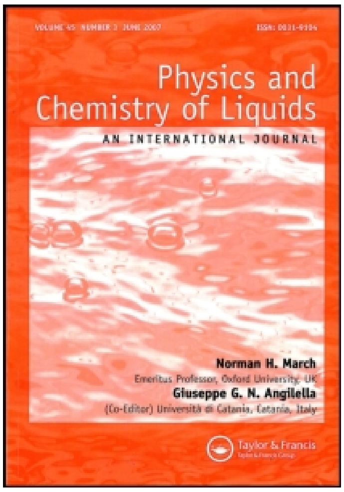

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THERMODYNAMIC INVESTIGATION OF VISCOSITY AND DIFFUSION IN BINARY LIQUID ALLOYS

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A simple formalism is provided to relate the viscosity and the chemical diffusion coefficient of binary liquid alloys. Only under simplified considerations, it reduces to the form of Stokes-Einstein relation. The positive and negative deviations of the viscosity from the additive rule of mixing have been ascribed to the role of energetic and size effects.

1. INTRODUCTION

A good deal of understanding of the structure and the binding at the microscopic level associated with the mixing of binary liquid alloys can be achieved through the knowledge of the atomic transport properties like viscosity (η) and diffusion coefficient (D). But these investigations for binary liquid alloys lag behind the other transport properties both in experimental and in theory. Temperature and composition dependent values of η and D are highly desirable.

Some results available [1] for few liquid alloys indicate that η and D (at a given temperature) may deviate either positive or negative from the linear additive rule of mixing, like any other thermodynamic functions. Through the thermodynamics of mixing, it has been possible, to obtain the thermodynamic functions of mixing from its

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partial values but the same is not as well understood for η and D. It is not very clear that how η and D of the alloy are related to its component values.

As regards to the relation between η and D a good relation ($\eta_A = k_B T/3\pi r D_A$; η_A and D_A are values referred to pure components, and r is the radius of diffusing particle) at least for pure liquids, exists due to Stokes-Einstein. This is also found to work satisfactorily well for dilute solution of spherical particles for relatively large diameters such as macromolecules and colloidal particles. But for a medium consisting of similarly sized particles and for non-dilute solutions, the applicability of Stokes-Einstein relation is yet to be established.

The present work is aimed towards these understandings. Based on a simple approach by considering a thermodynamic force and the related concentration gradient, a suitable relation can be obtained between η and D for binary liquid alloys. It is shown that Stokes-Einstein relation is only a simplified version of the general expression for the binary alloys. The effects of interchange energy and the size factor on viscosity are discussed. The implications of various diffusion coefficients used, in literature, for a binary mixture are analysed. A general formalism related to viscosity and the chemical diffusion coefficient (D_m) for a binary liquid mixture is provided in section 2. The simplified version and its relation to Stokes-Einstein equation are discussed in section 3. The role of energetics and the size factor in creating positive or negative deviations of viscosity from the additive rule of mixing are explained in section 4 followed by conclusion in section 5.

2. GENERAL FORMALISM

Consider a binary mixture consisting of Nc_A atoms of component A and Nc_B of B. Imagine that a gradient (small) of concentration c_A is maintained in an equilibrium condition along x-direction by the application of a force F_A. In case of thermodynamic equilibrium the force F_A, for an ideal dilute solution, can be expressed as

$$F_A = \frac{-k_B T d \ln c_A}{dx} \qquad (1)$$

Here k_B is the Boltzmann's constant and T the temperature. In the absence of the concentration gradient the force F_A will produce an average velocity v_A for A, i.e.

$$v_A = \beta_A F_A = \frac{F_A}{\sigma_A \eta} \tag{2}$$

where β_A is the mobility and $\beta_A^{-1} = \sigma_A \eta$ is the friction coefficient. σ_A depends on size and shape of the particle A. η is the coefficient of viscosity. Therefore, the flux of A per unit cross-sectional area per second is given by

$$J_A = v_A c_A = \frac{F_A c_A}{\sigma_A \eta} \tag{3}$$

Analogous to eq. (1), one can also express the force F_A for non-ideal solution, i.e.

$$F_A = -k_B T \frac{d \ln a_A}{dx} \tag{4}$$

where a_i ($i = A, B$) is the thermodynamic activity of component i. Then the flux for A becomes,

$$J_A = -k_B T \frac{c_A}{\sigma_A \eta} \frac{d \ln a_A}{dx} \tag{5}$$

Equating it to the flux due to Ficks first law, i.e.

$$J_A = -D_A \frac{dc_A}{dx} \tag{6}$$

where D_A is the intrinsic diffusion coefficient. From eqs. (5) and (6), one has

$$D_A = \frac{k_B T}{\sigma_A \eta} \frac{d \ln a_A}{d \ln c_A} \tag{7}$$

Similarly, one can write for the component *B*, i.e.

$$D_B = \frac{k_B T \, d \ln a_B}{\sigma_B \eta \, d \ln c_B} \tag{8}$$

Equations (7) and (8) can now be used to express the chemical diffusion coefficient

$$\begin{aligned} D_m &= c_A D_B + c_B D_A \\ &= \frac{k_B T}{\eta}\left\{\frac{c_A}{\sigma_B}\frac{d \ln a_B}{d \ln c_B} + \frac{c_B}{\sigma_A}\frac{d \ln a_A}{d \ln c_A}\right\} \end{aligned} \tag{9}$$

By virtue of Gibbs-Duhem relation, it can readily be shown that

$$\frac{d \ln a_A}{d \ln c_A} = \frac{d \ln a_B}{d \ln c_B} \tag{10}$$

Therefore, the viscosity η becomes

$$\eta = \frac{k_B T}{D_m}\left\{\frac{c_A}{\sigma_B} + \frac{c_B}{\sigma_A}\right\}\frac{d \ln a_A}{d \ln c_A} \tag{11}$$

The later function of eq. (11), i.e. $d \ln a_A / d \ln c_A$ can be identified as the concentration fluctuations, $S_{cc}(0)$, in the long wavelength limit. By virtue of thermodynamic definition (Bhatia and Thornton [2]), $S_{cc}(0)$ can be expressed as

$$S_{cc}(0) = c_B a_A \left(\frac{\partial a_A}{\partial c_A}\right)^{-1}_{T,p} = c_A a_B \left(\frac{\partial a_B}{\partial c_B}\right)^{-1}_{T,p} \tag{12}$$

one has

$$\frac{d \ln a_A}{d \ln c_A} = \frac{c_A c_B}{S_{cc}(0)} = \frac{S_{cc}^{id}(0)}{S_{cc}(0)} = \phi \tag{13}$$

where p is the pressure.

For a chemically ideal solution, $a_A \rightarrow c_A$, then one has

$$S_{cc}(0) \rightarrow S_{cc}^{id}(0) = c_A c_B; \quad \text{and} \quad \phi = 1 \tag{14}$$

Therefore for binary liquid alloys, η and D_m are related as,

$$\eta = \frac{k_B T}{D_m}\left(\frac{c_A}{\sigma_B} + \frac{c_B}{\sigma_A}\right)\phi \tag{15}$$

As regards to a relation between η and D_m, an equation of the type (15) has been arrived at by different workers independently (see for example, Glasstone, Laidler and Eyring [3], Hartly and Crank [4], Carman and Stein [5]).

Though the actual performance of eq. (15) in binary liquid alloys can not be assessed, at present, for want of specific informations, the general trend of $\eta(c)$ isotherms can be inferred. For sake of qualitative discussion, eq. (15) can be expressed as

$$\eta = \eta^0 \phi \tag{16}$$

with

$$\eta^0 = \frac{k_B T}{D_m}\left(\frac{c_A}{\sigma_B} + \frac{c_B}{\sigma_A}\right) \tag{17}$$

The experimental results available for few systems, by implications, suggest that the prefactor η^0 should be linear in c. Moelwyn-Hughes [6] in a separate analysis also assumed a linear behaviour of the prefactor η^0. Therefore the deviation of η-c isotherm from the additive rule of mixing can generally be ascribed to the factor ϕ (see eqs. (12) and (13)). The function ϕ has been widely investigated (for recent review see Singh and March [7], Singh and Sommer [8]) for different categories of binary liquid mixtures, $\phi \sim 1$ for simple liquid alloys, $\phi \gg 1$ for compound forming (large negative enthalpy of formation) liquid alloys and $\phi \ll 1$ for segregating and immiscible liquid alloys (large positive enthalpy of formation). Therefore η-c isotherms for simple liquid alloys such as Na-K, Ag-Au, Sn-Pb, Pb-Bi, Sb-Bi, etc are likely to be linear or slightly concave. Large positive deviation from the additive rule of mixing is expected for compound forming liquid alloys (such as Hg-Na, Hg-K, Mg-Sn etc) and negative deviation for segregating and immiscible liquid alloys.

The available experimental results on η-c isotherms for compound forming liquid alloys (see Shimoji and Itami [1]) also suggest large positive deviations from the linear law. Similarly the experimental data on segregating liquid alloys (Cd-In [9], Cd-Sn [10], Bi-Zn [11], Cd-Ga [12], Al-In [13]) exhibit values of η less than the linear values at respective compositions. However, the composition isotherm curves of $\eta(c)$ of liquid Bi-Ga and Ga-Hg, (both immiscible liquid alloys) exhibit [12] positive deviations.

3. ON RELATIONSHIP BETWEEN VISCOSITY AND DIFFUSION COEFFICIENTS

It is clear from eq. (15) that η and D_m are related through factors like T, c_i, σ_i and ϕ. It is of considerable interest to examine it under various simple conditions. For a thermodynamically ideal mixture, $\phi = 1$, and therefore eq. (15) becomes

$$\eta^{id} = \frac{k_B T}{D_m^{id}} \left(\frac{c_A}{\sigma_B} + \frac{c_B}{\sigma_A} \right) \tag{18}$$

with

$$D_m^{id} = c_A D_B^{id} + c_B D_A^{id} \tag{19}$$

and

$$D_A^{id} = \frac{k_B T}{\sigma_A \eta}; \; D_B^{id} = \frac{k_B T}{\sigma_B \eta} \tag{20}$$

If one further assumes that under ideal mixing condition, the constituent particles (A and B) are of the same size and shape, then one has

$$\sigma_A = \sigma_B = \sigma, \tag{21}$$

and so, D_A^{id} and D_B^{id} become

$$D_A^{id} = D_B^{id} = \frac{k_B T}{\eta} \tag{22}$$

Eq. (18) now reduces to

$$\eta^{id} = \frac{k_B T}{\sigma D_m^{id}} \tag{23}$$

which is Stokes-Einstein (SE) type relation with $\sigma = 6\pi r$, r is the radius of the diffusing particle. It is evident that η of a binary mixture reduces to this form of Stokes-Einstein relation only in special conditions. It may also be noted that equation of the type (23) is valid for dilute solution of spherical particles and should be strictly applicable for relatively large diameter particles such as macromolecule and colloidal particles. Many attempts [14, 15] have been made to generalize eq. (23) by treating σ as a parameter. It was found that σ may vary from $6\pi r$ to $4\pi r$.

Also, efforts have been made (see for example, Tyrell and Harris [15], Kirkaldy and Young [16]) to establish an empirical relationship between η and D_m for a binary mixture. It was found that these are not linearly related, as expected from SE relation, rather one has

$$D_m \eta^n = \text{constant}, \tag{24}$$

where the exponent n can be considered as the characteristic feature of the system. According to Hiss and Cussler [17], $n = 2/3$ whereas Davies *et al.* [18] reported that $n = 0.45$.

Following the work by Eyring (see Glasstone *et al.* [13]), a relation between η and D_m in a binary mixture can be expressed as

$$\eta = \frac{k_B T}{D_m} \frac{\lambda_1}{\lambda_2 \lambda_3} \phi \tag{25}$$

where λ_1 is the distance between two layers of particles in the liquid, λ_2 is the distance between two adjacent particles in the moving layer in the direction at right angles to the direction of motion, and λ_3 is the distance between neighbouring particles in the direction of motion. Obviously the pre-factor on r.h.s. of eq. (25) should have the same physical significance as in eq. (15). For ideal mixture ($\lambda_1 = \lambda_2 = \lambda_3 = \lambda$) eq. (25) reduces to

$$\eta^{id} = \frac{k_B T}{\lambda D^{id}} \tag{26}$$

4. EFFECT OF ENERGETICS AND SIZE FACTOR ON VISCOSITY

It is clear from the discussion of section 2 that η-c isotherms mainly depend on the factor ϕ. In this regard, the work of Osman and Singh [19] who have carried out a thermodynamic investigation of ϕ for enthalpic and entropic effects separately is of direct relevance. Taking into account of the enthalpic effects only, ϕ can be expressed as

$$\phi = 1 - c_A c_B \left(\frac{2\omega}{k_B T}\right) \tag{27}$$

where $\omega\left(= \varepsilon_{AB} - \frac{\varepsilon_{AA}+\varepsilon_{BB}}{2}\right.$, ε_{ij} are i–j bond strengths) is known as order energy or interchange energy. An ideal mixture is defined for additive bond strengths (i.e., $\varepsilon_{AB} = \frac{\varepsilon_{AA}+\varepsilon_{BB}}{2}$, i.e., $\omega = 0$). If $\omega < 0$ then unlike atoms ($A-B$) pairs are preferred over like atoms pairs (i.e. $A-A$ or $B-B$). Converse if true for $\omega > 0$.

Eqs. (27) and (16), yield

$$\eta = \eta^0 \left\{1 - c_A c_B \left(\frac{2\omega}{k_B T}\right)\right\} \tag{28}$$

or

$$\frac{\Delta\eta}{\eta^0} = -2 c_A c_B \left(\frac{\omega}{k_B T}\right) \tag{29}$$

where $\Delta\eta = [\eta - \eta^0]$. For $\omega = 0$, $\eta = \eta^0$. In a quite different approach, Moelwyn-Hughes [6], also approximated that $\eta^0 = c_A \eta_0^A + c_B \eta_0^B$, η_0^i is the viscosity of pure components. Eq. (28) suggests that the η-c isotherms exhibit positive deviation for $\omega < 0$ and reverse is true for $\omega > 0$. As an schematic representation $\Delta\eta/\eta^0$ for different values of ω is shown in Figure 1. It is clear from the Figure 1 that due to energetic effects alone, $\Delta\eta$ always exhibits maximum or minimum at equiatomic composition.

One can also express eq. (29) in terms of enthalpy of formation (H_M). In the light of conformal solution results, one has

$$\frac{H_M}{RT} = 2 c_A c_B \left(\frac{\omega}{k_B T}\right) \tag{30}$$

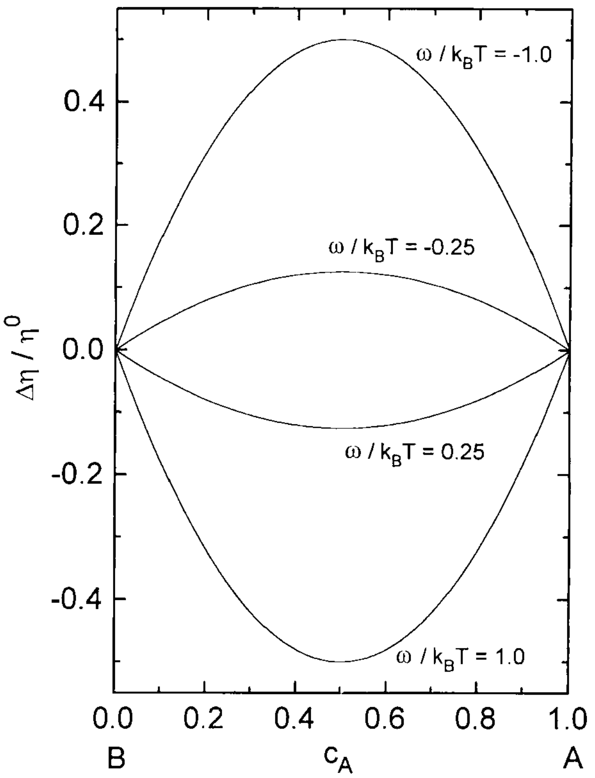

FIGURE 1 Effect of the order energy (ω/k_BT) on the viscosity.

Therefore eq. (29) becomes

$$\frac{\Delta\eta}{\eta^0} = -\frac{H_M}{RT} \tag{31}$$

where R is the gas constant.

Though eq. (31) has been derived under very simple conditions, it sets the right trend for η and H_M dependence.

On the other hand, by considering the entropic effects, Osman and Singh [19] showed that

$$\phi = 1 + c_A c_B \left(\frac{\gamma - 1}{c_A + \gamma c_B}\right)^2 \tag{32}$$

where $\gamma (\equiv \Omega_B/\Omega_A; \Omega_B > \Omega_A, \Omega_i$ is the atomic volume) is treated as the size factor. Due to entropic effect, eq. (16) becomes

$$\frac{\Delta\eta}{\eta^0} = c_A c_B \left(\frac{\gamma - 1}{c_A + \gamma c_B} \right)^2 \tag{33}$$

For $\gamma = 1$, $\eta = \eta^0$ eq. (31) reveals that asymmetry in $\Delta\eta$ about $c_A = c_B = 0.5$ is induced by size factor γ. The composition of asymmetry depends on γ. Also $\Delta\eta$ is always positive due to size effect. $\Delta\eta/\eta^0$ for different γ is shown in Figure 2.

In actual practice, η of a given mixture, however, depends collectively on both enthalpic and entropic effects. The combined role of

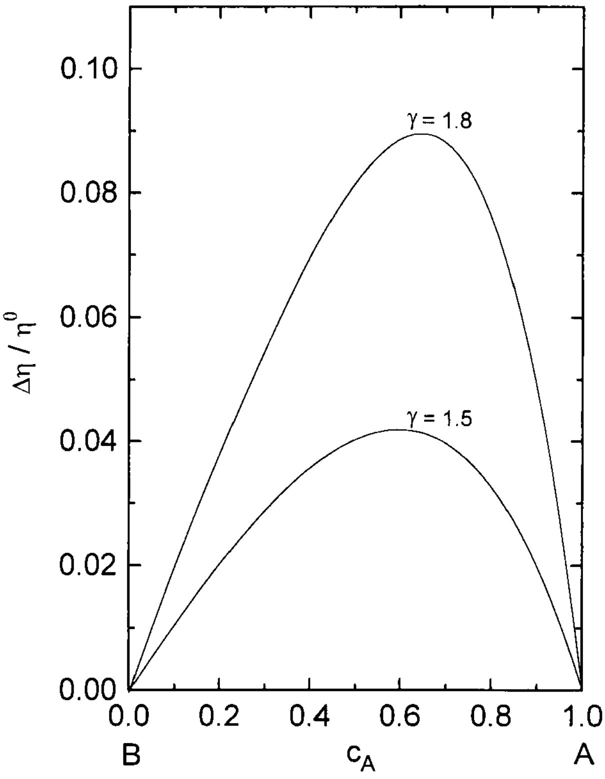

FIGURE 2 Effect of size factor $\gamma (= \Omega_B/\Omega_A, \Omega_B > \Omega_A, \Omega_i$ is the atomic volume) on viscosity.

these two effects was also discussed in ref. [19], which enables one to write,

$$\phi = 1 - c_A c_B g(\gamma, W) \tag{34}$$

with

$$g(\gamma, W) = \frac{2\gamma^2 W - (\gamma - 1)^2 \{c_A + \gamma c_B\}}{(c_A + \gamma c_B)^3} \tag{35}$$

$$W = \Omega_A \left(\frac{\omega}{k_B T}\right) \tag{36}$$

Therefore, $\Delta\eta/\eta^0$ becomes

$$\frac{\Delta\eta}{\eta^0} = -c_A c_B g(\gamma, W) \tag{37}$$

The factor $g(\gamma, W)$, which incorporates both energetic and size effects is responsible for the characteristic behaviour of $\Delta\eta$ for a given binary liquid alloys. The implications of the factor $g(\gamma, W)$ in eq. (37), and that of D_m and σ_i in eq. (15) shall be discussed for binary liquid alloys where reliable η, D_m and other thermodynamic data exist simultaneously, in the forthcoming publication.

5. CONCLUSIONS

A simple approach for binary liquid alloys encompassing the thermodynamic force and the related concentration gradient is used to obtain a suitable relation between η and D_m. It has been observed that the Stokes-Einstein type relation for liquid alloys can only be procured under very simplified approximations. It also paved the way to investigated the role of interchange energy and the size factor on viscosity of liquid alloys. Some important results are as follows:

(i) The deviation of η-c isotherm from the additive rule of mixing can be ascribed to the factor $\phi(= S_{cc}^{id}(0)/S_{cc}(0))$. Positive deviation is expected for compound forming liquid alloys and the negative deviation for segregating and immiscible liquid alloys.

(ii) Due to energetic effects alone, the viscosity deviation ($\Delta\eta$) could be positive or negative. $\Delta\eta$ is always positive due to size effect and the position of asymmetry depends on size factor. The characteristic behaviour of $\Delta\eta$ for a given binary liquid alloys depends on the coupled effects of energetic and the size factor.

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