Binary Systems Formed by Alkali Bromides with Barium or Strontium Bromide

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By DTA and visual methods the phase diagrams of the ten binary systems formed by lithium, sodium, potassium, rubidium and cesium bromide with barium or strontium bromide have been drawn. Moreover, the fusion thermal effects regarding the eutectics and the congruent compounds singled out in the systems have been evaluated.

The general thermodynamic behaviour of these systems is discussed in comparison with the ideal one.

As part of a research program on the thermodynamic properties of binary systems formed by couples of fused salts with mono-bivalent cations [1], in the present paper the systems formed by $BaBr_2$ or $SrBr_2$ with (Li, Na, K, Rb, Cs) Br have been studied. These systems have been investigated by means of DTA in order to determine both the solid-liquid equilibria (SL) and the thermal effects accompanying the fusion of the eutectics and of the congruent compounds.

Information about the general thermodynamic behaviour of these binary mixtures are still very poor: phase diagrams of $BaBr_2$ or $SrBr_2$ + (Li, Na, K) Br systems go back to 1917 [2].

Experimental Section

The apparatus and the measurements technique (DTA and visual method) have already been described [1, 3]. Platinel thermocouples have been used. All the salts (of BDH origin) have been dried following the usual methods suggested in the literature.

In order to state the composition of the incongruent compounds in $BaBr_2$ + (Rb,Cs) Br and $SrBr_2$ + (Li,K) Br systems, the research has been extended to the determination of X-ray powder diffraction patterns for various compositions in each system, at proper temperatures. The samples were pre-fused under N_2 and cooled down slowly. Measurements have been performed by means of a Philips apparatus fitted with a high temperature camera (Material Research Corporation mod. X-86 N-II), employing Ni-filtered Cu radiation.

Results and Discussion

In Figs. 1 and 2 the phase diagrams of all the ten systems investigated are shown.

The compositions of the incongruent compounds $2\,BaBr_2 \cdot RbBr$ and $2\,BaBr_2 \cdot CsBr$ have been stated by comparison of the X-ray diffraction spectra of samples at $x_{BaBr_2} = 1$; 0.8; 0.66; 0.5; 0.33.

In the analogous case of the systems $SrBr_2$ + (Li, K) Br, the composition of the incongruent compounds could not be singled out with the same certainty, because the formation reactions did not appear, on the basis of X-ray diffraction spectra, to be completed even after very long heating periods. However, the most likely compositions, based on DTA measurements, should be: $3\,SrBr_2 \cdot LiBr$ and $SrBr_2 \cdot 4\,KBr$.

The heats of fusion of all the congruent compounds singled out in the investigated systems have been measured: the corresponding values and the heats of fusion (ΔH_{calc}) calculated additively [1, 4] are reported in Table 1. With these data it is possible to evaluate the quantity $\Delta\Delta H \equiv \Delta H_{exp} - \Delta H_{calc}$ representing, as already discussed [1], the sum $\Delta H_{mix} + \Delta H_{diss}$ (ΔH_{mix} = heat of mixing of the pure salts; ΔH_{diss} = heat of dissociaton of the congruent compound in the pure and solid components).

Compounds	ΔH_{exp}	ΔH_{calc}	$\Delta\Delta H$
$BaBr_2 \cdot 2\,KBr$	16.1	18.1	− 2.0
$BaBr_2 \cdot 2\,RbBr$	15.7	17.1	− 1.4
$BaBr_2 \cdot 2\,CsBr$	14.4	17.0	− 2.6
$2\,SrBr_2 \cdot KBr$	15.9	15.6	+ 0.3
$2\,SrBr_2 \cdot RbBr$	16.4	15.5	+ 0.9
$SrBr_2 \cdot RbBr$	8.5	10.5	− 2.0
$SrBr_2 \cdot CsBr$	10.2	11.2	− 1.0

Table 1. Heat (kcal/mole) of fusion of the congruent compounds.

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[1] C. SINISTRI, R. RICCARDI, and A. MAGISTRIS, Ber. Bunsenges. Physik. Chemie **71**, 376 [1967].

[2] G. KELLNER, Z. Anorg. Chem. **99**, 137 [1917].

[3] R. RICCARDI and C. SINISTRI, Ric. Sci. **35** (II-A), 1026 [1965].

[4] For the calculations, the following data have been used: for $BaBr_2$ $\Delta H_f = 7.44$ kcal/mole, $\Delta C_{p,f} = 5.97$ cal·deg^{-1}·mole^{-1} (mean values between those reported by different AA. [5, 6]); for $SrBr_2$ [5] $\Delta H_f = 2.50$, $\Delta H_{\alpha,\beta} = 2.90$ kcal/mole, $C_{p,l} = 27.8$, $C_{p,\beta} = 27.5$ and $C_{p,\alpha} = 20.9$ cal·deg^{-1}·mole^{-1}; for the alkali bromides the ΔH_f reported by DWORKIN and BREDIG [7] and an estimated value of $\Delta C_{p,f} = 1$ cal·deg^{-1}·mole^{-1}.

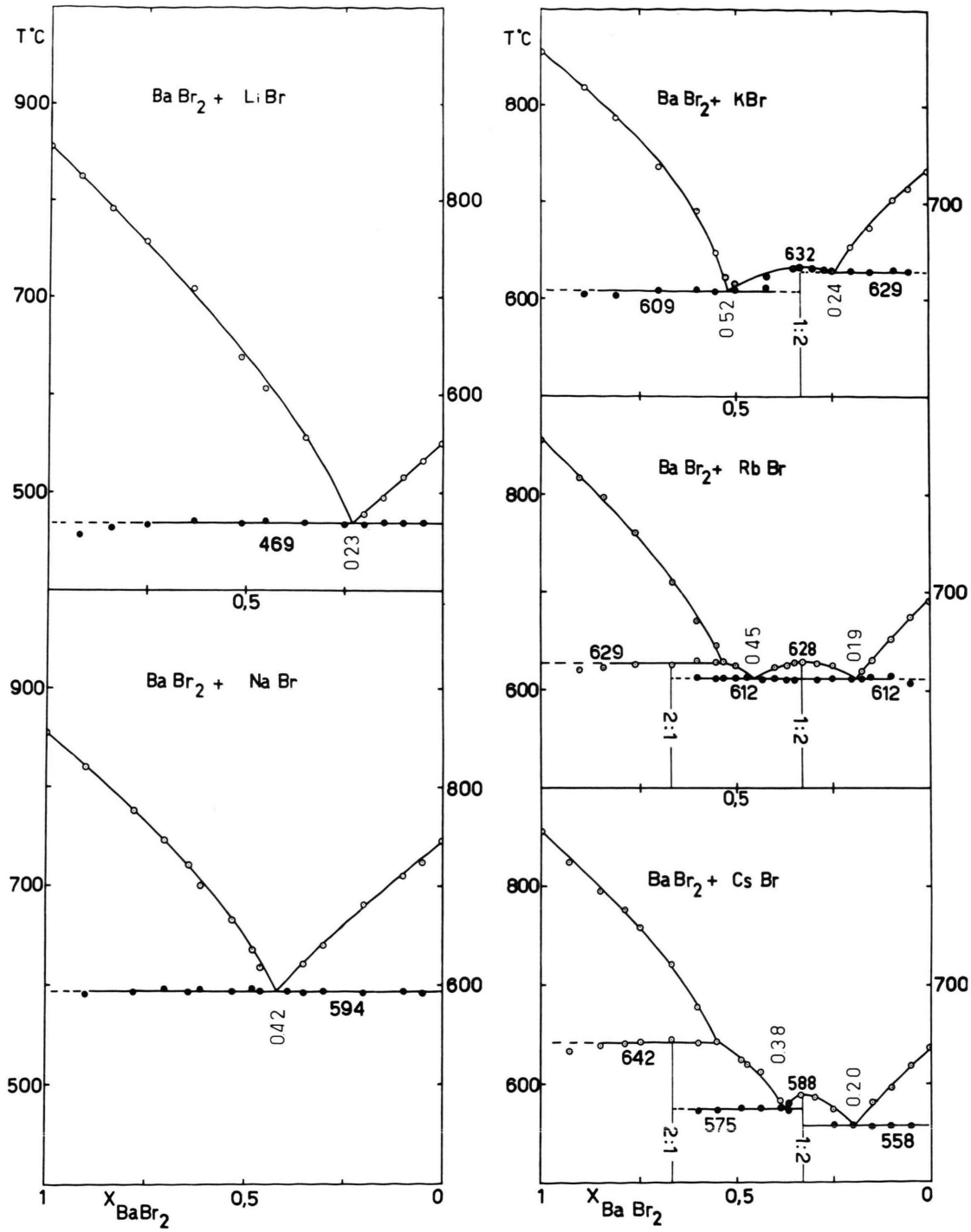

Fig. 1. Phase diagrams for the systems $BaBr_2$ + (Li, Na, K, Rb, Cs) Br. The m.p. of the pure salts are: $BaBr_2$ 855 °C (other values 847 [2], 857 [5], 853 [6] °C); LiBr 547 °C; NaBr 747 °C; KBr 734 °C; RbBr 692 °C and CsBr 636 °C.

[5] A. S. Dworkin and M. A. Bredig, J. Phys. Chem. **67**, 697 [1963].

[6] G. J. Janz, F. J. Kelly, and J. L. Perano, Trans. Faraday Soc. **59**, 2718 [1963].

[7] A. S. Dworkin and M. A. Bredig, J. Phys. Chem. **64**, 269 [1960].

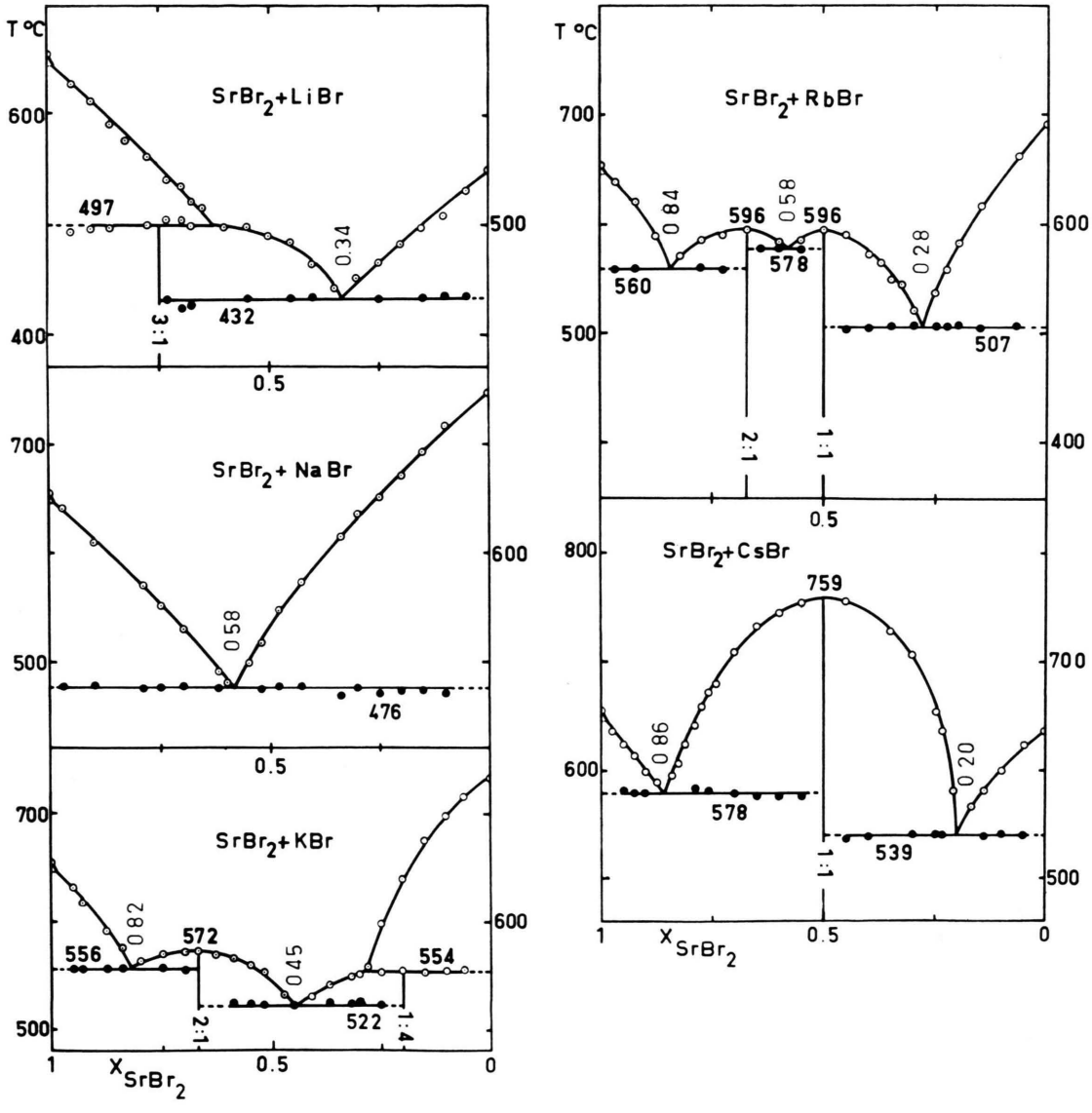

Fig. 2. Phase diagrams for the systems $SrBr_2$ + (Li, Na, K, Rb, Cs) Br. For pure $SrBr_2$ the m.p. is 655 °C (other values 643 [2], 657 [5] °C); the transition point is 646 °C (other values 645 [5] °C).

It can be noted that the $\Delta\Delta H$ values are in most cases negative, thus indicating an exothermic mixing effect in these systems ($\Delta H_{diss} \geqq 0$). Only the two compounds $2\,SrBr_2 \cdot MeBr$ (Me = K and Rb) show a positive $\Delta\Delta H$: this might indicate that for these compounds a particularly high ΔH_{diss} value is able to revers the sign of the sum $\Delta H_{mix} + \Delta H_{diss}$.

Similar measurements have been carried out on the eutectics formed by pure salts, and/or by congruent compounds. In Table 2, ΔH_{exp} and ΔH_{calc} are reported: these latter have been calculated additively.

In this case $\Delta\Delta H$ represents the heat of mixing of the eutectic components. Also these $\Delta\Delta H$ values show that, particularly for the systems containing (K, Rb, Cs) Br, an exothermic mixing effect is to be expected.

The $\Delta\Delta H$ in Tables 1 and 2, arising from differences of quantities known only with limited pre-

Eutectics	ΔH_{exp}	ΔH_{calc}	$\Delta\Delta H$
$BaBr_2(0.23) + LiBr$	4.7	4.4	+ 0.3
$BaBr_2(0.42) + NaBr$	5.9	6.0	− 0.1
$BaBr_2(0.54) + BaBr_2 \cdot 2\,KBr$	9.4	10.6	− 1.2
$BaBr_2 \cdot 2\,KBr(0.46) + KBr$	9.3	10.6	− 1.3
$BaBr_2 \cdot 2\,RbBr(0.31) + RbBr$	8.3	8.7	− 0.4
$BaBr_2 \cdot 2\,CsBr(0.33) + CsBr$	7.3	8.5	− 1.2
$SrBr_2(0.58) + NaBr$	5.1	5.0	+ 0.1
$SrBr_2(0.72) + 2\,SrBr_2 \cdot KBr$	6.9	7.9	− 1.0
$SrBr_2(0.76) + 2\,SrBr_2 \cdot RbBr$	6.4	7.6	− 1.2
$2\,SrBr_2 \cdot RbBr(0.35) + SrBr_2 \cdot RbBr$	10.6	11.3	− 0.7
$SrBr_2 \cdot RbBr(0.39) + RbBr$	5.2	6.6	− 1.4
$SrBr_2(0.83) + SrBr_2 \cdot CsBr$	5.4	5.8	− 0.4
$SrBr_2 \cdot CsBr(0.25) + CsBr$	5.2	6.7	− 1.5

Table 2. Heat (kcal/mole) of fusion of the eutectics.

cision (experimental errors on ΔH_{exp}, uncertainties on ΔC_p, etc.), are to be understood only as indicative and must be used with some caution.

Thermodynamic Behaviour

The liquidus curves regarding one of the two pure components, can be discussed with the equation [8]:

$$T_1 = \frac{\Delta\bar{H}_1 + \mu_1^e}{\Delta\bar{S}_1 - R \ln x_1} \qquad (1)$$

where:

1 = $BaBr_2$, $SrBr_2$ [9], or MeBr;
T_1 = SL equilibrium temperature (°K);
$\Delta\bar{H}_1$ = heat of fusion of 1, duly corrected to keep into account its dependence on the temperature [8];
μ_1^e = excess potential of 1, related to the activity coefficient f_1 by $\mu_1^e = R\,T_1 \ln f_1$;
$\Delta\bar{S}_1$ = $\Delta\bar{H}_1/T_{1,0}$ ($T_{1,0}$ = melting point of 1);
x_1 = molecular fraction of 1.

Equation (1) has been derived assuming that, for the couple of salts, the Temkin's model of the total dissociation and of random distribution of the cations are valid. If each ion behaves ideally, it must obviously be:

$$\mu_1^e = 0\,. \qquad (2)$$

By the use of (1) and (2) and the figures already reported [4], the ideal SL curves, drawn as continuous lines in Figs. 3 and 4 near the experimental data, have been calculated.

On the whole it may be said that the thermodynamic behaviour of the five systems with $BaBr_2$, is not too far from the ideal one (see Fig. 3) whereas more remarkable deviations are observed in systems with $SrBr_2$ (see Fig. 4). The negative deviation of the liquidus curves from ideality (experimental points lying under SL ideal curve) can be accounted for either by activity coefficients <1, or by the tendency to complex formation, as it has been already discussed in a previous paper [1].

As regards the effect of the alkali cations size it can be stated that in both cases the mixtures containing lithium or sodium salts are those less deviating from ideal behaviour, while the mixtures with potassium, rubidium or cesium show marked negative deviations.

As for the congruent compounds type Me_2BaBr_4, using again the model of total dissociation:

$$Me_2BaBr_4 \rightarrow 2\,Me^+ + Ba^{++} + 4\,Br^-$$

it is possible to calculate the ideal SL curves by the equation:

$$\ln a_{Me_2BaBr_4} = -\frac{\Delta H}{R\,T} + \left(\frac{\Delta H}{R\,T_0} + \ln 0.1481\right). \qquad (3)$$

In this equation, which is easily derived from (1):

$$a_{Me_2BaBr_4} = x^2_{MeBr} \cdot x_{BaBr_2}\,;$$
$$0.1481 = 0.667^2 \cdot 0.333\,;$$

ΔH and T_0 represent the heat and the temperature of fusion (°K) of the congruent compound.

In Fig. 5 the curves calculated by (3) are reported as continuous lines in comparison with the experimental data. It may be observed that the experimental points and the calculated curves satisfactorily agree in the case of the K_2BaBr_4 and Rb_2BaBr_4 compounds, whereas for Cs_2BaBr_4 there is a negative deviation from the ideal behaviour.

Similar calculations are shown in Fig. 6 for the congruent compounds, type $MeSr_2Br_5$ and $MeSrBr_3$.

Negative deviations from the ideal behaviour (which is again represented by a solid line) are shown also in this case: they are however more pronounced than in the case of the systems containing $BaBr_2$.

This is in agreement with the general behaviour of the systems with $SrBr_2$.

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[8] C. SINISTRI and P. FRANZOSINI, Ric. Sci. **33** (II-A), 419 [1963].

[9] In the evaluation of ΔH_1 and ΔS_1 for this salt, the transition effects (see Ref. [8]) should be also taken in to account.

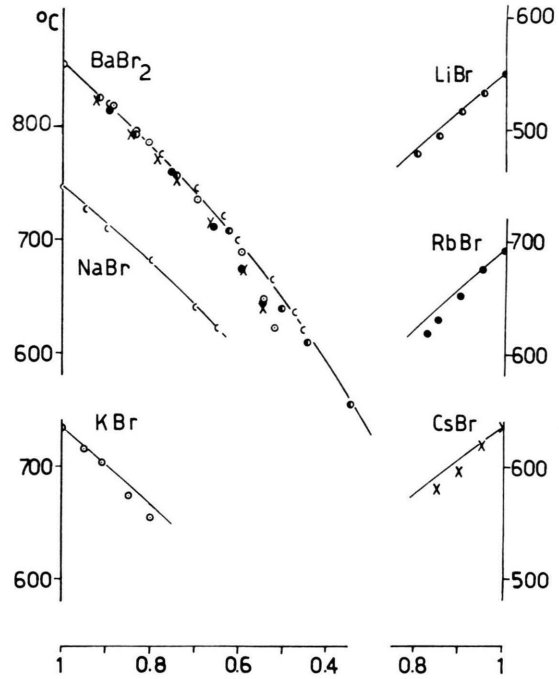

Fig. 3. Behaviour of the ideal curves rich in $BaBr_2$, LiBr, NaBr, KBr, RbBr, CsBr (continuous lines) in comparison with the experimental data.

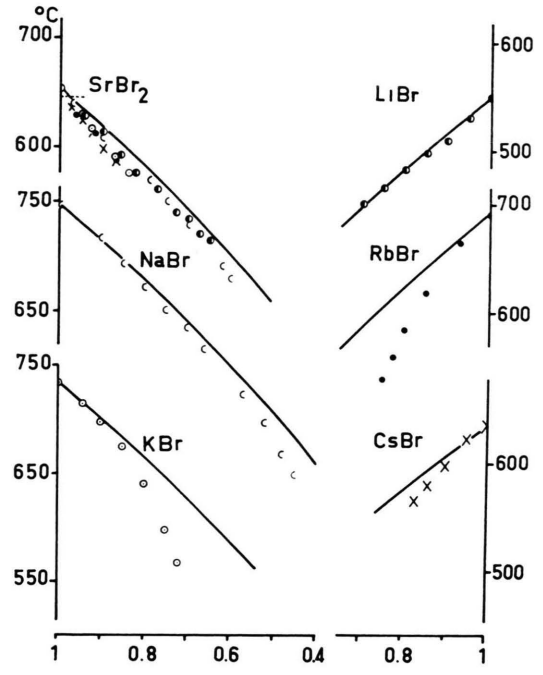

Fig. 4. Behaviour of the ideal curves rich in $SrBr_2$, LiBr, NaBr, KBr, RbBr, CsBr (continuous lines) in comparison with the experimental data.

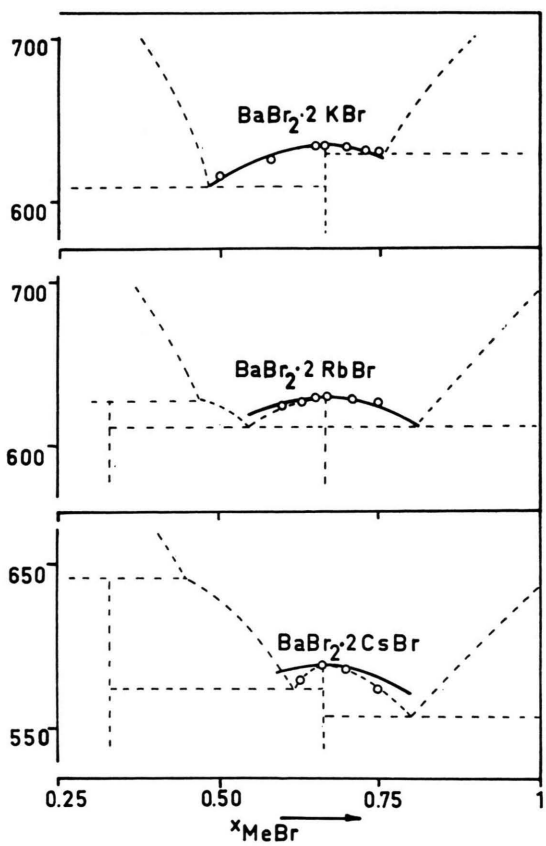

Fig. 5. Behaviour of the ideal curves regarding the congruent compounds Me_2BaBr_4 (continuous lines) in comparison with the experimental data (small circles).

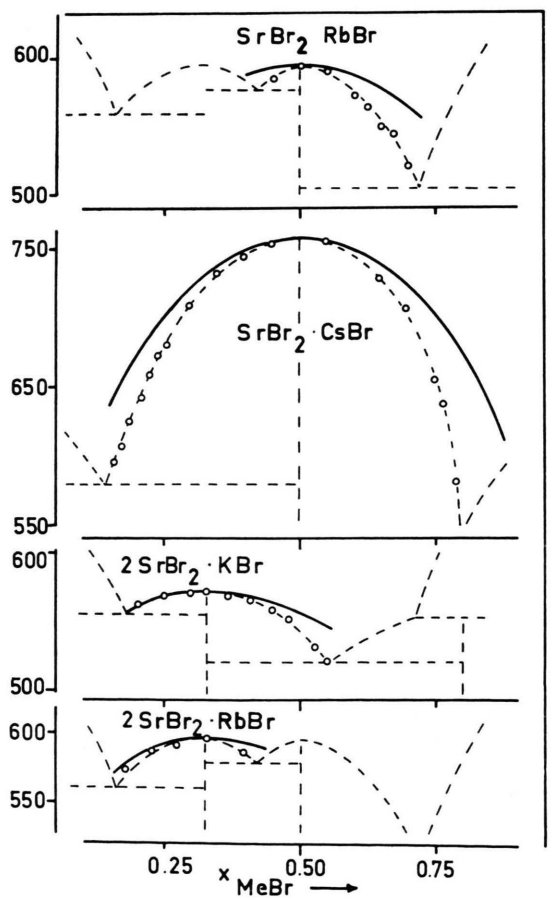

Fig. 6. Behaviour of the ideal curves regarding the congruent compounds $MeSr_2Br_5$ and $MeSrBr_3$ (continuous lines) in comparison with the experimental data (small circles).