one can calculate the partial molar volume of the components, and the following values are arrived at for salts in infinite dilution: $51._5$ (180 °C) and $57._8$ (100 °C) cm^3/mol for KCNS; $44._1$ (180 °C) and $45._7$ (100 °C) cm^3/mol for NaCNS.

The molar volumes of pure acetamide at 180 and 100 °C are $66._4$ and $60._6$ cm^3/mol, respectively, notably higher than the intrinsic volume, according to Bondi (*8*) of 35.9 cm^3/mol. This fact evidences a notable component of disorder volume and dead space in the packing of the molecules of acetamide. It is to be noted that the molar volumes of MCNS lessen with the increase of temperature; this fact depends upon an increase in the electrostriction component of the molar volume and can be imputed to an increase in the dissociation of salt as a function of the temperature, as well as to the natural trend of the electrostriction volume with the increasing temperature (*9*). The continuation of the research will serve to establish the entity and the influence of the dissociation of the electrolytes in acetamide as regards the properties of the solutions.

Glossary

x_i	mole fraction of the *i*th component
K_{cr}	cryoscopic constant
$\bar{V}_i$	partial molar volume of the *i*th component
V_m	mean volume
T	absolute temperature
ΔH_{fus}	fusion enthalpy
ΔS_{fus}	fusion entropy
d	density
eut	eutectic
per	peritectic

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Received for review August 1, 1980. Accepted December 18, 1980. Thanks are due to CNR (Rome) for financial support.

Liquid–Liquid and Solid–Liquid Equilibria in the Reciprocal Ternary System Ag,Li/Br,I

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The liquid–liquid and solid–liquid equilibria in the mixture Ag,Li/Br,I were studied as a function of composition and temperature. The system presents a miscibility gap, with the upper critical solution point at $x_{AgI} = 0.5 = x_{LiBr}$ and $T = 706$ °C. The projection of the gap occupies 45.6% of the composition square. Moreover, an "a priori" prediction of the gap was calculated by means of the CIS theory.

The characterization of liquid immiscibility in molten salts has been one of the objects of our investigations for many years (*1–3*). Demixing phenomena are particularly stimulating, being rather infrequent in fused salts and very interesting from both the theoretical and applicative viewpoints. To continue a systematic analysis of the salt mixtures which could possibly give rise to liquid–liquid equilibria, we took into account the reciprocal ternary systems (i.e., mixtures containing two cations and two anions) formed by lithium or sodium halides and silver halides. Preliminary experimental tests along with theoretical considerations suggested this family as a suitable one to study.

This paper reports detailed results for liquid–liquid (LL) and solid–liquid (SL) equilibria in the mixture Ag,Li/Br,I; to our knowledge no such data on this system have yet been reported.

Experimental Section

The experimental technique, based on direct visual observation of the sample possibly integrated by DTA, was the same as in ref *4*. The materials used were LiBr (Merck SP), LiI (Merck P), and AgI (Fluka puriss.), while AgBr was obtained from AgNO$_3$ (Fluka puriss.) and KBr (Fluka puriss.). Particular care was devoted to the drying of lithium salts following the procedures suggested in the literature (*5*).

Results

Figure 1 reports the SL equilibria of the four binaries which are the sides of the composition square. Dashed lines, which are mainly based on DTA measurements, should be taken as being only indicative; even working at very low heating rates, we found that the resolution of the two peaks in the thermogram was sometimes imprecise.

AgBr + LiBr: this system presents a peritectic point at 430 °C and $x_{AgBr} = 0.77$ (x = mole fraction).

LiBr + LiI: this system shows complete solubility in the solid phase with a minimum at 417 °C and $x_{LiBr} = 0.40$.

AgI + LiI: this system shows complete solubility in the solid phase with a minimum at 437 °C and $x_{AgI} = 0.20$.

AgBr + AgI: this system presents a eutectic at 364 °C and $x_{AgBr} = 0.77_5$. The extension of the various solid phases in this mixture is beyond the aim of the present research and is still under question (see, e.g., ref *6* and *7*).

The LL and SL equilibria temperatures along the two diagonal and the four off-diagonal cuts are reported in Table I. The off-diagonal cuts a and b were obtained by adding increasing amounts of LiI to mixtures of silver iodide and bromide with the fixed composition $x_{AgBr} = 0.20$ and 0.50, respectively. On the other hand, the off-diagonal cuts c and d were obtained by starting from a mixture of silver and lithium bromide with the fixed composition $x_{AgBr} = 0.50$ and 0.20, respectively, to which increasing amounts of LiI were added.

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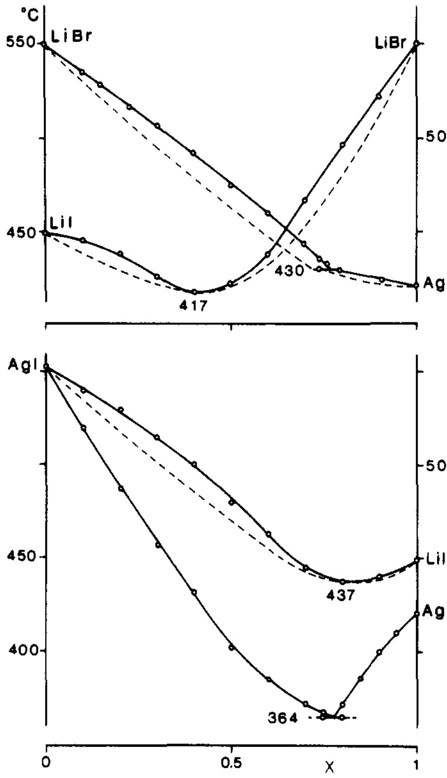

Figure 1. Phase diagrams for the binaries AgBr + LiBr, LiBr + LiI, AgI + LiI, and AgBr + AgI.

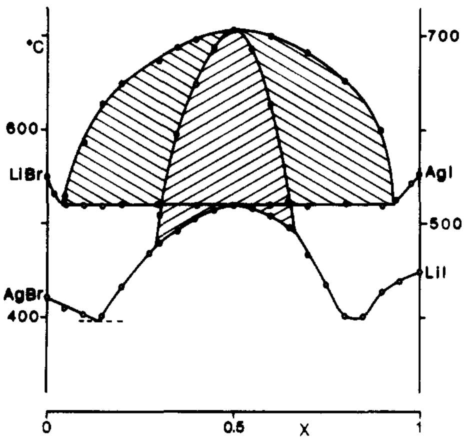

Figure 2. LL and SL equilibria for the stable and unstable diagonals. The area in which demixing occurs is shaded.

Next to the LL data (that represent the temperature at which demixing takes place while cooling and shaking) the table reports, in parentheses, the primary crystallization temperature (PCT), i.e., the temperature at which equilibrium between two liquid phases and one solid phase is reached. Figures 2 and 3 show the results obtained for the cuts studied. The LL equilibria areas are shaded.

The general topology of the system is reported in Figures 4 and 5. Figure 4 shows the projections of the examined cuts along with the temperatures of the LL equilibrium limits. The trend of the minimum of the SL equilibria is also shown by a dashed line; the point of the minimum along this curve was found at 388 °C and $x_{\mathrm{LiI}} = 0.60_5$, $x_{\mathrm{LiBr}} = 0.25$, and $x_{\mathrm{AgI}} = 0.14_5$. The projection of the stratification lens is dashed and occupies 45.6% of the composition square. The main axis of the lens coincides with the stable diagonal. Along this axis PCT is constant at 520 ± 1 °C.

Table I. SL and LL Equilibria Temperatures (°C) in the System Ag,Li/Br,I[a]

		Stable Diagonal AgI + LiBr			
x_{AgI}	SL eq	LL eq	x_{AgI}	SL eq	LL eq
0.000	550		0.600		700 (521)
0.020	532		0.700		682 (519)
0.050		530 (520)	0.800		652 (521)
0.100		586 (520)	0.900		600 (519)
0.150		628 (518)	0.935	526	
0.200		650 (520)	0.980	544	
0.300		675 (521)	1.000	553	
0.400		696 (519)			
0.500		706 (520)			
		Unstable Diagonal AgBr + LiI			
x_{LiI}	SL eq	LL eq	x_{LiI}	SL eq	LL eq
0.000	421		0.550		686 (516)
0.050	410		0.600		626 (509)
0.100	403		0.650		526 (496)
0.150	402		0.700	467	
0.200	433		0.750	336	
0.275	469		0.800	403	
0.300		508 (480)	0.850	402	
0.350		595 (492)	0.900	428	
0.400		648 (506)	0.950	438	
0.450		688 (515)	1.000	449	
0.500		706 (520)			
x_{LiI}	SL eq	LL eq	x_{LiI}	SL eq	LL eq
		Cut a: LiI + {AgI – AgBr(0.20)}			
0.000	487		0.350		538 (503)
0.050		513 (512)	0.405	491	
0.065		550	0.560	460	
0.100		585 (517)	0.670	440	
0.167		640 (520)	0.800	430	
0.200		633 (516)	0.930	438	
0.300		573 (505)	1.000	449	
		Cut b: LiI + {AgI – AgBr(0.50)}			
0.000	402		0.400		648 (513)
0.050	431		0.450		600
0.100	470		0.500		540 (500)
0.150		517 (500)	0.545	491	
0.200		575 (510)	0.600	470	
0.250		628	0.695	435	
0.300		668 (519)	0.800	416	
0.333		677 (520)	0.850	419	
			0.930	431	
			1.000	449	
		Cut c: LiI + {LiBr – AgBr(0.5)}			
0.000	475		0.350		681 (519)
0.050	470		0.400		659 (506)
0.100	469		0.465		602
0.130	477		0.500		550 (485)
0.150		494 (483)	0.550	470	
0.200		590 (490)	0.590	433	
0.300		670 (512)	0.700	393	
0.334		684 (521)	0.800	408	
			0.900	435	
			1.000	449	
		Cut d: LiI + {LiBr – AgBr(0.20)}			
0.000	521		0.350		516 (495)
0.021	514		0.400	477	
0.050		513 (508)	0.500	435	
0.080		574	0.620	412	
0.100		605 (512)	0.700	410	
0.167		634 (520)	0.800	423	
0.220		619 (512)	0.900	438	
0.300		575 (500)	1.000	449	

[a] The values given in parentheses represent the primary crystallization temperature. x values are mole fractions. The experimental equilibrium temperatures are reproducible within ±1 °C.

Figure 5 reports the projections of the interpolated LL isotherms at 550, 600, 650, and 700 °C. The upper critical solution point of the system is at $x_{\mathrm{AgI}} = 0.50$, $x_{\mathrm{LiBr}} = 0.50$, and $T = 706$ °C. The SL isotherms at 420, 460, 500, and 540 °C are also shown. The general topology of the system is in

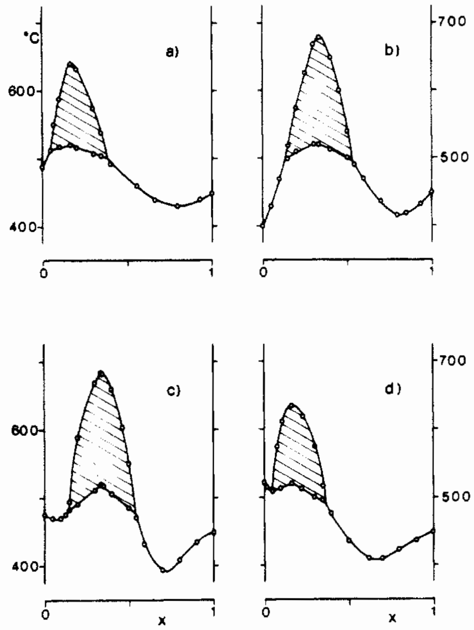

Figure 3. LL and SL equilibria along the four (a–d) studied cuts. Demixing areas are shaded.

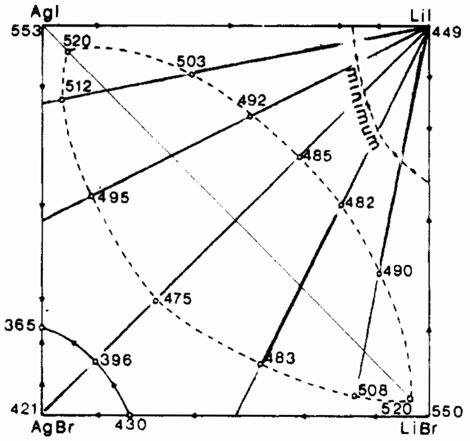

Figure 4. Diagonal and off-diagonal cuts studied in the reciprocal ternary Ag,Li/Br,I with the projection of the nonisothermal basis of the stratification dome.

agreement with the triangulation rules.

Discussion

As in previous papers (see ref *1* and *2*) an "a priori" prediction of the LL equilibria was carried out by means of the CIS theory (*8*). These calculations required the following data: the standard Gibbs free energy change for the metathetical reaction, ΔG°, the four binary mixture interaction parameters k, and the coordination number Z. On the basis of the literature data (*9*, *10*), the ΔG° value can be taken as $\Delta G^\circ = 7800 - T$(cal mol^{-1}); moreover (*11*, *12*) k(AgBr + LiBr) = 1800 and k(AgBr + AgI) = 1100 (cal mol^{-1}). No data for k(AgI + LiI) and k(LiBr + LiI) are available. Because of the symmetry shown by the miscibility gap along the main diagonal (see Figures 4 and 5), calculations were made by using symmetrical k values, i.e., assuming k(AgI + LiI) = 1800 and k(LiBr + LiI) = 1100. The results obtained by using this set of data and $Z = 6$ are shown in Figure *6*; the calculated upper critical solution point is at $x_{\mathrm{AgI}} = x_{\mathrm{LiBr}} = 0.50$ and $T = 703$ °C, to be compared with the experimental one found at the same composition and $T = 706$ °C.

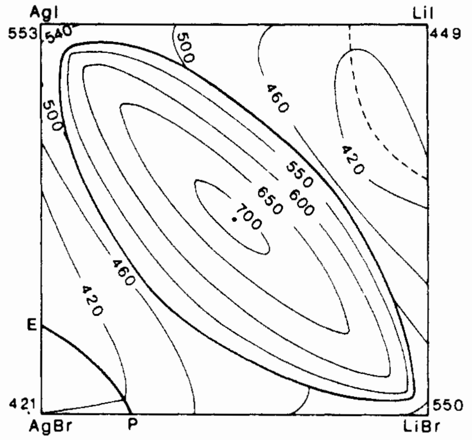

Figure 5. Interpolated SL (420, 460, 500, and 540 °C) and LL (550, 600, 650, and 700 °C) isotherms in the studied system. The temperature of the upper critical solution point is 706 °C.

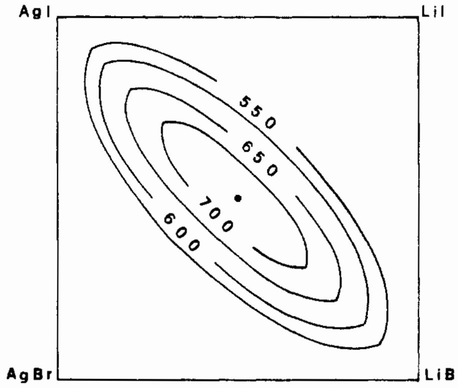

Figure 6. LL isotherms as calculated by means of the CIS theory.

It is interesting to observe that in this system the ΔG° value is not very large, and alone it cannot account for the wide stratification field. As previously observed (*3*), a big contribution to the occurrence of the MG is also given by the positive value of the four binary parameters k. In fact, the MG calculated by using the same ΔG° and Z values and all $k = 0$ shows an upper critical solution point at $T = 432$ °C.

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Received for review July 11, 1980. Accepted December 2, 1980.