Melting behaviour in the n-alkanol family. Enthalpy–entropy compensation

L. Ventolà,*[a] T. Calvet,[a] M. A. Cuevas-Diarte,[a] M. Ramírez,[a] H. A. J. Oonk,[b] D. Mondieig[c] and Ph. Negrier[c]

[a] *Departament de Cristal·lografia, Mineralogia i Dipòsits Minerals, Facultat de Geologia, Universitat de Barcelona, Martí i Franquès s/n, E-08028 Barcelona, Spain. E-mail: lourdes_ventola@yahoo.com; Fax: +34 934021340; Tel: +34 934021350*
[b] *Chemical Thermodynamics Group, Faculty of Chemistry, Debye Institute, Utrecht University, Padualaan 8, CH-3584 Utrecht, The Netherlands*
[c] *Centre de Physique Moléculaire Optique et Hertzienne, UMR 5798 au CNRS Université Bordeaux I, Cours de la Libération 351, F-33405 Talance Cedex, France*

The melting behaviour was studied in ten systems: $C_{15}OH$–$C_{16}OH$, $C_{16}OH$–$C_{17}OH$, $C_{17}OH$–$C_{18}OH$, $C_{18}OH$–$C_{19}OH$, $C_{19}OH$–$C_{20}OH$ with $\Delta n = 1$ (difference in chain length), $C_{15}OH$–$C_{17}OH$, $C_{16}OH$–$C_{18}OH$, $C_{17}OH$–$C_{19}OH$, $C_{18}OH$–$C_{20}OH$ with $\Delta n = 2$, and $C_{16}OH$–$C_{20}OH$ with $\Delta n = 4$. The phase that melts is either the monoclinic $R'_{IV}(C2/m, Z = 4)$ or the hexagonal $R'_{II}(R\bar{3}m, Z = 6)$ rotator form. One of the most important issues in the melting of these systems is that when the two original compounds of the system are isostructural, the phase diagram does not always show total miscibility. In the systems studied here, only the $C_{15}OH$–$C_{16}OH$, $C_{18}OH$–$C_{19}OH$ and $C_{19}OH$-$C_{20}OH$ systems show total miscibility. In the other systems in which the two original compounds are isostructural, miscibility is partial, as in the systems where the two original compounds are not isostructural. In this family, as in other families of mixed crystals, there is an excess enthalpy-entropy compensation. This compensation has a temperature dimension, and is called the compensation temperature (θ) of the family and/or subfamily. In the case of the R'_{II} and R'_{IV} rotator forms of the n-alkanols family its value is 362 K. This value is in line with the trend show by a large group of organic and inorganic mixed crystalline materials.

Introduction

Normal alkanols, CH_3–$(CH_2)_{n-1}$–OH (abbreviated here as C_nOH), are among the simplest of the substituted hydrocarbons. A single –OH group replaces a hydrogen atom at one end of the aliphatic chain, forming hydrogen bonds between the chains.

The study of these compounds and their mixtures is one of the research topics in the REALM (*Réseau Européen sur les Alliages Moléculaires*) network. The n-alkanols are interesting from both a fundamental and a practical point of view. Their high melting point means they can potentially be used as phase change materials (PCMs), for the storage of energy and for thermal protection. Mixing of different members of the family is a means to optimise the working temperature for heat storage for a given application. In fundamental terms, the n-alkanols family offers the opportunity of correlation of their properties with those of other families of mixed crystals, such as the n-alkanes.[1,2] Research into families of mixed crystals rather than isolated systems has a number of advantages. It allows correlation of results with one or more exo-thermodynamic parameters. Correlations of this kind, as a rule, improve the significance of the results and, what is more, often give rise to interesting empirical relationships.

This paper reports the melting behaviour of ten binary systems, $C_{15}OH$–$C_{16}OH$, $C_{16}OH$–$C_{17}OH$, $C_{17}OH$–$C_{18}OH$, $C_{18}OH$–$C_{19}OH$ and $C_{19}OH$–$C_{20}OH$ with $\Delta n = 1$ (difference in chain length), $C_{15}OH$–$C_{17}OH$, $C_{16}OH$–$C_{18}OH$, $C_{17}OH$–$C_{19}OH$ and $C_{18}OH$–$C_{20}OH$ with $\Delta n = 2$, and $C_{16}OH$–$C_{20}OH$ with $\Delta n = 4$, the majority of which have not been

published before. For these systems, we also crystallographically characterized the rotator forms that melt: R'_{II} ($R\bar{3}m$, $Z = 6$) and $R'_{IV}(C2/m, Z = 4)$, and determined the thermodynamic mixing properties, excess enthalpy and excess entropy. The experimental data and thermodynamic analysis, evidence a common characteristic temperature (θ) for R'_{II} and R'_{IV}.
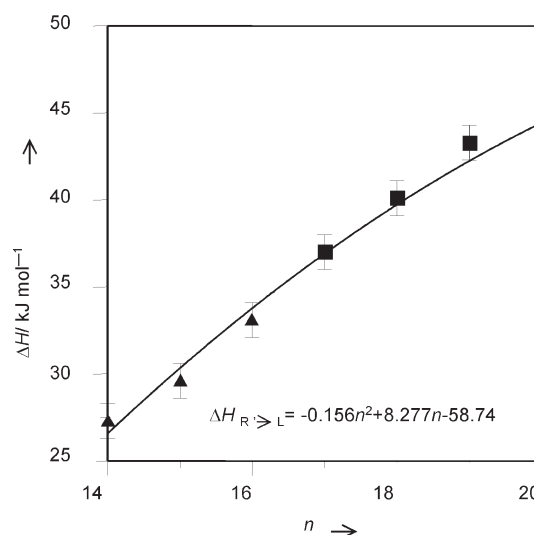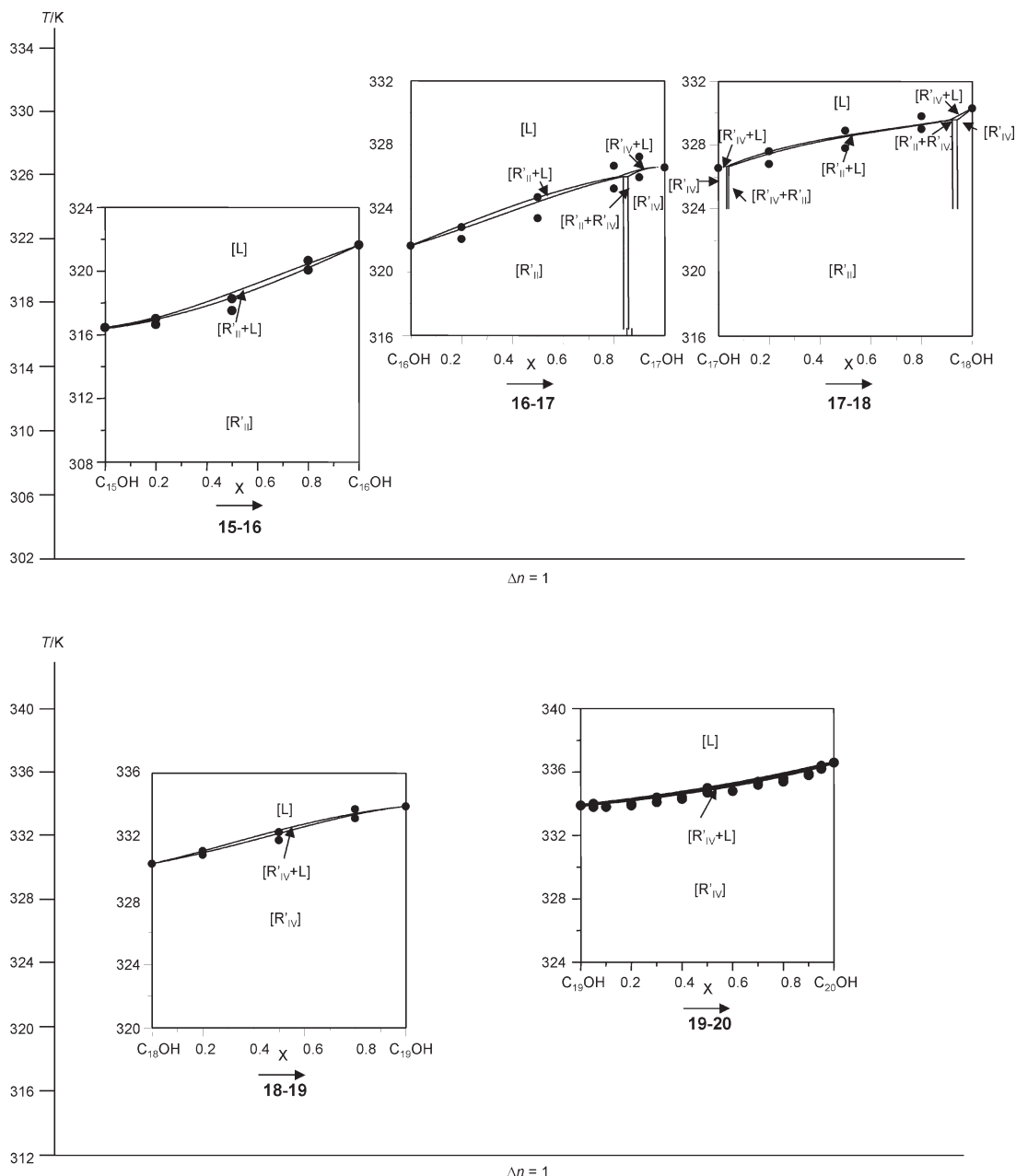

Fig. 1 Variation of the melting enthalpy *versus* n. ▲: R'_{II} form and ■: R'_{IV} form.

$$\Delta H_{R' \rightarrow L} = -0.156n^2 + 8.277n - 58.74$$

Fig. 2 Phase diagram of the systems with $\Delta n = 1$: $C_{15}OH$–$C_{16}OH$, $C_{16}OH$–$C_{17}OH$, $C_{17}OH$–$C_{18}OH$, $C_{18}OH$–$C_{19}OH$ and $C_{19}OH$–$C_{20}OH$. ●: experimental results and lines: calculated results.

Experimental data

All the experimental data comes from X-ray diffraction as a function of temperature and composition, and differential scanning calorimetry as a function of composition.

Pure substances

The pure substances show polymorphic behaviour. An ordered form (stable at room temperature) transforms into a rotator form a few degrees below the melting point.[3–7] In this form the molecules have rotational disorder around their long axis. In this paper's area of concern, which is the range in which the transition from solid to liquid takes place, two different rotator forms can be stabilized. The nature of these forms depends on chain length. In $C_{15}OH$ and $C_{16}OH$ the stable form before melting is R'_{II}.[4–6] For $C_{17}OH$, $C_{18}OH$, $C_{19}OH$ and $C_{20}OH$ the stable form before melting is the monoclinic R'_{IV}.[3,7] In energy terms the R'_{II} and the R'_{IV} forms are very similar. All

the $\Delta H_{R'II \to L}$ and $\Delta H_{R'IV \to L}$ *versus* n data can be correlated with a single polynomial function (degree 2) (Fig. 1).

Binary systems

The phase diagrams of the systems studied here are shown in Figs. 2 ($\Delta n = 1$), 3 ($\Delta n = 2$) and 4 ($\Delta n = 4$). Only the $C_{15}OH$–$C_{16}OH$, $C_{18}OH$–$C_{19}OH$ and $C_{19}OH$–$C_{20}OH^8$ binary systems, with $\Delta n = 1$, show total miscibility. In the $C_{16}OH$–$C_{17}OH$ system the miscibility (necessarily) is incomplete, because of the fact that the two pure substances do not have the same form. Out of the $\Delta n = 1$ systems $C_{17}OH$–$C_{18}OH$ is the exception: in spit of the fact that the two components have the same form (R'_{IV}), the form R'_{II} is stable one for intermediate compositions. The same situation is found for the $\Delta n = 2$ systems $C_{17}OH$–$C_{19}OH$ and $C_{18}OH$–$C_{20}OH$.[9] The phenomenon that by mixing a form is stabilized, that is metastable for the pure components, is also observed for n-alkane systems.
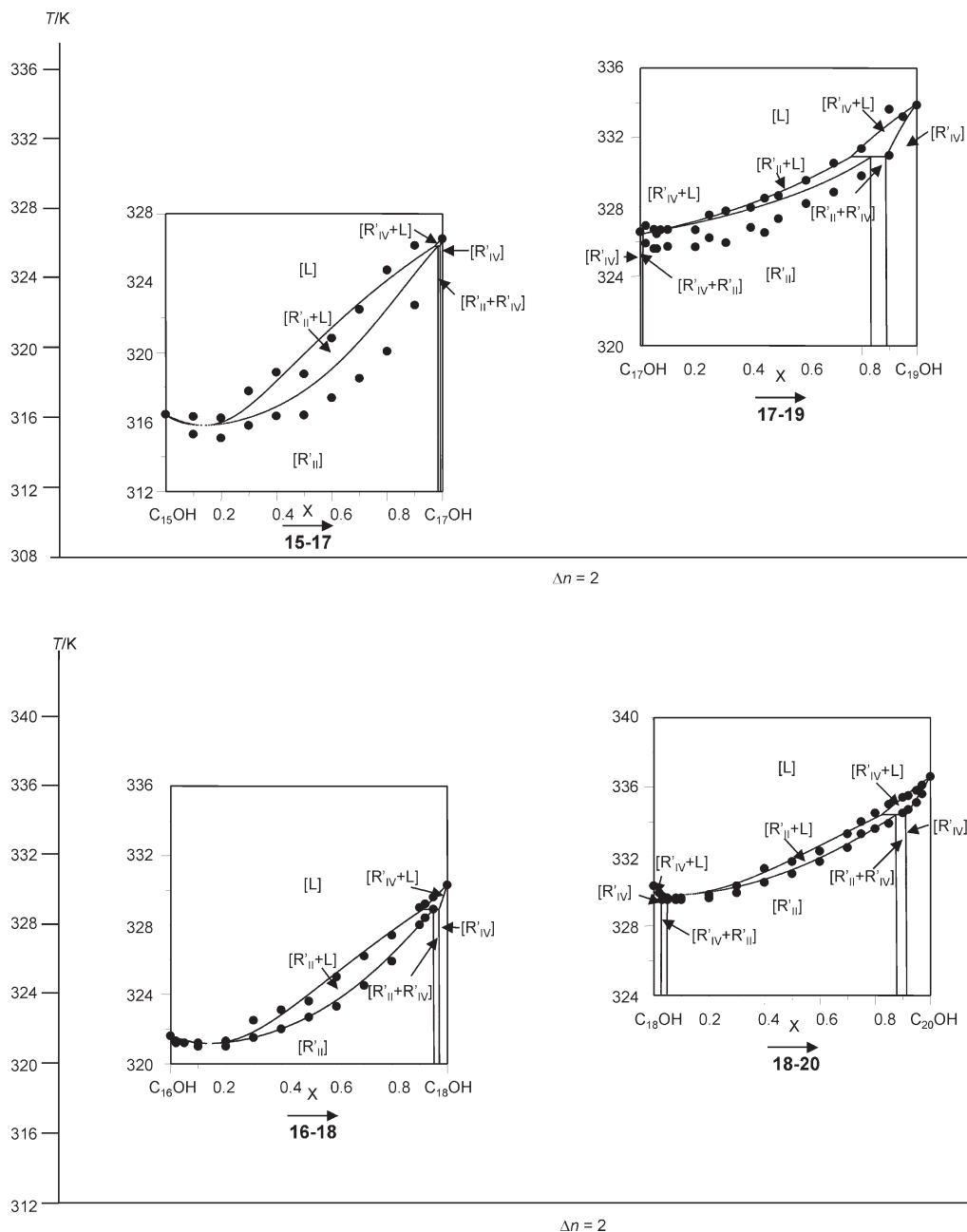
Fig. 3 Phase diagram of the systems with $\Delta n = 2$: $C_{15}OH$–$C_{17}OH$, $C_{16}OH$–$C_{18}OH$, $C_{17}OH$–$C_{19}OH$ and $C_{18}OH$–$C_{20}OH$. ●: experimental results and lines: calculated results.

Obviously, the alternation in a binary system of R'_{II} and R'_{IV} goes together with $(R'_{II} + R'_{IV})$ two-phase regions and with $(R'_{II} + R'_{IV} + L)$ three-phase equilibria of the eutectic or peritectic type, see Figs. 2–4.

The solid-liquid domains in all systems, are very narrow: less than 2 K in the $\Delta n = 1$ and $\Delta n = 2$ systems, and slightly less than 4 K in the $\Delta n = 4$ system. The width of the solid-liquid domains and the $R'_{II} + R'_{IV}$ domains increase with increasing Δn. The mixed samples of the systems are characterised by a large heat effect of melting: $\Delta H_{\text{melting}}$ between 30 and 43 kJ mol^{-1}.

Thermodynamic analysis

Each of the systems has been subjected to a thermodynamic analysis: in order to derive from the experimental data (i) thermodynamically correct phase diagrams; and (ii) the thermodynamic excess properties of the binary mixtures in their rotator state. The phase diagrams, along with the melting properties of the pure components, provide information on the excess Gibbs energy; more precisely, the difference between the excess Gibbs energies of liquid and rotator. The measured heats of melting as a function of composition provide the excess enthalpies. Details of the methodology, including the underpinning of the thermodynamic model and the approximations made, are given in ref. 1. The approximations concern the mixing properties of the liquid state, and the role of the (excess) heat capacity. Chemically similar substances that form mixed crystals generally give rise to liquid mixtures that, in first approximation, can be taken as ideal mixtures. It means that the excess properties, derived from the experimental data, fully are attributed to the rotator state. The heat capacity differences (liquid minus rotator) hardly have any influence on the results of the computations; and the more so because of the small temperature ranges. Therefore, the heats of melting of the components are taken as temperature independent. The excess Gibbs energies of mixed crystals, in good approximation and setting aside low temperatures, appear to be linear functions of
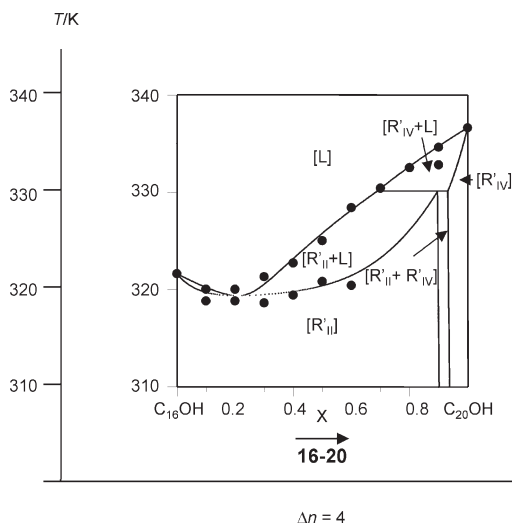
Fig. 4 Phase diagram of the $C_{16}H_{33}OH–C_{20}H_{41}OH$ systems with $\Delta n = 4$. ●: experimental results and lines: calculated results.

temperature; it means that their excess heat capacities virtually are zero. Against that background, the $AB\theta$ model has proved its usefulness. The excess Gibbs energy in terms of the model is given by eqn. (1), where A, B and θ are system-dependent parameters. The parameter A, with the dimension of energy, is a measure of the magnitude of the function; the dimensionless B expresses the asymmetry of the function; and θ, with the

dimension of temperature, its change with temperature. The expressions for the excess enthalpy and excess entropy are eqns. (2) and (3).

$$G^{E,sol}(T,x) = A(1 - T/\theta)x(1 - x)[1 + B(1 - 2x)] \quad (1)$$

$$H^{E,sol}(T,x) = H^{E,sol}(x) = Ax(1 - x)[1 + B(1 - 2x)] \quad (2)$$

$$S^{E,sol}(T,x) = S^{E,sol}(x) = (A/\theta)x(1 - x)[1 + B(1 - 2x)] \quad (3)$$

for $T = \theta$ the excess Gibbs energy ($G^E = H^E - TS^E$) goes through zero; θ is the temperature at which H^E and S^E (are said to) compensate one another; θ is the quotient of H^E and S^E. The thermodynamic computations were carried out with the LIQFIT[10] program, which is based on the EGC methodology.[11] By successive approximations, and using intermediate phase diagram calculations, the excess Gibbs energy of the rotator state is optimized and therewith the phase diagram. The deviation of the EGCs from a straight line is attributed to the rotator phases only.

The systems $C_{15}OH–C_{16}OH$, $C_{18}OH–C_{19}OH$, and $C_{19}OH–C_{20}OH$, display complete subsolidus miscibility in one of the rotator forms. The other systems have one or two two-phase regions of the type $[R'_{II} + R'_{IV}]$; their phase diagrams can be looked upon as the stable results of two, each other overlapping, $[R'_{II} + L]$ and $[R'_{IV} + L]$, melting loops. For the analysis of the diagrams with overlapping loops (one speaks of crossed[12,13]-and double crossed isodimorphism[13,14]), 'metastable' melting properties are needed for loops that do not end at a/the 'stable' melting point(s). The values of the stable

Table 1 Purity and thermophysical characteristics of the system compounds

	Purity (%GC)	$T_{melting}$/K	$\Delta H_{melting}$/kJ mol^{-1}	$\Delta S_{melting}$/J K^{-1} mol^{-1}	Transition
$C_{15}OH$	≥97%	316.4	29.6 ± 1.0	93.6	$R_{II} \to L$
$C_{16}OH$	~99%	321.6	33.1 ± 1.3	103.0	$R_{II} \to L$
$C_{17}OH$	≥97%	326.6	37.0 ± 1.0	113.3	$R_{IV} \to L$
		$(326.4)^a$	$(37.0)^a$	$(113.4)^a$	$(R_{II})^a \to L$
$C_{18}OH$	98.9	330.3	40.1 ± 1.0	121.3	$R_{IV} \to L$
		$(329.8)^a$	$(40.1)^a$	$(121.6)^a$	$(R_{II})^a \to L$
$C_{19}OH$	≥98%	333.9	43.3 ± 1.0	129.7	$R_{IV} \to L$
		$(333.0)^a$	$(43.3)^a$	$(130.0)^a$	$(R_{II})^a \to L$
$C_{20}OH$	≥98%	336.6	43.6 ± 1.3	129.5	$R_{IV} \to L$
		$(335.7)^a$	$(43.6)^a$	$(129.9)^a$	$(R_{II})^a \to L$

^{a} Metastable phases.

Table 2 Thermodynamic excess properties for the equimolar mixed crystalline R'_{II} form at the equimolar composition. Filled Circles: the rotator form is stable in the two n-alkanols. Open circles: the rotator form is not stable in the two n-alkanols, and half filled circles: the rotator form is stable in the n lower n-alkanol and metastable in the n higher n-alkanol.

| System	Code	$\bar{n}$	$\Delta n/\bar{n}$	T_{EGC}/K	$H^{E,R}$/J mol^{-1}	$G^{E,R}$/J mol^{-1}	$S^{E,R}$/J K^{-1} mol^{-1}	θ/K
$\Delta n = 1$								
15–16	●	15.5	0.065	318.2	295	62	0.73	404
16–17	◑	16.5	0.061	323.9	575	−41	1.90	303
17–18	○	17.5	0.057	328.4	938	−45	2.99	314
$18–19^a$	●	18.5	0.054	332.1	289	−18	0.92	314
$19–20^a$	●	19.5	0.051	334.9	231	40	0.57	405
$\Delta n = 2$								
15–17	◑	16	0.125	318.8	2136	313	5.72	373
16–18	◑	17	0.118	323.3	2287	309	6.12	374
17–19	○	18	0.111	328.5	1309	167	3.48	376
18–20	○	19	0.105	331.4	1751	169	4.77	367
$\Delta n = 4$								
16–20	○	18	0.222	322.5	4514	811	11.48	393

^{a} Concern to the R'_{IV} form.

and metastable melting properties are assembled in Table 1. The final phase diagrams have been calculated with PRO-PHASE.[15]

The calculated thermodynamic excess properties are given in Table 2, for the equimolar mixtures. The calculated phase diagrams are represented in Figs. 2 and 4 in the form of solid lining. The experimental phase diagram data are fully supported by the calculated phase diagrams. The mean difference between the experimental temperatures and the ones calculated, taken as abs $(T_{obs} - T_{calc})$, is 0.4 K. The value of 0.4 K is representative of the precision that is realizable by differential thermal analysis.[16] For the individual systems abs $(T_{obs} - T_{calc})$ ranges from 0.11 ($C_{18}OH$–$C_{20}OH$) to 0.9 ($C_{15}OH$–$C_{17}OH$).

Correlations and discussion

In Fig. 5 the calculated equimolar excess enthalpies are plotted *versus* the calculated equimolar excess entropies. The figure expresses the fact that the rotator state of the ten alkanol systems correspond to a class of similar systems in terms of enthalpy-entropy compensation. The compensation temperature, representative of the class, is calculated as 362 ± 38 K. The alkanol family is incorporated in Fig. 6, where for a variety of binary mixed crystals, families and isolated systems, the compensation temperature is plotted against the equimolar equal-G curve temperature. The latter is the melting temperature the equimolar mixture would have, if it were to melt isothermally (in a recent paper we have shown that alkane mixtures can be made to melt isothermally[29]). From Fig. 6 it follows that the alkanol systems are in line with the others. For families of systems that are homologous series of chain-molecule substances, the chain length of the molecules (the number of carbon atoms n) is a powerful and, at the same time, obvious parameter for correlating physical properties. This is clearly shown by Fig. 1 for the heats of melting; and from Figs. 2–4 and Table 1 it can be read that the melting points of the pure alkanols increase with n in a regular manner. The magnitude of the excess properties, read, the value of the model parameter A, stands in relation to the difference in chain length (of the component molecules of the binary systems), or rather to the difference in chain length, $\Delta n / \bar{n}$, where
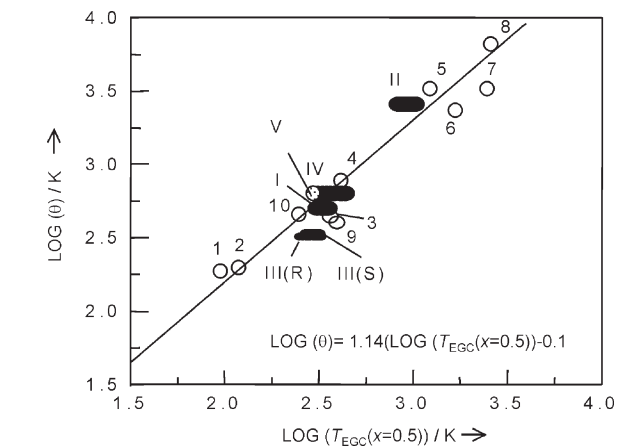
Fig. 6 log–log representation of compensation temperature θ *versus* T_{EGC} of mixed crystals of equimolar composition for different families of substances and isolated systems with known θ: (*V*) R'_{II} and R'_{IV} rotator forms of the n-alkanols, (*I*) 1,4-dihalobenzenes,[17] (*III(R)*) the rotator I and II, and (*III(S)*) 'ordered' forms of n-alkanes,[1,2,18] (*IV*) a group of plastic–crystalline neopentane derivatives,[19] (1) Ar+Kr and (2) Kr+Xe,[20] (3) l-carvoxime,[21] (5) Ni+Au,[22] (6) Pd+Au,[23] (8) MgO+CaO and (7) SrO+BaO,[24] (II) alkali halides,[25] (9) CBr4+C_2Cl_6,[26] (10) CCl_4+C(CH_3)$_4$[27] and (4) 1,2,4,5-tetrachloro-benzene +1,2,4,5-tetrabromobenzene.[28]

$\bar{n} = 0.5(n + n')$. In Fig. 7, the experimental equimolar H^E values (which are 0.25 times the parameter A) are plotted *versus* $\Delta n / \bar{n}$; in comparison with the data for the n-alkanes. In the case of the n-alkane systems, given the experimental uncertainties, it had not been possible to make a distinction between the excess properties of the forms R_I and R_{II}, for given $\Delta n / \bar{n}$. Obviously, same holds for the alkanol forms R'_{II} and R'_{IV}; in view of the lower number of systems, and, possibly, also because of higher experimental uncertainties. Unlike the situation for the parameter θ, for which Fig. 6 is evidence of a unifying principle, a correlation of the A parameters for the collection of (families of) systems is not yet available. From Fig. 7 it follows that for given $\Delta n / \bar{n}$, the alkanol systems have smaller excess properties than the alkane systems. A theoretical analysis of the differences, however, remains to be made.
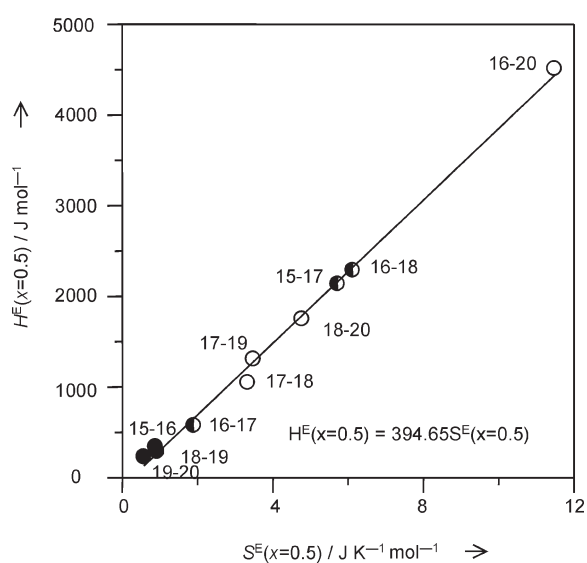
Fig. 5 Excess enthalpy *versus* excess entropy at equimolar composition. Filled circles: the rotator form is stable in the two n-alkanols. Open circles: the rotator form is not stable in the two n-alkanols. Half filled circles: the rotator form is stable in the n lower n-alkanol and metastable in the n higher n-alkanol.
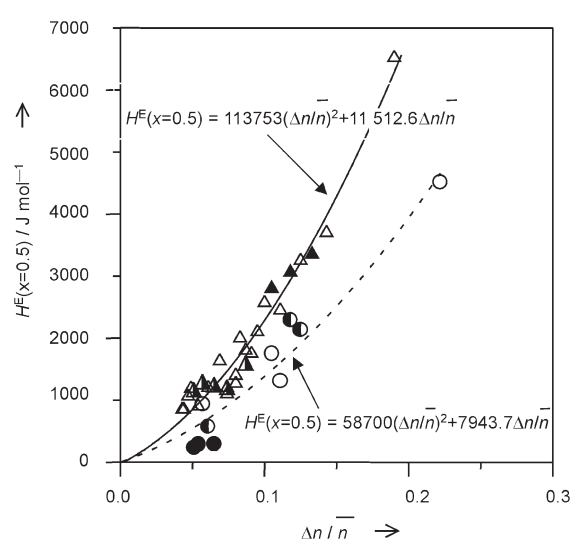
Fig. 7 Excess enthalpy as a function of $\Delta n / \bar{n}$. Circle: n-alkanol family. Triangle: n-alkane family.[1,30] Filled symbols: the rotator form is stable in the two n-alkanols. Open symbols: the rotator form is not stable in the two components. Half filled circles: the rotator form is stable in the *n* lower component and metastable in the n higher component.

Conclusions

i. Before melting, the n-alkanols studied, crystallise in either one of the two rotator forms R'_{II} and R'_{IV}. The two forms are structurally different; their thermodynamic properties, on the other hand, are very much alike.

ii. The excess Gibbs energies of the binary mixtures are well described by the $AB\theta$ formula, eqn. (1). Given the experimental uncertainties, a distinction between R'_{II} and R'_{IV}, as regard excess properties, was not made. The magnitude parameter A is system-dependent; its value can be related to the relative difference in chain length between the molecules of the components of a given system. The alkanol family of systems is characterized by a uniform value for the parameter θ, which is $\theta = 362$ K.

iii. The alkanol systems combine high heats of melting with narrow solid to liquid two-phase regions (less than 2 K for the $\Delta n = 1$ and $\Delta n = 2$ systems: less than 4 K for the $\Delta n = 4$ system). These properties, and the fact that by variation of composition the melting temperature can be optimised, make that the alkanols correspond to a large range of Phase Change Materials for thermal thermal protection and storage of energy.

Acknowledgements

References

1   H. A. J. Oonk, D. Mondieig, Y. Haget and M. A. Cuevas-Diarte, *J. Chem. Phys.*, 1998, **108**, 715.
2   D. Mondieig, P. Espeau, L. Robles, Y. Haget, H. A. J. Oonk and M. A. Cuevas-Diarte, *J. Chem. Soc. Faraday Trans.*, 1997, **93**, 3343.
3   L. Ventolà, M. Ramírez, T. Calvet, X. Solans, M. A. Cuevas-Diarte, N. Negrier, D. Mondieig, J. C. van Miltenburg and H. A. J. Oonk, *Chem. Mater.*, 2002, **14**, 508.
4   L. Ventolà, European Thesis, University of Barcelona, Spain, 2001.
5   M. Ramírez, European Thesis, University of Barcelona, Spain, 2002.
6   E. Frede and D. Precht, *Kiel. Milchwirtsch. Forschungsber*, 1974, **26**, 325.
7   T. Seto, *Mem. Collect. Sci. Univ. Kyoto*, 1962, **A30**, 89.
8   L. Ventolà, M. Calvet, M. A. Cuevas-Diarte, D. Mondieig and H. A. J. Oonk, *Phys. Chem. Chem. Phys.*, 2002, **4**, 1953.
9   L. Ventolà, M. Calvet, M. A. Cuevas-Diarte, D. Mondieig and H. A. J. Oonk, *Phys. Chem. Chem. Phys.*, submitted.
10 M. H. G. Jacobs and H. A. J. Oonk, LIQFIT program, Utrecht University, Netherlands, 1989.
11 J. A. Bouwstra, N. Brouwer, A. C. G. Van Genderen and H. A. J. Oonk, *Thermochimica Acta*, 1980, **38**, 97.
12 L. C. Pardo, M. Barrio, J. Ll. Tamarit, D. O. López, J. Salut, P. Négrier and D. Mondieig, *Phys. Chem. Chem. Phys.*, 2001, **3**, 2644.
13 M. A. Cuevas-Diarte, P. Espeau, Y. Haget, D. Mondieig, H. A. J. Oonk and L. Robles, *XXI Journées des Equilibres entre Phases*, Université Rouen, France, 1995, p. 63.
14 P. Espeau, European Thesis, Université Bordeaux I, France, 1995.
15 J. S. van Duijneveldt, F. S. A. Baas and H. A. J. Oonk, *PROPHASE program*, Utrecht University, Netherlands, 1988.
16 P. R. van der Linde, M. Bolech, R. den Besten, M. L. Verdonk, J. C. van Miltenburg and H. A. J. Oonk, *J. Chem. Thermodynamics.*, 2002, **34**, 613.
17 T. Calvet, M. A. Cuevas-Diarte, Y. Haget, P. R. van der Linde and H. A. J. Oonk, *Calphad*, 1991, **15**, 225.
18 F. Rajabalee, V. Metivaud, H. A. J. Oonk, D. Mondieig and P. Waldner, *Phys. Chem. Chem. Phys.*, 2000, **2**, 1345.
19 D. O. López, J. Salud, J. Ll. Tamarit, M. Barrio and H. A. J. Oonk, *Chem. Mater.*, 2000, **12**, 1108.
20 J. F. Walling and G. D. Halsey, *J. Phys. Chem.*, 1958, **62**, 756.
21 M. T. Calvet and H. A. J. Oonk, *Calphad*, 1995, **19**, 49.
22 C. M. Sellers and F. Maak, *Trans. Metall. Soc. AIME*, 1966, **236**, 457.
23 H. Okamoto and T. B. Massalsky, *Bull. Alloy Phase Diag.*, 1985, **6**, 229.
24 W. J. Van der Kemp, J. G. Blok, P. R. van der Linde, H. A. J. Oonk, A. Schuijff and M. L. Verdonk, *Calphad*, 1994, **18**, 225.
25 W. J. van der Kemp, J. G. Blok, A. C. G. van Genderen, P. J. van Ekeren and H. A. J. Oonk, *Thermochim. Acta*, 1992, **196**, 301.
26 J. van Braak, D. O. López, J. Salud, J. Ll. Tamarit, M. H. G. Jacobs and H. A. J Oonk, *J. Cryst. Growth*, 1997, **180**, 315.
27 J. Salud, D. O. López, J. van Braak, M. Barrio, M. H. G. Jacobs, J. Ll. Tamarit and H. A. J. Oonk, *XXIV Journées des Equilibres entre Phases*, ed. F. A. Kuhnast and J. J. Kuntz, Université Nancy, France, 1998, 261.
28 M. J. van Genderen, D. Mondieig, Y. Haget, M. A. Cuevas Diarte and H. A. J. Oonk, *Calphad*, 1992, **16**, 301.
29 D. Mondieig, V. Metivaud, H. A. J. Oonk and M. A. Cuevas-Diarte, *Chem. Mater*, 2003, **15**, 2552.
30 V. Metivaud, European Thesis, Université Bordeaux I, France, 1999.