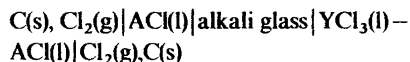


Thermodynamic Studies of Binary Charged Unsymmetrical Fused Salt Systems. Calorimetric and Electromotive Force Measurements of Yttrium(III) Chloride—Alkali Chloride Mixtures

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The thermodynamic quantities of mixing in liquid $YCl_3 - ACl$ ($A = Li, Na, K, Rb,$ or Cs) mixtures have been measured. The molar enthalpies of mixing (ΔH^M) for all the above binaries have been determined calorimetrically in the temperature range 998–1143 K. The partial Gibbs energies of mixing of ACl in the binaries ($A \neq Cs$) have been determined by emf measurements of the galvanic cell:



The partial Gibbs energies and entropies have been calculated.

The interaction parameters ($\lambda^M = \Delta H^M / x_1 x_2$) were found to be temperature independent and to increase to quite negative values as the size of the alkali metal cation increased. The systems have significant energetic asymmetries with more negative values of λ^M in the alkali chloride-rich than in the yttrium chloride-rich region. With the exception of the $YCl_3 - LiCl$ binary, all other binaries show a distinct minimum at YCl_3 concentration $X_{YCl_3} \leq 0.25$. The partial entropies of mixing ($A \neq Li$) show inflection points and a sharp dependence on composition in the concentration region $0.2 \leq X_{YCl_3} < 0.25$. The results are compared with recent thermodynamic data on the lanthanide(III) chloride—alkali chloride binary mixtures and discussed in view of recent Raman spectroscopic studies on the $YCl_3 - ACl$ binaries.

Recently, the thermodynamic and structural properties of a series of binary liquid $LaCl_3 - ACl$ and $CeCl_3 - ACl$ ($A = Li, Na, K, Rb, Cs$) mixtures have been investigated by means of calorimetric,^{1,2} electromotive force,^{1,3} and Raman spectroscopic^{4,5} measurements. The Raman studies of $LaCl_3 - KCl$ mixtures⁴ and especially the Raman spectral changes observed on melting $Cs_2NaLaCl_6$, Cs_3LaCl_6 and K_3LaCl_6 ⁵ solids, showed that in alkali chloride-rich mixtures $LaCl_6^{3-}$ configurations are formed. In this species the La^{3+} cation is in an octahedral chloride geometry. The thermodynamic quantities [integral enthalpy (ΔH^M), partial enthalpy ($\Delta \bar{H}_{ACl}$) and chemical potential ($\Delta \mu_{ACl}$)] for both the $LaCl_3 - ACl$ and $CeCl_3 - ACl$ systems were found to increase to quite large negative values as the size of the alkali metal cation increased in the sequence $Li < Na < K < Rb < Cs$. For mixtures with KCl , $RbCl$, and $CsCl$, the enthalpy interaction parameter $\lambda^M = \Delta H^M / X_i (1 - X_i)$, ($X_i = \text{mol fraction of component } i$), varies strongly with composition and shows a broad minimum at composition $X_{LaCl_3} < 0.25$.

A comparison of the interaction parameters for the sequences of binaries $LCl_3 - ACl$ ($L = La, Ce$) indicates that the λ^M 's could be fitted to a general curve of the form:^{3,5}

$$\lambda^M = a(T, P, X) + b(T, P, X)\delta_{12} + c(T, P, X)\delta_{12}^2 \quad (1)$$

Here $\delta_{12} = (d_1 - d_2) / d_1 d_2$ is the size parameter (d_1 and d_2 are characteristic interionic distances in the

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two salts which are mixed) and a , b , and c are functions of temperature, pressure, and composition. It was further argued that, since the characteristic physical and chemical properties (polarizabilities, interionic distances, *etc.*) of all lanthanide chlorides are similar, eqn. (1) should be general for lanthanide chloride-ACl mixtures.

However, more recent calorimetric data by Dienstbach and Blachnik⁶ on the sequence of binaries $GdCl_3-ACl$ show that the magnitudes of λ^M s are more positive than those expected from eqn. (1); also, the shape of the λ^M curves are similar to those of $LaCl_3-ACl$ or $CeCl_3-ACl$, with a pronounced broad minimum at $X_{GdCl_3} \lesssim 0.25$ ($A=K, Rb, Cs$).

It appears that a better understanding of the systematics of the thermodynamics of the lanthanide chloride-alkali chloride series requires some knowledge of the thermodynamics of binaries containing the end chlorides of the series (*i.e.*, $LuCl_3$). An alternative to the rare and expensive end members of the lanthanide chloride series is yttrium chloride, having physicochemical properties very similar to those of $YbCl_3$.⁷

In this paper we report the enthalpies, partial Gibbs energies, and entropies of mixing for YCl_3-ACl liquid mixtures. The results are compared with data of other LCl_3-ACl ($L=La, Ce, Gd$) systems and discussed in terms of the possible melt structures suggested by the recent Raman spectroscopic studies on these systems.⁸

The purpose of this study is to establish the systematics of the thermodynamic and structural properties of the liquid lanthanide chloride-alkali metal chloride mixtures.

EXPERIMENTAL

Yttrium(III) chloride for the calorimetric studies was prepared by dissolving yttrium oxide purchased from A. D. Mackay, Inc. in concentrated HCl. Slow evaporation of the solution gave the hydrated YCl_3 , which was dried according to procedures described previously.¹

Yttrium(III) chloride for the emf measurements was prepared by dissolving yttrium oxide from Research Chemicals in concentrated HCl. The hydrated YCl_3 was dried under vacuum at temperatures up to 200 °C. The salt was then treated with gaseous HCl and melted under HCl atmosphere. After this treatment, the melt was filtered through a quartz frit and distilled under vacuum (10^{-5} Torr). The source and methods of purifica-

tion of the alkali chlorides were the same as those previously used.^{1,2} The measurements of the integral enthalpies of mixing were of the "crucible-double breakoff" type, where both liquid salts were contained in fused silica containers.⁹ The calorimetric apparatus used, its calibration, and the required corrections have been described elsewhere.¹⁰ The cell used in the emf measurements is similar to the one described in previous papers.¹¹⁻¹³ The composition of the glasses and the experimental techniques are given elsewhere.¹⁴⁻¹⁶

By adding small crystals of YCl_3 or ACl in the anode compartment of the cell the composition of the mixture could be changed. One could then either start with a low YCl_3 concentration and add YCl_3 or start with a high YCl_3 concentration and add ACl.

The emf, E , of the cell is related to the chemical potential of the ACl salt in the mixture, $\Delta\mu_{ACl}$, through the equation

$$\Delta\mu_{ACl} = -FE$$

where F is the Faraday constant.

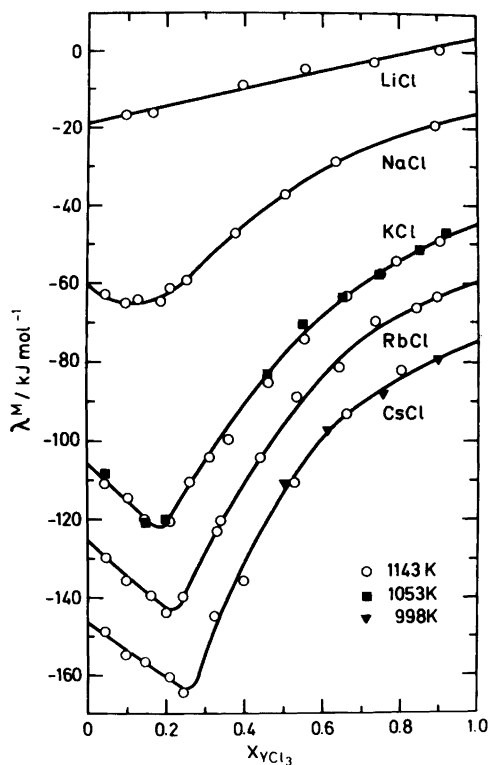


Fig. 1. Enthalpy interaction parameters in liquid mixtures of yttrium(III) chloride with the alkali chlorides.

RESULTS AND DISCUSSION

Fig. 1 presents the results of the liquid-liquid enthalpy of mixing experiments. In Fig. 1, the enthalpy interaction parameters are plotted *versus* mol fraction. The lines shown in the figure represent the "best" curves. The mean deviation of the actual experimental points from the interaction parameter curves is estimated to $\sim \pm 2\%$.

The enthalpy of mixing becomes more negative with increasing size of the alkali metal cation. For the YCl_3 –LiCl binary and at concentrations rich in YCl_3 , positive enthalpies of mixing have been observed. The values of the interaction parameter (Fig. 1) decrease sharply from about $+4 \text{ kJ mol}^{-1}$ for the YCl_3 –LiCl binary to about -165 kJ mol^{-1} for the YCl_3 –CsCl binary. Within experimental error, the interaction parameters are independent of temperature. All considered systems show more negative values of the interaction parameter in the alkali chloride-rich than in the yttrium chloride-rich region. For the mixtures containing CsCl, RbCl, and KCl, distinct minima are found for λ^M at concentrations $0.2 \leq X_{\text{YCl}_3} < 0.25$. A broad minimum is also present in the λ^M of the YCl_3 –NaCl mixtures, while the data for the λ^M of the YCl_3 –LiCl vary linearly with X_{YCl_3} , within experimental error.

These trends have been observed previously in the studies of other LCl_3 – ACl ^{1,2,6} binaries. However, the data for the YCl_3 – ACl binaries are unique in showing both the sharp minima near $X_{\text{YCl}_3} \sim 0.25$ and the high energetic asymmetry in the interaction parameter. Similar sharp minima at $X_{\text{ZnCl}_2} \sim 0.33$ and high energetic asymmetry have been observed previously for the ZnCl_2 – CsCl binary.⁹

Raman investigations⁸ have shown that at concentrations of YCl_3 , where $X_{\text{YCl}_3} < 0.25$, octahedral YCl_6^{3-} ions are present in the melts containing NaCl, KCl, RbCl, or CsCl. The shift of the minimum of λ^M towards smaller X_{YCl_3} values for the binaries containing RbCl, KCl, and NaCl (Fig. 1) can probably be attributed to the increasing polarizing strength of the solvent cation and/or interactions between YCl_6^{3-} species in these melts. The large volume of the YCl_6^{3-} ion and the large number of Cl^- anions associated with the Y^{3+} cation increase the probability of having two of these species as nearest neighbours at concentrations below $X_{\text{YCl}_3} = 0.25$. Consequently, the YCl_6^{3-} ions will share chlorides, the octahedra will be distorted,

and Y–Cl interactions will be weakened. These effects are expected to shift the minimum of λ^M to mol fractions below $X_{\text{YCl}_3} = 0.25$. It is worth noting that if one assumes binuclear species like $\text{Y}_2\text{Cl}_6^{3-}$ in equilibrium with YCl_6^{3-} , then the minimum in λ^M should shift to X_{YCl_3} values higher than 0.25.

The interaction parameter for the lithium chloride–yttrium chloride mixtures varies approximately linearly with composition. As has been argued previously¹ and shown by the Raman studies,⁸ the absence of the minimum does not necessarily imply the absence of YCl_6^{3-} configurations from the melt mixtures. The high ionic strength of Li is important in diminishing Y–Cl interactions and thus weakly bonded and probably distorted YCl_6^{3-} configurations are formed.

The validity of eqn. (1) for the YCl_3 – ACl binaries was tested by plotting the enthalpy interaction parameter at different compositions ($X_{\text{YCl}_3} = 0, 0.25, 0.50, 1$) as a function of δ_{12} ($r_{\text{Y}^{3+}} = 0.88$). It was found, however, that the data did not fit a smooth, second-order-in- δ_{12} equation. Therefore, it appears that eqn. (1) holds only for the first members of the lanthanide series where the ionic radii of the trivalent cations are very similar and that, as the L^{3+} cation radius is reduced, a more complex equation and/or more complex size parameters are needed. It was found, for example, that the use of a new size parameter

$$\delta'_{12} = \frac{Z_1}{d_1} - \frac{Z_2}{d_2}$$

where Z_1 and Z_2 are the charges of the cations in the binary mixture ($Z_1 = 1, Z_2 = 3$), yields a smooth, second-order-in δ'_{12} algebraic equation, results which fit all the present interaction parameters.

Tables 1 and 2 present experimental results of the calorimetric and emf measurements. Except for the LiCl system, emf measurements obtained by starting with a high YCl_3 concentration and adding ACl give results slightly different from results obtained by starting with a low YCl_3 concentration and adding YCl_3 . Measurements starting with a low YCl_3 concentration were more reproducible than measurements starting with a high YCl_3 concentration. The reason for the difference between the two sets of data are difficult to understand, but since data obtained by adding YCl_3 give higher and more reproducible potentials, we believe that this set of data is the more reliable.

Table 1. Enthalpies of mixing liquid ytterbium(III) chloride and alkali chlorides.

System	Mol fraction X_{YCl_3}	Molar enthalpy $-\Delta H^M/kJ mol^{-1}$	System	Mol fraction X_{YCl_3}	Molar enthalpy $-\Delta H^M/kJ mol^{-1}$
CsCl–YCl ₃ T=1148 K	0.047	6.61	CsCl–YCl ₃ T=998 K	0.502	27.67
	0.098	13.65		0.614	23.02
	0.149	19.80		0.753	16.41
	0.212	26.75		0.897	7.28
	0.247	30.64	KCl–YCl ₃ T=1143 K	0.045	4.73
	0.325	31.94		0.103	10.59
	0.400	32.48		0.146	14.94
	0.528	27.46		0.212	20.09
	0.658	20.89		0.263	21.39
	0.801	13.06		0.313	22.35
		0.363		23.02	
RbCl–YCl ₃ T=1143 K	0.049	6.07	0.463	21.18	
	0.099	12.06	0.555	18.29	
	0.161	18.84	0.662	14.06	
	0.201	23.15	0.749	10.80	
	0.245	25.83	0.785	9.17	
	0.333	27.29	0.901	4.35	
	0.343	27.04	KCl–YCl ₃ T=1053 K	0.048	4.90
	0.443	25.74		0.150	15.40
	0.536	22.06		0.201	19.21
	0.644	18.67		0.463	20.68
0.737	13.44	0.551		17.37	
0.843	8.75	0.652		14.40	
NaCl–YCl ₃ T=1143 K	0.047	2.80	0.748	10.84	
	0.0985	5.78	0.851	6.49	
	0.130	7.24	0.917	3.56	
	0.189	9.88	LiCl–YCl ₃ T=1143 K	0.096	1.47
	0.211	10.21		0.166	2.26
	0.253	11.18		0.397	2.09
	0.377	11.01		0.556	1.21
	0.505	9.25		0.735	0.54
	0.633	6.66		0.907	-0.08
	0.890	1.88			

In Fig. 2, $\Delta \bar{S}_{ACl}$ is plotted versus X_{YCl_3} for the binaries with A=Li, Na, K, and Rb. The entropies were obtained by combining the partial Gibbs energies calculated from the emf measurements and partial enthalpies calculated from integral data by the method of intercepts. The calculated partial entropies compared within 10% with entropies measured directly by the temperature dependence of the emf. This comparison was made for a few concentrations only. Except for the YCl₃–LiCl system, the partial entropies show inflection points at YCl₃ concentrations in the region $0.2 \leq X_{YCl_3} < 0.25$ and a sharp dependence on composition at

this concentration. Even if the errors in the $\Delta \bar{H}_{ACl}$ values calculated from integral data by the methods of intercepts are relatively great ($\pm 800 J mol^{-1}$) the results (Figs. 1 and 2) indicate a definite ordering on the cation lattice, *i.e.*, complex formation, around the composition $X_{YCl_3} = 0.25$.

For the YCl₃–LiCl system, no minimum occurs in the enthalpy interaction parameter, the partial entropies are more ideal, and the regular solution model seems to fit fairly well. For the YCl₃–NaCl system, the situation is different from that found for the LaCl₃–NaCl¹ and the CeCl₃–NaCl² binaries where no significant deviation from regular solution

Table 2. Emf's for the galvanic cell C(s), Cl₂(g)|ACl(l)|A-glass|YCl₃(l)–ACl(l)|Cl₂(g),C(s).

System	Mol fraction X_{YCl_3}	Emf E/mV	System	Mol fraction X_{YCl_3}	Emf E/mV
RbCl–YCl ₃ ^a T=1143 K	0.098	19	RbCl–YCl ₃ T=1143 K	0.199	63
	0.101	16		0.248	93
	0.150	39		0.249	94
	0.196	61		0.299	140
	0.206	75		0.349	186
	0.249	115		0.351	175
	0.253	115		0.398	246
	0.303	170		0.400	270
	0.351	220		0.449	290
	0.444	324		0.452	306
KCl–YCl ₃ ^a T=1143 K	0.101	18	KCl–YCl ₃ T=1143 K	0.501	370
	0.102	18		0.548	411
	0.103	20		0.548	415
	0.156	41		0.651	527
	0.196	65		0.654	523
	0.201	65		0.299	146
	0.201	66		0.334	172
	0.252	111		0.349	191
	0.300	154		0.400	244
	0.300	157		0.447	278
0.351	207	0.500	338		
0.403	257	0.547	381		
0.450	304	0.598	427		
0.498	348	0.650	477		
NaCl–YCl ₃ ^a T=1103 K	0.096	16	NaCl–YCl ₃ T=1103 K	0.696	514
	0.100	17		0.741	560
	0.197	53		0.150	31
	0.201	52		0.191	46
	0.251	78		0.199	49
	0.295	108		0.200	52
	0.300	108		0.249	75
	0.399	175		0.251	78
	0.401	170		0.299	104
	0.499	232		0.300	103
0.500	236	0.301	108		
LiCl–YCl ₃ ^a T=974 K	0.102	12	LiCl–YCl ₃ T=974 K	0.348	134
	0.202	34		0.399	172
	0.300	62		0.399	165
	0.400	96		0.400	162
	0.500	129		0.449	197
LiCl–YCl ₃ T=974 K	0.250	49	LiCl–YCl ₃ T=974 K	0.493	220
	0.349	80		0.500	240
	0.452	111		0.501	230
	0.549	142		0.543	254
	0.640	173		0.596	290
	0.751	215		0.598	305
				0.601	284
				0.649	315
		0.702	344		
		0.787	399		

^a Obtained from measurements starting with a low YCl₃ concentration.

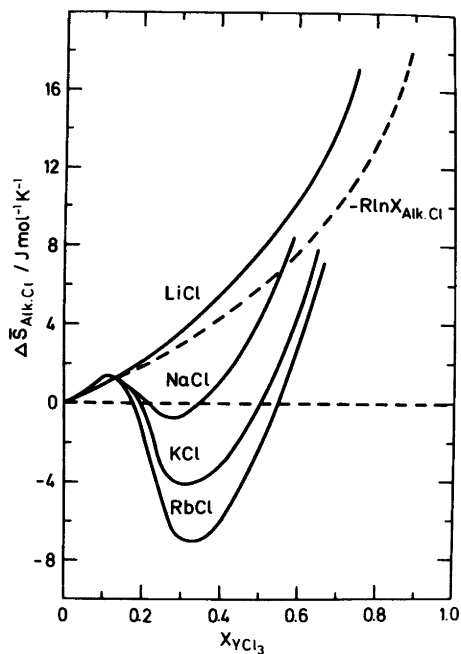


Fig. 2. Partial entropies of mixing of the alkali chlorides in mixtures with yttrium(III) chloride. The dotted line represents the ideal entropies given by $-R \ln X_{\text{Aik.Cl}}$.

behavior was observed. In the $\text{YCl}_3 - \text{NaCl}$ system, a minimum in the enthalpy interaction parameter is found around $X_{\text{YCl}_3} = 0.2$ and an inflection point in the curve for partial entropy versus mol fraction is observed at the same composition, an observation which is not surprising since the Y^{3+} ion is significantly smaller than the La^{3+} ion. As expected, these properties in the enthalpy and the partial entropy of mixing are more pronounced in the $\text{YCl}_3 - \text{KCl}$ and $\text{YCl}_3 - \text{RbCl}$ systems. This is consistent with the observations made for the $\text{LaCl}_3 - \text{AlCl}_3$ and $\text{MCl}_2 - \text{AlCl}_3$ ($\text{M} = \text{Mg}, \text{Co}, \text{and Mn}$) mixtures and is indicative of the formation of associated species in these melts.

The detailed Raman spectroscopic study⁸ of the $\text{YCl}_3 - \text{KCl}$ and the $\text{YCl}_3 - \text{CsCl}$ mixtures and the Raman changes occurring on melting the compound $\text{Cs}_2\text{NaYCl}_3$ have shown that at concentrations $X_{\text{YCl}_3} < 0.25$, octahedral YCl_6^{3-} species are present in these melts. At higher yttrium chloride concentrations, the YCl_6^{3-} octahedra appear to be distorted, sharing edges with each other. This

spectroscopic information reinforces the present thermodynamic data and our conclusions about the ionic geometry in binary $\text{YCl}_3 - \text{AlCl}_3$ systems.

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