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Solid-solution formation and phase segregation in binary systems of homologous extended-chain perfluorinated alkanes

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Dedicated to Professor Ronald K. Eby on the occasion of his 70th birthday

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Abstract

Using differential scanning calorimetry (DSC) and X-ray analysis it is shown that binary systems of perfluorinated alkanes form solid solutions or exhibit eutectic phase behaviour, depending on their difference in chain length. A simple model, which successfully correlated experimental results for this aspect of phase behaviour of binary *n*-alkane systems, is demonstrated to quantitatively describe the behaviour of perfluorinated alkanes as well. From the model parameters and experimental observations, it appears that, at equal number of carbon atoms, binary perfluorinated alkane systems allow for a larger chain difference than their hydrogenated analogues, before eutectic phase behaviour sets in.

Keywords: Eutectic phase behaviour; Phase segregation; Perfluorinated alkanes

1. Introduction

Since their discovery in nuclear power plants as radiation degradation products of poly(tetrafluoroethylene), perfluorinated alkanes have found wide spread application as fluoroadditives in material systems like thermoplastics, coatings and inks, to improve non-stick properties, lubricity and wear resistance [1]. Nevertheless, quantitative understanding of the phase behaviour of perfluorinated alkane compositions, the prime factor which determines their solid-state structure, and, hence, properties, is still lacking. Apart from commercial relevance, the phase behaviour of perfluorinated alkanes, being the paradigm for poly(tetrafluoroethylene), is of considerable academic interest as well.

The related case of binary *n*-alkane systems is well described in the literature [2–4]. In one aspect, homologous pairs of alkanes have been shown to form continuous solid solutions if their chain length and crystal symmetries are comparable [5]. Upon increasing the chain-length difference, the accommodation of strain in the paraffin lattices deviates from true Vegard's behaviour [6], and the resulting structure more resembles an interblock array [7]. If the difference in chain length is too large, demixing during, or prior to, crystallisation will occur, and ordinary eutectic phase behaviour is observed. It appears that a quantitative understanding of this phase behaviour can be obtained by careful consideration of factors like molecular size and shape [8].

Compared to *n*-alkanes, perfluorinated *n*-alkanes introduce a higher degree of conformational rigidity due to steric crowding of the fluorine atoms. *n*-Alkane chains crystallize in a zig-zag conformation, whereas short perfluoroalkyl chains maintain a helical conformation, even in an isolated state [9]. Owing to the inefficient packing of these shallow helices, the binary perfluorinated *n*-alkanes present a class of systems which is even more devoid of specific interactions than the *n*-alkanes [1], and for which, therefore, the phase behaviour is even more likely to be dominated by details of the van der Waals volume than their hydrogenated analogs. It is the objective of this communication to verify the theoretical quantitative predictions [8] regarding the chain-length difference dependent transition from solid-solution to eutectic phase behaviour, for a number of binary perfluorinated alkane systems. It is contemplated that the present results bear relevance to both academic considerations regarding the phase behaviour of polydisperse poly(tetrafluoroethylene) and most certainly their copolymers [10], as well as to the design of industrial products, such as high-performance ski-waxes and the like.

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Table 1
Melting points and melting enthalpies of the perfluorinated alkanes used, as measured by differential scanning calorimetry

	$C_{12}F_{26}$	$C_{14}C_{30}$	$C_{16}F_{34}$	$C_{20}F_{42}$	$C_{24}F_{50}$
T_m^0 (°C)	76.1	104.8	128.6	164.2	188.5
ΔH (kJ/mol)	21.6	31.9	37	49.4	56.0

2. Experimental

2.1. Materials

Perfluoro-dodecane ($C_{12}F_{26}$), -tetradecane ($C_{14}F_{30}$), -hexadecane ($C_{16}F_{34}$), -eicosane ($C_{20}F_{42}$) and -tetracosane ($C_{24}F_{50}$), and the *n*-alkanes: hexadecane ($C_{16}H_{34}$) and eicosane ($C_{20}H_{42}$) were purchased from Fluorochem Ltd (United Kingdom) and Aldrich, respectively, and used without further purification. The melting temperatures and enthalpies of these perfluorinated alkanes were measured with differential scanning calorimetry, and are listed in Table 1. Binary mixtures were prepared for carefully selected combinations, where the melting temperature of the higher perfluoroalkane did not exceed the boiling temperature of the lower perfluoroalkane.

2.2. Characterization

Differential scanning calorimetric (DSC) thermograms were recorded using a Netzsch differential scanning calorimeter (model 200), which was calibrated with indium. Samples of about 8 mg were heated at a rate of 10°C/min under N_2 atmosphere. Binary phase diagrams were constructed directly from DSC-curves at different concentrations. The melting temperatures of the pure components and eutectics correspond to peak maxima of the endotherms of once molten and cooled (rate: 10°C/min) material. The liquidus lines were constructed from the high-temperature onset at the end of the broad melting endotherms [11].

The pressure–volume–temperature (PVT) properties of the pure compounds were measured using a commercial high-pressure bellows-type dilatometer (Gnomix Inc. PVT Apparatus) using the standard isothermal operation mode with 10°C temperature and 10 MPa pressure steps. The measured pressures ranged from 10–100 MPa. Data at atmospheric pressure were extrapolated from high-pressure data using a fourth-order polynomial fit.

Powder X-ray diffraction graphs were recorded at room temperature using a Seifert ISO Debyeflex 1001 instrument, operated at 40 kV and 30 mA with CuKα radiation and Ni-filter, equipped with a Braun position-sensitive counter. The samples were placed on a background-free silicium single crystal plate (cut 13 degrees to the 111-direction) using Si-grease.

2.3. Theory

Upon crystallization, a binary mixture of short (lower) and tall (higher) alkanes will form a solid solution or a eutectic mixture depending on the difference in the chain length. Invoking the Bragg–Williams lattice approximation for solid solutions, Matheson et al. [8] developed a quantitative model to determine the critical condition for solid-solution stability, assuming random occupation of the lattice sites, and pairwise-additive nearest neighbour interactions, only. In this model it is assumed that ideal mixing (zero interaction energy) between the short and tall alkanes occurs as long as the van der Waals 'length' of the taller alkane partner is smaller than the lattice cell 'length' of the shorter partner (see Fig. 1). Now, let L_i denote the projected van der Waals length of species i, where i is s (short) or t (tall), K_i its lattice length, and c_i its number of carbon atoms. The projected van der Waals length of a perfluorinated alkane (L_i), consisting of c_i carbon atoms follows from its van der Waals volume a_i: [12] $a_i = 11.4 + 14.8c_i$ (a_i in cm^3/mol), and the projected length per CF_2-group, $p = 1.3$ Å:

$$L_i = 1 + 1.3c_i \quad (1)$$

Assuming that a lattice site has the same aspect ratio as the cylindrical van der Waals volume, the effective length of

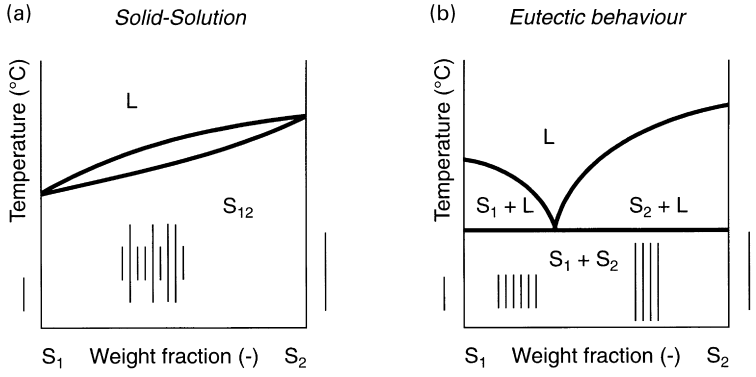

Fig. 1. Schematic representation of the limiting phase behaviour of binary alkane systems: (a) solid-solution behaviour when the van der Waals length of the taller alkane is smaller that the lattice length of the shorter partner; and (b) eutectic behaviour when the van der Waals length of the taller alkane exceeds the lattice length of the shorter partner.

Table 2
Calculation of c^*_t as a function of c_s as described in the text. Tabulated against the number of carbon atoms of the shorter partner, c_s, are: T_m, the melting point in Kelvin; $V_m(T_m)$, the molar volume at T_m in cm^3/mol; $\alpha^{1/3}$, the cube root of the expansion factor (dimensionless); $(dV/dT)_{T=T_m}\cdot 10^2$, the thermal expansion coefficient at T_m and atmospheric pressure as determined by PVT-measurements in cm^3/K; $\Delta(f=0.2)$ (dimensionless), computed according to Eq. (5) with $f=0.2$; $\Delta(f=0.4)$; $c^*_t(f=0.2)$, the maximum number of carbon atoms of the longer partner that will still form a solid solution upon crystallization, computed according to Eq. (5) with $f=0.2$; $c^*_t(f=0.4)$

C_s	T_m	$V_m(T_m)$	$\alpha^{1/3}$	$(dV/dT)_{T=T_m}\cdot 10^2$	$\Delta(f=0.2)$	$\Delta(f=0.4)$	$c^*_t(f=0.2)$	$c^*_t(f=0.4)$
12	348	319	1.19	0.05	1.06	1.11	15	16
14	376	369	1.19	0.07	1.11	1.22	18	20
16	399	419	1.19	0.08	1.10	1.21	21	23
20	436	519	1.19	0.09	1.09	1.19	26	28
24	463	619	1.19	0.13	1.18	1.37	34	39

a lattice site is written as:

$$K_i = \alpha_i^{1/3} L_i \tag{2}$$

Here α_i, is an expansion factor, defined as the ratio of the molar volume of the solid extrapolated to its melting point, $V_i(T_m)$, and the van der Waals volume, a_i, $\alpha_i = V_i(T_m)/a_i$. The number of carbon atoms of the tallest partner, c_t*, that will still mix ideally with a perfluoroalkane possessing c_s carbon atoms, then, follows from Eqs. (1) and (2):

$$c_t^* = c_s + \frac{K_s - L_s}{p} = 0.769(\alpha_s^{1/3} - 1) + \alpha_s^{1/3} c_s \tag{3}$$

The local lattice deformation which results when the van der Waals length of the taller perfluorinated alkane partner exceeds the lattice cell length of the shorter partner, is treated as a thermal expansion that reequilibrates over the entire *s*-lattice [13]. In view of the simple model in hand, the upper bound of the linear expansion coefficient of the *s*-lattice (in the chain direction) is set as one-third of the thermal expansion coefficient at the melting point of the perfluorinated *s*-alkane:

$$\left(\frac{d\varepsilon}{dT}\right)_s = f\left[\frac{1}{3}\left(\frac{dV}{V dT}\right)_s\right]_{T=T_m} \tag{4}$$

where ε is the initial, local strain of the *s*-lattice, $(d\varepsilon/dT)_s$ is the linear thermal expansion coefficient of the *s*-lattice, and *f* is an adjustable parameter obeying $0 \le f \le 1$. With this, solid solution behaviour is expected when:

$$c_t \le 0.769(\Delta\alpha_s^{1/3} - 1) + \Delta\alpha_s^{1/3} c_s$$
$$\text{with } \Delta = 1 + 2T\left(\frac{d\varepsilon}{dT}\right)_s \tag{5}$$

Parameters required by Eq. (5) are given in Table 2, and the loci of solutions are plotted in Fig. 2. This concludes in short the existing [8] model applied to binary perfluorinated alkane systems; for more details the reader is referred to the original article.

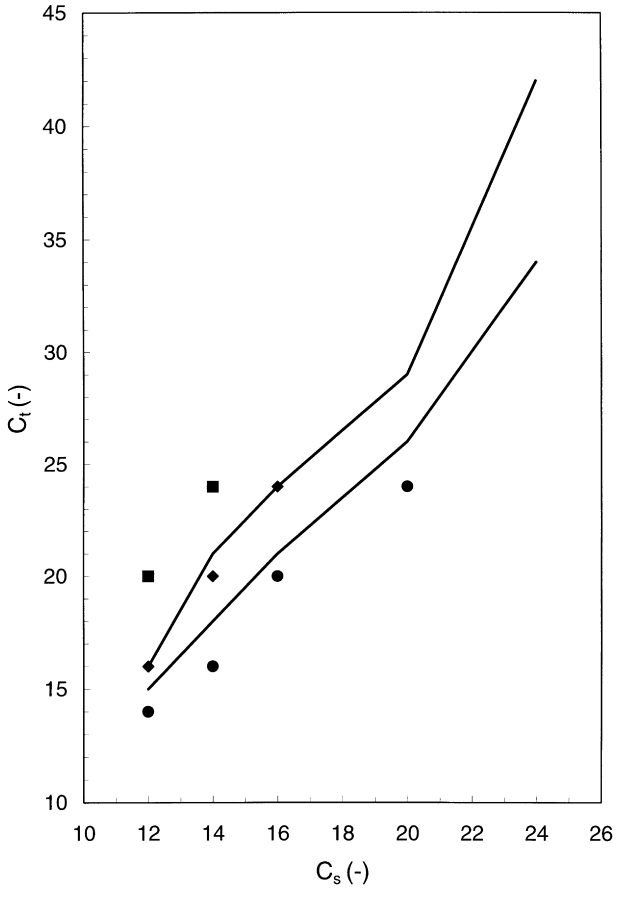

Fig. 2. Map of the experimentally observed phase behaviour of all studied perfluorinated alkane binary systems, compared to the loci of solutions to Eq. (5). (●): Solid-solution behaviour; (◆): Aspects of both solid-solution and eutectic phase behaviour; (■); Eutectic phase behaviour; (lines): Loci of solutions to Eq. (5) with $f=0.2$ (lower line) and $f=0.4$ (upper line); The lines act as a guide to the eye, connecting the calculated integer part of c_t* for selected values of c_s (see Table 1).

3. Results and discussions

Both differential scanning calorimetry and X-ray measurements revealed three types of phase behaviour for the binary perfluoroalkane systems studied in this work: solid-solution formation, eutectic behaviour, and what appears to be a combination of both solid-solution and eutectic behaviour. The experimentally observed phase behaviour for all the present systems, compared to the loci of solutions to Eq. (5) is depicted in Fig. 2.

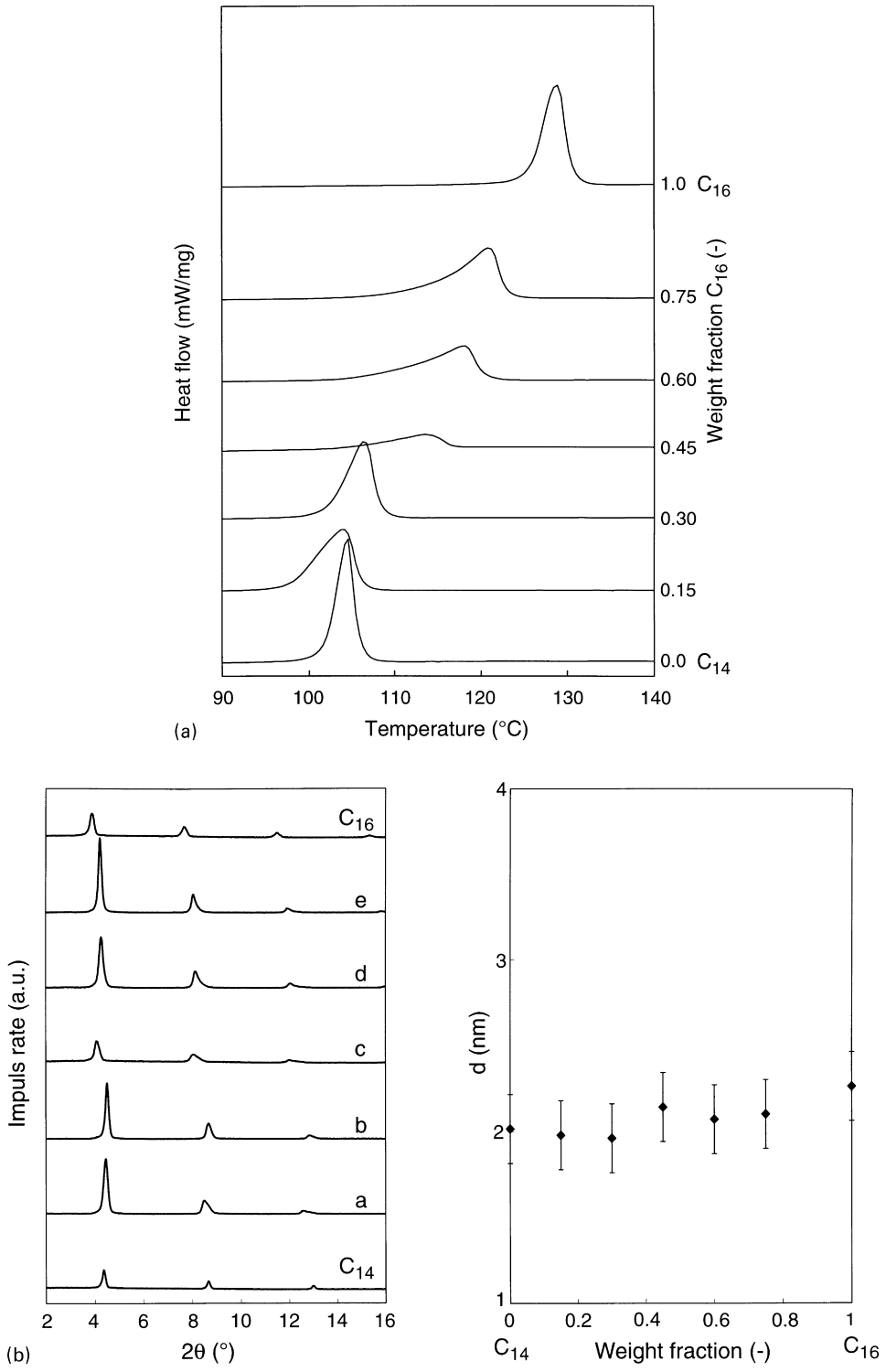

Fig. 3. (a) DSC-thermograms of the system perfluorotetradecane–perfluorohexadecane ($C_{14}F_{30}/C_{16}F_{34}$) as a function perfluorohexadecane concentration, indicative of solid-solution behaviour, (b) X-ray data of the system $C_{14}F_{30}/C_{16}F_{34}$ as a function of perfluorohexadecane concentration, indicative of solid-solution behaviour, (c) Partial phase diagram of the system $C_{14}F_{30}/C_{16}F_{34}$ based on DSC and X-ray data.

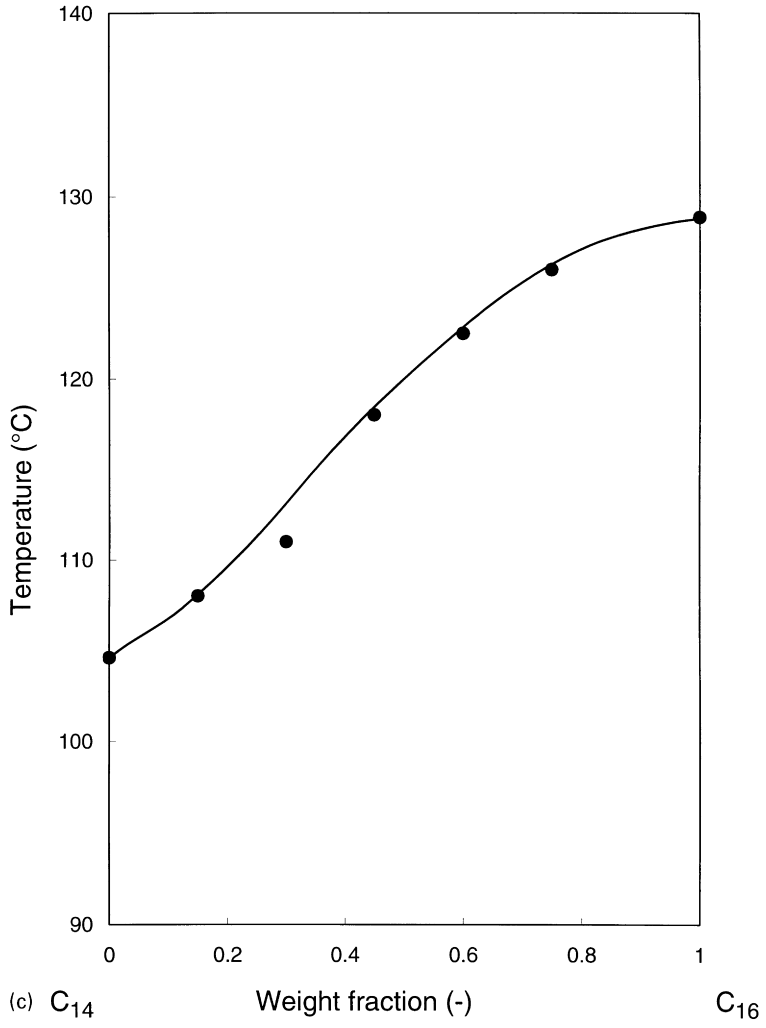

Fig. 3. (*continued*)

A typical example of solid-solution behaviour is observed for the system perfluorotetradecane–perfluorohexadecane ($C_{14}F_{30}/C_{16}F_{34}$) (see Fig. 3(c)). DSC-thermograms of binary mixtures of various concentrations display one (broad) melting range which is located in between the melting temperatures of the single components (Fig. 3(a)), and from the X-ray data (Fig. 3(b)) it can be seen that the (single) long period of the binary solid (associated with the 001-reflection) changes from 20 to 23 Å, approximately according to Vegard's rule. Fryer et al., [7] reported similar behaviour for binary mixtures of $C_{38}H_{78}/C_{37}H_{76}$, although it was concluded that the data deviated from true Vegard's behaviour and more resembled an interblock array structure.

Ordinary eutectic phase behaviour is found, for example, for the system perfluorotetradecane–perfluorotetracosane ($C_{14}F_{30}/C_{24}F_{50}$) (see Fig. 4(c)). The DSC-thermograms of mixtures of various $C_{24}F_{50}$-content of this system are presented in Fig. 4(a), clearly showing the eutectic melting transition at a constant temperature of 104°C and decreasing melting enthalpy upon increasing $C_{24}F_{50}$-content. Also the X-ray data for this system, Fig. 4(b), are indicative of eutectic phase behaviour, displaying approximately constant lamellar spacings equal to those of the pure components $C_{14}F_{30}$ (20 Å) and $C_{24}F_{50}$ (33 Å), at all compositions. The continuous lines in Fig. 4(c) represent the melting point depression for the ideal situation, and were calculated using the Flory–Huggins equation, assuming equal densities (weight fraction equals volume fraction ϑ) and zero interaction energy, using melting points and melting enthalpies from Table 1:

$$\frac{1}{T_m^0} - \frac{1}{T_m} = \frac{R}{\Delta H} \ln \varphi \tag{6}$$

The excellent agreement between experimental and predicted phase behaviour in Fig. 2, confirms the ideal mixing assumption (zero interaction energy), which was used in Section 2.3.

More complicated phase behaviour is observed, for example,

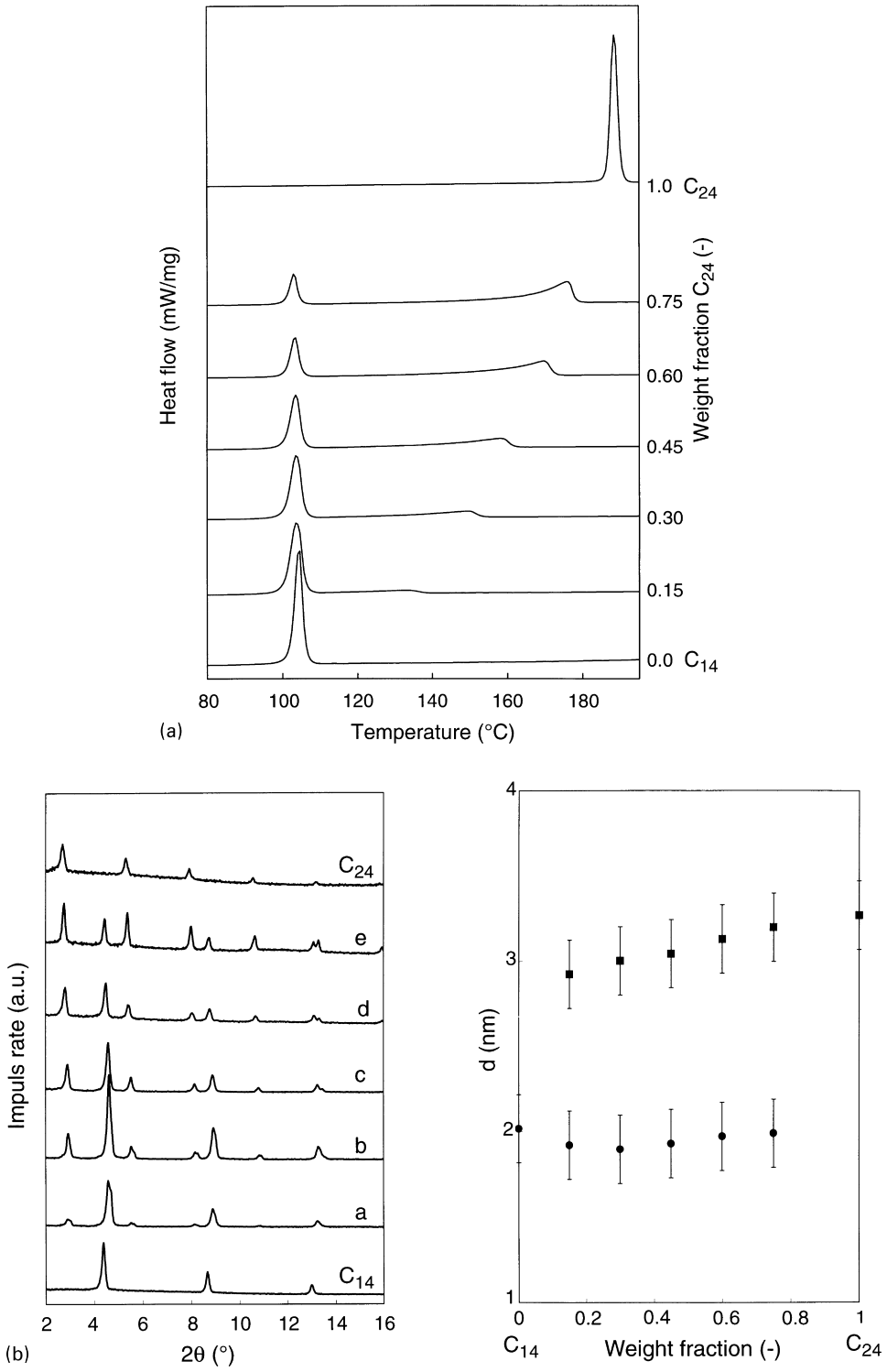

Fig. 4. (a) DSC-thermograms of the system perfluorotetradecane–perfluorotetracosane ($C_{14}F_{30}/C_{24}F_{50}$) as a function of perfluorotetracosane content, indicative of eutectic phase behaviour; (b) X-ray data of the system $C_{14}F_{30}/C_{24}F_{50}$ as a function of perfluorotetracosane content; (c) phase diagram of the system $C_{14}F_{30}/C_{24}F_{50}$ based on DSC and X-ray data, indicative of eutectic phase behaviour. The solid lines are calculated using the Flory–Huggins equation (see text).

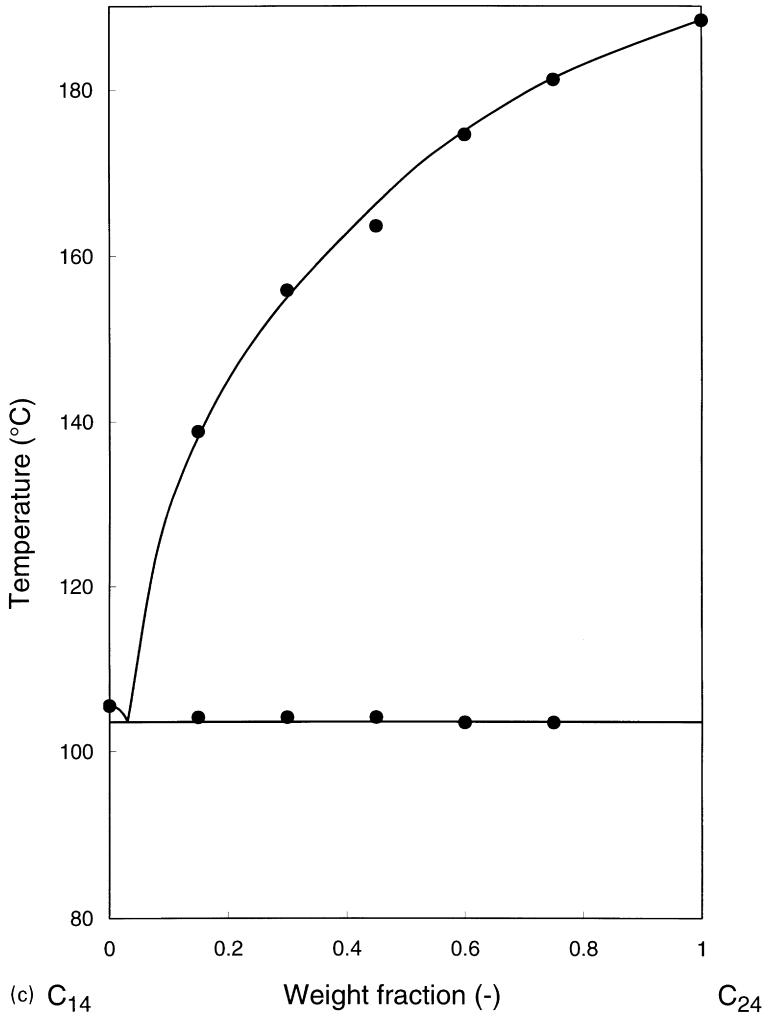

Fig. 4. (*continued*)

for the system perfluorotetradecane–perfluoroeicosane ($C_{14}F_{30}/C_{20}F_{42}$). The DSC-thermograms at various $C_{20}F_{42}$-concentrations (Fig. 5(a)) reveal several endotherms, some of them similar to those observed in the system $C_{14}F_{30}/C_{24}F_{50}$ and seemingly related to eutectic phase behaviour, but others having an origin which is less obvious. Moreover, in Fig. 6 it can be seen that many of the observed endotherms strongly depend on cooling rate, which implies that the DSC-thermograms in Fig. 5(a) do not necessarily reflect equilibrium phase behaviour. Similar complex behaviour can be found in binary *n*-alkane systems, for example the system *n*-hexadecane–*n*-octadecane, and is indicative of partial miscibility in the solid state [7]. Indeed, in the phase map, Fig. 2, all ''complex'' systems are found in a narrow band between solid-solution and eutectic behaviour. The X-ray data of various $C_{14}F_{30}/C_{24}F_{50}$ compositions cooled at 10°C/min in (Fig. 5(b)), exhibit the characteristic lamellar spacings of the single components, as well as intermediate reflections, which also suggests the occurrence of both solid-solution and eutectic phase behaviour.

On comparing the loci of solutions of Eq. (5) to the experimentally observed phase behaviour (Fig. 2), it is clear that the model is able to account quantitatively for the transition from solid-solution to eutectic behaviour. It is especially noteworthy, that in the phase map (Fig. 2), all ''complex'' systems, most probably owing to partial miscibility in the solid state, are found in the narrow band, defined by the line $f = 0.2$ and $f = 0.4$. With $0 \leq f \leq 0.4$, the model correctly describes all experimentally observed phase behaviour, rating the ''complex'' systems as eutectic systems.

In Fig. 7(a) a comparison is made between the phase behaviour of perfluorinated and *n*-alkanes, using the parameters for *n*-alkanes from Ref. [8]. It appears that, when compared at the same number of carbon atoms, *n*-alkane systems display a greater tendency to eutectic behaviour than its perfluorinated analogues. From the cube root of the expansion factor (Table 1 of Ref. [8], and Table 2) for

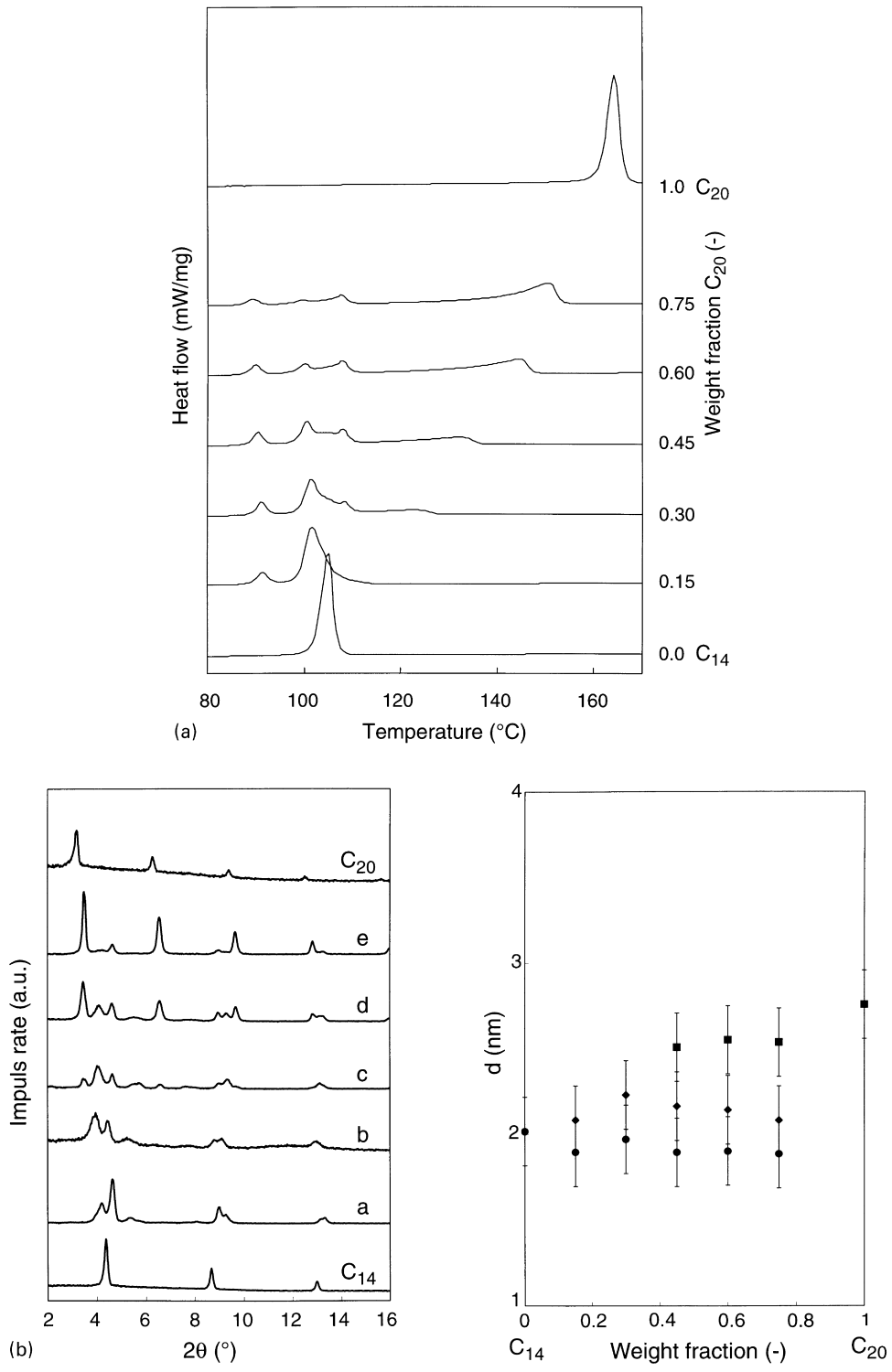

Fig. 5. (a) DSC-thermograms of the systems $C_{14}F_{30}/C_{20}F_{42}$ as a function of perfluoroeicosane content; (b) X-ray data of the system $C_{14}F_{30}/C_{20}F_{42}$ as a function of perfluoroeicosane content.

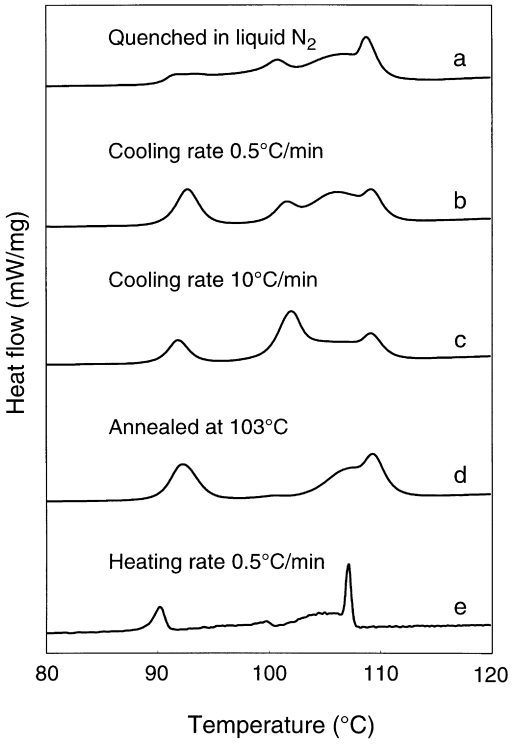

Fig. 6. DSC-thermograms ((a)–(d): heating rate 10°C/min) of the system 55 w/w% $C_{14}F_{30}$–45 w/w% $C_{24}F_{50}$, cooled at different rates: (a) quenched in liquid nitrogen; (b) cooling rate 0.5°C/min; (c) cooling rate 10°C/min; (d) annealed for 5 h at 103°C; and (e) heating rate 0.5°C/min (sample cooled with 10°C/min).

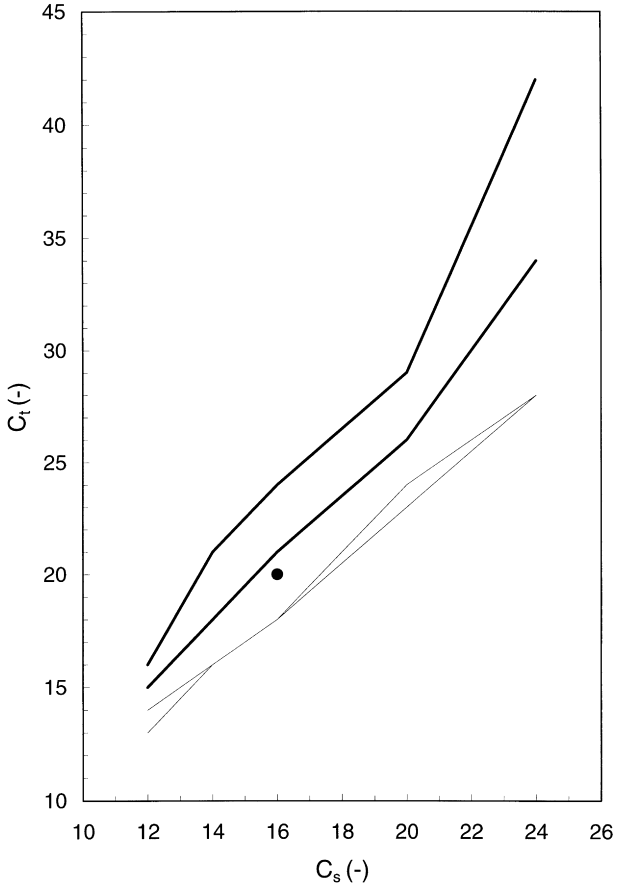

Fig. 7. Phase map for fluorinated alkenes (thick lines) and *n*-alkanes (thin lines) using Eq. (5) with $f = 0$, and $f = 0.5$. Parameters for *n*-alkanes from Matheson and Smith [8]. Also shown in this figure is experimental verification (●) for the systems $C_{16}F_{34}/C_{20}F_{42}$ (eutectic behaviour) and $C_{16}H_{34}/C_{20}H_{42}$ (solid solution).

the systems studied (up to thirty carbon atoms), it is clear that the maximum difference in chain length which allows ideal mixing behaviour (assuring solid-solution formation), is approximately 15% of the shorter partner in case of *n*-alkanes, compared to 19% in the case of perfluorinated alkanes. Taking into account a certain amount of allowable lattice strain, this maximum difference in chain length increases considerably for the perfluorinated alkanes, whereas it remains almost the same for the *n*-alkanes. This is consistent with the well known high entropy (high mobility) in the crystalline state of perfluorinated alkanes, which, together with their relatively low entropy in the melt [1,9], is also responsible for the high melting points of these compounds. Also depicted in Fig. 7, is the experimental verification for the system C_{16}–C_{20}, demonstrating that the model correctly predicts eutectic behaviour for the system hexadecane–eicosane ($C_{16}H_{32}/C_{20}H_{42}$) (see Fig. 8), and solid-solution behaviour for its perfluorinated analog ($C_{16}F_{32}/C_{20}F_{42}$).

4. Conclusions

Using differential scanning calorimetry and X-ray analysis it is shown that binary systems of perfluorinated alkanes form solid solutions or exhibit eutectic phase behaviour, depending on their difference in chain length. A simple model, which successfully correlated experimental results for this aspect of phase behaviour of binary *n*-alkane systems [8], was demonstrated to work for perfluorinated alkanes as well. The model, which has only one adjustable parameter, assumes ideal mixing behaviour (solid solution formation) if the van der Waals envelope of the taller partner is smaller or equal to the lattice size of the smaller partner. If the van der Waals size of the taller partner exceeds this value and the energy penalty associated with the resulting lattice strain becomes too large, eutectic phase behaviour sets in. From the model parameters and experimental observations, it appears that, at equal number of carbon atoms, binary perfluorinated alkane systems allow for a larger chain difference than their hydrogenated analogues, before eutectic phase behaviour sets in. Moreover, it was found experimentally that binary systems with a critical chain-length difference, display complex rate-dependent phase behaviour, exhibiting aspects of both solid-solution and eutectic phase behaviour, which might be due to partial miscibility in the solid state.

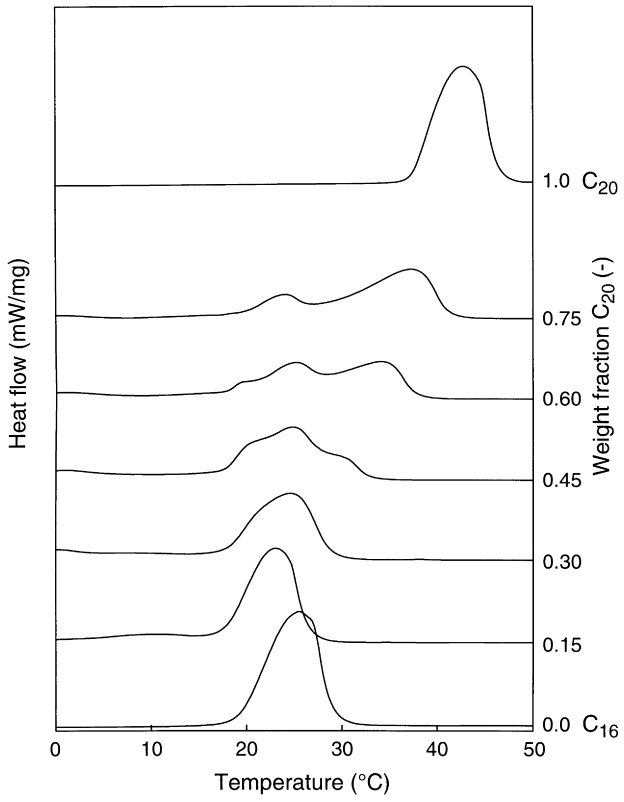

Fig. 8. DSC-thermograms of the systems $C_{16}H_{34}/C_{20}H_{42}$ as a function of eicosane content, indicative of eutectic phase behaviour.

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References

[1] Scheirs J. In: Scheirs J, editor. Modern fluoropolymers, Chichester: Wiley, 1997. p. 1.
[2] Wunderlich B. Macromolecular physics, 3. New York: Academic Press, 1976.
[3] Dorset DL, Snyder RG. Macromolecules 1995;28:8412.
[4] Dorset DL. J Phys Chem 1997;101:4870.
[5] Muyukh YV. J Struct Chem 1960;1:346.
[6] Vegard L, Dale H. Z Krist 1928;67:148.
[7] Mazee WM. A Chim Acta 1957;17:97.
[8] Matheson RR, Smith P. Polymer 1985;26:292.
[9] Rabolt JF, Fanconi B. Polymer 1977;18:1258.
[10] Eby RK, Wilson FC. J Appl Phys 1962;33:2951.
[11] Berghmans H. Chapter 8. In: Mathot VBF, editor. Calorimetry and thermal analysis of polymers, Munich: Hanser, 1994. p. 228.
[12] Van Krevelen DW. Properties of polymers. 3rd edition. Amsterdam: Elsevier, 1990.
[13] Eby RK. J Appl Phys 1962;33:2253.