

The C₁₉H₃₉OH–C₂₀H₄₁OH system: Experimental phase diagram and thermodynamic modelling

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The experimental phase diagram of the C₁₉H₃₉OH–C₂₀H₄₁OH system has been determined and, subsequently, subjected to thermodynamic modelling. The pure components of the system are polymorphic. At low temperature they have monoclinic phases that are different: a γ phase ($C2/c$, $Z = 8$) for C₂₀H₄₁OH and a β phase ($P2_1/c$, $Z = 8$) for C₁₉H₃₉OH. At high temperature, a few degrees before melting, the two components have the same monoclinic phase R'_{IV} ($C2/m$, $Z = 4$). The solid–liquid equilibrium can be explained by simple isomorphism, and the solid–solid equilibria by crossed isodimorphism. The solid–liquid domain ([R'_{IV} + L]) is very narrow (less than 0.2 K), and the enthalpy of fusion is high enough to consider the alloys of the system as promising candidates for thermal energy storage. Three solid–solid domains were observed ([β + R'_{IV}], [γ + R'_{IV}] and [β + γ]), these are related by a peritectoid invariant at ≈ 323 K, with compositions from 55 and 80 mol% in C₂₀H₄₁OH. One of the domains ([β + R'_{IV}]) has a minimum at ≈ 321 K and about 40 mol% in C₂₀H₄₁OH. The calculated phase diagram, obtained by thermodynamic analysis, is in full agreement with the experimental one.

1. Introduction

This article is part of a general study of the solid state miscibility in the family of the n-alkanols. We present the experimental phase diagram and a thermodynamic analysis of the C₁₉H₃₉OH–C₂₀H₄₁OH system. The work on the n-alkanols is one of the activities of the REALM† network (*Réseau Européen sur les Alliages Moléculaires*), dedicated to the preparation, structural and thermodynamic characterisation, modelling and application of molecular alloys.^{1–4} Normal alkanols are among the simplest of the substituted hydrocarbons. A single –OH group replaces a hydrogen atom at one end of the aliphatic chain. Alkanols are substances with a high heat of fusion. This implies that the alkanols and their alloys are promising candidates for storing thermal energy.

Some binary systems among n-alkanols have been studied before,^{5–8} but to our knowledge the phase diagram of this system has not been published yet. The system belongs to the category of binary system with $\Delta n = 1$ between two n-alkanols, one with an odd number of carbon atoms in the chain and the other with an even number. The two constituents of the title system are polymorphic; not in the same manner, however.⁹ At low temperature, the two constituents have ordered monoclinic phases: the phase β for C₁₉H₃₉OH (with $P2_1/c$, $Z = 8$);⁹ and the phase γ ($C2/c$, $Z = 8$) for C₂₀H₄₁OH.^{10–11} At high temperature, the two constituents have the same disordered, monoclinic phase, R'_{IV} ($C2/m$, $Z = 4$).⁹

For the preparation of mixed samples we have followed two different procedures: dissolution–evaporation (D + E), and melting–quenching (M + Q). In the case of D + E, mixed crystalline material is obtained by rapid precipitation from a solution in diethyl ether. In the case of M + Q, sealed liquid mixtures are brought into liquid nitrogen. We have observed that the behaviour of the mixed samples is dependent on the method of preparation.¹² Unlike the D + E samples, the M + Q samples, when kept at 279 K, undergo changes that evolve in time, even after a period of two years. In view of the observations, we have used, for the determination of the solid–solid part of the phase diagram, only the D + E samples. For the solid–liquid part, we have used both D + E and M + Q samples.

Experimental

The n-alkanols, CH₃–(CH₂)_(n–1)–OH (hereafter abbreviated C_nH_{2n+1}OH), used were purchased from Fluka Chemical with an estimated purity of better than 98%. The substances were used without further purification.

The mixed samples were obtained by the dissolution–evaporation (D + E), and melting–quenching (M + Q) methods. In the D + E method the components weighed in the desired proportions, are dissolved in diethyl ether, then precipitated by rapid evaporation of the solvent. In the M + Q method the components are weighed in the desired proportions, melted and mixed to get an entirely homogeneous sample and then quenched in liquid nitrogen. The phase diagram characteristics were determined by means of two techniques:

† The REALM consists of four European Universities: Universitat de Barcelona, Universitat Politècnica de Catalunya, University of Utrecht and Université Bordeaux I.

Differential scanning calorimetry (DSC)

Calorimetric measurements were made with a Perkin-Elmer DSC-7 calorimeter. The following conditions were adopted during the analysis:

- (i) Sample weight: between 3.9 and 4.1 mg
- (ii) Scanning rate: 2 K min^{-1}
- (iii) Six independent measurements for each sample
- (iv) The instrument was calibrated with the known melting point and enthalpy of indium and melting point of n-decane
- (v) The random part of the uncertainties was estimated using Student's method, with a 95% threshold of reliability. The uncertainties in temperature and heat-flow calibration coefficient for the DSC were estimated at $\pm 0.2 \text{ K}$ and 2%, respectively.

From the DSC curves the characteristic temperatures were determined with the use of the shape factor method.¹³ Enthalpy effects were evaluated by integration of the DSC signals.

X-ray powder diffraction analysis (XRD)

Two instruments were used: a Siemens D-500 diffractometer and a Guinier-Simon camera.

Siemens D-500 diffractometer: This instrument was used with a Bragg-Brentano geometry. Monochromatic Cu $K\alpha_1$ ($\lambda = 1.5406 \text{ \AA}$) radiation was selected by a secondary monochromator. The data were collected at different temperatures using an Anton PAAR TTK system, and applying a heating rate of 0.02 K s^{-1} and 5 min of stabilisation time. The analysis performed corresponds to a heating process from 298 K to the melting temperature. The patterns were scanned with a step size of 0.025° , step time of 5 s and the 2θ range was $1.6\text{--}60^\circ$. These patterns allow us to determine the cell parameters of the mixed crystals using the "Pattern Matching" option of the program FULLPROF.¹⁴

Guinier-Simon camera: This instrument works in transmission mode using Cu $K\alpha$ radiation, with a quartz crystal as the primary monochromator. The sample was mounted on a rotating sealed capillary of 0.5 mm diameter, perpendicular to the X-ray radiation beam; the window width used was 1.5 mm. The sample was heated at 0.5 K h^{-1} . The continuous evolution of the X-ray pattern is registered on a photographic film, which is moved perpendicularly to the beam at a constant rate of 1 mm h^{-1} .

Phase diagram determination

Different mixed samples of the system were studied to determine the phase diagram (Fig. 1): 5, 10, 20, 30, 40, 50, 60, 70, 80, 90 and 95 mol% in $\text{C}_{20}\text{H}_{41}\text{OH}$ for the characterisation of the melting phenomena, and 5, 20, 30, 50, 60, 85 and 90 mol% in $\text{C}_{20}\text{H}_{41}\text{OH}$ for the characterisation of solid-solid equilibria.

The information on the system comes from X-ray diffraction as a function of temperature and composition, and differential thermal analysis as a function of composition. The system is characterised by:

- (i) A solid-liquid domain: $[\text{R}'_{\text{IV}} + \text{L}]$. Its width is not larger than 0.2 K
- (ii) Three solid-solid domains: $[\gamma + \beta]$, $[\beta + \text{R}'_{\text{IV}}]$ and $[\gamma + \text{R}'_{\text{IV}}]$
- (iii) Four single-phase domains: $[\gamma]$, $[\beta]$, $[\text{R}'_{\text{IV}}]$ and $[\text{L}]$
- (iv) A minimum at $\approx 321 \text{ K}$ and $x \approx 40 \text{ mol\%}$ in $\text{C}_{20}\text{H}_{42}\text{O}$ for the $[\beta + \text{R}'_{\text{IV}}]$ domain. This has been deduced from a global phase diagram analysis, and it was corroborated by the thermodynamic analysis
- (v) A $[\beta + \gamma + \text{R}'_{\text{IV}}]$ peritectoid three-phase equilibrium at $\approx 323 \text{ K}$ for compositions between 55 and 80 mol% in $\text{C}_{20}\text{H}_{41}\text{OH}$; the coordinates follow from the XRD results for

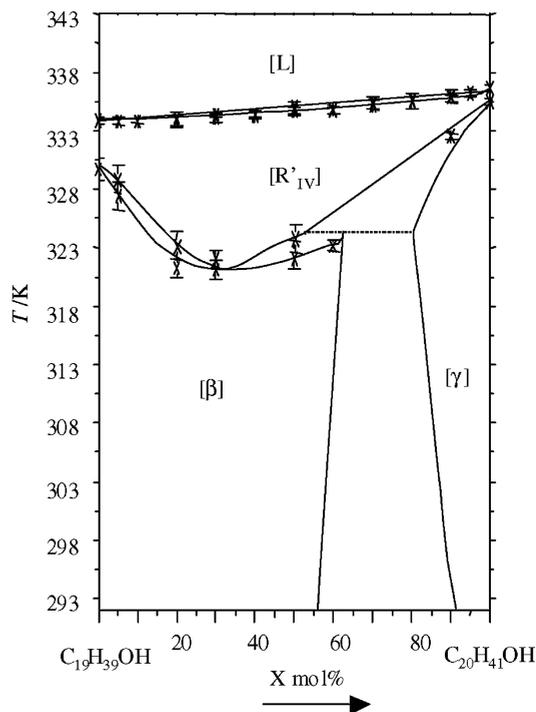


Fig. 1 $\text{C}_{19}\text{H}_{39}\text{OH}$ - $\text{C}_{20}\text{H}_{41}\text{OH}$ experimental phase diagram.

the samples with 60, 85 and 90 mol% $\text{C}_{20}\text{H}_{41}\text{OH}$, and are supported by the thermodynamic analysis.

Crystallographic characterisation

Different experiments under isothermal and isoplethic conditions were carried out for the compositions. The results have allowed us to identify and characterise the different alloys as well as the limits of their stability domains.

Isothermal analysis

Measurements at 293 K. The $[\gamma]$, $[\beta]$ and $[\gamma + \beta]$ domains were observed. The β phase is the stable phase of $\text{C}_{19}\text{H}_{39}\text{OH}$ and the γ phase is the stable phase of $\text{C}_{20}\text{H}_{41}\text{OH}$ at this temperature. The limits of the $[\gamma + \beta]$ domain were derived from the evolution as a function of composition of the lattice distances d_{006} of each of the two phases (Fig. 2). The β phase was found between pure $\text{C}_{19}\text{H}_{39}\text{OH}$ and 55 mol% in

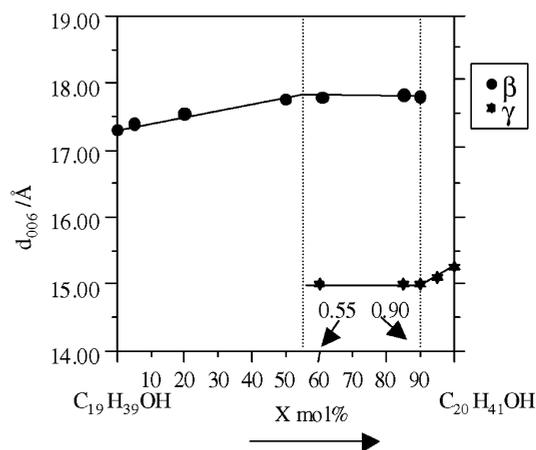


Fig. 2 Variation of d_{006} versus composition of the γ and β phases at 293 K.

$C_{20}H_{41}OH$. The γ phase was found for compositions rich in $C_{20}H_{41}OH$, from 90 mol% on.

Table 1 gives the results of the cell parameter refinement for the γ and β phases of the compositions studied.

Measurements at 333K. The R'_{IV} phase was observed in a wide range of composition: between pure $C_{19}H_{39}OH$ and 85 mol% in $C_{20}H_{41}OH$. This phase is the melting phase of each of the pure alkanols. For compositions rich in $C_{20}H_{41}OH$, we observe the $[\gamma + R'_{IV}]$ and $[\gamma]$ domains as $C_{20}H_{41}OH$ mole fraction increases.

In Table 2, are given the cell parameters for the R'_{IV} phase at 333 K for the studied compositions.

Isoplethic analysis

The isoplethic analysis of the different compositions has allowed us to determine the stability limits of the different phase domains as a function of temperature.

Energetic characterisation

The temperatures and enthalpy effects of the transitions in the mixed samples and the pure alkanols were determined (Table 3). In Fig. 3, DSC diagrams are shown for some of the compo-

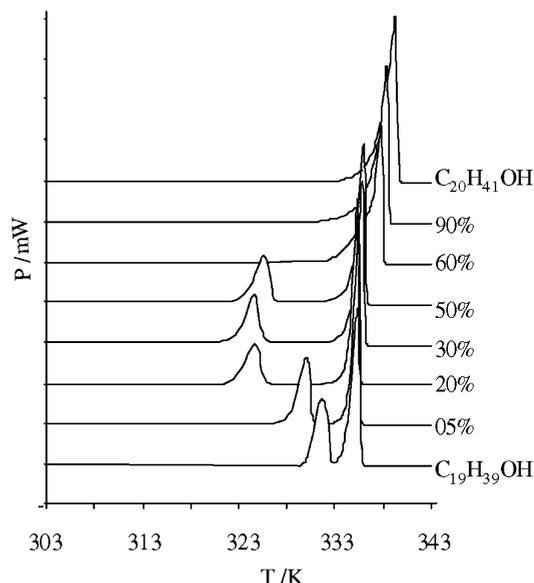


Fig. 3 Evolution of the DSC curves.

Table 1 Cell parameters of the β and γ phases at 293 K

$C_{20}H_{41}OH$ fraction	$a/\text{\AA}$	$b/\text{\AA}$	$c/\text{\AA}$	$\beta/^\circ$	Phase
0.20	5.036(1)	7.385(1)	106.95(2)	90.65(2)	β
0.30	5.029(1)	7.377(2)	107.29(3)	90.60(2)	β
0.50	5.034(1)	7.383(1)	108.20(2)	90.72(1)	β
0.95	9.000(6)	4.969(1)	108.49(7)	122.8(4)	γ^a

^a These parameters are for the γ phase with the space group $A2/a$ (non-conventional) to facilitate the comparison between the different phases.

Table 2 Cell parameters of the R'_{IV} phase at 333 K

$C_{20}H_{41}OH$ fraction	$a/\text{\AA}$	$b/\text{\AA}$	$c/\text{\AA}$	$\beta/^\circ$
0.20	8.328(6)	4.938(3)	51.25(8)	91.6(3)
0.30	8.330(9)	4.937(7)	51.63(9)	92.1(4)
0.50	8.328(6)	4.935(6)	52.18(9)	92.1(3)
0.60	8.320(7)	4.936(4)	52.68(9)	93.3(3)
0.85	8.334(5)	4.938(9)	53.17(7)	93.4(2)
0.90	8.340(6)	4.940(5)	53.24(9)	93.4(3)

Table 3 Transition temperatures and enthalpies of $C_{19}H_{39}OH$, $C_{20}H_{41}OH$ and mixed compositions

$x\%$ $C_{20}H_{41}OH$	$T_{\text{solvi}}/\text{K}$ $\beta \rightarrow R'_{IV}$	$T_{\text{solvi}}/\text{K}$	$\Delta H_{\text{trans}}/\text{kJ mol}^{-1}$	T_{sol}/K $R'_{IV} \rightarrow L$	T_{liq}/K	T_{fus}/K	$\Delta H_{\text{fus}}/\text{kJ mol}^{-1}$
$C_{19}H_{39}OH$	329.7 ± 0.9	29.1 ± 0.6				333.9 ± 0.5	43.3 ± 1.0
0.05	327.6 ± 1.4	328.5 ± 0.5	24.0 ± 1.0	333.8 ± 0.5	334.0 ± 0.4		43.2 ± 0.8
0.10				333.8 ± 0.4	333.8 ± 0.4		43.2 ± 1.0
0.20	321.3 ± 1.0	323.4 ± 0.7	22.0 ± 0.8	333.9 ± 0.7	334.0 ± 0.8		43.1 ± 0.9
0.30	321.3 ± 1.2	323.3 ± 0.5	23.1 ± 1.0	334.1 ± 0.6	334.4 ± 0.5		43.0 ± 0.9
0.40				334.3 ± 0.5	334.4 ± 0.5		43.3 ± 1.5
0.50	322.1 ± 0.6	324.2 ± 0.4	23.7 ± 1.0	334.7 ± 0.6	335.0 ± 0.7		43.3 ± 0.9
0.60	323.1 ± 0.5	324.8 ± 0.5		334.8 ± 0.5	334.8 ± 0.5		43.2 ± 1.0
0.70				335.2 ± 0.4	335.4 ± 0.8		43.3 ± 0.8
0.80				335.4 ± 0.7	335.6 ± 0.8		43.3 ± 0.8
0.90				335.8 ± 0.5	335.9 ± 0.7		43.1 ± 0.7
0.95				336.2 ± 0.5	336.4 ± 0.5		
$C_{20}H_{41}OH$	$\gamma \rightarrow R'_{IV}$	335.5 ± 0.5	28.4 ± 0.4			336.6 ± 0.5	43.6 ± 2.2

sitions studied. The most energetic DSC signal corresponds to melting, and the least energetic corresponds to the β to R'_{IV} transition in the samples containing 5, 20, 30, and 50 mol% of $C_{20}H_{41}OH$.

Thermodynamic analysis

In order to model the phase diagram, we have used the T_{EGC} concept introduced by Oonk.¹⁵ The thermodynamic computations, in terms of the above formalism, were carried out with the LIQFIT program.¹⁶ This program adjusts by successive approximations (with the EGC method) a liquidus curve to the experimental one, calculating G^E . Some simplifications: we have assumed: the liquid phase to be an ideal solution ($G^{E,liq} = 0$), neglected the ΔC_p of the original compounds, and considered $G^{E,sol}$, $H^{E,sol}$, $S^{E,sol}$ independent from the temperature.

For the solid–liquid [R'_{IV} + L] equilibrium we have used the melting properties of the pure component alkanols and the experimental liquidus data. The $G^{E,R'_{IV}}$ obtained, along with the temperatures and entropies of transitions of the pure components are needed for the modelling of the solid–solid equilibria [β + R'_{IV}] and [γ + R'_{IV}]. The transition properties of the stable forms were determined from DSC data, whereas the transition properties of metastable forms of the pure components were obtained from interpolation of a polynomial fit of the values of the n-alkanols where these forms are stable. These values are: $T_{\beta \rightarrow R'_{IV}}^m = 331.8$ K, $\Delta S_{\beta \rightarrow R'_{IV}}^m = 85.6$ J K mol⁻¹ for $C_{20}H_{41}OH$ and $T_{\gamma \rightarrow R'_{IV}}^m = 320.1$ K and $\Delta S_{\gamma \rightarrow R'_{IV}}^m = 90.9$ J K mol⁻¹ for $C_{19}H_{39}OH$. The LIQFIT computations were made with the superior solvus curve of each solid–solid equilibrium. After the LIQFIT computations on each of the three two-phase situations, the complete stable phase diagram was calculated by means of the PROPHASE program.¹⁷

In Fig. 4 the results of the different assessments are shown. We can observe that there is perfect agreement between the experimental data and the calculated phase diagram.

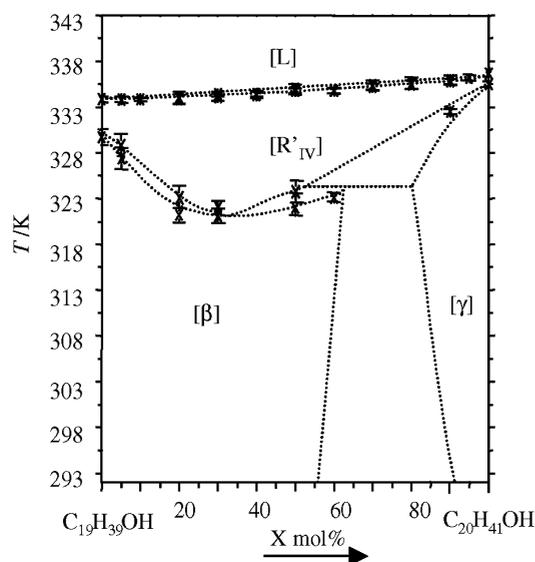


Fig. 4 Calculated phase diagram and experimental points.

Conclusions

The two pure-component alkanols have a different polymorphic behaviour. At room temperature there are two different ordered phases: β for $C_{19}H_{39}OH$ and γ for $C_{20}H_{41}OH$. At high temperature, a few degrees before melting, both ordered phases transform into an R'_{IV} rotator phase.

The phase diagram has a solid–liquid domain ($[R'_{IV} + L]$), that can be interpreted by simple isomorphism, and three solid–solid domains, ($[\gamma + \beta]$, $[\beta + R'_{IV}]$ and $[\gamma + R'_{IV}]$), that can be interpreted by crossed isodimorphism. The $[R'_{IV} + L]$ domain is very narrow (less than 0.2 K), and the melting enthalpy values are high enough to consider the domain as a good candidate for the storage of thermal energy. The three solid–solid domains are related by a peritectoid three-phase equilibrium at ≈ 323 K between 55 and 80 mol% in $C_{20}H_{41}OH$ compositions. This was derived from the XRD results. The $[\beta + R'_{IV}]$ domain shows a minimum at ≈ 321 K and ≈ 40 mol% in $C_{20}H_{41}OH$. This was deduced from a global phase diagram analysis.

The experimental phase diagram characteristics are fully supported by the outcome of the thermodynamic analysis.

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