$$\beta_s^E(T)/[\text{GPa}]^{-1} = 0.545 + (0.28 \times 10^{-2})(T/°\text{C}) - \beta_w(T) \quad (9)$$

$$c_s(T)/[m] = 6.044 + (0.28 \times 10^{-2})(T/°\text{C}) + (0.36 \times 10^{-4})(T/°\text{C})^2 \quad (11)$$

$$\beta^*(c^*) = 2.5c^* - 2.0c^{*2} + 0.5c^{*3}$$

with $c^* = c/c_s$.

In the above equations all viscosities are expressed in μPa s, pressure is expressed in MPa, temperature is expressed in °C, and concentration is expressed as a molality, m = mol of NaCl/kg of H_2O. The above set of equations reproduces the original data within a standard deviation of ±0.5% which is comparable with the uncertainty in the data values themselves. A comparison with other investigations reveals that our correlation agrees with the results of Goncalves and Kestin (*3*) and those of Korosi and Fabuss (*12*) to within the combined uncertainty. The results of Suryanarayana and Venkatesan (*20*) deviate from our correlation by as much as 1.6% with a standard deviation of ±0.75%; the deviations are predominantly on the negative side. The data of Lengyel et al. (*13*) Ezrohki (*1*), Ostroff et al. (*14*), and Janz et al. (*5*) are in reasonable agreement with the present correlation.

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Literature Cited

(1) Ezrokhi, L. L., *J. Appl. Chem. USSR (Engl. Transl.)*, **25**, 917 (1952).
(2) Fair, J. A., Ozbeck, H., "Viscosity and Density Tables of Sodium Chloride Solutions (compilation)", National Geothermal Information Resource, Lawrence Berkeley Laboratory, University of California.
(3) Goncalves, F. A., Kestin, J., *Ber. Bunsenges. Phys. Chem.*, **81**, 1156 (1977).
(4) Haas, J. L., Jr., *U. S., Geol. Surv., Bull.*, **No. 1421-B** (1976). See also *Am. J. Sci.*, **269**, 490 (1970).
(5) Janz, G. J., Oliver, B. G., Lakshminarayanan, G. R., Mayer, G. E., *J. Phys. Chem.*, **74**, 1285 (1970).
(6) Kestin, J., Khalifa, H. E., *Appl. Sci. Res.*, **32**, 483 (1976).
(7) Kestin, J., Khalifa, H. E., Ro, S. T., Wakeham, W. A., *J. Chem. Eng. Data*, **22**, 207 (1977).
(8) Kestin, J., Khalifa, H. E., Sookiazian, H., Wakeham, W. A., *Ber. Bunsenges. Phys. Chem.*, **82**, 180 (1978).
(9) Kestin, J., Leidenfrost, W., Liu, C. Y., *Z. Angew. Math. Phys.*, **10**, 558 (1959).
(10) Kestin, J., Sokolov, M., Wakeham, W. A., *J. Phys. Chem. Ref. Data*, in press.
(11) Kestin, J., Wang, H. E., *J. Appl. Mech.*, **79**, 197 (1957).
(12) Korosi, A., Fabuss, B. M., *J. Chem. Eng. Data*, **13**, 548 (1968).
(13) Lengyel, S., Tamas, J., Giber, J., Holderith, J., *Magy. Kem. Foly.*, **70**, 66 (1964).
(14) Ostroff, A. G., Snowden, B. S., Woessner, O. E., *J. Phys. Chem.*, **73**, 2784 (1969).
(15) Othmer, D. G., Yu, E. S., *Ind. Eng. Chem.*, **60**, 22 (1968).
(16) Potter, R. W., II, Brown, D. L., *U. S., Geol. Surv., Bull.*, **No. 1421-C** (1977).
(17) Potter, R. W., II, Shaw, D. R., Haas, J. L., Jr., *U. S., Geol. Surv., Bull.*, **No. 1417** (1975).
(18) Rowe, A. M., Jr., Chou, J. C. S., *J. Chem. Eng. Data*, **15**, 61 (1970).
(19) Seidell, A., "Solubilities of Inorganic and Metal Organic Compounds", Vol. 1, Van Nostrand, New York, N.Y., 1940.
(20) Suryanarayana, C. V., Venkatesan, V. K., *Trans. Faraday Soc.*, **54**, 1709 (1952).

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Supplementary Material Available: Figures 5–10, which display the viscosity of the six solutions as a function of pressure along various isotherms, and Figures 14–20, which contain plots of the deviations of the present experimental results (18 pages). Ordering information is given on any current masthead page.

Liquid–Liquid Equilibria in the Reciprocal Ternary System Cs, Li ‖ Cl, F

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The miscibility gap in the molten system Cs, Li ‖ Cl, F as a function of composition and temperature was completely measured. The upper critical solution temperature of this system was found at 912 °C and x_{LiF} = 0.540, x_{LiCl} = 0.235, and x_{CsF} = 0.225 (x = mole fraction). The experimental results were compared with those calculated on the basis of the conformal ionic solution theory.

In the past few years, a serial work (*5*), meant to systematically analyze the liquid immiscibility of ionic salts at high temperatures, was carried out in our laboratory; among the mixtures formed by lithium fluoride and alkali halides, the system Cs, Li ‖ Cl, F showed a large demixing phenomenon along the stable diagonal (LiF + CsCl) (*4*).

Solid–liquid (SL) equilibria for this system were given by Bukhalova and Sementsova (*2*); no data on the liquid–liquid (LL) equilibria were previously reported.

The present paper studies the miscibility gap in the whole composition square as a function of temperature.

Experimental Section

The apparatus employed, which allows direct observation of the sample contained in the quartz vessel, is fully described (*7*).

The materials used were CsCl, CsF, LiCl, and LiF "Merck Suprapur". Particular care was devoted to the drying of the samples to prevent loss of transparency of the vessel. Devetrification phenomena of silica caused no problems during the performance of the experiments.

Results

Table I reports the measured LL and SL equilibria temper-

Table I. LL and SL Equilibria Temperatures (°C) in the System Cs, Li‖Cl, F[a]

		Stable Diagonal LiF + CsCl			
x_{LiF}	SL eq	LL eq	x_{LiF}	SL eq	LL eq
0.000	645		0.450		870 (831)
0.020	635		0.565		894 (830)
0.050	668		0.650		907 (830)
0.075	706		0.765		912 (830)
0.115	738		0.800		910 (829)
0.175	776		0.900		890 (830)
0.250	808		0.950		850 (830)
0.325	828		0.965	834	
0.350		838 (830)	1.000	848	
0.425		864 (830)			
		Unstable Diagonal LiCl + CsF			
x_{LiCl}	SL eq	LL eq	x_{LiCl}	SL eq	LL eq
0.000	703		0.500		882 (830)
0.050	660		0.525		876 (828)
0.100	609		0.550		858 (823)
0.150	542		0.570		834 (816)
0.200	460		0.590	810	
0.225	429		0.620	792	
0.250	436		0.650	774	
0.260	460		0.750	686	
0.275	530		0.800	621	
0.300	603		0.850	540	
0.350	700		0.900	504	
0.400	762		0.925	531	
0.435	796		0.950	560	
0.460		842 (816)	1.000	610	
0.475		870 (822)			
x_{LiCl}	SL eq	LL eq	x_{LiCl}	SL eq	LL eq
		Cut a: LiCl + {CsF – LiF(0.875)}			
0.025	800		0.125		885 (829)
0.045	817		0.145		874 (826)
0.060		835 (823)	0.200		830 (814)
0.070		850 (826)	0.225	805	
0.100		886 (828)	0.250	785	
		Cut b: LiCl + {CsF – LiF(0.700)}			
0.100	750		0.275		903 (826)
0.140	800		0.310		880 (820)
0.160		838 (810)	0.345		840 (811)
0.175		868 (817)	0.370	798	
0.200		898 (824)	0.400	760	
0.230		912 (830)			
		Cut c: LiCl + {CsF – LiF(0.400)}			
0.250	760		0.400		902 (829)
0.285	795		0.425		884 (827)
0.305		820 (809)	0.470		832 (815)
0.320		860 (816)	0.490	808	
0.350		893 (826)	0.525	790	
0.375		904 (830)			
		Cut d: LiCl + {CsF – CsCl(0.350)}			
0.325	790		0.425		851 (829)
0.340	807		0.460		830 (823)
0.360		824 (819)	0.480	814	
0.375		840 (824)	0.525	787	
0.400		856 (830)			

[a] The values given in parentheses represent PCTs; x's are mole fractions. The a–d off-diagonal cuts were obtained by adding increasing amounts of LiCl to a binary mixture of fixed composition (given in parentheses in mole fraction). The experimental equilibrium temperatures are reproducible within ±1 °C.

atures for the two diagonal and four off-diagonal cuts. Along with the LL data (which represent the temperature at which by cooling and shaking demixing takes place) the table gives in parentheses the primary crystallization temperature (PCT), i.e., the temperature at which equilibrium between two liquid and one solid phase is reached.

Figures 1 and 2 bring into evidence the demixing area (shaded) along the studied cuts with LL equilibrium points.

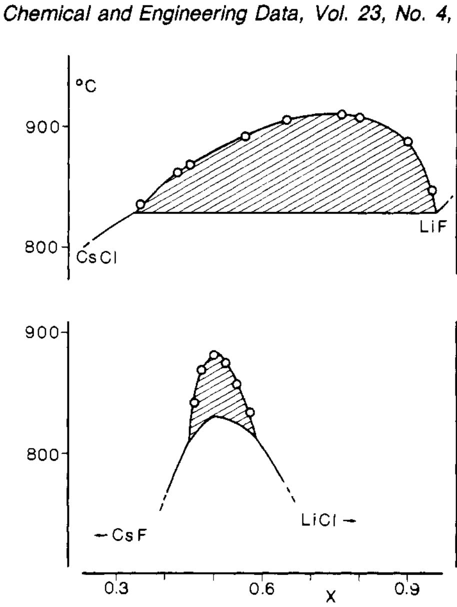

Figure 1. Demixing areas (shaded) along the stable (CsCl + LiF) and the unstable (CsF + LiCl) diagonals. LL equilibrium points are indicated by circles.

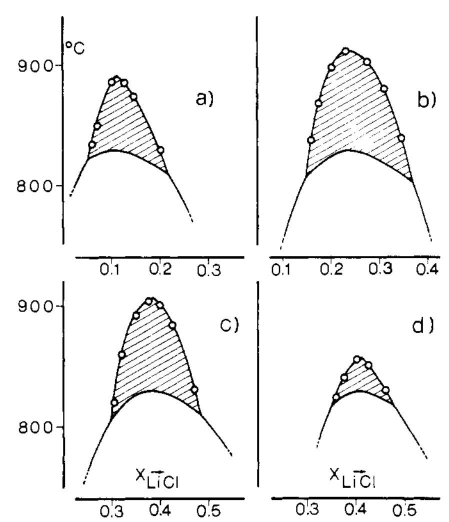

Figure 2. Demixing areas (shaded) along the four (a–d) studied off-diagonal cuts. LL equilibrium points are indicated by circles.

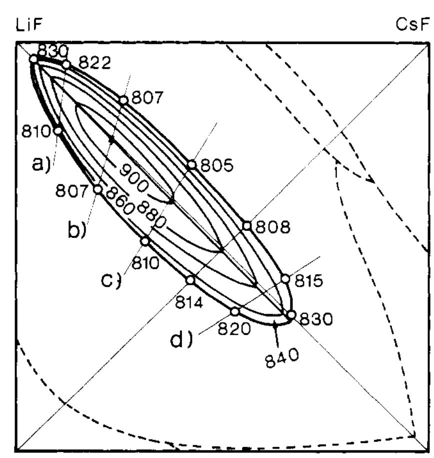

Figure 3. General topology of the studied system. The limits (dashed lines) of the crystallization field are those of ref 2; fine lines represent the projections of the examined cuts. In the demixing field four LL isotherms (at 840, 860, 880, 900 °C) are shown; the temperature of the upper critical point (starred) is 912 °C. The limiting temperatures of the nonisothermal basis of the stratification dome are also reported.

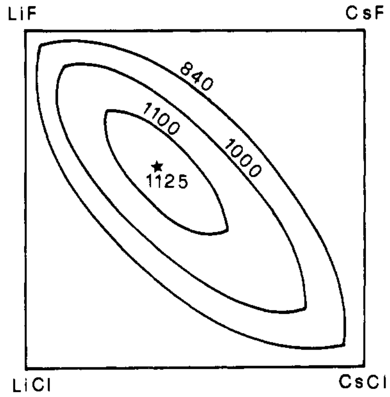

Figure 4. LL isotherms as calculated by means of the CIS theory using $Z = 6$, $\Delta G° = 22\,100 - 3.3T$, and k's from ref 3.

The general results are summarized in Figure 3 which reports the projections of the examined cuts (with the temperatures of the LL equilibrium limits) along with those of the interpolated LL isotherms at 840, 860, 880, and 900 °C. The system upper critical solution point was found at 912 °C for the composition (mole fraction) $x_{LiF} = 0.540$, $x_{LiCl} = 0.235$, and $x_{CsF} = 0.225$.

In order to give a complete view of the system thermal behavior, the SL equilibria (*2*) are also briefly reported by dashed lines. The stratification impinges over the LiF crystallization field and its projection occupies 14.3% of the composition square. The main axis of the lens is slightly shifted toward the LiCl corner. Along this axis the PCT is constant at 830 ± 1 °C.

Discussion

A satisfactory prediction of LL equilibria in the reciprocal molten salt system Na, Tl || Br, NO_3 was recently carried out by means of the conformal ionic solution (CIS) theory (*6*). This theory allows calculations of the topological features of systems A, B || C, D when the following data are known: the four binary mixture interaction parameters (k), the coordination number (Z), and the standard Gibbs free energy change ($\Delta G°$) for the metathetical reaction

$$AC + BD \rightarrow AD + BC$$

For the metathetical reaction LiF(l) + CsCl(l) → LiCl(l) + CsF(l), Lumsden calculated (*3*) the following values (in cal mol^{-1}): $\Delta G° = 22\,100 - 3.3T$; k(LiF + CsF) = −3000, k(CsF + CsCl) = 0, k(LiCl + CsCl) = −4200, k(LiCl + LiF) = −200. Since this system has a much larger $\Delta G°$ value than the previous one (Na, Tl || Br, NO_3: $\Delta G° = 8720 - 1.1T$), it was thought proper for testing the range of applicability of the CIS theory. Calculations on the present system using the Lumsden set of data with $Z = 6$ led to results which are only qualitatively acceptable (see Figure 4). In order to obtain better predictions, different values for the parameters, particularly $\Delta G°$ and Z, must be assumed. Figure 5 reports the results obtained using $\Delta G° = 19\,800 - 3.3T$ and $Z = 5$; the calculated miscibility gap compares well with the topology of the system, but the experimental stratification dome has a larger asymmetry toward the LiF corner.

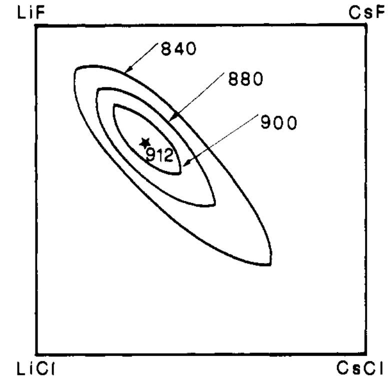

Figure 5. LL isotherms as calculated by means of the CIS theory using $Z = 5$, $\Delta G° = 19\,800 - 3.3T$, and k's from ref 3.

On the basis of these results it appears that the CIS theory, when applied to systems with large $\Delta G°$ and to phenomena as sensitive as LL equilibria, does not yield a quantitative picture of the system. Limitation to the second order of the theory (*1*) or the assumptions that Z and k are independent of composition and temperature are probably too drastic.

Literature Cited

(1) Blander, M., Yosim, S. J., *J. Chem. Phys.*, **39**, 2610 (1963).
(2) Bukhalova, G. A., Sementsova, D. V., *Russ. J. Inorg. Chem.*, **10**, 1027 (1965).
(3) Lumsden, J., "Thermodynamics of Molten Salt Mixtures", Academic Press, London, 1966, pp 19, 69, 158.
(4) Margheritis, C., Flor, G., Sinistri, C., *Z. Naturforsch. A*, **28**, 1329 (1973).
(5) Margheritis, C., Flor, G., Sinistri, C., *Z. Naturforsch. A*, **30**, 896 (1975), and previous papers of this series.
(6) Saboungi, M. L., Schnyders, H., Foster, M. S., Blander, M., *J. Phys. Chem.*, **78**, 1091 (1974).
(7) Sinistri, C., Franzosini, P., Timidei, A., Rolla, M., *Z. Naturforsch. A*, **20**, 561 (1965).

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