Journal of Thermal Analysis, Vol. 50 (1997) 685-704

VARIATION IN ENTHALPY OF THE SYSTEM *n*-TETRACOSANE–*n*-HEXACOSANE AS FUNCTIONS OF TEMPERATURE AND COMPOSITION

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(Received Januarr 26, 1996; in revised form September 10, 1996)

Abstract

Differential enthalpy analyses were performed on the binary *n*-alkane system *n*-$C_{24}H_{50}$–*n*-$C_{26}H_{54}$ with a Setaram DSC111 calorimeter of Tian Calvet type.

The measurements provided enthalpy data from 260 to 260 K on *n*-tetracosane, *n*-hexacosane and 19 binary mixtures.

An analytical expression, derived from the Einstein model, is proposed for every pure phase in its temperature domain, to represent the variation in the enthalpy with temperature.

A general expression for the enthalpy as a function of temperature and composition is also given.

Keywords: binary mixtures, calorimetry, Einstein's solid model, enthalpy variations, *n*-hexacosane, *n*-tetracosane

Introduction

The phase diagram of the binary *n*-alkane system *n*-tetracosane (*n*-$C_{24}H_{50}$)–*n*-hexacosane (*n*-$C_{26}H_{54}$) was determined by means of joint calorimetric and radiocrystallographic studies.

At room temperature, this system shows the existence of two limited terminal solid solutions and three orthorhombic intermediate phases. The terminal solid solutions, denoted γ_1 and γ_2, are isostructural with *n*-tetracosane and *n*-hexacosane [1, 2]. The intermediate phases, denoted β_1', β'' and β_2', are identical to those found in the system *n*-eicosane (*n*-$C_{20}H_{42}$–*n*-docosane (*n*-$C_{22}H_{46}$) [3], and *n*-docosane (*n*-$C_{22}H_{46}$)–*n*-tetracosane (*n*-$C_{24}H_{50}$) [2, 4, 5]. They are isomorphic with the structure of *n*-tricosane (*n*-$C_{23}H_{48}$) and *n*-pentacosane (*n*-$C_{25}H_{52}$) [2, 6–12].

0368–4466/97/ $ 5.00

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With increasing temperature, γ_1 and γ_2 behave in the same way as *n*-tetracosane and *n*-hexacosane [2, 13–15]. The solutions β_1', β'' and β_2' undergo the same solid-state transitions as those observed in *n*-tricosane [2, 6–12] and in the binary system *n*-docosane–*n*-tetracosane [12, 15].

In this work, we present a differential calorimetric analysis of the system *n*-$C_{24}H_{50}$–*n*-$C_{26}H_{54}$. The enthalpy variation *vs.* temperature is given for the different solid phases. The data concerning the phases γ_1, β_1', β'' and β_2' $\gamma_2$are then treated by using functions derived from the Einstein solid model.

Finally, a general expression is given for the enthalpy of the solid solutions as a function of temperature and composition.

Experimental

The enthalpy measurements were performed with a DSC111 differential scanning calorimeter manufactured by Setaram.

The low-temperature measurements were carried out by adding a cooling device to the calorimeter, allowing the circulation of cold nitrogen in the calorimeter.

The apparatus was calibrated with the help of the thermodynamic data on alumina reported in the N.B.S. table [16].

Principle of measurement

The difference in heat flow exchanged between the two cells and the calorimeter block is evaluated by measurement of the electromotive force (*e.m.f.*) developed in two thermopiles surrounding the calorimeter cells and connected together in opposition.

The *e.m.f.* ΔE, measured from time t_1 to time t_2, is related to the difference in heat Q_T exchanged between the cells and the calorimeter block, by means of the sensitivity coefficient S, determined by calibration:

$$Q_T = \frac{1}{S}\int_{t_1}^{t_2} \Delta E \mathrm{d}t$$

– Q_T is computed by numerical integration, for each temperature jump $\Delta T = T_2 - T_1$ (T_1 and T_2 correspond, respectively, to time t_1 and time t_2). Q_T is split into two terms, Q_D and Q_E.

– Q_D corresponds to the disymmetry of the two cells. It is determined in a 'blank' measurement, by introducing an empty crucible into each of the two cells.

– Q_E corresponds to the sample contribution and $Q_E = Q_T - Q_D$.

– Q_T is obtained by putting the sample in one of the previous crucibles, the second remaining empty as reference.

The molar enthalpy of heating of the sample at temperature T, referred to 260 K, is

$$H(T) - H(260) = \sum_i \frac{M}{m}(Q_E)_i$$

where M and m are, respectively, the molar weight and the mass of the sample introduced in the calorimeter.

$H(T)$ and $H(260)$ are the enthalpies at T and 260 K, respectively.

Operating conditions

The measurements were carried out by sequential programming of the temperature *vs.* time:

– The rising temperature period t_m was set at 180 s and corresponded to 1 or 0.5 K, depending on the temperature range.

– The temperature level duration t_p depends on a computer test, checking that the calorimeter signal returned to constant value, corresponding to a steady state. When no transition occurred in the sample, t_p=420 s (Fig. 1).

As the signal might stabilize at a value that was not exactly the base line, an automatic correction was made by the computer (Fig. 2).

The measurements were performed in two steps, for both blank and sample:

– from 260 to 300 K, at a temperature rate of 20 K h^{-1}, giving a temperature jump of 1 K, using the cooling device;

– from 290 to 360 K, at a temperature rate of 10 K h^{-1}, giving a temperature jump of 0.5 K.

These two series of measurement overlap in a range of 10 K; no significant differences between the operating conditions were observed.

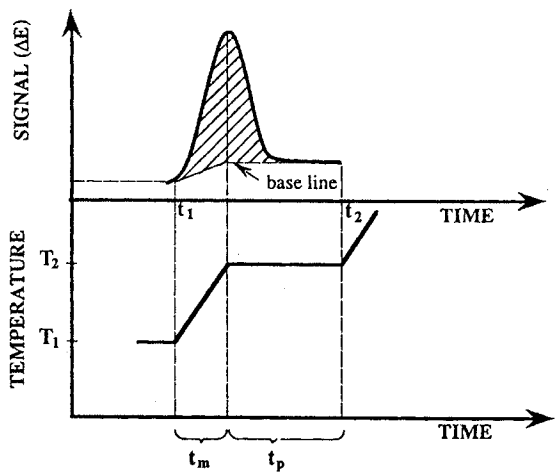

Fig. 1 Integration of the calorimetric signal

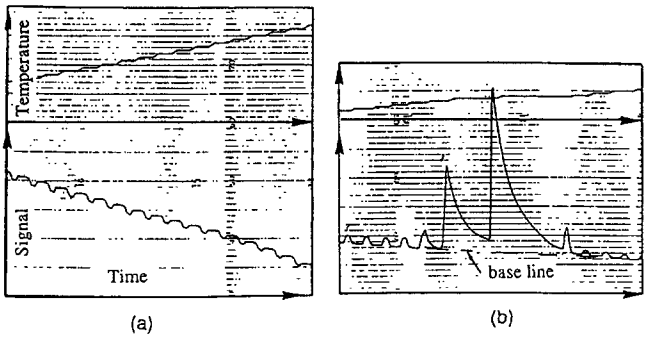

Fig. 2 Signal and temperature profils for a discontinuous experiment. a – blank; b – sample

Sample preparation

The *n*-tetracosane and *n*-octacosane were purchased from Aldrich: their purity grade was 99%, as determined by gas chromatography and mass spectroscopy.

The samples (pure *n*-alkanes and mixtures) were prepared by weighing the solid components, melting and thorough mixing. The homogeneous liquids thus obtained were quenched in a crystallizing dish, maintained at a very low temperature in a Dewar vessel with liquid air. Such a rapid cooling ensured an uniform steric concentration in the solid.

Experimental results

Variation in enthalpy with temperature

The reproducibility and the precision of the enthalpy measurements were determined by using *n*-hexacosane, for which the experimental enthalpy was com-

Table 1 Enthalpy variation of standard alumina from "National Bureau of Standard [16] *vs.* temperature

T/K	H_{exp}/J mol^{-1}	H_{lit}/J mol^{-1}	Deviation/J mol^{-1}	Relative deviation/%
289.4	0	0	0	0
300	874	826	48	5.4
310	1605	1631	–27	–1.7
320	2425	2456	–31	–1.3
330	3261	3301	–40	–1.2
340	4122	4163	–42	–1
350	4998	5043	–45	–1

T: temperature in Kelvins, H_{exp}: variation of the experimental enthalpy in J mol^{-1}, H_{lit}: variation of the enthalpy from literature in J mol^{-1}.

pared with literature data [16, 17]. The relative deviation was about 2% (Table 1 and 2).

The calorimetric measurements were made on *n*-tetracosane, *n*-hexacosane and 19 binary mixtures, covering the whole range of concentration. The results are presented in Tables 3–13. The enthalpy variations are given every 5 K, except for the solid transition and melting domains. Figure 3 presents the curve of the enthalpy for the mixture containing 32.5 mol% *n*-hexacosane.

Table 2 Enthalpy variation of *n*-hexacosane *vs.* temperature

T/K	H_{exp}/J mol^{-1}	H_{lit}/J mol^{-1}	Deviation/J mol^{-1}	Relative deviation/%
270	0	0	0	–
280	6061	5920	141	2.3
290	12381	12110	270	2.2
300	18961	18580	381	2
310	25669	25480	189	0.7
320	32720	32780	–60	0.2
330	134897	134780	117	0.1
340	142731	143280	–549	0.4

T: temperature in Kelvins, H_{exp}: variation of the experimental enthalpy in J mol^{-1}, H_{lit}: variation of the enthalpy from literature [17] in J mol^{-1}.

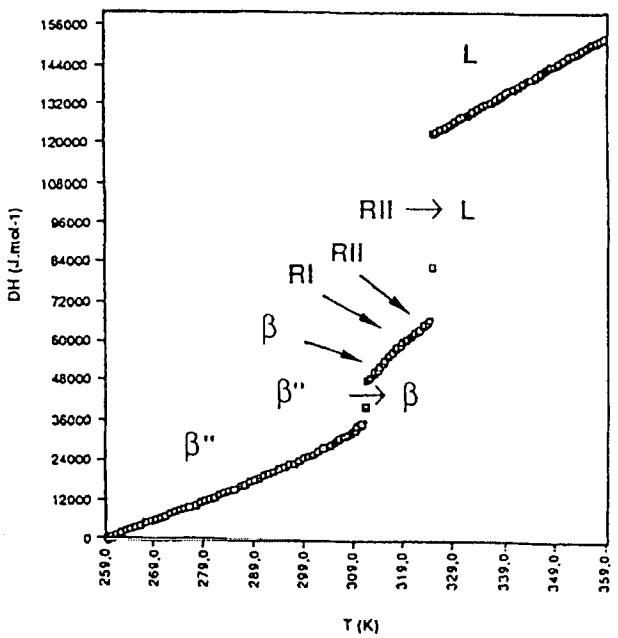

Fig. 3 Enthalpy curve for the mixture containing 32.5 mol% of *n*-hexacosane

Representation of the variations in enthalpy for the phases γ_1, β_1', β'', β_2' and γ_2

We proposed to represent the binary system with the help of the Einstein model. Such a binary behaves like a monoatomic solid of N atoms, having $3N$ independent vibrations, which are harmonic and have the same frequency. This frequency corresponds to a typical temperature θ, called Einstein's temperature.

For each composition, the enthalpy variations can be described by the following expression, derived from the Einstein model:

Table 3 Variations of the enthalpy *vs.* temperature

T/K	C_{24} $H^{260}(T)$/J mol^{-1}	Phase	T/K	C_{24}:1.1 mol% C_{26} $H^{260}(T)$/J mol^{-1}	Phase
259.5	0		259.5	0	
260.5	400		260.5	454	
265.5	2945		265.5	2545	
270.5	5134		270.5	5271	
275.5	7456		275.5	7860	
280.5	9856		280.5	9875	
285.4	12359		285.4	13477	
290.4	14866		290.4	16201	
295.4	17631		295.4	18689	
300.4	20434		300.4	21513	
305.4	25562	γ_1	305.4	24575	γ_1
310.4	26068		310.4	27984	
315.4	29113		315.4	32005	
318.3	31156		315.9	32375	
318.8	31546		316.4	32792	
319.3	31994		316.9	33293	
319.8	32567		317.4	32375	
320.3	34045		317.8	32792	
320.8	53497		318.3	33293	
321.3	63220		318.8	34151	
321.8	63837	α-RII	319.3	38891	
322.3	64512		319.8	45843	
322.8	65297		320.3	52533	
323.3	66745		320.8	58329	
323.8	120024		321.3	63222	α-RII
324.3	120454		321.8	65257	
324.8	120828		322.3	67231	
325.3	121138		322.8	68038	
325.8	121496		323.3	69745	
326.3	121848		323.8	107967	
326.8	122184		324.3	121812	
327.3	122554		324.8	122186	
325.8	122935		325.3	122540	
328.3	123312		325.8	122912	
328.8	123692		326.3	123252	
329.3	124063		326.8	123615	
329.8	124421		330.3	126232	L
330.3	124802	L	335.3	129973	
330.8	125175		340.3	133653	
331.3	125533		345.3	137378	
331.8	125898		350.3	141122	
335.3	128504		355.2	144942	
340.3	132407		329.2	148043	
345.3	136445				
350.2	140278				
355.2	144089				
359.2	147138				

T: temperature in Kelvins; $H^{260}(T)$: measured enthalpy, with T=260 K as reference, in Joule per mol; γ_1: triclinic primary solid solution; α-RII: rhombohedric rotator phase; L: liquid phase.

$$H(T) - H(260) = \frac{3NR\theta}{\exp(\theta/T)} - H_E$$

The parameters N, θ and the integration constant H_E, are optimized by using the Rosenbrock method [18], from the temperature and enthalpy data corresponding to γ_1, β_1', β'', β_2' and γ_2. The results are given in Table 14.

Table 4 Variations of the enthalpy *vs.* temperature

T/K	C_{24}:2.5 mol% C_{26} $H^{260}(T)$/J mol^{-1}	Phase	T/K	C_{24}:10 mol% C_{26} $H^{260}(T)$/J mol^{-1}	Phase
259.5	0		259.5	0	
260.5	469		260.5	478	
265.5	2958		265.5	3061	
270.5	5426		270.5	5676	
275.5	7903		275.5	8424	
280.5	10631		280.5	11381	
285.4	13514		285.4	14498	
290.4	16356		290.4	17391	
295.4	19628		295.4	20563	
300.4	23310	$\gamma_1 + \beta'_1$	300.4	23888	β'_1
305.4	26952		305.4	27253	
310.4	30760		308.4	29677	
312.4	32346		308.9	30080	
312.9	32778		309.4	30503	
313.4	33283		309.9	30927	
313.9	33664		310.4	31426	
314.4	34036		310.9	31900	
314.9	38662		311.4	32377	
315.4	45479		311.9	32934	
315.8	46453	$\gamma_1 + \beta'_1$	312.4	35240	
316.3	47594	$\gamma_1 + RI$	312.9	47212	
316.8	49150		313.4	48922	
317.3	51792		313.9	49828	
317.8	54911		314.4	50684	
318.3	57796		314.9	51586	
318.8	60713		315.4	52476	β
319.3	62879		315.8	53418	
319.8	64107		316.3	54351	
320.3	64854		316.8	55249	
320.8	65469		317.3	56129	
321.3	66133	$\gamma_1 + RI$	317.8	56942	
321.8	66727		318.3	57748	RI
322.3	67382		318.8	58460	
322.8	68105		319.3	59116	
323.3	69199	α-RII	319.8	59894	
323.8	95139		320.3	60496	
324.3	123140		320.8	61091	
324.8	123551		321.3	61754	
325.3	123978		321.8	62443	
325.8	124324		322.3	63185	α-RII
326.3	124698		322.8	63999	
326.8	125063		323.3	64977	
330.3	127795		323.8	67693	
335.3	131741	L	324.3	118712	
340.3	135729		324.8	119521	
345.3	139784		325.3	119912	
350.2	143824		325.8	120330	
355.2	147907		326.3	120732	
359.2	151205		326.8	121127	
			330.3	123756	L
			335.3	127545	
			340.3	131512	
			345.3	135426	
			350.2	139363	
			355.2	143254	
			359.2	146479	

T: temperature in Kelvins; $H^{260}(T)$: measured enthalpy, with T=260 K as reference, in Joule per mol; γ_1: triclinic primary solid solution; β_1': orthorhombic intermediate solid solution; β-RI: orthorhombic rotator phase; α-RII: rhombohedric rotator phase; L: liquid phase.

Table 5 Variations of the enthalpy *vs.* temperature

T/K	C_{24}:15.1 mol% C_{26} $H^{260}(T)$/J mol^{-1}	Phase	T/K	C_{24}:20 mol% C_{26} $H^{260}(T)$/J mol^{-1}	Phase
259.5	0		259.5	0	
260.5	423		260.5	564	
265.5	1847		265.5	3533	
270.5	3605		270.5	6678	
275.5	5322		271.5	7305	β''
280.5	7328		272.5	7921	
285.4	9388		273.5	8445	
290.4	11760	$\beta'_1+\beta''$	274.5	8897	
291.4	12314		275.5	9047	
292.4	12858		276.5	9381	
293.4	13354		277.5	9853	
294.4	13873		278.5	10380	
295.4	14424		279.5	10834	
296.4	15051		280.5	11333	
297.4	15501		285.4	13913	
298.4	16122		290.4	16850	
299.4	16656		295.4	20010	$\beta'_1+\beta''$
300.4	17262		300.4	23549	
305.4	20454		305.4	27043	
308.4	22779	β'_1	308.4	29260	
308.9	23168		308.9	29685	
309.4	23566		309.4	30082	
309.9	24015		309.9	30499	
310.4	24460		310.4	30921	
310.9	24971		310.9	31392	
311.4	25538		311.4	32092	
311.9	30422		311.9	43542	
312.4	39587		312.4	45444	
312.9	40482		312.9	46202	
313.4	41346		313.4	46954	
313.9	42184		313.9	47751	β
314.4	43081		314.4	48576	
314.9	43928		314.9	49384	
315.4	44770	β	315.4	50215	
315.8	45686		315.9	51081	
316.3	46585		316.4	51919	
316.8	47408		316.9	52751	
317.3	48205		317.4	53508	
317.8	48926		317.8	54175	
318.3	49602		318.3	54793	RI
318.8	50213	RI	318.8	55368	
319.3	50873		319.3	55957	
319.8	51512		319.8	56513	
320.3	52070		320.3	57072	
320.8	52667		320.8	57579	
321.3	53260		321.3	58143	
321.8	53810		321.8	58717	
322.3	54390		322.3	59302	α-RII
322.8	55004	α-RII	322.8	59879	
323.3	55679		323.3	60479	
323.8	56631		323.8	61234	
324.3	66636		324.3	62971	
324.8	110494		324.8	83645	
325.3	110866		325.3	114690	
325.8	111259		325.8	115022	
326.3	111628		326.3	115352	
326.8	112011		326.8	115657	
330.3	114636		327.3	116003	
335.3	118406	L	327.8	116335	L
340.3	122168		330.3	117978	
345.3	125951		335.3	121354	
350.2	129877		340.3	124690	
355.2	133717		345.3	128008	
359.2	136887		350.3	131544	
			355.2	135127	
			359.2	137920	

T: temperature in Kelvins; $H^{260}(T)$: measured enthalpy, with T=260 K as reference, in Joule per mol; β'_1, β'': orthorhombic intermediate solid solution; β-RI: orthorhombic rotator phase; α-RII: rhombohedric rotator phase; L: liquid phase.

Table 6 Variations of the enthalpy *vs.* temperature

T/K	C_{24}:25 mol% C_{26} $H^{260}(T)$/J mol^{-1}	Phase	T/K	C_{24}:30 mol% C_{26} $H^{260}(T)$/J mol^{-1}	Phase
259.5	0		259.5	0	
260.5	667		260.5	743	
265.5	3344		265.5	3510	
270.5	6284		270.5	6376	
275.5	9988	β"	275.5	9485	
279.5	12373		280.5	12728	
280.5	13035		285.4	15884	
281.4	13611		290.4	19380	
282.4	14179		295.4	22965	
283.4	14841		300.4	26677	β"
284.4	15440		305.4	30697	
285.4	16173		308.4	33314	
290.4	19609		308.9	33887	
295.4	22970		309.4	34353	
300.4	26768		309.9	34844	
305.4	30670	β" + β'$_1$	310.4	35266	
308.4	33309		310.9	35873	
308.9	33676		311.4	37101	
309.4	34081		311.9	48340	
309.9	34570		312.4	51076	
310.4	34993		312.9	51830	
310.9	35571		313.4	52540	
311.4	37063		313.9	53361	
311.9	49376		314.4	54202	β
312.4	50144		314.9	55080	
312.9	50935		315.4	56020	
313.4	51717		315.8	56954	
313.9	52559		316.3	57954	
314.4	53504		316.8	58763	
314.9	54339	β	317.3	59584	
315.4	55147		317.8	60340	
315.8	56071		318.3	60929	RI
316.3	56996		318.8	61544	
316.8	57794		319.3	62234	
317.3	58569		319.8	62895	
317.8	59259	RI	320.3	63497	
318.3	59945		320.8	64211	
318.8	60581		321.3	64779	
319.3	61221		321.8	65368	
319.8	61808		322.3	65907	
320.3	62413		322.8	66373	
320.8	62993		323.3	67056	α-RII
321.3	63596		323.8	67758	
321.8	64169		324.3	68627	
322.3	64752		324.8	72487	
322.8	65339	α-RII	325.3	100400	
323.3	65946		325.8	123833	
323.8	66523		326.3	124253	
324.3	67727		326.8	124658	
324.8	88404		327.3	125139	
325.3	121923		327.8	125554	
325.8	122330		330.3	127634	
326.3	122768		335.3	131686	L
326.8	123232		340.3	135625	
327.3	123627		345.3	139753	
327.8	124027		350.2	143828	
330.3	126213		355.2	148013	
335.3	130241	L	359.2	151321	
340.3	134160				
345.3	138511				
350.2	142738				
355.2	146833				
359.2	150336				

T: temperature in Kelvins; $H^{260}(T)$: measured enthalpy, with T=260 K as reference, in Joule per mol; β_1', β'': orthorhombic intermediate solid solution; β-RI: orthorhombic rotator phase; α-RII: rhombohedric rotator phase; L: liquid phase.

Table 7 Variations of the enthalpy *vs.* temperature

T/K	C_{24}:33 mol% C_{26} $H^{260}(T)$/J mol^{-1}	Phase	T/K	C_{24}:35.2 mol% C_{26} $H^{260}(T)$/J mol^{-1}	Phase
259.5	0*		259.5	0	
260.5	363		260.5	1832	
265.5	2730		265.5	4742	
270.5	5463		270.5	7606	
275.5	8495		275.5	10273	
280.5	11660		280.5	13004	
285.4	14826		285.4	16029	
290.4	18244		290.4	18976	
295.4	21500		295.4	22397	β"
300.4	25173	β"	300.4	25870	
305.4	29068		305.4	29942	
308.4	31743		308.4	32462	
308.9	32204		308.9	32916	
309.4	32569		309.4	33361	
309.9	33026		309.9	33780	
310.4	33530		310.4	34212	
310.9	34143		310.9	34741	
311.4	34761		311.4	36101	
311.9	40674		311.9	42444	
312.4	48870		312.4	48800	
312.9	49669		312.9	49688	
313.4	50533		313.4	50446	
313.9	51377		313.9	51328	
314.4	52179		314.4	52136	
314.9	53040	β	314.9	52984	β
315.4	53871		315.4	53928	
315.8	54757		315.8	54891	
316.3	55737		316.3	55773	
316.8	56466		316.8	56586	
317.3	57225	RI	317.3	57412	
317.8	57915		317.8	58134	RI
318.3	58572		318.3	58721	
318.8	59143		318.8	59324	
319.3	59783		319.3	59938	
319.8	60375		319.8	60611	
	60828		320.3	61248	
320.3	61412		320.8	61837	
320.8	61970		321.3	62437	
321.3	62534		321.8	62305	
321.8	63099		322.3	63518	
322.3	63689	α-RII	322.8	64276	α-RII
322.8	64282		323.3	65038	
323.3	64886		323.8	65895	
323.8	65564		324.3	67155	
324.3	66856		324.8	70647	
324.8	88457		325.3	86481	
325.3	121498		325.8	121252	
325.8	121931		326.3	121676	
326.3	122388		326.8	122043	
326.8	122805		327.3	122444	
327.3	123209		327.8	122839	
327.8	125347	L	330.3	124831	
330.3	129713		335.3	128967	L
335.3	134098		340.3	133060	
340.3	138189		345.3	137300	
345.3	142397		350.2	141457	
350.2	146488		355.2	145562	
355.2	149856		359.2	148834	
359.2					

T: temperature in Kelvins; $H^{260}(T)$: measured enthalpy, with T=260 K as reference, in Joule per mol; β": orthorhombic intermediate solid solution; β-RI: orthorhombic rotator phase; α-RII: rhombohedric rotator phase; L: liquid phase.

As an example, results obtained for pure n-$C_{24}H_{50}$ are presented in Fig. 4, which shows the variation in the error function F with θ.

Table 8 Variations of the enthalpy *vs.* temperature

T/K	C_{24}:40.1 mol% C_{26} $H^{260}(T)$/J mol^{-1}	Phase	T/K	C_{24}:45.1 mol% C_{26} $H^{260}(T)$/J mol^{-1}	Phase
259.5	0		259.5	0	
260.5	390		260.5	460	
265.5	2731		265.5	3220	
270.5	5645		270.5	5926	
275.5	8789		271.5	6477	β"
280.5	12053		272.5	6880	
285.4	15128		273.5	7259	
290.4	18490		274.5	7773	
295.4	21569	β"	275.5	8394	
300.4	25298		276.5	8948	
305.4	29257		277.5	9631	
309.4	32565		278.5	10221	
309.9	33059		279.5	10888	
310.4	33563		280.5	11335	
310.9	34017		285.4	14386	
311.4	34536		290.4	17633	
311.9	36313		295.4	21007	β" + β'$_2$
312.4	43461		300.4	24499	
312.9	48702		305.4	28321	
313.4	49773		309.4	31723	
313.9	50735		309.9	32177	
314.4	51511		310.4	32619	
314.9	52329		310.9	33055	
315.4	53206		311.4	33652	
315.8	54091	β	311.9	34911	
316.3	54971		312.4	38960	
316.8	55845		312.9	44666	
317.3	56661		313.4	48124	
317.8	57378		313.9	49067	
318.3	58086		314.4	49920	
318.8	58645	RI	314.9	50771	
319.3	59253		315.4	51690	
319.8	59876		315.8	52614	β
320.3	60438		316.3	53565	
320.8	61040		316.8	54425	
321.3	61605		317.3	55299	
321.8	62138		317.8	56024	
322.3	62719		318.3	56705	
322.8	63327		318.8	57327	
323.3	63924	α-RII	319.3	57971	RI
323.8	64515		319.8	58596	
324.3	65175		320.3	59189	
324.8	65927		320.8	59826	
325.3	68307		321.3	60474	
325.8	88454		321.8	61083	
326.3	121684		322.3	61668	
326.8	122117		322.8	62327	
327.3	122493		323.3	62851	
327.8	122884		323.8	63459	α-RII
328.3	123299		324.3	64030	
328.8	123692		324.8	64636	
329.3	124098	L	325.3	65760	
329.8	124456		325.8	80861	
330.3	124889		326.3	120761	
335.3	128882		326.8	121595	
340.3	132818		327.3	121987	
345.3	136851		327.8	122391	
350.2	140943		328.3	122800	
355.2	144870		328.8	123237	
359.2	147934		329.3	123654	
			329.8	124078	
			330.3	124519	L
			335.3	128601	
			340.3	132648	
			345.3	136787	
			350.2	140890	
			355.2	145076	
			359.2	148508	

T: temperature in Kelvins; $H^{260}(T)$: measured enthalpy, with T=260 K as reference, in Joule per mol; β", β'$_2$: orthorhombic intermediate solid solution; β-RI: orthorhombic rotator phase; α-RII: rhombohedric rotator phase; L: liquid phase.

Table 9 Variations of the enthalpy *vs.* temperature

T/K	C_{24}:49.8 mol% C_{26} $H^{260}(T)$/J mol^{-1}	Phase	T/K	C_{24}:60.1 mol% C_{26} $H^{260}(T)$/J mol^{-1}	Phase
259.5	0		259.5	0	
260.5	612		260.5	667	
265.5	3156		265.5	2995	
270.5	5644		270.5	5772	
275.5	8463		280.5	11900	β″ + β′$_2$
280.5	10976		294.4	20892	
285.4	14033		295.4	21486	
290.4	16829		296.4	22204	
295.4	18665	β″ + β′$_2$	297.4	22922	
300.4	21940		298.4	23639	
305.4	25426		299.4	24396	
309.4	28317		300.4	25212	
309.4	28746		305.4	29100	
310.4	29149		310.4	33276	β′$_2$
310.9	29567		310.9	33802	
311.4	30032		311.4	34258	
311.9	30537		311.9	34754	
312.4	31414		312.4	35303	
312.9	33830		312.9	36190	
313.4	38334		313.4	37608	
313.9	43284		313.9	40388	
314.4	46457		314.4	44697	
314.9	47307	β	314.9	48704	
315.4	48131		315.4	51868	
315.8	48974		315.9	53228	
316.3	49818		316.4	54232	
316.8	50686		316.9	55153	
317.3	51541		317.4	56043	
317.8	52326		317.8	56985	β
318.3	53017		318.3	57794	
318.8	53674		318.8	58595	
319.3	54258	RI	319.3	59264	
319.8	54847		319.8	59923	RI
320.3	55443		320.3	60475	
320.8	56005		320.8	61052	
321.3	56583		321.3	61687	
321.8	57122		321.8	62333	
322.3	57662		322.3	62903	
322.8	58216		322.8	63478	
323.3	58766		323.3	64128	
323.8	59346	α-RII	323.8	64770	α-RII
324.3	59926		324.3	65373	
324.8	60579		324.8	66000	
325.3	61368		325.3	66716	
325.8	63096		325.8	67545	
326.3	79507		326.3	70352	
326.8	115901		326.8	93601	
327.3	117423		327.3	124562	
327.8	117842		327.8	124996	
330.3	119712	L	328.3	125412	
335.3	123514		328.8	125778	
340.3	127349		329.3	126142	
345.3	131216		329.8	126535	
350.2	135081		330.3	126998	
355.2	139004		335.3	131109	L
359.2	142072		340.3	135350	
			345.3	139522	
			350.3	143752	
			355.2	148014	
			359.2	151528	

T: temperature in Kelvins; $H^{260}(T)$: measured enthalpy, with T=260 K as reference, in Joule per mol; β″, β′$_2$: orthorhombic intermediate solid solution; β-RI: orthorhombic rotator phase; α-RII: rhombohedric rotator phase; L: liquid phase.

Table 10 Variations of the enthalpy *vs.* temperature

T/K	C_{24}:75 mol% C_{26} $H^{260}(T)$/J mol^{-1}	Phase	T/K	C_{24}:77.1 mol% C_{26} $H^{260}(T)$/J mol^{-1}	Phase
259.5	0		259.5	0	
260.5	682		260.5	416	
265.5	3513		265.5	3276	
270.5	6550		270.5	6273	
275.5	9282		275.5	9636	
280.5	12393		280.5	12599	
285.4	15812		285.4	15794	
290.4	18986		290.4	19030	
295.4	22268	β'_2	295.4	22553	β'_2
300.4	25965		300.4	26178	
305.4	29822		305.4	30167	
310.4	34027		310.4	34328	
313.4	36703		314.4	37984	
313.9	37236		314.9	38618	
314.4	37930		315.4	39506	
314.9	38758		315.8	40794	
315.4	39894		316.3	42687	
315.8	41569		316.8	45410	
316.3	43905		317.3	48963	
316.8	47487		317.8	52636	
317.3	51901		318.3	56214	
317.8	55754		318.8	58454	
318.3	58379		319.3	59542	
318.8	59678		319.8	60427	
319.3	60836		320.3	61233	
319.8	61434	β	320.8	61931	β
320.3	62218		321.3	62583	
320.8	62898	RI	321.8	63206	RI
321.3	63576		322.3	63841	
321.8	64232		322.8	64454	
322.3	64881		323.3	65068	
322.8	65497		323.8	65695	
323.3	66147		324.3	66313	α-RII
323.8	66731		324.8	66924	
324.3	67383		325.3	67554	
324.8	68039	α-RII	325.8	68205	
325.3	68782		326.3	68934	
325.8	69470		326.8	69792	
326.3	70218		327.3	71990	
326.8	71254		327.8	89670	
327.3	75834		328.3	126301	
327.8	98933		328.8	126746	
328.3	128734		329.3	127209	
328.8	129166		329.8	127653	
329.3	129588		330.3	128072	
329.8	129995		335.3	132365	L
330.3	130425		340.3	136761	
335.3	134434	L	345.3	141157	
340.3	138514		350.2	145503	
345.3	142622		355.2	149931	
350.2	146579		359.2	153440	
355.2	150827				
359.2	154193				

T: temperature in Kelvins; $H^{260}(T)$: measured enthalpy, with T=260 K as reference, in Joule per mol; β'_2: orthorhombic intermediate solid solution; β-RI: orthorhombic rotator phase; α-RII: rhombohedric rotator phase; L: liquid phase.

The general function F is defined by

$$F(\theta,x) = \sum_{i=1}^{n} ((\Delta H(x)_{exp} - \Delta H(\theta,x)_{calc})^2$$

where $\Delta H(x)_{exp}$ is the variation in enthalpy measured for each molar fraction x; $\Delta H(\theta,x)_{calc}$ is the variation in enthalpy calculated for each molar fraction x; and n is the number of points taken into account for the optimization.

Deviations between calculated and experimental data are illustrated in Fig. 5. The agreement between the experimental and calculated values is very good (less then 2 J mol^{-1}).

Table 11 Variations of the enthalpy *vs.* temperature

T/K	C_{24}:80 mol% C_{26} $H^{260}(T)$/J mol^{-1}	Phase	T/K	C_{24}:90.1 mol% C_{26} $H^{260}(T)$/J mol^{-1}	Phase
259.5	0		259.5	0	
260.5	424		260.5	380	
265.5	3042		265.5	2065	
270.5	5795		270.5	4810	
275.5	8622		275.5	7441	
280.5	11496		280.5	10160	
285.4	14491		285.4	13084	
290.4	17434		290.4	16043	
295.4	20958	β'_2	295.4	19211	
300.4	24270		300.4	22451	$\beta'_2+\gamma_2$
305.4	27618		305.4	25981	
310.4	31283		310.4	29573	
314.4	34332		315.4	33335	
314.9	34857		318.3	35934	
315.4	35455		318.8	36533	
315.8	36221		319.3	37467	
316.3	37395		319.8	39279	
316.8	39262		320.3	43029	
317.3	42037		320.8	50663	
317.8	45326		321.3	58666	
318.3	50034		321.8	61051	
318.8	54487		322.3	62437	
319.3	57307		322.8	63692	
319.8	58464		323.3	64432	
320.3	59249		323.8	65043	β
320.8	59925		324.3	65622	
321.3	60591	β	324.8	66247	
321.8	61152		325.3	66834	RI
322.3	61759		325.8	67426	
322.8	62403		326.3	67985	
323.3	62945		326.8	68572	α-RII
323.8	63566		327.3	69154	
324.3	64115		327.8	69805	
324.8	64744		328.3	70607	
325.3	65386		328.8	83632	
325.8	66005		329.3	124016	
326.3	66682	α-RII	329.8	124108	
326.8	67450		330.3	124482	
327.3	69302		335.3	128884	
327.8	79710		340.3	133112	L
328.3	121862		345.3	137075	
328.8	125229		350.2	141253	
329.3	125660		355.2	145221	
329.8	126133		359.2	148493	
330.3	126515				
335.3	130537				
340.3	134586	L			
345.3	138749				
350.2	143033				
355.2	147281				
359.2	150826				

T: temperature in Kelvins; $H^{260}(T)$: measured enthalpy, with T=260 K as reference, in Joule per mol; β'_2: orthorhombic intermediate solid solution; γ_2: tricminic primary solid solution; β-RI: orthorhombic rotator phase; α-RII: rhombohedric rotator phase; L: liquid phase.

Table 12 Variations of the enthalpy *vs.* temperature

T/K	C_{24}:97 mol% C_{26} $H^{260}(T)$/J mol^{-1}	Phase	T/K	C_{24}:99 mol% C_{26} $H^{260}(T)$/J mol^{-1}	Phase
259.5	0		259.5	0	
260.5	585		260.5	651	
265.5	3363		265.5	3539	
270.5	6352		270.5	6157	
275.5	8958		275.5	8600	
280.5	11744		280.5	11734	
285.4	14526		285.4	14102	
290.4	17631		290.4	17443	
295.4	20567		295.4	20494	
300.4	23806		300.4	23907	
305.4	27235	γ_2	305.4	27374	γ_2
310.4	30722		310.4	30825	
315.4	34289		315.4	34358	
320.3	37980		320.3	38068	
320.8	38478		322.3	39664	
321.3	38965		322.8	40107	
321.8	39529		323.3	40642	
322.3	40321		323.8	41535	
322.8	41592		324.3	43780	
323.3	44263		324.8	51747	
323.8	50029		325.3	66645	
324.3	58861		325.8	74380	
324.8	70937		326.3	75039	
325.3	73408		326.8	75721	
325.8	74043		327.3	76433	α-RII
326.3	74699		327.8	77231	
326.8	75369	α-RII	328.3	78293	
327.3	76085		328.8	80818	
327.8	76803		329.3	94957	
328.3	77667		329.8	137278	
328.8	80875		330.3	137708	
329.3	113602		330.8	138108	
329.8	136918		331.3	138535	
330.3	137385		331.8	138971	
330.8	137835		335.3	141902	L
331.3	138279		340.3	146060	
331.8	138723		345.3	150291	
335.3	141741	L	350.2	154517	
340.3	146183		355.2	158768	
345.3	150666		359.2	162270	
350.3	155263				
355.2	159764				
359.2	163315				

T: temperature in Kelvins; $H^{260}(T)$: measured enthalpy, with T=260 K as reference, in Joule per mol; γ_2: triclinic primary solid solution; β-RI: orthorhombic rotator phase; α-RII: rhombohedric rotator phase; L: liquid phase.

A general expression for the enthalpy $H(T,x)$ as a function of temperature and composition can be established by study of the variation in the parameters N and θ with composition.

A dispersion of θ around 1300 K (Fig. 6) is observed and a mean value of 1367 K is chosen.

The parameter N is then calculated for each composition, with its Einstein temperature. Figure 7 presents the variation in N with composition.

The distribution of the points leads to a parabolic representation of N *vs.* composition:

$$N(x) = 107(1-x) + 118.5x + 98x(1-x)$$

where x is the molar fraction in n-$C_{26}H_{54}$ of the pure phases.

Table 13 Variations of the enthalpy *vs.* temperature

T/K	C_{24}:97 mol% C_{26} $H^{260}(T)$/J mol^{-1}	Phase
259.5	0	
260.5	274	
265.5	3432	
270.5	6310	
275.5	9195	
280.5	12349	
285.4	15383	
290.4	18679	
295.4	21968	γ_2
300.4	25213	
305.4	25562	
310.4	31935	
315.4	35366	
320.3	38989	
323.3	41337	
323.8	41767	
324.3	42241	
324.8	42828	
325.3	44529	
325.8	66706	
326.3	76661	
326.8	77304	
327.3	77961	α-RII
327.8	78623	
328.3	79323	
328.8	80076	
329.3	89017	
329.8	140083	
330.3	140498	
330.8	140930	
331.3	141359	
335.3	144717	
340.3	148983	L
345.3	153276	
350.2	157651	
355.2	162074	
359.2	165632	

T: temperature in Kelvins; $H^{260}(T)$: measured enthalpy, with T=260 K as reference, in Joule per mol; γ_2: triclinic primary solid solution; α-RII: rhombohedric rotator phase; *L*: liquid phase.

This expression is computed in the whole range of concentration as the phase domains are too narrow for individual numerical optimization.

Nevertheless, $N(x)$ is only valid in the pure phase domains.

Finally, a general expression for the enthalpy $H(T,x)$ as a function of temperature and composition is defined for the phases γ_1, β_1', β'', β_2' and γ_2:

$$H(T,x) = \frac{3R\theta N(x)}{\exp(\theta/T) - 1}$$

The agreement between the experimental and calculated values is good; the mean deviation is 5%.

Conclusion

In this work, we have determined the variation in the enthalpies of n-$C_{24}H_{50}$, n-$C_{26}H_{54}$ and 19 binary mixtures between 260 and 360 K. These data for binary

Table 14 Parameters N, θ and H_E *vs.* composition in n-$C_{26}H_{54}$

x/mol % in n-$C_{26}H_{54}$	Phase	Temperature domain/ K	N	θ/ K	H_E/ J mol^{-1}	Error function 10^{-5} F/ J mol^{-1}
0	γ_1	269.5–317.8	61.3	1093.8	24695	1.417792
1.1	γ_1	292.4–314.9	311.3	1869.4	7341	0.7135303
10	β_1'	270.5–309.4	82.8	1157	27915	4.878368
30.1	β''	270.5–309.4	113.5	1263.7	27327	1.025291
33	β''	270.5–307.4	99.9	1214.3	28844	5.314301
35.2	β''	270.5–307.4	245.7	1667.6	13823	4.443181
40.1	β''	270.5–306.4	122.0	1318.3	24966	10.12776
45.1	β''	270.5–309.9	158.8	1462.3	20331	4.890922
75	β_2'	294.4–321.4	352.6	1820	11556	4.589846
77.1	β_2'	295.4–313.4	118.1	1297.3	25299	4.927112
80	β_2'	270.5–313.4	86.6	1177.1	27325	2.765067
97	γ_2	294.4–318.3	69.7	1064.9	31227	0.4958911
99	γ_2	282.4–318.3	65.4	1020.5	33797	1.9759240
100	γ_2	270.5–321.8	45.3	774.3	46693	1.748367

mixtures of the different phases γ_1, β_1', β'', β_2' and γ_2, and also the phases of the pure *n*-alkanes, have been represented by an analytical expression, derived from Einstein's model of the solid state.

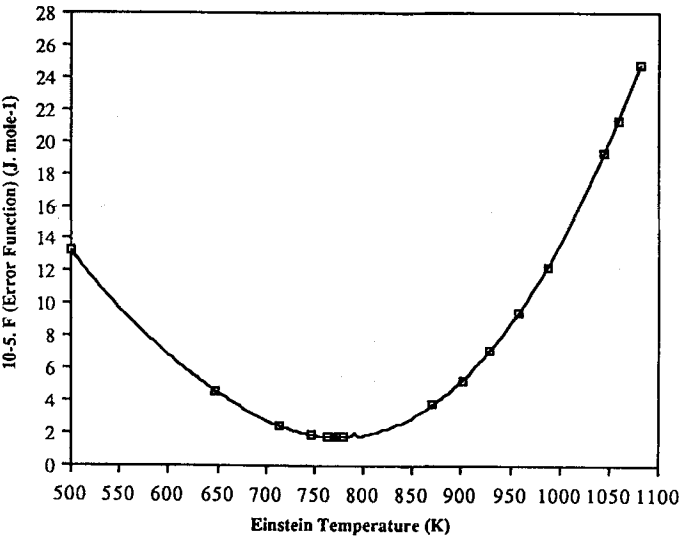

Fig. 4 Variation of the error function *vs.* the Einstein temperature of the *n*-hexacosane

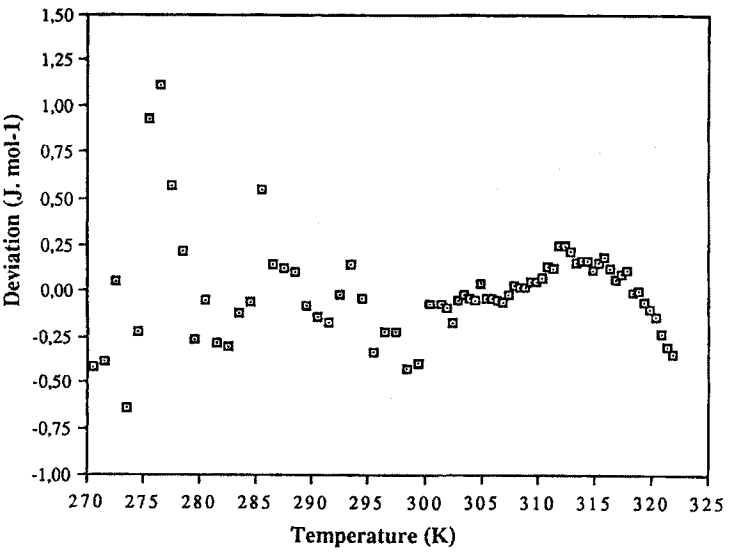

Fig. 5 Deviation between measured and calculated enthalpies

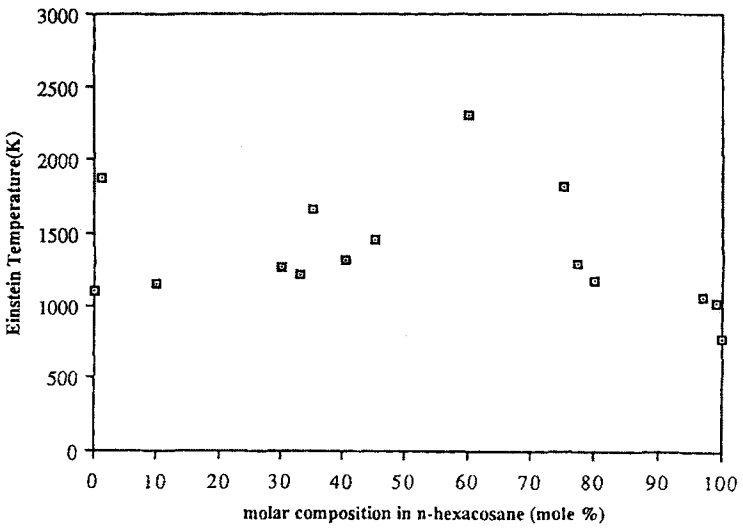

Fig. 6 Einstein temperature *vs.* composition

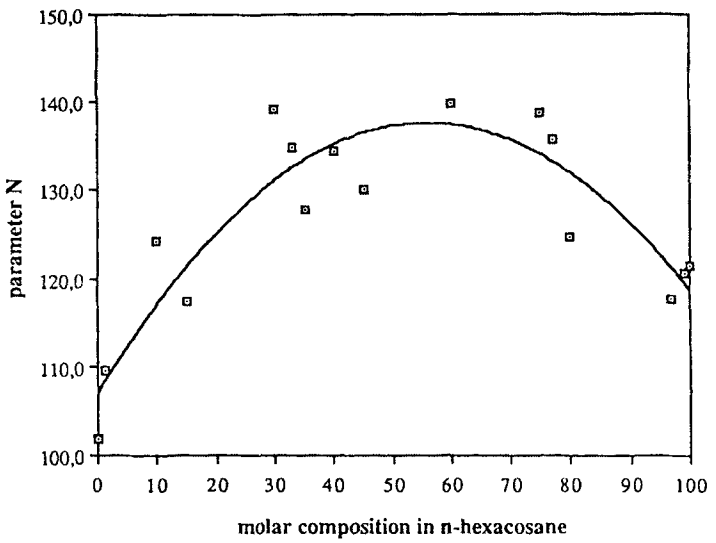

Fig. 7 Values of the parameter *N vs.* composition, with a constant Einstein temperature of 1367 K

A general expression has been defined for the enthalpy as a function of temperature and the molar fraction of n-$C_{26}H_{54}$.

This study gives new results on the binary system n-$C_{24}H_{50}$–n-$C_{26}H_{54}$. These results could be used for determination of the thermodynamic functions of mixing, necessary for calculations on the solid-solid equilibria.

References

1 Z. Achour, J. B. Bourdet, M. Bouroukba and M. Dirand, J. Chim. Phys., 90 (1993) 325.
2 Z. Achour-Boudjema, J. B. Bourdet, D. Petitjean and M. Dirand, J. Mol. Struct., 354 (1995) 197.
3 H. Lüth and S. G. Nyburg, Mol. Cryst. Liq. Cryst., 27 (1974) 337.
4 N. Hasnaoui, J. Dellacherie, L. Schuffenecker, M. Dirand and D. Balesdent, J. Chim. Phys., 85 (1988) 153.
5 Z. Achour, J. B. Bourdet, M. Bouroukba and M. Dirand, J. Chim. Phys., 89 (1992) 707.
6 J. Doucet, I. Denicolo, A. Craievich and A. Collet, J. Chem. Phys., 75 (1981) 5125.
7 R. G. Snyder, A. F. Maroncelli, S. P. Qi and H. L. Strauss, Science, 214 (1981) 188.
8 I. Denicolo, A. F. Craievich and J. Doucet, J. Chem. Phys., 80 (1984) 6200.
9 G. Ungar, J. Phys. Chem., 87 (1983) 689.
10 S. K. Filatov, E. N. Kotelnikova and E. A. Aleksandrova, Zeitschrift für Kristallographie, 172 (1985) 35.
11 G. Ungar and N. Masic, J. Phys. Chem, 89 (1985) 1036.
12 N. Hasnaoui, J. Dellacherie, L. Schuffenecker and M. Dirand, J. Chim. Phys., 85 (1988) 675.
13 I. Denicolo, J. Doucet and A. F. Craievich, J. Chem. Phys., 78 (1983) 1465.
14 J. Doucet and A. J. Dianoux, J. Chem, Phys., 81 (1984) 5043.
15 Z. Achour, J. B. Bourdet, M. Bouraoukba and M. Dirand, J. Chim. Phys., 89 (1992) 707.
16 D. A. Ditmars, S. Ishihara, S. S. Chang and G. Bernstein, J. Research, 87 (1982) 159.
17 R. J. L. Andon and J. F. Martin, J. Chem. Thermodynamics, 8 (1976) 1159.
18 H. H. Rosenbrock, J. 3., 175 (1960).