

Molecular thermodiffusion (thermophoresis) in liquid mixtures

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Thermodiffusion (thermophoresis) in liquid mixtures is theoretically examined using a hydrodynamic approach. Thermodiffusion is related to the local temperature-induced pressure gradient in the liquid layer surrounding the selected molecule and to the secondary macroscopic pressure gradient established in the system. The local pressure gradient is produced by excess pressure due to the asymmetry of interactions with surrounding molecules in a nonuniform temperature field. The secondary pressure gradient is considered an independent parameter related to the concentration gradient formed by volume forces, calculated from the generalized equations for mass transfer. Values of Soret coefficients for mixtures of toluene and *n*-hexane are calculated using parameters in the literature. When the molecules are assumed to be similar in shape, the calculated Soret coefficients are lower than the empirical values found in the literature. However, by introducing an asymmetry parameter, which is calculated from independent measurements of component diffusion in the literature, very good agreement is obtained.

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I. BACKGROUND

When a liquid mixture is placed in a temperature gradient, there is movement of the constituent components, generating a concentration gradient. This coupling between temperature and concentration gradients is known as thermodiffusion or the Ludwig-Soret effect. Since its discovery by Ludwig [1] and the first systematic investigations of thermodiffusion in liquid mixtures by Soret [2], the effect has been subject to numerous experimental and theoretical studies. Investigations of the Ludwig-Soret effect in liquid mixtures typically involve measurements of a so-called thermal diffusion coefficient, an ordinary (mass) diffusion coefficient, or a ratio of the two that is referred to as the Soret coefficient. Tools used to measure the Soret coefficient in liquid mixtures include the thermogravitational column [3] and thermal field-flow fractionation (TFFF) [4]. Thermal diffusion coefficients are measured by forced Rayleigh scattering (TDFRS) [5] and beam deflection methods [6]. A variety of techniques are used to measure mass diffusion coefficients, including TDFRS and dynamic light scattering [7]. Data provided by these methods have been used to compare values obtained by molecular dynamic (MD) simulations [8,9]. A summary of the information obtained by these methods can be found in Refs. [10,11].

TFFF has proven to be particularly adept at measuring the Soret coefficients of dissolved polymers and suspended particles. In one of the more comprehensive studies on polymer thermodiffusion [12] by TFFF, the independence of thermodiffusion on chain length and branching configuration was demonstrated, as predicted by scaling considerations [13,14].

In a later study of polymers [15] dissolved in binary solvent mixtures, the dependence of thermodiffusion on the relative concentration of solvent components in specific mixtures was found to be nonlinear. The curvature in these relationships, which can be either positive or negative,

provides evidence for the existence of multiple forces affecting the thermodiffusion of dissolved solutes in liquid mixtures.

The independence of polymer thermodiffusion on chain length and branching configuration means that the polymer chain moves at the same velocity as that of the individual monomer units (mers), at least for homopolymers. Therefore, we have modeled polymer thermodiffusion using a similar approach as that used for particle thermophoresis [16]. This hydrodynamic approach, which has been used to explain the thermodiffusion of hydrophobic homopolymers in pure solvents [17], considers the molecules surrounding a selected mer as a continuous medium, while the selected mer is considered a solid particle suspended in that medium. The flow of liquid around the particle is caused by a local pressure gradient in the surface layer of the particle, as defined by the Navier-Stokes equation

$$\eta\Delta u = -\nabla\Pi_{loc} + f_{loc}, \quad (1)$$

where u is the velocity of the liquid, Π_{loc} is the local pressure distribution around the particle due to its interaction with molecules of the liquid, η is the dynamic viscosity of the liquid, and f_{loc} is any local volume force in the liquid around the particle. In a temperature or concentration gradient, the local pressure distribution is not uniform due to asymmetry in the distribution of molecules around the particle. The same asymmetry also causes a local volume force on the particle. The validity of this approach does not depend on the size of the particle, provided the size is comparable or larger than the solvent molecules, because the model is based on the hydrodynamic motion of liquid in the layer surrounding the particle. However, the model's validity does depend on the frequency of intermolecular collisions being great enough to consider the solvent as a continuous medium.

In order to calculate the pressure gradient in Eq. (1), we use the condition of hydrostatic equilibrium in the absence of a temperature and concentration gradient:

$$-\nabla \Pi_{loc} + f_{loc} = 0. \quad (2)$$

Following the approach used in the theory of diffusiophoresis [18], we showed [17] that the local pressure distribution can be obtained from the condition of hydrostatic equilibrium in the surrounding liquid, where the local volume force f_{loc} is expressed through the intermolecular interaction potentials:

$$\frac{d\Pi_{loc}^i}{dr} + \sum_{j=1}^N \frac{\phi_j}{v_j} \frac{d\Phi_{ij}}{dr} = 0. \quad (3)$$

Here, r is the radial coordinate for a spherical molecule, ϕ_j is the volume fraction of molecules of the j th kind, v_j is the specific molecular volume occupied by the molecule of the j th kind, and Φ_{ij} is the interaction potential between molecules of the i th and j th kind. Equations (2) and (3) express the simple condition that for local equilibrium, any local volume force in the liquid is canceled by a local pressure gradient.

For liquids with low electrical conductivity, such that ions are absent and molecular dissociation does not occur to a significant extent, only dipole-dipole interactions play a role in the interaction potential [19]. Dipole-dipole interactions include those between permanent dipoles (the Keesom interaction), those between permanent and induced dipoles (the Debye induction interaction), and those that are induced spontaneously (the London or dispersion interaction). According to the Fowkes approach [19], dipole-dipole interactions have a common dependence on the distance between dipoles and may be written in the following form [20]:

$$\Phi_{ij}(r) = -\frac{16\sqrt{A_i A_j}(r_i r_j)^3}{9r^6}, \quad (4)$$

where A_i and A_j are the Hamaker constants for the respective liquids, and r_i and r_j are the molecular radii. Solving Eq. (3) using the assumption of uniform density in the surrounding liquid, we obtain the following equation for the local pressure established around the dissolved molecule of type i :

$$\Pi_{loc}^i = -\sum_{j=1}^N \frac{\phi_j}{v_j} \Phi_{ij}. \quad (5)$$

Equation (5) defines the local excess pressure in the liquid mixture due to the presence of a selected molecule of the i th kind and its interaction with other molecules.

In the presence of an imposed temperature gradient and consequent concentration gradient established by thermal expansion, the differentiation of Eq. (5) gives

$$\nabla \Pi_{loc}^i = \sum_{j=1}^N \frac{\phi_j}{v_j} \nabla T \left(\alpha_{Tj} \Phi_{ij} - \frac{\partial \Phi_{ij}}{\partial T} \right) - \Phi_{ij} \nabla \phi_j, \quad (6)$$

where $\alpha_{Tj} = \partial(\ln v_j) / \partial T$ is the cubic thermal expansion coefficient of the surrounding molecules of type j .

The temperature dependence of the intermolecular interaction potential also causes, besides the pressure gradient, a volume force that is defined by differentiation of the interaction potential:

$$f_{loc}^i = -\sum_{j=1}^N \frac{\phi_j}{v_j} \frac{\partial \Phi_{ij}}{\partial T} \nabla T. \quad (7)$$

In order to describe the hydrodynamic problem related to thermophoresis and diffusiophoresis, Eqs. (6) and (7) are substituted into Eq. (2), which upon rearrangement yields

$$\nabla \Pi_{loc}^i = \sum_{j=1}^N \frac{\Phi_{ij}}{v_j} (\alpha_{Tj} \phi_j \nabla T - \nabla \phi_j). \quad (8)$$

Equation (8) represents the expression for the local concentration and temperature-induced pressure gradient, which will be used to solve the hydrodynamic problem of liquid flow around the selected particle. The resulting expression is not related to any model equation of state for the liquid mixture and contains only those parameters that can be obtained independently.

Several authors have assumed the temperature dependence of the intermolecular interaction potential to be the main source of either a pressure gradient or a volume force that is responsible for flow of liquid around a particle [21–24]. In each case, the cancellation of the pressure gradient by a volume force, or vice versa, was ignored. In Ref. [24], for example, the temperature dependence of the Flory-Huggins interaction parameter and associated temperature-induced force are assumed to be the main source of polymer thermophoresis without any consideration of the related pressure gradient. In fact, the temperature dependence of the interaction potential is canceled by the resulting volume force created, as outlined above. This cancellation is implicit in the classical paper by Ruckenstein [25], where particle thermophoresis is based on the selective adsorption of solutes in a dilute system. Thus, the temperature dependence of the interaction energy cannot be responsible for thermodiffusion itself in a hydrodynamic model. Only a redistribution of the molecules in space due to thermal expansion can give a pressure gradient resulting in molecular motion.

In solving Eq. (1) for a spherical particle, we use the approach taken by Teubner [26], which utilizes the generalized reciprocal theorem for invariance of the following integral:

$$\eta \int_S u' \hat{\sigma} dS - \eta \int_V u' \nabla \Pi dV = \eta' \int_S u \hat{\sigma}' dS - \eta' \int_V u \nabla \Pi' dV. \quad (9)$$

Here, S is the outer surface of a moving body, V is the outer volume surrounding this surface, and $\hat{\sigma}$ is the hydrodynamic stress tensor expressed by the velocity gradient [27]. The primed and unprimed parameters in Eq. (9) are interrelated in two separate problems on the movement of the same body. Using this theorem, we employ the results of Ref. [26], which relates particle phoresis to the local pressure gradient and fluid velocity distribution in the space around a particle moving with constant unit velocity $U_1(r)$, where r is the radius vector directed from the particle center to the observation point. The velocity distribution $U_1(r)$, which corresponds to the conditions $U_1(r=r_i)=u_0$ and $U_1(r=\infty)=0$, is defined as

$$U_{1(i)}(r) = \frac{3}{4} \frac{r_i}{r} [u_0 + n_0(u_0 n_0)] + \frac{1}{4} \left(\frac{r_i}{r} \right)^3 [u_0 - 3n_0(u_0 n_0)], \quad (10)$$

where u_0 and n_0 are the unit vectors directed along the $U_{1(i)}$ and radius vector r , respectively. Using the condition of steady-state motion, where the sum of the hydrodynamic friction, diffusion and thermophoretic forces acting on the particle is equal to zero, we obtain the following general expression for the particle velocity U_i :

$$U_i = \frac{1}{6\pi\eta r_i} \int_0^\pi \sin \vartheta d\vartheta \times \int_{r_i}^\infty 2\pi r^2 dr \sum_{j=1}^N \frac{\Phi_{ij}}{v_j} (\nabla \phi_j - \alpha_{Tj} \phi_j \nabla T) U_{1(i)}, \quad (11)$$

where ϑ is the angle between r and the outer temperature gradient ∇T .

Next, we substitute the expressions for the local pressure gradient [Eq. (8)] and interaction potential [Eq. (4)] into Eq. (11). After carrying out some straightforward but cumbersome calculations, we obtain the following expression for the velocity of the selected particle:

$$U_i = \frac{8r_i^2}{27\eta} \sum_{j=1}^N \frac{\sqrt{A_i A_j}}{v_j} (\nabla \phi_j - \alpha_{Tj} \phi_j \nabla T). \quad (12)$$

Equation (12) allows for the introduction of the partial diffusiphoretic mobility (cross-diffusion coefficient), defined as the velocity of a selected particle of the i th kind per unit concentration gradient of the j th component:

$$b_{Dij} = \frac{8r_i^2}{27\eta} \frac{\sqrt{A_i A_j}}{v_j}. \quad (13)$$

Equation (12) also allows for the introduction of the partial cross-diffusion factor $S_{Dij}=b_{Dij}/D_i$, where $D_i=kT/6\pi\eta r_i$ is the Stokes-Einstein diffusion coefficient of the selected molecule. Using Eq. (13), the partial cross-diffusion factor can be cast in the following form:

$$S_{Dij} = \frac{4v_i^H \sqrt{A_i A_j}}{3v_j kT}, \quad (14)$$

where $v_i^H=(4\pi/3)r_i^3$ is the equivalent hydrodynamic volume of the molecule.

Next, we introduce the partial thermophoretic mobility (thermodiffusion coefficient), which represents the velocity of a selected particle of the i th kind per unit temperature gradient in a surrounding medium (solvent) of pure j th component:

$$b_{Tij} = -\alpha_{Tj} \frac{8r_i^2}{27\eta} \frac{\sqrt{A_i A_j}}{v_j}. \quad (15)$$

Using Eq. (15), the partial thermodiffusion factor $S_{Tij}=b_{Tij}/D_i$ is defined as

$$S_{Tij} = -\alpha_{Tj} \frac{4v_i^H \sqrt{A_i A_j}}{3v_j kT}. \quad (16)$$

Next, we substitute these newly defined parameters into a set of diffusion equations, in order to obtain the distribution of component concentrations in a temperature gradient. Here, however, we run into a problem related to a general defect in the standard formulation of diffusion equations for concentrated systems. Standard approaches use $N-1$ diffusion equations to define a multicomponent mixture of N components. In this approach, the volume fraction (or other expression of concentration) of the last component (the solvent) is obtained from the equation for conservation of mass, or from the Gibbs-Duhem equation, rather than another (N th) diffusion equation [27,28]. This approach is often referred to as the solvent reference frame in theories of mass diffusion and thermodiffusion. Such an approach is reasonable when one is considering a solvent that contains $N-1$ dissolved components at low concentrations because the solvent can be logically selected as the N th component with a concentration distribution that follows from those of the other components. However, this method fails when we consider systems having multiple components with similar concentrations, so that no single component can be unambiguously selected as the "solvent" component. In such a situation, the selection of the N th (solvent) component is arbitrary. Consequently, $N+1$ equations must be employed for N components, representing a mathematical problem with a nontrivial solution. A mathematical solution must exist that is independent of which component is selected to be the solvent.

This fundamental flaw in standard approaches to diffusion may arise from the assumption of an isobaric system, even though it is generally accepted that an osmotic pressure gradient should exist in nonuniform liquid mixtures. Thus, in stationary liquid mixtures, a volume force will arise, which must be balanced by a macroscopic pressure gradient ∇P , in order to maintain hydrostatic equilibrium. We recently proposed [29] an approach based on the obvious statement that whenever a volume force acts on a system and/or a concentration gradient is present, a pressure gradient will be established spontaneously. In our approach, this spontaneous pressure gradient plays the role of the ($N+1$)th unknown function in the system of diffusion equations. The observable

effect of this secondary pressure gradient on the process of molecular diffusion or drift motion is identified as the barodiffusion force on a molecule:

$$f_P^i = -\bar{v}_i \nabla P. \quad (17)$$

Here \bar{v}_i is the volume of molecules of the i th kind, which can be expressed as the partial molecular volume and identified with the change in system volume upon the addition of one molecule of the given (i th) kind. A well-known example of a barodiffusion force is the Archimedes force, where the pressure gradient is caused by gravity.

When we take into account the secondary macroscopic pressure gradient and associated barodiffusion force, the symmetrized system of diffusion equations for a liquid mixture placed in a temperature gradient takes the following form:

$$\frac{\partial \phi_i}{\partial t} = \nabla \left\{ D_i \left[\nabla \phi_i + \phi_i \left(\frac{\bar{v}_i}{kT} \nabla P - \sum_{j=1}^N S_{Dij} \nabla \phi_j - \sum_{j=1}^N S_{Tij} \phi_j \nabla T \right) \right] \right\} \quad (1 \leq i \leq N). \quad (18)$$

Using an Eq. (18) for each component and the equation for conservation of mass,

$$\sum_{i=1}^N \phi_i = 1, \quad (19)$$

we obtain the following equation for the macroscopic pressure gradient:

$$\nabla P = kT \frac{-J_\Sigma + \sum_{i,j=1}^N \phi_i b_{Dij} \nabla \phi_j + \sum_{i,j=1}^N \phi_i b_{Tij} \phi_j \nabla T - \sum_{i=1}^N D_i \nabla \phi_i}{\sum_{i=1}^N D_i \bar{v}_i \phi_i}. \quad (20)$$

Here $J_\Sigma = \sum_{i=1}^N J_i$ is the net flux of substance through boundaries of the considered volume.

Substituting Eq. (20) into the system of diffusion equations yields the following system of symmetrized diffusion equations:

$$\frac{\partial \phi_i}{\partial t} = \nabla D_i \frac{\sum_{j \neq i}^N p_{ij} \phi_j}{\sum_{j=1}^N p_{ij} \phi_j} \nabla \phi_i + \nabla \frac{-J_\Sigma - \sum_{j \neq i}^N D_j \nabla \phi_j + \sum_{i,j=1}^N b_{Dij} (\nabla \phi_j - \alpha_{Tj} \phi_j \nabla T) \left(\frac{r_j^2}{r_i^2} \sqrt{\frac{A_j}{A_i}} - p_{ij} \right) \phi_j}{\sum_{j=1}^N p_{ij} \phi_j} \phi_i \quad (1 \leq i, j \leq N), \quad (21)$$

where $p_{ij} = \bar{v}_j D_j / \bar{v}_i D_i$ is the parameter characterizing the contribution of barodiffusion. In Eq. (21), the relationship $b_{Tij} = -\alpha_{Tj} b_{Dij}$ is used, which follows from Eqs. (10) and (12).

The logical necessity for a macroscopic pressure gradient is interconnected with the hydrodynamic approach used to calculate thermodiffusion parameters. In this approach, if the acting force established by the temperature gradient is not compensated by another force or pressure gradient, then thermodiffusion motion would occur even in a pure liquid, which is hard to imagine. Equation (21) eliminates this possibility by compensating the thermophoretic force with a barodiffusion force described by Eq. (17).

The system that we will use to examine the consequences

of a macroscopic pressure gradient on the movement of mass in response to an applied field is a binary liquid mixture placed in a uniform temperature gradient. In this system, the dependence of thermodiffusion and barodiffusion on the macroscopic pressure gradient can be seen in a relatively simple form, especially if we ignore the flux of substance J_Σ through boundaries in the system. However, it should be recognized that such fluxes could occur in a more complex system. For example, such fluxes could result from adsorption-desorption processes, where certain molecules dissolve into the liquid at one wall and are removed at the opposite wall. In a temperature gradient, this could arise from a temperature dependence in the solubility or adsorption of solutes.

For this simple binary system without flux at the walls, $\phi_2 = \phi$ and $\phi_1 = 1 - \phi$, and Eq. (21) takes the following form:

$$\begin{aligned} \frac{\partial \phi}{\partial t} = \nabla & \frac{D_1 \phi + p(1 - \phi)D_2 + b_{D22} \left(1 - \frac{v_2}{v_1} \sqrt{\frac{A_1}{A_2}}\right) \left(\frac{r_1^2}{r_2^2} \sqrt{\frac{A_1}{A_2}} - p\right) (1 - \phi) \phi}{p(1 - \phi) + \phi} \nabla \phi \\ & + \nabla \frac{-J_1 - J_2 - b_{D22} \left(\frac{r_1^2}{r_2^2} \sqrt{\frac{A_1}{A_2}} - p\right) \left[\alpha_{T1}(1 - \phi) \frac{v_2}{v_1} \sqrt{\frac{A_1}{A_2}} + \alpha_{T2} \phi\right] \nabla T(1 - \phi)}{p(1 - \phi) + \phi} \phi. \end{aligned} \quad (22)$$

Here $J_{1(2)}$ are the fluxes of the respective components $p = p_{21} = \bar{v}_1 D_1 / \bar{v}_2 D_2$ and Eq. (19) is utilized. For the macroscopic pressure gradient in a binary mixture, we obtain

$$\begin{aligned} \nabla P = \frac{kT}{\bar{v}_2 [\phi + p(1 - \phi)]} \times & \left\{ -\frac{J_1 + J_2}{D_2} + \left(\frac{D_1}{D_2} - 1\right) \nabla \phi + S_{D22} \left[\left(1 - \frac{v_2}{v_1} \sqrt{\frac{A_1}{A_2}}\right) \nabla \phi \right. \right. \\ & \left. \left. - \left[\alpha_{T1}(1 - \phi) \frac{v_2}{v_1} \sqrt{\frac{A_1}{A_2}} + \alpha_{T2} \phi\right] \nabla T \right] \left[(1 - \phi) \frac{r_1^2}{r_2^2} \sqrt{\frac{A_1}{A_2}} + \phi \right] \right\}. \end{aligned} \quad (23)$$

As with the standard approach, conservation of mass [Eq. (19)] can be used for the concentration distribution of one component, but in our approach that component's distribution also satisfies the respective symmetrized diffusion equation.

II. MAIN OUTCOMES AND RESULTS: STATIONARY BINARY MIXTURE IN A CONSTANT-TEMPERATURE GRADIENT

For the steady state system in an impermeable vessel, Eq. (22) takes the form

$$\begin{aligned} \nabla \phi = \frac{S_{D22} \left(\frac{r_1^2}{r_2^2} \sqrt{\frac{A_1}{A_2}} - p\right) \left[\alpha_{T1}(1 - \phi) \frac{v_2}{v_1} \sqrt{\frac{A_1}{A_2}} + \alpha_{T2} \phi\right] (1 - \phi) \phi}{\frac{D_1}{D_2} \phi + p(1 - \phi) + S_{D22} \left(1 - \frac{v_2}{v_1} \sqrt{\frac{A_1}{A_2}}\right) \left(\frac{r_1^2}{r_2^2} \sqrt{\frac{A_1}{A_2}} - p\right) (1 - \phi) \phi} \nabla T. \end{aligned} \quad (24)$$

In many empirical studies of thermodiffusion, the distribution of component concentrations is characterized by the Soret coefficient, described empirically as $S_T = -\nabla \phi / \phi(1 - \phi) \nabla T$. Using Eq. (24), S_T can be expressed as

$$\begin{aligned} S_T = - \frac{S_{D22} \left(\frac{v_1^H \bar{v}_2}{v_2^H \bar{v}_1} \sqrt{\frac{A_1}{A_2}} - 1\right) \left[\alpha_{T1}(1 - \phi) \frac{v_2}{v_1} \sqrt{\frac{A_1}{A_2}} + \alpha_{T2} \phi\right]}{\phi + \frac{\bar{v}_1}{\bar{v}_2} (1 - \phi) + S_{D22} \left(1 - \frac{v_2}{v_1} \sqrt{\frac{A_1}{A_2}}\right) \left(\frac{v_1^H \bar{v}_2}{v_2^H \bar{v}_1} \sqrt{\frac{A_1}{A_2}} - 1\right) (1 - \phi) \phi}. \end{aligned} \quad (25)$$

Inserting the definition of S_{D22} from Eq. (14) into Eq. (25) yields

$$\begin{aligned} S_T = - \frac{\frac{4}{3} \frac{v_2^H A_2}{v_2 kT} \left(\frac{v_1^H \bar{v}_2}{v_2^H \bar{v}_1} \sqrt{\frac{A_1}{A_2}} - 1\right) \left[\alpha_{T1}(1 - \phi) \frac{v_2}{v_1} \sqrt{\frac{A_1}{A_2}} + \alpha_{T2} \phi\right]}{\phi + \frac{\bar{v}_1}{\bar{v}_2} (1 - \phi) + \frac{4}{3} \frac{v_2^H A_2}{v_2 kT} \left(1 - \frac{v_2}{v_1} \sqrt{\frac{A_1}{A_2}}\right) \left(\frac{v_1^H \bar{v}_2}{v_2^H \bar{v}_1} \sqrt{\frac{A_1}{A_2}} - 1\right) (1 - \phi) \phi}. \end{aligned} \quad (26)$$

When the volume fraction of the second component ϕ is low, we have

$$S_T = \frac{4\alpha_{T1}}{3} \frac{v_2^H}{v_1} \frac{\sqrt{A_1 A_2}}{kT} \left(1 - \frac{v_1^H \bar{v}_2}{v_2^H \bar{v}_1} \sqrt{\frac{A_1}{A_2}}\right). \quad (27)$$

An expression similar to Eq. (27) was obtained for the thermal diffusion coefficient of an isolated molecule of one component dissolved in another [29] by considering the action of a spontaneously established macroscopic pressure gradient. In that work, however, the macroscopic pressure gradient

was calculated directly as the source of a barophoretic force that compensates the thermophoretic force applied to the solvent molecules contained in a unit volume, in order to maintain the system at hydrostatic equilibrium. The introduction of a barophoretic force in that work resulted in much better agreement of the model with empirical values of the thermal diffusion coefficients for polystyrene in several organic solvents, compared to an earlier version of the theory where this factor was not taken into account [17].

When the volume fraction of the second component approaches unity, Eq. (26) is transformed into an equation simi-

TABLE I. Solvent parameters.

	<i>n</i> -Hexane		Toluene	
Molar mass M (g mol ⁻¹)	86.2	[33]	92.1	[5]
Density d (g/cm ³)	0.66	[35]	0.87	[35]
Thermal expansion $\alpha_T \times 10^3$ (K ⁻¹)	1.06	[36]	1.10	[36]
Surface tension γ (mN/m)	25.64	[35]	28.78	[35]
	25.24	[36]	28.52	[36]
Hamaker constant $A \times 10^{13}$ (erg)	5.57	[35]	5.40	[34]
Viscosity $\eta \times 10^4$ (N s/m ²)	3.1	[33]	5.9	[33]

lar to Eq. (27), except that the isolated molecule is the first component dissolved in a solvent of the second component. Comparing these two extremes, one can see that the sign of the Soret coefficient for a binary mixture is defined by the following factor:

$$1 - \frac{v_1^H \bar{v}_2}{v_2^H \bar{v}_1} \sqrt{\frac{A_1}{A_2}}. \quad (28)$$

Although both positive and negative Soret coefficients are allowed, Eq. (28) does not allow for a sign change in S_T with changes in the volume fraction of the components, which is contrary to empirical observations [5]. In certain mixtures, however, such a sign change could occur from the temperature dependence of the parameters, particularly in mixtures where the value expressed by Eq. (28) is close to zero. Inside a thermal diffusion cell, a change in the sign of S_T would occur at a position that varies with the hot- and cold-wall temperatures. In a given cell with given temperature parameters and a fixed observation point, the effect would be manifested as a change in the measured sign of S_T as a function of composition. A more quantitative discussion of this effect would require more precise information on the temperature dependence of the interaction potentials than that currently available and is therefore beyond the scope of this work.

Another possible explanation for the measured change in sign of S_T is thermoosmotic flow (convection), which can be

established even in thin thermodiffusion cells [20]. Such flow depends on the interaction of liquid molecules with the cell walls, and the direction of the resulting movement is defined by a parameter similar to that given by Eq. (28). Consequently, empirical results obtained in thermodiffusion cells depend on the wall material, which may explain the significant differences published in the literature. For example, in Ref. [30] a variation of $\pm 50\%$ is reported for values of S_T in toluene/*n*-hexane mixtures collected from five different sources.

Consideration of thermoosmotic flow and its role in thermodiffusion measurements is beyond the scope of this work. For the present, we will compare the predictions of our model with a self-consistent set of empirical data and show that our results are at least in qualitative agreement with that data. For our initial comparison we simplify Eq. (26), which contains three different volume parameters for each component. These parameters include the partial molecular volume $\bar{v}_{1(2)}$, the hydrodynamic volume $v_{1(2)}^H$, and the specific molecular volume $v_{1(2)}$. Because not all of these parameters are readily available for any system, we transform Eq. (26) into a form that contains the ratios of each volume parameter for the two components, so that for molecules with similar shapes we can assume the ratios of the different types of volume parameters to be about the same. With this assumption, it is only necessary to have one of the three types of volume parameters. Of the three, the specific molecular volumes are most readily available. The specific molecular volumes and their respective radii can be obtained using the following equation:

$$v_{1(2)} = \frac{4\pi r_{1(2)}^3}{3} = \frac{M_{1(2)}}{N_a d_{1(2)}}. \quad (29)$$

Here $M_{1(2)}$ is the molar mass, $d_{1(2)}$ is the density of the respective component, and N_a is Avogadro's number. The resulting simplified version of Eq. (26) is applicable to systems in which the different molecules have a similar shape and aspect ratio:

$$S_T = - \frac{\frac{4A_2}{3kT} \left(\sqrt{\frac{A_1}{A_2}} - 1 \right) \left[\alpha_{T1}(1-\phi) \frac{v_2}{v_1} \sqrt{\frac{A_1}{A_2}} + \alpha_{T2}\phi \right]}{\phi + \frac{v_1}{v_2}(1-\phi) + \frac{4A_2}{3kT} \left(\frac{v_2}{v_1} \sqrt{\frac{A_1}{A_2}} - 1 \right) \left(1 - \sqrt{\frac{A_1}{A_2}} \right) (1-\phi)\phi}. \quad (30)$$

Equation (30) is used below to compare the proposed theory with the most consistent subset of experimental data that could be found in Ref. [30]. These data include the concentration dependence of the Soret coefficient for mixtures of toluene and *n*-hexane, as measured by thermal diffusion forced Rayleigh scattering [31], a thermal diffusion cell [6],

and a thermogravitational column [32]. The necessary parameters and their sources are present in Table I. For *n*-hexane, the Hamaker constant was not available and was therefore calculated from the following expression for the dependence of surface tension γ on A in nonionic liquids [34]:

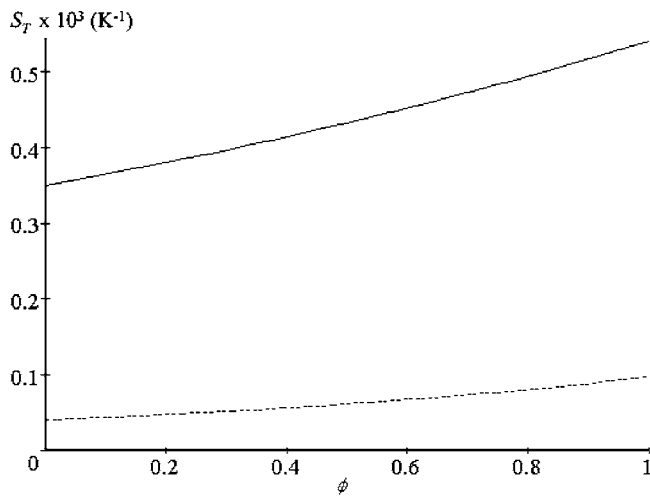


FIG. 1. Theoretical dependence of S_T on the volume fraction ϕ of toluene in n -hexane/toluene mixtures, using the assumption of spherical molecules $[(v_1^H/v_2^H)\bar{v}_2/\bar{v}_1=1]$ and a Hamaker constant ratio calculated from Eq. (31) and surface tension data from the literature. The upper curve is obtained using surface tension values from Ref. [35]. The lower curve (dashes) is calculated using surface tension values from Ref. [36]. $T=300$ K for all calculations.

$$\gamma_i = \frac{A_i}{48\pi r_i^2}. \quad (31)$$

The radius r_i in Eq. (31) was calculated from Eq. (29) using solvent parameters from Ref. [35]. Values of the surface tension were obtained from Refs. [35,36]. This approach to calculating molecular radii seems satisfactory considering that we need only the ratio of the Hamaker constants to calculate Soret coefficients from the model.

Because experimental data are expressed as a function of the mole fraction m of the second component (toluene), we can transform Eq. (30) using the relationship

$$\phi = \frac{m}{\frac{v_1}{v_2} + \left(1 - \frac{v_1}{v_2}\right)m}. \quad (32)$$

For this work, we neglect the difference between volume fraction and mole fraction for the miscible components under consideration, which have similar volume parameters.

In order to illustrate the sensitivity of the Soret coefficient to values of the Hamaker constants, Fig. 1 contains two plots of Eq. (30), each calculated using a different source for the surface tension values used to estimate the ratio of Hamaker constants according to Eq. (31). As illustrated in the figure, a difference in surface tension of 1%–2% yields Soret coefficients that differ by a factor of 5–6. This extremely high sensitivity arises from the fact that Hamaker constants for miscible components are very close to one another, making it difficult to perform a robust analysis of the model. Nevertheless, even the higher values predicted from Eq. (30) are 10 times lower than measured values, which are plotted in Fig. 2. However, the ratio of two Soret coefficients calculated

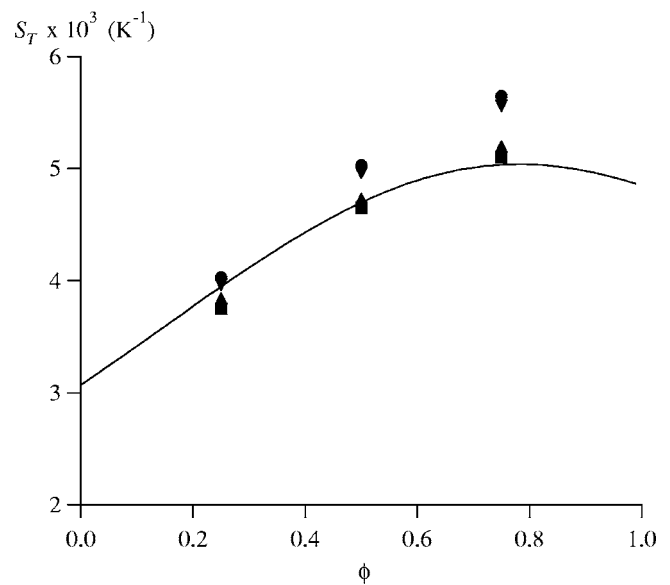


FIG. 2. Dependence of S_T on the volume fraction ϕ of toluene in n -hexane/toluene mixtures. Experimental points: (●) from Ref. [31], (▼) and (▲) from Ref. [6], and (■) from Refs. [3,32]. The solid curve is a fit to Eq. (26) using asymmetry parameter $(v_1^H/v_2^H)\bar{v}_2/\bar{v}_1=0.38$. $T=300$ K for all calculations.

from Eq. (30) matches the ratio of measured values quite well. The calculated ratio can be expressed by the following equation, which is obtained from Eq. (26):

$$\frac{S_T(1)}{S_T(0)} = \frac{\alpha_{T2}}{\alpha_{T1}} \left(\frac{v_1}{v_2}\right)^2 \sqrt{\frac{A_2}{A_1}}. \quad (33)$$

Using the solvent parameters in Table I, for example, we calculate $S_T(1)/S_T(0)=1.55$, while the empirical ratio is 1.6. The good agreement between theory and experiment indicates that the ratio of Hamaker constants is accurate, even if a systematic error exists in individual values.

The systematic error that leads to a discrepancy between theory and experiment for individual values of S_T may be eliminated by considering the asymmetry parameter $v_1^H\bar{v}_2/v_2^H\bar{v}_1$, which was set to a value of unity in simplifying Eq. (26). Even relatively small differences in shape between the molecules can significantly change the value of the parameter:

$$\frac{v_1^H\bar{v}_2}{v_2^H\bar{v}_1} \sqrt{\frac{A_1}{A_2}} - 1.$$

We can calculate the ratio \bar{v}_2/\bar{v}_1 in the asymmetry parameter using Eq. (29) and known values of the component molecular weights and densities. We can calculate the ratio v_1^H/v_2^H in the asymmetry parameter using the Stokes-Einstein equation and measured values of the diffusion coefficients:

$$\frac{v_1^H}{v_2^H} = \left(\frac{D_2\eta_1}{D_1\eta_2}\right)^3. \quad (34)$$

Using Eqs. (29) and (34) along with the viscosity and molecular weight data contained in Table I and diffusion coefficients taken from Ref. [6], we calculate an asymmetry pa-

parameter of 0.38 for the *n*-hexane/toluene system under consideration.

Equation (26) is plotted in Fig. 2 using the Hamaker constants listed in Table I, a value of 0.38 for the asymmetry parameter, and $\frac{4}{3}(v_2^H/v_2)A_2/kT$ as a fitting parameter to the most consistent set of data points from Ref. [30], which is a compilation of data from several studies. We note that other data in Ref. [30] varied by as much as 50% from the values plotted in Fig. 2, reflecting the large variability in empirical values of S_T measured by different techniques. The best-fit value of $\frac{4}{3}(v_2^H/v_2)A_2/kT=5.4$ corresponds to $v_2^H/v_2 \approx 0.3$. This ratio of molecular volumes matches the value calculated from Eqs. (29) and (34) using $D=2.4 \times 10^{-5}$ cm²/s reported for toluene at 298 K in Ref. [6]. This same value of $\frac{4}{3}(v_2^H/v_2)A_2/kT=5.4$ was also recently used to obtain good agreement between theory and experiment for the dependence of the effective diffusion coefficient on volume fraction in mixtures of toluene and *n*-hexane [37].

It would be desirable to check the model with other solvent mixtures. Unfortunately, only a small number of solvent mixtures exist for which a systematic study of thermal diffusion has been completed. Of these, very few have yielded a consistent set of data, and of these, toluene/*n*-hexane was the only system for which we could find the required solvent parameters. However, with the renewed interest in both ordinary (mass) and thermal diffusion, more empirical data will soon be available. The consistency and reliability of these new data will be greatly improved due to significant

advances in the design and implementation of instruments being used in these studies.

III. CONCLUSIONS

Our proposed hydrodynamic approach to thermodiffusion in concentrated liquid mixtures requires the introduction of a macroscopic pressure gradient into the mass transfer equations. The approach leads to the establishment of a closed system of equations for the resulting component concentrations in an established temperature gradient. Predicted Soret coefficients are highly sensitive to the inputted values of the Hamaker constants, and this sensitivity increases for highly miscible liquids where the Hamaker constants are similar in value. The model also predicts the Soret effect to be affected by differences in the shape of the component molecules. It is difficult to construct a robust validation test of the model due to the large variability of Hamaker constants reported in the literature. On the other hand, the sensitivity of the Soret effect to molecular interaction energies suggests that accurate measurements of the Soret coefficient could be used to calculate such energies with high accuracy and precision.

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