Molecular Origin of Thermal Diffusion in Benzene + Cyclohexane Mixtures

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The isotope effect in thermal diffusion (Soret effect) of benzene + cyclohexane mixtures has been investigated by a holographic grating technique. The Soret coefficient can be split into additive contributions. One contribution, the isotope effect, stems from the differences of both mass and moment of inertia, and is independent of composition. An additional "chemical" contribution depends on concentration and even changes its sign at a benzene mole fraction $x_{\mathrm{benz}} \approx 0.7$. The mass effect is in agreement with molecular dynamics calculations: the heavier component migrates to the cold side.

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A temperature gradient across a fluid or gaseous mixture generally leads to a net mass flux and the buildup of a concentration gradient. This effect is known as thermal diffusion or Ludwig-Soret effect [1,2]. The amplitude of the concentration gradient is determined by the Soret coefficient S_{T}. Compared to other transport properties, reliable experimental data and studies on thermal diffusion in binary liquids where only a few well-defined experimental parameters are varied in a systematic way are scarce. At the same time, there is no theory available that could predict the amplitude or at least the sign of S_{T} from molecular properties. Experimentally, even a change of sign of S_{T} has been observed for ethanol/water mixtures at an ethanol weight fraction of approximately 0.29 [3]. Rutherford [4,5] and Ma and Beyerlein [6] have investigated isotopic mixtures of organic liquids like benzene with a thermogravitational column and found that S_{T} depends not only on the mass difference but also on the difference of the mass distribution within the isotopically substituted molecules. Computer simulations of Lennard-Jones liquids with an interaction potential

$$U_{\mathrm{LJ}}(r) = 4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right] \tag{1}$$

have been carried out [7–12] in order to identify relevant molecular parameters. σ and ϵ are related to the molecular diameter and the depth of the potential, respectively, and r is the intermolecular distance. It has been found that the differences of molecular mass M, diameter, and interaction strength contribute almost additively to S_{T} [12], the mass effect being such that the heavier molecules accumulate on the cold side.

It is immediately evident that S_{T} must vanish for isotopic mixtures of identical substitution patterns, where both components become indistinguishable. To our knowledge, no study on the isotope effect in a mixture of two different liquids has been carried out so far. Since, in this case, the molecules differ not only with respect to their mass and mass distribution, a finite Soret coefficient is expected even if these two parameters agree for the two species. The questions that shall be addressed for liquid mixtures in this contribution are as follows.

(1) Is it possible to split S_{T} into different contributions, and, if so, are these contributions additive?

(2) Is the part caused by the differences in mass and mass distribution comparable to S_{T} of isotopic mixtures, and is the sign such that the heavy component tends towards the cold regions as predicted by computer simulations? What is the relative importance of mass and mass distribution?

(3) What are magnitude and origin of the remaining part?

(4) What is the composition dependence of the individual contributions?

In order to answer these questions, benzene/cyclohexane mixtures have been chosen. Both molecules are of high symmetry and almost identical with respect to size and interaction strength, as expressed by the Lennard-Jones parameters σ and ϵ in Table I [13].

The masses M of benzene (C_6H_6) and cyclohexane (C_6H_{12}) can be made equal by two different isotopic substitutions at all hydrogen or all carbon positions of benzene: H → D or $^{12}C \rightarrow {}^{13}C$. The natural abundances of D and ^{13}C are only negligible 0.0115% and 1.07%, respectively. The masses and the moments of inertia I for rotation around the z axis perpendicular to the plane of the molecule are listed in Table II. While M is identical for C_6D_6 and $^{13}C_6H_6$, the mass distribution as characterized by the moment of inertia

$$I = \sum_i m_i(x_i^2 + y_i^2) \tag{2}$$

is different. m_i is the mass and (x_i, y_i) are the coordinates in the xy plane of the ith atom.

For the measurement of the Soret coefficients, we employed a transient holographic grating technique with heterodyne detection and active phase tracking. It has been

TABLE I. Lennard-Jones parameters of benzene and cyclohexane.

Compound	M (amu)	σ (nm)	ϵ (kJ/mol)
C_6H_6	78.1	0.528	3.175
C_6H_{12}	84.2	0.564	3.175

TABLE II. Molecular mass m and moment of inertia I of the liquids.

Compound	M (amu)	I (amu Å^2)
C_6H_6	78.1	174.0
C_6DH_5	79.1	179.9
$C_6D_3H_3$	81.3	192.1
C_6D_5H	83.1	204.2
C_6D_6	84.2	210.3
$^{13}C_6H_6$	84.1	185.4
C_6H_{12}	84.2	198.8
C_6D_{12}	96.2	248.0

described in detail elsewhere [14,15]. Quinizarin was used as inert dye. Absorption of light within a holographic interference grating leads to a temperature and, due to the Ludwig-Soret effect, also to a concentration grating. Both gratings are read by Bragg diffraction and separated based on their different lifetimes of microseconds and milliseconds, respectively. The amplitude of the temperature grating was merely on the order of 10 μK. All data analysis is based on a solution of the diffusion equation [16]

$$\frac{\partial c}{\partial t} = D\Delta c + D_{\mathrm{T}}\nabla c(1 - c)\nabla T\,. \tag{3}$$

D is the mass diffusion, D_{T} the thermal diffusion coefficient, and $S_{\mathrm{T}} = D_{\mathrm{T}}/D$. The spatial and temporal temperature distribution $T(\vec{r}, t)$ is obtained from the heat equation with the periodic heating of the absorbed light field from the interference grating as the source term. All chemicals have been obtained from Aldrich with a purity of 98% (C_6DH_5, $C_6D_3H_3$), 99% (C_6D_5H, $^{13}C_6H_6$), and 99.5% (C_6H_6, C_6D_6, C_6H_{12}, C_6D_{12}).

Figure 1 shows a pronounced isotope effect for C_6H_6/C_6H_{12} and C_6D_6/C_6H_{12} mixtures at a benzene concentration of $c = 0.75$ (weight fraction). The heterodyne diffraction efficiencies are normalized to the diffraction efficiency of the temperature grating and plotted as a function of time after the grating has been switched on. Obviously, S_{T} even changes sign. The negative amplitude of the concentration mode in case of C_6H_6/C_6H_{12} corresponds to a negative Soret coefficient of C_6H_6 in C_6H_{12}, meaning that C_6H_6 migrates into the hot regions. After deuteration, benzene reverses its direction. It now prefers the cold areas, and S_{T} of C_6D_6 in C_6H_{12} is positive.

Figure 2 shows S_{T} as a function of the mass difference between cyclohexane and benzene for different isotopic substitution patterns as listed in the legend. The benzene mole fraction is $x = 0.5$. From this plot, it is immediately evident that the isotope effect is not a pure function of the mass difference ΔM. There are two mixtures with identical molecular masses of the two constituents: C_6D_6-C_6H_{12} and $^{13}C_6H_6$-C_6H_{12}. The corresponding Soret coefficients are significantly different and both are finite.

The lines a and a' correspond to the transition $C_6D_6 \rightarrow C_6H_6$, a reduction of M_{benz} by 6 amu, and the lines b and b' correspond to an increase of M_{chex} by 12 amu ($C_6H_{12} \rightarrow C_6D_{12}$). Some measurements have also been performed along line a with benzene of varying degrees of deuteration.

The same data are replotted in Fig. 3, where the isotope effect is not only accounted for by the mass difference but also by the difference of the moments of inertia:

$$S_{\mathrm{T}} = S_{\mathrm{T}}^0 + a_{\mathrm{M}}\delta M + b_{\mathrm{I}}\delta I\,, \tag{4}$$

$\delta M = (M_{\mathrm{chex}} - M_{\mathrm{benz}})/(M_{\mathrm{chex}} + M_{\mathrm{benz}})$, and $\delta I = (I_{\mathrm{chex}} - I_{\mathrm{benz}})/(I_{\mathrm{chex}} + I_{\mathrm{benz}})$. The isotopic part of Eq. (4) has already been introduced by Schirdewahn *et al.* for gaseous isotopic mixtures of hydrogen [17] and by Rutherford for isotopic mixtures of benzene [5]. Since we are dealing with chemically different species, an additional contribution S_{T}^0 has been added to account for the finite Soret effect that would still be observed if benzene and cyclohexane could be made identical

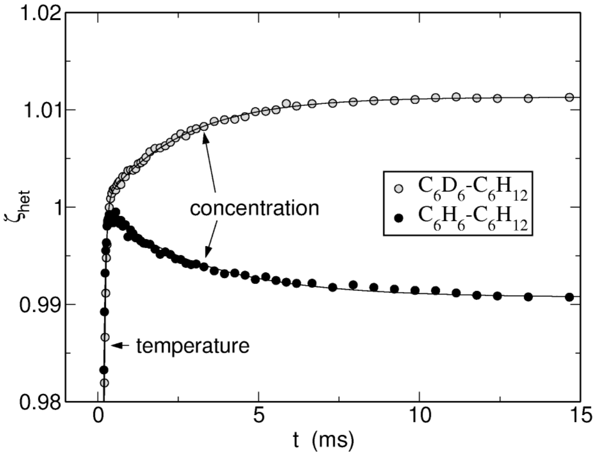

FIG. 1. Heterodyne diffraction efficiency for C_6H_6/C_6H_{12} and C_6D_6/C_6H_{12} mixtures. Benzene concentration $c = 0.75$. The diffraction efficiency of the temperature grating has a rise time of ≈40 μs and is normalized to unity.

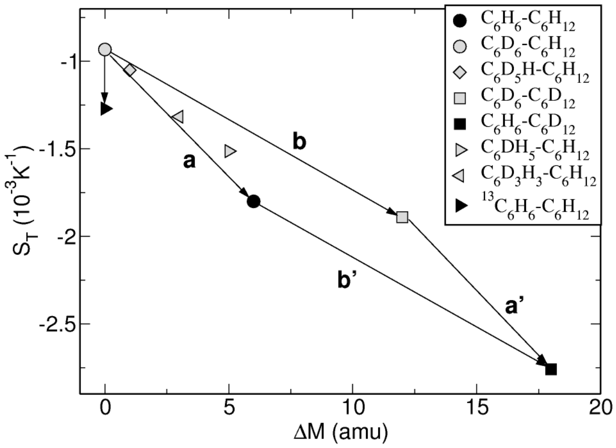

FIG. 2. Soret coefficient of benzene in cyclohexane as a function of the difference in molecular mass $\Delta M = M_{\mathrm{chex}} - M_{\mathrm{benz}}$. ($x_{\mathrm{benz}} = 0.5$, $T = 20\,^{\circ}$C.)

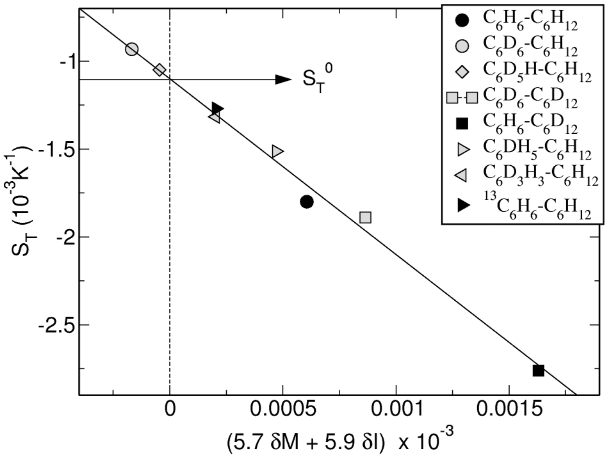

FIG. 3. Data of Fig. 2 plotted versus $-(a_M \delta M + b_I \delta I)$ according to Eq. (4). The intersection with the vertical line at $a_M \delta M + b_I \delta I = 0$ corresponds to S_T^0 ($x_{benz} = 0.5$, $T = 20\,^\circ C$).

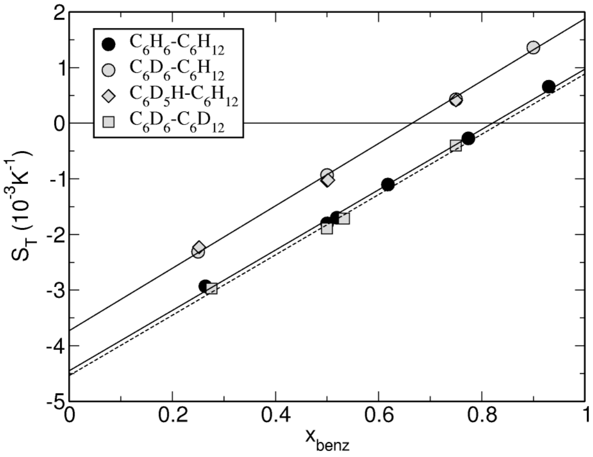

FIG. 4. Soret coefficients of benzene in cyclohexane as a function of composition for different degrees of deuteration of both benzene and cyclohexane ($T = 20\,^\circ C$).

with respect to M and I. $a_M = -5.7 \times 10^{-3}$ K^{-1}, $b_I = -5.9 \times 10^{-3}$ K^{-1}, and $S_T^0 = -1.10 \times 10^{-3}$ K^{-1} have been obtained from a least-squares fit of Eq. (4). Hence, the contributions of δM and δI to the Soret effect are almost identical in magnitude. The values of a_M and b_I are, considering the experimental uncertainty, remarkably close to the values found by Rutherford for isotopic mixtures of benzene ($a_M = -5.3 \times 10^{-3}$ K^{-1}, $b_I = -2.6 \times 10^{-3}$ K^{-1}).

Mass and moment of inertia show the same effect: molecules with higher mass and larger moment of inertia migrate to the cold side. This is best seen from Fig. 2, where S_T of benzene in cyclohexane is negative. The change of S_T is positive when the mass of benzene is increased ($C_6H_6/C_6H_{12} \rightarrow C_6D_6/C_6H_{12}$). A similar argument holds for cyclohexane, whose Soret coefficient in benzene is positive since it migrates to the cold side. The positive mass effect is in agreement with the behavior observed in molecular dynamics simulations [11,12].

There is a pronounced composition dependence of S_T, which even changes its sign at high benzene mole fractions (Fig. 4). Such a change of sign has previously been reported for ethanol/water mixtures [3]. Surprisingly, the isotope effect is independent of concentration, and the composition dependence of S_T is caused only by the linear concentration dependence of the "chemical" contribution S_T^0. The concentration independence of the contribution owed to the isotope effect, $a_M \delta M + b_I \delta I$, can be deduced from the parallel lines for the mixtures with different isotope substitutions in Fig. 4.

S_T^0 has been calculated according to Eq. (4) for all values of S_T measured for the different isotopically substituted mixtures. The linear concentration dependence of S_T^0 is obvious from the plot in Fig. 5, and a linear regression gives $S_T^0 = (-3.75 + 5.32 x_{benz}) \times 10^{-3}$ K^{-1}. At $x_{benz} \approx 0.7$, the straight line in Fig. 5 crosses zero and S_T^0 vanishes. At this concentration, the Soret effect is caused solely by the isotope effect and, due to the similar a_M and b_I, benzene/cyclohexane mixtures behave almost identically to isotopic mixtures of benzene.

It would be of interest to investigate the influence of isotopic substitution on the two transport coefficients D and D_T. In principle, the diffusion coefficient D could be obtained from the decay time of the concentration signal and the thermal diffusion coefficient from $D_T = S_T/D$. Unfortunately, the error of D diverges for $S_T \rightarrow 0$, where the amplitude of the concentration signal vanishes. For this reason, we restricted our discussion to the well-behaved Soret coefficient S_T.

In summary, we have, for the first time, been able to split the Soret coefficient of a mixture of two organic solvents, benzene and cyclohexane, into additive contributions utilizing a fast and sensitive optical grating technique. The isotope effect depends both on the differences of mass and moment of inertia (first and second moments) of the two

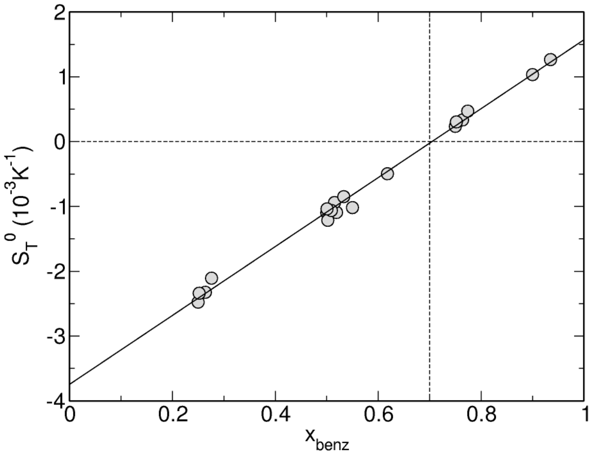

FIG. 5. S_T^0 as calculated from Eq. (4) for all measured isotopic substitutions of benzene and cyclohexane ($T = 20\,^\circ C$).

molecules, but not on composition of the mixture. The Soret coefficient caused by the isotope effect alone is comparable to the one in isotopic mixtures of benzene. An additional "chemical" contribution S_T^0 depends linearly on the benzene concentration and even changes its sign at a certain composition. The mass effect is in agreement with MD calculations, where the heavy component migrates to the cold side. So far, we have no molecular explanation for the source of S_T^0 and why it vanishes at a certain composition.

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