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DIFFUSIOPHORESIS OF LIQUID DROPS IN VISCOUS MEDIA WITH DUE CONSIDERATION OF INTERNAL FLOWS AND THE PHASE TRANSITION ON THEIR SURFACE

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A theory of diffusiophoresis of a spherical drop in a binary viscous mixture with nonuniform concentration is developed.

In construction of a theory of motion of liquid drops in viscous media with a phase transition occurring on their surface internal flows have not been taken into account so far [1-9]. In fact, drops whose viscosity is very much greater than the viscosity of the external medium surrounding them have been considered. In these conditions the presence of hydrodynamic flows inside the drop can be neglected.

It was shown in [10-12] by the examples of gravitational, thermophoretic, and diffusiophoretic motion of nonvolatile drops in viscous media that the contribution of internal flows to the velocity becomes very substantial if the viscosity of the internal region of the drop is comparable with the viscosity of the medium surrounding the drop. It has also been found that with increase in the radius of the nonvolatile drops of water their velocity of thermophoresis in gases (particularly in air) will depend significantly on the interphase surface tension, which varies over the surface of the drops [11].

Throughout the paper the term "nonvolatile drop" means a drop on whose surface there is no phase transition of the substance of which it consists. The term "volatile drop" means a drop on whose surface there is a phase transition of the substance of which it consists.

In this paper we consider the diffusiophoresis of a large volatile spherical drop of radius R in a binary viscous mixture. By a viscous mixture we mean either a gaseous or liquid mixture. Far from the drop gradients of the relative concentrations $(\nabla C_{1e})_\infty$ and $(\nabla C_{2e})_\infty$ of the mixture components are maintained in the volume of the medium. If the drop is surrounded by a binary gas mixture we choose as C_{1e} and C_{2e} the relative numerical concentrations of the molecules: $C_{1e} = n_{1e}/n_e$, $C_{2e} = n_{2e}/n_e$, $n_e = n_{1e} + n_{2e}$, n_{1e} and n_{2e} are the numbers of molecules of the first and second components of the mixture in unit volume. For the case of a liquid binary mixture external to the drop it is convenient to introduce relative mass concentrations C_{1e} and C_{2e} for the components:

$$C_{1e} = n_{1e}m_1/\rho_e \text{ and } C_{2e} = n_{2e}m_2/\rho_e,$$

where m_1 and m_2 are the masses of the molecules of the mixture components, and $\rho_e = n_{1e}m_1 + n_{2e}m_2$ is the density of the mixture.

The origin of the spherical system of coordinates r, θ, φ can be taken at the center of the drop. In this case the drop can be regarded as at rest, and the binary mixture as moving relative to the center of the drop at constant velocity $\mathbf{U}$. If we choose $(\nabla C_{1e})_\infty$ along the polar axis $Z = r\cos\theta$, then vector $\mathbf{U}$ will be directed along this axis.

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The procedure for solution of this problem is analogous to that described for the solution of problems of thermophoresis and diffusiophoresis of nonvolatile drops with internal flows taken into account [10-12].

The distributions of velocities $\mathbf{v}^{(e)}$ and $\mathbf{v}^{(i)}$, pressures $p^{(e)}$ and $p^{(i)}$, and temperatures $T^{(e)}$ and $T^{(i)}$, respectively, for the external [superscript (e)] and internal[(i)] regions relative to the drop are sought with the aid of the following system of equations:

$$\eta_e \nabla^2 \mathbf{v}^{(e)} = \nabla p^{(e)}, \tag{1}$$

$$\operatorname{div} \mathbf{v}^{(e)} = 0, \tag{2}$$

$$\eta_i \nabla^2 \mathbf{v}^{(i)} = \nabla p^{(i)}, \tag{3}$$

$$\operatorname{div} \mathbf{v}^{(i)} = 0, \tag{4}$$

$$\nabla^2 T^{(e)} = 0, \tag{5}$$

$$\nabla^2 T^{(i)} = 0. \tag{6}$$

In (1) and (3) η_e and η_i are the viscosities of the medium outside and inside the drop, respectively.

For concentrations C_{1e} outside the drop the equation

$$\nabla^2 C_{1e} = 0 \tag{7}$$

is valid. Equations (1)-(7) are presented in linearized form. Linearization is carried out if the relative change in all the quantities that vary with the coordinates [$\mathbf{v}^{(e)}$, C_{1e}, $\mathbf{v}^{(i)}$, T_e, T_i, $p^{(e)}$, and $p^{(i)}$] is small at distances on the order of the drop diameter. It was shown in [2-4] and [10-12] that this condition is equivalent to introduction of a single small parameter

$$(R\nabla) \ll 1. \tag{8}$$

At a great distance from the drop ($r \to \infty$) the boundary conditions

$$v_r^{(e)} = |\mathbf{U}| \cos\theta, \tag{9}$$

$$v_\theta^{(e)} = -|\mathbf{U}| \sin\theta, \tag{10}$$

$$C_{1e} = C_{01e} + (\nabla C_{1e})_\infty r \cos\theta, \tag{11}$$

$$T_e = T_{0e} \tag{12}$$

are valid. In (11), (12) and henceforth the subscript 0 (C_{01}, T_{0e}) denotes values of the quantities at a great distance from the drop.

The surface of the drop is impermeable to the second component of the binary mixture, which can be expressed by the relation

$$\left(n_{02e} v_r^{(e)} + n_{0e}^2 D_{12} \frac{m_1}{\rho_{0e}} \frac{\partial C_{1e}}{\partial r} \right)\Big|_{r=R} = 0 \tag{13}$$

for the case where the external medium is a binary gas mixture.

If the external medium consists of a binary mixture of liquids, we have the following condition for permeability of the second component:

$$\left(n_{02e} v_r^{(e)} + \frac{\rho_{0e}}{m_2} D_{12} \frac{\partial C_{1e}}{\partial r} \right)\Big|_{r=R} = 0. \tag{14}$$

In (13) and (14) n_{02e} is the number of molecules of the second component, and n_{0e} is the total number of molecules, in a unit volume of the mixture, ρ_{0e} is the density, and D_{12} is the coefficient of mutual diffusion.

The first terms on the left sides of (13) and (14) are the convective radial fluxes, and the second terms are the converted (i.e., expressed in terms of $\partial C_{1e}/\partial r$) radial diffusion fluxes of the second component of the mixture.

We assume that the drop retains its spherical shape. The nondeformability condition has the form [13]

$$\frac{\eta_e U}{R} \ll \frac{\sigma}{R}, \tag{15}$$

where σ is the interphase surface tension on the drop—external medium interface.

For the tangential components of the velocity outside $[v_\theta^{(e)}]$ and inside $[v_\theta^{(i)}]$ the drop at r = R the condition [11-12]

$$\left(v_\theta^{(e)} - v_\theta^{(i)}\right)\Big|_{r=R} = K_{Tse}^{(e)} \frac{\eta_e}{\rho_{0e}T_{0e}R} \frac{\partial T_e}{\partial \theta}\Big|_{r=R} + \frac{K_{se}^{(e)}D_{12}}{R} \frac{\partial C_{1e}}{\partial \theta}\Big|_{r=R} \tag{16}$$

is valid. Condition (16) shows that the difference in velocities of the internal and external media on the drop surface $[v_\theta^{(e)} - v_\theta^{(i)}]_{r=R}$ is equal to the sum of the thermal and diffusion slip velocities, which are proportional to the coefficients $K_{Tse}^{(e)}$ and $K_{se}^{(e)}$, respectively.

Condition (16) has the same general form for gaseous and liquid media outside the drop. The difference consists in the specific analytical expression for $K_{Tse}^{(e)}$ and $K_{se}^{(e)}$. Analytical expressions for $K_{Tse}^{(e)}$ and $K_{se}^{(e)}$ were obtained with different degrees of accuracy by different methods for binary gas mixtures in [14-19]. The most accurate results were obtained in [17-19]. The coefficients of thermal and diffusion slip for liquids and, in particular, liquid mixtures have not yet been calculated theoretically. This is due to the fact that a theory of an inhomogeneous liquid at a boundary with another phase must first be constructed. The construction of such a theory, however, involves mathematical difficulties that have not yet been overcome. Nothing we have said, however, rules out the experimental measurement of $K_{Tse}^{(e)}$ and $K_{se}^{(e)}$ for different binary liquid mixtures.

On the surface of the drop, in view of the phase transition of its substance, for the first component of the external mixture we have the condition

$$n_{1e}|_{r=R} = n_{1es}(T_e)|_{r=R}, \tag{17}$$

where $n_{1es}(T_e)$ is the absolute saturating concentration (in number of molecules) of the first component of the mixture at temperature T_e. We can then write

$$n_{1es}(T_e)|_{r=R} = n_{01es}(T_{0e})|_{r=R} + \delta T'_e|_{r=R}. \tag{18}$$

Equation (18) reflects the relation between the saturating concentration of the first component and the temperature; $n_{01es}(T_{0e})$ is the saturating concentration of the first component at temperature T_{0e}, and T'_e is the contribution made to T_{0e} by external temperature gradient. The constant δ in (15) is given by

$$\delta = \frac{dn_{1e}(T)}{dT}. \tag{19}$$

On the drop surface the temperature is continuous:

$$T_e|_{r=R} = T_i|_{r=R}. \tag{20}$$

The difference in heat fluxes outside and inside the drop is equal to the heat going towards phase transition of the drop in unit time for unit surface:

$$\alpha m_1 m_2 \frac{n_{0e}^2}{\rho_{0e}} D_{12} \frac{\partial C_{1e}}{\partial r}\Big|_{r=R} = \left(-\varkappa_e \frac{\partial T_e}{\partial r} + \varkappa_i \frac{\partial T_i}{\partial r}\right)\Big|_{r=R} \tag{21}$$

for the case of a gas phase outside the drop and

$$\alpha \rho_{0e} D_{12} \frac{\partial C_{1e}}{\partial r}\Big|_{r=R} = \left(-\varkappa_e \frac{\partial T_e}{\partial r} + \varkappa_i \frac{\partial T_i}{\partial r}\right)\Big|_{r=R} \tag{22}$$

for the case of a liquid phase outside the drop.

In (21) and (22) α is the specific heat of the phase transition; $\varkappa_e$ and $\varkappa_i$ are the thermal conductivities of the external medium and drop, respectively.

On the drop surface the flow of the first component of the mixture is continuous, which can be expressed by the relations

$$\left(n_{01e}v_r^{(e)} - D_{12}n_{0e}^2 \frac{m_2}{\rho_{0e}} \frac{\partial C_{1e}}{\partial r}\right)\Big|_{r=R} = n_{01i}v_r^{(i)}\Big|_{r=R}, \tag{23}$$

$$\left(n_{01e}v_r^{(e)} - D_{12} \frac{\rho_{0e}}{m_1} \frac{\partial C_{1e}}{\partial r}\right)\Big|_{r=R} = n_{01i}v_r^{(i)}\Big|_{r=R}. \tag{24}$$

Equation (23) is valid for the case of a gas phase external to the drop, and (24) for an external liquid phase. The first terms on the left sides of (23) and (24) are equal to the convective radial fluxes of the first component of the binary mixture, while the second terms are equal to the radial diffusion fluxes of the same component. The term $n_{01i}v_r^{(i)}|_{r=R}$ on the right sides of (23) and (24) is equal to the convective radial flux of matter within the drop at the drop—external medium interface.

On the drop—external medium interface the normal and tangential components of the total stress tensor are continuous (see [13, Chap. 2] or [11]):

$$\left(-p^{(e)}+2\eta_e\frac{\partial v_r^{(e)}}{\partial r}\right)\Bigg|_{r=R}-\frac{2\sigma}{R}=\left(-p^{(i)}+2\eta_i\frac{\partial v_r^{(i)}}{\partial r}\right)\Bigg|_{r=R}, \tag{25}$$

$$\eta_e\left(\frac{1}{r}\ \frac{\partial v_r^{(e)}}{\partial\theta}+\frac{\partial v_\theta^{(e)}}{\partial r}-\frac{v_\theta^{(e)}}{r}\right)\Bigg|_{r=R}+\frac{1}{r}\ \frac{\partial\sigma}{\partial T_e}\ \frac{\partial T_e}{\partial\theta}\Bigg|_{r=R}=\eta_i\left(\frac{1}{r}\ \frac{\partial v_r^{(i)}}{\partial\theta}+\frac{\partial v_\theta^{(i)}}{\partial r}-\frac{v_\theta^{(i)}}{r}\right)\Bigg|_{r=R}. \tag{26}$$

In (26) $1/r(\partial\sigma/\partial T_e)(\partial T_e/\mu\theta)|_{r=R}$ is the tangential component of the force due to temperature variation of the surface tension over the indicated interface.

The solution of the system of differential equations (1)-(7) with boundary conditions (9)-(14) and (16)-(26) can be put in the form [12, 20]

$$v_r^{(e)}=\left(\frac{A_e}{r^3}+\frac{B_e}{r}+|\mathbf{U}|\right)\cos\theta, \tag{27}$$

$$v_\theta^{(e)}=\left(\frac{A_e}{2r^3}-\frac{B_e}{2r}-|\mathbf{U}|\right)\sin\theta, \tag{28}$$

$$p^{(e)}=p_0^{(e)}+\eta_e\frac{B_e}{r^2}\cos\theta, \tag{29}$$

$$v_r^{(i)}=(c_i+D_ir^2)\cos\theta, \tag{30}$$

$$v_\theta^{(i)}=-(c_i+2D_ir^2)\sin\theta, \tag{31}$$

$$p^{(i)}=p_0^{(i)}+10\,\eta_iD_ir^2\cos\theta, \tag{32}$$

$$T_e=T_{0e}+\frac{\mu_1}{r^2}\cos\theta+\frac{\varphi_1}{r}, \tag{33}$$

$$T_i=T_{0i}+\mu_2r\cos\theta, \tag{34}$$

$$C_{1e}=C_{01e}+|(\nabla C_{1e})_\infty|\,r\cos\theta+\frac{\mu_3}{n_{0e}r^2}\cos\theta+\frac{\varphi_2}{r}. \tag{35}$$

Substitution of the solutions (27)-(35) in the boundary conditions (13)-(14), (16)-(18), and (20)-(26) gives a system of equations, with the aid of which we can calculate all the known constants: A_e, B_e, c_i, D_i, μ_1, μ_2, μ_3, $|\mathbf{U}|$, φ_1, and φ_2.

Knowing $|\mathbf{U}|$, we can write an expression for the velocity of the drop in the field of concentration gradient $(\nabla C_1)_\infty$:

$$\begin{aligned}\mathbf{U}_D=-\mathbf{U}=&-\frac{6\eta_i\eta_eK_{Tse}^{(e)}\,\alpha m_1\beta_\alpha(\nabla C_{1e})_\infty}{(2\eta_e+3\eta_i)\,\rho_{0e}T_{0e}\left(2\varkappa_e+\varkappa_i+\dfrac{2\alpha\delta m_1\beta_\alpha}{n_{0e}}\right)}-\frac{6\eta_iK_{se}^{(e)}D_{12}\delta\alpha m_1\dfrac{\beta_\alpha}{n_{0e}}(\nabla C_{1e})_\infty}{(2\eta_e+3\eta_i)\left(2\varkappa_e+\varkappa_i+\dfrac{2\alpha\delta m_1\beta_\alpha}{n_{0e}}\right)}+\\&+\frac{6\eta_i}{(2\eta_e+3\eta_i)}\,\frac{n_{01e}}{n_{01i}}\left(\frac{\beta_\alpha}{n_{01e}}+\frac{\beta}{n_{02e}}\right)\frac{(2\varkappa_e+\varkappa_i)(\nabla C_{1e})_\infty}{\left(2\varkappa_e+\varkappa_i+\dfrac{2\alpha\delta m_1\beta_\alpha}{n_{0e}}\right)}-\frac{2\alpha m_1\beta_\alpha R\dfrac{\partial\sigma_0}{\partial T_e}(\nabla C_{1e})_\infty}{(2\eta_e+3\eta_i)\left(2\varkappa_e+\varkappa_i+\dfrac{2\alpha\delta m_1\beta_\alpha}{n_{0e}}\right)}+\\&+\frac{3\beta(2\eta_e+\eta_i)(2\varkappa_e+\varkappa_i)(\nabla C_{1e})_\infty}{n_{02e}(2\eta_e+3\eta_i)\left(2\varkappa_e+\varkappa_i+\dfrac{2\alpha\delta m_1\beta_\alpha}{n_{0e}}\right)}.\end{aligned} \tag{36}$$

In (36) we have introduced symbols for a gas mixture external to the drop,

$$\beta = n_{0e}^2 D_{12} \frac{m_1}{\rho_{0e}}, \quad \beta_\alpha = n_{0e}^2 D_{12} \frac{m_2}{\rho_{0e}}, \tag{37}$$

and for a liquid mixture external to the drop,

$$\beta = \frac{\rho_{0e} D_{12}}{m_2}, \quad \beta_\alpha = \frac{\rho_{0e} D_{12}}{m_1}. \tag{38}$$

Thus, we have obtained a formula (36) for the velocity of diffusiophoresis of a liquid drop in a binary viscous mixture. The formula is valid for description of the motion of drops in both liquid and gaseous binary mixtures.

In the case of gas mixtures formula (36) can be directly compared with experiment, since all the quantities contained in it can be calculated theoretically. In the case of motion of drops of liquids, however, the coefficients $K_{Tse}^{(e)}$ and $K_{se}^{(e)}$ are unknown, as already mentioned.

The first two terms in (36) make a contribution to the velocity directed towards reduction of the concentration of the first component of the binary mixture, which undergoes a phase transition on the drop surface. The other three terms lead to the appearance of a velocity component directed towards increase in concentration of the same component of the mixture. Thus, the equation of motion of a drop depends significantly on the relative roles of two opposing effects. Owing to thermal and diffusion slip the drop moves in the direction of decrease in the concentration C_{1e}, and due to reactive evaporation and $\partial\sigma/\partial T_e$ it moves in the direction of increase in C_{1e}.

If the viscosity and thermal conductivity of the internal region of the drop η_i and $\varkappa_i$ become very much greater than the viscosity and thermal conductivity η_e and $\varkappa_e$ of the external medium (if the gas contains a highly viscous and highly heat-conducting drop), and $n_{01e}/n_{01i} \to 0$, from (37) we obtain

$$U_D = \frac{\beta}{n_{02e}} (\nabla C_{1e})_\infty = \frac{n_{0e}^2}{n_{02e}} D_{12} \frac{m_1}{\rho_{0e}} (\nabla C_{1e})_\infty. \tag{39}$$

The last formula coincides with the result of [8, 9].

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