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Parity Violation in Unstirred Crystallization from Achiral Solutions

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1. Introduction

Dissymmetry of the atomic arrangement in molecules or crystals of chiral substances leads to the existence of left (L) and right-handed (D) forms being a mirror image of the other. The two structural forms of crystals, i.e. L and D enantiomers have mirror macro- and micromorphology and exhibit opposite sense of optical rotation. The formation and identification of enantiomers or racemates, and determination of enantiomeric purity is very important to chiral drugs manufacturing, since L and D enantiomers of a large number of drugs exhibit quite different therapeutic, toxic and adverse side effects. The different biological activity of chiral compounds is caused by the preferred chirality of chemistry of life and breakage of mirror symmetry in nature is a general phenomenon. Origin, mechanisms and conditions of formation of chiral asymmetry for various physical, chemical and biological objects and processes are extensively studied. The progress in understanding of the spontaneous breakage of chiral symmetry in crystallization processes of simple substances can help in better establishing the causes of chiral asymmetry in nature.

Single enantiomers or racemates can be formed during crystallization. Unequal amounts of L- and D-forms can be produced in mirror-symmetric chemical reactions through a phenomenon called spontaneous symmetry breaking. Breakage of chiral symmetry has been discovered by Kondepudi and co-workers in their studies of sodium chlorate crystallization from stirred solution (Kondepudi et al., 1990). The phenomenon has been investigated both experimentally and theoretically (McBride & Carter 1991; Kondepudi et al., 1995 a,b; Kondepudi et al., 1993; Kondepudi et al., 1995 a,1995 b; Kondepudi & Sabanayagam, 1994; Qian & Botsaris, 1998, 2004). At present, efforts are made to establish the experimental conditions under which the phenomenon occurs, to determine all important parameters controlling its kinetics and mechanisms, and to develop a reliable theory (Veintemillas-Verdaguer et al, 2007; Viedma 2004; Cartwright et al., 2004; Martin et al. , 1996; Metcalfe & Ottino, 1994; Bushe et al., 2000). Our results for sodium chlorate have shown that even in unstirred solutions there is a finite probability of creation of large enantiomeric excess (Szurgot & Szurgot, 1995a) and pure enantiomeric forms (Szurgot & Szurgot, 1995b), what means that chiral symmetry is broken in sodium chlorate unstirred crystallization.

The aim of the paper was to prove that parity violation really takes place in unstirred solutions, to establish the effect of first crystals and effect of growth conditions (supersaturation, temperature, and crystallizer size) on chiral nucleation of sodium bromate. Sodium bromate crystallizes in the cubic structure (space group $P2_13$, class 23). A large number of nucleation experiments have been carried out to establish various dependencies and to describe the statistics of chiral nucleation. Presented results describe chiral nucleation of sodium bromate but the same types of dependencies have been established also for other compounds.

2. Experimental

Sodium bromate solutions were prepared of 99.0% pure AR grade NaBrO_3 powder dissolved in warm distilled water using magnetic, teflon coated stirrer and filtered with a glass filter. Then they were transformed to several flat-bottomed crystallizers and left for crystals to grow. Large flat-bottomed crystallizers of 2 l capacity and of 23 cm in diameters and Petri flasks of 3.5, 6, 8, 9, 11, 13 and 14 cm in diameter and of volume of 20-100 ml were used. Simultaneously about 10-20 crystallization runs were conducted. Slow solvent evaporation at a constant temperature between -2 and 109°C created the supersaturation necessary for nucleation and crystal growth. Crystals nucleated spontaneously at the air/solution interface and immediately on the flat bottom of crystallizers. First events of spontaneous nucleation or nucleation stimulated by L, D, and both L and D seeds occurred approximately 4-40 h after preparation of solution. Crystallizations were conducted at $-2, 0, 1.5, 4, 6.5, 8, 10, 14, 21, 25, 31, 33, 40, 50, 56, 58, 60, 62, 64, 66, 68, 70, 82, 88, 90, 92, 94, 96, 98, 100, 103, 105$, and 109°C (boiling point). Temperature of nucleation and crystal growth varied about $\pm 0.2^\circ\text{C}$. Crystals were identified and counted before and after completed crystallization, i.e. when the whole solvent evaporated and the whole material crystallized. The smallest of the crystals were about $100\text{ }\mu\text{m}$ and the largest about 2 cm in size. Nucleation and crystal growth were conducted in closed and in open crystallizers. In open crystallizers the whole surface of the solution evaporated freely, whereas in closed crystallizers evaporation was hindered since only the small slit was open to remove the molecules of the solvent. As a result supersaturation necessary for nucleation and crystal growth in open crystallizers was much higher than in closed crystallizers.

Chirality of the crystals was determined with a polariscope or polarizing microscope by optical activity. Laevorotatory $(-)\text{-NaBrO}_3$ crystals have the same absolute structural configuration as isomorphous sodium chlorate of the opposite sign of rotation, i.e. dextrorotatory $(+)\text{-NaClO}_3$ crystals (Vogl et al., 1995). In this paper $(-)\text{-NaBrO}_3$ enantiomers have been denoted as L forms, and $(+)\text{-NaBrO}_3$ enantiomers as D forms. Therefore sodium bromate D crystals rotated light clockwise, and L crystals counterclockwise. When white light was used to D crystals placed between polarizers the colour of the crystals changed from blue to orange when the analyser were rotated clockwise, and the L crystals from orange (or yellow) to blue.

As-grown surfaces of crystals were etched in formic acid for 1-10 s at room temperature. The crystals were then rinsed in acetone and dried between filter paper. As-grown and etched surfaces of crystals were examined under optical Zeiss microscopes in reflection and in transmission.

3. Results and discussion

3.1 Chiral nature of micromorphology of as-grown and etched surfaces

Sodium bromate crystals nucleated at the air/solution interface and immediately on the glass bottoms of the crystallizers and grew on {100} and {111} surfaces on the crystallizer bottoms. Macromorphology of high-temperature (growing above 85 °C) forms of sodium bromate was cubic (dominated by {100} faces) with small {111}, $\{1\bar{1}1\}$, {110} and {210} surfaces which occasionally appeared on the habit. Low temperature forms (growing below 40 °C), and medium temperature forms (growing between 40 and 85 °C) were tetrahedral with {111} and $\{1\bar{1}1\}$ as dominant surfaces and minor {100}, {110} and {210} surfaces. Figure 1 presents morphology of high-temperature L and D forms.

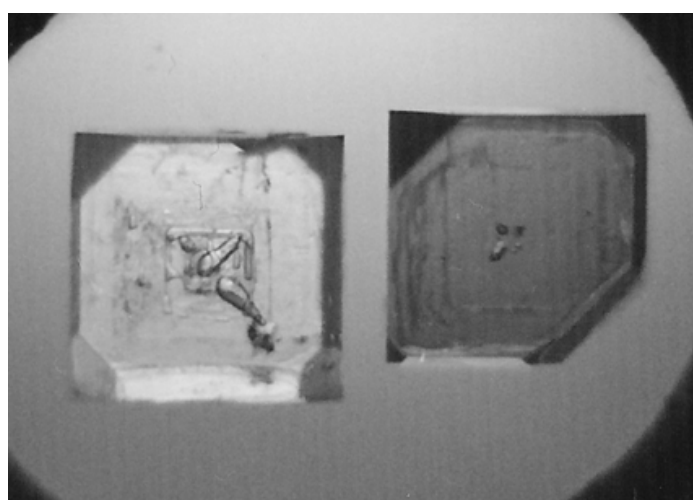
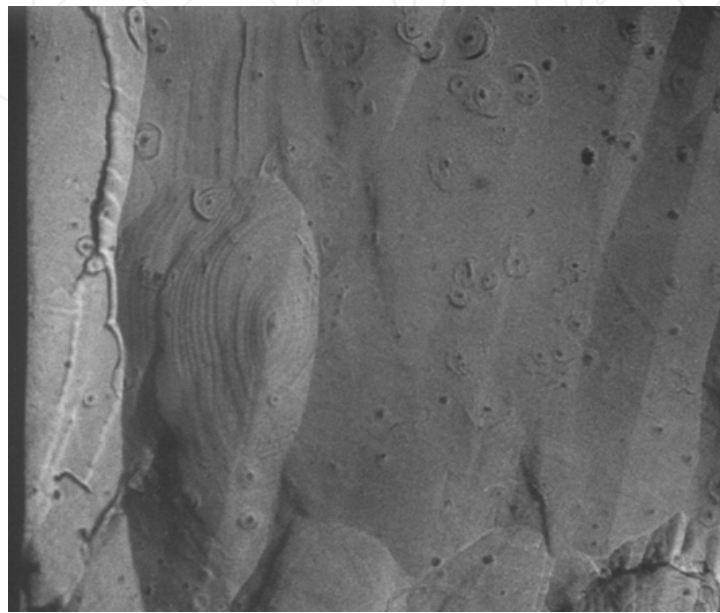


Fig. 1. L- NaBrO_3 , and D- NaBrO_3 crystals seen under crossed polarizers. Note: L (levorotatory) crystal is nearly white, and D (dextrorotatory) crystal is nearly black. In white light left crystal is blue and right is orange-brown. Growth temperature 86 °C. Field of view: 2.9 cm x 2 cm.

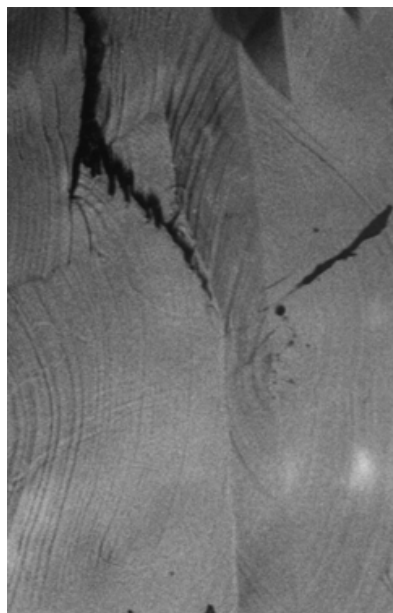
As grown {100} surfaces of low-temperature NaBrO_3 crystals exhibits elliptical growth hillocks which are dislocation growth centres. The hillocks are present on both enantiomorphous forms and depending on the type of enantiomer their major axes are inclined about +13° or -13° to the $\langle 100 \rangle$ edge of the crystal (Fig. 2).

Etching of L and D crystals of NaBrO_3 in formic acid reveals well-defined dislocation pits. The morphology of etch pits formed on {100} surfaces of both enantiomorphous forms is illustrated in Figure 3. The shape and orientation of growth hillocks and etch pits on {100} surfaces of NaBrO_3 crystals are similar to hillocks and pits revealed on NaClO_3 crystals as they belong to the same symmetry class (Szurgot & Szurgot, 1995a, Szurgot, 1995). Chiral nature of etch pits and growth hillocks reflects chirality of the internal structure of crystals. Etch pits formed on L crystals are mirror images of the pits formed on D crystals. As a result, L and D enantiomers of sodium bromate can be distinguished by the shape of growth and dissolution centers. Calculations of surface entropy factor (α factor) for sodium bromate crystals have shown that in the whole temperature region of growth from aqueous solution, i.e. between 271 and 381 K surface entropy factor varies between 5.6 and 4.8 for low and high-temperature limits. This means that the presence of growth

hillocks as dislocation growth centers is expected at low supersaturations. Values of α factor for sodium bromate are somewhat higher than those calculated for sodium chlorate (4.8-4.2) (Szurgot & Szurgot, 1994). This explains why etch pits and growth hillocks on sodium bromate crystals are more polygonal in comparison with the corresponding growth hillocks and etch pits formed by the same etchant on {100} surfaces of sodium chlorate.



(a)



(b)

Fig. 2. Growth hillocks on (100) surfaces of dextrorotatory and laevorotatory crystals of sodium bromate. (a) (+)-NaBrO₃, and (b) (-)-NaBrO₃ crystal. Growth temperature 25 °C. Field of view: (a) 4 mm x 3.3 mm, (b) 1.8 mm x 2.8 mm.

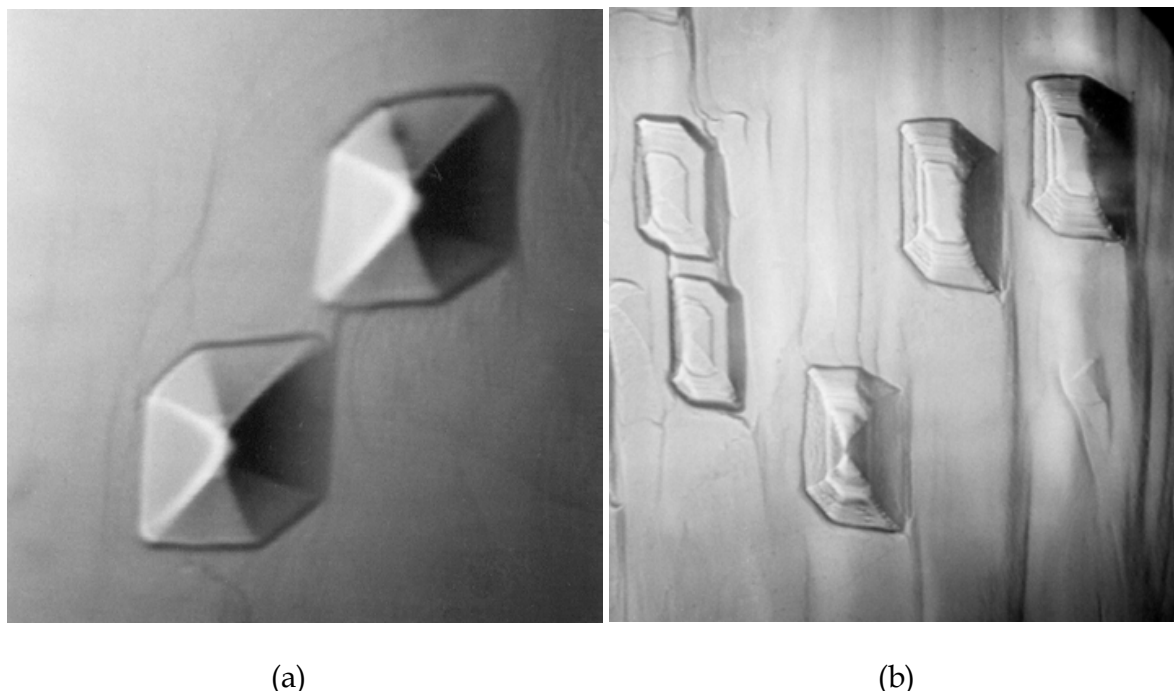


Fig. 3. Dislocation etch pits on (100) surfaces of dextrorotatory and laevorotatory sodium bromate crystals. (a) (+)-NaBrO₃, and (b) (-)-NaBrO₃ crystal. Etched in formic acid: (a) 3s, (b) 5s. Field of view: (a) 0.2 mm x 0.2 mm, (b) 0.3 mm x 0.32 mm.

3.2 Convection effects on surface morphology and distribution of inclusions

Convection effects on crystal growth embrace rate and kinetics of growth and nucleation, macromorphology, micromorphology and formation of defects. In the case of buoyancy-driven convection due to Earth's gravity various defects such as inclusions, dislocations, and growth bands are preferably formed at top sectors of the crystals, and at upper parts of side faces (Szurgot & Sangwal, 1987; Wilcox, 1983). Lateral segregation of impurities is another effect caused by the convection flow which has been recently revealed by etch topography (Szurgot, 2010). Differences in supersaturations in various parts of crystals growing from solution, transient instabilities in convection flow, creation of starvation zones depleted in solute in the laminar boundary layer and in the closed wake at the rear, are responsible for the observed effects. Differences in supersaturations in various parts of growing crystals are responsible for different thickness of growth layers in various places of the same surfaces. Szurgot established that growth layers present on vertical, side faces of potassium bichromate crystals growing in aqueous solution are thicker in upper parts of crystals than layers situated in the lower parts of the same faces (Szurgot, 1991). Figure 4 illustrates the same effect on a side, vertical or slightly inclined with respect to the vertical (111) surface of sodium bromate crystal grown at low temperature. The preferred capture inclusions by the upper, top faces, and by upper parts of vertical faces of two sodium bromate crystals grown at high temperature region is shown in Figure 5. Both figures prove that buoyancy-driven convection participates in growth of sodium bromate crystals.



Fig. 4. Micromorphology of a vertical, side (111) surface. U, L-upper and lower parts of a crystal. Arrow indicates direction of gravitational field. Growth temperature: 25 °C. Field of view: 2.7 mm x 4 mm.

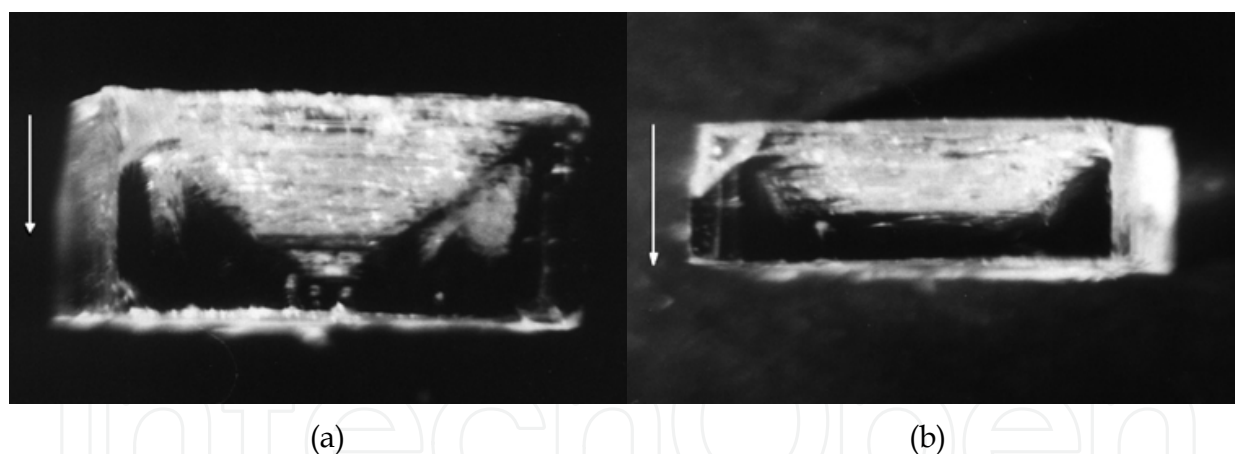


Fig. 5. Distribution of inclusions in NaBrO_3 crystals grown by self-nucleation at the bottom of growth vessel from unstirred solution at 90 °C. The planes of contact with the bottom are (100). Arrows indicate direction of gravitational field. Note: inclusions are captured by the upper, horizontal, top (100) face, and by upper parts of vertical (010) faces. Front planes: (001). Field of view: (a), (b) 4 mm x 2.5 mm.

3.3 Statistics of nucleation of chiral forms. Unimodal, bimodal and trimodal distribution of enantiomeric excess

The enantiomeric excess ee is a dimensionless coefficient used to characterize the formation of enantiomers in crystallization. It expresses the relative excess of L-forms in the whole population of enantiomers. This order parameter can be determined by the formula

$$ee = (N_L - N_D) / (N_D + N_L), \quad (1)$$

where N_L and N_D are the numbers of L- and D-forms.

If $ee = -1$ then exclusively D-crystals, if $ee = 1$ then exclusively L-crystals are formed but if D- and L-crystals nucleate with the same probability then $ee = 0$. Since our identification of sodium bromate enantiomers has been performed by the direction of rotation of light N_L is the number of laevorotatory (-)- NaBrO_3 crystals, and N_D is the number of dextrorotatory (+)- NaBrO_3 crystals.

Statistics of distributions of enantiomeric excess ee has been the main goal of our studies. It is based on an analysis of large number of crystallization runs (over 4300 crystal growth runs). Figures 6-11 and Table 1 present experimental data on the occurrence and relative participation of enantiomorphous forms of sodium bromate spontaneously nucleated at various temperatures and at various supersaturations. It may be noted from the data that in unseeded, unstirred solutions ee assumes all possible values between -1 and 1, and depending on the growth conditions various unimodal, bimodal and trimodal distributions are created. This means that in the case of sodium bromate uni-, bi- and the trimodal distributions of enantiomers are formed in unstirred solutions rather than monomodal, as it was reported previously for sodium chlorate (Kondepudi et al., 1990; Kondepudi et al., 1995b; Martin et al., 1996). This proves that in the case of spontaneous nucleation of sodium bromate enantiomers chiral symmetry is broken.

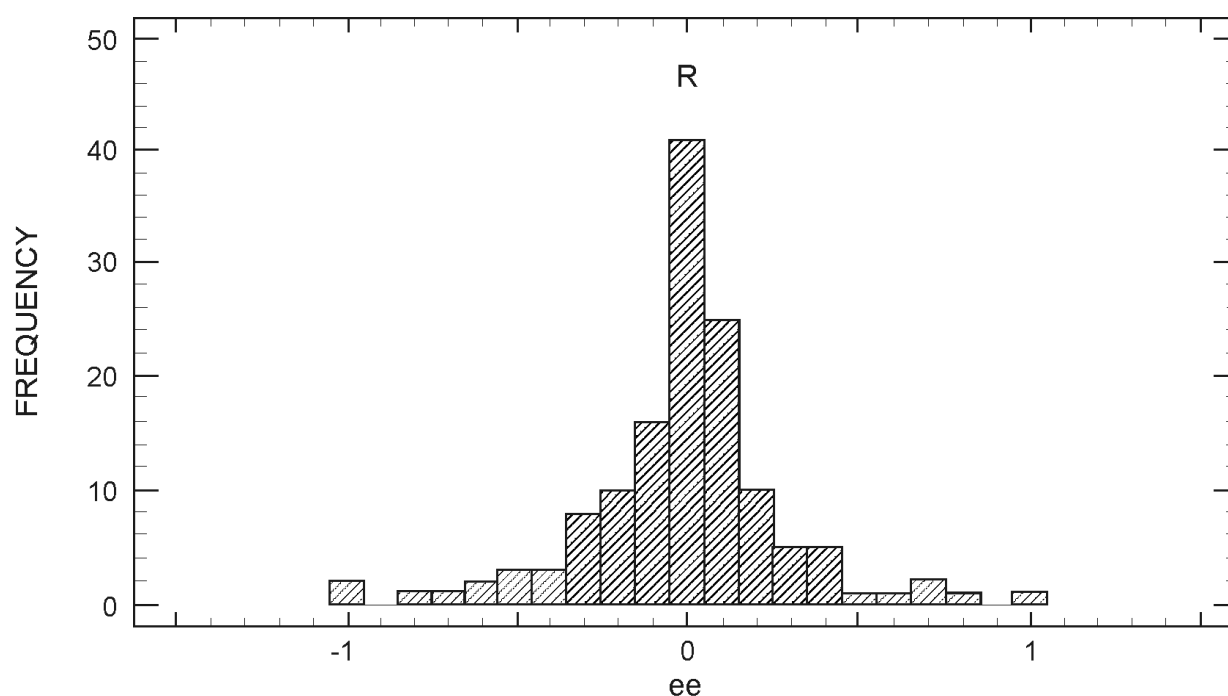


Fig. 6. Unimodal distribution of enantiomeric excess ee for NaBrO_3 crystals nucleated at 100°C in unstirred solutions in open crystallizers diameter of 6.2 cm. Note: high probability of nucleation of racemates (50:50 mixture) ($P = 0.30$), and close to zero probability nucleation of pure L ($PL = 0.007$) and pure D forms ($PD = 0.014$). Ratio: $PL/PD = 0.5$, $PR/(PL+PD) = 14.3$. Number of growth runs: 138, high supersaturation.

Experiments of unstirred crystallization of sodium chlorate enantiomers performed by various researchers revealed that only unimodal ee distribution is obtained in which only one peak occurs, i.e. peak for $ee = 0$ which corresponds to the same probability of creation of

L and D-crystals (Kondepudi et al., 1990; Kondepudi et al., 1995b; Martin et al., 1996). Our data show that unimodal distributions of ee with peaks at $ee = 0$ (or at $-0.05 < ee < 0.05$) which are here assigned as R peaks (R since $ee = 0$ means racemate 50:50 mixture) are formed only in certain conditions of crystallization: in open, large crystallizers at the lowest, and at the highest temperatures and at high supersaturations. Figure 6 is an example of such an unimodal distribution of enantiomeric excess ee for NaBrO_3 crystals nucleated at 100°C in unstirred solutions in open crystallizers diameter of 6.2 cm. It is seen that the probability PR of nucleation of racemate 50:50 mixture is high $PR = 0.30$, whereas probability of nucleation of pure L (PL, for $ee = 1$) and pure D (PD, for $ee = -1$) forms are close to zero ($PL = 0.007$, $PD = 0.014$). In this case supersaturation is high, ratio $PL/PD = 0.5$, and ratio $PR/(PL+PD) = 14.3$. Domination of formation of racemates over pure enantiomers is here evident.

Figure 7 reveals bimodal distribution of enantiomeric excess ee for NaBrO_3 crystals nucleated at 103°C in unstirred solutions in small, closed crystallizers diameter of 3.5 and 6.2 cm. Peak R is absent, instead peaks D and L are present. Peak D presents the largest enantiomeric excess of D forms (ee between -1 and -0.95), and peak L shows the largest excess of L-forms (ee between 0.95 and 1). Probabilities of nucleation of pure L forms, and pure D forms are high ($PL = 0.39$, and $PD = 0.35$), and the probability of nucleation of racemates (50:50 mixture) is close to zero ($PR = 0.02$). In this case supersaturation is low, ratio $PL/PD = 1.11$, and $(PL+PD)/PR = 37$. Since in the class ee is between -0.95 and -1 about 90-95 % of sodium bromate crystals were pure D enantiomers ($ee = -1$), and in the class between 0.95 and 1 were pure L enantiomers ($ee = 1$) our PL and PD are assigned as the probabilities of nucleation of pure enantiomers. According to the author's knowledge it is the first evidence for a such bimodal ee distribution which is typical of stirred crystallization rather than unstirred crystallization. The distribution proves that in the case of spontaneous nucleation of sodium bromate enantiomers chiral symmetry is broken.

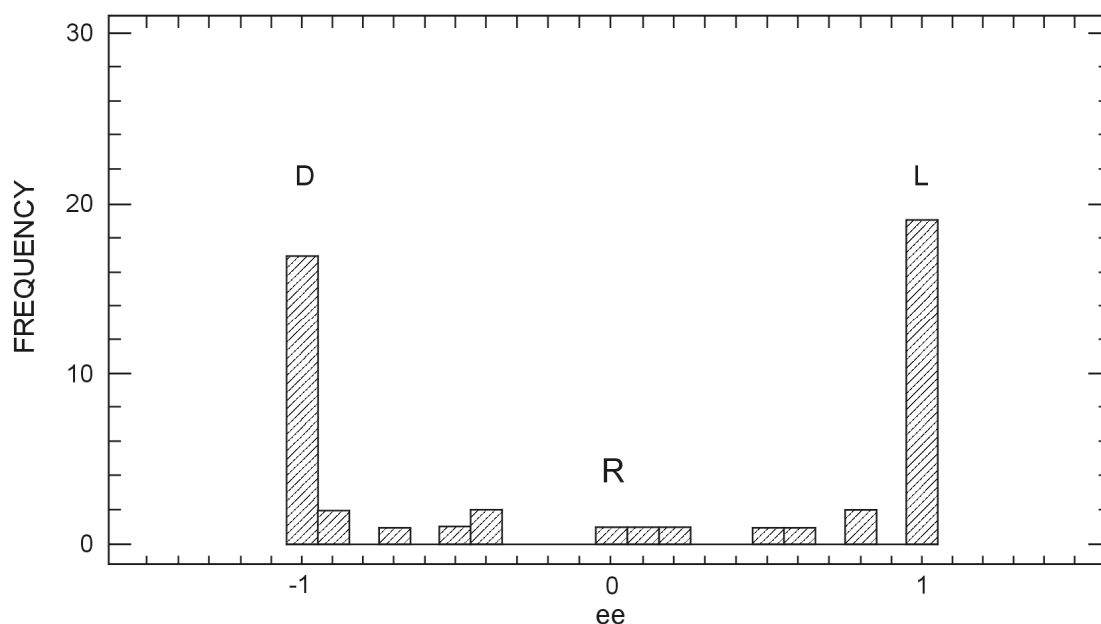


Fig. 7. Bimodal distribution of enantiomeric excess ee for NaBrO_3 crystals nucleated at 103°C in unstirred solutions in small, closed crystallizers diameter of 3.5 and 6.2 cm. Note: high probability of nucleation of pure L ($PL = 0.39$) and pure D ($PD = 0.35$) forms, and close to zero probability nucleation of racemates (50:50 mixture) ($PR = 0.02$). Ratio: $PL/PD = 1.11$, $(PL+PD)/PR = 37$. Number of growth runs: 49, low supersaturation.

Figure 8 and Table 1 reveal another bimodal distribution of enantiomeric excess ee for NaBrO_3 crystals in which high peaks D and L are present and have practically the same height. In this case crystals nucleated at different temperatures in the range between 0 and 105 °C in unstirred solutions in small, closed crystallizers with a different size. Number of growth runs is here large: 727. It is seen from the figure that number of events for which racemates are formed ($ee = 0$) is so low that peak R may be neglected as a separate peak ($PR = 0.02$). Probabilities of nucleation of pure L forms, and pure D forms are high and comparable with those presented in Figure 7 ($PL = 0.43$, and $PD = 0.41$). Ratio $PL/PD = 1.05$, and $(PL+PD)/PR = 42$. These results show that bimodal distributions of enantiomeric excess ee are common, occur in the whole temperature range used for unstirred crystallization and parity violation in unstirred crystallization is a real phenomenon. The phenomenon occurs in closed, small crystallizers for which supersaturation is low due to low evaporation rate. Experiments at boiling point (109 °C) in closed crystallizers revealed bimodal distribution of enantiomers with high probability of nucleation of pure L and D forms: 0.41 and 0.43, respectively. In this case vigorous movement of the growth medium takes place due to boiling and such a distribution is expected since it corresponds to intensive stirring. We can notice that probabilities PL and PD are the same as those noted in unstirred solution (Figs. 8 and 7).

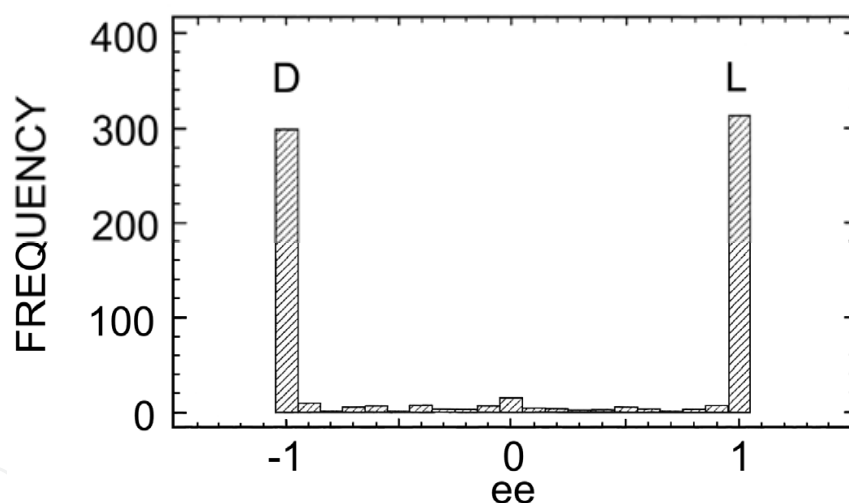


Fig. 8. Bimodal distribution of ee for crystals nucleated in closed, small crystallizers at low supersaturation at different temperatures. Probability of nucleation: $PD = 0.41$, $PR = 0.02$, $PL = 0.43$. Ratio: $PL/PD = 1.05$, $(PL+PD)/PR = 42$. Number of growth runs: 727.

Figure 9 reveals another type of bimodal distribution of ee . Here sodium bromate crystals nucleated spontaneously at 58 °C. The distribution presents results for 112 crystallization runs. It is seen from the figure that only R and L peaks are present in the distribution. Peak R is low and peak L is high. Peak D is absent. Probability of nucleation and probability ratios for this case are following: $PD = 0.009$, $PR = 0.05$, $PL = 0.70$, $PL/PD = 7.8$, $(PL+PD)/PR = 14.2$. Figures 7 and 9 show that distributions of ee and probabilities of nucleation are affected by temperature, and figures 6 and 7 reveal strong effect of evaporation rate, representing supersaturation.

Growth conditions	Total number of crystallization runs and probabilities PD, PR, PL of nucleation				Number of peaks and type of ee distribution
(°C)	Total	pure L form	Racemate	pure D forms	
Closed crystallizers (Tg = 0-105 °C)	727	PL = 0.43	PR = 0.02	PD = 0.41	2 (L,D) bimodal
Open crystallizers (Tg = 0-105 °C)	3312	PL = 0.16	PR = 0.16	PD = 0.05	3 (L, R, D) trimodal
Open crystallizers HT region (Tg = 98-105 °C)	423	PL = 0.002	PR = 0.16	PD = 0.01	1 (R) Unimodal

Table 1. Spontaneous nucleation of NaBrO₃ enantiomers in unstirred aqueous solutions under various conditions. (For L forms ee = 1 or 0.95 ≤ ee ≤ 1, for D forms ee = -1 or -1 ≤ ee ≤ -0.95, R – racemate 50:50 mixture (equal number of L- and D-crystals ee ≈ 0 i.e. -0.05 < ee < 0.05, HT-high- temperature growth, Tg-growth temperature).

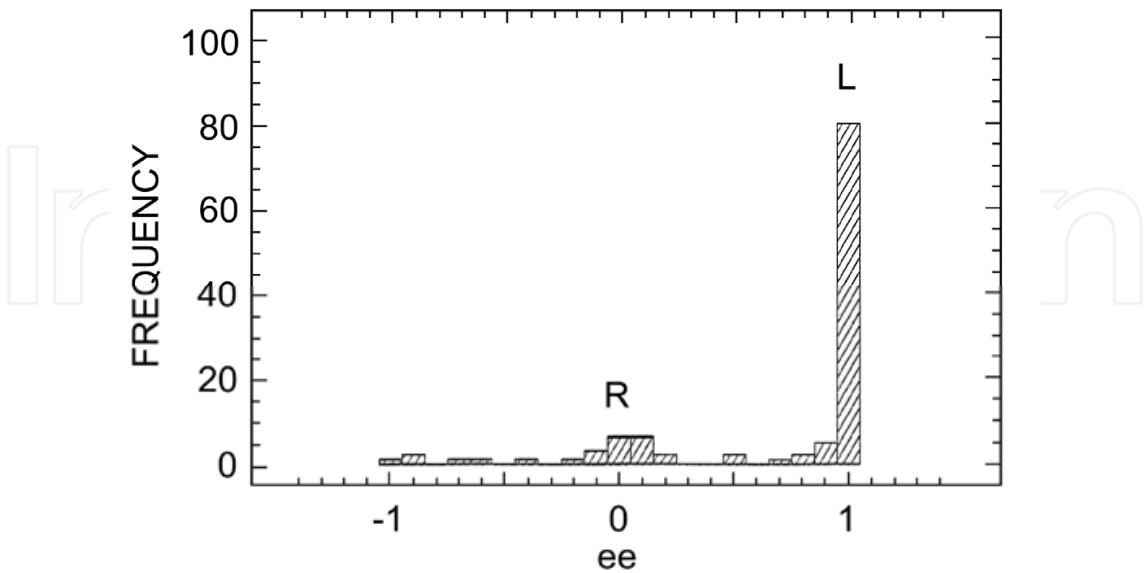


Fig. 9. Bimodal distribution of ee for crystals nucleated spontaneously at 58 °C. Probability of nucleation and probability ratios: PD = 0.009, PR = 0.05, PL = 0.70, PL/PD = 7.8, (PL+PD)/PR = 14.2. Number of growth runs: 112.

Trimodal distributions of enantiomeric excess *ee* are formed when sodium bromate crystals nucleated in closed and open crystallizers. Figure 10 shows an example of *ee* distribution when crystals nucleated spontaneously at constant temperature 105 °C in small, medium and large crystallizers. During nucleation and crystal growth in open crystallizers operating supersaturation was high, and in closed crystallizers low. The distribution presents results for 354 crystallization runs. It is seen from the figure that three peaks are present: peak D, peak R and peak L. The peaks are high and well defined. Probability of nucleation and probability ratios for this case are following: $PD = 0.23$, $PR = 0.18$, $PL = 0.21$, $PL/PD = 0.91$, $(PL+PD)/PR = 2.4$. This results deal with crystallization at high temperature, but trimodal distributions were obtained at any temperature. Trimodal distributions of *ee* are in fact combined bimodal distributions (peaks D and L), and unimodal distributions contributing to the central peak R.

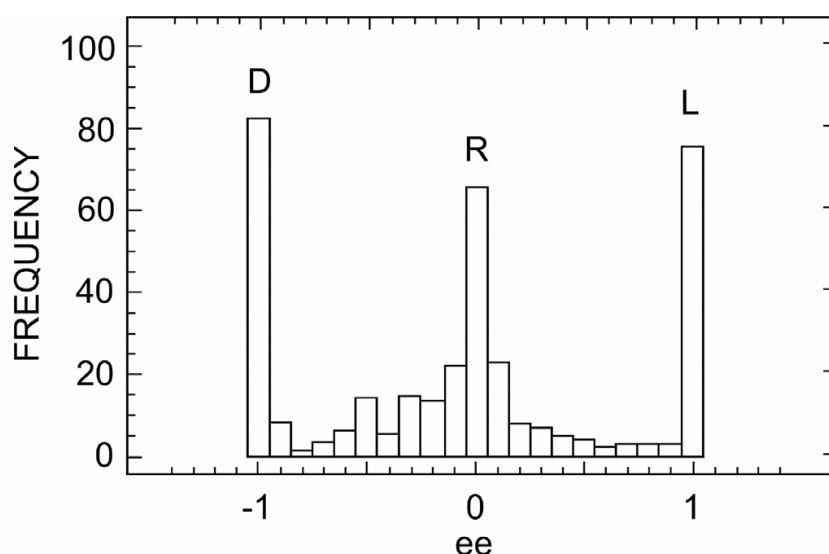


Fig. 10. Trimodal distribution of *ee* for crystals nucleated spontaneously in unstirred solution in open and closed crystallizers at 105 °C. Probability of nucleation: $PD = 0.23$, $PR = 0.18$, $PL = 0.21$. Ratio: $PL/PD = 0.91$, $(PL+PD)/PR = 2.4$. Number of growth runs: 354, low and high supersaturations.

Figure 11 shows trimodal *ee* distribution when crystals nucleated spontaneously at constant, but various temperatures (between -2 and 105 °C), in small, medium and large, open and closed crystallizers. The distribution includes a large number of nucleation runs (2201 runs). Operation supersaturation was low, medium and high. The figure reveals that, as previously, three peaks are present in the distribution, but peak D is smaller than peak R, and smaller than peak L, which is the highest of the three. Probability of nucleation and probability ratios for these results are following: $PD = 0.06$, $PR = 0.12$, $PL = 0.23$, $PL/PD = 3.8$, $(PL+PD)/PR = 2.4$. The results show that crystallization at low, medium and high temperatures and at various supersaturations leads inevitably to the trimodal *ee* distributions.

Bimodal and trimodal *ee* distributions with peaks D and L prove that for certain growth conditions the probability of the creation of exclusively L- and D- crystals is high in unstirred crystallization, and probability of creation of racemates is low. This means that it is not true that only unimodal distributions of enantiomeric excess with exclusively peaks R

are created in unstirred crystallization. Chiral symmetry is broken in spontaneous nucleation of sodium bromate from unstirred solutions.

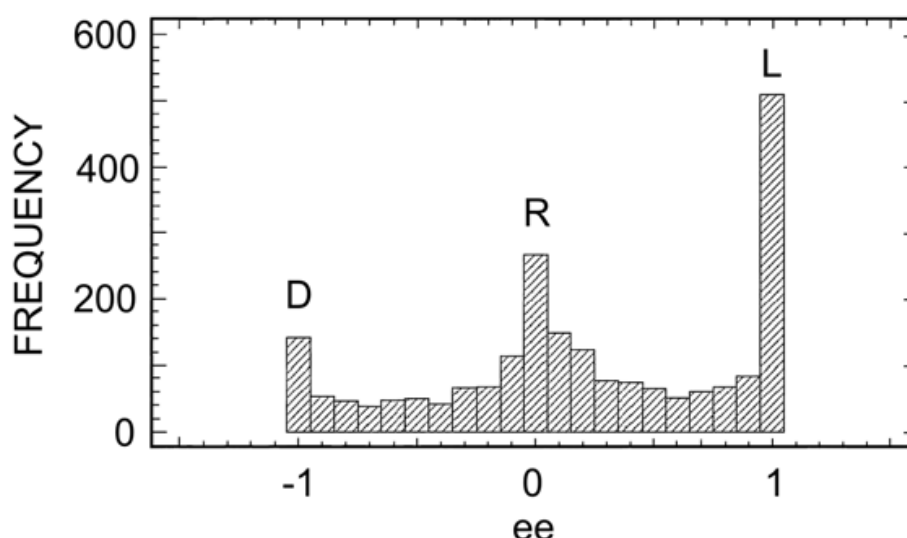


Fig. 11. Trimodal distribution of ee for crystals nucleated spontaneously in unstirred solution. Distribution includes a large number of nucleation runs conducted at various temperatures, various supersaturations with various crystallizer sizes. Probability of nucleation: PD = 0.06, PR = 0.12, PL = 0.23. Ratio: PL/PD = 3.8, (PL+PD)/PR = 2.4. Number of growth runs: 2201.

Comparison of probabilities for both trimodal distributions presented in Figures 10 and 11 shows that PR and PL are practically the same, but PD decreased. This means that L enantiomers of sodium bromate are preferentially formed with respect to D enantiomers. Figures 7 and 8 reveal that asymmetry between D and L enantiomers is not created during nucleation in closed crystallizers since ratio PL/PD for nucleation in closed crystallizers varies between 1.05 and 1.11, and both values of PL/PD are close to one, whereas PL/PD resulting from figure 11 is about four.

In stirred crystallization, in forced convection regime the bimodal distribution of enantiomeric excess is preferentially obtained since the high efficiency of cloning of the single parent crystal by the collision breeding e.g. by breaking off the whiskers from the crystal surface of the parent crystal. In unstirred crystallization when the mechanisms connected with free convection operate as it was suggested by Szurgot and Szurgot (Szurgot & Szurgot, 1995b), and supported by the Cartwright and coworkers (Cartwright et al., 2004) the efficiency of cloning of the first crystal is expected to be much lower due to slow velocity of movement of the solution. Much time is needed prior to the next crystal will nucleates in unstirred solution. When small, closed crystallizers are used in unstirred crystallization then for a small volume of the solution and at low supersaturation it is possible that nearly all secondary crystals will acquire the handedness of the first crystals (Figs 7, 8). In this case, in a single growth run in a small crystallizer either L pure or D pure enantiomers will be created and bimodal distribution will result for a large number of experiments.

In unstirred crystallization it is highly probable that two or more initial crystals will control the secondary nucleation, rather than the single parent crystal. In the case of two initial

crystals which may be either LL, DD or LD pairs the trimodal distribution will result (Figs 10, 11). In large crystallizers due to the huge volume of the mother solution, and at additionally high supersaturation, which are reachable especially in open crystallizers, three, or larger number of initial crystals is formed and the racemate peak (peak R at $ee = 0$) will play an important role. Unimodal distribution is thus preferentially formed (Fig 6), or multimodal distribution with the dominating racemate peak.

Figure 12 presents dependence of ratio PL/PD on temperature for sodium bromate crystals nucleated in open and closed crystallizers. Diamonds present experimental points for nucleation in open crystallizers, and squares nucleation in closed crystallizers. It is seen from the figure that in the case of nucleation in closed crystallizers PL/PD is independent of temperature in the whole temperature range and is nearly constant. Values of PL/PD are spread in the narrow range between 0.95 and 1.1 which means that they are very close to one. Since $PL \approx PD$, nucleation in closed crystallizers leads to symmetric distributions of enantiomeric excess. In the case of nucleation in open crystallizers at higher supersaturation PL/PD values are spread in the wide range between 0 and 20. On an average PL/PD increases with the increasing temperature what can be approximated by the linear function $PL/PD = 0.035t + 1.454$, where t is temperature in Celsius degrees. At most temperatures $PL > PD$, at selected temperatures $PL = PD$, and at certain temperatures $PL/PD = 0$ what means that $PL = 0$, and L forms are not created. Values of PL/PD are scattered between two curves, lower limit is the straight line $PL/PD = 0$, the upper limit is curve UL. It is seen that spreading PL/PD values is relatively narrow at low temperatures and wide at high temperatures.

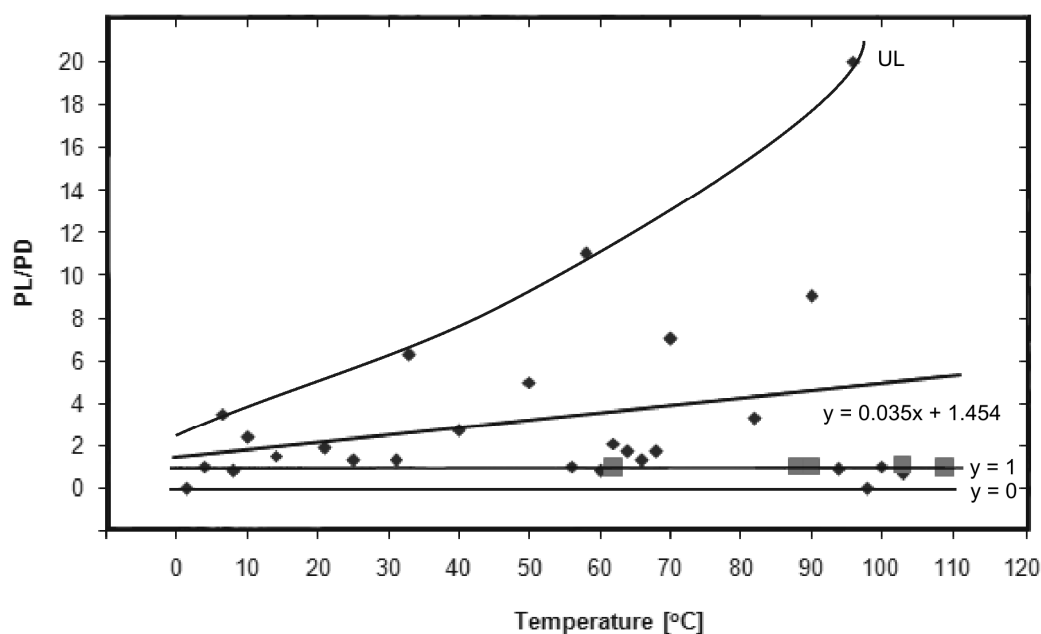
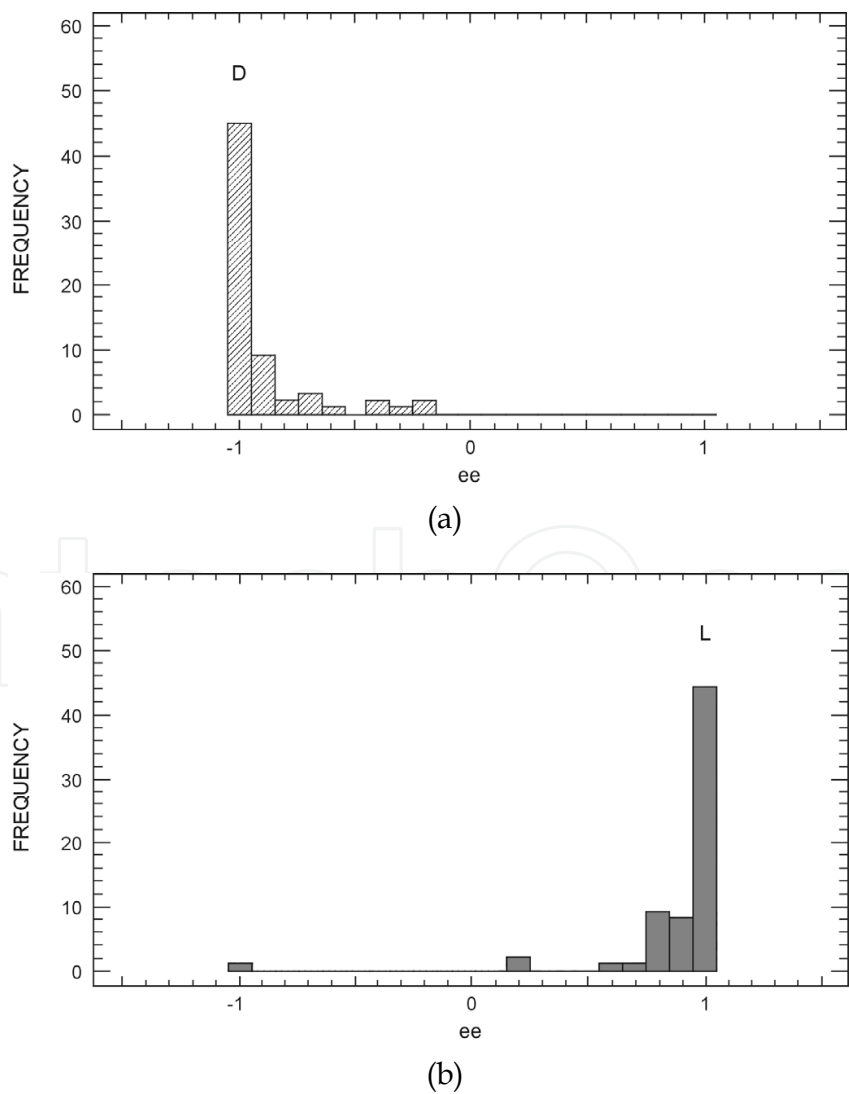


Fig. 12. Effect of temperature on the ratio PL/PD, where PL is the probability of nucleation of L forms, and PD is the probability of creation of D forms. Diamonds-nucleation in open crystallizers, squares- nucleation in closed crystallizers. Curve UL represents the upper limit values of ratio PL/PD.

3.4 Effect of handedness of first nucleated crystals on the handedness of secondary crystals

Appearing of the first crystal or a group of initial crystals and an introduction of a seed into growth medium, in our case into the aqueous solution, initiate secondary nucleation. As a result, secondary and primary heterogeneous or homogeneous nucleation participates in the formation of enantiomers, and various parameters controlling primary and secondary nucleation affect handedness of the nucleated crystals. Figure 13 and Table 2 present the effect of handedness of initial crystals on the formation of sodium bromate enantiomers. Figure 13 shows the effect of seeds on handedness of daughter crystals created by the secondary nucleation processes. It is seen that if the single L-crystal, or a group of L crystals nucleate as the first, mainly or exclusively L-crystals are formed, but if D-crystal is the first mainly D-crystals nucleate (Fig 13 a,b). In the first case peak L, and in the second case peak D is formed, similarly as in the case of sodium chlorate (Szurgot & Szurgot, 1995b). The scatter of ee values is high between -1 and 0, in spite of the fact that high enantiomeric excess is obtained, and probability PD for seeded crystals equals 0.68, whereas PL = 0.68 (Table 2, Fig 13 a,b).



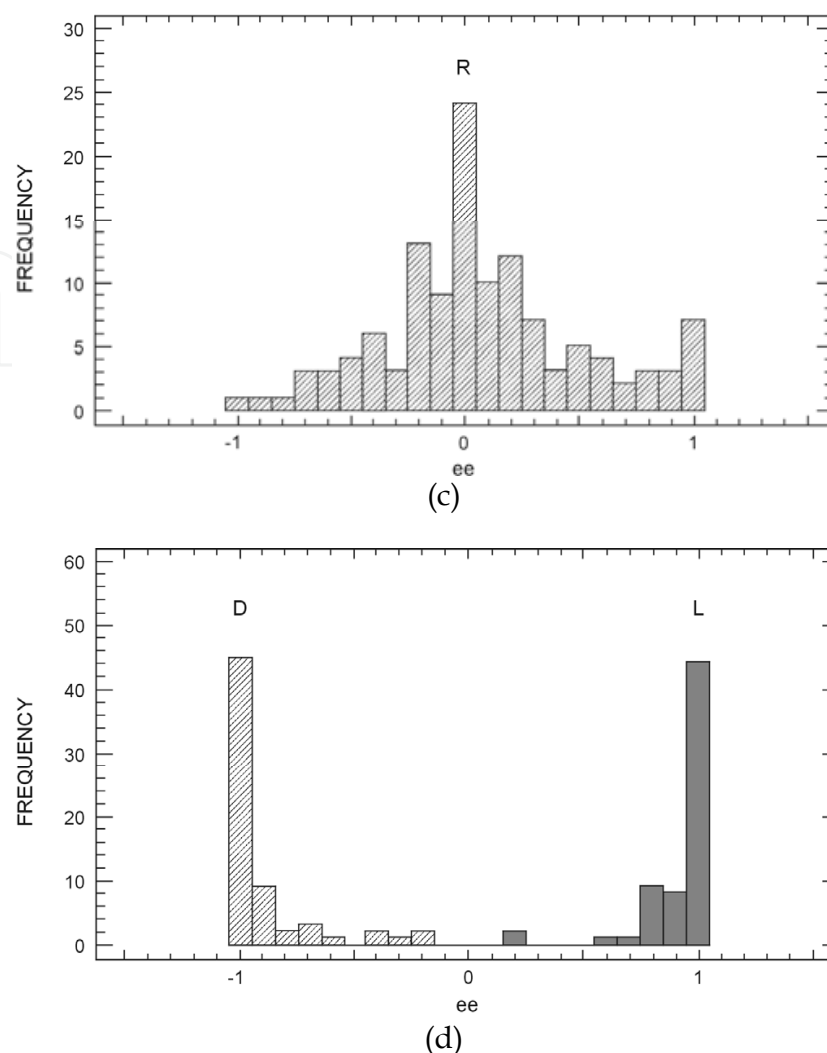


Fig. 13. Effect of handedness of seed crystals on the formation of NaBrO_3 enantiomers in unstirred solution. Distributions of ee values conditioned by secondary nucleation induced by: (a) D forms, (b) L forms, (c) a pair of L and D forms. (d) Combined data for single D forms (dashed), and single L forms (filled). Probability of nucleation and probability ratios: (a) $\text{PD} = 0.68$, $\text{PL} = 0$, $\text{PR} = 0$, (b) $\text{PD} = 0.015$, $\text{PL} = 0.68$, $\text{PR} = 0$, (c) $\text{PD} = 0.008$, $\text{PR} = 0.19$, $\text{PL} = 0.06$, $\text{PL}/\text{PD} = 7.5$, $\text{PR}/(\text{PL}+\text{PD}) = 2.8$, (d) $\text{PD} = 0.34$, $\text{PL} = 0.34$, $\text{PR} = 0$, $\text{PL}/\text{PD} = 1$, $\text{PR}/(\text{PL}+\text{PD}) = 0$. Number of growth runs: (a) 65, (b) 65, (c) 124, (d) 130. Here three independent cases of secondary nucleation induced by single D, single L, and a pair LD of initial crystals are presented (Figs. (a), (b), and (c) respectively), whereas the bimodal distribution presented in Figure (d) reveals the combined data secondary nucleation for single D (Fig (a)), and single L (Fig (b)) initial crystals. Since of 130 experiments presented in Fig (d) 65 represents seeding by a single D enantiomers, and the same number 65 experiments represents seeding by a single L enantiomers this binomial distribution proves that $\text{PL}=\text{PD}$.

We can notice that there exists the finite probability of the formation of enantiomers with the opposite handedness with respect to the initial crystals, i.e. L crystals for D initial enantiomers, and D crystals for L parent enantiomers. The probabilities are low but different

from zero ($PD = 0.015$ for L seed, Fig 13b, Table 2). The last results show that during secondary nucleation of sodium bromate enantiomers there exist processes responsible for generation of opposite handedness as it was predicted by Frank in 1953 (Frank, 1953), although the dominant role in unstirred crystallization play processes of chiral autocatalysis. In unstirred crystallization of sodium bromate cloning of initial crystals has 68 % efficiency. The dominant role of handedness of the initial crystals in the formation of enantiomers has been proven.

If a pair LD (or a group of LD pairs) crystals nucleate as first, then central maximum, i.e. peak R appears (Figs 13c, for a single LD pair). Such a situation has been shown earlier for sodium chlorate in which LD pairs of seeds played the role of first crystals (Szurgot, Szurgot, 1995b). Thus, the presence of peaks D, L, and R in distributions of ee values is conditioned by the handedness of first crystals.

Type of seed	Number of crystallization runs and probabilities PL, PR, PD of nucleation				Number of peaks and type of ee distribution
	Total	L	R	D	
Single D	65	0 PL = 0	0 PR = 0	44 PD = 0.68	1 (D) unimodal
Single L	65	44 PL = 0.68	0 PR = 0	1 PD = 0.015	1 (L) unimodal
LD pair	129	7 PL = 0.06	24 PR = 0.19	1 PD = 0.008	2 (R dominant, L) Bimodal

Table 2. Secondary nucleation of NaBrO₃ enantiomers induced by chiral seeds in unstirred aqueous solutions. (L - left forms with ee = 1 or $0.95 \leq ee \leq 1$, D - right forms with ee = -1 or $-1 \leq ee \leq -0.95$, R -racemate 50:50 mixture with ee ≈ 0 or $-0.05 < ee < 0.05$).

The distributions of enantiomeric excess resulted from the effect of handedness of initial crystals enable one to explain experimental ee distributions and predict the possibilities of the formation of new distributions, that have not been discovered yet. Combined results presented in Figures 13a,b,c lead to obtaining various types of ee distributions presented in Figs. 6-11. Figure 13d shows that the bimodal distribution with D and L peaks is the result of nucleation exclusively single D and single L enantiomers as initial. This type of distribution has been obtained in closed, small crystallizers in which supersaturation was relatively low (Figs. 7 and 8), and at 109 °C, i.e. at boiling point when the mother solution was violently moved. The trimodal ee distributions with peaks D, L and R are the result of initial nucleation of single L, single D, and a pair of LD enantiomers. Figures 10 and 11 resulting from the crystallization in open, and in closed crystallizers are just such a type, so we now know that in these crystallization conditions both single L and single D enantiomers, as well as pairs of LD enantiomers are nucleated as the initial crystals. The type of bimodal distribution shown in Figure 9 for nucleation at 58 °C results from the initial nucleation of single L forms and a pair of LD forms.

Values of probabilities PD, PL, and PR revealed in secondary nucleation experiments are in relatively good agreement with the experimentally determined probabilities. For example, values of PD and PL in the bimodal distribution with D and L peaks shown in Figure 7 are equal to about 0.37 (PD = 0.35, PL = 0.39), those in Fig 8 about 0.42 (PD = 0.41, PL = 0.43), those in Fig 13d are equal to 0.34 (PD = 0.34, PL = 0.34). The unimodal distribution with peak R presented in Figure 6 gives PR = 0.30, and peak R in Figure 13c gives PR = 0.19, somewhat smaller, but acceptable value.

3.5 Effect of supersaturation on probability of nucleation of enantiomers and racemates

The number of nucleated crystals in one growth run varies markedly between 8 and 273. This means that the supersaturation of the solution at which nuclei are formed also assumes very different values from low to high. In most of our experiments supersaturation was not very high. Formation of pure enantiomers and the high enantiomeric excess takes place when the number of nucleated crystals and the supersaturation is relatively low. Spontaneous nucleation at relatively low or medium supersaturation in unstirred solutions (in closed crystallizers, and in small open crystallizers) leads to high enantiomeric excess and to the bimodal and trimodal distributions of ee. In open, large crystallizers, the supersaturations are higher, both enantiomers nucleate simultaneously, ee tends to zero, and monomodal distributions of ee result. Peak R is the one and the only peak in the distributions.

The supersaturation is, however, not the only factor affecting the formation of enantiomers. Kondepudi and co-workers showed in 1995 that the stirring rate is the critical parameter in chiral symmetry breaking in stirred crystallization of sodium chlorate (Kondepudi et al., 1995 a,b). Secondary nucleation studies of sodium chlorate enantiomers in aqueous solution conducted by Denk & Botsaris (Denk & Botsaris, 1972) have shown that apart from supersaturation, stirring rate and impurities, also handedness of seeds plays an important role in the formation of chiral forms during crystallization of sodium chlorate. Our previous results for sodium chlorate (Szurgot & Szurgot, 1995b) and present results for isomorphous sodium bromate confirmed the important role of handedness of initial crystals.

To explain appearing of D, R, and L peaks and various values of ee occurring in the ee distributions the effect of supersaturation on the formation of enantiomers will be analysed. The first crystals appear during the primary nucleation at the supersaturation above the metastable limit, which is here assumed as 10% at 30 °C for sodium bromate. This leads to the drop of supersaturation, as it was monitored by Kondepudi for sodium chlorate, and confirmed by the analysis of distribution of sizes of sodium bromate crystals. Further acts of nucleation occur at lower supersaturations, in the secondary nucleation region. Denk and Botsaris' secondary nucleation results (Denk & Botsaris, 1972) are our base for explaining of the distributions of sodium bromate enantiomers. The way we applied here is the same as applied earlier for sodium chlorate (Szurgot & Szurgot, 1995b).

Figure 14 presents three possible relations ee and supersaturation: the upper curve for first L crystal, the lower curve for first D crystal, and the central, straight line for two initial, one L, and one D crystal nucleated spontaneously. Dashed lines indicate possible scatter in ee values for each of the dependencies. Four regions of supersaturations are distinguished to describe the formation of sodium bromate enantiomers.

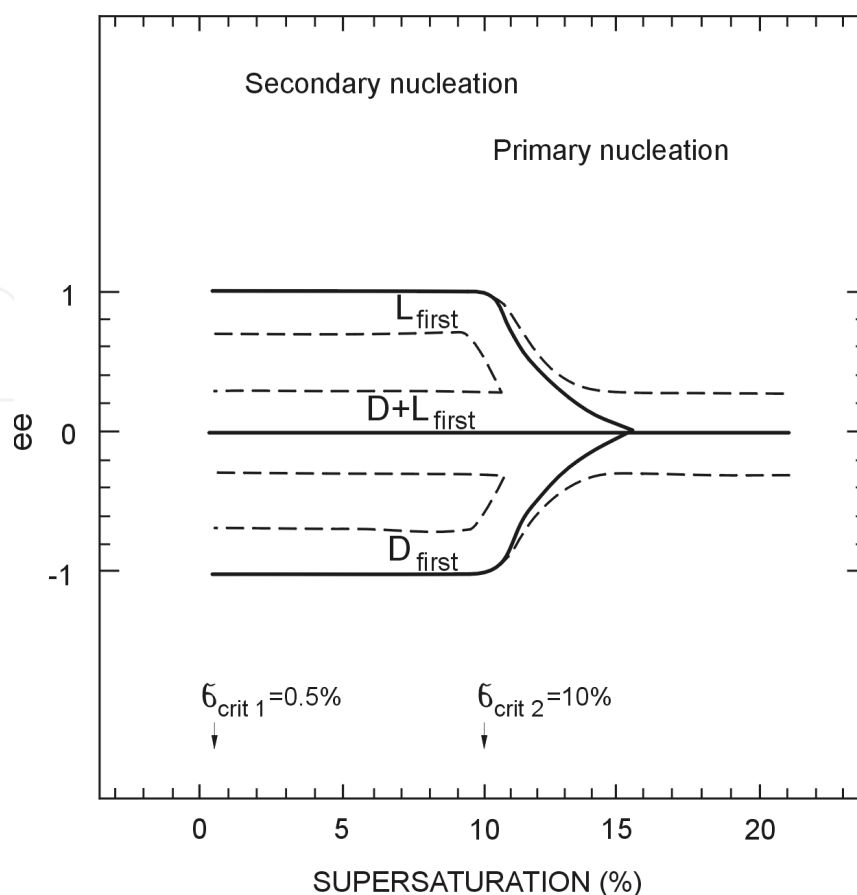


Fig. 14. Expected dependence of the nucleation of D- and L-forms of sodium bromate on supersaturation in an unstirred solution at constant temperature 30 °C.

At very low supersaturations (0-0.5%, region I) no nucleation takes place. At low, and medium supersaturations (0.5-10%, region II) secondary nucleation produces the crystals with the same structure as the first crystals. Strictly speaking a large part of the population between 60% and 100 % of the crystals have the same structure as the parent crystal. This means that for the first D enantiomer we have ee between -1 and -0.7, and for the first L crystal ee values will be between 0.7 and 1 with maximal values ee = -1 and ee = 1, as it has been shown in our experiments with the secondary nucleation (Fig. 13). In the case of pair of LD initial crystals peak R is formed at ee = 0, and in the dashed range of ee values, between -0.3 and +0.3 about 70 % (between 60 and 80 %) of crystals is then nucleated (Figs. 13c, 6).

At still higher supersaturations (above 10 %) primary nucleation begins and exists together with the secondary nucleation or is the only mechanism, forming crystals. In the transitional region (10-15%, region III) ee tends to zero, and any value of ee between -1 and 1 is possible. In the highest supersaturation range (above 15 %, region IV) racemates are only formed, and racemate 50:50 mixture (ee = 0) is the only peak in ee distributions. In any region ee may be equal to 0 if both L and D enantiomers nucleate as first (the central straight).

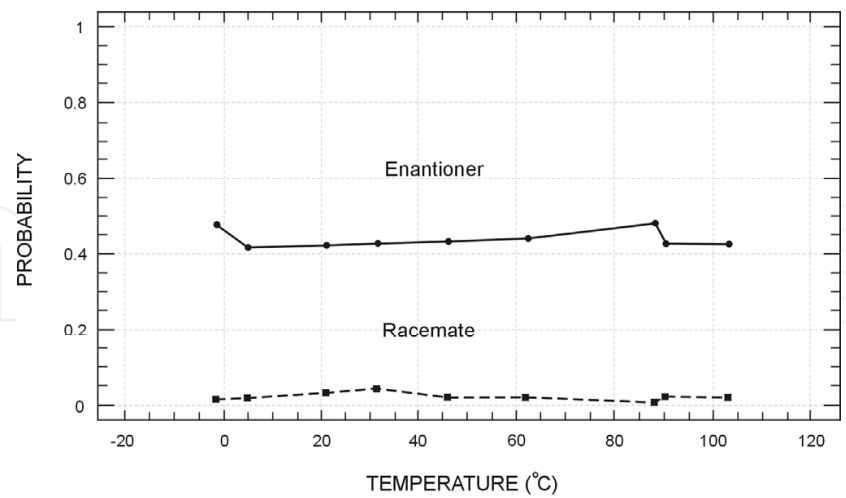
As Figure 14 summarises the results on the formation of enantiomers in various runs, at various supersaturations, and various first crystals, it reflects various possibilities resulting from the above analysed model. This includes the creation of peaks D, R and L as a consequence of autocatalysis caused by the first crystals but also explains the scatter

in ee values. Bimodal distributions of enantiomers with peaks for pure L and D enantiomers (peaks D and L) and absence of the peak R prove that in closed, small crystallizers at low supersaturations only single enantiomers are created, and simultaneous nucleation of a pair of D and L forms is not in these conditions sufficiently competitive process.

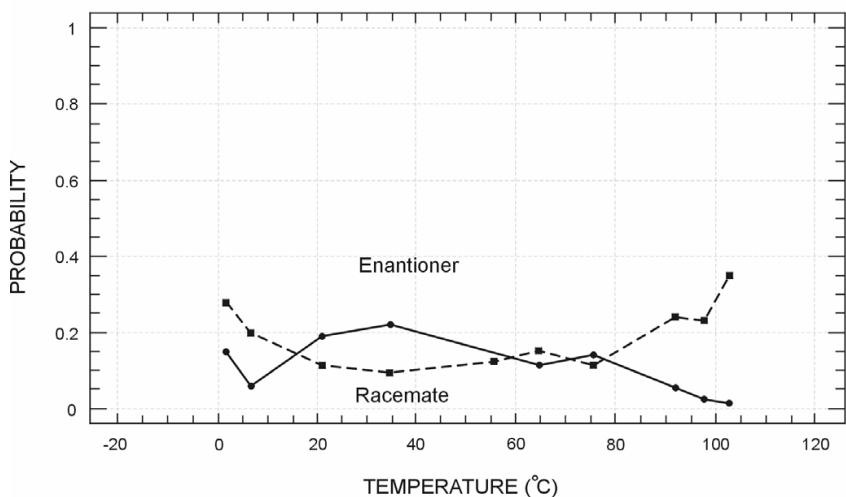
Our results show that chiral symmetry breaking takes place in unstirred solution so it is not a forbidden process. Since in unstirred crystallization there exist natural convection, and fluid movement around the growing crystals takes place with the velocities of the order of 0.01-0.1cm/s, the convection-induced transport of the solution from the parent crystal region to the other parts of the crystallizer should operate. In small crystallizers the volume of the solution is small and at low supersaturations when closed crystallizers are used there is enough time to transport the solution from the parent crystal to each place of the crystallizer before a new crystal has nucleated spontaneously. It is enough time because the nucleation rate is low at low supersaturation. Conversely, at high supersaturations, in open crystallizers new spontaneously created crystals of various handedness can be effectively formed during short period of time, and if additionally the crystallizer is large the formation of racemates will be preferred. In stirred crystallization fluid velocities are high (order of 10 cm/s) and process of transport of whiskers formed on the surfaces and broken off the parent crystals is highly probable. Collisions of parent crystals with the stirrer contribute to the cloning of the crystals in stirred solution. Thus bimodal distributions of enantiomers in stirred crystallization are commonly formed. The preferred formation of bimodal distributions of enantiomers in stirred solutions instead of the monomodal racemate distribution can be also caused by much deeper drop in supersaturation in stirred solution after first acts of nucleation in comparison to unstirred crystallization as it was established by Kondepudi and co-workers (Kondepudi et al., 1993) The supersaturation drop occurring in stirred and unstirred solutions leads to the transition from regions IV or from III to region II in which only one type of enantiomer is formed and to region I where no nucleation takes place. In unstirred solution supersaturation drop also contributes to interruption of primary nucleation. This is why bimodal distributions of enantiomers occur in sodium bromate unstirred crystallization. But not only pure enantiomers are formed in unstirred solutions but also this process is highly probable, and expected in small, closed crystallizers. As a result, the effective cloning of crystals in unstirred solutions exist no matter what the microscopic mechanisms of autocatalysis and competition between both chiral forms are.

3.6 Effect of temperature on probability of nucleation of enantiomers and racemates

A large number of nucleation experiments have been conducted to establish the effect of temperature on nucleation of sodium bromate enantiomers. Figures 15 and 16 show the results for crystallization in closed and in open crystallizers in a wide temperature range between -2 and 109 °C. Does temperature affect the formation of enantiomers? Figures 15 and 16 reveal that in closed crystallizers the probability of the creation of L and D enantiomers is very high, about 0.4 for each of the enantiomers, and probability PR of the formation of racemates is very low (about 0.01). Bimodal distributions in these conditions have much in common. It is seen that in small crystallizers and at low supersaturations temperature does not affect the distribution of enantiomers.



(a)



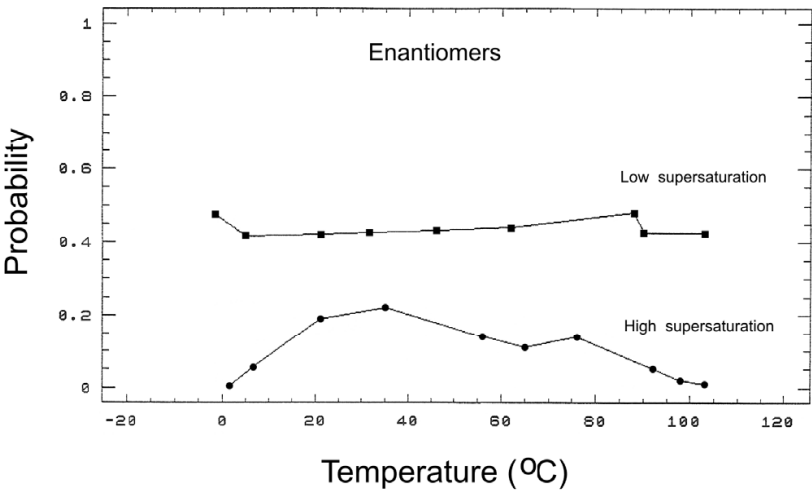
(b)

Fig. 15. Effect of temperature on probability of nucleation of pure enantiomers and racemates (50:50 mixture) of sodium bromate in unstirred solution. Growth conditions: (a) low supersaturation (closed, small crystallizers), and (b) high supersaturation (open crystallizers). Probability of nucleation of pure enantiomers is arithmetic average of L and D form.

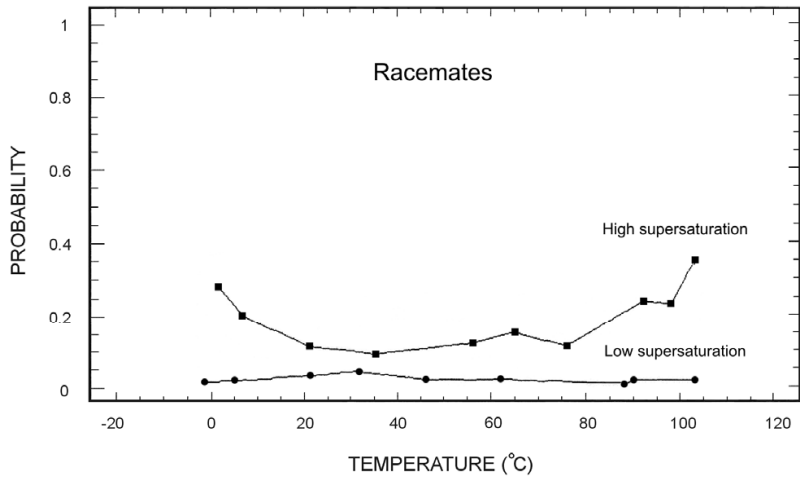
In open crystallizers temperature affects the formation of enantiomers and racemates (Figures 15 (b), 16 (b)). It is seen that three temperature regions may be considered: low-temperature region (between -2 and +10 °C), medium-temperature region (between +10 and 80 °C), and high temperature region (between 80 and 109 °C). We can see that in open crystallizers, at high supersaturations PR is relatively high (between 0.10 and 0.27) in the whole temperature range, and the probabilities PL and PD of the formation of enantiomers are relatively low (between 0.01 and 0.2) in comparison with nucleation in closed crystallizers. At medium temperatures both probabilities PR and the mean probability of the formation of

enantiomers $(PL+PD)/2$) are comparable, and does not vary significantly with the temperature. At low and at high temperatures probability PR of formation of racemates is high, and probabilities of formation of enantiomers are low.

To reveal both effects: temperature and the supersaturation the probabilities of formation of enantiomers and racemates have been drawn separately, one for enantiomers (Fig. 16 (a)) and another for racemates (Fig. 16 (b)). Figs. 15 (a) and 16 (a) illustrate that parity violation in unstirred crystallization occurs at any temperature and this is a common phenomenon, with high values of probabilities for the formation of enantiomers, on an average about 0.4 for each of enantiomers. Such a high probability cannot be neglected in the considerations of chiral symmetry breaking phenomenon.



(a)



(b)

Fig. 16. Effect of temperature and supersaturation on probability of nucleation of: (a) enantiomers, (b) racemates.

4. Conclusions

First nucleated crystals govern the handedness of secondary crystals and depending on their handedness, nucleation temperature and supersaturation various unimodal, bimodal and trimodal distributions of enantiomeric excess are obtained. Nucleation temperature affects the distribution of enantiomers. Simultaneous seeding of L and D enantiomers leads to a unimodal, broad distribution of enantiomeric excess with maximum at $ee = 0$, i.e. for a 50:50 racemate mixture. L forms of sodium bromate have a greater probability of spontaneous nucleation than D forms. Unstirred crystallization of sodium bromate leads to a strong breakage of chiral symmetry, formation of pure enantiomers and bimodal distributions of enantiomeric excess, the same type as discovered in stirred solutions.

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6. References

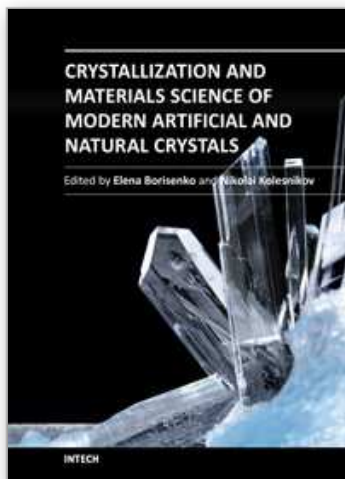
- Kondepudi, D.P.; Kaufman, R.J. & Singh N. 1990. Chiral Symmetry Breaking in Sodium Chlorate Crystallization. *Science*, Vol.250, (16 November 1990), pp. 975-976, ISSN 0036-8075
- Kondepudi, D.P.; Bullock, K.L.; Digits, J.A.; Hall, J.K.; & Miller, J.M. 1993. Kinetics of Chiral Symmetry Breaking in Crystallization. *Journal of the American Chemical Society*, Vol.115, No.22 (November 1993), pp. 10211-10216, ISSN 0002-7863
- Kondepudi, D.P.; Bullock, K.L.; Digits, J.A.; Hall, J.K. & Yarborough, P.D. 1995a. Stirring Rate as a Critical Parameter in Chiral Symmetry Breaking Crystallization. *Journal of the American Chemical Society*, Vol.117, No.1 (January 1995), pp. 401-404, ISSN 0002-7863
- Kondepudi, D.P.; Digits, J.A.; Bullock, K.L.; & . 1995b. Studies in Chiral Symmetry Breaking Crystallization I: The Effects of Stirring and Evaporation Rates. *Chirality*, Vol.7, No.2 (March 1995), pp. 62-68, ISSN 1520-636
- Kondepudi, D.P. & Sabanayagam, C. 1994. Secondary nucleation that leads to Chiral Symmetry Breaking in Stirred Crystallization. *Chemical Physics Letter*, Vol.217, No.4 (21 January 1994), pp. 364-367, ISSN 0009-2614
- McBride, J.M. & Carter R.L. 1991. Spontaneous Resolution by Stirred Crystallization. *Angewandte Chemie*, Vol.30, No.3 (March 1991), pp. 293-295, ISSN 0570-0833
- Qian, R.Y. & Botsaris, G.D. 1998. Nuclei Breeding from a Chiral Crystal Seed of NaClO_3 . *Chemical Engineering Science*, Vol.53, No.9 (1 May 1998), pp. 1745-1756, ISSN 0009-2509
- Qian, R.Y. & Botsaris, G.D. 2004. Effect of Seed Preparation on the Chirality of the Secondary Nuclei. *Chemical Engineering Science*, Vol.59, No.14 (July 2004), pp. 2841-2852, ISSN 0009-2509

- Veintemillas-Verdaguer, S.; Osuna Esteban S. & Herrero, M.A. 2007. The Effect of Stirring on Sodium Chlorate Crystallization under Symmetry Breaking Conditions. *Journal of Crystal Growth*, Vol.303, No. 2 (15 May 2007), pp. 562-567, ISSN 0022-0248
- Viedma, C. 2004. Experimental Evidence of Chiral Symmetry Breaking in Crystallization from Primary Nucleation. *Journal of Crystal Growth*, Vol.261, No.1 (15 January 2004), pp. 118-121, ISSN 0022-0248
- Cartwright, J.H.E.; Garcia-Ruiz, J.M.; Piro, O.; Sainz-Diaz, C.I.; & Tuval, I. 2004. Chiral Symmetry Breaking During Crystallization: An Advection-Mediated Nonlinear Autocatalytic Process. *Physical Review Letters*, Vol.93, No.3 (16 July 2004), pp. 035502-1-035502-4, ISSN 0031-9007
- Martin, B.; Tharrington, A. & Wu X-I. 1996. Chiral Symmetry Breaking in Crystal Growth: Is Hydrodynamic Convection Relevant? *Physical Review Letters*, Vol.77, No.13 (23 September 1996), pp. 2826-2829, ISSN 0031-9007
- Metcalfe, G. & Ottino, J.M. 1994. Autocatalytic Processes in Mixing Flows. *Physical Review Letters*, Vol.72, No.18 (2 May 1994), pp. 2875-2878, ISSN 0031-9007
- Bushe, T.; Durand, D.; Kondepudi, D.; Laudadio, J. & Spilker, S. 2000. Chiral Symmetry Breaking in Crystallization: Role of Convection. *Physical Review Letters*, Vol.84, No.19 (8 May 2000), pp. 4405-4408, ISSN 0031-9007
- Szurgot, J. & Szurgot, M. 1995a. Enantiomorphism in Sodium Chlorate Crystals. *Crystal Research and Technology*, Vol.30, No.1 (January 1995), pp. 71-79, ISSN 1521-4079
- Szurgot, M. & Szurgot, J. 1995b. Chiral Symmetry Breaking in Sodium Chlorate Crystallization from Unstirred Solution. *Crystal Research and Technology*, Vol.30, No.7 (September 1995), pp. 949-956, ISSN 1521-4079
- Vogl, O., Qin, M., Bartus, J. & Jaycox G.D. 1995. Chiral Nucleation. *Monatshefte fur Chemie*, Vol.126, No. 1 (January 1995), pp. 67-73, ISSN 0026-9247
- Szurgot, M. 1995. Chiral Etch Pits on Sodium Chlorate Crystals. *Crystal Research and Technology*, Vol.30, No.5 (July 1995), pp. 621-628, ISSN 1521-4079
- Szurgot, J. & Szurgot, M. 1994. On the Nature of Growth Hillocks on Sodium Chlorate Crystals. *Crystal Research and Technology*, Vol.29, No.6 (June 1994), pp. 829-836, ISSN 1521-4079
- Szurgot, M. & Sangwal, K. 1987. Influence of Free Convection on the Formation of Growth Defects in Potassium Bichromate Crystals Grown from Aqueous Solutions. *Crystal Research and Technology*, Vol.22, No.12 (December 1987), pp. 1477-1484, ISSN 1521-4079
- Wilcox, W.R. 1983. Influence of Convection on the Growth of Crystals from Solutions. *Journal of Crystal Growth*, Vol.65, No.1-3 (2 December 1983), pp. 133-142, ISSN 0022-0248
- Szurgot, M. 2010. Investigations of Impurity Striations in Potassium Bichromate Crystals. *Crystal Research and Technology*, Vol.45, No.4 (June 2010), pp. 347-354, ISSN 1521-4079
- Szurgot, M. 1991. Effect of Buoyancy-driven Convection on Surface Morphology and Macromorphology of Potassium Bichromate Crystals. *Crystal Research and Technology*, Vol.26, No.1 (January 1991), pp. 43-52, ISSN 1521-4079

- Frank, F.C. 1953. On Spontaneous Asymmetric Synthesis. *Biochimica et Biophysica Acta*, Vol.11, (1953), pp. 459-463, ISSN 0006-3002
- Denk, E.G & Botsaris, G.D. 1972. Fundamental Studies in Secondary Nucleation from Solution. *Journal of Crystal Growth*, Vol.13/14, No.14 (May 1972), pp. 493-499, ISSN 0022-0248

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