Journal of Thermal Analysis, Vol. 54 (1998) 785-802

ENTHALPY VARIATION OF THE NINE SOLID PHASES OF THE BINARY MOLECULAR ALLOYS (*n*-TRICOSANE:*n*-PENTACOSANE) *VS.* TEMPERATURE

M. B. Jouti, M. Bouroukba, D. Balesdent and M. Dirand

Laboratoire de Thermodynamique des Séparations, Ecole Nationale Supérieure des Industries Chimiques, Institut National Polytechnique de Lorraine, 1, rue Grandville – B. P. 451 – F-54001 Nancy Cedex, France

Abstract

The enthalpy variations of pure *n*-tricosane (n-$C_{23}H_{48}$), pure *n*-pentacosane (n-$C_{25}H_{52}$) and sixteen binary mixtures were determined from 282 to 360 K. The differential enthalpy analyses were carried out on the pure components, on the four terminal solid solutions, denoted $\beta_o(C_{23})$, $\beta_o'(C_{23})$, $\beta_o'(C_{25})$, $\beta_o(C_{25})$ and on the three intermediate phases, called β_1'', β_1', β_2'' of the binary system (C_{23}:C_{25}) using a calorimeter of the Tian Calvet type. These variations can be represented by an analytical expression, which is derived from Einstein's model. The two Rotator phases β-RI and α-RII were also studied.

Keywords: binary mixtures, enthalpy variations, Einstein's solid model, *n*-pentacosane, *n*-tricosane

Introduction

An estimate of the crystallization point of solid *n* alkanes (hereafter denoted by C_n) in paraffinic petroleum or middle-distillate fuels is possible only when the thermodynamic properties of the pure components and their respective mixtures are known. In our laboratory joint studies by calorimetry and X-ray diffraction are carried out currently on the liquid/solid and solid/solid equilibria occurring in pure C_n ($17<n<27$) [1], in solution with ethylbenzene [2, 3] and in their respective binary mixtures [4–17]. These studies allowed to determine:

i) the binary phase diagrams of C_{22}:C_{24} [5, 8], C_{24}:C_{26} [9, 10], C_{23}:C_{24} [12], C_{21}:C_{23} [13, 14] and C_{23}:C_{25} [15, 16].

ii) the general rules of the thermodynamic and structural behaviour of consecutive [even:even numbered], [even:odd-numbered] and [odd:odd-numbered] *n*-alkane binary mixtures [17].

As for the C_{24}:C_{26} system [18], the aim of this work is to present the differential enthalpimetric analyses carried out on the solid phases which have been observed in the C_{23}:C_{25} mixtures [15, 16]. The phase diagram [16] shows the existence of nine solid solution ranges:

1418–2874/98/ $ 5.00

Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

i) at low temperature, four terminal solid solutions, denoted $\beta_o(C_{23})$, $\beta'_o(C_{23})$, $\beta'_o(C_{25})$ and $\beta_o(C_{25})$ and three orthorhombic intermediate solutions: two isostructural phases called β''_1 and β''_2 on both sides of the phase β'_1.

ii) when the temperature increases, all these phases undergo the same solid/solid transitions as the pure C_{23} and C_{25}, except the δ transition, with appearance of the β phase (Fmmm) which is a second order transition with the Rotator RI state, and just below the solidus line the Rotator phase α-RII ($R\bar{3}m$).

The enthalpy variations *vs.* temperature are given for the different solid phases. Then data concerning the low temperature phases are treated using a function derived from the Einstein solid model.

Experimental

Measurement principle

The enthalpy measurements were performed with a differential scanning calorimeter of the TIAN-CALVET type [19], a DSC 111 manufactured by SETARAM, using a discontinuous mode of temperature programming.

The calorimeter principle has been described before [18, 20]. It is based on the measurement of the difference of heat Q exchanged between two cells and the calorimeter block during a temperature jump from T_1 to T_2. On the one hand, the calorimeter asymmetry term Q_D is determined by a blank experiment, in which only the sample support is placed in the measurement cell. On the other hand, the sample is put in its support to measure the overall heat Q_o. The sample contribution Q_S corresponds to the difference between the measurement Q_o and blank Q_D values: $Q_S=Q_o-Q_D$. For each temperature jump j, the molar enthalpy variation is:

$$H(T_2)-H(T_1)=\frac{M}{m}(Q_S)_j$$

where M and m are the molar mass and the mass of the sample, respectively.

The molar enthalpy of sample heating at temperature T, referred to 282K, is:

$$H(T)-H(282)=\sum_j \frac{M}{m}(Q_s)_j$$

where $H(T)$ and $H(282)$ are the enthalpies at T and 282 K, respectively.

The calibration of the apparatus was performed with the help of the thermodynamic data of alumina reported by the N.B.S. Table [21]. The reproductibility and the precision of the enthalpy measurement were determined by using C_{26} for which the experimental enthalpy was compared to that in the literature [22]. The relative standard deviations is about 2% [18].

Operating conditions

The measurements were carried out with a discontinuous programming of the temperature *vs*. time:

– the rising temperature period was set at 200 s and corresponded to 1 or 0.5 K, depending on the temperature range.
– the temperature level duration depends on a computer test, checking that the calorimeter signal returned to constant value, corresponding to a steady state.
The measurements were carried out in two steps, for both blank and sample:
– from 282 K to 310 K, with a temperature rate of 18 K h^{-1}, giving a temperature jump of 1 K.
– from 300 to 310 K, with a temperature rate of 9 K h^{-1}, giving a temperature jump of 0.5 K.

These two series of measurements overlap over 10 K; no significant differences between the operating conditions were observed.

Sample preparation

The *n*-alkanes C_{23} and C_{25} were obtained from Aldrich Chemical Company and had a stated purity of 99% for C_{25} and over 99% for C_{23}, as determined by gas chromatography and mass spectroscopy. The mixtures were prepared by mixing together appropriate proportions of C_{23} and C_{25}. The samples were obtained by melting, thorough mixing and quenching in a crystallizing dish within a Dewar vessel containing liquid air. Such a rapid cooling ensured a uniform steric concentration of each component in the solid state.

Experimental results

Variation of the enthalpy vs. temperature

The calorimetric measurements were made on pure C_{23} and C_{25} and 16 binary mixtures, covering the whole range of concentrations. The results are presented in Tables 1 to 9. Figure 1 represents the curve of the enthalpy for pure C_{25} and the mixture containing 30 mol% of C_{25}.

Representation of the variations of enthalpy for low temperature phases

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

Table 1 Variations of the enthalpy *vs*. temperature

T/K	C_{23}: 0 mol% C_{25} $H^{282.8}(T)$/J mol^{-1}	Phase
282.8	0	
283.8	587	
284.8	1210	
285.9	1878	
286.9	2491	
287.9	3090	
288.9	3715	
289.9	4341	
290.9	4967	
292.0	5640	
293.0	6316	$\beta_0(C_{23})$
294.0	6944	
295.0	7572	
296.0	8225	
297.0	8864	
298.1	9499	
299.1	10186	
300.1	10876	
301.1	11562	
302.1	12208	
303.1	12891	
304.1	13575	
304.9	14282	
305.4	14654	
305.9	15058	
306.5	15446	
307.0	15846	
307.5	16251	
308.0	16658	
308.5	17083	
309.1	17502	$\beta'_0(C_{23})$
309.6	17924	
310.1	18358	
310.6	18812	
311.1	19324	
311.6	19890	
312.2	20419	
312.7	20982	
313.2	28519	
313.7	41799	
314.2	42942	
314.8	44178	
315.3	45516	
315.8	46827	β-RI
316.3	47695	
316.8	48686	
317.4	49616	
317.9	50485	
318.4	51587	
318.9	52401	
319.4	53348	α-RII
319.9	54605	
320.5	83772	
321.0	102749	
321.5	103239	
322.0	103729	
322.5	104208	
323.1	104719	
323.6	105211	
324.1	105706	
324.6	106221	
325.1	106717	
325.6	107222	
326.2	107724	
326.7	108237	
327.2	108744	
327.7	109253	
328.2	109759	
328.8	110258	L
329.3	110783	
329.8	111271	
330.3	111789	
330.8	112303	
331.4	112811	
331.9	113329	
332.4	113848	
332.9	114356	
333.4	114872	
333.9	115381	
334.5	115898	
335.0	116408	
335.5	116926	
336.0	117437	
336.5	117944	
337.1	118455	
337.6	118964	
338.1	119478	
338.6	119987	
339.1	120506	
339.6	121025	
340.2	121547	

T/K	C_{23}: 0.3 mol% C_{25} $H^{282.8}(T)$/J mol^{-1}	Phase
282.8	0	
283.8	605	
284.8	1211	
285.9	1819	
286.8	2411	
287.9	3025	
288.9	3646	
289.9	4274	
290.9	4885	
292.0	5500	
293.0	6131	$\beta_0(C_{23})$
294.0	6766	
295.0	7394	
296.0	8026	
297.0	8661	
298.1	9314	
299.1	9958	
300.1	10613	
301.1	11261	
302.1	11919	
303.1	12579	
304.1	13241	
304.9	13807	
305.4	13959	
305.9	14332	
306.4	14701	
306.9	15095	
307.4	15498	
308.0	15907	
308.5	16350	
309.0	16784	$\beta'_0(C_{23})$
309.5	17248	
310.0	17675	
310.5	18102	
311.0	18549	
311.6	19018	
312.1	19681	
312.6	28140	
313.1	38842	
313.6	39682	
314.1	40993	
314.7	42211	
315.2	43353	
315.7	44420	β-RI
316.2	45372	
316.7	46247	
317.2	47097	
317.7	47921	
318.3	48878	α-RII
318.8	49835	
319.3	50588	
319.8	52348	
320.3	82832	
320.8	99919	
321.3	100351	
321.8	100787	
322.4	101178	
322.9	101611	
323.4	102032	
323.9	102448	
324.4	102854	
324.9	103280	
325.5	103678	
326.0	104090	
326.5	104514	
327.0	104940	
327.5	105352	L
328.0	105786	
328.6	106210	
329.1	106632	
329.6	107050	
330.1	107487	
330.6	107913	
331.1	108331	
331.6	108769	
332.2	109207	
332.7	109642	
333.2	110084	
333.7	110529	
334.2	110984	
334.7	111412	
335.2	111852	
335.8	112286	
336.3	112733	
336.8	113175	
337.3	113604	
337.8	114035	
338.3	114484	
338.8	114912	
339.4	115348	
339.9	115789	
340.4	116228	

T: temperature in K; $H^{282.8}(T)$: measured enthalpy, with T=282.8 K as reference, in joule per mole; $\beta_0(C_{23})$: orthorhombic primary solid solution; $\beta'_0(C_{23})$: orthorhombic primary solid solution; β-RI: orthorhombic rotator phase; α-RII: rhombohedric rotator phase; *L*: liquid phase

Table 2 Variations of the enthalpy *vs.* temperature

T/K	C_{23}: 0.5 mol% C_{25} $H^{282.8}(T)$/J mol^{-1}	Phase
282.8	0	
283.8	650	
284.8	1315	
285.9	1972	
286.9	2622	
287.9	3258	
288.9	3955	
289.9	4608	
290.9	5214	
292.0	5856	$\beta_o(C_{23})$
293.0	6513	
294.0	7187	
295.0	7824	
296.0	8463	
297.0	9103	
298.1	9724	
299.1	10374	
300.1	11037	
301.1	11693	
302.1	12346	
303.1	13013	
304.1	13693	
304.9	14042	
305.4	14364	
305.9	14719	
306.4	15052	
306.9	15373	
307.4	15696	
308.0	16036	
308.5	16378	$\beta'_o(C_{23})$
309.0	16686	
309.5	17052	
310.0	17404	
310.5	17761	
311.0	18103	
311.6	18457	
312.1	18916	
312.6	35942	
313.1	38582	
313.6	39516	
314.1	40525	
314.7	41876	
315.2	42786	
315.7	43771	β-RI
316.2	44716	
316.7	45569	
317.2	46341	
317.7	47089	
318.3	47996	
318.8	48651	
319.3	49446	α-RII
319.8	50692	
320.3	58983	
320.8	97622	
321.3	97970	
321.8	98295	
322.4	98617	
322.9	98931	
323.4	99249	
323.9	99571	
324.4	99889	
324.9	100216	
325.5	100536	
326.0	100855	
326.5	101181	
327.0	101511	L
327.5	101839	
328.0	102173	
328.6	102499	
329.1	102825	
329.6	103153	
330.1	103476	
330.6	103820	
331.1	104146	
331.6	104485	
332.2	104823	
332.7	105145	
333.2	105455	
333.7	105776	
334.2	106112	
334.7	106435	
335.2	106757	
335.6	107075	
336.3	107397	
336.8	107709	
337.3	108024	
337.8	108346	
338.3	108667	
338.8	109000	
339.4	109319	
339.9	109639	
340.4	109982	

T/K	C_{23}: 1.5 mol% C_{25} $H^{282.8}(T)$/J mol^{-1}	Phase
282.8	0	
283.8	582	
284.8	1199	
285.9	1836	
286.9	2455	
287.9	3180	
288.9	3805	
289.9	4430	
290.9	5093	
292.0	5731	$\beta'_o(C_{23})$
293.0	6380	
294.0	7078	
295.0	7725	
296.0	8346	
297.0	8995	
298.1	9631	
299.1	10305	
300.1	10980	
301.1	11684	
302.1	12354	
303.1	13049	
304.4	13753	
304.9	14157	
305.4	14637	
305.9	15243	
306.4	16094	
307.0	16660	
307.5	17422	
308.0	17867	
308.5	18314	β''_1
309.0	18724	
309.6	19147	
310.1	19564	
310.6	20105	
311.1	31907	
311.6	36586	
312.2	37601	
312.7	38587	
313.2	39660	
313.7	40617	
314.2	41924	
314.7	42921	β-RI
315.3	43684	
315.8	44792	
316.3	45840	
316.8	46370	
317.3	47100	
317.9	47850	
318.4	48588	
318.9	49329	α-RII
319.4	50284	
319.9	54430	
320.5	101048	
321.0	101440	
321.5	101620	
322.0	102210	
322.5	102590	
323.1	102969	
323.6	103379	
324.1	103787	
324.6	104205	
325.1	104635	
325.7	105042	
326.2	105457	
326.7	105859	
327.2	106261	
327.7	106689	
328.3	107142	
328.8	107565	L
329.3	107977	
329.8	108374	
330.3	108772	
330.9	109218	
331.4	109635	
331.9	110038	
332.4	110448	
332.9	110874	
333.5	111307	
334.0	111714	
334.5	112107	
335.0	112513	
335.5	112931	
336.1	113341	

T: temperature in K; $H^{282.8}(T)$: measured enthalpy, with T=282.8 K as reference, in joule per mole; $\beta_o(C_{23})$: orthorhombic primary solid solution; $\beta'_o(C_{23})$: orthorhombic primary solid solution; β''_1: orthorhombic intermediate solid solution; β-RI: orthorhombic rotator phase; α-RII: rhombohedric rotator phase; L: liquid phase

Table 3 Variations of the enthalpy *vs.* temperature

T/K	C_{23}: 1.8 mol% C_{25} $H^{282.8}(T)$/J mol^{-1}	Phase
282.8	0	
283.8	648	
284.8	1290	
285.9	1916	
286.9	2529	
287.9	3159	
288.9	3791	
289.9	4443	$\beta'_o(C_{23})$
290.9	5085	
292.0	5758	
293.0	6406	
294.0	7044	
295.0	7699	
296.0	8362	
297.0	9044	
298.1	9704	
299.1	10368	
300.1	11050	
301.1	11726	
302.1	12423	
303.1	13112	
304.1	13604	
304.9	14276	
305.4	14787	
305.9	15418	
306.4	16009	
306.9	16529	
307.4	17041	
308.0	17492	
308.5	17924	
309.0	18372	β''_1
309.5	18838	
310.0	19295	
310.5	19687	
311.0	20782	
311.6	33701	
312.1	36328	
312.6	37270	
313.1	38211	
313.6	39188	
314.1	40253	
314.7	41301	β-RI
315.2	42260	
315.7	43222	
316.2	44119	
316.7	44807	
317.2	45244	
317.7	45610	
318.3	46338	
318.8	46989	
319.3	47710	α-RII
319.8	48753	
320.3	52377	
320.8	99774	
321.3	100584	
321.8	100901	
322.4	101233	
322.9	101567	
323.4	101891	
323.9	102227	
324.4	102569	
324.9	102888	
325.5	103256	
326.0	103602	
326.5	103943	
327.0	104275	L
327.5	104607	
328.0	104948	
328.6	105284	
329.1	105644	
329.6	105988	
330.1	106339	
330.6	106676	
331.1	107009	
331.6	107349	
332.2	107704	
332.7	108045	
333.2	108385	
333.7	108741	
334.2	109077	
334.7	109410	
335.2	109736	
335.8	110068	
336.3	110441	
336.8	110771	
337.3	111094	
337.8	111427	
338.3	111758	
338.8	112102	
339.4	112430	
339.9	112755	
340.4	113079	

T/K	C_{23}: 2 mol% C_{25} $H^{282.8}(T)$/J mol^{-1}	Phase
282.8	0	
283.8	644	
284.8	1270	
285.9	1907	
286.9	2565	
287.9	3191	
288.9	3825	
289.9	4479	
290.9	5112	
292.0	5771	
293.0	6460	$\beta'_o(C_{23})$
294.0	7138	
295.0	7788	
296.0	8443	
297.0	9100	
298.1	9779	
299.1	10458	
300.1	11168	
301.1	11898	
302.1	12708	
303.1	13590	
304.1	14590	
304.9	14984	
305.4	15381	
305.9	15814	
306.5	16212	
307.0	16586	
307.5	16979	
308.0	17375	
308.5	17775	
309.1	18201	β''_1
309.6	18628	
310.1	19070	
310.6	19541	
311.1	20893	
311.6	35428	
312.2	36389	
312.7	37301	
313.2	38247	
313.7	39264	
314.2	40336	
314.8	41417	
315.3	42430	β-RI
315.8	43416	
316.3	44314	
316.8	45150	
317.3	45946	
317.9	46882	
318.4	47575	
318.9	48211	
319.4	48883	α-RII
319.9	49731	
320.6	51522	
321.0	91657	
321.5	97089	
322.0	97465	
322.5	97838	
323.1	98215	
323.6	98601	
324.1	98973	
324.6	99359	
325.1	99745	
325.6	100123	
326.2	100505	
326.7	100884	
327.2	101254	
327.7	101635	
328.2	102063	
328.8	102457	
329.3	102837	L
329.8	103216	
330.3	103589	
330.8	103984	
331.3	104372	
331.9	104781	
332.4	105140	
332.9	105522	
333.4	105907	
333.9	106295	
334.5	106679	
335.0	107065	
335.6	107443	
336.0	107827	
336.5	108214	
337.1	108604	
337.6	108980	
338.1	109374	
338.6	109759	
339.1	110145	
339.6	110524	
340.2	110908	
340.7	111283	

T: temperature in K; $H^{282.8}(T)$: measured enthalpy, with T=282.8 K as reference, in joule per mole; $\beta'_o(C_{23})$: orthorhombic primary solid solution; β''_1: orthorhombic intermediate solid solution; β-RI: orthorhombic rotator phase; α-RII: rhombohedric rotator phase; L: liquid phase

Table 4 Variations of the enthalpy *vs.* temperature

T/K	C_{23}: 3 mol% C_{25} $H^{282.8}(T)$/J mol^{-1}	Phase
282.8	0	
283.8	657	
284.8	1316	
285.9	1966	
286.9	2625	
287.9	3293	
288.9	3967	
289.9	4672	
290.9	5334	
292.0	5928	β''1
293.0	6657	
294.0	7334	
295.0	8066	
296.0	8798	
297.0	9530	
298.1	10284	
299.1	11024	
300.1	11777	
301.1	12516	
302.1	13285	
303.1	14029	
304.1	14787	
304.9	15104	
305.4	15548	
305.9	15937	
306.5	16324	
307.0	16699	
307.5	17119	
308.0	17491	
308.5	17866	
309.1	18263	
309.6	18663	
310.1	19160	
310.6	24566	
311.1	34284	
311.6	35173	
312.2	36028	
312.7	36864	
313.2	37720	
313.7	38729	
314.2	39732	β-RI
314.8	40707	
315.3	41666	
315.8	42586	
316.3	43434	
316.8	43796	
317.4	44190	
317.9	44906	
318.4	45717	α-RII
318.9	46328	
319.4	46961	
319.9	47769	
320.5	48625	
321.0	80002	
321.5	82967	
322.0	83350	
322.5	83715	
323.1	84070	
323.6	84413	
324.1	84765	
324.6	85111	
325.1	85452	
325.6	85818	
326.2	86182	
326.7	86563	L
327.2	86900	
327.7	87242	
328.2	87592	
328.8	87979	
329.3	88331	
329.8	88694	
330.3	89059	
330.8	89432	
331.3	89837	
331.9	90233	
332.4	90618	
332.9	91022	
333.4	91450	
333.9	91829	
334.5	92170	
335.0	92533	
335.5	92890	
336.0	93256	
336.5	93618	
337.1	93982	
337.6	94330	
338.1	94679	
338.6	95035	
339.1	95367	
339.6	95719	
340.2	96089	
340.7	96409	

T/K	C_{23}: 4 mol% C_{25} $H^{282.8}(T)$/J mol^{-1}	Phase
282.8	0	
283.8	630	
284.8	1281	
285.9	1936	
286.9	2592	
287.9	3219	
288.9	3859	
289.9	4524	
290.9	5200	β''1
292.0	5883	
293.0	6560	
294.0	7231	
295.0	7919	
296.0	8605	
297.0	9287	
298.1	9967	
299.1	10705	
300.1	11420	
301.1	12154	
302.1	12870	
303.1	13638	
304.1	14415	
305.4	15204	
305.9	15552	
306.5	15925	
307.0	16323	
307.5	16748	
308.0	17205	
308.5	17690	
309.0	18188	
309.6	27405	
310.1	32757	
310.6	33570	
311.1	34374	
311.6	35192	
312.2	36042	
312.7	36922	
313.2	37861	β-RI
313.7	38772	
314.2	39669	
314.7	40584	
315.3	41462	
315.8	42242	
316.3	43005	
316.8	43694	
317.3	44379	
317.9	45182	
318.4	45867	α-RII
318.9	46653	
319.4	47779	
319.9	50186	
320.4	57688	
321.0	59097	
321.5	84528	
322.0	84846	
322.5	85162	
323.0	85499	
323.6	85841	
324.1	86167	
324.6	86497	
325.1	86803	
325.6	87096	L
326.1	87432	
326.7	87760	
327.2	88080	
327.7	88388	
328.2	88723	
328.7	89035	
329.3	89337	
329.8	89678	
330.3	89986	
330.8	90313	
331.3	90618	
331.8	90937	
332.4	91289	
332.9	91583	
333.4	91896	
333.9	92203	
334.4	92523	
334.9	92825	
335.5	93147	
336.0	93467	
336.5	93803	
337.0	94109	
337.5	94427	
338.1	94740	
338.6	95050	
339.1	95351	
339.6	95669	
340.1	95995	

T: temperature in K; $H^{282.8}(T)$: measured enthalpy, with T=282.8 K as reference, in joule per mole; 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_{23}: 25 mol% C_{25} $H^{282.8}(T)$/J mol^{-1}	Phase
282.8	0	
283.8	682	
284.8	1362	
285.9	2061	
286.9	2751	
287.9	3436	
288.9	4124	
289.9	4813	
290.9	5515	
292.0	6238	
293.0	6963	β'_1
294.0	7689	
295.0	8418	
296.0	9158	
297.0	9886	
298.1	10644	
299.1	11417	
300.1	12196	
301.1	12986	
302.1	13814	
303.1	14630	
304.1	15444	
304.9	15883	
305.4	16304	
305.9	16759	
306.5	17557	
307.0	28039	
307.5	28898	
308.0	29807	
308.5	30327	
309.1	31061	
309.6	31825	
310.1	32595	β-RI
310.6	33358	
311.1	34136	
311.6	34920	
312.2	35749	
312.7	36547	
313.2	37379	
313.7	38188	
314.2	38977	
314.6	39736	
315.3	40429	
315.6	41080	
316.3	41704	
316.8	42269	
317.4	42919	
317.9	43473	
318.4	44013	
318.9	44592	α-RII
319.4	45203	
319.9	45796	
320.5	46478	
321.0	47451	
321.5	51135	
322.0	83511	
322.5	92015	
323.1	92414	
323.6	92704	
324.1	93112	
324.6	93454	
325.1	93813	
325.6	94166	
326.2	94513	
326.7	94863	
327.2	95214	
327.7	95576	
328.2	95965	L
328.6	96321	
329.3	96661	
329.8	97049	
330.3	97395	
330.8	97735	
331.3	98084	
331.9	98441	
332.4	98793	
332.9	99130	
333.4	99520	
333.9	99865	
334.5	100200	
335.0	100584	
335.5	100921	
336.0	101273	
336.5	101625	
337.1	101963	
337.6	102303	
338.1	102650	
338.6	103020	
339.1	103356	
339.6	103699	
340.2	104040	

T/K	C_{23}: 30 mol% C_{25} $H^{282.8}(T)$/J mol^{-1}	Phase
282.8	0	
283.8	686	
284.8	1309	
285.9	1976	
286.9	2658	
287.9	3367	
288.9	4079	
289.9	4798	
290.9	5524	
292.0	6247	
293.0	6986	
294.0	7721	β'_1
295.0	8458	
296.0	9209	
297.0	9943	
298.1	10682	
299.1	11461	
300.1	12228	
301.1	13014	
302.1	13823	
303.1	14630	
304.1	15478	
304.9	15858	
305.4	16355	
305.9	16947	
306.4	20169	
306.9	27305	
307.4	28902	
308.0	29881	
308.5	30431	
309.0	31219	
309.5	32056	
310.0	32910	
310.6	33798	
311.1	34686	β-RI
311.6	35617	
312.1	36523	
312.6	37455	
313.1	38350	
313.7	39256	
314.2	40155	
314.7	40970	
315.2	41704	
315.7	42415	
316.3	43123	
316.8	43905	
317.3	44578	
317.8	45280	
318.3	45985	
318.8	46744	α-RII
319.4	47616	
319.9	48697	
320.4	50094	
320.9	52352	
321.4	57934	
322.0	78013	
322.5	96736	
323.0	97346	
323.5	97631	
324.0	98334	
324.6	98797	
325.1	99254	
325.6	99718	
326.1	100166	
326.6	100654	
327.1	101120	
327.7	101591	
328.2	102075	
328.7	102559	L
329.2	103021	
329.7	103496	
330.3	103963	
330.8	104413	
331.3	104896	
331.8	105367	
332.3	105842	
332.8	106315	
333.4	106813	
333.9	107301	
334.4	107781	
334.9	108248	
335.4	108732	
336.0	109204	

T: temperature in K; $H^{282.8}(T)$: measured enthalpy, with T=282.8 K as reference, in joule per mole; β'_1: 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_{23}: 40 mol% C_{25} $H^{282.8}(T)$/J mol^{-1}	Phase
282.8	0	
283.8	697	
284.8	1425	
285.9	2108	
286.9	2789	
287.9	3588	
288.9	4289	
289.9	5028	
290.9	5742	
292.0	6438	
293.0	7157	β'₁
294.0	7898	
295.0	8625	
296.0	9359	
297.0	10121	
298.1	10891	
299.1	11671	
300.1	12438	
301.1	13221	
302.1	14004	
303.1	14784	
304.1	15545	
304.9	15985	
305.4	16403	
305.9	16872	
306.4	17414	
306.9	18493	
307.4	24865	
308.0	29222	
308.5	30314	
309.0	31086	
309.5	31834	
310.0	32613	
310.5	33425	
311.0	34217	
311.6	35044	
312.1	35880	β-RI
312.6	36754	
313.1	37648	
313.6	38537	
314.1	39434	
314.7	40287	
315.2	41056	
315.7	41845	
316.2	42525	
316.7	43162	
317.2	43853	
317.7	44440	
318.3	45057	
318.8	45629	
319.3	46231	α-RII
319.8	46867	
320.3	47515	
320.8	48171	
321.3	48941	
321.9	50588	
322.4	62168	
322.9	95680	
323.4	98863	
323.9	99086	
324.4	99522	
324.9	99968	
325.5	100397	
326.0	100805	
326.5	101243	
327.0	101678	
327.5	102094	L
328.0	102509	
328.6	102929	
329.1	103364	
329.6	103798	
330.1	104219	
330.6	104663	
331.1	105100	
331.6	105539	
332.2	105965	
332.7	106384	
333.2	106809	
333.7	107223	
334.2	107689	
334.7	108116	
335.2	108557	
335.8	108993	
336.3	109433	
336.8	109893	
337.3	110333	
337.8	110765	
338.3	111202	
338.8	111645	
339.4	112085	
339.9	112521	
340.4	112960	

T/K	C_{23}: 53 mol% C_{25} $H^{282.8}(T)$/J mol^{-1}	Phase
282.8	0	
283.8	734	
284.8	1413	
285.9	2117	
286.9	2838	
287.9	3543	
288.9	4261	
289.9	4956	
290.9	5686	β'₁
292.0	6418	
293.0	7127	
294.0	7846	
295.0	8604	
296.0	9338	
297.0	10085	
298.1	10610	
299.1	11594	
300.1	12379	
301.1	13158	
302.1	13980	
303.1	14784	
304.4	15829	
304.9	16115	
305.4	16633	
305.9	17164	
306.5	17726	
307.0	18951	
307.5	24085	
308.0	28590	
308.5	29964	
309.1	30800	
309.6	31621	
310.1	32454	
310.6	33303	
311.1	34141	
311.6	35011	
312.2	35917	
312.7	36826	
313.2	37778	β-RI
313.7	38712	
314.2	39641	
314.8	40516	
315.3	41330	
315.8	42103	
316.3	42835	
316.8	43532	
317.4	44272	
317.9	44906	
318.4	45549	
318.9	46184	
319.4	46826	
319.9	47482	α-RII
320.5	48140	
321.0	48614	
321.5	49534	
322.0	50582	
322.5	60502	
323.1	91693	
323.6	97310	
324.1	97759	
324.6	98225	
325.1	98676	
325.6	99151	
326.2	99612	
326.7	100091	
327.2	100559	
327.7	101039	L
328.2	101516	
328.8	102004	
329.3	102485	
329.8	102942	
330.3	103423	
330.8	103908	
331.3	104384	
331.9	104861	
332.4	105342	
332.9	105814	
333.4	106289	
333.9	106778	
334.5	107282	
335.0	107733	
335.5	108207	
336.0	108680	
336.5	109166	
337.1	109647	
337.6	110132	
338.1	110612	
338.6	111097	
339.1	111584	
339.6	112071	
340.2	112552	
340.7	113028	
341.2	113486	

T: temperature in K; $H^{282.8}(T)$: measured enthalpy, with T=282.8 K as reference, in joule per mole; β'₁: 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_{23}: 80 mol% C_{25} $H^{282.8}(T)$/J mol^{-1}	Phase
282.8	0	
283.8	692	
284.8	1380	
285.9	2073	
286.9	2779	
287.9	3476	
288.9	4185	
289.9	4876	
290.9	5596	β''_2
292.0	6306	
293.0	7018	
294.0	7741	
295.0	8475	
296.0	9212	
297.0	9939	
298.1	10702	
299.1	11485	
300.1	12245	
301.1	13031	
302.1	13823	
303.1	14623	
304.1	15423	
304.6	15774	
305.4	16145	
305.9	16494	
306.4	16823	
306.9	17141	
307.4	17515	
308.0	17886	
308.5	18341	
309.0	18693	
309.5	19077	
310.0	19502	
310.5	19935	
311.1	20476	
311.6	21007	
312.1	21944	
312.6	23085	
313.1	24631	
313.7	26746	
314.2	29428	
314.7	32105	
315.2	36663	
315.7	39616	
316.2	41041	
316.6	41988	
317.3	42969	
317.8	43814	
318.3	44564	
318.8	45285	
319.4	45957	
319.9	46581	
320.4	47161	
320.9	47682	β-RI
321.4	48212	
321.9	48809	
322.5	49395	
323.0	49941	
323.5	50533	α-RII
324.0	51142	
324.5	52000	
325.0	62441	
325.6	89274	
326.1	103509	
326.6	104144	
327.1	104479	
327.6	104797	
328.2	105145	
328.7	105520	
329.2	105878	
329.7	106285	
330.2	106669	
330.7	107001	
331.3	107335	
331.8	107699	L
332.3	108070	
332.8	108432	
333.3	108803	
333.9	109186	
334.4	109554	
334.9	110007	
335.4	110359	
335.9	110687	
336.4	111082	
337.0	111461	
337.5	111859	
338.0	112273	
338.5	112652	
339.0	113003	
339.6	113423	
340.1	113843	

T/K	C_{23}: 84 mol% C_{25} $H^{282.8}(T)$/J mol^{-1}	Phase
282.8	0	
283.8	682	
284.8	1343	
285.9	2023	
286.9	2764	
287.9	3488	
288.9	4191	
289.9	4917	
290.9	5643	
292.0	6368	β''_2
293.0	7078	
294.0	7781	
295.0	8494	
296.0	9235	
297.0	10003	
298.1	10753	
299.1	11528	
300.1	12292	
301.1	13058	
302.3	13836	
302.8	14174	
303.3	14522	
303.8	14866	
304.4	15235	
304.9	15575	
305.4	15929	
305.9	16290	
306.4	16639	
306.9	17006	
307.4	17336	
308.0	17673	
308.5	18039	
309.0	18412	
309.5	18778	
310.0	19168	
310.5	19566	
311.1	19952	
311.6	20367	
312.1	20921	
312.6	21695	
313.1	22674	
313.6	24069	
314.1	25809	
314.7	28350	
315.2	31816	
315.7	36247	
316.2	40092	
316.7	41777	
317.2	42774	
317.7	43743	
318.3	44544	β-RI
318.8	45254	
319.3	45912	
319.8	46529	
320.3	47170	
320.8	47716	
321.3	48258	
321.9	48831	
322.4	49393	α-RII
322.9	49979	
323.4	50546	
323.9	51153	
324.4	51976	
325.0	56830	
325.5	68228	
326.0	99051	
326.5	99382	
327.0	99710	
327.5	100051	
328.0	100387	
328.6	100732	
329.1	101078	
329.6	101418	
330.1	101776	
330.6	102121	
331.1	102474	
331.6	102826	
332.2	103148	
332.7	103447	
333.2	103745	L
333.7	104076	
334.2	104390	
334.7	104722	
335.2	105065	
335.8	105361	
336.3	105702	
336.8	106029	
337.3	106347	
337.8	106647	
338.3	106961	
338.8	107287	
339.4	107605	
339.9	107934	
340.4	108284	

T: temperature in K; $H^{282.8}(T)$: measured enthalpy, with *T*=282.8 K as reference, in joule per mole; β''_2: orthorhombic intermediate solid solution; β-RI: orthorhombic rotator phase; α-RII: rhombohedric rotator phase; *L*: liquid phase

Table 8 Variations of the enthalpy *vs.* temperature

T/K	C_{23}: 88 mol% C_{25} $H^{282.8}(T)$/J mol^{-1}	Phase	T/K	C_{23}: 95 mol% C_{25} $H^{282.8}(T)$/J mol^{-1}	Phase
282.8	0		282.8	0	
283.8	711		283.8	653	
284.8	1429		284.8	1309	
285.9	2155		285.9	1073	
286.9	2867		286.9	2325	
287.9	3596		287.9	2888	
288.9	4347		288.9	3321	
289.9	5069		289.9	4007	
290.9	5822	β''_2	290.9	4865	$\beta_0(C_{25})$
292.0	6539		292.0	5313	
293.0	7314		293.0	5968	
294.0	8060		294.0	6652	
295.0	8799		295.0	7342	
296.0	9574		296.0	8040	
297.0	10318		297.0	8720	
298.1	11072		298.1	9409	
299.1	11853		299.1	10104	
300.1	12632		300.1	10839	
301.1	13432		301.1	11583	
302.1	14173		302.1	12311	
303.1	14936		303.1	13072	
304.1	15715		304.1	13837	
304.8	16094		304.8	14173	
305.4	16442		305.4	14806	
305.9	16795		305.9	15073	
306.4	17145		306.4	15518	
306.9	17512		306.9	15924	
307.4	17872		307.4	16379	
308.0	18228		308.0	16847	
308.5	18594		308.5	17353	
309.0	18942		309.0	17828	
309.5	19295		309.5	18334	
310.0	19664		310.0	18839	
310.5	20037		310.5	19306	
311.1	20400		311.1	19777	
311.6	20768		311.6	20275	
312.1	21161		312.1	20752	
312.6	21578		312.6	21190	
313.1	22001		313.1	21623	
313.7	22479		313.7	22053	$\beta'_0(C_{25})$
314.2	23070		314.2	22419	
314.7	23631		314.7	22825	
315.2	24939		315.2	23268	
315.7	26727		315.7	23720	
316.2	29685		316.2	24187	
316.8	34437		316.8	24674	
317.3	40205		317.3	25454	
317.8	44050		317.8	26921	
318.3	45181		318.3	30801	
318.8	46137		318.8	40549	
319.4	46928		319.4	47312	
319.9	47655	β-RI	319.9	48570	
320.4	48330		320.4	49903	
320.9	48991		320.9	50462	β-RI
321.4	49630		321.4	51189	
321.9	50179		321.9	51971	
322.5	50738		322.5	52853	
323.0	51298		323.0	53302	
323.5	51886	α-RII	323.5	53944	
324.0	52450		324.0	54825	α-RII
324.5	53039		324.5	55322	
325.0	53684		325.0	56053	
325.6	55384		325.6	56994	
326.1	82022		326.1	60417	
326.6	102724		326.6	97009	
327.1	103092		327.1	105048	
327.6	103433		327.6	105477	
328.2	103784		328.2	105908	
328.7	104131		328.7	106346	
329.2	104474		329.2	106811	
329.7	104837		329.7	107247	
330.2	105201		330.2	107681	
330.7	105542		330.7	108131	
331.3	105876		331.3	108561	
331.8	106227	L	331.8	108997	
332.3	106581		332.3	109453	
332.8	106943		332.8	109904	
333.3	107279		333.3	110369	
333.9	107630		333.9	110810	L
334.4	107999		334.4	111245	
334.9	108318		334.9	111695	
335.4	108659		335.4	112155	
335.9	108852		335.9	112585	
336.4	109018		336.4	113035	
337.0	109365		337.0	113476	
337.5	109708		337.5	113927	
338.0	110061		338.0	114357	
338.5	110406		338.5	114806	
339.0	110734		339.0	115262	
339.6	111079		339.6	115718	
340.1	111436		340.1	116159	
340.6	111789		340.6	116598	

T: temperature in K; $H^{282.8}(T)$: measured enthalpy, with T=282.8 K as reference, in joule per mole; β''_2: orthorhombic intermediate solid solution; $\beta_0(C_{25})$: orthorhombic primary solid solution; $\beta'_0(C_{25})$: orthorhombic primary 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_{23}: 97.5 mol% C_{25} $H^{282.8}(T)$/J mol^{-1}	Phase
282.8	0	
283.8	722	
284.8	1367	
285.9	2028	
286.9	2685	
287.9	3336	
288.9	4013	
289.9	4703	
290.9	5380	
292.0	6035	
293.0	6707	$\beta_0(C_{25})$
294.0	7383	
295.0	8077	
296.0	8769	
297.0	9470	
298.1	10189	
299.1	10848	
300.1	11563	
301.1	12273	
302.1	12991	
303.1	13713	
304.3	14455	
304.8	14828	
305.4	15228	
305.9	15601	
306.4	15967	
306.9	16379	
307.4	16782	
308.0	17245	
308.5	17618	
309.0	18007	
309.5	18383	
310.0	18792	
310.5	19218	
311.1	19666	
311.6	20100	
312.1	20573	
312.6	21045	
313.1	21545	
313.7	22086	
314.2	22722	
314.7	23522	
315.2	24322	
315.7	24950	
316.2	25430	$\beta'_0(C_{25})$
316.8	25874	
317.3	26335	
317.8	26821	
318.3	27489	
318.8	29348	
319.4	37307	
319.9	49728	
320.4	50945	
320.9	52096	
321.4	52829	
321.9	53680	
322.5	54432	
323.0	55084	β-RI
323.5	55731	
324.0	56363	
324.5	57021	α-RII
325.0	57705	
325.6	58460	
326.1	60130	
326.6	60566	
327.1	110147	
327.6	110561	
328.2	110969	
328.7	111429	
329.2	111846	
329.7	112276	
330.2	112698	
330.7	113126	
331.3	113558	
331.8	113986	L
332.3	114408	
332.8	114827	
333.3	115244	
333.9	115669	
334.4	116138	
334.9	116564	
335.4	116996	
335.9	117424	
336.4	117851	
337.0	118300	
337.5	118738	
338.0	119182	
338.5	119625	
339.0	120062	
339.6	120490	
340.1	120919	

T/K	C_{25} $H^{282.8}(T)$/J mol^{-1}	Phase
282.8	0	
283.8	632	
284.8	1288	
285.9	1918	
286.9	2542	
287.9	3203	
288.9	3883	
289.9	4546	
290.9	5207	
292.0	5866	
293.0	6549	
294.0	7212	
295.0	7873	
296.0	8560	$\beta_0(C_{25})$
297.0	9274	
298.1	9918	
299.1	10641	
300.1	11342	
301.1	12044	
302.1	12693	
303.1	13362	
304.1	14104	
305.4	14808	
305.9	15134	
306.4	15476	
306.9	15817	
307.4	16165	
308.0	16510	
308.5	16849	
309.0	17187	
309.5	17530	
310.0	17875	
310.5	18220	
311.1	18571	
311.6	18936	
312.1	19342	
312.6	19723	
313.1	20092	
313.7	20476	
314.2	20856	
314.7	21237	
315.2	21610	
315.7	21988	
316.2	22361	
316.8	22742	
317.3	23123	
317.8	23506	
318.3	23916	
318.8	24353	$\beta'_0(C_{25})$
319.4	25129	
319.9	27443	
320.4	40295	
320.9	48968	
321.4	50129	
321.9	51154	
322.5	51985	β-RI
323.0	52638	
323.5	53243	
324.0	53855	α-RII
324.5	54481	
325.0	55093	
325.6	55718	
326.1	56386	
326.6	57523	
327.1	111747	
327.6	113069	
328.2	113471	
328.7	113845	
329.2	114222	
329.7	114590	
330.2	114963	
330.7	115323	
331.3	115686	
331.8	116049	
332.3	116414	
332.8	116782	
333.3	117152	
333.9	117522	L
334.4	117894	
334.9	118265	
335.4	118626	
335.9	118991	
336.4	119358	
337.0	119714	
337.5	120090	
338.0	120473	
338.5	120854	
339.0	121225	
339.6	121602	
340.1	121974	
340.6	122343	

T: temperature in K; $H^{282.8}(T)$: measured enthalpy, with T=282.8 K as reference, in joule per mole; $\beta_0(C_{25})$: orthorhombic primary solid solution; $\beta'_0(C_{25})$: orthorhombic primary solid solution; β-RI: orthorhombic rotator phase; α-RII: rhombohedric rotator phase; L: liquid phase

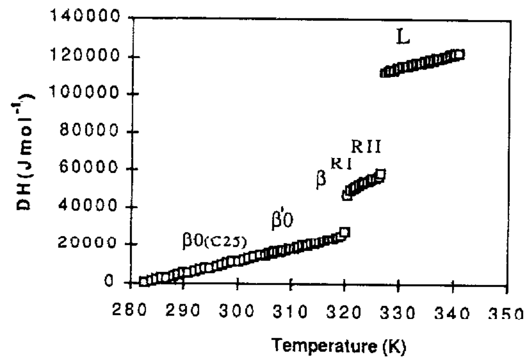

Fig. 1a Enthalpy curve for pure *n*-pentacosane

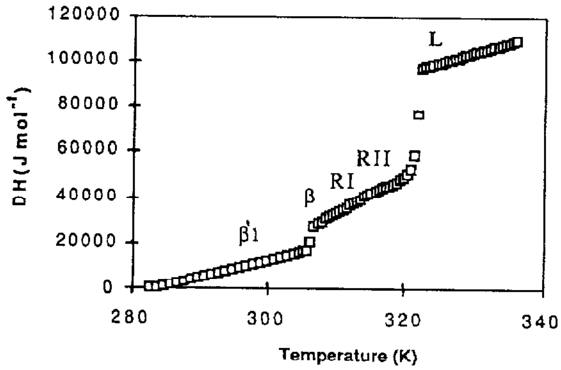

Fig. 1b Enthalpy curve for the mixture containing 30 mol% of *n*-pentacosane

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

$$H(T) - H(282) = \frac{3NR\theta}{\exp(\theta/T)} - H_E$$

The parameters N, θ and the integration constant H_E, are optimised using the Rosenbrock method [23], from the temperature and enthalpy data corresponding to $\beta_o(n\text{-}C_{23})$, $\beta_o'(n\text{-}C_{23})$, β_1'', β_1', β_2'' and $\beta_o(n\text{-}C_{25})$ with the error function which 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 of enthalpy measured for each molar fraction x.
$\Delta H(\theta,x)_{calc}$ is the variation of enthalpy calculated for each molar fraction x.
n is the number of points taken into account for the optimization.

For instance, Table 11 presents the values of the enthalpy variations calculated from the best parameters N,θ and H_E (Table 10), compared to the experimental data for a mixture of 30% molar in C_{25}: the agreement between experimental and calculated values is good; the relative standard deviation is 1.5% as maximum, except for the first value which is always imprecise.

Expressions of the enthalpy $H(T,x)$ as function of the temperature and composition can be defined by the study of the variation of the parameters N and θ *vs.* composition.

Table 10 Parameters N, θ, H_E *vs.* composition in n-$C_{25}H_{52}$

x/mol% in $C_{25}H_{52}$	Phase	Temperature domain/K	N	θ/ K	H_E/ J mol^{-1}	Error function/ J mol^{-1}
0	$\beta_o(C_{23})$	282.8–307.2	60.2	981.9	47276	9716
0.3	$\beta_o(C_{23})$	282.8–309.2	60.4	999.3	45268	19073
0.5	$\beta_o(C_{23})$	282.8–306.2	72.4	1096.3	41884	20559
1.5	$\beta'_o(C_{23})$	282.8–306.2	56.9	937.2	50252	33078
2	$\beta'_o(C_{23})$	282.8–302.1	82.2	1145.9	41576	21096
1.8	$\beta'_o(C_{23})$	282.8–305.2	71.7	1076.2	43761	17116
3	β''_1	282.8–308.2	137.3	1385.7	35578	19520
4	β''_1	282.8–307.2	146.1	1428.6	33464	34729
25	β'_1	282.8–305.2	172.9	1477.9	34395	18531
30	β'_1	282.8–305.2	157.2	1429.0	36038	17256
53	β'_1	282.8–306.2	142.9	1379.9	37588	54337
40	β'_1	282.8–307.2	115.3	1269.7	41370	85523
80	β''_2	282.8–308.2	144.9	1391.8	36865	24780
84	β''_2	282.8–310.2	96.1	1178.7	44428	22140
87.9	β''_2	282.8–310.2	58.8	871.9	61459	6575
95	$\beta_o(C_{25})$	282.8–306.2	72.2	1048.2	47466	9276
97.5	$\beta_o(C_{25})$	282.8–308.2	73.0	1061.9	46239	21185
100	$\beta_o(C_{25})$	282.8–310.2	59.9	953.1	50668	12680

A dispersion of θ 1100 K (Fig. 2) is observed. The parameters N and H_E are again calculated for each composition, with an Einstein temperature equal to 1100 K. Figure 3 and Table 12 present the variations of N and H_E *vs.* composi-

Table 11 Calculated enthalphies and deviations from the experimental enthalpies, for the mixture containing 30 mol% n-C_{25}

T/K	ΔH_{exp}/	ΔH_{calc}/	Deviations
	J mol^{-1}		
282.8	0	−3	3
283.8	686	658	28
284.8	1308	1327	−19
285.8	1975	2004	−29
286.9	2657	2689	−32
287.9	3367	3380	−13
288.9	4079	4080	−1
289.9	4798	4786	12
290.9	5523	5500	23
291.9	6246	6221	25
292.9	6965	6950	15
294.0	7720	7687	33
295.0	8457	8431	26
296.0	9205	9182	23
297.0	9942	9941	1
298.0	10681	10708	−27
299.0	11460	11482	−22
300.0	12228	12264	−36
301.1	13014	13053	−39
302.1	13822	13850	−28
303.1	14630	14654	−24
304.1	15477	15466	11
305.2	16355	16286	69

tion. Finally, a general expression of the enthalpy $H(T,x)$ as a function of the temperature and composition is defined by the following expression:

$$H(T,x) = \frac{3R1100N(x)}{\exp\left(\frac{1100}{T}\right) - 1}$$

with: i) in the terminal solid solution ranges:
for $\beta_o(C_{23})$ and $\beta_o'(C_{23})$: $N(x)$=138.38x+72.66

for $\beta_o(C_{25})$ and $\beta_o'(C_{25})$: $N(x)=-49.115x+125.32$
where x is the molar fraction of C_{25}.

ii) for the orthorhombic intermediate solution β_1'', β_1' and β_2'', the parameter $N(x)$:

$$N(x) = 83.5\pm2$$

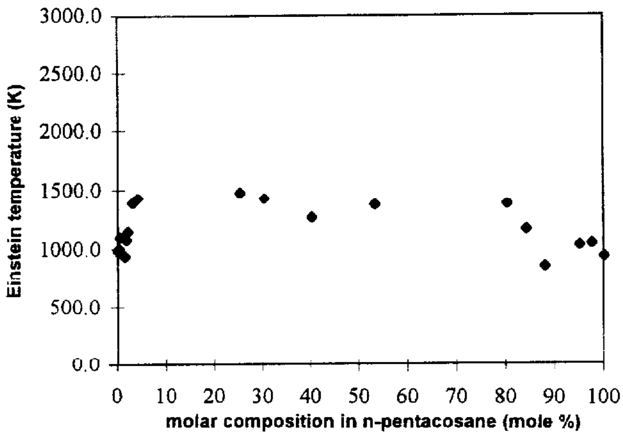

Fig. 2 Einstein temperature *vs.* composition

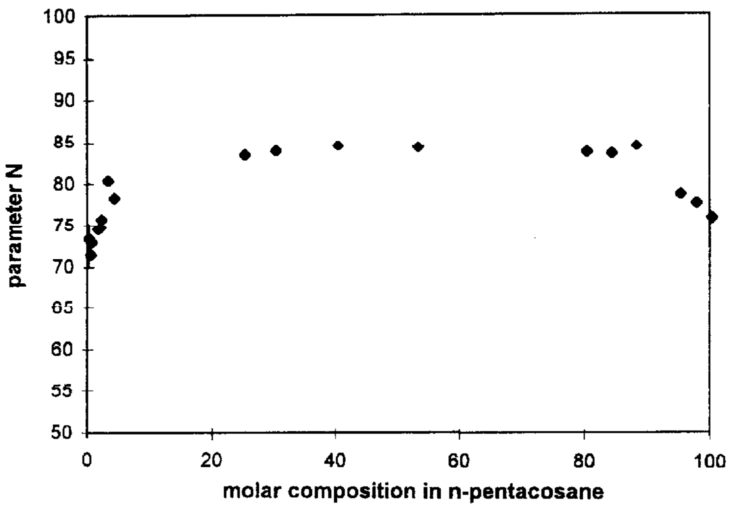

Fig. 3 Values of the parameter N *vs.* composition, with a constant Einstein temperature of 1100 K

Table 12 Parameters N, θ, H_E *vs.* composition in n-$C_{25}H_{52}$

x/mol% in $C_{25}H_{52}$	Phase	Temperature domain/K	N	θ/ K	H_E/ J mol^{-1}	Error function/ J mol^{-1}
0	$\beta_o(C_{23})$	282.8–307.2	73.4	1100	42002	17343
0.3	$\beta_o(C_{23})$	282.8–309.2	71.5	1100	40895	26291
0.5	$\beta_o(C_{23})$	282.8–306.2	72.9	1100	41737	20564
1.5	$\beta'_o(C_{23})$	282.8–306.2	74.5	1100	42644	44854
1.8	$\beta'_o(C_{23})$	282.8–302.1	74.7	1100	42766	17319
2	$\beta'_o(C_{23})$	282.8–305.2	75.8	1100	43389	21534
3	β''_1	282.8–308.2	80.4	1100	46150	94538
4	β''_1	282.8–307.2	78.3	1100	44921	113240
25	β'_1	282.8–305.2	83.4	1100	47848	96066
30	β'_1	282.8–305.2	83.9	1100	48177	76579
40	β'_1	282.8–306.2	84.6	1100	48453	108628
53	β'_1	282.8–307.2	84.4	1100	48371	107006
80	β''_2	282.8–308.2	83.8	1100	48077	108995
84	β''_2	282.8–310.2	83.6	1100	47947	30935
87.9	β''_2	282.8–310.2	84.6	1100	48385	67952
95	$\beta_o(C_{25})$	282.8–306.2	78.9	1100	45118	10412
97.5	$\beta_o(C_{25})$	282.8–308.2	77.8	1100	44532	22072
100	$\beta_o(C_{25})$	282.8–310.2	76.1	1100	43539	30884

Conclusions

In this work, we determined the variation of the enthalpy of C_{23}, C_{25} and 16 binary mixtures between 282 K and 350 K. These data concerning binary mixtures of the phases $\beta_o(C_{23})$, $\beta'_o(C_{23})$, $\beta_o(C_{25})$, $\beta'_o(C_{25})$, β''_1, β'_1, β''_2 as well as the phases of the pure n-alkanes C_{23} and C_{25}, have been represented by an analytical expression, derived from Einstein's model of the solid state.

Expressions of the enthalpy, as a function of the temperature and molar fraction of C_{25}, has been defined for the ranges of the terminal solid solutions and of the intermediate solid solution, respectively. This study gives new results about the binary systems C_{23}:C_{25} and these results could be used for the determination of the thermodynamic functions of mixing, necessary to calculate solid–solid equilibria.

References

1 P. Barbillon, L. Schuffenecker, J. Dellacherie, D. Balesdent and M. Dirand, J. Chim. Phys., 88 (1991) 91.
2 P. M. Goghomu, J. Dellacherie and D. Balesdent, J. Chem. Thermodyn., 21 (1989) 925.
3 P. M. Goghomu, J. Dellacherie and D. Balesdent, Thermochim. Acta, 157 (1990) 241.
4 N. Hasnaoui, J. Dellacherie, L. Schuffenecker, M. Dirand and D. Balesdent, J. Chim. Phys., 85(2) (1988) 153.
5 N. Hasnaoui, J. Dellacherie, L. Schuffenecker, M. Dirand and D. Balesdent, J. Chim. Phys., 85(6) (1988) 675.
6 Z. Achour, J. B. Bourdet, M. Bouroukba and M. Dirand, J. Chim. Phys., 89 (1992) 707.
7 Z. Achour, P. Barbillon, M. Bouroukba and M. Dirand, Thermochim. Acta, 204 (1992) 187.
8 Z. Achour, J. B. Bourdet, M. Bouroukba and M. Dirand, J. Chim. Phys., 90 (1993) 325.
9 Z. Achour-Boudjema, J. B. Bourdet, D. Petitjean and M. Dirand, J. Mol. Struct., 354(3) (1995) 197.
10 Z. Achour-Boudjema, M. Bouroukba and M. Dirand, Thermochim. Acta (in press).
11 M. Dirand and Z. Achour-Boudjema, J. Mol. Struct., 375 (1996) 243.
12 A. Sabour, J. B. Bourdet, M. Bouroukba and M. Dirand, Thermochim. Acta, 269 (1995) 249.
13 B. Jouti, D. Petitjean, E. Provost, M. Bouroukba and M. Dirand, J. Mol. Struct., 356(3) (1995) 191.
14 B. Jouti, E. Provost, D. Petitjean, M. Bouroukba and M. Dirand, J. Mol. Struct., (in press).
15 B. Jouti, J. B. Bourdet, M. Bouroukba and M. Dirand, Mol. Cryst. Liq. Cryst., 270 (1995) 159.
16 B. Jouti, E. Provost, D. Petitjean, M. Bouroukba and M. Dirand, Mol. Cryst. Liq. Cryst., (in press).
17 M. Dirand, Z. Achour, B. Jouti, A. Sabour and J. C. Gachon, Mol. Cryst. Liq. Cryst., 275 (1996) 293.
18 Z. Achour-Boudjema, M. Bouroukba, D. Balesdent, E. Provost and M. Dirand, J. Thermal Anal. (in press).
19 E. Calvet et H. Prat, Microcalorimétrie. Applications physico-chimiques et biologiques (lère édition), Masson et Cie, Paris, 1956.
20 F. Hanrot, D. Ablitzer, J. L. Houzelot and M. Dirand, FUEL, 73(2) (1994) 305.
21 D. A. Ditmars, S. Ishibara, S. S. Chang and G. Bernsten, J. Res. Nat. Bur. Ltds, 87(2) (1982) 159.
22 R. J. Andon and J. F. Martin, J. Chem. Therm., 8 (1976) 1159.
23 H. H. Rosenbrock, J. 3, 175 (1960).