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Miscibility of Lithium with Lithium Chloride and Lithium Chloride–Potassium Chloride Eutectic Mixture

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Synopsis. The mutual solubilities of Li-LiCl and Li-LiCl-KCl systems were determined both in liquid-liquid and solid-liquid equilibrium regions. No critical solution temperature was observed for Li-LiCl system. The enthalpy of solution of LiCl in Li was estimated and compared with those for other alkali metal-alkali halides.

The phase diagrams and electric conductivity data for metal-salt systems are important information for the elucidation of the metal fog in molten salt electrolysis or the development of molten salt battery. Bredig *et al.*¹⁾ have reported a number of phase diagrams for alkali metal–alkali halides systems and Pitzer²⁾ has given a theoretical analysis primarily based on the regular solution theory and the electronic nature of metal bonding. However, only a few data were obtained with lithium–lithium halides systems. In this work, the mutual solubilities of lithium–lithium chloride and lithium–lithium chloride–potassium chloride eutectic mixture systems were determined and a thermodynamic interpretation was given.

Experimental

The determination of solubilities between 294 and 850 °C were made by a static equilibration (saturation)-and-sampling method. The apparatus for the measurement of solubility of lithium in molten salt and the analytical methods were the same as those described previously.³⁾ An apparatus of the same type was used for the solubility measurement of salts in molten lithium. The amounts of chloride ion in the sample were determined with the Mohr method.

Furthermore, in order to determine the solubilities at temperature above 850 °C, differential thermal analysis was carried out using the molybdenum cell in which lithium and salts were sealed by means of electron beam welding. A Shimadzu Model DT-20B micro DTA apparatus was used.

Results and Discussion

Solubility Data. All the solubility data obtained in this work are shown in Table 1, and the phase diagram based on the data for lithium–lithium chloride system is given in Fig. 1. In the same figure, the data obtained by Bredig¹⁾ and by Smirnov⁴⁾ for the solubility of Li in LiCl are also included. It is seen that our values are in good agreement with theirs. From the present measurement, the monotectic points for Li–LiCl system can be determined with reasonable accuracy. The monotectic temperature is estimated to be 608 °C which is about two degrees lower than the

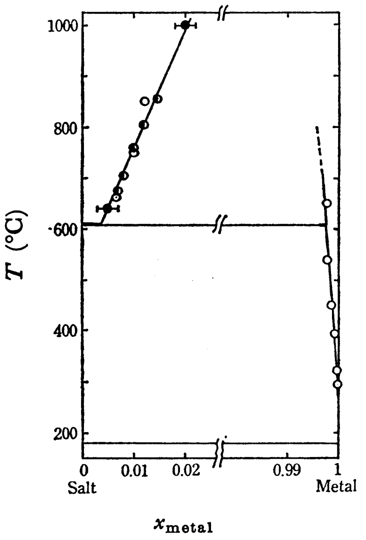

Fig. 1. Phase diagram of Li-LiCl system.
○ This work, ◐ Smirnov *et al*, ● Bredig *et al.*

Table 1. Equilibrium compositions in Li-LiCl and Li-LiCl-KCl eutectic mixture systems

System	Li-LiCl		Li-LiCl-KCl eutectic	
Temp. (°C)	Salt rich phase (mole% metal)	Metal rich phase (mole% salt)	Salt rich phase (mole% metal)	Metal rich phase (mole% salt)
294		0.007		
322		0.019		
394		0.069		
450		0.14±0.02	0.083±0.002	0.098±0.001
540		0.21		
550			0.23±0.01	0.15±0.01
650		0.23±0.01	0.38±0.01	0.20
662	0.66±0.10³⁾			
750	1.00±0.02		0.53±0.02	
850	1.22±0.01		0.65±0.03	

melting points of LiCl. The monotectic compositions are $X_{Li}=0.0045$ for salt-rich phase and $X_{LiCl}=0.0022$ for metal-rich phase (X: mole fraction). It is found that the mutual solubilities for Li–LiCl system are considerably smaller than those for Na–NaX or K–KX (X: halides) systems,[1] and accordingly their temperature coefficients are also very small. On the other hand, the mutual solubilities of Li–LiCl–KCl(eut. mixture) is still smaller than those for Li–LiCl system. This may be attributed to the fact that the equilibrium constant of the following equation, $Li+KCl \rightleftharpoons LiCl+K$, is 0.052.[5]

Critical Solution Temperature. Most of alkali (or alkali earth) metal-salt solutions are confirmed to exhibit an upper critical solution point at elevated temperatures.[1] One of the purposes of this work was to determine the critical point for Li–LiCl system. However, the upper critical solution temperature for this system could not be detected in spite of raising temperature of the system up to 1350 °C. This is higher than the boiling point of lithium metal. It may therefore be concluded that the present system has no upper critical point, though decisive observation could not be made.

Enthalpy of Solution of LiCl in Li. The plot of the logarithm of the solubility of solid LiCl in molten Li against the reciprocal of the absolute temperature are found to be linear within the experimental error, and the enthalpy of solution ΔH_{sol} of solid LiCl in molten Li was estimated to be about 14 kcal/mol. This is fairly small value when one compare this with those for NaCl in Na (20 kcal/mol)[6,7] or KCl in K (20 kcal/mol).[6,7] Since the enthalpy of solution ΔH_{sol} is the sum of the heat of fusion ΔH_f and the partial molar heat of mixture $\Delta \overline{H}_{mix}$, the ΔH_f values for these three salts are of comparable magnitude, this means that $\Delta \overline{H}_{mix}$ of LiCl in Li–LiCl solution is relatively smaller than those for Na–NaCl or K–KCl solution. This is rather unexpected result, because the cohesive energy of lithium metal is larger than those for Na or K metal and lithium is believed to be energitically unfavorable for the mixing with salt.

Excess Entropy. It is interesting to examine the sign and magnitude of the excess entropy of the present system. Since the mutual solubilities of, say, Na–NaCl system is larger than those of Li–LiCl, the excess free energy ΔG^E for Na–NaCl system should be positive and smaller in magnitude than that for Li–LiCl system. But they will be of comparable magnitude if comparison is made at the same lower temperature by extrapolation of the data for Na–NaCl system. Now ΔH^E for Na–NaCl is larger than that for Li–LiCl, then ΔS^E for Li–LiCl system will become smaller than that for Na–NaCl system. Possible contributions to the ΔS^E of metal-salt solutions were discussed by Pitzer[2] and the above result coincides with his analysis.

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