

Orientationally Disordered Mixed Crystals Sharing Methylchloromethanes [(CH₃)_{4-n}CCl_n, n = 0, ..., 4]

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The experimental systems studied are the five methylchloromethanes [(CH₃)_{4-n}CCl_n, n = 0, ..., 4] and seven of their binary combinations, the accent being on the thermodynamic mixing properties in the plastic crystalline (orientationally disordered) state with its three forms (rhombohedral, face-centered cubic and simple cubic). It is demonstrated that a uniform description can be given of the thermodynamic excess properties characterized by a uniform temperature (420 K) of enthalpy/entropy compensation. The magnitude of the excess properties is related to volumetric mismatch between the components of a system, and, to a relatively small extent, to the dipolar nature of the molecules.

Introduction

The experimental systems, dealt with in this paper, are five pure substances, referred to as the methylchloromethanes, and seven of their binary combinations. The substances are characterized by the formula (CH₃)_{4-n}CCl_n, with 0 ≤ n ≤ 4; they are 2,2-dimethylpropane (or neopentane, Cl:0 for short), 2-chloro-2-methylpropane (Cl:1), 2,2-dichloropropane (Cl:2), 1,1,1-trichloroethane (Cl:3), and tetrachloromethane (carbon tetrachloride, Cl:4).

Like many other substances with globular molecules, the methylchloromethanes give rise to a plastic crystalline state—a mesostate, between “normal” solid and liquid, in which the molecules have rotational freedom.^{1,2} The plastic crystalline state is the subject of this paper, in particular, the binary mixed state and its structural and thermodynamic characteristics.

Within the plastic crystalline state the methylchloromethanes exhibit a polymorphic nature such that maximally three forms are involved: (i) FCC (face-centered cubic), (ii) SC (cubic), and (iii) R (rhombohedral). FCC is the stable form of Cl:0³ and Cl:1⁴, and R is the stable form of Cl:2, Cl:3, and Cl:4.^{5–8} As an invariably metastable form, FCC has a real appearance for Cl:3 and Cl:4, and so has SC for Cl:2.^{4–15}

At present, and thanks to the techniques of X-ray diffraction and (micro)calorimetry, the phase behavior is known for seven out of the 10 possible binary combinations of the five methylchloromethanes.^{9–15} In addition to the phase behavior, in the form of temperature vs composition (TX) phase diagrams, the calorimetric measurements have provided the heats of phase transitions as a function of composition. The available information, when combined with the thermodynamic mixing properties of the mixtures in the liquid state, can be used to elucidate the thermodynamic mixing properties of the plastic crystalline mixtures in the forms FCC and R.

In our investigation, reported in this paper, we have brought together the experimental data and subjected the data to a thermodynamic analysis. As a subsequent step, we have explored the possibility of combining the results obtained for the individual binary systems to a coherent, unifying description of the thermodynamic mixing properties, in the plastic crystalline state, for the ensemble of binary systems. Correlations between pure compound properties, which fall outside the scope of this paper, have been detailed elsewhere.^{16,17}

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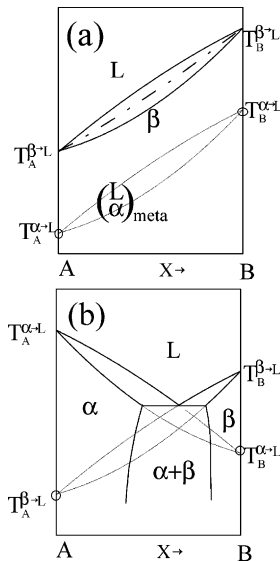


Figure 1. Two kinds of polymorphic phase behavior, representative of the systems studied. Solid and dashed curves represent stable and metastable behavior, respectively. Open circles represent so-called metastable melting points. The dotted-dashed line in Figure 1a represents the EGC-curve.

Thermodynamic Background

The thermodynamic background presented in this section consists of two parts. The first is related to the thermodynamic analysis of the phase diagrams and the second to the thermodynamic description of the mixed plastic crystalline state.

For our purpose it is expedient to distinguish between the two types of phase behavior that are presented by Figure 1. Three phases are involved: liquid (L) and the two solid phases, α and β .

For the case represented by Figure 1a, the form α is metastable for the pure components and also for the binary mixtures. The lower loop of the diagram represents the change from α to liquid. The (so-called) metastable loop emanates from component A's metastable melting point, and ends in B's metastable melting point.

For the other case, referred to as crossed isodimorphism,^{12,18–23} the form α is stable for component A, and the form β is stable for component B (β is metastable for A and α is metastable for B). The “stable” phase diagram can be looked upon as the stable result of two, each other crossing, solid–liquid loops. The two crossing loops imply a stable three-phase equilibrium ($\alpha + \beta + L$), which, in the case of Figure 1b, is eutectic.

Each of the three forms (α , β , L), in which $(1 - X)$ mole of component A mixes with X mole of component B, is characterized by its own Gibbs function

$$G^j(T, X) = (1 - X)G_A^{*j}(T) + XG_B^{*j}(T) + RT[X \ln(X) + (1 - X) \ln(1 - X)] + G^{Ej}(T, X) \quad (1)$$

where $j = \alpha, \beta, L$; T is the thermodynamic temperature; and R is the gas constant ($R = 8.314\,472\text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$). G_A^* and G_B^* denote the (molar) Gibbs energies of the components, and G^E is the excess Gibbs energy, the deviation from ideal-mixing behavior.

To have equilibrium, at a given temperature, between (say) a β phase and a liquid phase, it is necessary that, for that temperature, their Gibbs functions intersect. In the TX plane the locus of the points of intersection is the equal- G curve (EGC), having an intermediate position between solidus and liquidus, the boundaries of the solid–liquid loop (see Figure 1a).^{12,24}

For every point on the EGC the forms β and liquid have equal Gibbs energies: the EGC is the solution of the equation

$$\Delta G(T, X) = G^L(T, X) - G^\beta(T, X) = 0 \quad X^L = X^\beta \quad (2)$$

After substitution of the individual Gibbs functions (eq 1), eq 2 takes the form

$$(1 - X)\Delta G_A^*(T) + X\Delta G_B^*(T) + \Delta G^E(T, X) = 0 \quad (3)$$

The course of the EGC in the TX plane, as follows from eq 3, is determined by the pure-component properties ΔG_A^* and ΔG_B^* along with the difference between the excess Gibbs energies of liquid and solid β . The other way round the excess Gibbs energy difference along the EGC ($\Delta G_{EGC}(X)$) can be calculated from a given course of the EGC, if the properties ΔG_A^* and ΔG_B^* are known.

From the general definition of Gibbs energy $G = H - TS$, the properties ΔG^* are given by $\Delta G^*(T) = \Delta H^*(T) - T\Delta S^*(T)$. ΔH^* is the enthalpy change on melting, the heat of melting, and ΔS^* the change in entropy; their change with temperature is related to the difference (liquid minus β) in heat capacity, ΔC_p^* . In the case of the present investigation, ΔC_p^* has practically a negligible influence: $\Delta H_A^* = \Delta H_A^*/T_A^0$, and ΔH_B^* and $\Delta S_B^* = \Delta H_B^*/T_B^0$ are given constant values.

The formula that now results for the EGC is²⁴

$$T_{EGC}(X) = \frac{((1 - X)\Delta H_A^* + X\Delta H_B^*) + \Delta G_{EGC}^E(X)}{(1 - X)\Delta S_A^* + X\Delta S_B^*} \quad (4)$$

According to this formula, the difference in excess Gibbs energy (liquid minus β), along the EGC, is calculated from the positions of the EGC in the TX plane, along with the heats of melting and the melting points (T_A^0 and T_B^0) of the pure components. In this context, the type of behavior displayed by Figure 1a is more accessible than the type of behavior displayed by Figure 1b. For the latter, some of the metastable properties—heats of melting and melting points—have to be obtained in an indirect manner.

Information on the excess properties of the liquid mixtures is available in the form of excess Gibbs energies (typically

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derived from isothermal liquid–vapor equilibria) and excess enthalpies (from heat mixing experiments). The combination of $G^{E,L}$, for given T , and $H^{E,L}$ gives $S^{E,L}$ and as a result $G^{E,\beta}$ along the EGC.

Generally, the experimental data for the liquid mixtures are given in the form of adjusted constants of the Redlich–Kister expressions

$$Z^{E,L}(X) = X(1 - X)\{Z_1^L + Z_2^L(1 - 2X) + Z_3^L(1 - 2X)^2\} \quad (5)$$

where Z^E is G^E for a given T , or H^E . The number of constants given usually is two but sometimes is three or only one. This situation, in combination with the circumstance that for the systems at hand the excess properties are relatively small, has the effect that reliable values can be obtained only for the parameters Z_1^β and occasionally for Z_2^β (where β is plastic crystalline R or FCC). In practice, this comes down to reliable values for the equimolar mixtures.

Research, over the last 2 decades on families of mixed crystals has revealed that their excess Gibbs energies generally conform to the $AB\theta$ model,^{23,25–30} for which

$$G^E(T,X) = A(1 - T/\theta)X(1 - X)[1 + B(1 - 2X)] \quad (6)$$

$$H^E(T,X) \Rightarrow H^E(T,X) = AX(1 - X)[1 + B(1 - 2X)] \quad (7)$$

$$S^E(T,X) \Rightarrow S^E(T,X) = (A/\theta)X(1 - X)[1 + B(1 - 2X)] \quad (8)$$

A , B , and θ are system-dependent parameters; they express the magnitude (A), the change with temperature (θ), and the asymmetry (B) of the excess Gibbs energy. At $T = \theta$ the excess Gibbs energy goes through zero. The property θ is often referred to as the “compensation temperature”: At $T = \theta$, H^E and S^E compensate one another in that $H^E - TS^E = 0$. The $AB\theta$ model, therefore, is such that H^E and S^E have the same sign; their quotient, H^E/S^E , is equal to the compensation temperature.

A key role in mixed crystals research is played by the degree of geometric mismatch between the molecules of the two components of a system.^{27,29} A convenient parameter, m , to describe the geometric mismatch is

$$m = |\Delta V|/V_m \quad (9)$$

where ΔV is the difference between the molar volumes of the components and V_m their mean.

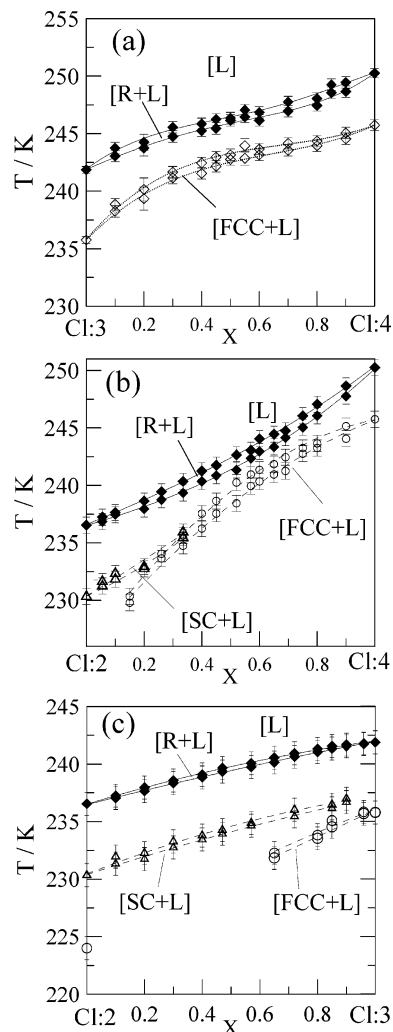


Figure 2. Phase behavior of the systems composed of Cl:2, Cl:3, and Cl:4. Full symbols are for the experimental data on stable equilibria and open symbols for data on metastable equilibria: [R+L] (◆), [FCC+L] (○), [SC+L] (△).^{9,11,15}

Within a family of related systems the system-dependent parameters A can be represented by the expression

$$A = a + bm + cm^2 \quad (10)$$

where the constants b and c have positive values.

For families of systems for which the component substances belong to a chemically coherent group (like the alkali halides²⁹ or n -alkanes²⁷), the constant a generally has a negligible value. The constant a has a negative value for the family of systems where 2-methylnaphthalene is one of the components and 2-R-naphthalene ($R = F, Cl, Br, SH$) is the other. The negative value is an indication of an attractive effect between the methyl-substituted and the halogen-substituted compound (in the case of the methylchloromethane systems, one or more methyl groups of the first component are replaced by chloro substituents in the second component).²⁸

The parameter B of the $AB\theta$ model is also system-dependent. Its absolute value, as a rule, is less than 0.5.^{25,27,29} Generally, B is positive if the system is defined such that, in the system definition [(1 - X) mole of substance A + X mole of substance B], component B is the one with the

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greater molar volume (it means that, in our definition of the systems studied, negative B values are expected).

For θ it is generally found that, within a family of systems, its value is system-independent, the value of θ being a characteristic of the family as a whole.^{25,27,29}

As a rule, the compensation temperature is above the melting temperature of the mixed crystals and such that the (relative) difference between the two increases with increasing melting temperature. In a robust way the relation between the compensation temperature and a characteristic melting temperature of the mixed crystals, the equimolar melting temperature, is given by the empirical formula³⁰

$$\log(\theta/K) = (1.10 \pm 0.05) \log\{T_{EGC}(X=0.5)/K\} \quad (11)$$

As an example, for the family of mixed crystals of common alkali halides having the NaCl type of structure, the value of θ is 2565 K, and the mean of the equimolar EGC temperatures is 913 K.²⁹

Experimental Section

Phase Behavior. The phase behavior of the binary methylchloromethane systems, as far as the change from the plastic crystalline state to liquid is concerned, is known for seven out of the 10 possible combinations. The three plastic diagrams shared by Cl:2, Cl:3, and Cl:4 are shown in Figure 2.^{9,11,15} The diagrams conform to Figure 1a, the stable solid form being plastic crystalline R.

Cl:1 differs from Cl:2, Cl:3, and Cl:4 in that its stable form is FCC. Accordingly, the phase behavior shown by the binary combinations of Cl:1 with each of the three (Figure 3) is in conformity with Figure 1b, crossed isodimorphism.¹²⁻¹⁴

A common characteristic of the three systems is that the metastable extension of the [FCC+L] branch has a real appearance, whereas the other, [R+L], has not.

Another system showing crossed isodimorphism and, having a rich experimental history,^{31,32} is the combination of neopentane (Cl:0) and carbon tetrachloride (Cl:4). The system has been the subject of a recent reinvestigation.¹⁰

Metastable Melting Points. The rhombohedral form (R) is stable for Cl:2, Cl:3, and Cl:4. For Cl:0 and Cl:1 it is not only metastable, but also physically absent. In the case of Cl:0 the metastable melting point has been assessed by thermodynamic analysis of the system Cl:0 + Cl:4.¹⁰ The metastable melting point of Cl:1 has been obtained by extrapolation, as is shown in Figure 4a.

With the exception of Cl:2, the melting points of the methylchloromethanes in the form FCC can be obtained in a direct manner. In Figure 4b it is shown how the melting point of Cl:2 has been determined by extrapolation.

For the simple cubic form (SC), invariably being metastable, the information is rather scarce. Values have been obtained for Cl:2 (direct measurement⁸), Cl:3 (extrapolation over a small distance), and Cl:4 (also by extrapolation) (see Figure 4c).

All of the melting point numerical data have been assembled in Table 1, along with the heats of melting, as detailed hereafter.

Heat Effects. In addition to the temperature characteristics of the transitions, represented in Figures 2 and 3 by the isoplethic data pairs, all of the heat effects have been determined, simultaneously, by differential scanning calorimetry. The ensemble of data not only provides the heats of melting of the pure components in

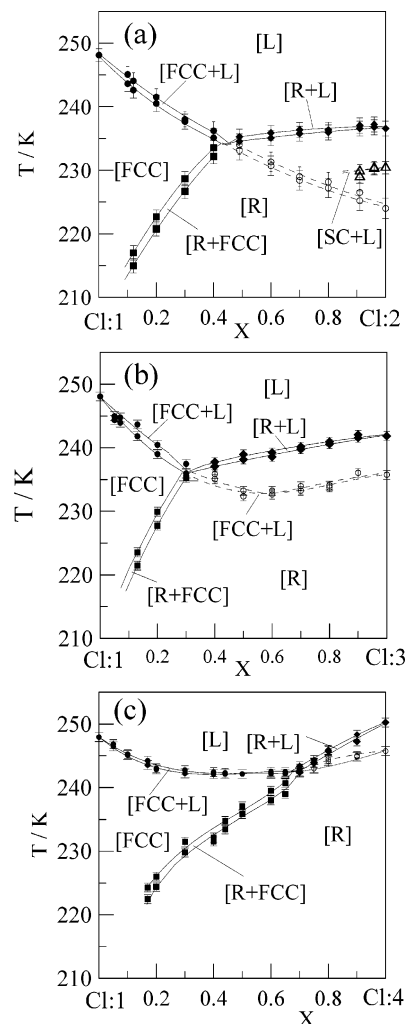


Figure 3. Phase behavior of the system of Cl:1 with Cl:2,¹⁴ Cl:3,¹³ and Cl:4,¹² examples of crossed isodimorphism. Full symbols are for the experimental data on stable equilibria and open symbols for data on metastable equilibria: [R+L] (\blacklozenge), [R+FCC] (\blacksquare), [FCC+L] (\circ), [SC+L] (\triangle).

their different forms, but also the excess enthalpy differences (liquid minus solid) of the binary combinations.

A speaking result is shown by Figure 5, the energetic companion of Figure 3. The energetic data, as follows from a comparison of Figures 5 and 3, have the advantage that the heat effect of the transition from R to FCC can be combined with the heat of melting of FCC to give the heat of melting of form R:

$$\Delta H^{R \rightarrow \text{FCC}} + \Delta H^{\text{FCC} \rightarrow \text{L}} = \Delta H^{R \rightarrow \text{L}} \quad (12)$$

The three systems (Figure 5) have component Cl:1 in common. For this component the data for the three systems are mutually consistent, not only as regards to the heat effect of the transition from FCC to liquid but also for the virtual change from R to liquid.

In Figure 6a,b, it is shown how the heat effects are obtained for the virtual changes from FCC to liquid for Cl:2 and from SC to liquid for Cl:3 and Cl:4.

In Figure 5b, for the combination of Cl:1 and Cl:3, the FCC heat of melting values of the two components have been connected by a straight line. The distance from this line, for a given composition, to the measured heat of melting is equal to the difference (liquid minus solidus) in excess enthalpy, ΔH^E , for that

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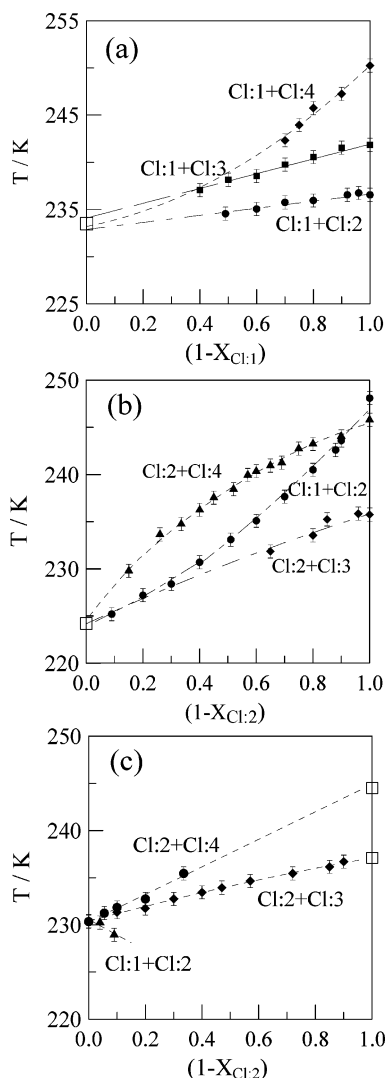


Figure 4. Extrapolation of metastable melting points (open squares) from the solidus temperatures: (a) melting of form R of Cl:1 (Figure 3), (b) melting of form FCC of Cl:2 (Figures 2b,c and 3a), (c) melting of form SC of Cl:3 and Cl:4 (Figure 2b,c).

Table 1. Melting Point and Heats of Melting of the Methylchloromethanes in Their Different Forms

substance	melting form	mp/K	$\Delta H^*/$ $\text{kJ}\cdot\text{mol}^{-1}$	$\Delta S^*/$ $\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$
Cl:0	FCC	256.8 ^a	3.09 ^a	12.03 ^a
	R	220.0 ^c	2.35 ^c	10.68 ^c
Cl:1	FCC	248.1 ^a	1.76 ^a	7.09 ^a
	R	234.0 ^b	2.60 ^b	11.11 ^b
Cl:2	R	236.6 ^a	2.30 ^a	9.72 ^a
	SC	230.4 ^a	1.93 ^a	8.25 ^a
	FCC	224.0 ^b	0.86 ^b	3.84 ^b
Cl:3	R	241.9 ^a	2.42 ^a	10.01 ^a
	SC	237.1 ^b	2.35 ^b	9.91 ^b
	FCC	235.8 ^a	1.55 ^a	6.57 ^a
Cl:4	R	250.3 ^a	2.52 ^a	10.07 ^a
	SC	245.8 ^b	1.82 ^b	7.40 ^b
	FCC	244.0 ^a	1.80 ^a	7.38 ^a

^a Experimental values. ^b Values obtained from the extrapolation of experimental values. ^c Values obtained from the thermodynamic assessment.

composition. For $X = 0.5$, as can be read from the figure, $\Delta H^{\text{E,FCC}}(X=0.5) \approx -0.45 \text{ kJ}\cdot\text{mol}^{-1}$.

The full range of ΔH^{E} values for the system's FCC form, as follows from a least-squares calculation in terms of

$$\Delta H^{\text{E}}(X) = X(1-X)\{\Delta H_1 + \Delta H_2(1-2X)\} \quad (13)$$

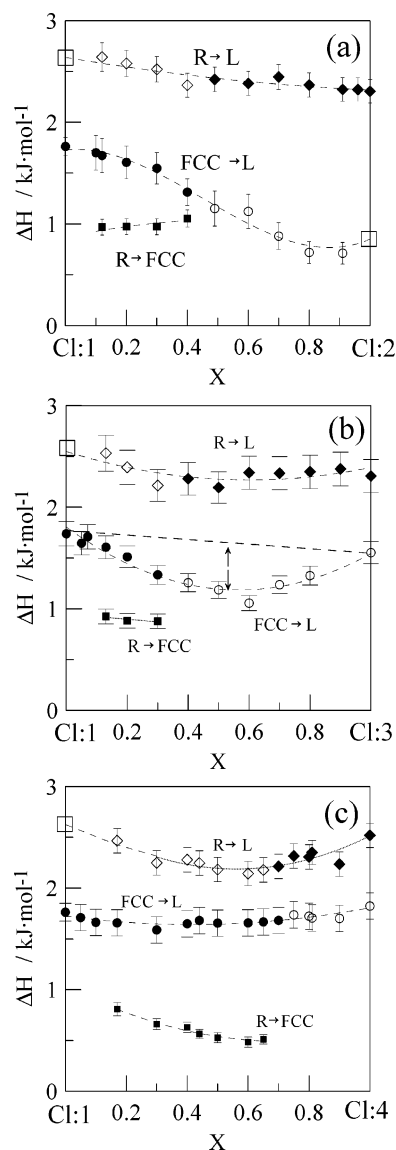


Figure 5. Experimental heat effects of the transitions in the systems Cl:1 + Cl:2,¹⁴ Cl:3,¹³ Cl:4.¹² The open diamonds for the transitions of R to liquid are according to eq 12.

is represented by $\Delta H_1 = -1749 \text{ J}\cdot\text{mol}^{-1}$, and $\Delta H_2 = 191 \text{ J}\cdot\text{mol}^{-1}$. These values are included in Table 2, along with the values calculated for the other systems/forms.

It may be observed that the ΔH_1 and ΔH_2 values are given as integers in joule per mole. From a point of view of experimental uncertainties, an integer in decajoule per mole would be more appropriate (vide infra).

Phase-Diagram Analysis. Taking, again, the FCC to liquid change in the system Cl:1+Cl:3 as an example, it can be read from Figure 3b that the equimolar EGC temperature is 232.6 K. This temperature, along with the melting properties of the two components, given in Table 1, corresponds to a ΔG^{E} value of $-65 \text{ J}\cdot\text{mol}^{-1}$ according to eq 4.

In laboratory practice, EGC-directed calculations to determine $\Delta G^{\text{E}}_{\text{EGC}}(X)$ are carried out by means of the program WINIFIT.³³

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Table 2. Survey of Excess Enthalpy and Excess Gibbs Energy Changes at Melting, in the Form of the Constants of the Two-Parameter Redlich–Kister Expressions, Obtained by Calorimetry and Thermodynamic Phase-Diagram Analysis

system	solid form	calorimetry		phase-diagram analysis		
		$\Delta H_1/\text{kJ}\cdot\text{mol}^{-1}$	$\Delta H_2/\text{kJ}\cdot\text{mol}^{-1}$	$T_{\text{EGC}}(X=0.5)/\text{K}$	$\Delta G_1/\text{J}\cdot\text{mol}^{-1}$	$\Delta G_2/\text{J}\cdot\text{mol}^{-1}$
Cl:0+Cl:4	R	-1.43	0.66	230.0	-56	449
	FCC	-2.70	0.40	237.0	-602	9
Cl:1+Cl:2	R	-0.20	-0.10	234.7	-6	-62
	FCC	-0.77	1.62	232.6	-154	-40
Cl:1+Cl:3	R	-0.67	-0.67	237.9	28	-16
	FCC	-1.75	0.19	232.6	-263	-62
Cl:1+Cl:4	R	-1.48	0.11	238.0	-100	-25
	FCC	-0.68	-0.18	242.0	-141	-66
Cl:2+Cl:3	R	0.10	0.04	239.6	14	-9
	FCC	0.00	0.00	234.4	-18	0
Cl:2+Cl:4	R	-0.40	0.34	242.0	-67	13
	FCC	0.70	0.05	238.6	14	8
Cl:3+Cl:4	R	-0.23	-0.13	246.2	-20	54
	FCC	0.15	0.23	243.2	29	55

Table 3. Thermodynamic Mixing Properties of the Liquid Mixtures in the Form of the Two Redlich–Kister Coefficients for the Excess Enthalpy and Two for the Excess Gibbs Energy, All Expressed in $\text{J}\cdot\text{mol}^{-1}$ and Valid for the Temperatures Given

system	$H_1/\text{J}\cdot\text{mol}^{-1}$	$H_2/\text{J}\cdot\text{mol}^{-1}$	T/K	ref	$G_1/\text{J}\cdot\text{mol}^{-1}$	$G_2/\text{J}\cdot\text{mol}^{-1}$	T/K	ref
Cl:0+Cl:4	1550	0	293.15	34	1380	15	273.15	35
Cl:1+Cl:2	44		298.15	36	89	122	298.15	37
Cl:1+Cl:3	10		298.15	36	186	-198	298.15	37
Cl:1+Cl:4	210	-338	298.15	38	812	363	298.15	39
Cl:2+Cl:3	23	-7	298.15	36	72	3	298.15	37
Cl:2+Cl:4	541	-317	298.15	36	547	132	298.15	37
Cl:3+Cl:4	437	-115	298.15	38	330	-143	298.15	40

One of the options of the program is the calculation of ΔG_1 and ΔG_2 , the coefficients of the G^E analogue of eq 13.

For all of the systems and their forms, the calculated ΔG_1 and ΔG_2 values are included in Table 2, as well as the equimolar EGC temperatures.

The complete set of independent experimental data, i.e., the calorimetrically determined ΔH coefficients and the ΔG coefficients and temperatures provided by the phase diagram, allow the calculation of the coefficients of the entropy analogue of eq 13; the calculated values of ΔS_1 and ΔS_2 are included in Table 4.

Discussion

The Significance of the Computed Redlich–Kister Constants. The outcome of the thermodynamic analysis of the individual systems in their different forms is assembled in Table 4. The table is a collection of Redlich–Kister constants, two for the excess enthalpies and two for the excess entropies. The numerical values follow from the difference properties in Table 2 and the properties of the liquid mixtures in Table 3.

For each of the systems and forms, the computed values are mutually consistent and mathematically precise; in the sense that they can be used—in combination with the pure-component data in Table 1—to perform an accurate calculation

of the phase diagram. As regards the physical significance of the computed constants, read the accuracy of the computed excess properties, the situation is less favorable. The fact is that all of the H and S values in Table 4 are the result of a number of successive arithmetical operations, starting from data that have been determined in an indirect manner, whether including extrapolations.

The values in the table, as a result, are affected with uncertainties, in a rather intransparent manner, varying from case to case. It means, at any rate, that some reserve should be exercised in drawing conclusions with regard to the fine structure of the excess behavior of the group of systems.

The Role of the Geometric Mismatch. The chlorine substituent has a smaller van der Waals radius than the methyl group. This fact finds expression in Figure 7, where the molar volumes of the methylchloromethanes, Cl: n , are plotted against n for the liquid state and the plastic crystalline forms R and FCC.

The molar volumes, expressed in $\text{cm}^3\cdot\text{mol}^{-1}$, are represented by the formulas

$$V^L(T=298\text{K}) = 121.7 - 11.24n + 1.30n^2 \quad (14)$$

$$V^R(T=232\text{K}) = 100.64 - 5.166n + 0.395n^2 \quad (15)$$

$$V^{\text{FCC}}(T=230\text{K}) = 103.24 - 6.036n + 0.506n^2 \quad (16)$$

The Redlich–Kister coefficient H_1 , like the A parameter of the $AB\theta$ model, is equal to 4 times the equimolar excess enthalpy. In Figure 8 calculated H_1^{SOL} values, taken from Table 4, are plotted against their corresponding values of the mismatch parameter m . The value of m for a given form in a given system is calculated from the molar volumes of the components, as contained in eqs 15 and 16 and according to eq 9. For the rhombohedral form, all of the H_1^{SOL} values have been taken; for the FCC form, just the values for three of the systems. The reason for leaving out four of the FCC values is that they might deviate too much from reality, because of the extrapolations made (and therefore could give rise to false conclusions).

Passing over any details, as regards the nature of the systems (vide infra), one can observe that Figure 8, in an unambiguous manner, reflects the influence of mismatch in size. Putting everything in the same category, the behavior displayed by the straight line in Figure 8 can be represented by

$$A(m) = (-0.7 + 26m) (\text{kJ}\cdot\text{mol}^{-1}) \quad (17)$$

where $A(m)$ is the A parameter of the $AB\theta$ model.

The Asymmetry of the Excess Properties. The “asymmetry parameter” B of the $AB\theta$ model corresponds to the quotient $H_2^{\text{SOL}}/H_1^{\text{SOL}}$ of the two parameters of the Redlich–Kister expression for the excess enthalpy (under the assumption that $H_2^{\text{SOL}}/H_1^{\text{SOL}} = S_2^{\text{SOL}}/S_1^{\text{SOL}}$). For systems where the second component is the one with the smaller molecules, a positive H_1^{SOL} generally goes together with a negative H_2^{SOL} . The numbers in Table 4 comply with this rule (when allowance is made for the fact that, owing to the experimental uncertainties, only the cases with large H_1^{SOL} values should

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Table 4. Survey of Excess Enthalpy and Excess Entropy Changes at Melting of the Solid Forms^a

system	solid form	$\Delta H_1^{L-SOL}/$ $J \cdot mol^{-1}$	$\Delta H_2^{L-SOL}/$ $J \cdot mol^{-1}$	$\Delta S_1^{L-SOL}/$ $J \cdot mol^{-1} \cdot K^{-1}$	$\Delta S_2^{L-SOL}/$ $J \cdot mol^{-1} \cdot K^{-1}$	$H_1^L/$ $J \cdot mol^{-1}$	$H_2^L/$ $J \cdot mol^{-1}$	$S_1^{Liq}/$ $J \cdot mol^{-1} \cdot K^{-1}$	$S_2^{Liq}/$ $J \cdot mol^{-1} \cdot K^{-1}$	$H_1^{SOL}/$ $J \cdot mol^{-1}$	$H_2^{SOL}/$ $J \cdot mol^{-1}$	$S_1^{SOL}/$ $J \cdot mol^{-1} \cdot K^{-1}$	$S_2^{SOL}/$ $J \cdot mol^{-1} \cdot K^{-1}$
Cl:0+Cl:4	R	-1428	656	-5.97	0.90	1550	0	0.62	-0.05	2978	-656	6.59	-0.95
	FCC	-2703	396	-8.86	1.63					4253	-396	9.48	-1.68
Cl:1+Cl:2	R	-196	-103	-0.81	-0.18	44	0	-0.15	-0.44	240	103	0.66	-0.26
	FCC	-774	1618	-2.66	7.13					818	-16.8	2.51	-7.57
Cl:1+Cl:3	R	-673	-671	-2.94	-2.75	10	0	-0.57	0.66	683	671	2.35	3.41
	FCC	-1749	191	-6.39	1.08					1757	-191	5.80	-0.42
Cl:1+Cl:4	R	-1475	110	-5.78	0.57	210	-338	-2.02	-2.35	1684	-477	3.76	-2.91
	FCC	-679	-181	-2.22	-0.48					888	-156	0.2	1.87
Cl:2+Cl:3	R	101	37	0.36	0.19	23	-7	-0.16	-0.06	-78	-44	-0.52	-0.22
	FCC	0	0	0.08	0.00					23	7	-0.24	-0.03
Cl:2+Cl:4	R	-398	343	-1.37	1.36	541	-317	-0.02	1.51	939	-660	1.35	-2.87
	FCC	703	55	2.89	0.19					-162	-372	-2.91	1.70
Cl:3+Cl:4	R	-227	-128	-0.84	-0.74	437	-115	0.36	0.09	664	13	1.20	0.83
	FCC	148	230	0.49	0.72					280	-345	-0.13	-0.63

^a Their combination with the excess enthalpy and entropy in the liquid-phase allowed the calculation of the excess enthalpy and entropy in the solid phases. The thermodynamic properties in all phases are in the form of two-parameter Redlich–Kister expressions.

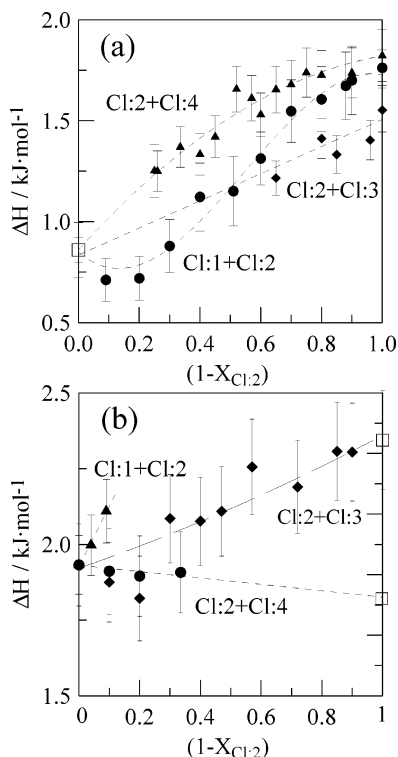


Figure 6. Experimental heat effects of the transitions from FCC to liquid (a) and SC to liquid (b) for the systems Cl:2 + Cl:1,¹⁴ Cl:3,¹⁵ Cl:4.¹¹ The open squares are the extrapolated values proposed for the FCC to liquid transition of Cl:2 (a) and for the SC to liquid transitions of Cl:3 and Cl:4 (b).

be taken into consideration). For these cases, $B = -0.2$ seems to be a representative value (which, besides, is in line with the degree of asymmetry shown by the majority of mixed-crystal systems).

The Compensation Temperature. In the $AB\theta$ model the compensation temperature θ is the quotient of the excess enthalpy and the excess entropy. Concentrating on the equimolar composition, that quotient is equal to the quotient of H_1^{SOL} and S_1^{SOL} . In Figure 9 the values of H_1^{SOL} are plotted against their corresponding values of S_1^{SOL} , both from Table 4, and for all of the cases included in Figure 8.

The line which is drawn in Figure 9 is for $\theta = 420$ K. This compensation temperature is more or less representative for the ensemble of systems, the mean equimolar EGC temperature of which is 238 K. The quotient of $\log \theta$ and

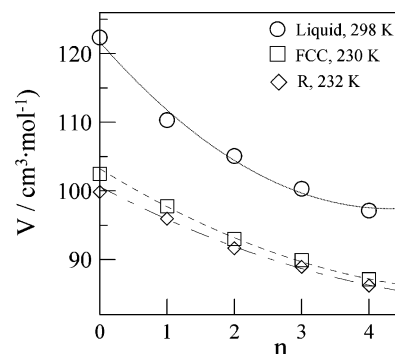


Figure 7. Molar volumes of the methylchloromethanes, Cl: n , as a function of the number of chlorine atoms, n .

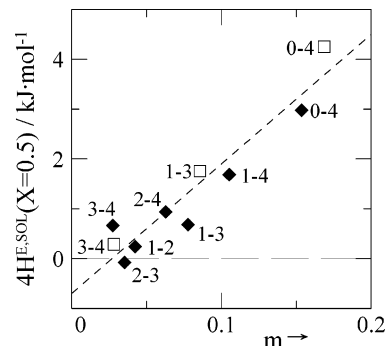


Figure 8. Equimolar excess enthalpies of the rhombohedral (◆) and FCC (□) plastic mixed crystals, plotted against the mismatch parameter m , defined by eq 9.

$\log[T_{EGC}(X=0.5)]$ is equal to 1.10, indicating that the mixed plastic crystals in the methylchloromethane systems comply with the general trend implied in eq 11.

The Role of Dipoles. Up to this point the only factor put into action to explain the magnitude of the excess properties of mixed crystals has been the geometric mismatch, the mismatch in size. An obvious second factor, to further rationalize the excess properties, is dipole dilution, as we will call it. The methylchloromethanes having a dipole moment are Cl:1 ($\mu = 2.14$ D), Cl:2 (2.33 D), and Cl:3 (1.78 D). The idea is that, when one of the three is mixed with Cl:0 or Cl:4, there will be a positive enthalpy effect, due to the unfavorable circumstance that upon mixing the distances between the dipoles are increased.

To demonstrate that the idea has some viability, we constructed the excess enthalpy vs mismatch diagram (Figure

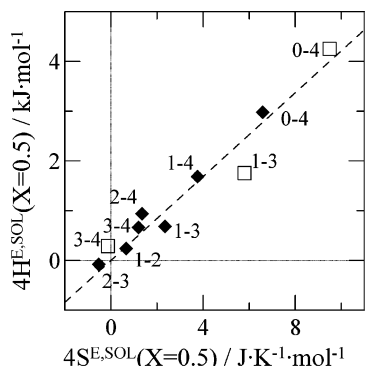


Figure 9. Equimolar excess enthalpies of the rhombohedral (◆) and FCC (□) plastic mixed crystals, plotted against the corresponding equimolar excess entropies.

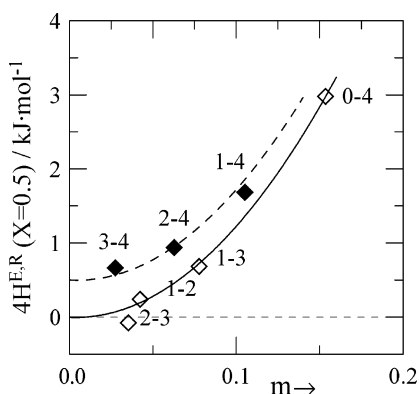


Figure 10. Equimolar excess enthalpies of the rhombohedral plastic mixed crystals plotted against the mismatch parameter m , defined by eq 9 for systems with (◆) and without (◇) dipole dilution.

10) from the rhombohedral data from Figure 8. In Figure 10, the influence of mismatch only is reflected by the solid curve (which respects the data for the systems without dipole

dilution). The curve, which is convex and emanates from the origin, is typical of families of systems (like binary combinations of n -alkanes²¹ and common-ion alkali halides²⁹), where mismatch in size is the only factor responsible for the magnitude of the excess properties. The evidence of an additional contribution to the magnitude of the excess properties, due to the dipole dilution, is reflected by the dashed curve (which respects the data for the systems Cl:1+Cl:4, Cl:2+Cl:4, and Cl:3+Cl:4). In terms of the $AB\theta$ model, the additional contribution to the A parameter, which is given by the distance between the dashed curve and the solid one, is about $0.5 \text{ kJ}\cdot\text{mol}^{-1}$.

Conclusions

The thermodynamic mixing properties of the binary systems of the different forms of the plastic crystalline state have been derived from calorimetric and phase-diagram data and the thermochemical properties of the pure components. Some of the pure-component data have been obtained by extrapolation and correlation of binary data.

The $AB\theta$ model for the excess Gibbs energy allows for an adequate description of the mixing properties such that (i) the forms of the mesostate are characterized by a uniform θ value of 420 K and (ii) the magnitude parameter A can be related to the mismatch in molar volume of the components of an individual system, making allowances for the effect of dipole dilution.

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