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Excess thermodynamic properties of some binary solutions of ethylbenzene + *n*-alkanes

P.M. Ghogomu[a], M. Bouroukba[b], J. Dellacherie[b], D. Balesdent[b], M. Dirand[b,*]

[a] *Department of Inorganic Chemistry, Faculty of Science, University of Yaounde I, P.O. Box 812, Yaounde, Cameroon*

[b] *Laboratoire de Thermodynamique des Séparations, Ecole Nationale Supérieure des Industries Chimiques, 1 Rue Grandville, BP No. 451, 54001 Nancy Cedex, France*

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Abstract

Some thermodynamic properties (excess enthalpies, entropies and Gibbs energies of mixing) have been determined for binary solutions of ethylbenzene + *n*-alkanes (eïcosane, $C_{20}H_{42}$; heneïcosane, $C_{21}H_{44}$; docosane, $C_{22}H_{46}$; tricosane, $C_{23}H_{48}$; and tetracosane, $C_{24}H_{50}$), at crystallization temperatures in the (260–305) K range. The calculated properties vary with the chain lengths of the *n*-alkanes, and show the alternation effect occurring in the general behaviour of *n*-alkanes. Simple analytical expressions have been established to describe the excess properties. © 1997 Elsevier Science B.V.

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1. Introduction

Normal paraffin hydrocarbons with chain lengths ranging from 18 to 24 carbon atoms are the principal constituents of the solid wax deposits responsible for the restriction of the flow of oils at low temperatures. These organic substances have therefore been the subject of several research works over the past years. Unfortunately, most of these works have been concerned, in the most part, with the structural properties of the pure *n*-alkanes and some of their binary mixtures. A lesser amount of work has been carried out on their physico-chemical properties, let alone on their thermodynamic properties in solution. Solution thermodynamics has hitherto been applied to binary mixtures of organic solvents + lower *n*-alkanes [1–6].

Experimental investigations of the solubility of the higher members of the homologous series in various simple and mixed solvents have been reported, [7–17] while theoretical studies have been limited to the correlation of these results with the use of predictive equations [10,11,16,17].

In particular, many workers have been engaged in the development of theories of solution which render possible the interpretation and the prediction of the thermodynamic excess properties of binary solutions in which at least one component is an *n*-alkane. This has led to tractable analytical expressions derived through extensions of the corresponding-states principle [18,19], Prigogine's theory [20–22], the Flory theory [23–26], and general group-contributions methods [27,28]. These works have been very impor-

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*Corresponding author. Tel.: 00 33 03 83 17 50 00; fax: 00 33 03 83 35 08 11; e-mail: mdirand@ensic.u-nancy.fr.

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tant for a better understanding of the thermodynamic behaviour of non-electrolyte mixtures.

In this paper, we report the values of some excess properties calculated from experimental measurements carried out in this laboratory. The solubility of n-alkanes from C_{20} to C_{24} in ethylbenzene has been measured, for temperatures in the (260–305) K range [29,30]. The corresponding heats of mixing have also been determined by calorimetry [38] while the enthalpy functions of the pure n-alkanes in the solid and liquid states were measured using a differential scanning calorimeter [36]. In the next section, we show how these results lead to the calculation of the excess thermodynamic properties of the binary mixtures.

2. Theory

The solubility of non-polymorphous solids in liquids has been thoroughly investigated in most texts on non-electrolyte solutions. When a solid-phase transition is present, the solubility equations for temperatures below the transition point must include terms for the effect of the phase transition. The n-alkanes studied here show transition in the solid phase below their melting points. While the values of thermodynamic quantities relative to the melting transition of these compounds are known with some accuracy, the values relevant to their solid-phase transitions have continued to be the object of much controversy. The values given for the enthalpy of transition for docosane, for example, may differ from one author to another by as much as 5 kJ mol^{-1}. This would obviously lead to defects in the calculation of the activity coefficients. We have therefore decided to use basic first principles.

Let us consider the process of crystallization in which the deposited solid crystal is in equilibrium with the saturated liquid solution. The thermodynamic condition for this equilibrium is the equality of the chemical potentials (g) of each component (i) in the crystal and in the liquid solution:

$$g_i^{\text{crystal}}(T,y) = g_i^{\text{solution}}(T,x) \qquad (1)$$

where T is the crystallization temperature, and y and x represent the compositions of crystal and solution, respectively. The chemical potential of the paraffin (component 2) may be expressed as a sum of two terms: one relative to pure liquid (2) and the other to the effect of mixing. Also, we consider that the crystal deposited is pure solid (2) in its stable crystalline form at temperature T. Eq. (1) applied to component 2, thus, becomes

$$g_2^{\text{pure solid}}(T) = g_2^{\text{pure liquid}}(T) + g_2^{\text{m}}(T,x) \qquad (2)$$

where $g_2^{\text{m}}(T,x)$ is the partial molar Gibbs free energy of mixing for component 2.

The molar Gibbs free energy, g, may be given in terms of the molar enthalpy h, molar entropy s and the absolute temperature T by the fundamental thermodynamic equation:

$$g = h - Ts \qquad (3)$$

Eq. (2) may then be rewritten in the following form:

$$g_2^{\text{m}}(T,x) = [h_2(T) - Ts_2(T)]^{\text{pure solid}} - [h_2(T) - Ts_2(T)]^{\text{pure liquid}} \qquad (4)$$

The terms on the right-hand side may be calculated from calorimetric measurements carried out in this laboratory [36]. The mixing energy function $g_2^{\text{m}}(T,x)$ can be given in two parts:

$$g_2^{\text{m}}(T,x) = RT\ln x_2 + g_2^{\text{e}}(T) \qquad (5)$$

where $RT\ln x_2$ represents the Gibbs free energy of mixing for an ideal solution, and $g_2^{\text{e}}(T)$ the excess partial molar Gibbs free energy for component 2. Solubility results, reported elsewhere [29], give values of the saturation concentrations x_2 at given temperatures. The $g_2^{\text{e}}(T)$ terms may then be calculated.

3. Thermodynamic functions (H,S) for pure n-alkanes

While low-temperature thermal data are available in the literature for the n-alkanes C_5 to C_{18} [32,33], for n-hexacosane [34] and for other high-molecular weight hydrocarbons [35], n-alkanes from C_{19} to C_{25} have surprisingly not been the object of thermal analysis; their thermodynamic properties have often been calculated through extrapolations from the existing values available in literature [8–17]. However, some of these alkanes were studied by many authors [39–42], and particularly by Hasnaoui [36], using DSC and the values for the C_{18}–C_{26} homologues have been revised by Barbillon et al. [31]. In the present work, we use the synthesis developed by Ghogomu [17].

Table 1
Numerical values of the constants in the expressions of the thermodynamic state functions of *n*-alkanes (*n* is the number of carbon atoms in the molecule)

n	β_0/ K	β_1/ J mol^{-1}	β_2/ J mol^{-1}	β_3/ J mol^{-1} K^{-1}	β_4/ J mol^{-1} K^{-2}	$s^0_{\beta,260}$/ J mol^{-1} K^{-1}	$S^0_{1,260}$/ J mol^{-1} K^{-1}	L_0/ J mol^{-1}	L_1/ J mol^{-1} K^{-1}
20	450	633	179100	−1262	2.21	462	662	−4000	634
21	455	673	179700	−1279	2.270	484	693	−41460	660
22	423	648	94940	−664	1.16	503	718	−44090	697
23	487	784	190940	−1338	2.34	524	750	−45890	724
24	449	741	121160	−838	1.44	543	773	−47920	757

The enthalpy function for each of the compounds in the low-temperature (β)[1] crystal form at the temperature T (260$^2T^2$ 340 K) is expressed as:

$$H^0_{\beta,T} = \frac{\beta_0\beta_1}{(e^{\beta_0/T} - 1)} + \beta_2 + \beta_3 T + \beta_4 T^2$$

where β_0, β_1, β_2, β_3 and β_4 are constants, characteristic of each *n*-alkane. For the liquid state, the enthalpy fitted a linear relationship with temperature:

$$H^0_{1,T} = L_0 + L_1 T$$

Other expressions have been reported for the high-temperature stable solids ('rotator' phases), but will not be given here as they do not enter into our calculations.

The entropy functions were derived from these expressions in conjunction with the second law of thermodynamics. The standard molar entropies at 260 K were extrapolated from literature values as explained by Ghogomu [17]. The integral form of the entropy functions can be expressed as:

$$S^0_{\varphi,T} = S^0_{\varphi,260} + \int_{260}^{T} \frac{dH}{T}$$

where φ is the state of matter (β-form solid, or liquid), and $S^0_{\varphi,T}$ the standard molar entropy at absolute temperature T. The numerical values of $S^0_{\beta,260}$ and $S^0_{1,260}$ are given in Table 1 together with those of the constants $\beta_0, \ldots, \beta_4$, L_0 and L_1. The expressions of $S^0_{\varphi,T}$ are given in Table 3(a).

4. Thermodynamic properties of the *n*-alkanes in solution

4.1. Activities and activity coefficients

The enthalpy and entropy functions given in Section 3 were used to calculate the Gibbs free energy of mixing $g^m_2(T,X)$ according to Eq. (4). Since this mixing property is related to activity by the expression:

$$g^m_2(T,x) = RT \ln a_2(T,x) \qquad (6)$$

the activity of each paraffin may be calculated for a given temperature T (it should be noted that the $T = f(x)$ relationship is univocal such that any property will simultaneously be a function of T and x). Activity is related to composition (x_2) by Eqs. (5) and (6); it is therefore possible to calculate the activity coefficients γ_2 given by:

$$g^e_2(T) = RT \ln\gamma_2(T) \qquad (7)$$

We present, in Table 2, the values of x_2, γ_2 and a_2 for each *n*-alkane at crystallization temperature T.

4.2. Excess properties

The excess partial molar Gibbs free energy for each paraffin i, in the liquid binary mixture with ethylbenzene, may be calculated from the partial molar Gibbs free energy of mixing as given by Eq. (5):

$$g^e_i(T) = g^m_i(T,x) - RT \ln x_i$$

This excess property is related to the excess partial molar enthalpy and entropy by

$$g^e_i(T) = h^e_i - Ts^e_i$$

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[1] Orthorhombic structure (Pbcm) for the odd-numbered *n*-alkanes or triclinic structure for the even-numbered homologues [43]. Both structures are herein designated β.

Table 2
Activities (a) and activity coefficients (γ) of n-paraffins in solution in ethylbenzene. x is the solubility at temperature T

T/ K	x	a	γ
2(a): n-Eïcosane			
266.51	0.0095	0.0142	1.490
270.31	0.0150	0.0214	1.434
272.71	0.0195	0.0276	1.415
275.6	0.0265	0.0379	1.430
278.21	0.0364	0.0489	1.344
281.96	0.0536	0.0717	1.337
282.81	0.0614	0.0782	1.273
284.96	0.0790	0.0972	1.228
286.16	0.0904	0.109	1.209
287.11	0.104	0.121	1.165
288.26	0.116	0.134	1.153
289.66	0.136	0.154	1.138
290.51	0.151	0.168	1.113
291.26	0.164	0.180	1.101
292.96	0.179	0.200	1.118
292.96	0.191	0.212	1.109
293.91	0.204	0.232	1.133
2(b): n-Heneïcosane			
262.51	0.0047	0.0097	2.067
268.01	0.0100	0.0182	1.815
275.51	0.0260	0.0413	1.589
278.56	0.0366	0.0571	1.561
281.91	0.0550	0.0811	1.475
284.96	0.0739	0.111	1.505
286.61	0.0950	0.132	1.385
288.46	0.115	0.159	1.376
290.00	0.140	0.185	1.322
291.16	0.164	0.207	1.264
293.16	0.201	0.252	1.259
294.56	0.234	0.290	1.236
295.71	0.263	0.324	1.232
2(c): n-Docosane			
268.66	0.0044	0.0051	1.161
274.21	0.0085	0.0098	1.155
277.46	0.0123	0.0143	1.161
281.31	0.0202	0.0223	1.103
284.41	0.0294	0.0313	1.064
286.56	0.0381	0.0395	1.038
289.51	0.0539	0.0545	1.011
291.71	0.0702	0.0690	0.982
293.51	0.0865	0.0838	0.969
295.46	0.107	0.103	0.962
296.91	0.127	0.119	0.941
297.86	0.143	0.132	0.922
298.81	0.156	0.145	0.932
299.86	0.171	0.162	0.948
300.56	0.186	0.174	0.933
301.26	0.198	0.187	0.944
302.01	0.213	0.202	0.951
302.46	0.226	0.211	0.931
2(d): n-Tricosane			
271.11	0.0037	0.0086	2.316
280.11	0.0136	0.0249	1.833
285.86	0.0295	0.0484	1.641
288.61	0.0415	0.0658	1.586
292.61	0.0699	0.1020	1.459
295.01	0.0940	0.132	1.407
297.36	0.124	0.169	1.367
298.76	0.146	0.197	1.341
300.51	0.173	0.236	1.367
300.91	0.184	0.245	1.335
2(e): n-Tetracosane			
272.01	0.0027	0.0023	0.849
279.76	0.0069	0.0061	0.885
285.61	0.0142	0.0125	0.882
289.10	0.0224	0.0190	0.848
292.76	0.0346	0.0291	0.842
296.00	0.0511	0.0424	0.831
299.01	0.0732	0.0598	0.817
301.51	0.0997	0.0791	0.794
303.06	0.117	0.0941	0.803
304.86	0.144	0.115	0.798
306.16	0.163	0.132	0.807

The enthalpy term may be calculated from the experimental results obtained from calorimetry [38]; and the entropy term may then be deduced.

4.2.1. Excess partial molar enthalpy, h_i^{e}

We have measured the enthalpies of mixing ethylbenzene + n-alkanes in the liquid phase at temperatures in the (298.15–330.00) K range, for concentrations of n-alkanes < 15 mol%, using a Setaram C80D calorimeter [38]. The results show that the total molar mixing enthalpy h^{m}, may be expressed in terms of mole fraction x, the number of carbon atoms n, and temperature T, by an expression of the form:

$$h^{\mathrm{m}} = x(1-x)[A(n,T) + (2x-1)B(n,T)]$$

where A and B are constants, independent of x, but functions of n and T. The root-mean-square deviation calculated for all the experimental points (n varied from 16 to 25 and T from 298.15 to 330.00 K) was 0.0267.

The excess partial molar enthalpy h_i^{e} for each paraffin i is then given by:

$$h_i^{\mathrm{e}} \equiv h^{\mathrm{m}} + (1-x)\frac{\partial h^{\mathrm{m}}}{\partial x} = (1-x)^2[A(n,T) + (4x-1)B(n,T)]$$

Table 3

(a) Expressions of the entropy function of pure *n*-alkanes

Solid β:

$$S^0_{\beta,T} = S^0_{\beta,260} + \beta_0\beta_1\left[\frac{1}{T}\left(\frac{e^{\beta_0/T}}{e^{\beta_0/T}-1}\right) - \frac{1}{260}\left(\frac{e^{\beta_0/260}}{e^{\beta_0/260}-1}\right)\right] + \beta_3\ln(T/260) + 2\beta_4(T-260)$$

Liquid:

$$S^0_{1,T} = s^0_{1,260} + L_1\ln\left(\frac{T}{260}\right)$$

(b) Numerical values of the constants in the analytical expressions of h^e and s^e:

$A(n,T) = A_0 + A_1 n + A_2 T + A_3 T^2$

$B(n,T) = B_0 + B_1 n + B_2 n^2 + B_3 T$

$A_0 = -40475\ \mathrm{J\ mol^{-1}}$	$B_0 = -16255\ \mathrm{J\ mol^{-1}}$
$A_1 = -329.8\ \mathrm{J\ mol^{-1}}$ (carbon atom)$^{-1}$	$B_1 = -791\ \mathrm{J\ mol^{-1}}$ (carbon atom)$^{-1}$
$A_2 = 268.9\ \mathrm{J\ mol^{-1}K^{-2}}$	$B_2 = 3.6\ \mathrm{J\ mol^{-1}}$ (carbon atom)$^{-2}$
$A_3 = 0.37\ \mathrm{J\ mol^{-1}K^{-2}}$	$B_3 = 82.6\ \mathrm{J\ mol^{-1}K^{-1}}$

(c)$S^e_i(n,x,260) = (1-x)^2(a+bx+cx^2)$

n-alkane	*a*	*b*	*c*
Eïcosane (C2O)	11.4	−138	−67.3
Heneïcosane (C21)	20.9	−132	−15.3
Docosane (C22)	16.1	−161	−54.9
Tricosane (C23)	12.7	−147	−157
Tetracosane (C24)	24.4	−178	22

The expressions and numerical values of $A(n,T)$ and $B(n,T)$ are given on Table 3(b).

4.2.2. Excess partial molar entropy, s^e_i

The excess partial molar entropy may be derived from the excess partial molar enthalpy by:

$$s^e_i(n,x,T) = \int_{T_0}^{T} \frac{1}{T}\left(\frac{\partial h^e_i}{T}\right)_{n,x} \mathrm{d}T + s^e_i(n,x,T_0)$$

where $s^e_i(n,x,T_0)$ is a constant at T_0, depending only on x. For each paraffin, it is possible to calculate this constant at various points on the solubility curve $T_s = f(x)$. At $T = T_s$:

$$s^e_i(n,x,T_s) = \frac{h^e_i(n,x,T_s) - g^e_i(n,x,T_s)}{T_s}$$

such that:

$$s^e_i(n,x,T_0) = s^e_i(n,x,T_s) - (1-x)^2[(A_2 + (4x-1)B_3)\ln\left(\frac{T_s}{T_0}\right) + 2A_3(T_s - T_0)]$$

This function can take an expression of the form:

$$s^e_i(n,x,T_0) = (1-x^2)[a(n) + b(n)x + c(n)x^2]$$

$a(n)$, $b(n)$, and $c(n)$ are found to have no simple relationship with n. So, for each paraffin we define a constant

$$s^e_i(n,x,T_0) = (1-x^2)[a + bx + cx^2]$$

The values of a, b and c are given in Table 3(c). The r.m.s. deviation is < 0.04 for all the *n*-alkanes.

For each *n*-alkane, it is possible to calculate the excess partial molar entropy at constant concentration (respectively, constant temperature) for various values of temperature (respectively, concentration ranges) according to the final equation:

$$s^e_i(n,x,T) = (1-x)^2[(A_2 + (4x-1)B_3)\ln\left(\frac{T}{260}\right) + 2A_3(T-260) + a + bx + cx^2]$$

We have plotted $s^e_i = f(T)$ for $x = 0.05$ for all *n*-alkanes studied here (Fig. 1(a)). In Fig. 1(b) we

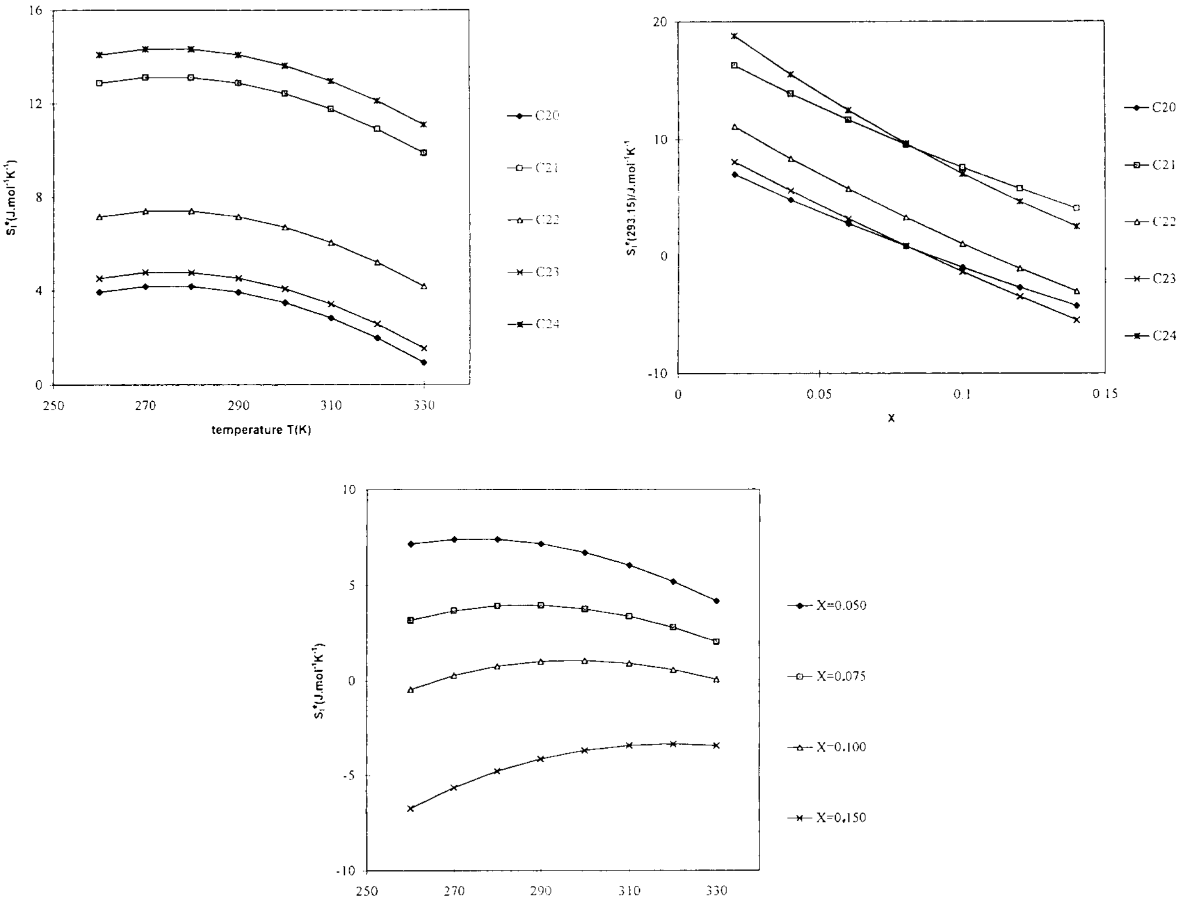

Fig. 1. (a) – Excess partial molar entropies for $x = 0.05$; (b) – $S_i^e(293.15) = f(x)$; and (c) – $S_i^e = f(T)$ for docosane.

have plotted $s_i^e = f(x)$ for $T = 293.15$ K for all the n-alkanes. Finally, we have plotted $s_i^e = f(T)$ for docosane at $x = 0.050$, 0.075 and 0.100 (Fig. 1(c)).

These curves show that the values for the even-numbered homologues show a simple increasing relationship with the number of carbon atoms, but the odd n-alkanes do not seem to follow this scheme. Such a behaviour could be a result of the alternation effects seen in the solubilities of the n-alkanes [29]. Since excess enthalpies show regular increments with n at constant temperature, it may be said that entropy effects account for the differences in solubility between the odd- and even-numbered n-alkanes.

4.2.3. Excess partial molar free enthalpy, g_i^e

A combination of the analytical expressions of h_i^e and s_i^e leads to that of g_i^e at given concentration x_i and temperature T:

$$g_i^e(T, x_i) = (1 - x)^2 \Bigg[A(n, T) + (4x - 1)B(n, T) - T\left[(A_2 + (4x - 1)B_3) \ln\left(\frac{T}{260}\right) + 2A_3(T - 260) + a + bx + cx^2 \right] \Bigg]$$

5. Conclusion

The results of calorimetric measurements and solubility have permitted the calculation of the activities,

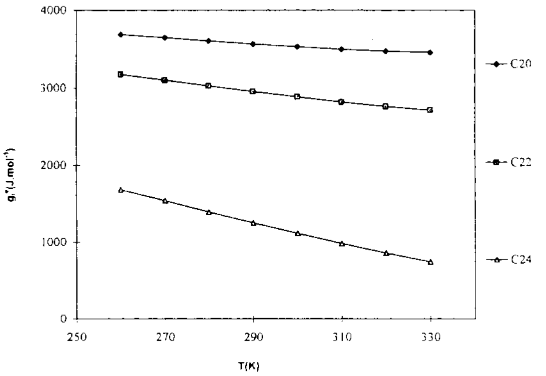

Fig. 2. Excess partial molar Gibbs energy of even-numbered alkanes according to the temperature for a molar fraction $x = 0.05$ in the ethylbenzene.

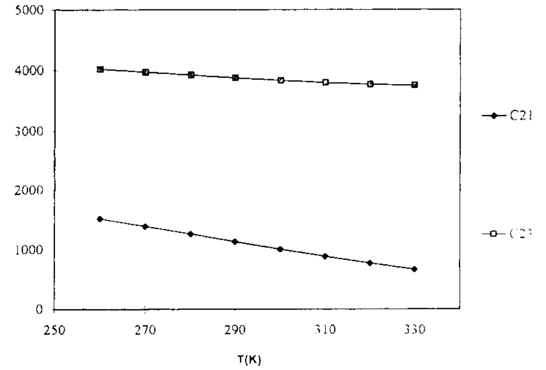

Fig. 3. Excess partial molar Gibbs energy of the odd-numbered alkanes vs. temperature for a molar fraction $x = 0.05$ in ethylbenzene.

activity coefficients and partial molar excess properties of *n*-alkanes in dilute solutions in ethylbenzene. Simple analytical expressions have been used to describe the molar excess enthalpies, entropies and Gibbs energies.

The thermodynamic properties of *n*-alkanes reported in this work, show that their variations with chain length are different for even-numbered and odd-numbered compounds (Figs. 2 and 3). The structure and properties of *n*-alkane liquids seem to be intimately linked to the corresponding solid structures. In effect, the structure of *n*-alkane liquids may influence their thermodynamic mixing properties, as shown by Lichtenthaler and Heintz [37]. Their work was, unfortunately, restricted to even-numbered *n*-alkanes and their isomers. More work is needed, for a better comprehension of the entropy effects on solubility.

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