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Self diffusion in liquid Na–K alloy

R V GOPALA RAO and A K MURTHY
Physical Chemistry Section, Jadavpur University, Calcutta 700 032

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Abstract. Self diffusion coefficients, D_i, in liquid Na-K alloy at 373 K have been computed in the linear trajectory approximation of Helfand, with square well as an attractive tail. From the computed D_{Na} and D_{K}, the mutual diffusion coefficient, D_{NaK} has also been determined. D_{Na}, D_{K} and D_{NaK} all increase with increase of concentration of potassium, while the ratio, $D_{\text{Na}}/D_{\text{K}}$ remains constant (1·45±0·01) over the entire concentration range.

Keywords. Liquid binary; self and mutual diffusion coefficients; linear trajectory approximation; square well model.

1. Introduction

Recently the authors have calculated the self diffusion coefficients for various liquid metals (Gopala Rao and Murthy 1975a; hereafter referred to as I), in the linear trajectory (LT) approximation (Helfand 1964) with square well as an attractive tail. In this paper we propose to extend the same to liquid binary alloys, taking Na-K system as an example, to calculate the self diffusion coefficients, D_i, of the species i in the binary system.

Largely because of its mathematical simplicity, the square well potential has been used to describe the interaction energy of dense fluids. Recent studies also proved its usefulness in the theoretical studies of conducting fluids like liquid metals (Gopala Rao and Murthy 1975a; 1975b) and alloys (Gopala Rao and Murthy, 1975c; 1975d).

2. Theory

According to the LT approximation of Helfand (1964), extended to binary mixtures by Davis and Polyvos (1967), the D_i in the binary mixture are given by the equations:

$$D_i = k_B T/\zeta_i \tag{1}$$

the friction coefficients ζ_i of the species i being,

$$\zeta_i = \zeta_i^H + \zeta_i^S + \zeta_i^{SH} \tag{2}$$

with

$$\zeta_i^H = \sum_{j=1}^{2} \tfrac{8}{3}\, \sigma_{ij}^2\, g_{ij}(\sigma_{ij})\, \rho_j\, (2\pi\mu_{ij} k_B T)^{\frac{1}{2}} \tag{3}$$

$$\zeta_i{}^S = \sum_{j=1}^{2} \frac{\rho_j}{3} (2\pi\mu_{ij}/k_B T)^{\frac{1}{2}} (2\pi)^{-2} \int_0^\infty k^3 \tilde{V}_{ij}{}^S(k)\, \tilde{G}_{ij}(k)\, dk \tag{4}$$

and

$$\zeta_i{}^{SH} = -\sum_{j=1}^{2} \frac{2\rho_j}{3} g_{ij}(\sigma_{ij}) (2\mu_{ij}/\pi k_B T)^{\frac{1}{2}} \times \int_0^\infty dk (k\sigma_{ij} \cos k\sigma_{ij} - \sin k\sigma_{ij})\, V_{ij}{}^S(k) \tag{5}$$

$\zeta_i{}^H$, $\zeta_i{}^S$ and $\zeta_i{}^{SH}$ are the friction coefficients due to the repulsive core interactions, soft interactions and to the cross effects between the hard and soft forces in the pair potential respectively. ρ_i is the number density of the species i. $\tilde{G}_{ij}(k)$ and $\tilde{V}^S{}_{ij}(k)$ are the Fourier transforms, respectively, of the total correlation function, $(g_{ij}(r) - 1)$, and soft part of the potential, $V_{ij}(r)$, σ_i is the rigid sphere diameter of species i. The reduced mass, μ_{ij}, is related to the atomic masses, m_i, as

$$\mu_{ij} = m_i m_j/(m_i + m_j). \tag{6}$$

Under the square well model (I), extended to binary mixtures (Gopala Rao and Murthy 1975c; 1975d), $G_{ij}(k)$ and $V^S{}_{ij}(k)$ become,

$$G_{ij}(k) \doteq [S_{ij}(k) - \delta_{ij}] (\rho_i \rho_j)^{-\frac{1}{2}} \tag{7}$$

$$V^S{}_{ij}(k) = \frac{4\pi\epsilon_{ij}}{k^3} (Ak\,\sigma_{ij} \cos Ak\,\sigma_{ij} - \sin Ak\,\sigma_{ij} - k\sigma_{ij} \cos k\sigma_{ij} + \sin k\sigma_{ij}) \tag{8}$$

where ϵ_{ij} and A represent the depth and breadth, respectively, of the square well used; δ_{ij} is the Kronecker delta function; and $S_{ij}(k)$ are the partial structure factors. Square well partials have been derived elsewhere (Gopala Rao and Murthy 1975c) and we directly use the same in the computation of D_i's for liquid Na-K alloy at 373K.

3. Results and discussion

Presented in table 1 are the results for the various ζ_i's for liquid Na-K alloy at 373K, at various concentrations of potassium. The 'like' potential parameters used are those given in I and the 'unlike' parameters have been determined by the Lorentz-Berthelot rules. The density data has been taken from Abowitz and Gordon (1962).

As in I, the $\zeta_i{}^H$ contributes nearly 55% of the total ζ_i. Table 2 shows the self diffusion coefficients for sodium and potassium at various concentrations. To our knowledge there are no experimental data for D_i to compare with our theoretical results. As can be seen from table 2, both D_{Na} and D_{K} increase with increasing concentration of potassium, while the ratio, $D_{\text{Na}}/D_{\text{K}}$ remains constant ($1{\cdot}45 \pm 0{\cdot}01$) over the entire concentration range. Exactly the same behaviour has been observed, very recently by Jacucci and McDonald (1975) for rare gas liquid mixtures by computer "experiments".

Table 1*. Various friction coefficients for liquid Na-K alloy at 373 K

Concentration (%K)	ζ_i^H/k_BT		ζ_i^S/k_BT		ζ_i^{SH}/k_BT	
	Na	K	Na	K	Na	K
0·1	0·1375	0·2063	0·0298	0·0358	0·0723	0·1034
0·2	0·1316	0·1977	0·0288	0·0348	0·0688	0·0985
0·3	0·1262	0·1901	0·0279	0·0339	0·0656	0·0941
0·4	0·1216	0·1834	0·0271	0·0331	0·0629	0·0903
0·5	0·1170	0·1767	0·0263	0·0323	0·0602	0·0866
0·6	0·1127	0·1705	0·0256	0·0316	0·0577	0·0832
0·7	0·1090	0·1651	0·0250	0·0309	0·0556	0·0802
0·8	0·1054	0·1598	0·0244	0·0302	0·0536	0·0774
0·9	0·1016	0·1542	0·0238	0·0296	0·0515	0·0744

*ζ_i/kT are in units of 10^5 sec/cm^2.

Table 2.* Self and mutual diffusion coefficients for liquid Na-K at 373 K.

Concentration (%K)	D_{Na}	D_K	D_{NaK}	D_{Na}/D_K
0·1	4·169	2·894	3·021	1·441
0·2	4·360	3·019	3·287	1·444
0·3	4·547	3·142	3·563	1·447
0·4	4·723	3·257	3·844	1·450
0·5	4·909	3·380	4·144	1·452
0·6	5·097	3·504	4·461	1·454
0·7	5·270	3·618	4·775	1·456
0·8	5·451	3·738	5·108	1·458
0·9	5·649	3·870	5·471	1·463

*D_i and D_{NaK} are in units of 10^{-5} cm^2/sec.

Table 3. Shear viscosity times and self diffusion coefficients.

Concentration (%K)	Shear viscosity η(in cp)	ηD_{Na} (gm.cm/sec^2)	ηD_K (gm.cm/sec^2)
0·1	0·6531	2·723	1·890
0·2	0·6201	2·704	1·873
0·3	0·5871	2·670	1·845
0·4	0·5580	2·635	1·818
0·5	0·5323	2·613	1·799
0·6	0·5096	2·597	1·785
0·7	0·4869	2·565	1·762
0·8	0·4628	2·523	1·730
0·9	0·4455	2·517	1·697

Constancy of this ratio is also expected from the regular solution theory (Bearman and Jones 1960; Bearman 1961). Under the regular solution hypothesis, ηD_1 and ηD_2 are independent of composition. Here η is the shear viscosity of the mixture or alloy. Alternatively the ratio, D_1/D_2 is independent of composition. Table 3 shows the values ηD_{Na} and ηD_{K} with η values taken from the data of Ewing *et al* (1951). In the present case also, ηD_1 and ηD_2 remain nearly constant with the average values being 2·616 for ηD_{Na} and 1·792 for ηD_{K}.

The ratio in table 2 is well given by the square of the inverse ratio of the corresponding molecular diameters i.e. $D_1/D_2 = (\sigma_2/\sigma_1)^2$, a relation found useful in Ar-Kr mixtures (Jacucci and McDonald 1975). Presently this ratio, $(\sigma_{\mathrm{K}}/\sigma_{\mathrm{Na}})^2$ turns out to be 1·53 and is in good agreement with that given in table 2.

Since the diffusion also depends on the atomic masses, the ratio, $(m_2/m_1)^{\frac{1}{2}}$, has been tried in the present Na-K system. This ratio gives a lower value of 1·3. In addition to the above relations, we may obtain a relation expressing the ratio, D_1/D_2, in terms of both atomic masses and molecular diameters, σ_i's. To this, we start with eqs (1) and (3) and assume, as a first approximation, that D_i values are mostly given by the hard core part. Hence from eqs (1) and (3), it follows that,

$$D_1/D_2 \approx \zeta_2^H/\zeta_1^H \tag{9}$$

$$\begin{aligned}
&= \left\{\frac{8\rho_1}{3}\sigma^2_{12}\, g_{12}\,(2\pi\,\mu_{12}\,k_B T)^{\frac{1}{2}} + \right.\\
&\qquad \left.\frac{8\rho_2}{3}\sigma^2_{22}\, g_{22}\,(2\pi\, k_B T\,\mu_{22})^{\frac{1}{2}}\right\} \times\\
&\qquad \left\{\frac{8\rho_1}{3}\sigma^2_{11}\, g_{11}\,(2\pi\,\mu_{11}\,k_B T)^{\frac{1}{2}} + \right.\\
&\qquad \left.\frac{8\rho_2}{3}\sigma^2_{12}\, g_{12}\,(2\pi\,\mu_{12}\,k_B T)^{\frac{1}{2}}\right\}^{-1}\\
&\equiv \{\rho_1 D + E\}\;\{F + \rho_2 D\}^{-1}.
\end{aligned} \tag{10}$$

To simplify the above equation further, we consider eq. (10) in the limit $\rho_2 \to 0$. In this limit, eq. (10) becomes,

$$D_1/D_2 = \rho_1\, D/F \tag{11}$$

$$= \frac{g_{12}}{g_{11}}\left(\frac{\mu_{12}}{\mu_{11}}\right)^{\frac{1}{2}}\left(\frac{\sigma_{12}}{\sigma_{11}}\right)^2$$

$$= \frac{g_{12}}{g_{11}}\left(\frac{2M_2}{M_1 + M_2}\right)^{\frac{1}{2}}\left(\frac{\sigma_{12}}{\sigma_{11}}\right)^2. \tag{12}$$

Considering eq. (10) in the other limit, i.e. $\rho_1 \to 0$, we obtain

$$D_1/D_2 = \rho_2\, E/D$$

$$= \frac{g_{22}}{g_{12}}\left(\frac{M_1 + M_2}{2M_1}\right)^{\frac{1}{2}}\left(\frac{\sigma_{22}}{\sigma_{12}}\right)^2 \tag{13}$$

The calculated ratios from eqs (12) and (13), respectively, are 1·489 and 1·526, deviating by about 2% from each other. These values are in very good agreement with those given in table 2. Since the values for the ratio, D_1/D_2, in the two limits are very close to the observed ones, we may expect that eq. (10), which is valid at all concentrations, would give a value in between the above two values.

Two other relations,

$$\begin{aligned} D_{\text{Na}}/D_{\text{K}} &= (\sigma_{\text{K}}\, M_{\text{K}}/\sigma_{\text{Na}}\, M_{\text{Na}})^{\frac{1}{2}} \\ &= 1{\cdot}454 \end{aligned} \tag{14}$$

and

$$\begin{aligned} D_{\text{Na}}/D_{\text{K}} &= \left(\frac{\sigma_{\text{NaK}}}{\sigma_{\text{Na}}}\right)\left(\frac{M_{\text{K}}}{M_{\text{Na}}}\right)^{\frac{1}{2}} \\ &= \left(\frac{\sigma_{\text{K}}}{\sigma_{\text{NaK}}}\right)\left(\frac{M_{\text{K}}}{M_{\text{Na}}}\right)^{\frac{1}{2}} \\ &= 1{\cdot}445 \end{aligned} \tag{15}$$

have also been found to reproduce the results in table 2.

So far no concrete theory has been developed to relate the mutual diffusion coefficients to the self diffusion coefficients of species in the mixture. Ebbsjo *et al* (1974) for isotopic mixtures, Parrinello *et al* (1974) for conformal mixtures of equal mass, Jacucci and McDonald (1975) for rare gas liquid mixtures, studied a relation,

$$D_{12} = c_2 D_1 + c_1 D_2 + \text{correction term} \tag{16}$$

which is a sum of terms of linear in the D_i's and a 'correction term' to account for the cross correlations and concluded that the correction term is negligible except for ionic liquids.

Table 2 shows (in column 4) the D_{NaK} values calculated from eq. (16) without the correction term and these values also increase with increase of concentration of potassium. This behaviour of D_{NaK} is in best accord with that expected from the concentration isotherm of the shear viscosity of this liquid alloy (Ewing *et al* 1951). The concentration isotherms of the shear viscosity of liquid Na-K alloy show no apparent discontinuity at any temperature and the present results also predicts the same since no discontinuity in the diffusion results (table 2) has been observed.

Finally it is worthwhile to mention that the potential parameters used are those fitted to give the correct first peak heights in the structure factor curves and thus the present calculations of self diffusion coefficients contain no adjustable (with respect to diffusion calculations) parameters.

Thus the present model also represents the structure of liquid alloys quite satisfactorily.

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