



A unit-cell model for predicting the viscosity of binary molten salts



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ABSTRACT

Molten salts and their mixtures are widely used as heat transfer fluid in the research area of solar energy applications. Measured viscosities of molten salts often show large discrepancies due to difficulties of measurement at elevated temperatures, especially for molten salt mixtures. In this paper, a theoretical model is presented for predicting the viscosity of binary molten salts, in which only data of viscosity, density and fraction of each component salt are needed. Comparisons with experimental data show that the model gives prediction of viscosity with errors less than 9.94%, though part of this error may probably come from experiment. In comparison, the Eyring equation always gives larger errors, reaching 11.4% in the worst case. The present work indicates that the model shows improved ability in prediction of viscosity of molten salt mixtures.

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1. Introduction

Molten salt is popularly used in the studies of solar energy utilization due to its advantages such as thermodynamic stability up to high temperatures, stability to radiation (no radiolysis decomposition), low pressure at the operating temperature and wide range of solubility, etc [1,2]. One of the researchers' interests is to develop molten salt mixtures with various components and compositions to increase the temperature range of receiving solar energy by reducing the melting temperature. Designing a solar power plant requires various thermophysical properties of molten salts such as thermal conductivity, viscosity, specific heat, etc. Measuring all thermophysical properties of molten salt mixtures would be tedious and not necessary. It is of great significance to develop theoretical models to predict these thermophysical properties.

In the previous work [3], the authors developed a unit-cell model for predicting the thermal conductivity of binary molten salts. This paper aims to develop a unit-cell model for predicting the viscosity of binary molten salts with better precision. In the published literatures, viscosity data of various molten salts can be found but they displayed large discrepancy [4,5]. Sometimes their difference may reach 70%. On the other hand, when molten salt mixtures are prepared, it would be very tedious to obtain their viscosity data all by experiment. A good theoretical approach can significantly reduce the quantity of measurement work.

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To theoretically predict viscosity of molten salt mixtures, Abe and Nagashima [6] modified the corresponding-states principle for alkali halide binary mixtures. Some basic parameters such as ionic radii, potential energy, molecular mass, etc, are simply obtained by taking proportional mean of mole fraction of components. Though accuracy was claimed to be within 10%, exceptional results were also found in their binary systems. In comparison, the semiempirical corresponding-states correlation by Janz et al. [4] was used to estimate the viscosity of pure molten salts with errors of 16–25%, and no data of binary molten salts were presented. Empirical expressions are often cited in literatures [7,8], among which Eyring equation [7] is a simple expression with moderate accuracy

$$\ln \eta = x_1 \ln \eta_1 + x_2 \ln \eta_2 \quad (1)$$

where x is the mole fraction, η the viscosity, subscripts 1 and 2 denote two components. It has been noted that this equation, and other similar ones, predict monotonic changes of viscosity with composition. Such monotonicity is often not observed in practice [8]. Though effort has been made to modify Eq. (1) theoretically [8,9], the calculated results are still not in good agreement with experimental data.

In this paper, the authors aim to develop a theoretical approach for calculating the viscosity of binary molten salts from the viewpoint of shear force in fluid flow. It is expected that the new approach is simple and convenient to use without involving additional parameters to be experimentally determined.

2. Theoretical

It has been verified that molten salt mixtures will decompose at high temperature [10]. In the following, however, decomposition will not be considered. That is, it is assumed that there are no chemical reactions among component fluids. Though it is evidenced that up to 40% chemical change from nitrate to nitrite in binary nitrate salt mixtures doesn't affect viscosity [11], it is still important to make this assumption since the basic thermoproperties such as density, viscosity, mole or mass fraction of component salts must be exactly identified. During mixing of liquid organic substances, new chemical bond may form. In this paper, however, it is assumed that there is not any kind of new chemical bonds between component ions after mixing. This means that mixing of two component liquids is simply a physical process in which thermophysical properties of component substances will not be changed. The continuous fluid body will also be discretized into some type of unit cells, like the case for theoretical work on the thermal conductivity [3,12].

In published literatures, Einstein equation [13,14] and Taylor equation [15] have been used for calculation of the viscosity of solution or emulsion systems. Though formulas are simple to use, too large errors will be produced if they are applied for molten salt mixtures (sometimes over 100%). Methods for calculating the viscosity of liquid hydrocarbon mixtures have been well reviewed by Mehrotra et al. [16], but it is difficult to apply these methods in molten salt mixtures because there are more parameters to be determined in them.

The unit cell concept has been used in many research areas such as permittivity in dielectric materials [17,18], heat conductivity in solids [19], etc. In this paper, the unit cell means the representative unit of a mixture obtained by discretizing a macroscopic fluid into many small parts. It does not mean microscopic particle like a molecule, ion, or nucleus.

Viscosity is a measure of the friction between fluid layers, and the result of friction is velocity gradient in the direction normal to fluid flow. From the viewpoint of frictional force, the friction between fluid layers in a binary mixture will include two parts: frictions due to the first component and due to the second component. Imagining a mixed fluid made up of a viscous component and an ideal fluid component, its velocity gradient in the direction normal to fluid flow will be mainly produced by the viscous compo-

nent while another component will contribute nothing to velocity gradient but change the volumetric structure of the fluid mixture. To extend this idea into molten salt mixtures, the component A with high viscosity will be considered to predominate in the total frictional force, whereas the component B with low viscosity will be of secondary importance. In the limit case, an ideal fluid in place of component B will function as the filling fluid that holds the volumetric structure of binary mixture and that contributes nothing to the total frictional force. The component A will act as the matrix in fluid as is used for electronic devices [20,21]. Under this background, the component (denoted by A in the following context) with high viscosity will be defined as the continuous phase, no matter its fraction is high or low, and another component B, with low viscosity, will be modeled as the dispersed phase. This definition of continuous or dispersed phase does not represent the real micro-structures of two components, but reflects the degree of importance of components in their contributions to the viscosity of mixtures.

Another problem is the shape of unit cells. It can be imagined that the shape of dispersed fluid phase in a real fluid mixture will not be simple, fixed and easy to be experimentally justified. As a matter of fact, it is of no significance to know the real shape of dispersed phase since classification of continuous and dispersed phases here is not based on physical phenomenon but is to reflect their mechanistic characteristic in describing friction force in fluid flow. Such a consideration immediately leads to the choice of cube as the shape of unit cells of dispersed and continuous phases due to its simplified feature in the following development of theoretical model, in a Cartesian coordinate system.

The unit cell thus constructed is illustrated in Fig 1.

Fig. 1(a) displays the choice of cube as the unit-cell shape with sidelength a . Fig. 1(b) gives a whole unit cell containing dispersed phase (component with low viscosity) and continuous phase (component with high viscosity), in which x is the direction of fluid flow and y the direction of velocity gradient. The cube with sidelength b , denoting the dispersed phase, is centrally located in the cube with sidelength a . The ratio of b/a is determined by

$$\frac{b^3}{a^3} = \frac{v_B}{v_A + v_B} \quad (2)$$

where v is the volume fraction. In the case of binary system, $v_A + v_B = 1$. The macroscopic fluid is discretized into a lot of unit

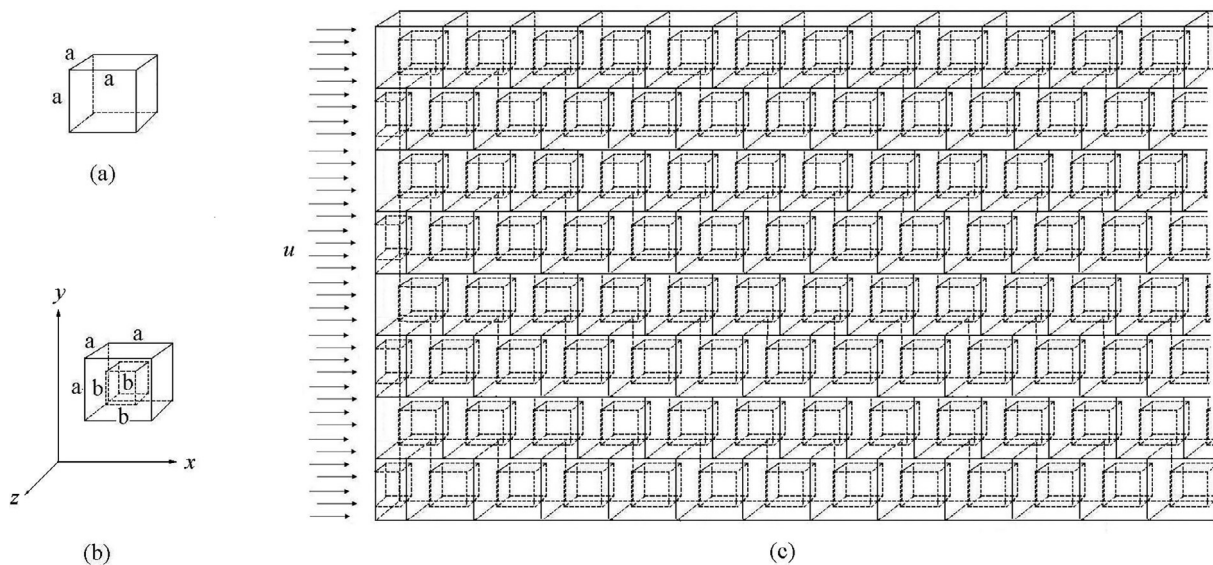


Fig. 1. discretization of binary molten salt. (a) shape of unit cell; (b) a whole unit cell of two component; (c) unit cell arrangement.

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