Estimation of the Enthalpy of Formation of Multialkane Synthetic Mixtures: Measurement by Mixing Calorimetry and Modeling by the UNIQUAC Model

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Measurements of the dissolution enthalpies in heptane at ambient temperature were carried out by mixing calorimetry on multialkane synthetic mixtures with an exponentially decreasing distribution of the *n*-alkane mole compositions, as observed in petroleum cuts. These experimental results and those of literature concerning the pure *n*-alkane dissolution enthalpies in the same experimental conditions allow us to determine the enthalpy of the formation of one or several crystallized solid solutions of these mixtures and thus, to highlight the influence of the characteristic parameters of the paraffinic distribution (theoretical average chain length, *n*-alkanes number, monophasic or polyphasic state) on the excess properties in the solid state. Second, this data bank permits us to test the predictive capacities of the UNIQUAC thermodynamic model. After modifying the expression of the interaction energy λ_{ij} to take into account the effect of the size difference between the *n*-alkanes of the mixture and the internal disorder induced by the *n*-alkane distribution length, this model gives very good results for the prediction of the excess enthalpy of complex multialkane samples.

Introduction

Accumulation of waxy deposits is a commonly occurring problem during the exploitation and the transport of paraffinic crude oils in very cold regions. Removal of these undesirable solids increases production costs and could cause damage to industrial equipment. An adequate thermodynamic model to describe solid/liquid equilibrium would be helpful to predict the solid deposition conditions and thus to adjust exploitation parameters. In recent years, more effort has been spent on the development of a model[1−4] able to represent the solubility and the solid/liquid equilibrium, and this requires a lot of experimental data. Consequently, the measurements of the solubility of pure *n*-alkanes[5−29] (hereafter denoted by C_n for simplification, *n* being the carbon atom number of the chain) and of binary,[16,27,30] ternary,[30] synthetic, and real complex mixtures[31−37] of C_ns in solvents are numerous because they constitute an essential data bank.

However there are very few experimental data on the enthalpies of formation of solid phases formed by complex multi-C_n mixtures. This lack of experimental data does not allow us to determine the excess enthalpies of these phases and to improve the mathematical representation of these excess properties. Indeed, the UNIQUAC model is very successful with solid phases of simple mixtures of C_ns whose chain lengths are close, but it is not really appropriate for complex systems where the C_n chain lengths disparity can be great.

This paper will bring a contribution to the two aspects of the problem by:

(1) The experimental measurement of the enthalpies of formation of solid phases of synthetic multi-C_n mixtures, differing by their average chain length and the C_n number, to highlight correlations between the characteristic parameters of the C_n mole compositions distribution and the evolution of the enthalpy of formation of the solid solutions.

(2) The use of the UNIQUAC model, after adjustment, for the prediction of the excess values.

Measurement of Dissolution Enthalpies and Estimation of the Formation Enthalpies of the Solid Phases of Complex Synthetic Multi-C_n Mixtures

Principle of Estimation of the Enthalpies of Formation of Solid Phases. To determine the formation enthalpies of the solid phases of multi-C_n mixtures, we undertook the measurement of their dissolution enthalpies in heptane at ambient temperature (T = 296.15 K) by mixing calorimetry. To obtain the different thermodynamic properties involved with the dissolution of synthetic multi-C_n samples in heptane, we represented the thermochemical cycle of the dissolution of a polyphasic mixture, at a given temperature T, in Figure 1. The following general equation was derived

$$\Delta_{\text{diss}}H(\text{mixture}) = \sum_{k=1}^{p} x_k \Delta_{\text{diss}}H(C_k) + \Delta H_{\text{liq}}^{\text{exc}} - \sum_{j=1}^{q} \Delta_{\text{form}}H(\varphi_j) \quad (1)$$

where $\Delta_{\text{diss}}H$(mixture) is the dissolution enthalpy of the mixture in a solvent, $\Delta_{\text{diss}}H(C_k)$ is the dissolution enthalpy of the pure C_ns of the mixture in the same experimental conditions, $\Delta_{\text{form}}H(\varphi_j)$ is the enthalpy of formation of φ_j in the solid phase, $\Delta H_{\text{liq}}^{\text{exc}}$ is the excess enthalpy in the liquid phase, p is the C_n number in the mixture, q is the phase

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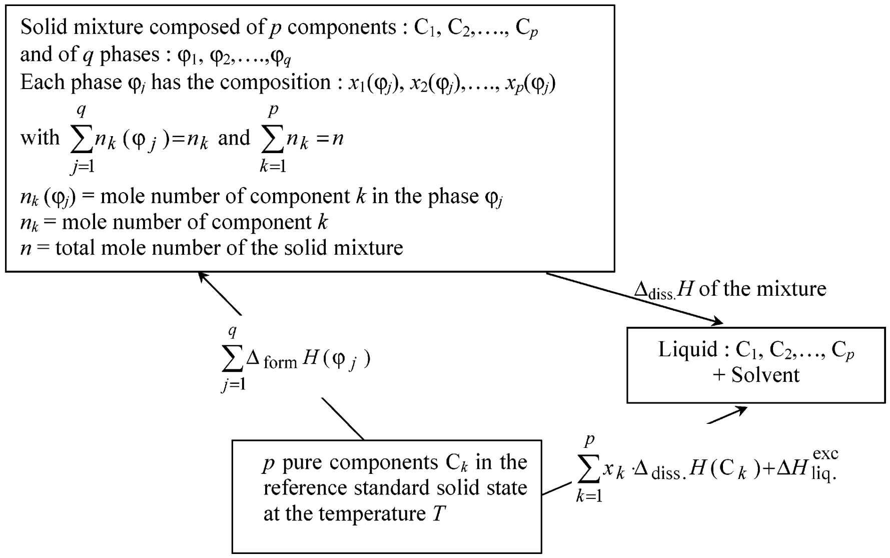

with : $\Delta_{\text{diss.}}H$ = enthalpy of dissolution of a multi-C_n solid mixture or of a pure solid C_n
$\Delta_{\text{form.}}H$= enthalpy of formation of a solid solution from pure solid C_n
$\Delta H_{\text{liq}}^{\text{exc}}$ = enthalpy of mixing of pure C_n in the liquid phase

Figure 1. Thermochemical cycle of the dissolution of a multi-C_n polyphasic mixture, at a given temperature T.

number in the mixture, and x_k is the C_n mole fraction in the mixture.

According to literature results,[38,39] the enthalpy of mixing of C_ns in the liquid phase is almost equal to zero and the mixing enthalpy[24−26,38] of two paraffinic complex liquid phases is always lower than 1 J·g^{-1}; thus, $\Delta H_{\text{liq}}^{\text{exc}} = 0$ for the multi-C_n mixtures. In a previous paper,[39] we determined the enthalpies of dissolution in heptane of C_ns with chain lengths ranging from 22 to 36 carbon atoms at ambient temperature ($T = 296.15$ K) and highlighted (1) a linear relation between the enthalpies of dissolution and the n carbon atom number and (2) the athermal character of the mixing process of a C_n in the liquid phase with a solvent of the same nature.

From experimental enthalpy data of dissolution of pure C_ns and of their multi-C_n mixtures in the same experimental conditions and according to the eq 1, it is possible to evaluate the enthalpy of formation of one or several solid solutions of synthetic mixtures

$$\sum_{j=1}^{q} \Delta_{\text{form}} H(\varphi_j) = \sum_{k=1}^{p} x_k \Delta_{\text{diss}} H(C_k) - \Delta_{\text{diss}} H(\text{mixture}) \quad (2)$$

The excess enthalpy in the solid phase can be calculated from the enthalpy of formation and the transition enthalpies of the reference states of pure components. Indeed, the excess enthalpy of a solid phase φ is equivalent to the enthalpy of formation of this phase from the pure constituents taken in the same crystalline state as that of the solid phase φ at the considered temperature. However, for polyphasic mixtures, it is impossible to separate the contribution of each phase to the total measured enthalpy of formation.

Samples Preparation. Up to now, most of the industrial and commercial multi-C_n samples, which have been studied in the literature,[40−44] show a continuous distribution of consecutive C_n mole compositions of the "normal logarithmic" type. However, in the petroleum fluids, the C_n mole composition decreases regularly as a function of the carbon atom number. These synthetic mixtures with a C_n mole composition distribution of the "decreasing exponential" type were prepared by mass of the solid pure C_ns, melting, and thoroughly mixing. The homogeneous paraffinic liquid solution was allowed to cool at ambient temperature. All the pure C_ns used were purchased from Fluka; their purity grade is ≥98%, as determined by our gas chromatography analyses. All the samples were composed of successive C_ns whose mole fraction x_n decreases regularly according to the recurrence relationship $x_{n+1} = \alpha x_n$, where the coefficient α was fixed at 0.858, which matched the average compositions observed in waxy crude oils. Seventeen multi-C_n synthetic mixtures were split them into three characteristic families:

(i) Family 1:8, monophasic simple systems whose C_n numbers, k, were $2 \leq k \leq 6$: $C_{24}-C_{25}$, $C_{22}-C_{24}$, $C_{23}-C_{25}$, $C_{24}-C_{26}$, $C_{22}-C_{25}$, $C_{21}-C_{25}$, $C_{22}-C_{26}$, and $C_{22}-C_{27}$.

(ii) Family 2:5, more complex *monophasic* systems whose C_n numbers were $7 \leq k \leq 11$ with distributions going from $C_{22}-C_{28}$ to $C_{22}-C_{32}$, which differentiate them by the addition of heavier C_n.

(iii) Family 3:4 *diphasic* mixtures whose C_n numbers were $12 \leq k \leq 15$ with distributions going from $C_{22}-C_{33}$ to $C_{22}-C_{36}$, which differentiate them by the addition of heavier C_n.

(iv) The first short C_n of families 2 and 3 was always C_{22}.

The first part of this experimental study will be focused on the evolution of the enthalpy of formation of the solid phases of complex multi-C_n mixtures and on the effect of the parameters of the paraffinic distribution: theoretical average chain length, number of components, number of crystallized solid solutions.

Samples Characterization by X-ray Diffraction. All the synthetic solid samples were analyzed by X-ray diffraction at ambient temperature ($T = 294.15$ K) by a combination of two methods: a Guinier De Wolff Nonius camera and a counter diffractometer (CGR Theta 60). The main observation is that the number of crystallized solid solutions increases with the C_n number of the paraffinic distribution:

(i) All systems containing 2−11 consecutive C_ns (families 1 and 2) form a single solid phase, whose orthorhombic structure is isostructural to the β' and β'' ordered intermediate phases of binary and ternary C_n molecular alloys;[45−47] a single periodicity of the molecule layer stacking along the long crystallographic c-axis is observed; it is equivalent to the chain length of an hypothetical orthorhombic pure odd-numbered C_n, whose number of carbon atoms is equal to the $\bar{n}$ theoretical mean number of carbon atoms of multi-C_n mixtures with an excess value close to one carbon atom.[40,41] Thus, all C_ns combine them into a single molecular layer; the longer molecules bend to insert themselves between the stacking planes and associate them with shorter molecules to obtain a single solid solution with a dense structure.

(ii) Samples from $C_{22}-C_{33}$ to $C_{22}-C_{36}$ (family 3) crystallize in two solid solutions with the same orthorhombic structure β' but with different mean carbon atom numbers; the successive addition of heavier C_n to the distribution induces the instability of the paraffinic system and the emergence of a second solid solution, richer in high molecular weight C_ns. The increase of the chain-length disparity into the lamellar structure by gradual extension of the C_n distribution requires two molecular layer thicknesses to combine all C_ns into dense and stable orthorhombic structures: the chains of the heavy C_n, added between each sample, insert themselves into the crystallographic structure of the solid phase whose stacking periodicity is compatible with their own chain length to minimize the molecular gaps; they crystallize into the new heavy phase, whose average chain length gradually increases. The lighter phase, with a lower layer thickness, could not accommodate these heavy C_ns and thus has unchanged average composition.

Note: The $\bar{n}$ theoretical average carbon atom number per molecule of a synthetic mixture is calculated by the following relationship

$$\bar{n} = \sum_{n_{\min}}^{n_{\max}} x_n n$$

with $n_{\max}$ and $n_{\min}$, respectively, the carbon atom numbers of the longest and the shortest C_n of the distribution and x_n, the mole fraction of each C_n.

These structural analyses by X-ray diffraction allow us to confirm that all the solid solutions of the synthetic samples are in a low-temperature ordered structure, as pure C_ns, at the study temperature of the dissolution experiments (T = 296.15 K).

Measurement and Operating Conditions. Enthalpies of dissolution were measured using a Setaram C80 differential calorimeter. The calorimeter principle and the scheme of the cell have been described before.[39] The solid sample and the solvent are initially in two compartments of the cell, separated by a mercury joint, and the mixture is made by reversal of the calorimeter. A differential assembly involves the presence of two cells in the calorimeter: the measurement cell, containing the sample to be analyzed and the solvent, and the reference cell, filled only with solvent. To accurately measure the enthalpy of dissolution and to minimize the asymmetry effect of the two cells (the cells are linked in opposition), the quantities of material (sample, solvent, and mercury) must be identical between each compartment of the two cells, the solid reagent mass in the measurement cell being replaced by an equivalent mass of solvent in the reference cell. The reversal of the calorimeter occurs in a linear stable baseline. The dissolution of the samples in C_7 is associated, in each case, with an endothermic effect.

Table 1. Specific and Mole Experimental Enthalpies of Dissolution in C_7 (T = 296.15 K) and Enthalpies of Formation of Solid Phases for Synthetic Mixtures with an Exponentially Decreasing Distribution of the C_n Mole Compositions xC_n

		xC_n	$\Delta_{\mathrm{diss}}h$	$\Delta_{\mathrm{diss}}H$	$\Delta_{\mathrm{form}}h$	$\Delta_{\mathrm{form}}H$
mixtures	$\bar{n}$	%	$J \cdot g^{-1}$	$J \cdot mol^{-1}$	$J \cdot g^{-1}$	$J \cdot mol^{-1}$
$C_{24}-C_{25}$	24.5	0.089	226.0	77922	34.9	12020
$C_{22}-C_{24}$	22.9	0.094	222.6	71874	38.0	12258
$C_{23}-C_{25}$	23.9	0.090	227.7	76711	30.8	10388
$C_{24}-C_{26}$	24.9	0.088	226.9	79623	31.4	11035
$C_{22}-C_{25}$	23.3	0.093	223.1	73295	36.2	11887
$C_{21}-C_{25}$	22.7	0.095	223.0	71372	34.6	11082
$C_{22}-C_{26}$	23.7	0.092	227.0	75827	31.1	10395
$C_{22}-C_{27}$	24.1	0.093	225.2	76371	35.2	11939
$C_{22}-C_{28}$	24.4	0.089	225.2	77452	35.7	12279
$C_{22}-C_{29}$	24.7	0.086	220.9	76950	39.5	13775
$C_{22}-C_{30}$	25.0	0.088	224.1	78970	37.0	13053
$C_{22}-C_{31}$	25.3	0.085	217.2	77392	43.9	15637
$C_{22}-C_{32}$	25.5	0.085	219.7	79048	41.8	15029
$C_{22}-C_{33}$	25.8	0.085	212.0	76967	49.3	17888
$C_{22}-C_{34}$	26.0	0.084	214.4	78474	47.1	17261
$C_{22}-C_{35}$	26.2	0.084	221.8	81820	39.8	14685
$C_{22}-C_{36}$	26.4	0.083	222.1	82485	39.4	14641

Experiments were performed at the temperature of 296.15 K, determined within ±0.2 K of the set point, the solvent is the heptane C_7H_{16} (purity ≥ 99%), the reagent quantities are of 9.3 mg for the multi-C_n mixtures and 3 g for heptane, all experimental values of the enthalpies of dissolution are the average of two reproducible experiments, and the experiments were carried out under atmospheric pressure.

Heptane is used as solvent because it is cheap and nontoxic. Furthermore, a significant difference between the carbon atom number of the solvent and the mean carbon atom number of the multi-C_n sample decreases the risk of forming a solid solution and improves the dissolution without increasing the temperature. The masses of reagent and solvent are chosen so as to have a total dissolution of the mixture in the solvent, whatever its average mole mass. The dissolution enthalpy values were reproducible with uncertainties lower than 3%.

Results and Discussion

The mole and specific experimental enthalpies of dissolution and of formation (T = 296.15 K) are reported in Table 1 as a function of the mole composition of solute of each binary system (multi-C_n mixture + C_7) and the $\bar{n}$ theoretical mean carbon atom number of each distribution. The enthalpies of formation of one or several solid phases are obtained from eq 2. The dissolution enthalpies as the enthalpies of formation are always positive values.

The experimental dissolution and formation enthalpies are of the same order for all the synthetic samples studied here. However, to better display the influence of the parameters of the paraffinic distribution on the solubility of multi-C_n mixtures, the variations of the enthalpy of formation are represented as a function of the C_n number of the distribution in Figure 2, and their analysis shows three characteristic evolutions:

(i) For the simple monophasic systems of family 1 (distributions containing 2−6 consecutive C_ns), the enthalpy of formation of the solid solution is invariant and independent of the length of the distribution and of the carbon atom number of the first short C_n of the mixture, the C_n arrangement in the molecular layers and the

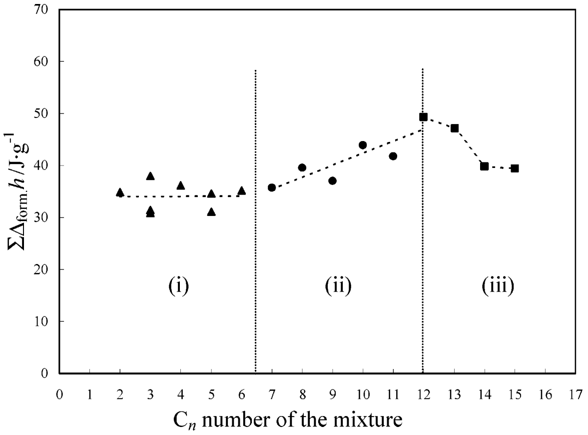

Figure 2. Evolution of the enthalpy of formation of solid phases as a function of the C$_n$ number of the mixture.

internal disorder being similar for a low number of components.

(ii) For the more complex monophasic systems of family 2 (distributions containing 7−11 consecutive C$_n$s), the enthalpy of formation of the solid phase increases linearly with the C$_n$ number of the sample, and this raising is closely related to that of the disorder in the lamellar structures during the addition of heavier C$_n$ to the distribution; when the number of constituents and the disparity of chain lengths become important, the system has more and more difficulties to combine all of the C$_n$s in a single dense stacking and the miscibility gap in the solid state is the reaction to a too strong instability.

(iii) For the biphasic systems of family 3 (distributions containing 12−15 consecutive C$_n$s): the enthalpy of formation of the two solid phases decreases to finally reach a constant value, because the miscibility gap in the solid state (for a C$_n$ number >11) involves the appearance of two new solid solutions more ordered than the original phase that generates them (the C$_n$s combine them by chain lengths affinity).

It can be also noticed that, for a same C$_n$ number (in the case of the ternary and quinary multi-C$_n$ samples of family 1), the mole dissolution enthalpy increases with the $\bar{n}$ theoretical mean carbon atom number of the distribution (enrichment in heavier C$_n$), while the mole enthalpy of formation of the solid phase shows any noticeable evolution according to the mixture average composition.

Modeling of the Enthalpies of Formation of the Solid Phases

The aim of the second part of this study is now to try to restore these experimental results by using the expression of the free excess enthalpy of the UNIQUAC model and to test its predictive capacity. Because the measured properties were close to the excess enthalpies, we were interested only in the residual part of the UNIQUAC model, taking into account the deviations to ideality due to the molecular interactions.

General Presentation and Choice of the Model of the Free Excess Enthalpy Used in this Study. For strongly nonideal systems, which is apparently the case for all our multi-C$_n$ synthetic mixtures with an exponentially decreasing distribution, two models are available: UNIQUAC and Wilson. The UNIQUAC model[50] and the Wilson equation[51] are purely predictive (knowing the sublimation enthalpies of pure components). However, we chose the UNIQUAC model for two reasons:

(i) The UNIQUAC model allows us to separate the excess enthalpy and the excess entropy, which is not the case for the Wilson equation, which gives only access to a global expression of the free excess enthalpy.

(ii) The UNIQUAC model is applicable to systems showing a partial miscibility in the solid state, which concerns a part of our synthetic multi-C$_n$ mixtures.

The UNIQUAC model, which rests on the concept of local composition of Wilson,[51] was initially developed by Abrams and Prausnitz[50] in the aim to have a general equation to take into account the differences of size and shape of molecules (entropic contribution), as well as the molecular energetic interactions (enthalpic contribution). The expression of the residual part of the Gibbs function (close to the formation enthalpies) of a binary system is the following

$$\frac{g_{\mathrm{r}}^{\mathrm{E}}}{RT} = -q_1x_1\ln(\theta_1 + \theta_2\tau_{21}) - q_2x_2\ln(\theta_2 + \theta_1\tau_{12})$$

$$\theta_1 = \frac{x_1q_1}{x_1q_1 + x_2q_2}$$

$$\theta_2 = \frac{x_2q_2}{x_1q_1 + x_2q_2}$$

and

$$\ln\tau_{12} = -\frac{\Delta u_{12}}{RT}$$

$$\ln\tau_{21} = -\frac{\Delta u_{21}}{RT}$$

where $g_{\mathrm{r}}^{\mathrm{E}}$ is the mole residual Gibbs function, q_i is the molecular surface-area parameter, relating to the area occupied by a molecule i, θ_i is the surface-area fraction of a molecule i within the mixture, τ_{ij} is the coefficient of binary interaction, defined from the energies of interaction u_{ij} and u_{ii}, x_i is the mole fraction of component i, R/J·K^{-1}·mol^{-1} is the universal gas constant (8.314), and T/K is the temperature.

Extrapolation to the Multicomponent Systems. In the case of multi-C$_n$ mixtures, the expression of the excess enthalpy used in this study is written according to the following expression

$$H^{\mathrm{E}} = -RT\left(\sum_{i=1}^{N} x_iq_i\ln\left(\sum_{j=1}^{N}\theta_j\exp\left(-\frac{\lambda_{ij}-\lambda_{ii}}{RT}\right)\right)\right) = -RT\left(\sum_{i=1}^{N} x_iq_i\ln\left(\sum_{j=1}^{N}\theta_j\Lambda_{ij}\right)\right) \quad (3)$$

where H^{E}/J·mol^{-1} is the mole excess enthalpy, R/J·K^{-1}·mol^{-1} is the universal gas constant (8.314), T/K is temperature = 296.15 K (in our study), x_i is the mole fraction of component i, q_i is the molecular surface-area parameter, relating to the area occupied by a C$_n$ molecule i, θ_i is the surface-area fraction of a C$_n$ molecule i within the multi-C$_n$ mixture, λ_{ij}/J·mol^{-1} is the energy of interaction between two different C$_n$ molecules i and j, λ_{ii}/J·mol^{-1} is the energy of interaction between two identical C$_n$ molecules i, Λ_{ij} is the coefficient of binary interaction, defined from the energies of interaction λ_{ij} and λ_{ii}, and N is the C$_n$ number in the mixture.

The C$_n$ characteristic parameters are related to the n carbon atom number by the following equations:

(i) ***Surface-Area Fraction θ_i and Structural Surface-Area Parameter q_i***

$$\theta_i = \frac{x_i q_i}{\sum_{i=1}^{N} x_i q_i} \tag{4a}$$

and

$$q_i = 0.1n_i + 0.1141 \tag{4b}$$

The expression connecting the structural parameter q_i to the n carbon atom of the considered C_n is obtained by a method of group contribution[52] by taking a carbon chain of 10 CH_2 groups as a reference unit for molecular interactions (UNIQUAC-10). The q parameters estimated by the method of groups contribution are so divided by the q value of 10 CH_2 groups

$$\left(q_i = \frac{(n_i - 2)q_{CH_2} + 2q_{CH_3}}{10q_{CH_2}} = \frac{0.848n_i + 2(0.848 - 0.540)}{10(5.40)} = 0.1n_i + 0.1141\right) \tag{5}$$

(ii) ***Energy of Interaction λ_{ii} between Two Identical Molecules.*** Scatchard and Hildebrand were the first to link the energies of interaction between two identical molecules to the energy of vaporization of the saturated liquid to the ideal gas. The adaptation of this concept to the Wilson equation requires the replacement of the volume fractions by the mole fractions and the introduction of the coordination number Z. Moreover, its transposition to the solid phases implies the use of the sublimation enthalpies instead of the vaporization enthalpies. The energy of interaction λ_{ii} between two identical molecules i is thus only a function of the sublimation enthalpy $\Delta_{sub}H_i$ and of the coordination number Z

$$\lambda_{ii} = -\frac{2}{Z}(\Delta_{sub}H_i - RT) = -\frac{1}{3}(\Delta_{sub}H_i - RT) \tag{6}$$

(with $Z = 6$ for the solid solutions with orthorhombic structures).[1]

The term $\Delta_{sub}H_i$ corresponds to the sublimation enthalpy of a C_n molecule i and can be written, for pure C_n, into the sum of the enthalpy variations of the successive phase changes

$$\Delta_{sub}H_i(296.15\ \text{K}) = \Delta H_{T_{o-d}}^{T_{fus}}{}_i\,(296.15\ \text{K}) + \int_{T_{fus}}^{T_{vap}} C_{p(l)i}\,dT + \Delta_{vap}H_i(296.15\ \text{K}) \tag{7}$$

where $\Delta_{sub}H_i$ is the sublimation enthalpy of C_n molecule i, $\Delta H_{T_{o-d}}^{T_{fus}}{}_i$ is the enthalpy variation from the order/disorder transition temperature T_{o-d} up to the melting point T_{fus} of C_n molecule i, $\Delta_{vap}H_i$ is the vaporization enthalpy of C_n molecule i, $C_{p(l)i}$ is the heat capacity of C_n molecule i in the liquid phase.

According to literature,[39] the $\Delta H_{T_{o-d}}^{T_{fus}}$ enthalpy variation of a C_n is equivalent to its enthalpy $\Delta_{diss}H$ required to entirely dissolve in a solvent, at a reference temperature ($T = 296.15$ K). As the heat capacity term is very weak by comparison to the phase change enthalpies, it can be neglected and eq 7 becomes

$$\Delta_{sub}H_i(296.15\ \text{K}) = \Delta_{diss}H_i(296.15\ \text{K}) + \Delta_{vap}H_i(296.15\ \text{K}) \tag{8}$$

The linear fitting of the experimental data for the dissolution enthalpies of pure C_n proposed by Briard et al.[39] and of results by Chickos[53] for the vaporization enthalpies lead to the following relations as functions of the n carbon atom number

$$\Delta_{diss}H_i(296.15\ \text{K})/\text{J·mol}^{-1} = 3687n \quad (20 \le n \le 36) \tag{9}$$

$$\Delta_{vap}H_i(296.15\ \text{K})/\text{J·mol}^{-1} = 5222n \quad (5 \le n \le 30) \tag{10}$$

Although the vaporization enthalpies provided by Chickos were measured at the temperature of 298.15 K, a difference of 2 K does not modify these enthalpy values, and by summation of eqs 9 and 10, the expression linking the sublimation enthalpy of pure C_n becomes

$$\Delta_{sub}H_i(296.15\ \text{K})/\text{J·mol}^{-1} = 8909n \tag{11}$$

(iii) ***Energy of Interaction λ_{ij} between Two Different Molecules i and j.*** Numerous authors[1,2,4,34,54,55] put forward the hypothesis according to which the energy of interaction between a short molecule i and a longer molecule j is similar to the energy of interaction between two short molecules i, which involves the following equality: $\lambda_{ij} = \lambda_{ii}$ ($i < j$). To take into account the differences of chain lengths, a new expression for these energies of interaction λ_{ij} is proposed.

So, the energy required to replace a molecule i, in a crystal built only by molecules i, by a molecule j of different size, is proportional to the difference of the carbon chain lengths between these two molecules i and j, noted ($n_i - n_j$). For a multi-C_n mixture, we multiply this term by a factor of disorder, reflecting the number of components of the distribution; this factor of disorder is equivalent to the ratio ($1/(n_{max} - n_{min})$), n_{max} being the chain length of the longest C_n and n_{min} that of the shortest C_n of the multi-C_n mixture. The new relation for the energy of interaction λ_{ij} corresponds to the eq 12

$$\lambda_{ij} = \left(1 - \left|\frac{n_i - n_j}{n_{max} - n_{min}}\right|\lambda_{ii}\right) \tag{12}$$

And the parameter of binary interaction Λ_{ij}, proportional to the difference (λ_{ii}–λ_{ij}) of the interaction energies between molecules i and j, becomes eq 13

$$\Lambda_{ij} = \exp\left(\frac{\lambda_{ii} - \lambda_{ij}}{RT}\right) = \exp\left(\frac{\left|\frac{n_i - n_j}{n_{max} - n_{min}}\right|\lambda_{ii}}{RT}\right) \tag{13}$$

where λ_{ij}/J·mol^{-1} is the energy of interaction between two different C_n molecules i and j, λ_{ii}/J·mol^{-1} is the energy of interaction between two identical C_n molecules i, Λ_{ij} is the coefficient of binary interaction, defined from the energies of interaction λ_{ij} and λ_{ii}, n_i is the carbon atom number of C_n molecule i, n_j is the carbon atom number of C_n molecule j, n_{min} is the carbon atom number of the shortest C_n of the distribution, and n_{max} is the carbon atom number of the longest C_n of the distribution.

Comparison between Experimental and Predicted Values. The excess enthalpies calculated by the UNIQUAC model are gathered in Table 2, with the experimental mole enthalpies of formation of solid phases of multi-C_n synthetic

Table 2. Comparison between the Experimental Mole Enthalpies of Formation of Solid Phases of Multi-C_n Synthetic Mixtures with an Exponentially Decreasing Distribution and Excess Enthalpies Calculated by the UNIQUAC Model

mixtures	$\bar{n}$	$\Delta_{\text{form}}H^{\text{exp}}$ $J \cdot mol^{-1}$	$\Delta_{\text{exc}}H^{\text{calc}}$ $J \cdot mol^{-1}$	relative gap(14) %
$C_{24}-C_{25}$	24.5	12020	4359	63.7
$C_{22}-C_{24}$	22.9	12258	6478	47.1
$C_{23}-C_{25}$	23.9	10388	6747	35.0
$C_{24}-C_{26}$	24.9	11035	7016	36.4
$C_{22}-C_{25}$	23.3	11887	8298	30.2
$C_{21}-C_{25}$	22.7	11082	9363	15.5
$C_{22}-C_{26}$	23.7	10395	9756	6.1
$C_{22}-C_{27}$	24.1	11939	10968	8.1
$C_{22}-C_{28}$	24.4	12279	11990	2.3
$C_{22}-C_{29}$	24.7	13775	12858	6.7
$C_{22}-C_{30}$	25.0	13053	13597	4.2
$C_{22}-C_{31}$	25.3	15637	14228	9.0
$C_{22}-C_{32}$	25.5	15029	14767	1.7
$C_{22}-C_{33}$	25.8	17888	15227	14.9
$C_{22}-C_{34}$	26.0	17261	15618	9.5
$C_{22}-C_{35}$	26.2	14685	15950	8.6
$C_{22}-C_{36}$	26.4	14641	16231	10.9

mixtures, having an exponentially decreasing distribution of the C_n mole fractions.

The relative gap between the calculated and the experimental results is obtained by the following expression

$$\left|\frac{\Delta_{\text{form}}H^{\text{exp}} - \Delta_{\text{exc}}H^{\text{calc}}}{\Delta_{\text{form}}H^{\text{exp}}}\right|100 \qquad (14)$$

This modified UNIQUAC model gives good results in the prediction of the enthalpies of formation of solid phases of complex multi-C_n mixtures; for all mixtures containing 5−15 consecutive C_n, the gap between the calculated and experimental values is, on average, of the order of 8%. However, the capacity of prediction of this model is more limited in the case of simple mixtures going from the binary to the quaternary mixtures of family 1. This inadequacy finds its origin in the fact that the UNIQUAC model was developed to represent the behavior of strongly nonideal compounds. Now, a calorimetric study carried out on these mixtures put in evidence that, in the case of synthetic multi-C_n samples with an exponentially decreasing distribution, the deviation to ideality of the ordered solid phases increases with the C_n number of the distribution. The increase of the chain lengths disparity in the lamellar layers induces a more important internal disorder in the structure, which raises the nonideal character of family 2 mixtures. The model proposed is thus more appropriate to the prediction of the formation enthalpies of solid phases of complex multi-C_n samples (those whose interest within the framework of the modeling of the crystallization of paraffinic solid deposits) than C_n binary or ternary paraffinic mixtures, whose behaviors are closer to ideality.

Nevertheless, although this model gives good agreement in the case of complex monophasic or polyphasic mixtures (families 2 and 3), it will be always difficult for it to represent with accuracy the notion of internal disorder and molecular rearrangement into the lamellar structures, because this predictive model is based only on pure compounds properties; the enthalpies of formation calculated by this model regularly increases with the C_n number of the mixture, while experimentally the miscibility gap in the solid state, which appears from a C_n number >11, leads to the formation of new solid phases, which are more ordered, and to a decrease of the formation enthalpies of the polyphasic mixtures of family 3.

Note: The use of the UNIQUAC model, by keeping the hypothesis collectively admitted according to which $\lambda_{ij} = \lambda_{ii}$, gives much less satisfactory results than ours, obtained by modifying the expression of the energy of binary interaction λ_{ij}. Indeed, the calculated excess enthalpies are, on average, of the order of 3700 $J \cdot mol^{-1}$. Now, these values are much lower than the experimental enthalpies of formation or than the calculated excess enthalpies presented in Table 2. So, this strengthens the taking into account of the chain lengths difference and of the factor of disorder in the expression of the energy of binary interaction λ_{ij}.

Conclusion

This paper was focused on two main objectives: first, the measurement of the dissolution enthalpies in heptane of synthetic multi-C_n mixtures to point out the influence of the parameters of the C_n distribution (theoretical average chain length, C_n number, monophasic or polyphasic state) on their enthalpies of formation; second, the estimation, by means of this experimental data bank, of the predictive capacity of the Uniquac model, concerning the formation enthalpies of solid phases of complex multi-C_n samples.

In the case of synthetic mixtures showing an exponentially decreasing distribution of the C_n chain lengths, the value of the formation enthalpy of solid phases is closely related to the internal disorder in the lamellar structures:

(1) It is constant for simple monophasic mixtures, composed of 2−6 successive C_ns,

(2) it increases with the C_n number for more complex monophasic samples, composed of 7−11 consecutive C_ns, but

(3) it decreases after the miscibility gap in the solid state, which leads to a C_n reorganization in two more ordered solid phases, for the polyphasic systems, composed of a C_n number > 11.

According to the literature, the UNIQUAC model allows a good prediction of the crystallization onset temperatures and of the crystallized deposit quantities as a function of the temperature.[1,2,34−36,54,55] Also, the use of the Uniquac model in this study, after modification of the expression of the energy of interaction λ_{ij} in order to take into account the effect of size difference between two C_n and of the internal disorder induced by the length of the distribution, leads to satisfactory results in the prediction of the enthalpies of formation of solid phases of complex multi-C_n mixtures (from 5 consecutive C_n). However, the predictive capacities of this UNIQUAC model will inevitably be limited by its difficulty to represent the disorder and the molecular rearrangements in the lamellar structures, because being purely predictive, the writing of the characteristic expressions of this model only rests on the pure C_n properties.

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