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Abstract

On the basis of the isostructural relationship between the low temperature monoclinic ($C2/c$, $Z = 32$) phases of the halogenomethane $CBr_{4-n}Cl_n$ ($n = 0, \dots, 4$), a set of mixed crystals has been analysed by means of high resolution X ray powder diffraction. It is shown that the monoclinic structure of pure and mixed crystals does not depend of the particularities of the dipolar (or dipole induced) interactions of the pure compound, neither on the composition of the mixed crystal, but on the relative content of the halogen atoms which controls the size of the molecule or the average molecule for the case of mixed crystals.

Keywords: Mixed crystals; Disorder; Vegard law; Halogenomethanes

1. Introduction

Simple organic compounds with molecules of almost globular shape possess molecular reorientational freedom within a certain range of temperatures [1]. The phase showing orientational disorder is called the plastic phase and such compounds are known as plastic crystals or orientationally disordered crystals. Among them, halogenomethane $CBr_{4-n}Cl_n$ ($n = 0, \dots, 4$) have been the focus of many studies [2–24]. Several reasons making this series of compounds of great interest can be claimed. They exhibit a series of thermally induced solid–solid phase transitions before melting that are attributed to the ability to gain rotational degrees of freedom in the crystalline state (orientationally disordered phases) due to the little hindrance for reorientational processes produced by the more or less globular shape of the molecules. Moreover, minor changes in the

molecular size or in the molecular symmetry can be induced by the change of one of the halogen atoms, giving rise to changes in the intermolecular interactions and thus, in the phase sequence, i.e., in the polymorphic behavior [9,14].

One of the reasons to delve into the study of the halogenomethane $CBr_{4-n}Cl_n$ ($n = 0, \dots, 4$) materials is the strong geometrical and electrostatic similarities. As a consequence it has been shown that the low-temperature “ordered” phase of all the compounds of this family (except for CBr_3Cl , which is unknown) are isostructural with a complex crystal structure having 32 molecules per monoclinic unit cell [2–6,14].

For the halogenomethanes with T_d molecular symmetry, a high number of experimental and molecular dynamics simulation studies have been published [9–12,19,20,24] while for the compounds with lower symmetry (C_{3v} or C_{2v}) only a few preliminary experiments have been done [6,7,23].

Cohen et al. [2] were able to grow a single crystal of CCl_4 for the low-temperature ordered phase, at 195 K. They concluded that the asymmetric unit cell ($C2/c$) contains four independent molecules (with $Z = 32$ molecules

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per unit cell) and, within the experimental error, all of them being regular tetrahedra. This result confirmed previous refinement procedure of the structure performed by Schoemaker and Trueblood [5] who considered each of the involved molecules in the asymmetric unit as a rigid body. As far as the low-temperature of the CBr_4 compound, Powers [25] redetermined the structure of the isostructural low-temperature phase of CBr_4 , initially solved by More et al. [4], confirming that also for such a compound the tetrahedral character of the molecule is fulfilled.

The crystal structures of the low-temperature phases of CBrCl_3 and CBr_2Cl_2 were attempted by Binbrek et al. [6] from neutron powder diffraction experiments. They described the structure of these phases on the basis of the hypothesis of the isostructural character of the low-temperature ordered phases for all four members of the $\text{CBr}_4-n\text{Cl}_n$ ($n = 0, \dots, 4$) family in terms of the $C2/c$ space group with $Z = 32$. For this low-temperature phase of CBrCl_3 and CBr_2Cl_2 compounds the molecules were assumed to be disordered so that sites have fractional occupancies of 0.75 and 0.25 for CBrCl_3 and 0.5 for CBr_2Cl_2 for each of Cl and Br atoms, respectively. Such an “occupational disorder” was confirmed by adiabatic calorimetry [7], which clearly revealed the existence of a glass transition at around 90 K related to the frozen of the exchange of positions between Cl and Br atoms, and by the appearance of an anomaly in the asphericity coefficient, which accounts for the anisotropy of the intermolecular interactions [14].

The isostructural relationship between low-temperature phases of CBrCl_3 and CCl_4 has been recently confirmed from the continuous variation of the lattice parameters as a function of concentration (at 223.2 K) for a series of substitutional monoclinic mixed crystals of the binary phase diagram between both compounds [23]. Data corresponding to mixed crystals between CBr_2Cl_2 and CCl_4 prove the same conclusion and make then evident the isostructural character of all the compounds of this family. These data will be published soon [26]. It should be stressed that substitutional mixed crystals correspond to a disordered structure, from a compositional distribution point of view, in which molecules of the two components are distributed regularly over the sites of the lattice.

In terms of fundamentals, the study of this family of substances offers the opportunity to define behavioral rules inside the family and correlate their properties in order to establish predictive tools without the requirement of strong hypothesis of a physical model. Then, the principal aim of this study is to examine to what extent the low-temperature structures, for pure compounds as well as for their mixed crystals will allow a uniform description of the ensemble.

2. Experimental section

2.1. Samples

The chemicals CCl_4 and CBrCl_3 were obtained from Across with purity of 99+% and 99%, respectively, and

used as received. CBr_4 was purchased from Flucka (99%) and CBr_2Cl_2 was obtained from Aldrich with of 98% and fractionally distilled.

2.2. X-ray diffraction

X-ray high-resolution diffraction patterns were recorded by means of a horizontally mounted INEL cylindrical position-sensitive detector (CPS 120) [27] equipped with a liquid nitrogen 600 series Cryostream Cooler from Oxford Cryosystems. The detector, used in Debye Scherrer geometry (transmission mode), consisted of 4096 channels and enables a simultaneous recording of the profile over a 2θ range between 4° and 120° (angular step of 0.029° in 2θ). Monochromatic $\text{CuK}\alpha_1$ ($\lambda = 1.54059 \text{ \AA}$) radiation was selected by means of an asymmetric focusing incident-beam curved quartz monochromator. The generator power was set to 1.0 kW (40 kV and 25 mA). PEAKOC application from DIFFRACTINEL software was used for the calibration and for the peak position determinations after pseudo-Voigt fittings [28].

The samples were introduced into 0.3- or 0.1-mm-diameter Lindemann glass capillaries in the liquid state at room temperature and were rotated perpendicularly to the X-ray beam during data collection to improve averaging of the crystallites.

Patterns were obtained at $220.2 \pm 1.0 \text{ K}$ (except for $\text{CCl}_4 + \text{CBrCl}_3$ mixed crystals, which were measured previously at $223.2 \pm 1.0 \text{ K}$ [23]) with acquisition times of at least 120 min and a stabilization time of at least 10 min before the data acquisition.

3. Results

3.1. X-ray high-resolution powder diffraction measurements

X-ray powder diffraction measurements were undertaken at $220.2 \pm 1.0 \text{ K}$ for the pure compounds $\text{CBr}_4-n\text{Cl}_n$ for $n = 0, 1, 2$ and 4, as well as for substitutional mixed crystals with mole fraction values distributed along the whole range of concentrations. The reason for the missing compound $n = 3$ (CBr_3Cl) is the non-commercial availability.

As far as the $\text{CCl}_4 + \text{CBrCl}_3$ mixed crystals are concerned values for the lattice parameters were taken from a previous work, in spite that temperature of the measurements was slightly higher ($223.2 \pm 1.0 \text{ K}$) [23]. Results for the isobaric thermal expansion tensor of the monoclinic phase of CBrCl_3 show that for the softer principal direction of the tensor, on the $(0k0)$ crystallographic plane, principal coefficient is around $1.5 \times 10^{-4} \text{ K}^{-1}$ [14]. It means that, in the worst case, a 3 K temperature difference would imply that lattice parameter changes less than $5 \times 10^{-3} \text{ \AA}$. Thus, it can be concluded that such a temperature difference does not hinder the use of published values for the aforementioned two-component system to be compared with results of the present work.

As for the two-component systems (CCl_4) + (CBr_2Cl_2), (CBrCl_3) + (CBr_2Cl_2) and (CBr_2Cl_2) + (CBr_4), three mixed crystals with compositions along the full range were measured.

3.2. Structural analysis

Experimental X-ray diffraction patterns were profile refined by using the Rietveld method. The process was checked first for pure compounds CCl_4 and CBr_4 , for which single-crystal structural analyses have been published [2,4]. The values obtained compare well with those published for single crystals, within the experimental error.

Next, the procedure was applied to CBrCl_3 and CBr_2Cl_2 pure compounds, following the model used by Binbrek et al. [6] which is briefly detailed. Structural parameters of CBr_4 were used as the starting point for the atomic coordinates of the four independent molecules in the asymmetric unit cell. To model the mixed crystals, the molecules were assumed to be uniformly disordered, i.e., the fractional occupancies of the halogen sites were set according to the compound analyzed: 0.25 and 0.75 for Br and Cl atoms for CBrCl_3 and 0.5 for each atom for CBr_2Cl_2 . A rigid-body of a pseudo-molecule with superimposed angular tetrahedral-symmetry in which Br and Cl atoms were placed according to standard distances from the central

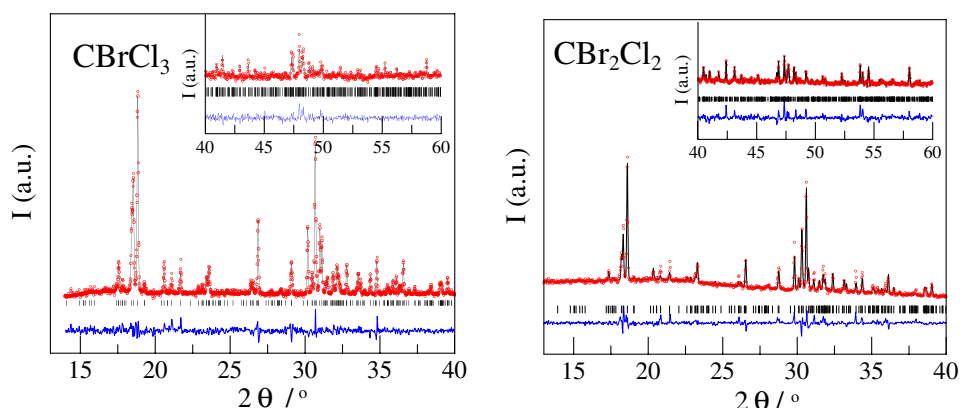


Fig. 1. Experimental (○, red circles) and calculated (—, black line) diffraction patterns along with the difference profile of monoclinic phase for pure compounds CBrCl_3 (at 223.2 K) and CBr_2Cl_2 (at 220.2 K). Inset correspond to a five times expanded vertical scale for the data from $2\theta > 40^\circ$. (For interpretation of the references in color in this figure legend, the reader is referred to the web version of this article.)

Table 1
Monoclinic lattice parameters (at 220.2 K) for halogenomethane compounds ($\text{CBr}_4 - n\text{Cl}_n$) and their mixed crystals for several molar compositions (X) as a function of the fractional occupational of chlorine halogen (X_{Cl}), together with the reliability indices (R_p and R_{wp}) of the Rietveld refinement r_{vdW} stands for the Associated van der Waals radii (see text)

Pure compound or mixed crystal	X	X_{Cl}	Lattice parameters				R_p (%)	R_{wp} (%)	r_{vdW} (Å)
			a (Å)	b (Å)	c (Å)	β (in °)			
CCl_4		1	20.303(4)	11.441(3)	19.903(4)	111.28(1)			2.756
CBrCl_3		0.75	20.631(3)	11.619(2)	20.201(3)	111.19(1)	4.9	6.6	2.824
CBr_2Cl_2		0.50	20.872(4)	11.747(2)	20.434(4)	111.19(1)	7.1	9.9	2.888
CBr_3Cl^a		0.25	21.082(4)	11.886(2)	20.659(5)	111.18(1)			2.949
CBr_4		0	21.2396(8)	12.0005(4)	20.8373(7)	111.136(2)			3.008
$(\text{CCl}_4)_1 - X(\text{CBrCl}_3)_X^a$ ($\alpha = 0.976$)	0.19	0.9525	20.393(4)	11.483(2)	19.978(3)	111.26(1)	5.7	7.5	2.843
	0.50	0.875	20.485(10)	11.531(5)	20.051(10)	111.27(3)	4.7	6.8	2.853
	0.80	0.800	20.580(3)	11.588(2)	20.150(3)	111.23(1)	7.4	9.6	2.869
$(\text{CCl}_4)_1 - X(\text{CBr}_2\text{Cl}_2)_X$ ($\alpha = 0.954$)	0.30	0.850	20.505(3)	11.542(2)	20.084(3)	111.24(1)	5.2	7.3	2.797
	0.49	0.755	20.625(3)	11.611(2)	20.200(3)	111.28(1)	5.3	7.4	2.822
	0.73	0.635	20.750(4)	11.681(2)	20.322(4)	111.24(1)	5.1	6.8	2.853
$(\text{CBrCl}_3)_1 - X(\text{CBr}_2\text{Cl}_2)_X$ ($\alpha = 0.978$)	0.30	0.675	20.698(5)	11.654(2)	20.262(4)	111.23(1)	5.5	7.3	2.843
	0.45	0.6375	20.752(3)	11.687(2)	20.319(3)	111.21(1)	5.3	7.2	2.853
	0.70	0.575	20.804(3)	11.722(2)	20.378(4)	111.21(1)	5.8	8.6	2.869
$(\text{CBr}_2\text{Cl}_2)_1 - X(\text{CBr}_4)_X$ ($\alpha = 0.960$)	0.25	0.375	20.974(3)	11.823(2)	20.557(2)	111.19(1)	4.6	5.9	2.919
	0.50	0.250	21.073(3)	11.886(1)	20.661(2)	111.19(1)	5.3	6.9	2.949
	0.74	0.125	21.174(5)	11.941(2)	20.755(2)	111.18(1)	6.5	8.8	2.979

The parameter α stands for the van der Waals ratio r_1/r_2 , $r_2 > r_1$ between the pure compounds involved in the binary mixed crystals.

^a Extrapolated values from the correlation (Table 2).

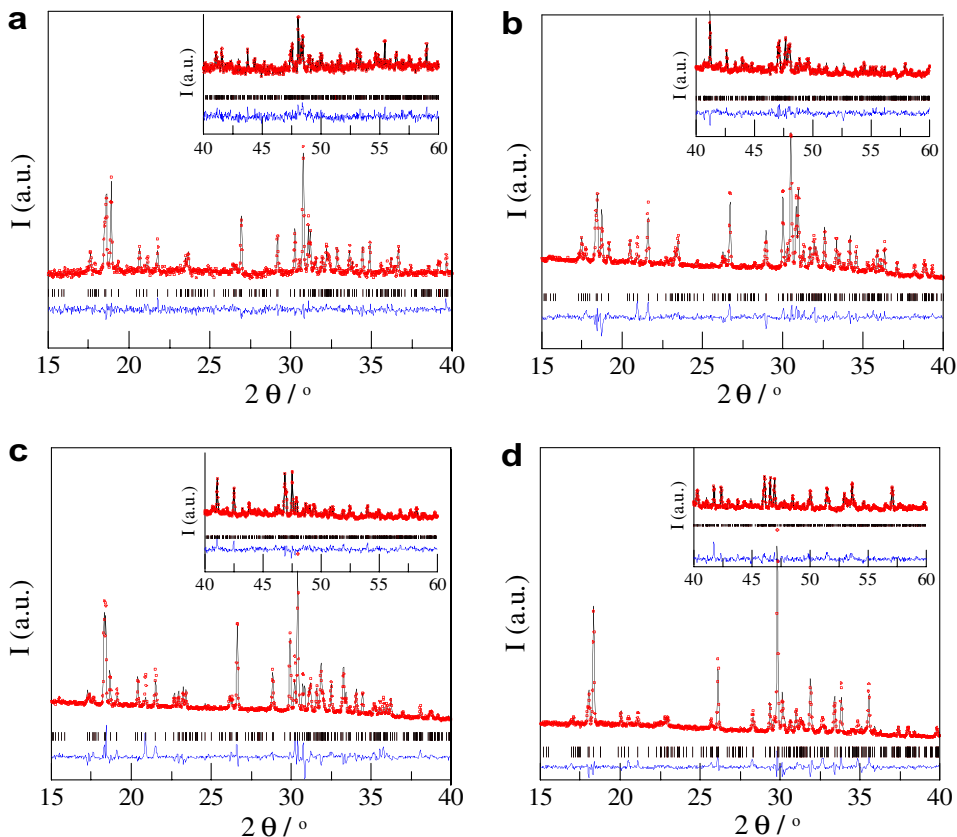


Fig. 2. Experimental (○, red circles) and calculated (—, black line) diffraction patterns along with the difference profile of monoclinic phase at 223.2 K for (a) $(\text{CCl}_4)_{0.20}(\text{CBrCl}_3)_{0.80}$ ($X_{\text{Cl}} = 0.800$), (b) $(\text{CCl}_4)_{0.27}(\text{CBr}_2\text{Cl}_2)_{0.73}$ ($X_{\text{Cl}} = 0.635$), (c) $(\text{CBrCl}_3)_{0.30}(\text{CBr}_2\text{Cl}_2)_{0.70}$ ($X_{\text{Cl}} = 0.575$) and (d) $(\text{CBr}_2\text{Cl}_2)_{0.26}(\text{CBr}_4)_{0.74}$ ($X_{\text{Cl}} = 0.125$). Each inset corresponds to a five times expanded vertical scale for the data from $2\theta > 40^\circ$. (For interpretation of the references in color in this figure legend, the reader is referred to the web version of this article.)

carbon atom (1.939 and 1.772 Å, respectively) was used. It should be noticed that the structural model imposes a dynamic disorder involving the exchange of Cl and Br atoms on fixed sites (due to the site symmetry requirements) making it impossible to define the orientation of the molecular dipole and, thus, a more detailed description of the structure. But, we must bear in mind that such a condition agrees with the results of specific heat [17], which clearly state that above the glass transition temperature (90 K) there is a dynamic disorder involving the exchange of Br and Cl atoms between fixed sites. In fact, individual molecules in the present case do not have perfect tetrahedral symmetry because of the size and bonding differences between Cl and Br atoms, but this symmetry is a reasonable constraint to impose upon the pseudo-molecule, which represents an average over all the disordered molecules.

Fig. 1 shows examples of the experimental and calculated profiles together with the difference between them for CBrCl_3 and CBr_2Cl_2 compounds (the range cutoff is due to the absence of diffraction lines at lower angles and poor signal at higher angles).

A similar process was applied to a set of mixed crystals. In these cases the fractional occupancies of the halogen atoms were set according to the composition. It means that the fractional occupancy of Chlorine halogen (X_{Cl}) is calcu-

lated, for a given mixed crystal $(\text{CBr}_4)_x(\text{CBr}_n\text{Cl}_m)_{1-x}$ ($(\text{CBr}_4)_x(\text{CBr}_m\text{Cl}_n)_{1-x}$) of molar composition X , as $X_{\text{Cl}} = 1/4[X \cdot m + (1 - X) \cdot n]$.

Continuous variation of the lattice parameters vs mole fraction X for the monoclinic mixed crystals was found whatever the analyzed case which proves the formation of monoclinic substitutional mixed crystals in the whole composition range. Table 1 summarizes lattice parameters and the R factors for the refinement procedure. Examples for some mixed crystals are given in Fig. 2.

4. Discussion

Vegard's law is an old empirical rule which holds a linear relation, at constant temperature, between the crystal lattice parameters of a mixed crystal and the concentration of the constituents, elements or molecules. Original law was established between the crystal lattice parameter and concentration by Vegard when analyzing ionic salt alloys [29]. It is well-known that several factors are responsible for the crystal structures of the mixed crystals: the relative atomic size of the constituents, the relative volume per valence electron in crystals of the constituents, Brillouin-zone effects or electrochemical differences between constituents. For a simple binary mixture of hard spheres, it has

been demonstrated that such a rule is based on the relative atomic or molecular sizes constituents [30].

When analyzing the lattice parameter variation as a function of mole fraction for each particular two-component system studied in this work, small but noticeable deviations from the Vegard’s law are evidenced. Thus, whether the structural properties of pure halogenomethane compounds and their molecular mixed crystals are governed by the relative common size or by some other particular parameter can be disclosed by analyzing lattice parameters as a function of the fractional occupancy of one of the halogen atoms (chlorine in our case). Fig. 3 shows the lattice parameters for pure halogenomethanes as well as for their mixed crystals as a function of the X_{Cl} . Surprisingly, whatever the pure compound and whatever the mixed crystal is considered, all of them are well located on the same (almost straight) curve. It means then that packing of the low-temperature phase of halogenomethanes, pure or mixed crystals, are purely controlled by the relative content of the halogen atoms. Table 2 gathers the coefficients of the polynomial equations for the lattice parameters as a function of

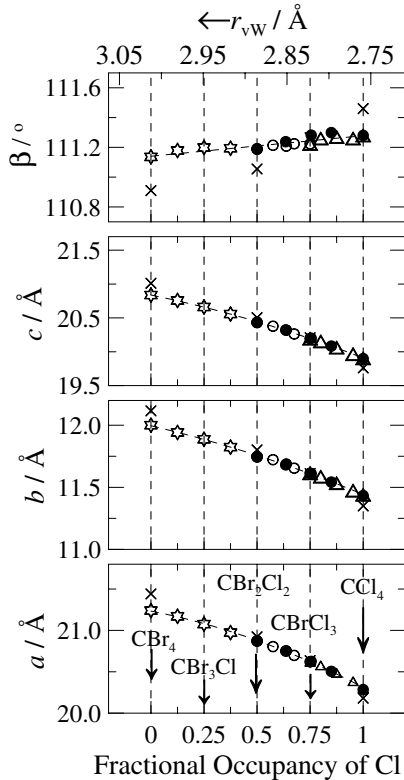


Fig. 3. Lattice parameters as a function of the fractional occupancy of Chlorine atom for pure compounds $\text{CBr}_4 - n\text{Cl}_n$ for $n = 0, 1, 2,$ and 4 (vertical dashed lines) as well as for molecular mixed crystals of the systems: $\text{CCl}_4 + \text{CBr}_2\text{Cl}_2$ (Δ), $\text{CBr}_2\text{Cl}_2 + \text{CBr}_4$ (\star) and $\text{CBr}_2\text{Cl}_2 + \text{CBr}_4 + \text{CBrCl}_3$ (\circ) at 220.2 K and $\text{CCl}_4 + \text{CBrCl}_3$ (\bullet) at 223.2 K . The upper X axis corresponds to the associated van der Waals molecular radius. It should be noticed that value for $X_{\text{Cl}} = 0.25$ which should correspond to the unavailable compound CBr_3Cl has been obtained from $(\text{CBr}_2\text{Cl}_2)_{0.5}$ (CBr_4) $_{0.5}$ mixed crystal. Crosses are for values from literature at different temperatures: CBr_4 at 296 K and CCl_4 at 195 K from Ref. [3], CBrCl_3 at 225 K and CBr_2Cl_2 at 250 K from Ref. [6].

X_{Cl} . The agreement between the calculated and experimental values has been estimated with the help of the reliability factor, defined as $R = \sum(p_{\text{exp}} - p_c)^2 / p_c^2$, where p_{exp} and p_c are the measured and calculated lattice parameters, respectively, assuming second-order (R_2) or linear (R_1) variations.

For a fine-tuning of the Vegard’s law (as a function of X_{Cl}) deviation, it is necessary to go deeper onto the structural details and, in particular, in the anharmonicity effects involved. Although such effects are unknown for the mixed crystals due to the lack of information about thermal expansivity or Grüneisen parameter, some reasons can be argued in a tentative way. As can be seen from Fig. 3 and from the reliability factors quoted in Table 2 for the second-order and linear fitted polynomials, the lattice parameter with the lowest deviation from a “perfect” Vegard’s line, is b . This result matches up with the well-known spatial distribution of intermolecular interactions for some of the pure compounds [14–20], for which the shortest distances (and then the strongest interactions) lie in the $[010]$ plane while soft intermolecular interactions are present between (010) direction. It means then that deviation from hard-sphere behavior due to low-frequency rotation-vibrational motions associated to a certain degree of anharmonicity will be stronger in the $[010]$ planes.

To estimate the influence of the relative size of the molecule (or the *average* molecule in the case of mixed crystals), a van der Waals molecular radius has been calculated for each entity. Molecular volumes of pure halogenomethanes have been calculated using the values of the van der Waals radii and interatomic chemical bonds following Kitaigorodsky’s method [31]. Owing to the fact that we are dealing with nearly spherical or pseudo-globular molecules, a van der Waals radius was associated to each pure halogenomethane or mixed crystal, r_{vdW} . Values of such a mean radii are consigned in Table 1, and correspond to the upper x -axis of Fig. 3, because a linear dependence, due to the detailed hypothesis, exists between the fractional occupancy of halogen atoms and the associated van der Waals radius.

Using the calculated molecular volumes one can calculate the packing coefficient, defined as $\eta = V_m / (V/Z)$, where V_m is the molecular volume and V/Z the volume occupied by a molecule in the monoclinic lattice, can be calculated. Fig. 4 depicts the variation of the packing coefficient as a function of the fractional occupancy of Chlorine halogen. The strong correlation evidences, in fact, that such a packing corresponds to equal-sphere closest-packing principle as was early revealed by Powers and Rudman [3] when comparing CCl_4 and CBr_4 monoclinic structures.

Finally, we would like to show the power of the correlation between lattice parameters and the fractional occupancy. In addition to the mixed crystals studied in this work, several other can be formed, which, on the basis of the isostructural character on the low-temperature phase of the pure compounds, should display the monoclinic $C2/c$ symmetry. This would be a crystallographic requirement, although it is well-known that the existence of a

Table 2

Polynomial equations $p_0 + p_1 X_{\text{Cl}} + p_2 X_{\text{Cl}}^2$ (p in Å or in degree for β parameter) to which the lattice parameters were fitted as a function of fractional occupancy of chlorine

Lattice parameter	p_0	p_1	p_2	$R_2 \times 10^6$	$R_1 \times 10^6$
a	21.233(0.009)	0.500(0.032)	0.423(0.029)	4.8	64.0
b	11.996(0.005)	0.403(0.021)	0.150(0.018)	6.1	29.6
c	20.837(0.007)	0.643(0.025)	0.286(0.022)	2.9	31.0
β	111.141(0.011)	0.1380(0.016)			0.6

R is the reliability factor (see text) for second order (R_2) and first order polynomial (R_1).

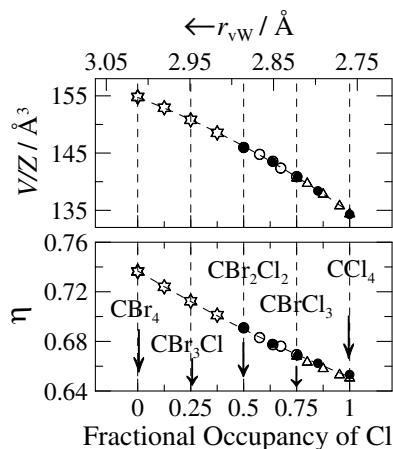


Fig. 4. Volume occupied by a molecule and packing coefficient of the monoclinic pure halogenomethane compounds and mixed crystals as a function of the fractional occupancy of the Chlorine halogen. The upper x axis corresponds to the associated van der Waals molecular radius.

unique Gibbs function for the whole mole fraction range is also required. Nevertheless, it has been shown that the ratio between hard-sphere diameter, $\alpha = \sigma_1/\sigma_2$, $\sigma_2 > \sigma_1$, univocally determines the shape of the phase diagram for a binary system of hard spheres. In such a way, for $\alpha > 0.87$ solid state displays complete miscibility, while for $\alpha < 0.87$ a eutectic, below which two solid solutions coexist (demixing region), appears [30]. For the halogenomethane molecules, assuming them as hard-spheres with an associated van der Waals radius, all the studied systems would have α values much higher than the limiting value for miscibility (see Table 1). Even for the binary combination between the chloro-bromo-methane compounds with the lowest α value, that relating CCl_4 and CBr_4 , $\alpha = 0.916$, would display complete miscibility and then a continuous series of mixed crystals, if, of course, the hard-sphere hypothesis is retained.

Also from the correlation found, the lattice parameters of a possible monoclinic $C2/c$ phase of CBr_3Cl can be obtained, the results being: $a = 21.082(4)$ Å, $b = 11.886(2)$ Å, $c = 20.659(5)$ Å, $\beta = 111.18(1)$ at 220.2 K. It should be stressed that although the authors did not find any structural report on this compound, some works published about 50 years ago [32] showed by means of dielectric permittivity studies the close behavior, as far as phase transitions and dipole disorder are concerned, of several

halogenomethane compounds, among them CBr_3Cl compound.

5. Conclusion

This work shows that the low-temperature phases of the halogenomethane compounds $\text{CBr}_4 - n\text{Cl}_n$, $n = 0, \dots, 4$ are isostructural and can form a continuous series of mixed crystals. It has been, moreover, identified that the fractional occupancy of the halogen atoms fully controls the lattice dimensions in spite of the dipole-dipole or dipole-induced dipole interactions that can appear as a function of the halogen composition. Lattice parameters as a function of the fractional occupancy of chlorine atom slightly deviate from the Vegard's law, the b parameter displaying the most linear behavior as a consequence of the soft van der Waals interactions in such a crystallographic direction.

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