PHYSICAL REVIEW E **70**, 031202 (2004)

Symmetric diffusion equations, barodiffusion, and cross-diffusion in concentrated liquid mixtures

Martin E. Schimpf[1] and Semen N. Semenov[2]
[1]*Department of Chemistry, Boise State University, Boise, Idaho 83725, USA*
[2]*Institute of Biochemical Physics RAS, Kosygin Street 4, 117977 Moscow, Russia*

(Received 21 January 2004; published 30 September 2004)

In models of diffusion in multicomponent mixtures, the current practice is to derive equations for an isobaric system. The equations are nonsymmetric in relation to the components of the mixture, and the concentration of solvent is assumed to be governed by the conservation of mass instead of its own corresponding diffusion equation. For concentrated mixtures, the solvent component is selected arbitrarily, which makes interpretation of the experimental data dependent on the choice of the interpreter. In this work, we derive a symmetric system of equations, made possible by the introduction of a spontaneously produced secondary pressure gradient. The effect of that pressure gradient is barodiffusion (barophoresis), defined by the force expressed as the secondary pressure gradient multiplied by the molecular volume. The model also considers the cross-diffusion (diffusiophoresis) that results from the hydrodynamic stresses associated with the local concentration-induced pressure gradient in liquid layers surrounding individual molecules. The resulting system of diffusion equations, which contains the secondary pressure gradient and component concentrations, is applied to a binary (nonionic) mixture of benzene and 1,2-dichloroethane. The steady-state system is placed in a uniform force field, and the effect of the secondary pressure gradient on the field-induced migration is discussed. Fluctuation dynamics in a system with no external force field is also discussed. The numerical results predict the establishment of lower concentration gradients compared to standard theory. Also, the predicted concentration dependence in the effective diffusion coefficient measured by dynamic light scattering is different compared to standard theory. Finally, experiments are proposed to further evaluate differences between the new model and the standard approach.

DOI: 10.1103/PhysRevE.70.031202 PACS number(s): 66.10.Cb

I. BACKGROUND

Molecular diffusion is a phenomenon that is important for a number of natural and technological processes, and it is studied intensively by both theory and experimentation. The equations that are used to describe the diffusion process were derived nearly 100 year ago. The most general form of the diffusion equations is obtained by nonequilibrium thermodynamics [1], or by the Maxwell-Stefan approach [2]. Some approaches to diffusion rely on specific models of the media. For example, Hunter [3] derives a diffusion equation in which the medium is considered to be a system of hard spheres. All these systems of equations, beginning from the oldest papers to the most recent publications [4,5], contain an important simplification. Thus, for a multicomponent mixture containing N components, N-1 diffusion equations are written, and for the last component, the concentration is obtained from the equation for the conservation of mass, instead of using an Nth diffusion equation. This simplification for the Nth component is sometimes called the solvent reference frame in diffusion and thermodiffusion measurements. In the Maxwell-Stefan and nonequilibrium thermodynamic approaches, the problem is formulated as a system of equations that relate the molar fluxes for N-1 components to the gradients of their chemical potentials, while the chemical potential of the Nth component is found from the Gibbs-Duhem equation, or from an equation that expresses the conservation of mass [4,5]. In order to test the theory with experimental data, the general equations are reformulated to include component concentrations instead of chemical potentials.

This approach is reasonable when one considers a solvent that contains dissolved components at low concentrations because the solvent can nonarbitrarily be selected as the secondary component, having a concentration distribution that follows from that of the other components, as described by their respective diffusion equations. However, the approach fails in concentrated systems, where the concentrations of all components are of the same relative magnitude. In such situations, selection of the component to be described by conservation of mass instead of its respective diffusion equation is arbitrary, even in more generalized thermodynamic formulations. Consequently, current theories of diffusion rely on $N+1$ equations for N components, yielding a mathematical problem that lacks a trivial solution. Certainly, a mathematical solution must exist that yields the same result, independent of which component is selected to be the solvent.

The current approach to diffusion also uses a system of equations derived for an isobaric system [1–5], which neglects the backward action of any pressure gradients in the system. Yet it is generally accepted that an osmotic pressure gradient should exist in nonuniform liquid mixtures. Thus, when a volume force $\vec{f}$ is present in a stationary system, a macroscopic pressure gradient $\vec{\nabla}\Pi_{\mathrm{macro}}$ must be established to compensate the volume force, in order to maintain hydrostatic equilibrium in the mixture. The general equation for hydrostatic equilibrium is written as [6]

$$\vec{\nabla}\Pi_{\mathrm{macro}} - \vec{f} = \vec{0}. \tag{1}$$

In Ref. [6], for example, the authors discuss the production of a pressure gradient produced by an external field, which is assumed to arise from the pressure dependence of the chemical potentials, and they arrive at the molecular mass transfer process termed barodiffusion. However, there is no discussion of the spontaneous establishment of such a pressure gradient, and its possible role in the system.

In Ref. [3], Eq. (1) is formulated as a condition for the absence of convection-diffusion flux of the considered component,

$$\frac{1}{\zeta}\frac{\partial \Pi_{\mathrm{macro}}}{\partial n}\vec{\nabla} n - \frac{\vec{f}_0}{\zeta} n = \vec{0}. \tag{2}$$

Here ζ is the hydrodynamic friction coefficient, n is the numeric concentration of the considered species, and $\vec{f}_0 = \vec{f}/n$ is the force acting on a single particle. In that work, the following equation, which relates the diffusion coefficient D to the pressure gradient, was obtained:

$$D = \frac{1}{\zeta}\frac{\partial \Pi_{\mathrm{macro}}}{\partial n}. \tag{3}$$

In Ref. [7], Eq. (3) is discussed in the context of irreversible thermodynamics and statistical physics, and the osmotic pressure gradient is considered to be the main driving force for diffusion.

In this paper, we propose an approach based on the obvious statement that when a volume force acts on a system, or when a concentration gradient is present, a pressure gradient is established spontaneously. This pressure gradient plays the role of the $(N+1)$th unknown function in the system of diffusion equations. In the context of nonequilibrium thermodynamics, this adds the term $\overline{v_i}\Pi_{\mathrm{macro}}$ to the chemical potentials of the molecules, where $\overline{v_i}$ is the molecular volume of the ith component in the mixture. Parameter $\overline{v_i}$ can be expressed as the partial molecular volume, and determined by a change in the volume of the system by the addition of one molecule of the given kind. Also, for such a nonisobaric system, the Gibbs thermodynamic potential should be considered instead of the Helmholz thermodynamic potential, which has previously been used in deriving the system of diffusion equations [1,2,5]. The observable effect of the secondary pressure gradient on molecular diffusion is a drift motion that can be described as the respective barodiffusion force acting on the molecule,

$$\vec{f}_P^{\,i} = -\overline{v_i}\vec{\nabla}\Pi_{\mathrm{macro}}. \tag{4}$$

In Ref. [7], a term similar to $\overline{v_i}\Pi_{\mathrm{macro}}$ in the chemical potential was considered, but no conclusion was made as to its possible role in molecular motion.

A common example of a barodiffusion force is the Archimedes force, where the pressure gradient is caused by gravity [8]. We call this force barophoretic, and the resulting motion barophoresis rather than barodiffusion, because the induced motion of the molecule is directed, whereas diffusion is a random walk. A similar situation is raised in the theory of ion movement in electrolytes [9], where the diffusion equations are supplemented by an equation that defines the electric field required to maintain electrical neutrality in the system.

In any nonuniform mixture, an osmotic pressure gradient will be present. For multicomponent mixtures, this pressure gradient balances the volume force, which is present even in the absence of an external field. This volume force can be considered a diffusiophoretic force, which acts on molecules placed in a concentration gradient [10]. Diffusiophoresis can be described as the process of one component's movement in the presence of a concentration gradient in another component. Because we are not aware of any theory developed to date that is based on a kinetic approach, calculation of the cross-diffusion coefficient is part of this paper. In order to determine the secondary pressure gradient in a multicomponent mixture, we first calculate the diffusiophoretic mobilities (cross-diffusion coefficients) for the components. These parameters are substituted into a symmetrized system of diffusion equations, where the barophoretic force expressed by Eq. (4) is taken into account. The resulting system of equations is a closed system that describes the diffusion process.

In our calculations, we use a hydrodynamic approach taken in the theory of particle diffusiophoresis [10], as well as in theories of thermophoresis (the movement of mass in response to a temperature gradient) of molecules and polymers [11]. In this microscopic-kinetic approach, diffusiophoresis is considered to result from hydrodynamic stresses on the molecule. These hydrodynamic stresses are expressed by gradients in the velocity profile of the liquid, as calculated by the Navier-Stokes equation [6],

$$\eta\Delta\vec{u} = -\vec{\nabla}\Pi_{\mathrm{loc}}. \tag{5}$$

Here $\vec{u}$ is the velocity of the liquid, Π_{loc} is the local pressure distribution around the molecule due to its interaction with other molecules, and η is the viscosity of the liquid. The local pressure distribution is obtained by the condition of the local equilibrium, which is expressed as the equation of hydrostatic equilibrium in the liquid around the molecule of the ith kind [see Eq. (1)],

$$\frac{d\Pi_{\mathrm{loc}}^{i}}{dr} + \sum_{j=1}^{N}\frac{\phi_j}{v_j}\frac{d\Phi_{ij}}{dr} = 0. \tag{6}$$

Here, r is the radial coordinate for a molecule, ϕ_j is the volume fraction of molecules of the jth kind, v_j is the specific molecular volume occupied in the liquid by a molecule of the jth kind, and Φ_{ij} is the respective interaction potential. For liquids with low electrical conductivity, such that ions are absent and molecular dissociation does not occur, only dipole-dipole interactions play a role [12]. Dipole-dipole interactions include those between permanent dipoles (the Keesom interaction), those between permanent and induced dipoles (the Debye induction interaction), and those induced spontaneously (the London or dispersion interaction). According to the Fowkes approach [12], these dipole-dipole interactions have a common dependence on the distance between dipoles, and may be written in the following simple form:

$$\Phi_{ij}(r) = -\frac{16\sqrt{A_iA_j}(r_ir_j)^3}{9r^6}, \tag{7}$$

where A_i and A_j are the Hamaker constants for the respective liquids, and r_i and r_j are the corresponding molecular radii.

II. THEORY

A. Local pressure distribution around the molecule

In order to define the pressure resulting from the interaction of molecules, we assume that the fraction of free volume in liquids is small enough that intermolecular interactions do not induce appreciable variations in the liquid molecule concentration around a selected molecule. Consequently, we use a constant (unperturbed) volume fraction ϕ_i in solving Eq. (4) to obtain the pressure profile around the molecule,

$$\Pi^i_{\mathrm{loc}} = -\sum_{j=1}^{N}\frac{\phi_j}{v_j}\Phi_{ij}. \tag{8}$$

Equation (8) defines the local excess pressure in the liquid mixture due to the presence of molecules of the ith kind and their interaction with other molecules. Using Eq. (5), we calculate the resulting local pressure gradient in the liquid mixture:

$$\vec{\nabla}\Pi^i_{\mathrm{loc}} = -\sum_{j=1}^{N}\frac{\Phi_{ij}}{v_j}\vec{\nabla}\phi_j + \sum_{j,k=1}^{N}\frac{\Phi_{ij}}{v_j}\beta_{jk}\vec{\nabla}\phi_k. \tag{9}$$

Here $\beta_{jk}=[\partial(\ln v_j)]/[\partial(\ln \phi_k)]$ is a dimensionless coefficient that defines the relative change in the specific volume of the jth component due to a relative change in volume fraction of the kth component (so-called volume effect). The magnitude of this coefficient will be similar to the relative "synergistic" change in volume upon mixing organic solvents and water, i.e., 10^{-3}–10^{-2}. Thus, when the number of the components is not too high (less than ten), the second term on the right side of Eq. (9) can be neglected, and the expression for the local pressure gradient can be written as

$$\vec{\nabla}\Pi^i_{\mathrm{loc}} = -\sum_{j=1}^{N}\frac{\Phi_{ij}}{v_j}\vec{\nabla}\phi_j. \tag{10}$$

Equation (10) represents the expression for the local concentration-induced pressure gradient, which will be used to solve the hydrodynamic problem of solvent flow around the selected molecule. This expression is not related to any model equation of state for the liquid mixture, and contains only parameters that can be independently obtained.

B. Flow velocity profile around the selected molecule and its diffusiophoretic mobility

In solving Eq. (3) for a spherical particle, we use the approach taken in Ref. [13], which utilizes the generalized reciprocal theorem on the invariance of the following integral:

$$\eta\int_S \vec{u}'\cdot\hat{\sigma}\,d\vec{S} - \eta\int_V \vec{u}'\cdot\vec{\nabla}\Pi\,dV = \eta'\int_S \vec{u}\cdot\hat{\sigma}'\,d\vec{S} - \eta'\int_V \vec{u}\cdot\vec{\nabla}\Pi'\,dV. \tag{11}$$

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 components of the flow velocity gradient [6]. The primed and unprimed parameters in Eq. (11) are interrelated in two separate problems on the movement of the same body. The theorem was proven for the case in which only a volume force is acting in the liquid, i.e., in the absence of a pressure gradient. However, the Navier-Stokes equation allows the external volume force in a liquid to be interchanged with a predetermined "external" pressure gradient. Thus, the reciprocal theorem can be "generalized" to situations in which a predetermined pressure gradient, related to the excess pressure, is present in a liquid. Using this generalization, we employ the results of Ref. [13], which relates particle phoresis to the volume force and fluid velocity distribution $\vec{U}_1(\vec{r})$ around a particle moving at unit velocity. Here, $\vec{r}$ is the radius vector directed from the particle center to the observation point. The velocity distribution $\vec{U}_1(\vec{r})$ corresponds to the boundary conditions $\vec{U}_1(r=r_i)=\vec{u}_0, \vec{U}_1(r=\infty)=\vec{0}$, and is defined as [6]

$$\vec{U}_{1(i)}(\vec{r}) = \frac{3}{4}\frac{r_i}{r}[\vec{u}_0 + \vec{n}_0(\vec{u}_0\cdot\vec{n}_0)] + \frac{1}{4}\left(\frac{r_i}{r}\right)^3[\vec{u}_0 - 3\vec{n}_0(\vec{u}_0\cdot\vec{n}_0)], \tag{12}$$

where $\vec{u}_0$ and $\vec{n}_0$ are unit vectors directed along $\vec{U}_1$ and $\vec{r}$, respectively. Using the steady-state condition in which the sum of the hydrodynamic friction and diffusiophoretic forces acting on the particle is zero, we obtain the following general expression for diffusiophoretic velocity U_{Di}:

$$U_{Di} = \frac{1}{6\pi\eta r_i}\int_0^{\pi}\sin\,\vartheta d\vartheta\int_{r_i}^{\infty}2\pi r^2 dr\sum_{j=1}^{N}\frac{d\Pi_i}{d\phi_j}(\vec{U}_{1(i)}\cdot\vec{\nabla}\phi_j). \tag{13}$$

Here, ϑ is the angle between the vectors $\vec{u}_0$ and $\vec{n}_0$. Next, we substitute the expressions for the local pressure gradient [Eq. (10)] and interaction potential [Eq. (7)] into Eq. (13). After carrying out some simple but cumbersome integral calculations, the following expression for diffusiophoretic velocity is obtained:

$$U_{Di} = \frac{8r_i^2}{27\eta}\sum_{j=1}^{N}\frac{\sqrt{A_iA_j}}{v_j}\vec{\nabla}\phi_j. \tag{14}$$

Using Eq. (14), we can define the partial diffusiophoretic mobility (cross-diffusion coefficient), which represents the velocity of a molecule of the ith kind in unit concentration gradient of the jth component, as follows:

$$b_{Dij} = \frac{8r_i^2}{27\eta}\frac{\sqrt{A_i A_j}}{v_j}. \tag{15}$$

From Eq. (15), the partial cross-diffusion factor, defined as $S_{Dij}=b_{Dij}/D_i$, where $D_i=kT/6\pi\eta r_i$ is the Stokes-Einstein diffusion coefficient of the selected molecule, can be expressed as

$$S_{Dij} = \frac{4v_i^H}{3v_j}\frac{\sqrt{A_i A_j}}{kT}, \tag{16}$$

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

For a binary mixture, Eq. (14) takes the following form:

$$U_{D1(2)} = \frac{8r_{1(2)}^2}{27\eta}\frac{A_{1(2)}}{v_{1(2)}}\left(1 - \frac{v_{1(2)}}{v_{2(1)}}\sqrt{\frac{A_{2(1)}}{A_{1(2)}}}\right)\nabla\phi, \tag{17}$$

where the subscript 1(2) refers to the value of the given parameter for component 1 in the presence of component 2, and vice versa. Equation (17) predicts diffusiophoresis in binary mixtures under the following condition:

$$\frac{v_{1(2)}}{v_{2(1)}}\sqrt{\frac{A_{2(1)}}{A_{1(2)}}} \neq 1.$$

Consequently, even in systems with a single type of molecule, diffusiophoresis cannot be neglected when the molecules form aggregates, because the aggregates will have a larger specific volume, even in isotropic mixtures. For such aggregated species, a positive diffusiophoresis is predicted, i.e., movement toward regions of lower concentration of the single molecules. By contrast, in a liquid consisting largely of associated molecules, any molecules that dissociate into smaller fragments will undergo negative diffusiophoresis, moving toward regions of higher concentration of the associated molecules. This prediction can be easily checked by experiment, after substituting the equation for diffusiophoretic mobility into the appropriate diffusion equations to obtain the expected concentration distributions. Thus, Eq. (14) provides the means for writing the complete system of diffusion equations for any system with multiple components.

C. General system of symmetrized diffusion equations

While the most general form of diffusion equations is written using chemical potentials, this form is difficult to compare with experimental data without certain additional assumptions regarding the concentration dependence of the chemical potential. Thus, the concentration dependence of the chemical potential is often impossible to derive theoretically, or to extract from experimental results. Therefore, we will rely on equations of mass balance and use expressions based on Fick's law for the diffusive flux of components [5]. Although this approach is not as general as those based on diffusion equations derived in the context of nonequilibrium thermodynamics, they have a clear physical sense, and can be evaluated with experimental data obtained in a wide range of situations, with different applied fields.

When we consider the secondary macroscopic pressure gradient and related barophoretic force in a system, the diffusion equation takes the following form:

$$\frac{\partial\phi_i}{\partial t} = \vec{\nabla}\cdot\left\{D_i\left[\vec{\nabla}\phi_i + \phi_i\left(\frac{\overline{v_i}}{kT}\vec{\nabla}P - \sum_{j=1}^{N} S_{Dij}\vec{\nabla}\phi_j - \frac{\vec{u}_i}{D_i}\right)\right]\right\} \tag{18a}$$

$$(1 \leqslant i \leqslant N).$$

In Eq. (18a), $\vec{u}_i$ is the velocity of molecules of the *i*th kind due to the presence of an external field or flow. Equation (18a) is the conventional material balance equation for the *i*th component. The corresponding mass flux equation is

$$\vec{J}_i = -\frac{D_i}{\nu_i}\left[\vec{\nabla}\phi_i + \phi_i\left(\frac{\overline{v_i}}{kT}\vec{\nabla}P - \sum_{j=1}^{N} S_{Dij}\vec{\nabla}\phi_j - \frac{\vec{u}_i}{D_i}\right)\right]. \tag{18b}$$

Equation (18b) contains, from left to right, the diffusion, barodiffusion, cross-diffusion, and drift (convective) terms.

Of course, the component concentrations must also satisfy the requirement for conservation of mass,

$$\sum_{i=1}^{N}\phi_i = 1. \tag{19}$$

By summing Eq. (18a) for all components, and utilizing the mass balance equation, we obtain the following expression for the macroscopic pressure gradient:

$$\vec{\nabla}P = kT\frac{-\vec{J}_\Sigma + \sum_{i,j=1}^{N} b_{Dij}\vec{\nabla}\phi_j\phi_i - \sum_{i=1}^{N} D_i\vec{\nabla}\phi_i + \sum_{i=1}^{N}\vec{u}_i\phi_i}{\sum_{i=1}^{N} D_i\overline{v_i}\phi_i}, \tag{20}$$

where $\vec{J}_\Sigma=\sum_{i=1}^{N}\vec{J}_i$ is the net flux of substance through the boundaries of the considered volume.

Note that while conservation of mass is used to obtain Eq. (20), all components are included in the system of diffusion equations, in contrast to the classical approach where the concentration of the "solvent" is determined solely by conservation of mass. Thus, Eq. (20) can be considered as a generalization of the Gibbs-Duhem equations to an open nonequilibrium system, where substance exchange with the surrounding medium is included. The Gibbs-Duhem equations are used in Ref. [5] to obtain a relationship between the gradients of the component chemical potentials in an isolated system. When one incorporates the concentration and pressure dependence of the component chemical potentials, as done in Ref. [6], the Gibbs-Duhem equation in the gradient form (see Ref. [5], supplement 1 to Chap. 15) can be transformed into Eq. (20) with $\vec{J}_\Sigma=\vec{0}$. As outlined in Ref. [6], this equation can be interpreted as one that formulates the condition of mechanical (hydrostatic) equilibrium in the system under consideration. Because the Gibbs-Duhem equation is closely related to the equation expressing the condition of local equilibrium, one can state that mechanical equilibrium is an essential condition of irreversible thermodynamics.

Equation (20) is similar to the expression for electric field strength in an electrolytic cell [9]. Parameter $\vec{J}_\Sigma$ is analogous to the electric current produced by electrochemical processes at the electrode, which induce a current in the cell. This field is established in electrolytic cells even when a concentration gradient is absent. In Eq. (20), the term proportional to $\vec{J}_\Sigma$ describes the component of the macroscopic pressure gradient that is related to the flux of substance passing through the system, i.e., the flux pressure gradient. The term proportional to $\Sigma_{i=1}^{N} D_i \vec{\nabla}\phi_i$ is analogous to the field produced by the so-called concentration or diffusion potential, and is due to the difference in diffusion rates of the components, i.e., the diffusion pressure gradient. The diffusion pressure gradient can also be considered as a generalization of the osmotic pressure gradient. The term proportional to $\Sigma_{i=1}^{N}\vec{u}_i\phi_i$ corresponds to the field produced from drift and convective ion transport in an external field or flow, i.e., the convection pressure gradient; it becomes zero in an electrolytic cell due to electric neutrality. The term proportional to b_{Dij}, which contains the Hamaker constants of the components, has no direct analog, as it is related to diffusiophoresis, which has not been studied in the theory of electrolytic cells. As stated above, the contribution of diffusiophoresis can be neglected in systems of molecules with small differences in both their Hamaker constants and their molecular volumes. In general, the diffusiophoresis effect is a measure of the difference in physicochemical properties of the components.

Substituting Eq. (20) for the pressure gradient into the system of diffusion equations [Eq. (18a) and (18b)], we can write the symmetrized system of diffusion equations as

$$\frac{\partial \phi_i}{\partial t} = \nabla D_i \frac{\sum_{j\neq i}^{N} p_{ij}\phi_j}{\sum_{j=1}^{N} p_{ij}\phi_j} \nabla \phi_i + \vec{\nabla}\cdot \frac{-\vec{J}_\Sigma - \sum_{j\neq i}^{N} D_j \vec{\nabla}\phi_j + \vec{u}_i \sum_{j=1}^{N}\left(\frac{u_j}{u_i} - p_{ij}\right)\phi_j + \sum_{j=1}^{N} b_{Dij}\vec{\nabla}\phi_j \sum_{k=1}^{N}\left(\frac{r_k^2}{r_i^2}\sqrt{\frac{A_k}{A_i}} - p_{ik}\right)\phi_k}{\sum_{j=1}^{N} p_{ij}\phi_j}\phi_i \quad (1 \leqslant i,j \leqslant N), \tag{21}$$

where $p_{ij} = \overline{v_j} D_j / \overline{v_i} D_i$ is the parameter characterizing the contribution of barophoresis. Equation (21) is structured such that the effective diffusion coefficient and effective velocity of a given molecule depend only on the concentration of other components. Equation (21) demonstrates the important role played by the macroscopic pressure gradient in the logical structure of the theory of diffusiophoresis. Among other things, it eliminates diffusiophoresis in pure liquids, which is indeed very hard to imagine. Thus, the logical necessity of a macroscopic pressure gradient is closely interconnected with the approach used in calculating the parameters of diffusiophoresis. Because this approach gives a nonzero partial (diagonal) cross-diffusion factor b_{Dii}, which formally should cause diffusiophoresis in a pure liquid, its effect should be compensated by another force, which is the barophoretic force described by Eq. (4).

As Eq. (21) shows, the macroscopic pressure gradient plays a role in mixtures placed in a force field. For nonionic systems, this could be a temperature gradient, a gravitational field, or a centrifugal force field. The interrelationship between thermal diffusivity and mass diffusion is particularly interesting. For example, Nieuwoudt and Law [14,15] discussed the influence of a temperature gradient on random molecular motions in binary liquid mixtures, while Anisimov *et al.* [16] discussed the role of thermal diffusivity on random molecular motions in binary gas mixtures near the vapor-liquid critical line. We recently discussed the role of temperature-induced macroscopic pressure gradients in solvents on the thermophoresis of dissolved solutes [17]. In this work, we consider gravitational and centrifugal fields.

Macroscopic pressure gradients may be established in systems where liquid flows or external forces are applied, as well as in systems where mass transfer occurs only at the boundaries. If we consider the latter case, in the absence of any liquid flow or external forces, then the flux of substance $\vec{J}_\Sigma$ in Eq. (18a) and (18b) includes only the mass transfer across interface boundaries. This transfer of molecules across a boundary could be related to an adsorption-desorption process, in which specific molecules are dissolving into solution from one wall of a vessel and removed from solution by adsorption at another wall. Such a situation could occur, for example, in a temperature gradient, where the adsorption and desorption of molecules differ at the cold and hot walls.

In the case of a uniform steady-state mixture, where no macroscopic external force is applied and no mass transfer at the boundaries occurs, the secondary pressure gradient and related coupling between different components can be established locally. In this case, the pressure gradient is related to fluctuations in the local concentration gradients and the related cross-diffusion (diffusiophoresis). Such processes may play a role in the fluctuation dynamics of multicomponent equilibrium systems, where the concentration fluctuations of the different components are coupled, contributing to collective-mode fluctuations in the system. However, the simplest situation for examining the consequences of an established pressure gradient is a binary steady-state liquid mixture placed in a constant force field. In this work, we examine the processes in such a system, where the contributions of diffusiophoresis and barophoresis can be seen in their simplest form.

For a binary system, let $\phi_2=\phi$ and $\phi_1=1-\phi$, so that Eq. (21) takes the following form:

$$\frac{\partial \phi}{\partial t} = \nabla \frac{D_1\phi + p(1-\phi)D_2 + b_{D22}\left(\frac{v_2}{v_1}\sqrt{\frac{A_1}{A_2}} - 1\right)\left(\frac{r_1^2}{r_2^2}\sqrt{\frac{A_1}{A_2}} - p\right)(1-\phi)\phi}{p(1-\phi)+\phi}\vec{\nabla}\phi + \vec{\nabla}\cdot\frac{-\vec{J}_1 - \vec{J}_2 + (\vec{u}_1 - p\vec{u}_2)(1-\phi)}{p(1-\phi)+\phi}\phi. \quad (22)$$

Here $J_{1(2)}$ are the fluxes of the respective components, $p=p_{21}=\overline{v_1}D_1/\overline{v_2}D_2$, and Eq. (16) is utilized. The resulting macroscopic pressure gradient in a binary mixture is

$$\vec{\nabla}P = kT \times \frac{-\vec{J}_1 - \vec{J}_2 + \left\{b_{D22}\left(1 - \frac{v_2}{v_1}\sqrt{\frac{A_1}{A_2}}\right)\left[(1-\phi)\frac{r_1^2}{r_2^2}\sqrt{\frac{A_1}{A_2}} + \phi\right] + D_1 - D_2\right\}\vec{\nabla}\phi + \vec{u}_2\phi + \vec{u}_1(1-\phi)}{D_2\overline{v_2}\phi + D_1\overline{v_1}(1-\phi)}. \quad (23)$$

III. MAIN OUTCOMES AND RESULTS

A. Stationary binary mixture in a force field

For a stationary system in an impermeable vessel, Eq. (22) takes the form

$$\vec{\nabla}\phi = -\frac{(\vec{u}_1 - p\vec{u}_2)(1-\phi)\phi}{D_1\phi + p(1-\phi)D_2 + b_{D22}\left(\frac{v_2}{v_1}\sqrt{\frac{A_1}{A_2}} - 1\right)\left(\frac{r_1^2}{r_2^2}\sqrt{\frac{A_1}{A_2}} - p\right)(1-\phi)\phi}. \quad (24)$$

When the volume fraction of component 2 is low ($\phi\approx 0$), Eq. (24) is transformed into the equation for a Boltzmann concentration distribution of that component,

$$\vec{\nabla}\phi = \frac{p\vec{u}_2 - \vec{u}_1}{pD_2}\phi. \quad (25)$$

When the volume fraction of component 2 is high ($\phi\approx 1$), Eq. (24) is transformed into the equation for the Boltzmann concentration distribution of the first component,

$$\vec{\nabla}\phi_1 = \frac{\vec{u}_1 - p\vec{u}_2}{D_1}\phi_1. \quad (26)$$

In a gravitational or centrifugal field, parameter $(p\vec{u}_2 - \vec{u}_1)/pD_2$ in Eq. (25) can be written as $[\overline{v_2}(\rho_2-\rho_1)\vec{G}]/kT$, where $\vec{G}$ is the acceleration of the respective force. Likewise, parameter $(\vec{u}_1 - p\vec{u}_2)/D_1$ in Eq. (26) can be written as $[\overline{v_1}(\rho_1-\rho_2)\vec{G}]/kT$. These terms correspond to the Archimedes force acting on one component suspended in a second component, where the second component can be considered the solvent in standard theory. Thus, the velocity of the second component at low concentration is determined by the known expression for the Archimedes force. The resulting expression takes into account the "barophoretic" force [Eq. (4)], and while this relationship has been known for a long time, it is obtained here without assuming any concrete form of the pressure gradient in the system.

When no barophoresis or diffusiophoresis is taken into account, Eq. (24) can be written using the standard theory of sedimentation for concentrated mixtures, where the concentration dependence of the density of the medium $\rho(\phi) = \rho_1(1-\phi)+\rho_2\phi$ is taken into account,

$$\vec{\nabla}\phi = -\frac{\overline{v_2}(\rho_2-\rho_1)\vec{G}}{kT}(1-\phi)\phi. \quad (27)$$

Thus, the denominator of Eq. (24) reflects changes in the mixture behavior due to diffusiophoresis and barophoresis.

In order to evaluate the consequences of diffusiophoresis and barophoresis, we will now simplify Eq. (24). Consider the three parameters having dimensions of volume, namely the partial molecular volume $\overline{v_{1(2)}}$, the hydrodynamic volume $v_{1(2)}^H$, and the specific molecular volume $v_{1(2)}$. Equation (24) can be transformed into a form that contains only ratios of these volume parameters for the respective components, or ratios of the associated radii. Then, for molecules with shapes that are not too far from spherical, we can assume these ratios to be about the same for any parameter used as the characteristic volume. Among the possibilities, the specific molecular volumes are convenient because these volumes, and the respective molecule radii, are related by

$$v = \frac{4\pi r^3}{3} = \frac{M}{N_a d}, \quad (28)$$

where M is the molar mass, d is density, and N_a is Avogadro's number. Using this simplification, we can write Eq. (24) in the following form:

$$\vec{\nabla}\phi = -\frac{\vec{u}_1 - p\vec{u}_2}{pD_2}\,\frac{(1-\phi)\phi}{1 + \left(\frac{v_2}{v_1} - 1\right)\phi + \frac{4}{3}\frac{A_2}{kT}\frac{v_1^{2/3}}{v_2^{2/3}}\left(\frac{v_2}{v_1}\sqrt{\frac{A_1}{A_2}} - 1\right)\left(\sqrt{\frac{A_1}{A_2}} - 1\right)(1-\phi)\phi}. \tag{29}$$

An additional assumption made in Eq. (29) is that the hydrodynamic volume of a molecule is equivalent to its specific molecular volume.

The relevant data for benzene and 1,2 dichloroethane (Table I) were taken from Ref. [18], except for the value of benzene's Hamaker constant, which was taken from Ref. [19]. These two solvents were selected because they have unlimited mutual miscibility, so that mixtures can be made with any desired volume fraction. Unfortunately, the value of the Hamaker constant for 1,2-dichloroethane is not available. Instead, we used the solubility parameter δ, which expresses the square-root of the interaction energy of the molecules per unit volume of liquid [18]. For organic solvents, where the van der Waals intermolecular interactions are prevailing, one expects the Hamaker constant $A \approx \delta^2/v^2$. We can express the number of molecules contained in unit volume as $1/v$, and the number of the interacting pairs of molecules to be about $1/v^2$. Using these approximations, the following equation is obtained that relates an unknown Hamaker constant to that of a known value in a different liquid:

$$A_2 \cong A_1 \frac{\delta_2^2 v_1^2}{\delta_1^2 v_2^2}. \tag{30}$$

Equation (29) can be used for any pair of nonpolar liquids, provided we know the solubility parameters and specific molecular volumes for both. The Hamaker constant for 1,2-dichloroethane in Table I was calculated using this approximation.

In order to investigate the effect of diffusiophoresis and barophoresis, we will look at the deviation in the concentration dependence of the concentration gradient from that computed using standard theory [Eq. (27)]. For low molecular-weight species, spatial changes in the component distribution will be very small, except in very strong centrifugal fields. In such cases, Eqs. (24)–(27) can be used to predict the concentration dependence of the concentration gradient, and the gradients can be measured using an optical grating technique [20].

For mixtures of benzene and 1,2-dichloroethane, the reduced concentration gradient is expressed by

$$F(\phi) = \frac{(1-\phi)\phi}{1 - \phi + \frac{v_2}{v_1}\phi + \frac{4}{3}\frac{A_2}{kT}\frac{v_1^{2/3}}{v_2^{2/3}}\left(\frac{v_2}{v_1}\sqrt{\frac{A_1}{A_2}} - 1\right)\left(\sqrt{\frac{A_1}{A_2}} - 1\right)(1-\phi)\phi}. \tag{31}$$

A plot of Eq. (31) is illustrated in Fig. 1, along with a plot of $(1-\phi)\phi$, which expresses the prediction of standard theory. The difference between Eq. (31) and standard theory is quite significant, even for these two highly miscible liquids. Because the function $(1-\phi)\phi$ is universal, the difference between this function and the concentration gradients given by Eq. (31) can be used to obtain values of the Hamaker constant. Thus, parameter $[\overline{v_2}(\rho_2-\rho_1)\vec{G}]/kT$ can be obtained from the concentration dependence of the concentration gradient at low volume fractions [Eq. (25)], and the derivative of the concentration gradient calculated as a function of concentration. Then, by measuring $F(\phi)$ at several volume fractions, calculation of the Hamaker constants will be possible, as specific molecular volumes are readily available in the literature. The relevant parameters can also be obtained by fitting the experimental data to the theoretical concentration dependence. Conversely, experiments on the partitioning of liquids with known Hamaker constants in a sedimentation field can be used to check the theory.

The characteristic value of the stationary concentration gradient $[\overline{v_2}(\rho_2-\rho_1)\vec{G}]/kT$ for mixtures of benzene and 1,2-dichloroethane in a gravitational field can be evaluated using

TABLE I. Solvent parameters.

Solvent	Specific molecular volume, v (10^{21} cm^3)	Molar mass, M (g/mol)	Density, d (g cm^{-3})	Hamaker constant, A ($\times 10^{13}$ erg)	Solubility parameter δ (cal cm^{-3})
1,2-dichloroethane	1.02	99	1.28	8.5	9.78
Benzene	1.16	78	0.89	5.0	9.17

the equation for gravitational acceleration $g = 10^3$ cm/s^2 and the data in Table I. The resulting value is $\sim 10^{-5}$ cm^{-1}. This value could be checked by the optical grating method [20], which is sensitive enough to make such measurements.

We note that the concentration dependence of the stationary concentration gradient contains only thermodynamic parameters of the liquid components, and no dynamic parameters such as viscosity. However, dynamic parameters will be present in expressions that describe the fluctuation behavior of uniform liquid mixtures.

B. Fluctuations in a uniform mixture

According to Eq. (24), the symmetrized diffusion equation for fluctuations in the concentration $\delta\phi$ of a uniform binary mixture, where no external force is applied, taking into account barophoresis effects, is defined by

$$\frac{\partial\,\delta\phi}{\partial t} = \nabla D_2 \frac{\dfrac{D_1}{D_2}\phi + p(1-\phi) + S_{D22}\left(\dfrac{v_2}{v_1}\sqrt{\dfrac{A_1}{A_2}} - 1\right)\left(\dfrac{r_1^2}{r_2^2}\sqrt{\dfrac{A_1}{A_2}} - p\right)(1-\phi)\phi}{p(1-\phi) + \phi} \vec{\nabla}\,\delta\phi. \tag{32}$$

Equation (32) has been linearized because we want to study small fluctuations $\delta\phi$ around a uniform stationary state having volume fraction ϕ. We neglected the term in Eq. (22) related to molecular drift because, as we discussed in the previous section, such effects are very small (although observable by light diffraction techniques) compared to diffusion for low molecular weight species in a gravitational field. Thus, the concentration fluctuations in a binary mixture are dominated by diffusion processes. The concentration fluctuations in liquid mixtures studied by dynamic light scattering [20,21] are a coupled diffusion mode with an effective diffusion coefficient given by

$$D_{\mathrm{eff}} = D_2 \frac{\dfrac{D_1}{D_2}\phi + p(1-\phi) + S_{D22}\left(\dfrac{v_2}{v_1}\sqrt{\dfrac{A_1}{A_2}} - 1\right)\left(\dfrac{r_1^2}{r_2^2}\sqrt{\dfrac{A_1}{A_2}} - p\right)(1-\phi)\phi}{p(1-\phi) + \phi}. \tag{33}$$

Applying Eq. (33) using the same simplification procedure as that used to obtain Eq. (24), we have

$$D_{\mathrm{eff}} = D_2 \frac{\phi + \dfrac{v_1}{v_2}(1-\phi) + \dfrac{4A_2}{3kT}\dfrac{v_1}{v_2}\left(\dfrac{v_2}{v_1}\sqrt{\dfrac{A_1}{A_2}} - 1\right)\left(\sqrt{\dfrac{A_1}{A_2}} - 1\right)(1-\phi)\phi}{\dfrac{v_1}{v_2}(1-\phi) + \dfrac{v_1^{1/3}}{v_2^{1/3}}\phi}. \tag{34}$$

In the use of Eq. (34), we should consider the concentration dependence of the diffusion coefficient that results from a concentration dependence in the viscosity. Assuming the simplest linear concentration dependence of viscosity $\eta(\phi) = \eta_1(1-\phi) + \eta_2\phi$, we obtain

$$\frac{D_{\mathrm{eff}}(\phi)}{D_2^0} = \frac{\phi + \dfrac{v_1}{v_2}(1-\phi) + \dfrac{4A_2}{3kT}\dfrac{v_1}{v_2}\left(\dfrac{v_2}{v_1}\sqrt{\dfrac{A_1}{A_2}} - 1\right)\left(\sqrt{\dfrac{A_1}{A_2}} - 1\right)(1-\phi)\phi}{\left[\dfrac{v_1}{v_2}(1-\phi) + \dfrac{v_1^{1/3}}{v_2^{1/3}}\phi\right]\left[1 + \left(\dfrac{\eta_2}{\eta_1} - 1\right)\phi\right]}, \tag{35}$$

where D_2^0 is the diffusion coefficient of the second component at high dilution. Using the ratio of the viscosities of 1,2-dichloroethane and benzene [18], which is equal to 1.51, we plot Eq. (35) in Fig. 2, along with the concentration dependence of the diffusion coefficient based on standard theory with benzene as the solvent. Our theory predicts a markedly different concentration dependence in the diffusion coefficient measured by dynamic light scattering. Thus, our theory predicts a maximum in the concentration dependence, which can easily be tested in the laboratory.

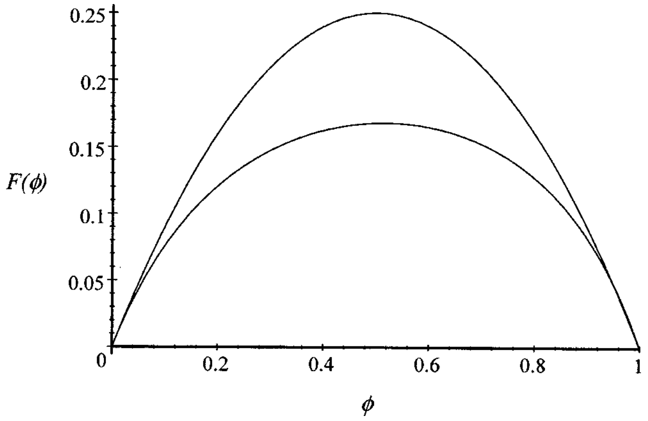

FIG. 1. Dependence of the reduced concentration gradient in 1,2-dichloroethane–benzene mixtures on solvent composition, expressed as the volume fraction ϕ of 1,2-dichloroethane. The lower curve, which has a maximum value of 0.18, is a plot of Eq. (31) (present theory); the upper curve, which has a maximum value of 0.25, represents standard theory [i.e., a plot of $\phi(1-\phi)$].

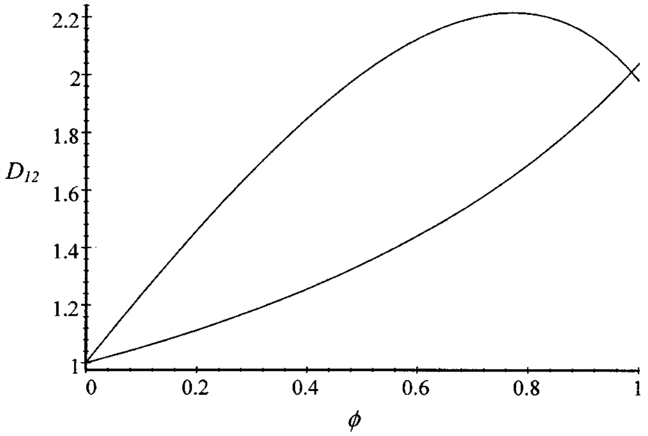

FIG. 2. The dependence of the effective diffusion coefficient D_{12} in 1,2-dichloroethane–benzene mixtures on solvent composition, expressed as the volume fraction ϕ of 1,2-dichloroethane. The concave curve, which has a maximum value of 2.2, plots Eq. (35); the convex curve shows the results obtained using standard theory, which is based on the concentration dependence of the viscosity.

The following function expresses the ratio of the concentration dependence of diffusion predicted by our theory to that of standard theory:

$$\frac{\phi+\frac{v_1}{v_2}(1-\phi)+\frac{4A_2}{3kT}\frac{v_1}{v_2}\left(\frac{v_2}{v_1}\sqrt{\frac{A_1}{A_2}}-1\right)\left(\sqrt{\frac{A_1}{A_2}}-1\right)(1-\phi)\phi}{\frac{v_1}{v_2}(1-\phi)+\frac{v_1^{1/3}}{v_2^{1/3}}\phi}.$$

Analogous to the situation with a stationary concentration gradient, this ratio depends only on thermodynamic parameters of the components.

IV. CONCLUSIONS

The proposed approach to modifying the system of diffusion equations in concentrated liquid mixtures is shown to be reasonable in perspective. Differences between the proposed and standard theory are large enough that they can be evaluated in the laboratory using mixtures of benzene and 1,2-dichloroethane. Those differences increase with the volume fraction of the dilute component, and are observable at a volume fraction of 10%.

The method presented in this work for symmetrizing the diffusion equations may be extended to systems that contain both electric fields and pressure gradients, such as those containing ions. Another potential application of the proposed approach is to the thermophoresis and diffusiophoresis of particles and polymers in solvent mixtures. In such systems, where concentration gradients are established under the action of temperature gradients, gravity, or a centrifugal force, both the barophoretic force and the thermophoretic or diffusiophoretic force must be considered.

Our approach compels us to take a fresh look at theories of separation. For example, in the centrifugation of biological molecules in a density gradient, it is assumed that the molecules are focused into regions where the density of the molecule is equal to the density of the surrounding medium. However, when one considers the barophoretic force, this assumption requires additional consideration. A similar situation occurs in isoelectric focusing, where the barophoretic force can shift the focusing point away from the isoelectric point. Other preparative separation methods may also be affected by barophoresis, such as liquid chromatography and electrophoresis, where concentrated mixtures are processed in an electric field or in hydrodynamic flow. Finally, a number of industrial and natural processes may be affected by barophoresis, such as the distribution of components in a subsurface oil reservoir, or any process that is carried out in a flow reactor or electric field.

---

[1] S. R. De Groot, *Thermodynamics of Irreversible Processes* (North-Holland Publishing Company, Amsterdam, 1952).
[2] R. Krishna and J. A. Wesselingh, Chem. Eng. Sci. **52**, 861 (1997).
[3] R. J. Hunter, *Foundations of Colloid Science* (Clarendon, London, 1989), Vol. 1.
[4] A. A. Shapiro, Physica A **320**, 211 (2003).
[5] D. Kondepudi and I. Prigogine, *Modern Thermodynamics* (Wiley, New York, 1999).
[6] L. D. Landau and E. M. Lifshitz, *Fluid Mechanics* (Pergamon, London, 1959).
[7] B. U. Felderhof, J. Chem. Phys. **118**, 11 326 (2003).
[8] A. Vailati and M. Giglio, Phys. Rev. E **58**, 4361 (1998).
[9] V. G. Levich, *Physicochemical Hydrodynamics* (Prentice-Hall, Englewood Cliffs, NJ, 1962).
[10] J. L. Anderson, Annu. Rev. Fluid Mech. **21**, 61 (1989).

[11] M. E. Schimpf and S. N. Semenov, J. Phys. Chem. B **104**, 9935 (2000).
[12] S. Ross and I. D. Morrison, *Colloidal Systems and Interfaces* (Wiley, New York, 1988).
[13] M. Teubner, J. Chem. Phys. **76**, 5564 (1982).
[14] B. M. Law and J. C. Nieuwoudt, Phys. Rev. A **40**, 3880 (1989).
[15] J. C. Nieuwoudt and B. M. Law, Phys. Rev. A **42**, 2003 (1990).
[16] M. A. Anisimov, V. A. Agayan, A. A. Povodyrev, J. V. Sengers, and E. E. Gorodetskii, Phys. Rev. E **57**, 1946 (1998).
[17] S. Semenov and M. Schimpf, Phys. Rev. E **69**, 011201 (2004).
[18] *Organic Solvents. Physical Properties and Methods of Purifications*, 4th ed., edited by J. A. Riddik, W. B. Bunger, and T. K. Sakano (Wiley, New York, 1986).
[19] A. W. Adamson and A. P. Gast, *Physical Chemistry of Surfaces* (Wiley, New York, 1997).
[20] S. Wiegand and W. Koeler, *Measurement of Transport Coefficients by an Optical Grating Technique, in Thermal Nonequilibrium Phenomena in Fluid Mixtures*, edited by S. Wiegand and W. Koeler (Springer, Berlin, 2002).
[21] *Photon Correlation and Light Beating Spectroscopy*, edited by H. Z. Cummings and E. R. Pike (Plenum Press, New York, 1974).