



Study on surface tension and surface phase of molten MCl-CeCl₃ (M = Li, Na, K, Cs): A comparison of Butler's equation and a newly-proposed model



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ABSTRACT

The thermodynamic optimization of NaCl-CeCl₃ has been carried out through CALPHAD method, and a set of reliable parameters has been obtained to supplement the thermodynamic database. Based on Butler's equation and thermodynamic database established by CALPHAD method, the calculated surface tensions of molten salt mixtures MCl-CeCl₃ (M = Li, Na, K, Cs) agree quite well with experimental results reported in the literature. The model parameter β was determined to be 0.95, 1.04, 1.09 and 1.12 for LiCl-CeCl₃, NaCl-CeCl₃, KCl-CeCl₃ and CsCl-CeCl₃, respectively, by fitting the experimental data of surface tension of these mixtures, since it is out of the question to get a universal β applicable to all molten salt mixtures. The new model proposed lately by Santos et al. to describe the thermodynamics in surface phase of liquid solution has been reduced to a much simpler form which is nearly numerically equivalent to it by eliminating the derivative of molar surface area with respect to pressure. The surface compositions and surface activity coefficients from Butler's equation were compared with those from Santos model. For LiCl-CeCl₃ and NaCl-CeCl₃, the results from the two models are almost the same due to the similar surface tensions of LiCl, NaCl and CeCl₃. Whereas for KCl-CeCl₃ and CsCl-CeCl₃, the mole fraction of CeCl₃ in surface phase from Butler's equation is overestimated compared with that from Santos model, leading to a slight underestimation of surface activity coefficients of CeCl₃ and also a slight overestimation of those of KCl and CsCl, since the surface tensions of KCl and CsCl are much smaller than that of CeCl₃.

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1. Introduction

The electrolysis of molten salt mixtures consisting of rare earth and alkali halides has been widely used in the industry to produce pure rare earth metals and alloys [1,2]. The surface tension of the electrolyte plays an important role in the rare earth metal metallurgy since various processes (e.g., the formation and growth of solid metal crystallites at the electrode) are closely related with it. Nevertheless, there have not been sufficient experimental data for surface tension of molten halides containing rare earths due to the difficulties in high temperature measurement. Therefore, it is indispensable to develop theoretical or empirical models to calculate the surface tension of these melts. A few decades ago, Butler [3] derived a series of equations which are now in common use to

connect the surface tension of solution with the compositions and thermodynamic properties of surface and bulk phase. Based on Butler's equation, Sprow et al. [4] and Speiser et al. [5,6] established the corresponding models to calculate the surface tension of simple liquid mixtures, such as N₂-Ar and N₂-CO at low temperatures, and binary liquid alloys, respectively. Tanaka et al. [7–12] developed several models to evaluate the surface tension of molten alloys, slags, oxides and alkali halides etc. combining Butler's equation with thermodynamic database built by CALPHAD method [13]. Qiao et al. [14–16] modified Tanaka's model with special attention to the model parameter β , and then calculated the surface tension of molten LaCl₃-MCl (M = Li, Na, K, Rb, Cs), LaCl₃-CaCl₂ and LaCl₃-NaCl-CaCl₂. However, as pointed out by Tanaka et al. [11], there are still some discrepancies between the calculated and experimental results when applying their model to halides, and the same case also exists in Qiao's model. Lately, Santos et al. [17,18] put forward a new and "almost exact" thermodynamic formalism to describe the surface phase of liquid mixtures based on fewer approximations

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than Butler's equation. The compositions and activity coefficients in the surface phase can be calculated in an innovative way with the use of Santos model.

In our previous work [19,20], we have performed the thermodynamic assessments of some molten halides containing rare earths using CALPHAD method. In order to investigate further such molten salt mixtures, we have attempted to solve the problem in Tanaka's and Qiao's models and calculated the surface tension of binary systems MCl–CeCl₃ (M = Li, Na, K, Cs) in this work. Before that, owing to the lack of thermodynamic parameters of NaCl–CeCl₃ we have to optimize this system using CALPHAD method to supplement the thermodynamic database. In addition, Santos model has been reduced to a much simpler form according to the theory of equivalent infinitesimal. Butler's equation, Santos model and the simplified Santos model have been applied to these systems to get the properties of surface phase. The compositions and activity coefficients in surface phase from classic Butler's equation have been compared with those from Santos model to elucidate the link between them.

2. Theory

2.1. Thermodynamic model for NaCl–CeCl₃

Thermodynamic optimization of NaCl–CeCl₃ was performed in this work using the same approach presented in the literature [19,20]. The Gibbs energy of the liquid phase is described by a two-sublattice ionic solution model [21,22] which can be written as (Na⁺, Ce³⁺)_P(Cl[−])_Q. According to the conservation of mass and charge, the relationship among the number of moles of solution components and ions within each sublattice can be expressed as

$$N_{\text{NaCl}} = n_{\text{Na}^+} \quad (1)$$

$$N_{\text{CeCl}_3} = n_{\text{Ce}^{3+}} \quad (2)$$

$$n_{\text{Cl}^-} = n_{\text{Na}^+} + 3n_{\text{Ce}^{3+}} \quad (3)$$

where N_i and n_j are the number of moles of solution component i and ion j , respectively. The site fraction of cation i ($i = \text{Na}^+, \text{Ce}^{3+}$) on cation sublattice is defined as

$$y_i = \frac{n_i}{n_{\text{Na}^+} + n_{\text{Ce}^{3+}}} \quad (4)$$

The numbers of cation and anion sites on the sublattice, P and Q , are calculated from the following equations:

$$P = \sum y_i (-v_i) = y_{\text{Cl}^-} = 1 \quad (5)$$

$$Q = \sum y_j v_j = y_{\text{Na}^+} + 3y_{\text{Ce}^{3+}} \quad (6)$$

where y_i and v_i , y_j and v_j represent the site fraction and charges of anion i and cation j , respectively.

The molar Gibbs energy expression of liquid phase is:

$$G_m^L (\text{J} \cdot \text{mol}^{-1}) = y_{\text{Na}^+} y_{\text{Cl}^-} {}^0G_{\text{NaCl}}^L + y_{\text{Ce}^{3+}} y_{\text{Cl}^-} {}^0G_{\text{CeCl}_3}^L + RT [P(y_{\text{Na}^+} \ln y_{\text{Na}^+} + y_{\text{Ce}^{3+}} \ln y_{\text{Ce}^{3+}}) + Q y_{\text{Cl}^-} \ln y_{\text{Cl}^-}] + E_{G_m} \\ = y_{\text{Na}^+} {}^0G_{\text{NaCl}}^L + y_{\text{Ce}^{3+}} {}^0G_{\text{CeCl}_3}^L + RT (y_{\text{Na}^+} \ln y_{\text{Na}^+} + y_{\text{Ce}^{3+}} \ln y_{\text{Ce}^{3+}}) + E_{G_m} \quad (7)$$

where R is the gas constant; T is the absolute temperature; ${}^0G_{\text{NaCl}}^L$ and ${}^0G_{\text{CeCl}_3}^L$ are the Gibbs energies of pure components NaCl and CeCl₃ in liquid state, respectively. E_{G_m} is the excess Gibbs energy of liquid phase which describes the interaction between the ions within each sublattice and can be expressed by a Redlich-Kister Polynomial, as shown below.

$$E_{G_m} (\text{J} \cdot \text{mol}^{-1}) = y_{\text{Na}^+} y_{\text{Ce}^{3+}} \left[(a_0 + b_0 T) + (y_{\text{Na}^+} - y_{\text{Ce}^{3+}}) \times (a_1 + b_1 T) + a_2 (y_{\text{Na}^+} - y_{\text{Ce}^{3+}})^2 \right] \quad (8)$$

where a_i ($i = 0, 1, 2$) and b_i ($i = 0, 1$) are coefficients to be optimized. Since there are no experimental data of heat capacity of Na₃Ce₅Cl₁₈, the Gibbs energy function of this intermediate compound ${}^0G_{\text{Na}_3\text{Ce}_5\text{Cl}_{18}}^S$ is described by the Neumann-Kopp rule as:

$${}^0G_{\text{Na}_3\text{Ce}_5\text{Cl}_{18}}^S (\text{J} \cdot \text{mol}^{-1}) = 3{}^0G_{\text{NaCl}}^S + 5{}^0G_{\text{CeCl}_3}^S + A + BT \quad (9)$$

where ${}^0G_{\text{NaCl}}^S$ and ${}^0G_{\text{CeCl}_3}^S$ are the Gibbs energies of pure components NaCl and CeCl₃ in solid state, respectively. The coefficients A and B are connected with the enthalpy and entropy of formation of Na₃Ce₅Cl₁₈ from NaCl and CeCl₃.

2.2. Combination of Butler's equation and CALPHAD method

Assuming a thermodynamic equilibrium between the bulk phase and the hypothetical monolayer surface phase, Butler [3] deduced the relationship between surface tension and thermodynamic properties of the liquid solution. For an A-B binary system, Butler's equation has the form:

$$\sigma = \sigma_A + \frac{RT}{A_A} \ln \frac{x_A^S}{x_A^B} + \frac{RT}{A_A} \ln \frac{\gamma_A^S}{\gamma_A^B} \quad (10)$$

$$\sigma = \sigma_B + \frac{RT}{A_B} \ln \frac{x_B^S}{x_B^B} + \frac{RT}{A_B} \ln \frac{\gamma_B^S}{\gamma_B^B} \quad (11)$$

where σ is the surface tension of the binary system; σ_i is the surface tension of pure component i ; A_i is the molar surface area of pure component i ; the superscripts S and B indicate the surface phase and bulk phase, respectively; x_i^S , x_i^B and γ_i^S , γ_i^B are the mole fraction and activity coefficient of component i , respectively. The molar surface area of pure component A_i is defined in a simple form [23] as

$$A_i = N_0 \left(\frac{V_i}{N_0} \right)^{2/3} = N_0^{1/3} V_i^{2/3} = N_0^{1/3} \left(\frac{M_i}{\rho_i} \right)^{2/3} \quad (12)$$

where N_0 is Avogadro's number; V_i , M_i and ρ_i are molar volume, molar mass and density of pure component i , respectively. γ_i^B can be obtained through the thermodynamic database established by CALPHAD method. According to the fundamental thermodynamic equations, the chemical potential of component i in the bulk phase μ_i^B can be written as

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