

Solid-Liquid and Liquid-Liquid Equilibria in the Reciprocal Ternary System Li,Rb/Br,F

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The solid-liquid and liquid-liquid equilibria in the molten system Li,Rb/Br,F as a function of composition and temperature were fully characterized. The system presents four invariant points and a miscibility gap which impinges on the LiF crystallization field and occupies 41.5% of the composition square. The upper critical solution point of the system was found at 1050 °C and $x_{\text{LiF}} = 0.76$ and $x_{\text{RbBr}} = 0.24$. The experimental miscibility gap was compared with the one predicted on the basis of the conformal ionic solution theory.

Data concerning phase diagrams of reciprocal ternary systems, that is mixtures containing two cations and two anions, have received a great impulse in the past few years. Among

the different measurements, those on liquid-liquid equilibria are of particular interest: demixing of inorganic molten salts is a rather infrequent phenomenon and also a possible tool for industrial high-temperature work. Moreover, reciprocal ternary systems formed by simple ionic salts can be a useful test for the current theories.

Following previous research in this field (2, 5), we report the solid-liquid (SL) and liquid-liquid (LL) equilibria relative to the reciprocal ternary system Li,Rb/Br,F. To our knowledge, no data on this system were previously reported except those concerning the stable diagonal (LiF + RbBr) which had been measured by our group (4).

Experimental Section

The experimental procedure was the same as in ref 2. The materials used were LiBr, LiF, RbBr, and RbF "Merck Suprapur".

Table I. SL and LL Equilibria Temperatures (°C) in the System Li, Rb/Br, F^a

x_{LiF}	SL eq	LL eq	x_{LiBr}	SL eq	LL eq	x_{LiF}	SL eq	LL eq	x_{LiBr}	SL eq	LL eq
stable diagonal: LiF + RbBr			unstable diagonal: LiBr + RbF			stable diagonal: LiF + RbBr			unstable diagonal: LiBr + RbF		
0.000	694		0.000	794		0.850		1044 (833)	0.600		953 (810)
0.020	686		0.100	680		0.900		1030 (834)	0.628		886
0.040	702		0.175	520		0.945		957	0.650		810 (790)
0.105	800		0.195	488		0.975		865 (834)	0.700	730	
0.155	828		0.205	550		0.980	840		0.750	655	
0.175		850 (834)	0.225	625		1.000	848		0.800	576	
0.200		876 (833)	0.250	690					0.845	452	
0.240		912 (834)	0.295	766					0.850	424	
0.300		950 (835)	0.350		870 (807)				0.900	460	
0.400		991 (834)	0.400		950 (821)				0.950	506	
0.500		1018 (834)	0.450		1004 (830)				1.000	550	
0.600		1034 (834)	0.500		1018 (834)						
0.700		1048 (835)	0.560		990						
x_{LiF}	SL eq	LL eq	x_{LiBr}	SL eq	LL eq	x_{LiF}	SL eq	LL eq	x_{LiBr}	SL eq	LL eq
cut a: LiBr + {RbF-LiF(0.80)}			cut b: LiBr + {RbF-LiF(0.50)}			cut c: LiBr + {RbF-RbBr(0.40)}			cut d: LiBr + {RbF-RbBr(0.70)}		
0.010	792		0.050	740		0.000	589		0.000	583	
0.020	804		0.090	792		0.025	540		0.010	594	
0.028		850 (811)	0.125		855 (805)	0.045	500		0.025	608	
0.050		946 (814)	0.150		911 (810)	0.065	514		0.050	618	
0.100		1012 (823)	0.200		966 (821)	0.080	526		0.100	662	
0.150		1044 (831)	0.300		1034 (833)	0.100	540		0.125	718	
0.200		1043 (832)	0.340		1043 (834)	0.115	568		0.150	758	
0.275		1016 (823)	0.400		1020 (825)	0.130	660		0.175		840 (811)
0.335		950 (810)	0.450		976 (814)	0.150	725		0.200		880 (821)
0.375		870 (800)	0.500		900 (802)	0.200		810 (786)	0.225		903 (830)
0.425	776		0.525		855 (794)	0.235		874 (802)	0.262		898 (832)
0.550	690		0.575	770		0.300		945 (822)	0.300		878 (822)
0.650	600		0.600	735		0.375		991 (834)	0.312		850 (810)
0.720	533		0.700	626		0.450		950 (828)	0.325		816 (800)
0.775	466		0.750	548		0.525		856 (800)	0.380	752	
0.800	448		0.800	473		0.575	770		0.450	678	
0.900	496		0.850	432		0.675	683		0.590	525	
1.000	550		0.900	473		0.740	580				
			0.950	518		0.775	490				
			1.000	550		0.795	426				
						0.830	408				
						0.900	480				
						1.000	550				

^a The values given in parentheses represent the primary crystallization temperature. x values are mole fraction. The a-d off-diagonal cuts were obtained by adding increasing amounts of LiBr to a binary mixture of fixed composition (given in parentheses in mole fraction). The experimental equilibrium temperatures are reproducible within ± 1 °C.

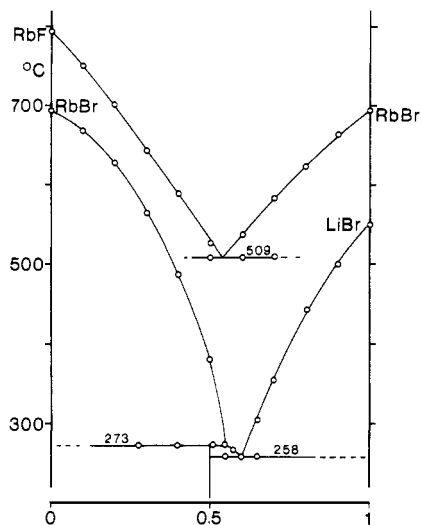


Figure 1. Phase diagrams for the binaries RbBr + RbF and LiBr + RbBr.

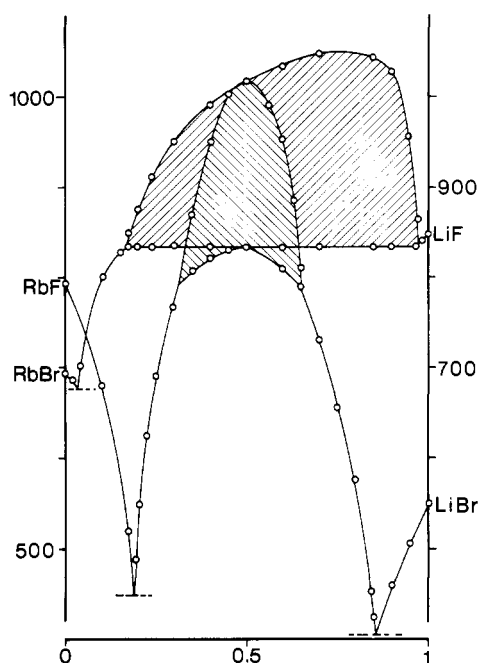


Figure 2. SL and LL equilibria for the stable and unstable diagonals. The area in which demixing occurs is shaded.

Results

Figure 1 reports the SL equilibria of the two binaries RbBr + RbF and LiBr + RbBr which represent two sides of the composition square. The corresponding data on the other two sides were previously reported. LiF + RbF (by ref 1): the system presents an incongruent 1:1 compound. The peritectic is at $x_{\text{LiF}} = 0.47$ and 475 °C and the eutectic is at $x_{\text{LiF}} = 0.44$ and 470 °C. RbBr + RbF (see Figure 1): the eutectic is at $x_{\text{RbBr}} = 0.54$ and 509 °C. LiBr + RbBr (see Figure 1): the system presents an incongruent 1:1 compound. The peritectic is at $x_{\text{LiBr}} = 0.55$ and 273 °C and the eutectic is at $x_{\text{LiBr}} = 0.60$ and 258 °C. LiBr + LiF (by ref 5): the eutectic is at $x_{\text{LiF}} = 0.24$ and 448 °C.

Table I reports the SL and LL equilibria temperatures along the two diagonal and the four main off-diagonal cuts. Next to the LL data (which represent the temperature at which by cooling and shaking demixing takes place) the table reports, in parentheses, the primary crystallization temperature (PCT), i.e., the temperature at which equilibrium between two liquid and one solid phase is reached.

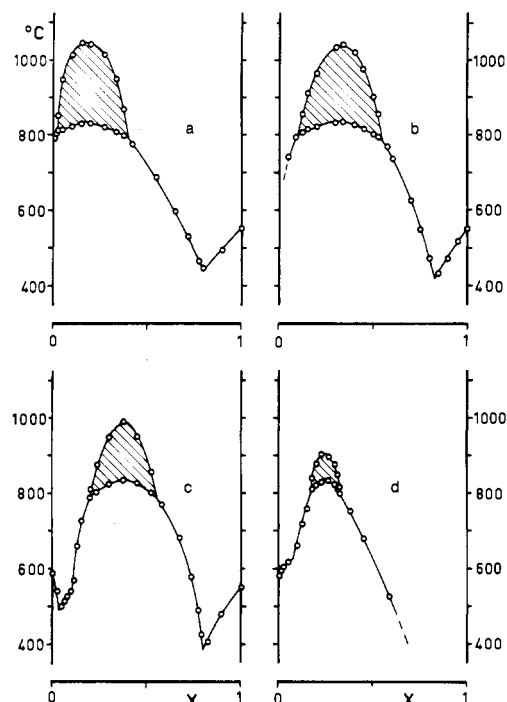


Figure 3. Demixing areas (shaded) along the main four (a-d) studied off-diagonal cuts.

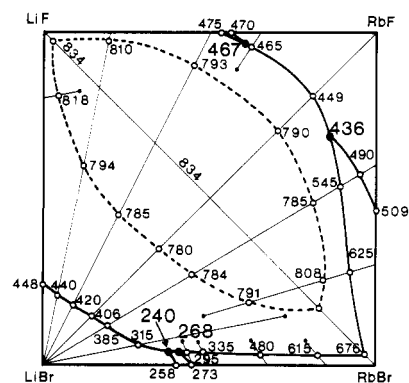


Figure 4. Diagonal and off-diagonal cuts studied in the reciprocal ternary Li,Rb/Br,F with the limits of the crystallization fields and the projection of the nonisothermal basis of the stratification dome.

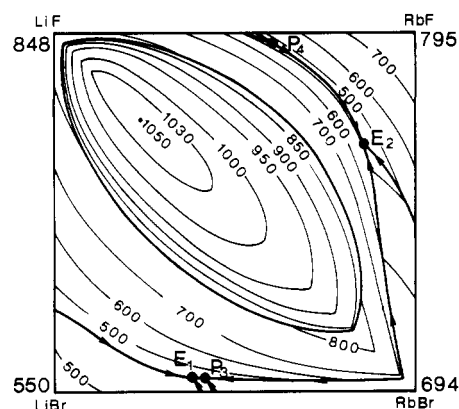


Figure 5. General topology of the studied system. The SL isotherms (at 500, 600, 700, and 800 °C) and the LL isotherms (at 850, 900, 950, 1000, and 1030 °C) are shown; the temperature of the upper critical solution point is 1050 °C.

Figures 2 and 3 show the demixing areas (shaded) along the studied cuts.

The general topology of the system is shown in Figures 4 and 5. Figure 4 reports the projections of the 13 examined cuts

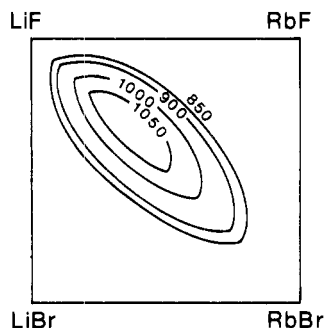


Figure 6. LL isotherms as calculated by means of the CIS theory.

along with the temperatures of the corresponding eutectics and of the LL equilibrium limits. The stratification lens (dashed) impinges on the LiF crystallization field and occupies 41.5% of the composition square. The main axis of the lens coincides with the stable diagonal. Along this axis PCT is constant at 834 ± 1 °C.

Figure 5 reports the projections of the interpolated LL isotherms at 850, 900, 950, 1000, and 1030 °C. The upper critical solution point of the system is at $x_{LiF} = 0.76$ and 1050 °C. The SL isotherms at 500, 600, 700, and 800 °C are also reported. Moreover, the figure brings into evidence the four invariant points presented by the system with the following coordinates: eutectic E_1 at $t = 240$ °C and $x_{LiF} = 0.04$, $x_{LiBr} = 0.58$, $x_{RbBr} = 0.38$; eutectic E_2 at $t = 436$ °C and $x_{LiF} = 0.14$, $x_{RbF} = 0.55$, $x_{RbBr} = 0.31$; peritectic P_3 at $t = 268$ °C and $x_{LiF} = 0.04$, $x_{LiBr} = 0.55$, $x_{RbBr} = 0.41$; peritectic P_4 at $t = 467$ °C and $x_{LiF} = 0.395$, $x_{RbF} = 0.57$, $x_{RbBr} = 0.035$. The general topology of the system agrees with the triangulation rules.

Discussion

In order to extend the test of the conformal ionic solution (CIS) theory (7) carried out in ref 2, we made attempts to predict the LL equilibria in the present system. The required data (see ref 2) are the standard Gibbs free energy change for the me-

tathetical reaction, ΔG° , the four binary mixture interaction parameters k , and the coordination number Z . Literature (3) reports the following values (in cal mol⁻¹): $\Delta G^\circ = 23400 - 3.4T$, $k(LiBr + LiF) = -900$, $k(LiBr + RbBr) = -4300$, $k(LiF + RbF) = -3200$. Calculations carried out by using this set of data with $k(RbBr + RbF) = 0$ and $Z = 6$ led to the following results: the system presents the demixing phenomenon but the MG is too large and its symmetry is incorrect. A sensitive improvement can be reached by taking into account a possible temperature dependence of the k values; this is in agreement with the findings for the system K,Li/Br,F (6).

An analysis of the experimental data on the phase diagrams of the four binaries, assuming that k varies only with temperature, gives the following results: $k(LiBr + LiF) = -3160 + 3.7T$; $k(RbBr + RbF) = -1250$; $k(LiBr + RbBr) = -7400 + 3.7T$; $k(LiF + RbF) = -3200$.

This new set of data, with $\Delta G^\circ = 19700 - 3.4T$ and $Z = 6$, provides the prediction shown in Figure 6; the topology of the system compares well with the experimental one, but still the agreement is not quantitative. The reservations on the CIS theory reported in ref 2 seem to be confirmed by the present results.

Literature Cited

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Vapor-Liquid Equilibrium Data for Binary Systems of Chlorobenzene with Acetone, Acetonitrile, Ethyl Acetate, Ethylbenzene, Methanol, and 1-Pentene

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Total pressure vapor-liquid equilibrium data were measured for the following six binaries containing chlorobenzene: acetone + chlorobenzene at 313.15, 353.00, and 386.66 K; acetonitrile + chlorobenzene at 293.15, 343.15, and 393.15 K; ethyl acetate + chlorobenzene at 313.15, 353.15, and 393.15; chlorobenzene + ethylbenzene at 293.15 K; methanol + chlorobenzene at 293.15, 338.15, and 385.15 K; 1-pentene + chlorobenzene at 280.00, 320.00, and 360.00 K. The P, T, x data were reduced to y, γ , and G^E values by the Mixon-Gumowski-Carpenter method. The virial equation of state truncated after the second coefficient was used to calculate the vapor-phase fugacity coefficients. The Tsonopoulos correlation was used to predict the second virial coefficients.

Introduction

The data reported were measured as part of an ongoing effort to expand the experimental vapor-liquid equilibrium (VLE) data base for a general correlation of mixture properties. Systems were chosen to provide examples of the interactions of a

Table I. Chemicals Used

component	vendor	stated purity, %
acetone	Burdick and Jackson	99.9+
acetonitrile	Burdick and Jackson	99.9+
chlorobenzene	Burdick and Jackson	99.9+
ethyl acetate	Burdick and Jackson	99.9+
ethylbenzene	Phillips Petroleum	99.944
methanol	Fisher Scientific	99.9
1-pentene	Phillips Petroleum	99.9+