

Excess Entropies of Mixing in the Binary Molten Salt Mixtures AlkCl-MgCl₂ and CaCl₂-MgCl₂

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The well known Temkin¹ expression for ionic fractions has frequently been used to calculate entropies of mixing in molten salt mixtures (see Førland²).

$$\Delta S_{\text{ideal}}^M = -R(n_1 \ln N_1 + n_2 \ln N_2) \quad (1)$$

The excess entropy of mixing can be obtained from

$$S^E = \Delta S_{\text{exp}}^M - \Delta S_{\text{ideal}}^M \quad (2)$$

Experimental data have shown that in simple mixtures of the type AX-BX (common anion) and AX-AY (common cation) deviations from the ideal Temkin entropy (eqn. (2)) are rather small. However, in unsymmetrical mixtures of the type AlkCl-MgCl₂, one can expect more pronounced deviations from the ideal entropy of mixing. The excess free energies given by Ikeuchi and Krohn³ for the systems NaCl-MgCl₂, KCl-MgCl₂, and CsCl-MgCl₂ together with the enthalpies of mixing given by Kleppa and McCarty⁴ makes it possible to evaluate excess entropies of mixing for these systems. These values together with the excess entropies for mixtures of CaCl₂-MgCl₂ found by Grjotheim, Holm and Malmo⁵ give a new basis for discussion of excess entropies and their dependence of the other excess functions in these systems.

By plotting the excess entropy as a function of the enthalpy of mixing at $N_{\text{MgCl}_2} = 0.5$, it is found that the data closely fit a straight line. The most interesting feature is shown by the fact, that the line does not go through (0,0); instead it intercepts the y -axis at about $\Delta H^M = -700$ cal/mole. This is consistent with the suggestions made by Grjotheim, Holm and Malmo⁵ that the configurational part of the excess entropy could be divided into two principal parts namely $S^E = S_1^E + S_2^E$. The first of these effects, S_1^E , is due to a reduction in the number of independent units in the system, which results in a *negative* contribution and is the major factor in the case of very strong

association. Secondly, the introduction of new species will make a *positive* contribution S_2^E , and is the controlling factor when the association is feeble, *i.e.* in systems where the enthalpy of mixing is small negative or positive.

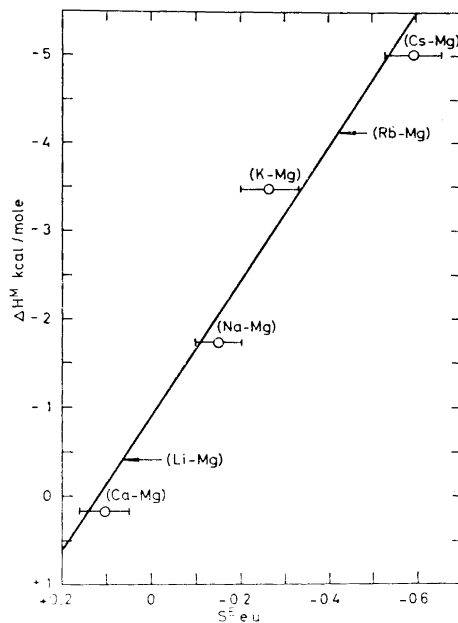


Fig. 1. The excess entropy S^E at $N_{\text{MgCl}_2} = 0.5$ as a function of the enthalpy of mixing in the corresponding system.

If this is applied to the systems mentioned above, it can easily be seen that the S_1^E term always determines the sign of S^E in the systems AlkCl-MgCl₂, where Alk⁺ = Na⁺, K⁺, Rb⁺, Cs⁺. The excess entropy will in this case probably be associated with the loss in the number of orientations of the chloride ions, due to formation of complex or associated species. In the system MgCl₂-CaCl₂ the interactions are weak and the S_2^E term will in this case be the most important. From the curve one can easily find the excess entropy for the LiCl-MgCl₂ system. Since the enthalpy of mixing in this system according to Kleppa and McCarty⁴ is about -400 cal/mole, S^E should be slightly positive, about

+0.08 e.u. EMF measurements carried out by using the galvanic cell ⁶

$\text{Cl}_2(\text{g})$, graphite/LiCl(l)/(Li-Mg)Cl(l)/graphite, $\text{Cl}_2(\text{g})$

show that the partial excess entropy of LiCl in the mixture is positive and of the same magnitude as given above, thus indicating that the S_2^E term will be the most important in this case.

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