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An empirical approach: estimation of enthalpy of mixing in the MCl–$ReCl_3$ melts (M = alkali metals, Re = rare earth metals)

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Abstract

In the view of the physical properties an empirical approach is well developed for estimating enthalpy of mixing in the MCl–$ReCl_3$ melts from experimental data (M = alkali metals and Re = rare earth metals). The interaction parameter of enthalpy of mixing at constant temperature, constant pressure and specific composition is expressed as $\lambda_i = a + bY + cY^2 + dY^3$, where Y is so-called the modified relative ionic potential, related to the valence, radius of the ionic and electronegativity of relative element M or Re. The coefficients a, b, c, d can be obtained from a multi-regression method with experimental data. The calculated results by present method agree well with the experimental data.

Keywords: Estimation of enthalpy of mixing; Interactive parameter of enthalpy; Alkali chloride and rare earth chloride melts

1. Introduction

Thermodynamic information of the melts involving rare earth halides and alkali halides plays an important role in the preparation of rare earth metals by molten salt electrolysis and by metallothermic reduction. Also the knowledge of thermodynamics of molten salts containing rare earth is useful in the understanding the recycle processing of spent fuel from fast nuclear reactors. From the point of view of fundamental study, the enthalpy of mixing is one of most important thermodynamic properties to understand the interionic interactions and structures in the melts. Since it is considerable difficult to measure accurately the enthalpy of mixing in the melts, which presents the energetic asymmetry in the charge unsymmetrical systems, some efforts are made to predict the enthalpy of mixing both empirically and theoretically [1–5]. The conformal solution theory [1] predicts that the interaction parameter, λ, of enthalpy in the liquid melts is a function of the size parameter, δ_{12}, with a second-order approximation.

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

The coefficients a, b and c are complicated integral functions of T, P and x. Size parameter $\delta_{12} = (d_1 - d_2)/d_1 d_2$, where d_1 and d_2 are the characteristic interionic distances in the two salts which are mixed. However, previous study [6] indicates that the conformal solution theory and the quasichemical theory [7] have not been developed to the point when there exists a sharp minimum in the interaction parameter of

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Table 1
Electronegativity of elements and ionic radius of alkali or rare earth metals

	Li	Na	K	Rb	Cs	La	Ce	Y
Electronegativity	1.0	0.9	0.8	0.8	0.7	1.1	1.1	1.2
r_M^+ or r_{Re}^{3+} (pm)	68	95	133	148	169	106	103	83

enthalpy of mixing. To the modified quasichemical model [8], the typical curve with a sharp minimum can be described. But it is, in some degree, difficult to fit the coefficients with experimental data due to complicated formula. Kleppa indicated that the interaction parameter of enthalpy of mixing is linearly dependent on the relative ionic potential [2]. When these data were collected and rearranged in the function of the relative ionic potential, we find the data is too scattered. It may result in terrible error for thermodynamic calculation.

To the melts mixed with rare earth chlorides and alkali chlorides, numerical experimental results reveal that the species present strong interaction. The purpose of present study is tentative to develop an empirical approach to estimating enthalpy of mixing in the MCl–$ReCl_3$ melts (M = alkali metals and Re = rare earth metals). It is significance to thermodynamic

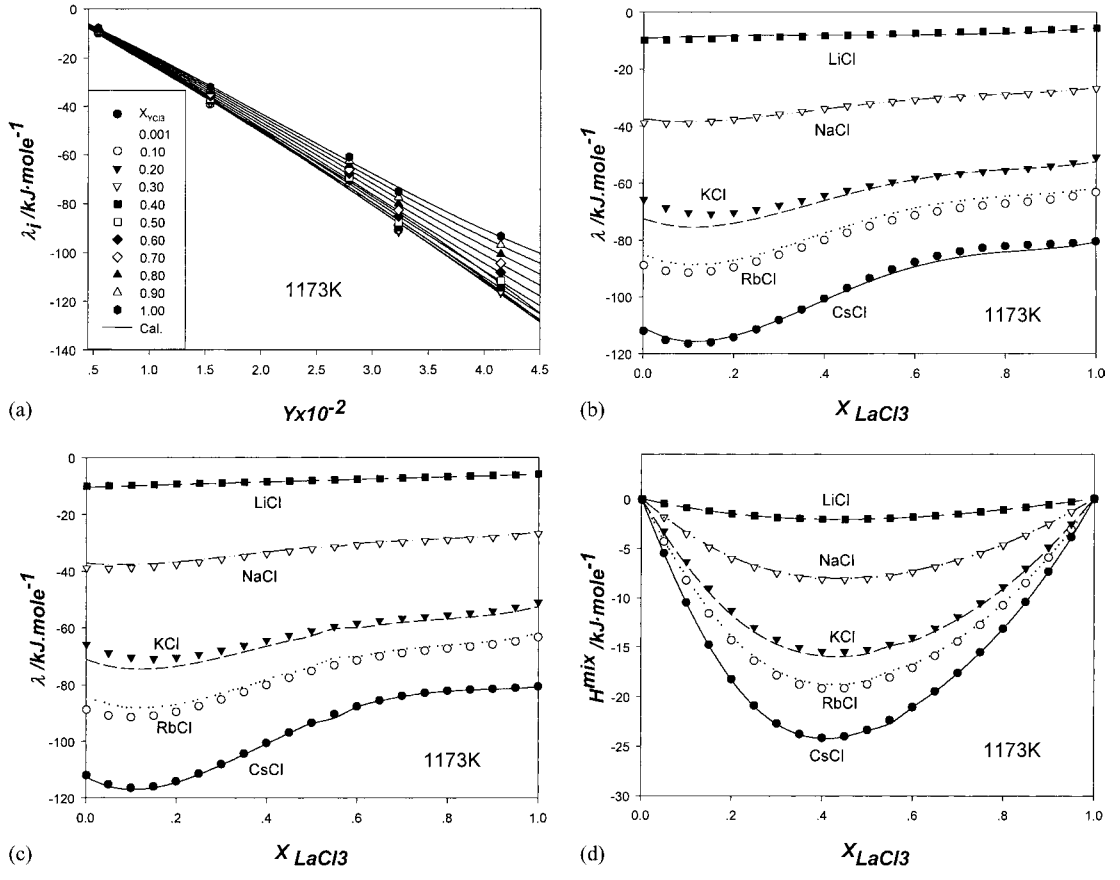

Fig. 1. (a) Interaction parameter dependence with the modified relative ionic potential in the $LaCl_3$–MCl melts; (b) interaction parameter of the enthalpy of mixing in the $LaCl_3$–MCl melts ($\lambda_i = a + bY$); (c) interaction parameter of the enthalpy of mixing in the $LaCl_3$–MCl melts ($\lambda_i = a + bY + cY^2 + dY^3$); (d) estimated enthalpy of mixing in the $LaCl_3$–MCl melts (dotted data derived from [6]).

optimization of phase diagrams and thermodynamic properties in the case of less experimental data available.

2. Empirical approach

Considering the polarization forces, coulombic forces, dispersion of Van der Waals forces of ions in the MCl–$ReCl_3$ melts, the thermodynamic quantities should be estimated with valuable experiment data available. The characteristic properties of metal elements or cation used in the following calculation were selected from Pauling's works [9], and were tabulated in Table 1.

In the MCl–$ReCl_3$ melts (M = alkali metals and Re = rare earth metals), the interaction parameter of enthalpy of mixing, in terms of mole fraction of rare earth chloride, is expressed as

$$\lambda = \frac{\Delta_{\text{mix}}H}{x(1-x)} \tag{2}$$

Based on the definition of the relative ionic potential [2], we similarly define the modified relative ionic potential, Y

$$Y = \left|\frac{Z_{\text{Re}}}{r_{\text{Re}}^{3+}} - \frac{Z_{\text{M}}}{r_{\text{M}}^{+}}\right| \times [1 + (E_{\text{Re}} - E_{\text{M}})] \times \frac{r_{\text{M}}^{+}}{r_{\text{Re}}^{3+}} \tag{3}$$

where Z_i, r_i, and E_i are the valence, radius of the ionic and electronegativity of relative element M or Re. Therefore, the interactive parameter of enthalpy of mixing in terms of the specific temperature, specific pressure (usually $P = 1$ atm) and specific composition, λ_i, could be described by following equation.

$$\lambda_i = a + bY + cY^2 + dY^3 \tag{4}$$

The coefficients a, b, c, d can be obtained from a multi-regression method with experimental data. The set of coefficients is dependent on the temperature, pressure and composition in the MCl–$ReCl_3$ melts.

3. Results and discussion

Fig. 1a shows the results calculated in Eq. (4). It obviously indicates that the interactive parameter of enthalpy of mixing in the MCl–$LaCl_3$ melts, λ_i, is almost linearly dependent on the modified relative ionic potential. Taking the first-order ($\lambda_i = a + bY$) and third-order approximations of Eq. (4), respectively, to estimate the interactive parameter of enthalpy dependent with mole fraction of $LaCl_3$, it turns out the estimated results are less difference between them (shown in Fig. 1b and c). In such case, Kleppa's linearly method [2] accords with present first approximation. To the MCl–$CeCl_3$ system, interactive parameter, λ_i, varies smoothly with the modified relative ionic potential. With the third-order approximation of Eq. (4), it accurately estimates the enthalpy of mixing in melts as shown in Fig. 2a and b. Similar results were obtained and were shown in Fig. 3a and b in the MCl–YCl_3 melts.

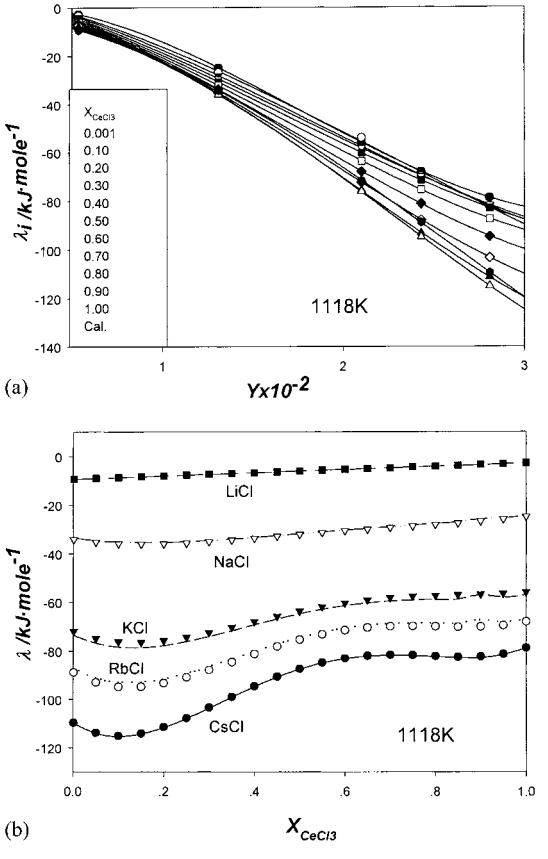

Fig. 2. (a) Interaction parameter dependence with the modified relative ionic potential in the $CeCl_3$–MCl melts; (b) interaction parameter of the enthalpy of mixing in the $CeCl_3$–MCl melts ($\lambda_i = a + bY + cY^2 + dY^3$) (dotted data derived from [10]).

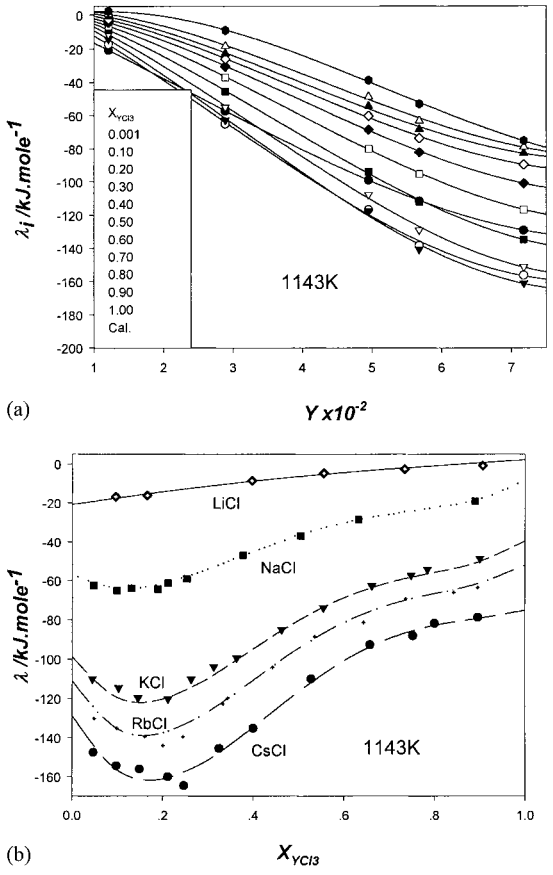

Fig. 3. (a) Interaction parameter dependence with the modified relative ionic potential in YCl_3–MCl melts; (b) interaction parameter of the enthalpy of mixing in the YCl_3–MCl melts ($\lambda_i = a + bY + cY^2 + dY^3$) (dotted data derived from [11]).

As mentioned in [6,10–12], all interactive parameters of enthalpy of mixing in the MCl–$ReCl_3$ melts are negative except for the LiCl–YCl_3 system. The considerable small positive values of enthalpy in the range of $0.9 < X_{YCl_3}$ are presumably due to the experimental uncertainties. In the view of polarizibility, the enthalpy of mixing increases with the increasing of the radii of alkali metal from Li to Cs. The minimum of interaction parameter of enthalpy was observed in the MCl–$ReCl_3$ melts from Na to Cs. The experimental measurements confirmed that there existed the complex $ReCl_6^{3-}$ and the short ordering occurred in those melts. The composition shift of the sharp peak to $ReCl_3$ from La to Y probably is attributed to the enhancement of particle interaction in the melts with the shrinkage of radii of rare earth element (shown in Fig. 1b and Fig. 3b).

Comparing the conformation solution theory and the present method, it is very interesting to find that the presentations in Eqs. (1) and (4) are very similar. All coefficients are the functions of temperature, composition and pressure. But it should be noted that the variable in Eq. (1) be the size parameter, thereby, variable in Eq. (4) be related to the properties of ionic charge, radii and electronegativity. The present work is just the empirical approach dependent on the reliable experimental determination.

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