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Microscopic study and modeling of thermodiffusion in binary associating mixtures

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Thermodiffusion in associating mixtures is a complex phenomenon, owing to the strong dependence of the molecular structure of such mixtures on concentration. In this paper, we attempt to elucidate this phenomenon and propose a qualitative mechanism for the separation of species in binary associating mixtures. A correlation between the sign change in the thermal diffusion factor and a change in the molecular structure, mixture viscosity, and the excess entropy of mixing in such mixtures is established. To quantify this correlation, we modify our recently developed dynamic model based on the Drickamer nonequilibrium thermodynamic approach [M. Eslamian and M. Z. Saghir, Phys. Rev. E **80**, 011201 (2009)] and propose expressions for the estimation of thermal diffusion factor in binary associating mixtures. The prediction power of the proposed expressions, as well as other widely used models, are examined against the experimental data. The proposed theoretical expressions are self-contained and only rely on the viscosity data as input and predict a sign change in the thermal diffusion factor in associating mixtures.

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I. INTRODUCTION

Mass diffusion in a mixture of two or more components may occur due to any or a combination of the following forces: spatial gradient of concentration, temperature, and pressure within the mixture, bearing in mind that these gradients are coupled through the Gibbs-Duhem equation. The problem of our interest is thermodiffusion or Soret effect, which is the coupled heat and mass diffusion due to a temperature gradient.

At the presence of a temperature gradient and therefore thermodiffusion in a binary or multicomponent liquid system, when complete transport equations are written to describe the problem in the differential form, in addition to the molecular or Fickian mass diffusion coefficients, thermal diffusion coefficients are also considered as input parameters. The most reliable way of obtaining the thermal diffusion coefficients is through performing proper experiments. However, conducting experiments is expensive and impractical in some cases. Therefore, reliable theoretical models to predict the thermal diffusion coefficients or factors are highly desirable.

The physics of thermodiffusion in nonassociating mixtures, such as hydrocarbons, is much less complicated than in the associating mixtures such as alcohol-water mixtures. This statement is supported by the fact that thermodiffusion models, used to emulate thermodiffusion process and estimate the thermal diffusion coefficients, are generally more successful and capable in predicting the experimental data in nonassociating mixtures. None of the thermodiffusion models, in the general form, can predict a sign change in the thermal diffusion factor in associating mixtures. This may be attributed to a large degree of structural dependence of associating mixtures on concentration. In other words, the presence of the hydrogen bonding in such mixtures and the strong and varying interaction between the alike and unlike molecules and a possible rearrangement of the molecular structure at various concentrations play important roles in thermodiffusion in associating mixtures. A theoretical model has to be highly sophisticated to incorporate such effects, some of which still unraveled.

The most popular and capable thermodiffusion models that have been evaluated against the experimental data include the Drickamer and co-workers' model, e.g., [1–3], Haase model [4], Kempers model [5], Firoozabadi and co-workers' binary [6] and multicomponent model [7], and our recently developed dynamic model [8]. A review of the above mentioned and some other models is provided by the authors in Ref. [9]. The only expressions that can somehow predict a sign change in the thermal diffusion factor of alcohol-water mixtures are those of Saghir and co-workers, e.g., (Pan *et al.* [10] and Abbasi *et al.* [11]), which both should be considered as modified versions of Drickamer [1] and Shukla-Firoozabadi binary models [6]. Due to the relevance of Pan *et al.* [10] and Abbasi *et al.* [11] approaches, we critically review their works in detail in the following sections.

In addition to the theoretical models that have considered the thermodiffusion problem as a whole, continued theoretical and experimental investigations have helped understand some of other dark sides of this phenomenon. For instance, Wiegand and co-workers [12–14] noticed that the concentration at which the thermal diffusion factor vanishes is close to the concentration at which the water hydrogen bonds break down in the mixture. This is in fact an important finding in thermodiffusion in associating mixtures. Using the molecular-dynamics (MD) simulation approach, Rousseau and co-workers studied this problem as well. In one study, MD simulation approach combined with a nonequilibrium algorithm that allows maintaining a constant heat flow through the system and another algorithm that accounts for the molecular interactions, such as the hydrogen bonds, was used [15]. A very good agreement between the methanol-water experimental data and the MD simulations was observed including a sign change in the thermal diffusion fac-

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tor. However, MD still cannot explain the mechanism of thermodiffusion in such mixtures. To investigate this problem in the molecular level, Rousseau *et al.* [15] used the model of Prigogine and co-workers [16], which is based on the Eyring rate processes theory outlined in Ref. [17] and the activation energy of viscous flow concept. By varying the particle-particle interaction parameters in that model, they realized that the slope of the thermal diffusion factor with concentration may change from positive to negative and a sign change may occur. In their work, Rousseau *et al.* [15] mentioned about the inadequacy of models, such as Kempers, in that they assume that the system is in thermodynamic equilibrium and therefore miss the kinetic or dynamic effects. Nieto-Draghi *et al.* [18] employed a boundary-driven MD method to compute the thermal diffusion factor in several associating mixtures. In the boundary-driven method, there is no need to estimate the phenomenological coefficients and, therefore, more accurate results may be obtained. Their simulations are successful in predicting a sign change in the studied mixtures.

In all of above-mentioned studies, a fundamental and physical model that can describe a structural change in the species and mixture and its effect on thermodiffusion is still lacking. Hence, more systematic research is needed to address issues such as:

(1) How a continuous change in the concentration and therefore molecular structure of associating mixtures directly affects the thermal diffusion factor?

(2) To what extent, the existing thermodiffusion models are applicable to associating mixtures?

(3) How the structural changes in the mixture can be modeled and incorporated into the existing thermodiffusion models?

The objective of this paper is to attempt to answer the above questions. To do so, we study the molecular structure of selected associating mixtures at various concentrations. We establish a qualitative relationship between the molecular structure and thermodiffusion and propose expressions for the estimation of thermal diffusion factor in associating mixtures. In addition, we evaluate the performance of the existing models of Haase [4], Kempers [5], Shukla-Firoozabadi [6], and our recently developed model for nonassociating mixtures [8] against the experimental data.

II. BACKGROUND OF THE EXISTING MODELS

Although other somewhat unconventional and new approaches, such as the kinematic [19], hydrodynamic [20,21], fluctuation [22], Brownian motion [23], and statistical- or probability-based methods [24,25] have been also employed to model thermodiffusion, apparently so far only the statistical thermodynamic approach of Kempers [5] and the nonequilibrium thermodynamics approach of Prigogine [16] and Drickamer [1] can be practically used to estimate thermal diffusion factors in liquid solutions. Our previously developed model [8] and the expressions proposed here are based on the Drickamer nonequilibrium thermodynamics. Using the nonequilibrium thermodynamic framework, for an n-component system, mass or molar fluxes of $n-1$ components are independent and one can write the molar diffusion flux of component i (j_i) as a function of the gradients of temperature $\nabla \ln T$ and chemical potential $\nabla_T(\mu_k)$, and the net heat of transport Q_i^* and the phenomenological coefficients L_{ik} as follows (e.g., [9]):

$$j_i = -\sum_{k=1}^{n-1} L_{ik}[(Q_k^* - Q_n^*)\nabla \ln T + \nabla_T(\mu_k - \mu_n)], \tag{1}$$

where Q_i^* is the heat flow per mole of the diffusing component i required to be absorbed by the region to keep the temperature constant.

Due to the dependence of pressure, temperature, and concentration gradients, imposed by the Gibbs-Duhem relationship, if concentration and temperature gradients are applied on a system, a local pressure gradient will be induced at each point as well. Due to the smallness of the pressure diffusion, however, we neglect its effect on mass diffusion. Hence, for a binary system, the conventional diffusive molar flux equation may be written as follows:

$$j_1 = -cD\left[\nabla x_1 + \frac{\alpha x_1 x_2}{T}\nabla T\right], \tag{2}$$

where c is the molar density, D is the molecular mass diffusion coefficient, x_1 and x_2 are the mole fractions of components 1 and 2, and α is the thermal diffusion factor of component 1. At the presence of a spatial temperature gradient, at steady-state condition, the molar fluxes vanish. Therefore, Eqs. (1) and (2) and the Gibbs-Duhem relation at local constant pressure and temperature result in the following approximate equation for the thermal diffusion factor in a binary system:

$$\alpha = \frac{Q_1^* - Q_2^*}{x_1(\partial \mu_1/\partial x_1)}. \tag{3}$$

Based on the convention we used to define α in Eq. (2), if α (of component 1) obtained from Eq. (3) is positive, this component is enriched on the cold side of the solution. Note that even though an induced global pressure gradient due to temperature and concentration gradients has been neglected in our nonequilibrium thermodynamic approach, Semenov and Schimpf [21,22] developed a thermodiffusion model based on a local pressure gradient that is induced around the diffusing particles in a mixture. Comparison and validation of these two approaches deserve more investigation.

Although the derivation of the approximate expression for the thermal diffusion factor, i.e., Eq. (3) is straightforward and rational, the estimation of the thermal diffusion factor remains challenging because the quantity "the net heat of transport" is rather vague and dependent upon several local and global properties of the *flowing* mixture. One of the most widely used thermodiffusion models based on Eq. (3) is the model that has been initiated by Prigogine [16] and established by Drickamer and co-workers [1–3] and later modified and extended to multicomponent mixtures by Firoozabadi and co-workers [6,7]. This model correlates thermal diffusion factor with the thermostatic properties of the mixture and a matching parameter, which is a dynamic property, but it is usually considered as a constant (=4). The prediction ability of this model will be examined in this paper. Drickamer model [1–3] has benefited from the Eyring theory of rate processes [17]. Eyring and co-workers independently developed thermodiffusion models as well, e.g., Mortimer and Eyring [24] and Prager and Eyring [25]; however, a statistical- and probability-based approach has been followed rather than the linear nonequilibrium approach, although both Drickamer and Eyring thermodiffusion models employ the concept of the activation energy. It seems that the combination of the nonequilibrium thermodynamic-based model of Drickamer and the activation energy of viscous flow concept of Eyring has been qualitatively successful when tested on various liquid mixtures. As shown by several workers (e.g., [6–8]), the Drickamer-Eyring modeling approach is quite successful for hydrocarbon systems. Its prediction power when tested against complex systems is also rather acceptable. For instance, Schimpf and Giddings [26] applied the Emery and Drickamer expression [27] on several polymer mixtures and obtained a good qualitative match between theory and their experimental data. Also, Winter and Drickamer [28] applied their model on liquid metal systems and found a rather good prediction power for the model. This suggests that the Drickamer-Eyring modeling approach potentially may be applicable to associating mixtures as well, if required modifications and refinements are made to account for the complex structure of associating mixtures, which also changes with concentration.

The Haase [4] and Kempers [5] thermodiffusion models, which are very similar but written in mass and volume frames of reference, respectively, are frequently used as well. Derivation of Haase and Kempers expressions has been done by Kempers following a statistical thermodynamic approach rather than the nonequilibrium thermodynamics approach given above. These models correlate the thermal diffusion factor with the species partial molar enthalpies and are applicable to gas, liquid, and solid mixtures, whereas Drickamer-type models are limited to liquid mixtures.

Recently, inspired from the work of Drickamer (e.g., [3]), we have proposed a model correlating the net heat of transport with the activation energy of viscous flow [8]. This model has been extended to multicomponent mixtures as well [29]. We have assumed that the net heat of transport of each component equals to (or correlates) with the activation energy of viscous flow of that component in pure state (E^{vis}) at given mixture pressure and temperature. E^{vis} has been defined by Eyring's rate theory [17] and is proportional to the natural logarithm of liquid viscosity. The main expression of that model is obtained from Eq. (3) and written as follows:

$$\alpha = \frac{E_1^{vis} - E_2^{vis}}{x_1(\partial \mu_1/\partial x_1)}. \qquad (4)$$

Equation (4) was successful in predicting the experimental data in nonassociating mixtures [8]. This is because some of the molecular features that influence the thermodiffusion phenomenon, such as the molecular size, shape, and moment of inertia, to some extent, directly affect the viscosity data and as a result the activation energy of viscous flow. However, due to the complex structure of associating mixtures and since the viscosity and the activation energy of viscous flow of each component in pure state [as assumed in Eq. (4)] differ significantly from that in the mixture, Eq. (4) is not adequate for associating mixtures. In fact, there is no model, in its original form, that could predict a sign change in such mixtures, although several attempts have been made to improve the prediction ability of the existing models for associating mixtures. For instance, Saghir and co-workers [10,11,30] followed a semiempirical approach to modify the matching parameter in Shukla-Firoozabadi expression [6]. In 2006, Pan *et al.* [30] used the perturbed-chain statistical associating fluid theory (PC-SAFT) equation of state (EOS) to predict the thermodynamic properties of the constituent species in associating mixtures such as alcohol-water mixtures. They combined the PC-SAFT EOS with Haase [4], Kempers [5], and Shukla-Firoozabadi [6] binary expressions to predict the thermal diffusion factor. Comparison against the experimental data revealed that, none of the models could predict a sign change in thermal diffusion factor. By inspecting the model results and the experimental data, they noticed that if the matching parameter (τ, which is the ratio of vaporization energy to activation energy of viscous flow) instead of 4, which is suggested by Drickamer and Eyring, is chosen to be 20, for low and moderate water mole fractions, a good match is obtained; but still a sign change in the thermal diffusion factor could not be predicted. However, a value of 20 for the matching parameter (τ) of associating liquids, which has a physical meaning (the ratio of the vaporization energy to the activation energy of viscous flow), is not justified. Later, Pan *et al.* [10] proposed several semiempirical mixing rules to convert the matching parameter (τ) in Shukla-Firoozabadi expression [6] into a variable parameter that changes with concentration. This is because in a binary associating mixture, due to the strong interaction between the molecules and a significant change in the molecular structures, assuming a constant or even variable τ for each component in the pure state is not adequate, as the viscosity of the mixture changes anomalously with concentration and, therefore, the activation energy of viscous flow of each component in the mixture is significantly different from that in the pure state. Pan *et al.* [10] obtained two constants of their correlation empirically, i.e., by extrapolation of the existing experimental data, when the mole fractions of the components approach 0. They managed to predict a sign change in the alcohol-water mixtures, although the error in the magnitude of the thermal diffusion factor was significant.

Abbasi *et al.* [11] modified the approach followed by Pan *et al.* [10] and proposed semiempirical expressions for estimating the activation energy of viscous flow of each component in several associating mixtures. The change in the activation energy of viscous flow is in fact a response to a change in the molecular structure of the mixture components. Their expressions combined with the Shukla-Firoozabadi model [6] are successful in predicting a sign change and estimating the magnitude of the thermal diffusion factor in alcohol-water and acetone-water mixtures, with reasonable errors. However, similar to Pan *et al.*'s [10] work, their correlations still rely on finding two constants based on the existing thermal diffusion experimental data. Besides, their

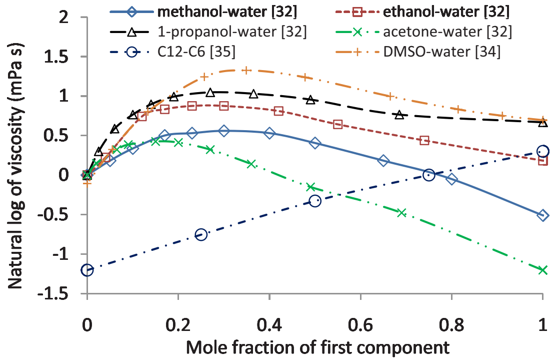

FIG. 1. (Color online) Anomalous behavior of viscosity in associating mixtures compared to nonassociating mixtures: natural logarithm of viscosity of selected aqueous mixtures and an *n*-alkane mixture (C12-C6) versus concentration.

physical interpretation of the activation energy of viscous flow requires reconsideration, as the activation energy of viscous flow defined by Eyring [17] is directly related to the viscosity of the liquid. The trend of the variation in the activation energy of viscous flow with concentration, estimated by Abbasi *et al.* [11] correlations (not shown here), strongly disagrees with the variation in viscosity data with concentration shown in Fig. 1 (the viscosity data in Fig. 1 are taken from Refs. [31–35]). Activation energy of viscous flow is somewhat proportional to the natural logarithm of liquid viscosity. Abbasi *et al.*'s [11] estimations of the activation energy of viscous flow in associating mixtures predicted a drastic decrease (up to several orders of magnitude) in the activation energy of viscous flow with concentration, whereas the logarithm of the viscosity data versus concentration shown in Fig. 1 reveals a much smaller change in the logarithm of viscosity (proportional to activation energy of viscous flow) with concentration.

III. PROPOSED MODEL

Despite the relative success in estimating the thermal diffusion factors by semiempirical correlations of Pan *et al.* [10] and Abbasi *et al.* [11], what are still lacking are the sound physical model and mathematical framework that link the activation energy of viscous flow and the net heat of transport with the concentration-dependent molecular structure in associating mixtures.

In Eq. (4), the variation in concentration has an insignificant effect on the computed thermal diffusion factors [8], and in fact, to some extent, this is the case in nonassociating mixtures, in which molecules behave individually in the mixture and a change in the mixture concentration mainly causes a change in the population of each species. In contrast, in associating mixtures the molecular structure of the mixture is highly dependent upon the relative mole fraction of the components. Before proposing expressions and a mechanism for thermodiffusion in associating mixtures, a brief review of the structure of aqueous associating mixtures studied here is necessary. Table I lists these mixtures as well as the sources of the thermal diffusion experimental data used for model verification. These mixtures include methanol-water [3], ethanol-water [3,36], 1-propanol-water [14], acetone-water [12], and dimethyl sulfoxide (DMSO)-water [12].

TABLE I. Selected mixtures studied in this work.

Binary mixture	Temperature (°C)	Ref.
Methanol-water	40	[3]
Ethanol-water	25	[3,36]
1-Propanol-water	25	[14]
Acetone-water	25	[12]
DMSO-water	25	[12]

A. Molecular structure of associating species and mixtures

Thermodiffusion in associating mixtures is significantly different from that in nonassociating mixtures, such as *n* alkanes. This is mainly because both water and alcohols, for instance, in the pure state and in the mixture have hydrogen bonds and form complex clusters. This causes such associating mixtures to exhibit several anomalousness in some of their properties, such as viscosity. In nonassociating mixtures, such as hydrocarbons, the mixture viscosity usually varies linearly with mole fraction (e.g., do-decane-hexane (C12-C6) shown in Fig. 1 [35]). In associating mixtures, on the other hand, the viscosity graph has a bell shape and increases with the increase in mole fraction of either component until a maximum value is reached ($x_w \sim 0.7-0.8$) (see Fig. 1). The anomalous change in the viscosity of associating mixtures is attributed to a significant change in the structure of such mixtures with concentration in the molecular level. Song and Peng [32] attributed this anomalous behavior of viscosity to the formation of micelles of alcohol or acetone in water because of the hydrophobic attraction between the hydrocarbon chains. The micelles surfaces are surrounded by hydration layers and this may cause an increase in the viscosity because the hydration layers are more viscous and denser than bulk water.

In general, in the microscopic level, the structural change in associating aqueous mixtures, such as alcohol-water, may be attributed to the presence of hydrogen bonds among the OH groups of water and alcohol and other water molecules and the opposing effect of hydrophobic interactions among the alkyl groups of alcohol molecules in such mixtures [37]. Variation in temperature and concentration alters the strength and configuration of hydrogen bonds and molecular structure. In pure water, the presence of hydrogen bonds results in the formation of water clusters, which are composed of several molecules. In alcohol-water mixtures (also acetone-water and DMSO-water mixtures), depending on the temperature and concentration and the interaction between water and alcohol molecules and clusters, the original clusters may be altered and new complex clusters may form. Although water and alcohols are miscible, their mixture is not homogenous. Experimental and theoretical investigations have revealed that the binary alcohol-water mixtures in the microscopic levels are mixed incompletely and association and/or probably restructuring of the molecules result in the coexistence of water-rich and alcohol-rich clusters in the system. These complexities and uncertainties make the modeling of thermodiffusion process in such mixtures really challenging.

Using x-ray emission spectroscopy, it has been deduced that molecules in the pure liquid methanol are predominantly hydrogen bonded and form open chains and closed chains (rings) with six and/or eight molecules of equal abundance. In the mixture, the bonded clusters are composed of both water and methanol molecules and water molecules seem to bridge methanol chains to form closed or semiclosed ringlike water-methanol clusters [38,39]. Ethanol consists predominantly of winding chains, similar to methanol. Closed chain hexamer clusters may survive in small quantities within the liquid at room temperature [40]. In ethanol-water mixture, depending on the concentration, the cluster structure of water or ethanol may prevail or both clusters may breakdown and new hybrid clusters form. Three major cluster structures in the mixture over the entire concentration span have been identified [41]. For pure water, clusters composed of 21 and 28 molecules are predominant. At low ethanol concentration (<10 vol %), overall, the structure of pure water prevails in the mixture, and some of the water molecules in water clusters are replaced by ethanol molecules. At 10 vol % ethanol concentration, separate water-rich and ethanol-rich clusters start to form in the microscopic level. In a wide range of ethanol concentration from 10 to 90 vol %, both water and ethanol self-associating clusters coexist. In pure ethanol, ethanol tetramer clusters are observed. Addition of up to 10 vol % of water to ethanol promotes self-association of ethanol molecules and larger ethanol clusters form, containing several water molecules.

In pure 1-propanol, hydrogen-bonded chain clusters of 1-propanol molecules are formed [42]. In 1-propanol mole fraction range of $0.7<x_{1\ \mathrm{pr}}\leq 1$, the 1-propanol chain clusters are dominant in binary 1-propanol-water mixtures. In $0.1<x_{1\ \mathrm{pr}}<0.7$, both 1-propanol chains and water clusters coexist in the mixtures in a heterogeneous fashion and the interactions between 1-propanol and water molecules are insignificant. When $x_{1\ \mathrm{pr}}\leq 0.1$ (where the sign of the thermal diffusion factor changes), the tetrahedral-like structure of water predominates in 1-propanol-water mixtures.

Takamuku *et al.* [43] summarized the results they obtained based on a series of studies performed on the structure of alcohol-water mixtures. At room temperature, with an increase in alcohol concentration, the structure of alcohol-water clusters starts to deviate from the tetrahedral-like structure of water clusters to hydrogen-bonded alcohol chains at a specific mole fraction for each alcohol. The transition mole fractions for methanol, ethanol, 1-propanol, and 2-propanol are 0.3, 0.2, 0.1, and 0.1, respectively. Thus, the larger the hydrophobic group, the more rapidly the tetrahedral-like structure of water is disturbed with increasing the alcohol concentration. We will investigate a possible correlation between these structural changes and the sign change in thermal diffusion factors of the studied associating mixtures.

In contrast to alcohols, no intermolecular hydrogen bonds can form in pure acetone. However, in aqueous acetone mixture, hydrogen atoms of water can hydrogen bond with oxygen atoms of either water or acetone [44]. Toryanik and Taranenko [45] proposed a two-dimensional model for the structure of water-acetone mixtures. Based on that model, at low concentrations of acetone, each acetone molecule is surrounded by a few water molecules, forming two hydrogen bonds with two water molecules in a cluster. As acetone concentration increases, the number of free water molecules decreases and at a specific acetone mole fraction ($x_a=0.22$), all water molecules participate in closed clusters. If the concentration of acetone is further increased, there will be inadequate water molecules to form closed clusters, but the hydrogen bonds between acetone and water molecules remain intact. This model has been verified by recent works, as well [44].

DMSO, a polar solvent, is miscible in water, although the binary DMSO-water mixture is heterogeneous in the molecular level. At high water concentrations ($x_W\sim 0.97$), small DMSO molecules tend to occupy cavities within the structure of water clusters without disturbing the hydrogen bond network of water clusters. The water mole fraction at which a sudden destruction of water clusters and the formation of DSMO clusters occurs ranges from 0.91 to 0.93. Below this water mole fraction, there is not enough room inside water clusters to accommodate more DMSO molecules. Therefore, due to the hydrophobic interactions among DMSO molecules in aqueous mixtures and the much stronger hydrogen bonding between water and DMSO species, the hydrogen bond network of water structures deteriorates and the more favored DMSO clusters form [46].

Using the thermal diffusion factors experimental data [3,12,14,36], the mole fraction of the nonwater species (x), at which the thermal diffusion factor vanishes, and its sign changes have been extracted and listed in Table II. Here we seek out whether there is a correlation between the sign change in thermodiffusion and mixture viscosity and/or a change in the structure of the selected associating mixtures. Therefore, the approximate mole fractions of the nonwater component, at which the mixture viscosity attains its maximum value and a rather significant change occurs in the molecular structure of the mixtures are also listed in Table II. Moreover, since the structural order of a mixture, to some extent, is quantified by the excess entropy of mixing, we have obtained the mole fraction at which this quantity (negative for mixtures studied here) becomes a minimum [47–49]. Table II shows that at concentration wherein the mixture viscosity reaches its maximum value, the entropy of mixing becomes a minimum and a major change occurs in the molecular structure of the mixtures. In addition, the mole fraction at which the thermal diffusion factor vanishes is smaller but still close to aforementioned mole fractions. In conclusion, we may deduce a correlation between the measurable viscosity data and the thermal diffusion factor. This is a basis for the modification of our recently developed thermal diffusion model for nonassociating mixtures [8].

Although the above-mentioned research works confirm a heterogeneous mixing and restructuring of molecules in associating mixtures, Dixit *et al.* [50] particularly stated that mixing of water and methanol results in incomplete mixing and *not* water restructuring. They studied a mixture with methanol to water mole fraction of 7:3 and found that 13%

TABLE II. Approximate mole fraction of nonwater species (x) at which several major changes occurs in the behavior of the studied binary mixtures.

Binary mixture	$\alpha=0$	Mixture structure changes[a] at	Viscosity attains its maximum value at	Excess entropy[b] of mixing attains its minimum value at
Methanol-water	0.15	$x=0.3$	$x=0.3$ [c]	$x=0.35$ [d]
Ethanol-water	0.14	$x=0.2$	$x=0.28$ [c]	$x=0.3$ [e]
1-Propanol-water	0.08	$x=0.1$	$x=0.26$ [c]	Not available
2-Propanol-water	0.1	$x=0.1$	$x=0.26$ [c]	Not available
Acetone-water	0.11	$x=0.2$	$x=0.17$ [f]	$x=0.28$ [g]
DMSO-water	0.2	$x=0.08$	$x=0.32$ [h]	Not available

[a] Reference [43].

[b] Excess entropy is the difference between entropy of a real mixture and that of the ideal mixture.

[c] Reference [32].

[d] Reference [47].

[e] Reference [48].

[f] Reference [33].

[g] Reference [49].

[h] Reference [34].

of water molecules exist as isolated water clusters and the rest of water molecules participate in the formation of methanol-water clusters (rings or chains). Based on the forgoing discussion on the molecular structure of associating mixtures, we may propose a mechanism for species separation and segregation in thermodiffusion in associating mixtures. Generally speaking, when a temperature gradient is applied on a homogenous mixture, the thermal field exerts forces on all molecules in a direction opposite to that of the thermal field, i.e., all molecules are naturally pushed toward the cold side. However, in response to the species migration, a concentration gradient is developed gradually as well such that at a steady state, forces due to the temperature and concentration gradients become balanced. In nonassociating mixtures, especially those with simple and rather spherical molecules, species migration is affected by molecular weight and size, moment and inertia of molecules, and the interaction between alike and unlike molecules is probably less significant [Fig. 2(a)]. In contrast, in associating mixtures, molecular interactions and a continuous change in the molecular structure play an important role in separation of molecules [Fig. 2(b)]. In this figure, for simplicity we have assumed a dimer structure for water clusters, whereas in reality isolated water clusters in pure state are composed of more molecules. Nonetheless, note that in hybrid alcohol-water mixtures, only few water molecules participate in the clusters [38]. In Fig. 2(b), we have assumed that a portion of water and methanol molecules remain isolated in the mixture, whereas the rest of the molecules form hybrid methanol-water clusters. In the presence of a temperature gradient, it is easier for the isolated molecules or clusters to move in the mixture toward either the cold side or the hot side. The response of the hybrid clusters, however, is more complicated. Imagine at a given mixture concentration water molecules at a steady state are enriched on the cold side, and the methanol molecules on the hot side (low to moderate water mole fractions). Initially, the temperature field applies forces on isolated and alcohol-water clusters in a direction from the hot side to the cold side. However, once a large enough concentration gradient has formed, the temperature and concentration gradients will apply forces on water and methanol molecules of a hybrid cluster most likely in opposite directions. This may cause the breakdown of the cluster due to opposing forces, or the cluster may move toward one end or even remains in its place and intact. Also, note that the local temperature may have an effect on hydrogen bonds, as at higher temperatures hydrogen bonds break easier [41].

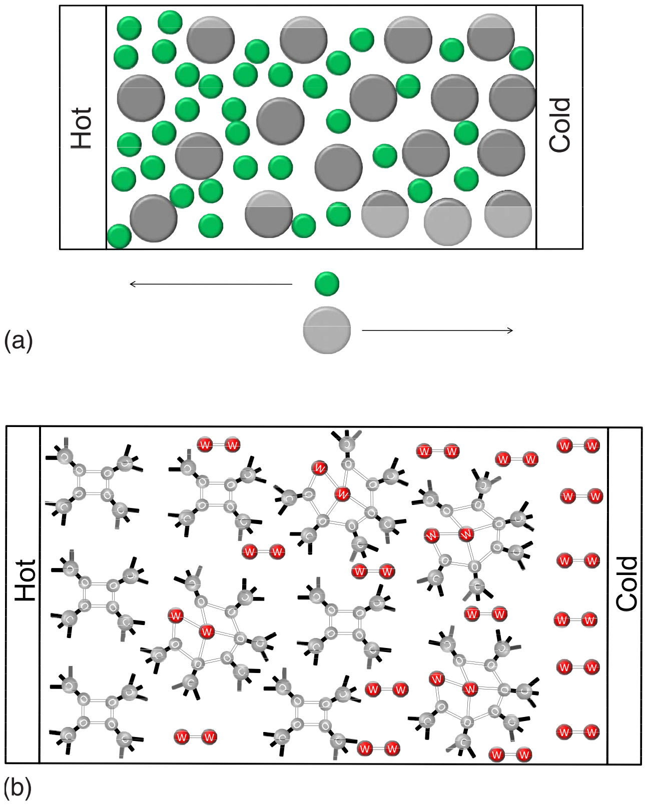

FIG. 2. (Color online) Thermodiffusion in (a) a typical nonassociating mixture versus (b) thermodiffusion in an associating mixture (methanol-water). Isolated water clusters have been assumed to be dimers and methanol clusters to be tetramers. The hydrogen atoms are not shown; "=" symbols denote the hydrogen bonds between molecules.

In the next section, we attempt to incorporate the effect of concentration on the molecular structure in associating mixtures into our model developed mainly for nonassociating mixtures [8]. Since the molecular structure in such mixtures is still in debate and has been only explained qualitatively, it is unrealistic to expect a model to quantitatively mimic the thermodiffusion phenomenon, which is highly dependent upon the mixture molecular structure.

B. Model development

In the development of Eq. (4), the net heat of transport of each component has been approximated by the activation energy of viscous flow of the same component in the pure state, regardless of the mixture concentration. This assumption might be acceptable for nonassociating mixtures, which undergo a minimum change in the molecular structure with variation in concentration. Obviously Eq. (4) cannot predict a sign change, as regardless of concentration, it always returns either a positive or negative value depending on the relative magnitudes of E_1^{vis} and E_2^{vis}. In order to take into account the effect of concentration on the activation energy of viscous flow, we may follow two approaches as outlined below.

1. Relative activation energy of viscous flow approach

Equation (4) may be alternatively written in other frames of reference as proposed by Eslamian and Saghir [8] following the work of Drickamer and co-workers [2]. Theoretically, the right choice of the frame of reference for comparison with the experimental data is still in debate. In Ref. [8], in addition to Eq. (4), we have also proposed the following expressions for nonassociating mixtures in mass and volume frames of reference, respectively:

$$\alpha = \frac{M_2 E_1^{vis} - M_1 E_2^{vis}}{(M_1 x_1 + M_2 x_2) x_1 (\partial \mu_1 / \partial x_1)}, \tag{5}$$

$$\alpha = \frac{\bar{V}_2 E_1^{vis} - \bar{V}_1 E_2^{vis}}{(\bar{V}_1 x_1 + \bar{V}_2 x_2) x_1 (\partial \mu_1 / \partial x_1)}, \tag{6}$$

where M_1 and M_2 are the molecular weights and $\bar{V}_1$ and $\bar{V}_2$ are the partial molar volumes of components 1 and 2, respectively. In contrast to Eq. (4), potentially the sign of the thermal diffusion factors obtained from Eqs. (5) and (6) may change, depending on the relative molecular weights and molar volumes of the two species. Therefore, these equations seem to be more suitable for associating mixtures.

The activation energy of viscous flow of a mixture (E_{mix}^{vis}) is proportional to the natural logarithm of the mixture viscosity. As mentioned before, in associating mixtures, viscosity and activation energy of viscous flow vary anomalously with concentration (see Fig. 1). This anomaly has to be accounted for somehow. In the absence of a model to directly estimate the net heat of transport or the activation energy of viscous flow of a component in the mixture, in Eqs. (5) and (6), we replace E_i^{vis} by $E_i^{vis} - E_{mix}^{vis}$. In other words, the activation energy of viscous flow of a component in the mixture is estimated by the difference between the activation energy of viscous flow of the mixture at a given concentration and that in pure state. Therefore, Eqs. (5) and (6) are modified as follows:

$$\alpha = \frac{M_2(E_1^{vis} - E_{mix}^{vis}) - M_1(E_2^{vis} - E_{mix}^{vis})}{(M_1 x_1 + M_2 x_2) x_1 (\partial \mu_1 / \partial x_1)}, \tag{7}$$

$$\alpha = \frac{\bar{V}_2(E_1^{vis} - E_{mix}^{vis}) - \bar{V}_1(E_2^{vis} - E_{mix}^{vis})}{(\bar{V}_1 x_1 + \bar{V}_2 x_2) x_1 (\partial \mu_1 / \partial x_1)}. \tag{8}$$

The values of the mixture activation energy of viscous flow at various concentrations are given in Table III. These values were calculated using the mixture viscosity data [31–35] obtained at various concentrations and temperatures, following the same method used for pure components [9]. Note that based on the Eyring reaction-rate theory [17], E_{mix}^{vis} is the energy required to overcome the mixture viscosity and cause the bulk mixture to flow. Equations (7) and (8) imply that the energy required for species segregation by thermodiffusion ($E_i^{vis} - E_{mix}^{vis}$) is different from but correlated with the energy required to cause the mixture to flow (E_{mix}^{vis}) as a whole. The validity and performance ability of above expressions are examined in the "results and discussions" section.

2. Mixture viscosity approach

Based on Eyring's rate theory [17], viscosity (η) of a liquid is related to the activation energy of viscous flow (E^{vis}) as $\eta = (A/V)\mathbf{exp}(E^{vis}/RT)$, where A may be assumed a constant, V is the fluid's molar volume, R is the universal gas constant, and T is the fluid temperature. Experimental data show that when the natural logarithm of η (or ηV) is plotted against $1/RT$ over a limited temperature range, a line is obtained whose slope equals E^{vis}. In other words, the activation energy of viscous flow of each component in pure state may be expressed as follows:

$$E_i^{vis} \sim \left(\frac{\partial \ln \eta}{\partial (1/T)} \right). \tag{9}$$

For a nonassociating mixture, such as C12-C6 shown in Fig. 1, the natural logarithm of viscosity varies linearly with concentration. In other words, the mixture viscosity is only dependent upon the mole fraction of each species. In associating mixtures (shown in Fig. 1 also), however, viscosity varies anomalously with concentration indicating that with a change in concentration, the structure of the mixture and the way molecules interact with each other change. Therefore, we may argue that the activation energy of viscous flow in an associating mixture may be considered to be proportional to the rate of change in the natural logarithm of mixture viscosity with respect to concentration,

$$E_{mix}^{vis} \sim \left(\frac{\partial \ln \eta_{mix}}{\partial x} \right). \tag{10}$$

Equation (9) has been already used to obtain the activation energy of viscous flow of each component in pure state required for the calculation of the thermal diffusion factor ac-

TABLE III. Activation energies of viscous flow of selected aqueous mixtures calculated at various mixture concentrations at given temperatures.

Methanol-water, at T=40 °C

Mole fraction[a]	E^{vis} (J/mole)	Mole fraction	E^{vis} (J/mole)
x=0.0	15384	x=0.675	15500
x=0.125	19000	x=0.75	14406
x=0.25	20358	x=0.875	12500
x=0.375	19500	x=1.0	10288
x=0.5	18022		

Ethanol-water, at T=25 °C

Mole fraction[a]	E^{vis} (J/mole)	Mole fraction	E^{vis} (J/mole)
x=0.0	16896	x=0.6	19677
x=0.1	22000	x=0.8	17000
x=0.2	24692	x=0.9	15500
x=0.4	22254	x=1.0	13871

1-Propanol-water, at T=25 °C

Mole fraction[a]	E^{vis} (J/mole)	Mole fraction	E^{vis} (J/mole)
x=0.0	16896	x=0.5	24118
x=0.125	25500	x=0.675	22000
x=0.25	27525	x=0.75	21307
x=0.3	27115	x=0.875	20000
x=0.4	25500	x=1.0	18163

Acetone-water, at T=25 °C

Mole fraction[a]	E^{vis} (J/mole)	Mole fraction	E^{vis} (J/mole)
x=0.0	16896	x=0.5	13475
x=0.06	20001	x=0.7	11003
x=0.14	20869	x=0.85	8076
x=0.3	17715	x=1.0	6892

DMSO-water, at T=25 °C

Mole fraction[a]	E^{vis} (J/mole)	Mole fraction	E^{vis} (J/mole)
x=0.0	16896	x=0.478	19884
x=0.133	19943	x=0.665	17036
x=0.257	21990	x=0.814	15451
x=0.349	21681	x=1.0	10770

[a] Mole fraction of the first component, i.e., the nonwater component.

cording to Eq. (4). To incorporate the effect of the mixture viscosity on the overall thermal diffusion factor, we propose the following modified expression:

$$\alpha = -\frac{E_1^{vis} - E_2^{vis}}{x_1(\partial \mu_1/\partial x_1)} \frac{\partial \ln \eta_{mix}/\eta_0}{\partial x_1}, \qquad (11)$$

where η_0 is a reference viscosity to make the second term in Eq. (11) dimensionless (here η_0 is assumed to be equal to water viscosity, which is 1cP at room temperature). Figure 1 shows that in nonassociating mixtures, the derivative of the natural logarithm of mixture viscosity with respect to mole fraction is a constant number, whereas in associating mixtures, its magnitude and sign change with concentration. Therefore, Eq. (11) is able to predict a sign change in thermal diffusion factor, as shown in the results and discussion section. The sign changes when the derivative of the natural logarithm of viscosity versus concentration vanishes. This is justified, as according to the findings of the previous section, listed in Table II, the sign of the thermal diffusion factor changes almost when the mixture viscosity attains its maximum value. The negative sign in Eq. (11) has been introduced empirically and its physical meaning is closely related to the variation in the natural logarithm of the mixture viscosity with respect to the mole fraction of the first component (nonwater component in this study).

IV. RESULTS AND DISCUSSION

Simplified versions of Haase [4] and Kempers [5] models, as outlined in Ref. [8], Shukla-Firoozabadi binary expression [6], our expressions proposed for nonassociating mixtures [8], as well as Eqs. (7), (8), and (11) developed in this work are evaluated against the experimental data (see Table I).

Cubic plus association and PC-SAFT are two popular EOSs that are applicable to associating mixtures, as they directly account for the hydrogen bonding interactions. In this study, all models are equally linked with the PC-SAFT EOS. Pan *et al.* [30] investigated the capability of PC-SAFT EOS in predicting the density and residual partial molar enthalpy of several aqueous alkanol mixtures. They found a very good agreement between the measured density data and the PC-SAFT EOS predictions, when the mole fraction of the alcohols was greater than 0.4. For low alcohol concentration mixtures, the error for density predictions was larger but well below 10%. Since a great deal of approximation is already involved in the development of thermodiffusion models, the 10% error associated with the PC-SAFT EOS is considered acceptable. The required input parameters for PC-SAFT EOS are taken from Ref. [10]. For water molecules, a 4C scheme is used, where a 4C molecule refers to a molecule with two equivalent electron donor and two electron acceptor sites. For all associating nonwater molecules, a 2B scheme has been employed, where a 2B molecule represents a molecule with one-electron donor and one-electron acceptor sites. The binary interaction parameters for alcohols and acetone were taken from Refs. [10,11], respectively. For DMSO, the binary interaction coefficient was unavailable and therefore was assumed 0. The binary interaction coefficients, if known, improve the accuracy of the EOS.

The Haase [4] and Kempers [5] models largely overestimate the thermal diffusion factors of the studied associating mixtures. Therefore, their corresponding results are only shown in Table IV. Table IV also contains the results of Eq. (7) of this work and Eq. (8) of Ref. [8]. The experimental data, predictions of Shukla-Firoozabadi formula, our nonassociating expression [Eq. (4)], and the expressions (8) and (11) are shown in Figs. 3–7. These figures display variation

TABLE IV. Thermal diffusion factor estimated using several models (not given in the figures).

x [a]	Haase [[4]]	Kempers [[5]]	Equation (8) of Eslamian-Saghir [[8]]	This work [Eq. (7)]
		Methanol-water		
0.125	−13.9	−19.2	−4.2	−0.84
0.25	−14.4	−19.7	−4.4	−0.47
0.375	−14.8	−20.1	−4.7	−0.75
0.5	−14.4	−19.6	−4.7	−1.18
0.675	−12.5	−16.9	−4.2	−1.7
0.75	−11.3	−15.4	−3.9	−1.8
0.875	−9.3	−12.7	−3.35	−1.92
		Ethanol-water		
0.1	−31	−38	−7.15	2.2
0.2	−35	−43	−8.5	4.7
0.4	−38	−47.7	−9.9	3.1
0.6	−26.1	−33.6	−7.3	0.6
0.8	−14.9	−19.7	−4.5	−0.7
0.9	−11.4	−15.2	−3.62	−1.0
		1-Propanol-water		
0.125	−22.8	−27.8	−4.8	4.8
0.25	−25.4	−31.2	−5.1	6.7
0.3	−27	−33	−5.8	6.9
0.5	−28	−34.5	−6.1	5.1
0.675	−21	−26	−4.8	2.8
0.75	−18	−22.4	−4.1	2
0.875	−13.8	−16.9	−3.2	1.1
		Acetone-water		
0.06	−77	−88	−19.9	−2.1
0.14	−213	−244	−59.4	−2.3
0.5	−172	−203	−59.5	−30.7
0.7	−33.6	−39	−12.9	−8.2
0.85	−17.5	−21	−7.3	−5.7
		DMSO-water		
0.055	−74	−84	−16.6	−2.7
0.133	−190	−217	−44.8	1.1
0.665	−40	−48	−12.6	−2.5
0.814	−20.1	−24	−6.6	−2
0.911	−14	−17	−4.9	−1.7

[a] Mole fraction of the first component in the mixture.

in the thermal diffusion factor of the first component (nonwater component) versus the mole fraction of the same component. All mixtures are at the atmospheric pressure and 25 °C, except for the methanol-water mixture, which is at 40 °C.

Figures 3–5 show a very similar trend and magnitude for the measured thermal diffusion factor in aqueous mixtures of methanol, ethanol, and 1-propanol. This is due to the similarity of the molecular structure of these alcohols. Figures 6 and 7 show that overall, the trend of the variation in the measured thermal diffusion factor of aqueous acetone and DMSO mixtures with concentration is similar to that of alcohol-water mixtures, although the acetone-water mixture has a larger thermal diffusion factor at moderate water concentrations and the graph has a clear minimum at acetone mole fraction of a about 0.5–0.6.

For all mixtures, the sign of the thermal diffusion factor changes at rather small concentrations of the nonwater com-

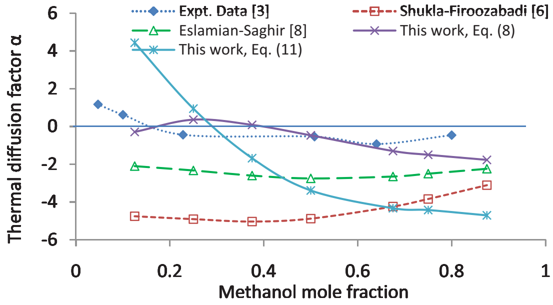

FIG. 3. (Color online) Thermal diffusion factor of methanol in methanol-water mixture versus methanol mole fraction: performance of several models compared with experimental data. $T=40\ ^\circ\mathrm{C}$, $P=1$ atm.

ponent. At low concentrations of alcohols, acetone and DMSO, the measured thermal diffusion factors are positive and therefore these species migrate to the cold side, whereas water moves to the hot side. After a sign change occurs, it becomes the opposite. This implies that in mixtures with low alcohol/acetone/DMSO concentration, these molecules/clusters move in the direction of the heat transfer from the hot side to the cold side. Note that water is the denser component in these associating mixtures; in nonassociating mixtures, usually the denser component is enriched on the cold side because in such mixtures the molecules are activated and move individually and not as clusters [Fig. 2(a)]. In associating mixtures with low to medium water mole fraction, in fact, this is the case and water is enriched on the cold side. When water concentration is high, water anomalously migrates to the hot side.

Both Table IV and Figs. 3–7 show that the Haase [4], Kempers [5], and Shukla-Firoozabadi [6] formulas fail to predict a sign change in thermal diffusion factors; they highly overestimate the magnitude of the thermal diffusion factors as well. Our formula previously developed and used for nonassociating mixtures [8] fails to predict a sign change; nevertheless, for low to moderate water concentrations, it fairly estimates the magnitude of the thermal diffusion factors. Our proposed expressions in this work, i.e., Eqs. (7), (8), and (11) predict a sign change, although at different mole fractions. Equation (11) shows the best predictive power. In fact, the way we have derived Eq. (11) necessitates a change in the sign of the thermal diffusion factor when the mixture viscosity reaches its maximum value. Also note that the graphs of the thermal diffusion factors based on Eq. (8) have a maximum because this expression incorporates the activation energy of viscous flow of the mixtures E_{mix}^{vis}, which have a maximum as well.

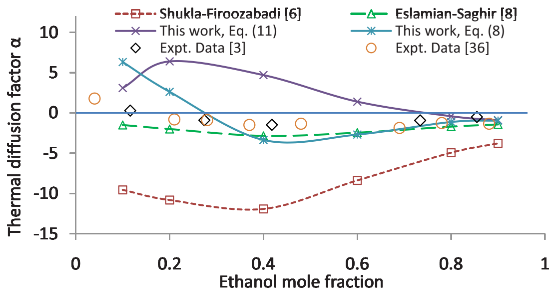

FIG. 4. (Color online) Thermal diffusion factor of ethanol in ethanol-water mixture versus ethanol mole fraction: performance of several models compared with experimental data. $T=25\ ^\circ\mathrm{C}$, $P=1$ atm.

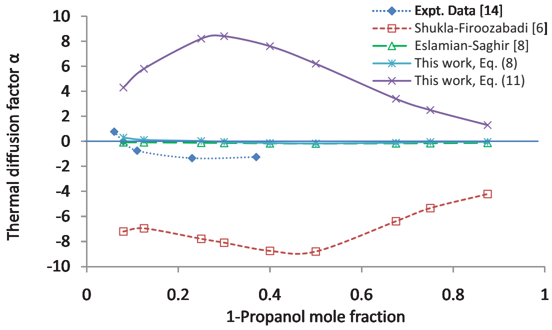

FIG. 5. (Color online) Thermal diffusion factor of 1-propanol (n-propanol) in 1-propanol-water mixture versus propanol mole fraction: performance of several models compared with experimental data. $T=25\ ^\circ\mathrm{C}$, $P=1$ atm.

The magnitude of the activation energy of viscous flow of 1-propanol and water are close and, therefore, Eqs. (4) and (11) that correlate the thermal diffusion factor directly with the difference between the activation energy of viscous flow of the two components estimate small values for the thermal diffusion factor (see Fig. 5), although the measured thermal diffusion factors for 1-propanol are in the same range as those of methanol and ethanol.

In addition to the associating mixtures, such as alcohol-water mixtures, a sign change in thermal diffusion factor has been also reported in benzene-cyclohexane mixture [51], where both components have comparable molecular weights. We may explain this based on the alteration of the mixture molecular structure. Pure benzene (C_6H_6) is a dense aromatic hydrocarbon with stable cyclic structure. Cyclohexane is a nonpolar solvent (C_6H_{12}) with a three-dimensional so-called chair conformation. The molecular order of benzene is quadrupolar due to the presence of a large positive quadrupole moment, corresponding to the accumulation of negative charge in the middle of the ring and positive on the outside. Cyclohexane has an almost negligible quadrupole moment and, therefore, there is a net breaking of structure associated

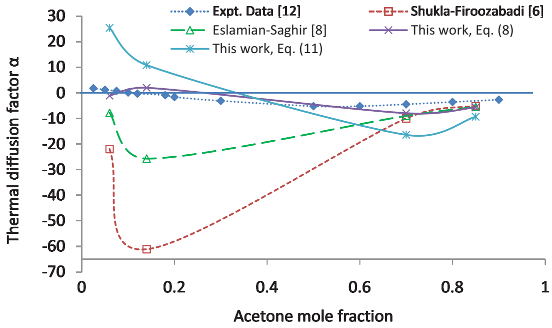

FIG. 6. (Color online) Thermal diffusion factor of acetone in acetone-water mixture versus acetone mole fraction: performance of several models compared with experimental data. $T=25\ ^\circ\mathrm{C}$, $P=1$ atm.

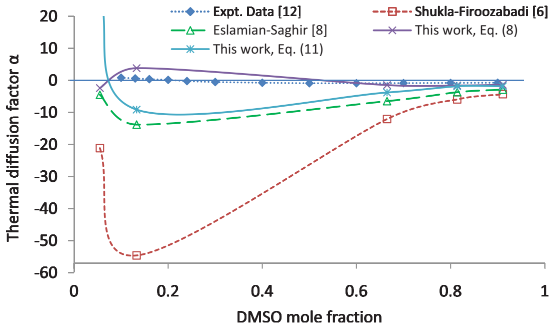

FIG. 7. (Color online) Thermal diffusion factor of DMSO in DMSO-water mixture versus DMSO mole fraction: performance of several models compared with experimental data. $T=25\ ^{\circ}\mathrm{C}$, $P=1$ atm.

with the mixing process [52]. In other words, mixing of benzene with cyclohexane leads to the destruction of the molecular structure of cyclohexane. It is not clear to us that at what concentration this destruction of structure occurs. Nevertheless, this structural change might be responsible for a sign change in the thermal diffusion factor of benzene-cyclohexane.

V. CONCLUSIONS

Thermodiffusion in binary associating mixtures, which is strongly dependent on the molecular structure and hydrogen bonds in such mixtures, was explored. It was found that the concentration at which the sign of the thermal diffusion factor changes is close to the concentration at which a significant change in the structure of mixture occurs, the mixture viscosity reaches a maximum, and the excess entropy of mixing attains its minimum value. With an increase in alcohol concentration, the structure of alcohol-water clusters starts to deviate from the tetrahedral-like structure of water clusters to hydrogen-bonded alcohol chains at a specific mole fraction for each alcohol. Compared to the nonassociating mixtures, such as hydrocarbons, the mixture viscosity varies anomalously in such mixtures and reaches a maximum, which is higher than the viscosity of both components in the pure state. We believe that such anomalous behaviors in the properties of associating mixtures are responsible for the anomalous behavior in thermodiffusion, i.e., a sign change in the thermal diffusion factor.

A mechanism for the separation of species in associating mixtures was proposed. At a moderate alcohol concentration, a portion of water and nonwater molecules remain isolated in the mixture, whereas the rest of the molecules may form hybrid clusters. When a temperature gradient is applied across the mixture, it is easier for the isolated molecules to move in the mixture toward either the cold side or the hot side. The response of the hybrid clusters, however, is more complicated. A temperature and the induced concentration gradients may apply forces on different molecules of a hybrid cluster in different directions. This may cause the breakdown of the cluster or the cluster may move toward one end or even remains in its place.

Starting from the nonequilibrium thermodynamics principles, our previously proposed expressions [8] were modified using two approaches. The developed expressions are only dependent on the viscosity data of pure components and the mixture. Although the magnitude of the thermal diffusion factor cannot be estimated adequately, the estimation of the proposed expressions is significantly better than those of Haase [4], Kempers [5], and Shukla-Firoozabadi [6]. In particular, Eq. (11) of this work best estimates the thermal diffusion factor, it is physically sound, and predicts a sign change when the derivative of the natural logarithm of viscosity with respect to concentration vanishes.

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