the substance in the vapor phase, must be subtracted from C_t. This correction term can be calculated quite well, if ideal behavior is assumed in the vapor phase. The ideal heat capacity is taken from the literature, and the value of n^g at each temperature is calculated with the experimental measurements of the total amount of substance inside the sample cell, the vapor pressure, the density of the liquid, and the total volume of the cell.

The second correction concerns the third term, $\Delta_{vap}H(\partial n^g/\partial T)_{sat}$, which provides the contribution of the enthalpy of vaporization (or condensation) during measurement. $\Delta_{vap}H$ is obtained from the literature, and the derivative factor is evaluated by calculating the change of n^g in the short temperature interval.

The cell is always filled almost completely with the liquid in order to have a very small vapor phase, and although corrections are very small and in many cases negligible, they have been applied to all the heat capacity measurements presented in this paper.

Materials. Hexane (Fluka AG, puriss p.a.; ≥99.5 mol %), heptane (Fluka AG, puriss p.a.; ≥99.5 mol %), decane (Fluka AG, puriss p.a.; ≥99 mol %), dodecane (Aldrich Chem. Co. Inc; >99 mol %), cyclohexane (Fluka AG, puriss p.a.; ≥99.5 mol %), benzene (Fluka AG, puriss p.a.; ≥99.5 mol %), toluene (Fluka AG, puriss p.a.; ≥99.5 mol %), methanol (Fluka AG, puriss p.a.; ≥99.5 mol %), 1-butanol (Fluka AG, puriss p.a.; ≥99.5 mol %), and 2,5,8,11-tetraoxadodecane (Aldrich Chem. Co. Inc; >99 mol %) were used without further purification. Prior to measurements the liquids were stored over Fluka molecular sieves type 4 Å to reduce any traces of water.

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

	$c_{sat}/(J{\cdot}K^{-1}{\cdot}mol^{-1})$		$c_{sat}/(J{\cdot}K^{-1}{\cdot}mol^{-1})$	
T/K	step	scan	step	scan
	Hexane		Heptane	
348.15	213.72	213.70	245.10	245.30
338.15	210.00	209.72	241.09	241.01
328.15	206.30	205.96	237.11	236.76
318.15	202.62	202.53	233.13	232.68
308.15	198.89	198.70	229.12	228.63
298.15	195.23	195.29	225.10	224.85
288.15	191.27	191.26	220.94	220.73
278.15	187.22		216.57	
	Decane		Dodecane	
348.15	340.07	340.28		
338.15	335.01	334.69	398.13	
328.15	329.96	329.45		
318.15	325.00	324.16	386.66	
308.15	320.04	319.16		
298.15	314.88	314.80	375.76	
288.15	309.78	310.13		
278.15	304.53		364.38	
	Toluene		Cyclohexane	
348.15	172.12	172.27		176.14
338.15	169.15	169.02		171.96
328.15	166.18	166.02		167.96
318.15	163.24	162.85		164.17
308.15	160.22	159.83		160.06
298.15	157.15	157.06		156.09
288.15	154.10	154.12		151.97
278.15	150.80			
	Methanol		1-Butanol	
348.15	93.25	93.43	217.97	217.63
338.15	90.59	90.64	209.54	208.88
328.15	88.06	88.06	201.06	200.39
318.15	85.68	85.65	192.78	192.05
308.15	83.42	83.37	184.81	184.12
298.15	81.26	81.36	177.21	177.06
288.15	79.24	79.41	170.34	170.44
278.15	77.30		163.68	

Experimental Results

With the aim of checking our new heat capacity cells and the experimental technique, saturated heat capacities of several pure organic liquids (hexane, heptane, decane, dodecane, cyclohexane, toluene, methanol, and 1-butanol) have been measured in the temperature range (5 to 75) °C by the scanning and/or step-by-step methods. Furthermore the excess heat capacities of the liquid mixtures (benzene + cyclohexane) at (25, 35, and 45) °C and (2,5,8,11-tetraoxadodecane + dodecane) at (25, 45, and 65) °C with the step-by-step procedure have been measured. The temperature intervals have been selected so as to be able to compare the main part of our results with the literature. For the mixtures studied, only direct experimental data of c^E_p at 25 °C can be found in the literature; nevertheless, for the (benzene + cyclohexane) mixture, there exist excess enthalpy data[26] measured with great care at different temperatures which enable us to calculate the $c^E_p(T)$. The reported values with the step-by-step method correspond to the average of six consecutive experimental determinations, with heating and cooling, alternatively.

The experimental values of the saturated heat capacities of the organic liquids are presented in Table 1. For each pure liquid and each method of measurement, a polynomial function

$$c_{sat}/(J{\cdot}K^{-1}{\cdot}mol^{-1}) = a_0 + a_1 T/K + a_2(T/K)^2 + a_3(T/K)^3 \tag{6}$$

was used to correlate the experimental values of c_{sat} with temperature using the method of least-squares with all

Table 2. Parameters a_i of Eq 6 and Standard Deviations, s

liquid	method	a_0	a_1	a_2	a_3	s / $\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$
hexane	step	−190	2.9	−0.007 9	0.000 008 1	0.04
	scan	84.9	6.554			0.17
heptane	step	−140	2.7	−0.007 0	0.000 007 2	0.02
	scan	140	0.16	0.000 39		0.09
decane	step	148	0.61	−0.000 16		0.07
	scan	280	−0.23	0.001 14		0.13
dodecane	step	208.5	0.561			0.17
toluene	step	46	0.44	−0.000 22		0.05
	scan	103	0.07	0.000 36		0.07
cyclohexane	scan	36.6	0.4006			0.09
methanol	step	73.2	−0.155	0.000 611		0.018
	scan	99	−0.318	0.000 87		0.02
1-butanol	step	640	−5.4	0.018	−0.000 017	0.09
	scan	970	−8.2	0.026	−0.000 025	0.09

Table 3. Experimental Excess Molar Saturated Heat Capacities, $c^{\mathrm{E}}_{\mathrm{sat}}$, at 298.15, 308.15,and 318.15K of the Benzene (1) + Cyclohexane (2) System

$T = 298.15$ K		$T = 308.15$ K		$T = 318.15$ K	
x_1	$c^{\mathrm{E}}_{\mathrm{sat}}$ / $\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$	x_1	$c^{\mathrm{E}}_{\mathrm{sat}}$ / $\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$	x_1	$c^{\mathrm{E}}_{\mathrm{sat}}$ / $\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$
0.1044	−1.01	0.1040	−0.88	0.1040	−0.83
0.1997	−1.84	0.1995	−1.63	0.1995	−1.57
0.2934	−2.37	0.2984	−2.30	0.2984	−2.21
0.3995	−2.72	0.3968	−2.70	0.3968	−2.57
0.5004	−2.91	0.4979	−2.84	0.4979	−2.71
0.5969	−2.82	0.5982	−2.80	0.5982	−2.66
0.7034	−2.60	0.7017	−2.43	0.7017	−2.29
0.8022	−2.09	0.8063	−1.81	0.8063	−1.69
0.8979	−1.18	0.8979	−1.15	0.8979	−1.05

Table 4. Experimental Excess Molar Saturated Heat Capacities, $c^{\mathrm{E}}_{\mathrm{sat}}$, at 298.15, 318.15, and 338.15 K of the 2,5,8,11-Tetraoxadodecane (1) + Dodecane (2) System

$T = 298.15$ K		$T = 318.15$ K		$T = 338.15$ K	
x_1	$c^{\mathrm{E}}_{\mathrm{sat}}$ / $\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$	x_1	$c^{\mathrm{E}}_{\mathrm{sat}}$ / $\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$	x_1	$c^{\mathrm{E}}_{\mathrm{sat}}$ / $\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$
0.0529	−1.45	0.0529	−1.10	0.0529	−1.01
0.1014	−2.09	0.1014	−1.94	0.1014	−1.86
0.1564	−2.28	0.1564	−2.24	0.1564	−2.29
0.2073	−1.55	0.2073	−2.21	0.2073	−2.48
0.2972	0.09	0.2972	−1.27	0.2972	−1.96
0.4065	2.45	0.4065	−0.08	0.4065	−1.17
0.4562	3.42	0.4562	0.50	0.4562	−0.75
0.4970	3.86	0.4970	0.72	0.4970	−0.70
0.5470	3.66	0.5470	0.82	0.5470	−0.52
0.5956	3.39	0.5956	0.54	0.5956	−0.68
0.6567	2.39	0.6567	0.08	0.6567	−0.94
0.7524	0.92	0.7524	−0.48	0.7524	−1.09
0.8007	−0.18	0.8007	−1.05	0.8007	−1.49
0.8497	−0.45	0.8497	−0.81	0.8497	−1.03
0.8979	−0.42	0.8979	−0.57	0.8979	−0.73
0.8956	−0.48	0.8956	−0.63	0.8956	−0.79
0.9495	−0.48	0.9495	−0.39	0.9495	−0.48

points weighted equally. The number of coefficients used in eq 6 for each fitting was determined by applying an F-test. Table 2 gives the coefficients a_i together with the standard deviations s defined as

$$s = [\sum_{i=1}^{N} (c^{\mathrm{exp}}_{\mathrm{sat},i} - c^{\mathrm{cal}}_{\mathrm{sat},i})^2/(N - n)]^{1/2} \qquad (7)$$

where N is the number of experimental values and n is the number of adjustable parameters.

Binary mixtures were prepared by mass. Caution was taken to prevent evaporation. The uncertainties in the mole fractions are estimated to be less than 0.0001. Conversion to molar quantities was based on the relative atomic mass table of 1985 issued by IUPAC.[20]

The experimental excess molar saturated heat capacities of the systems (benzene + cyclohexane) and (2,5,8,1-tetraoxadodecane + dodecane) are reported in Tables 3 and 4, respectively. The Redlich−Kister smoothing equation

$$c^{\mathrm{E}}_{\mathrm{sat}}/(\mathrm{J \cdot K^{-1} \cdot mol^{-1}}) = x_1(1 - x_1)\sum_{i=1}^{k} A_i(2x_1 - 1)^{i-1} \qquad (8)$$

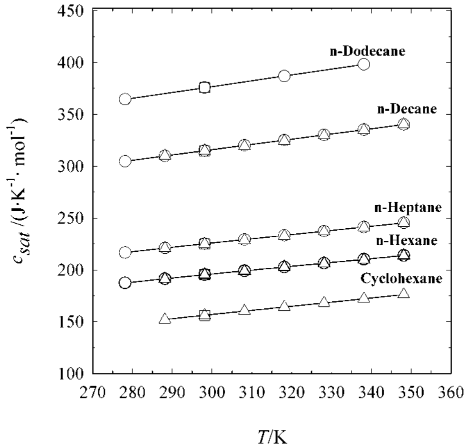

Figure 2. Saturated heat capacities of normal alkanes or cycloalkane as a function of temperature: ○, experimental data (step-by-step method); △, experimental data (scanning method); □, literature values[2,9] at 298.15 K. The full curves represent the smoothing of eq 6 with the coefficients of Table 2.

Table 5. Parameters A_i and Standard Deviation, s, for the Redlich−Kister Eq 8 Corresponding to the Excess Molar Saturated Heat Capacities, $c^{\mathrm{E}}_{\mathrm{sat}}$, for the Benzene (1) + Cyclohexane (2) System at Different Temperatures

T/K	A_1	A_2	A_3	A_4	A_5	s / $\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$
298.15	−11.48	−1.2	−4.1	−0.3	5.4	0.03
308.15	−11.44	−1.20	1.0			0.04
318.15	−10.91	−0.90	1.4			0.04

Table 6. Parameters A_i and Standard Deviation, s, for the Redlich−Kister Eq 8 Corresponding to the Excess Heat Capacities, $c^{\mathrm{E}}_{\mathrm{sat}}$, for the 2,5,8,11-Tetraoxadodecane (1) + Dodecane (2) System at Different Temperatures

T/K	A_1	A_2	A_3	A_4	A_5	s / $\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$
298.15	14.8	8.2	−70	4	37	0.14
308.15	2.8	5.7	−45	4.4	29	0.10
318.15	−2.5	5.0	−33	3.2	23	0.10

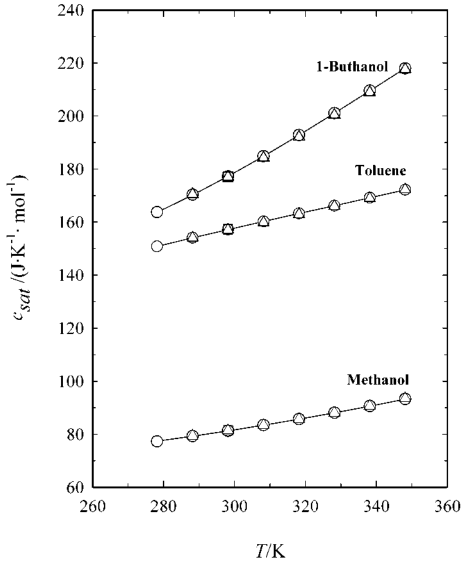

Figure 3. Saturated heat capacities of methanol, 1-butanol, and toluene as a function of temperature: ○♀ experimental data (step-by-step method); △, experimental data (scanning method); □, literature values[2] at 298.15 K. The full curves represent the smoothing of eq 6 with the coefficients of Table 2.

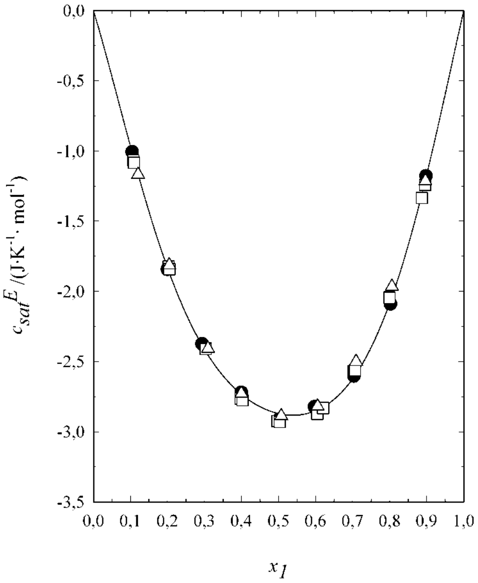

Figure 4. Excess heat capacity, $c_{\mathrm{sat}}^{\mathrm{E}}$, of the system benzene (1) + cyclohexane (2) at 298.15 K: ●, experimental data (this work); △, literature values;[22] □, literature values.[21] The full curve represents the smoothing of eq 8 with the coefficients of Table 5.

where x_1 is the mole fraction of benzene or 2,5,8,1-tetraoxadodecane, respectively, was fitted to the measurements by the method of least-squares with all points weighted equally. The coefficients A_i together with the standard deviations s, defined as before, obtained in the regression for each system and temperature are shown in Tables 5 and 6. The F-test has been employed to determine the number of coefficients.

Graphical representations of our measurements of saturated heat capacities, c_{sat}, of pure liquids according to temperature, with the two experimental procedures, are given in Figure 2 for alkanes or cycloalkane and in Figure 3 for methanol, 1-butanol, and toluene. The literature value[2,9] at 298.15 K and the values (full line) given by eq 6 with coefficients of Table 2 have been also represented.

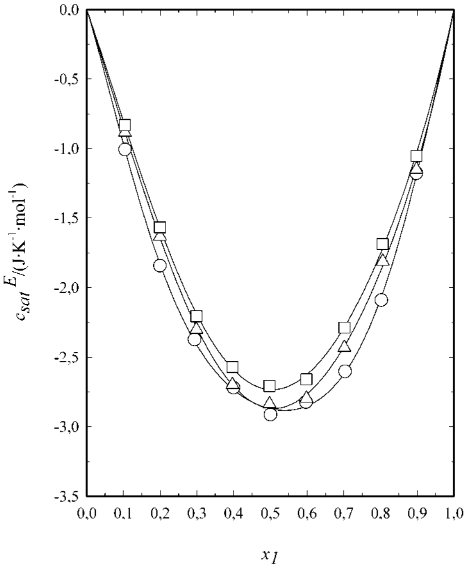

Figure 5. Excess heat capacities, $c_{\mathrm{sat}}^{\mathrm{E}}$, of the system benzene (1) + cyclohexane (2): ○, 298.15 K; △, 308.15 K; □, 318.15 K. The full curves represent the smoothing of eq 8 with the coefficients of Table 5.

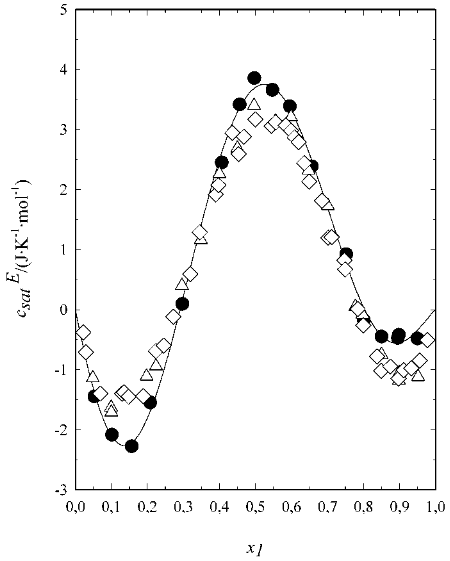

Figure 6. Excess heat capacities, $c_{\mathrm{sat}}^{\mathrm{E}}$, of the system 2,5,8,11-tetraoxadodecane (1) + dodecane (2): ●, 298.15 K; △, literature values;[23] ◇, literature values.[24] The full curves represent the smoothing of eq 8 with the coefficients of Table 6.

In Figure 4, the excess heat capacities of the system (benzene + cyclohexane) at 298.15 K have been represented along with literature experimental data[21,22] for comparison. Full curves represent smoothing eq 8 with the coefficients of Table 5. In Figure 5, all our experimental measurements of that mixture at the temperatures (298.15, 308.15, and 318.15) K with the corresponding smoothing curves have been collected.

In Figure 6, the excess heat capacities of the system (2,5,8,11-tetraoxadodecane + dodecane) at 298.15 K are presented along with literature experimental data[23,24] for comparison. Full curves represent smoothing eq 8 with the coefficients of Table 6. In Figure 7, a graphical representation of all our experimental measurements of that mixture at the temperatures (298.15, 318.15, and 338.15) K is given with the corresponding smoothing curves.

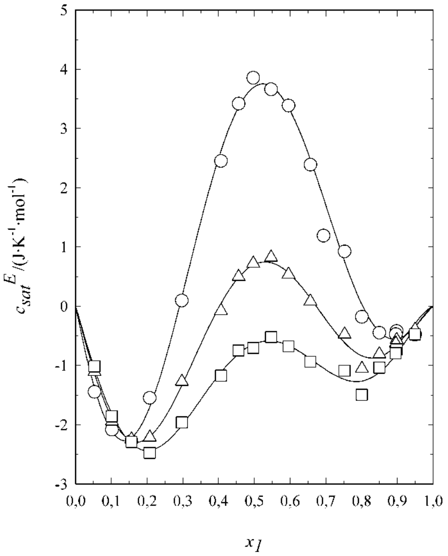

Figure 7. Excess heat capacities, $c_{\mathrm{sat}}^{\mathrm{E}}$, of the system 2,5,8,11-tetraoxadodecane (1) + dodecane (2): ○, 298.15 K; △, 318.15 K; □, 338.15 K. The full curves represent the smoothing of eq 8 with the coefficients of Table 6.

Table 7. Molar Saturated Heat Capacities of Pure Compounds at 298.15 K and Atmospheric Pressure

	molar sat. heat capacity/(J·K^{-1}·mol^{-1})	
liquid	exptl	lit.
hexane	195.23	195.48[2] 195.67[3] 195.33[4]
heptane	225.10	224.98[2] 224.76[5] 224.78[6]
decane	314.88	314.54[2] 315.46[7] 314.21[8]
dodecane	375.76	375.70[9] 376.00[10] 375.26[11]
cyclohexane	156.09	156.01[2] 156.03[12] 156.1[13]
benzene	135.58	135.76[2] 135.707[14] 135.64[15]
toluene	157.15	157.29[2] 157.15[16] 157.057[17]
methanol	81.26	81.47[2] 81.92[18] 81.04[13]
1-butanol	177.21	177.08[2]
2,5,8,11-tetraoxadodecane	368.01	367.78[19]

Discussion

To assess experimental data of the saturated heat capacities of pure and liquid mixtures measured by means of the new calorimetric cells, a comparison with literature values has been done.

Pure Liquids. In general, the best literature values of heat capacities of liquids have been determined at 298.15 K and atmospheric pressure; for that the c_{sat} values of the pure liquids studied under those conditions are listed in Table 7 with some literature values. Agreement between the two sets of measurements is particularly good. In Figures 8 and 9 the percentage deviations of our experimental measurements with respect to those proposed in the literature,[25] defined as $100(c_{\mathrm{sat}} - c_{\mathrm{lit.}})/c_{\mathrm{sat}}$, are represented as a function of the temperature. In each diagram two dashed lines are drawn which correspond to the upper and lower levels of uncertainty assigned in the reference cited.

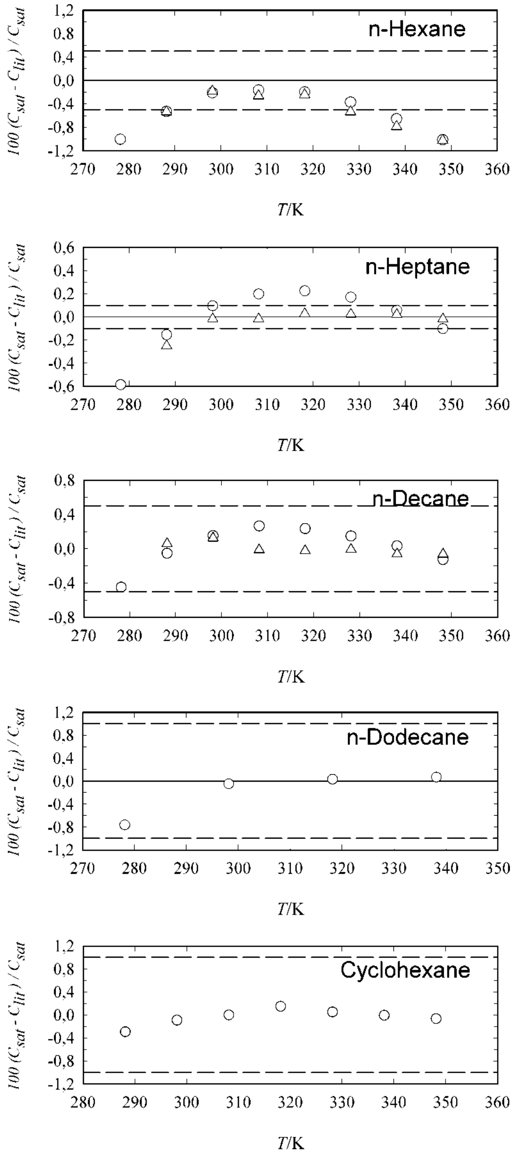

Figure 8. Percentage deviations of the measurements of this work with respect to the literature[25] for the pure liquids hexane, heptane, decane, dodecane, and cyclohexane as a function of temperature: ○, step-by-step method; △, scanning method.

Only in the case of hexane did all the experimental points show a negative deviation, which may denote a systematic error. However, we should bear in mind that most of the experimental points come within the uncertainty interval (±0.5%) and that the literature monograph[25] assigns an uncertainty of ±1% for temperatures over 330 K. In addition, the temperature interval analyzed in this reference is wider than ours, and in fact the data covering our interval generally manifest significant deviation with respect to the final correlation. This leads us to believe that the correlation polynomials overestimate the heat capacities in this temperature range.

For all the other liquids, especially for heptane, which is one of the better studied liquids, the experimental determinations of this work are within the uncertainty interval recommended.[25] This very close concordance with the data recommended in the above-mentioned monograph gives us confidence in our measurement methods.

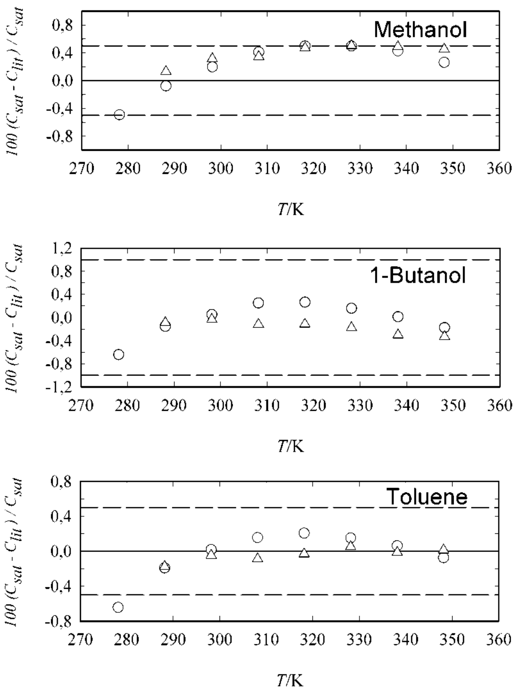

Figure 9. Percentage deviations of the measurements of this work with respect to the literature[25] for the pure liquids methanol, 1-butanol, and toluene as a function of temperature: ○, step-by-step method; △, scanning method.

It is also observed that, in the case of pure liquids, there is no significant difference between the data measured with the step-by-step method and those determined by the scanning method.

Liquid Mixtures. Figure 4 shows the experimental data of the excess heat capacity, $c_{\mathrm{sat}}^{\mathrm{E}}$, of the system benzene (1) + cyclohexane (2) at 298.15 K, with those of the literature,[21,22] and the smoothing of eq 7 (full curve) with coefficients of Table 5. Although a determination by the scanning method was attempted, it was not possible to obtain acceptable values. The data correspond to the average of six consecutive experimental determinations. It can be observed that there is very close agreement between our determinations and the values of the bibliography.

Measurements at the temperatures 308.15 and 318.15 K, for which no direct experimental determinations exist in the bibliography, have also been carried out and are represented in Figure 5. It is possible to calculate $c_{\mathrm{p}}^{\mathrm{E}}(T)$ from very precise excess enthalpy measurements at different temperatures[26] for comparison. Our results at the two temperatures differ less than 2% in the central range of concentration, which is very satisfactory.

Experimental determinations of the $c_{\mathrm{sat}}^{\mathrm{E}}$ of the system 2,5,8,11-tetraoxadodecane (1) + dodecane (2) have been performed at 298.15, 318.15, and 338.15 K; this exhibits a W-shape, and its determination is consequently dependent upon a good calorimetric measurement system. In Figure 6, a comparison is made between the values obtained at 298.15 K and those of the literature.[23,24] It can be seen that there is a discrepancy in the maximum and the two minimum areas. The quality and sensitivity of the equipment employed and the conditions at which the experiments have been carried out—the fact that each experimental point of the graph actually represents the mean of eight independent determinations with minimum dispersion (and always less than the difference with data in the bibliography)—give us complete confidence in our experimental measurements.

Finally, in Figure 7 the $c_{\mathrm{sat}}^{\mathrm{E}}$ values are presented at the three temperatures and the variation in this function can be observed. In the three cases, the characteristic W curve is found, where the maximums decrease and the two minimums approach each other as the temperature increases and moves away from the critical point of phase separation.

Conclusions

The new "batch" cells for a Micro DSC (Setaram) presented in this work have been designed to avoid any leakage during measurement. With the step-by-step and the scanning methods, many heat capacity experimental determinations of several pure organic liquids and binary organic liquid mixtures over wide temperature ranges have been carried out. A very close concordance with the literature values has been obtained, which proves their suitability for these kinds of measurements even with volatile liquids.

Literature Cited

(1) Calvet, E.; Prat, H. *Microcalorimêtrie. Applications Physico-Chimiques et Biologiques*; Masson et Cie: Paris, 1956.

(2) Riddick, J. A.; Bunger, W. B.; Sakano, T. K. *Organic Solvents, Physical Properties and Methods of Purification*, 4th ed.; Wiley: New York, 1986.

(3) Inglese, A.; Grolier, J.-P. E.; Roux, A. H.; Wilhelm, E. Thermodynamics of (1-chloronaphthalene + *n*-alkane): excess enthalpies, excess volumes and excess heat capacities. *Ber. Bunsen-Ges. Phys. Chem.* **1981**, *85* (9), 768−72.

(4) Wilhelm, E.; Inglese, A.; Quint, J. R.; Grolier, J.-P. E. Molar excess volumes and excess heat capacities of (1,2,4-trichlorobenzene) + an *n*-alkane. *J. Chem. Thermodyn.* **1982**, *14*, 303−308.

(5) Kimura, F.; D'Arcy, P. J.; Benson, G. C. Excess enthalpies and heat capacities for (di-*n*-propyl ether + *n*-heptane). *J. Chem. Thermodyn.* **1983**, *15*, 511−516.

(6) Lainez, A.; Rodrigo, M. M.; Wilhelm, E.; Grolier, J.-P. E. Thermodynamics of liquid mixtures containing *n*-alkanes and strongly polar components: V^E and C_p^E of mixtures with either pyridine or piperidine. *J. Solution Chem.* **1992**, *21*, 49−65.

(7) Costas, M.; Patterson, D. Excess Heat Capacity. Benzene + Decane System. *Int. DATA Ser., Sel. Data Mixtures, Ser. A* **1985**, *3*, 214.

(8) Roux, A. H.; Grolier, J.-P. E.; Inglese, A.; Wilhelm, E. Excess molar enthalpies, excess molar heat capacities and excess molar volumes of (fluorobenzene + an *n*-alkane). *Ber. Bunsen-Ges. Phys. Chem.* **1984**, *88* (10), 986−92.

(9) Faradjzadeh, A.; Grolier, J.-P. E. Excess Heat Capacity. Ethylbenzene + Dodecane System. *Int. DATA Ser., Sel. Data Mixtures, Ser. A* **1979**, *2*, 136.

(10) Costas, M.; Patterson, D. Excess Heat Capacity. Benzene + Dodecane system. *Int. DATA Ser., Sel. Data Mixtures, Ser. A* **1985**, *3*, 215.

(11) Grolier, J.-P. E.; Benson, G. C. Thermodynamic properties of binary mixtures containing ketones VIII. Heat capacities and volumes of some *n*-alkanone + *n*-alkane mixtures at 298.15 K. *Can. J. Chem.* **1984**, *62* (5), 949−53.

(12) Tanaka, R. Determination of excess heat capacities of (benzene + tetrachloromethane and + cyclohexane) between 293.15 and 303.15 K by use of a Picker flow calorimeter. *J. Chem. Thermodyn.* **1982**, *14*, 259−268.

(13) *CDATA: Database of Thermodynamic and Transport Properties for Chemistry and Engineering*; Department of Physical Chemistry, Institute of Chemical Technology: Prague, 1991.

(14) Tanaka, R. Excess heat capacities of mixtures of benzene with *n*-heptane at 293.15, 298.15, and 303.15 K. *J. Chem. Eng. Data* **1987**, *32*, 176−177.

(15) Grolier, J.-P. E.; Roux-Desgranges, G.; Berkane, M.; Wilhelm, E. Heat capacities and densities of mixtures of very polar substances 1. Mixtures containing acetonitrile. *J. Chem. Thermodyn.* **1991**, *23*, 421−429.

(16) Grolier, J.-P. E.; Faradjzadeh, A. Excess Heat Capacity. Toluene + 2,3-Dimethylbutane System. *Int. DATA Ser., Sel. Data Mixtures, Ser. A* **1981**, *1*, 36.

(17) Fortier, J. L.; Benson, G. C. Heat capacities of some binary aromatic hydrocarbon mixtures containing benzene or toluene. *J. Chem. Eng. Data* **1979**, *24* (1), 34−37.

(18) Villamañan, M. A.; Casanova, C.; Roux-Desgranges, G.; Grolier, J.-P. E. Thermochemical behaviour of mixtures of n-alcohol + aliphatic ether: heat capacities and volumes at 298.15 K. *Thermochim. Acta* **1982**, *52*, 279−283.

(19) Trejo, L. M.; Costas, M.; Patterson, D. Effect of molecular size on the W-shaped excess heat capacities: Oxaalkane–Alkane systems. *J. Chem. Soc., Faraday Trans.* **1991**, *87* (18), 3001–3008.

(20) IUPAC Commission on Atomic Weights and Isotopic Abundances. Atomic weights of the elements 1985. *Pure Appl. Chem.* **1986**, *58* (12), 1677–1692.

(21) Tanaka, R. Excess Enthalpy. Benzene + Cyclohexane System. *Int. DATA Ser., Sel. Data Mixtures, Ser. A* **1988**, *1*, 61.

(22) Wilhelm, E.; Grolier, J.-P. E. Excess Enthalpy. Benzene + Cyclohexane system. *Int. DATA Ser., Sel. Data Mixtures, Ser. A* **1985**, *3*, 165.

(23) Trejo, L. M.; Costas, M.; Patterson, D. Excess Heat Capacity. Benzene + Dodecane System. *Int. DATA Ser., Sel. Data Mixtures, Ser. A* **1991**, *1*, 40.

(24) Fortier, J. L.; Benson, G. C. Excess heat capacities of binary liquid mixtures determined with a Picker flow calorimeter. *J. Chem. Thermodyn.* **1976**, *8*, 411–423.

(25) Zábranský, M.; Ruzicka, V., Jr.; Majer, V.; Domalski, E. S. Heat Capacity of Liquids: Volume I—Critical Review and Recommended Values; *J. Phys. Chem. Ref. Data*, Monograph No. 6; American Chemical Society and American Institute of Physics: 1996.

(26) Elliot, K.; Wormald, C. J. A precision differential flow calorimeter. The excess enthalpy of benzene + cyclohexane between 280.15 K and 393.15 K. *J. Chem. Thermodyn.* **1976**, *8*, 881–893.

Received for review August 17, 2001. Accepted January 21, 2002.

JE0155103