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PAPER

The isotope Soret effect in molecular liquids: a quantum effect at room temperatures†

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Diffusion in multicomponent mixtures is not only driven by concentration but also by temperature gradients. Although this so-called Soret effect plays an important role in such diverse phenomena as the composition variation in oil reservoirs or prebiotic evolution, the underlying molecular mechanisms are still not clear. Here we show that the thermodynamic part of the isotopic contribution to the Soret effect of binary liquids is a quantum effect originating at room temperature from librational and vibrational motions of the molecules. Remarkably, the 'isotopic' contribution is not limited to true isotopic substitution but can be the dominating effect in mixtures of chemically similar molecules. We have tested the theory for the binary mixtures from the homologous series of halobenzenes and for halobenzenes in toluene and cyclohexane.

1 Introduction

More than one and a half centuries ago Ludwig described diffusion between unevenly heated locations in salt solutions of constant composition,¹ but it took another 23 years until the phenomenon was investigated in more detail by Soret in 1879.² In memory of these pioneering works the effect, which is also known as thermal diffusion or thermodiffusion, is now termed the Ludwig–Soret effect or, briefly, the Soret effect. Over the years it has become clear that thermal diffusion plays a crucial role in a number of quite diverse phenomena such as the magmatic differentiation in the mantle of earth,³ the separation of isotopes in silicate melts,⁴ the spatial variation of the composition in crude oil reservoirs,⁵ the prebiotic evolution of precursors of life near hot spots in the ancient ocean,⁶ oscillatory convection in double-diffusive systems,⁷ the analytical fractionation of polymers,⁸ tritium permeation through fusion reactor structures,⁹ or thermoelectricity.¹⁰

In a macroscopic description the diffusion flux \mathbf{J} in a binary fluid of density ρ not only originates from a concentration but also from a temperature gradient:¹¹

$$\mathbf{J} = -\rho D \nabla c - \rho D_T c (1 - c) \nabla T \quad (1)$$

where c is the mass fraction of the independent component. D and D_T are the mass and the thermal diffusion coefficient,

respectively. The amplitude of the concentration gradient in the stationary state, where the total flux vanishes, is determined by the Soret coefficient $S_T = D_T/D$. Typical values for small molecules are of the order of 10^{-3} K^{-1} and a positive sign corresponds to thermophobic motion down the temperature gradient.

2 The isotope Soret effect

A systematic investigation of the influence of molecular properties on the Soret effect has started with the study of the isotope effect in liquid mixtures initiated by Ma and Beyerlein¹² and by Rutherford.¹³ They investigated isotopic binary mixtures of chemically identical compounds and recognized, besides the mass difference, the mass distribution within the molecules as additional relevant property.

The scope of the isotope Soret effect has been widened significantly in ref. 14 and 15, where isotopic mixtures of *different* liquids were investigated. It has been shown experimentally that the differences between both the masses and the moments of inertia of both molecules contribute additively to the Soret coefficient, now referred to as the *isotopic* contribution.^{12,14}

The composition independent isotope effect is in sharp contrast to the frequently observed strong composition dependence of the so-called chemical contribution to the Soret coefficient, which may even lead to a sign change of S_T .^{4,14} These findings, together with general trends, like an increasing thermophobicity with increasing mass, could be reproduced both experimentally^{15,16} and in non-equilibrium molecular dynamics simulations.^{17–21} Very recently, Huang *et al.* were able to show that the characteristic patterns of the isotope effect are not limited to organic liquid mixtures but also prevail in very different inorganic systems, namely network modifiers such as iron, calcium or magnesium in silicate melts.⁴

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3 Quantum effects in liquids

Although a complete quantitative treatment of the Soret effect is still out of reach, we will show that the ‘isotopic’ mechanism of thermal diffusion is a general property of any liquid mixture and not restricted to true isotopic substitution. We propose a theoretical description, where the ‘isotopic’ mechanism is of dynamic nature and eventually stems from librational and translational vibrations of the molecules in the mixture. It is based on the assumption that molecular motion is due to forces acting on a molecular level,²² which, according to Bearman and Kirkwood,²³ originate from the gradient of the partial pressure of the constituents. Our most remarkable and surprising result is the quantum nature of the isotopic Soret effect (ISE) in molecular liquids.

The ISE belongs to the wide class of condensed phase isotope effects. Most studied is the so-called vapor pressure isotope effect, which was treated by Lindemann as early as 1919²⁴ and has thoroughly been investigated since then.²⁵ Other condensed phase isotope effects comprise changes of molar volume, compressibility, or surface tension.^{25,26}

After almost a century of research the generic characteristics of all these isotope effects are well understood and the vibrational properties have been identified as being essential.²⁶ This means that eventually all isotope effects are quantum in nature, even though this quantum character may often be hidden under some simplifying assumptions.

Contrary to the other isotope effects in condensed matter, where only small corrections to the main effect (e.g. the vapor pressure^{25,26}) are observed when the particles of the mixture become indistinguishable, this ‘main state’ does not exist in case of the Soret effect. It corresponds to the case of a pure substance where the Soret effect vanishes by definition. Moreover, in the case of chemically like molecules, the ISE can be the dominating or even sole contribution to the Soret effect, which leads to the astounding conclusion that in these mixtures the whole Soret effect can be due to quantum effects and non-classical in nature.

Other than the aforementioned equilibrium condensed phase isotope effects, the ISE is a non-equilibrium phenomenon in presence of a temperature gradient. As a result, in its most general form the Soret coefficient of a mixture contains both kinetic and thermodynamic contributions.²⁷ The former are due to molecular collisions whereas the latter are expressed *via* an appropriate thermodynamic potential, which varies spatially in non-equilibrium systems.

4 Microscopic statistical theory

Let us clarify the essence of the problem and a particular approach to it by a qualitative example. Consider a *solid body* composed of molecules of two sorts undergoing librational (hindered rotational) motion. The averaged energy of the quantum harmonic oscillator with frequency ν is

$$\langle E_{\text{osc}} \rangle = \frac{h\nu}{2} \coth \frac{h\nu}{2k_{\text{B}}T}. \quad (2)$$

where h is the Planck constant and $k_{\text{B}}T$ the thermal energy. In case of high temperature or low oscillator frequency ($h\nu/2k_{\text{B}}T \ll 1$) eqn (2) reduces to the classical result $\langle E_{\text{osc}} \rangle = k_{\text{B}}T$, where the

energy is uniformly distributed among the particles of either sort and their mutual rearrangement cannot be energetically profitable.

For $h\nu/(2k_{\text{B}}T) \leq 1$, however, the oscillator energy becomes frequency dependent and a shift of heavier particles into colder fluid layers would lower the energy of the mixture. Exactly this situation is realized in liquids, where the molecules have translational freedom and participate in librational motions similar to the solid state.

An intuitive understanding of the effect can be obtained from the following consideration, where we keep the force constant fixed and allow only for the variation of the mass or moment of inertia and, consequently, the vibrational or librational frequency ν (eqn (8)). For simplicity, we restrict ourselves for the moment to translational oscillations with $\nu = (K/M)^{1/2}$, but identical arguments hold for the librational degrees of freedom. Let us now transfer a heavy particle of mass M_2 from the hot (T_2) to the cold (T_1) side and a light particle of mass $M_1 < M_2$ in the opposite direction. The mechanism is easiest seen in the most extreme case, where the heavy particle belongs to the classical limit with $h\nu \ll k_{\text{B}}T$, corresponding to $\langle E_{\text{osc}} \rangle = k_{\text{B}}T$. For the light particle we assume the other extreme, $h\nu \gg k_{\text{B}}T$, where higher oscillator states cannot be occupied and eqn (2) reduces to the temperature independent ground state energy $\langle E_{\text{osc}} \rangle = h\nu/2$. From the displacement of the heavy particle to the cold side the system gains the energy $k_{\text{B}}(T_2 - T_1)$, whereas the opposite displacement of the light particle does not cost any energy. Hence, the whole process is energetically favorable.

It should be noted that a more detailed treatment for the here interesting case $h\nu \leq 2k_{\text{B}}T$ along the lines discussed below with a linear expansion of eqn (2) and for small temperature and mass (or moments of inertia) differences yields an energy gain for the particle exchange of

$$\Delta E = \frac{k_{\text{B}}T}{3} \left(\frac{h\nu}{2k_{\text{B}}T} \right)^2 \frac{M_2 - M_1}{M} \frac{T_2 - T_1}{T} \quad (3)$$

in case of translational oscillation. M and T are the average mass and temperature, respectively. An equivalent expression is obtained for the librational contribution.

Besides this *thermodynamic mechanism* there is also a *kinetic mechanism* of thermal diffusion, which is independent of an energetic gain by the relative motion of the particles. The easiest way to understand it is to consider the Soret effect in the gas phase, where the librational motion of molecules is replaced by the classical free rotation. The source of the Soret effect in gaseous mixtures are scattering phenomena, *i.e.*, collisions between the molecules. Thus, in gases the prevailing mechanism of thermal diffusion is of kinetic origin, whereas in solids it would be the thermodynamic mechanism. In liquid mixtures both mechanisms can be present simultaneously.

In the following we will pursue the thermodynamic approach, which allows for a solution of the problem in a closed form. The starting point is the notion of Bearman and Kirkwood²³ that the forces responsible for the thermodynamic contribution to the Soret effect originate from the gradient of the partial pressure.²² The molecules are modeled as unstructured attracting hard spheres and two additive contributions owing to steric repulsions and attractive interactions have been taken into account in

ref. 22. In case of complex n -atomic molecules, however, there is an additional contribution due to the three translational and three rotational degrees of freedom of the molecule. In the condensed (solid or liquid) phase these are subject to harmonic restoring forces^{25,26} similar to the $3n - 6$ internal vibrational degrees of freedom. In the following we will first consider the contribution of the rotational oscillations (librations) and later generalize to other types of molecular motion.

From eqn (2) the contribution of the librations to the free energy of the *pure* liquid in the quasi-harmonic approximation follows as

$$F^{\text{lib}} = Nk_{\text{B}}T \sum_{i=1}^3 \ln \left(2 \sinh \frac{h\nu_i}{2k_{\text{B}}T} \right), \quad (4)$$

where N is the number of molecules and the $\nu_i = c\tilde{\nu}_i$ (c being the speed of light) are the librational frequencies. They are on the order of $\tilde{\nu} \leq 100 \text{ cm}^{-1}$ and measurable in the far-infrared absorption spectrum.²⁸ Within the quasi-harmonic approximation the librational frequencies do not explicitly depend on temperature, *i.e.* $(\partial\nu_i/\partial T)_V = 0$,²⁹ whereas their volume derivative can be expressed *via* the so-called pseudo-Grüneisen parameter³⁰

$$\gamma_i = -\frac{V}{\nu_i} \left(\frac{\partial\nu_i}{\partial V} \right)_T. \quad (5)$$

From eqn (4) and (5) follows the contribution of the librational motions to the pressure:

$$p^{\text{lib}} = -\frac{\partial F^{\text{lib}}}{\partial V} = \rho k_{\text{B}}T \sum_{i=1}^3 \gamma_i \xi_i \coth \xi_i. \quad (6)$$

Here, ρ is the number of molecules per unit volume, and $\xi_i = h\nu_i/2k_{\text{B}}T$. The above estimation of the librational frequencies gives $\xi_i < 1$. Thus, for the librational contribution to the compressibility factor Z we have

$$Z^{\text{lib}} = p^{\text{lib}}/\rho k_{\text{B}}T \approx \sum_{i=1}^3 \gamma_i (1 + \xi_i^2/3). \quad (7)$$

Here, the quadratic term is nothing but the high-temperature quantum correction of Herzfeld and Teller.³¹ Just this term is responsible for the effect.

Let us now consider the case of a dilute liquid *mixture*, where component 1 (solute) is dissolved in low-concentration in component 2 (solvent). The most simple representation of the librational frequency is:

$$\nu = \sqrt{K/I}, \quad (8)$$

where the force constant K is a property of the surrounding fluid (solvent) and I is the moment of inertia of the librating molecule (solute). This means that

$$\gamma_{1,i} = \gamma_{2,i}, \quad \frac{\nu_{1,i}}{\nu_{2,i}} = \sqrt{I_{2,i}/I_{1,i}}. \quad (9)$$

It is convenient to express the partial pressures p_j in terms of the so-called compressibility factor – the pressure value normalized to its ideal gas value $\rho_j k_{\text{B}}T$. It is obvious that the compressibility factor Z_2 of pure solvent, *i.e.*, of a one-component system, is entirely determined by the properties of the solvent molecules (see left part of eqn (7)). The compressibility

factor Z_{12} of the solute molecules in the solvent, $Z_{12} = p_1/\rho_1 k_{\text{B}}T$, on the other hand, generally depends on characteristic properties of both molecules, like their sizes and interaction potentials. Thus, two indices are required to denote the compressibility factor of the solute.

The difference $Z_{12}^{\text{lib}} - Z_2^{\text{lib}}$ between the compressibility factors of the solute in the solvent and of the pure solvent follows from eqn (7) and (9):

$$Z_{12}^{\text{lib}} - Z_2^{\text{lib}} = \frac{1}{3} \sum_{i=1}^3 \gamma_{2,i} \xi_{2,i}^2 (I_{2,i}/I_{1,i} - 1). \quad (10)$$

This value determines the additional librational contribution to Soret effect as²²

$$S_T^{\text{lib}} = \frac{1}{\rho_2 T} \left[\frac{\partial(\rho_2 T \{Z_{12}^{\text{lib}} - Z_2^{\text{lib}}\})}{\partial T} \right]_p. \quad (11)$$

Taking the derivative with the help of eqn (5) and the definition of the thermal expansibility $\alpha = -\partial(\ln \rho_2)/\partial T$ of the solvent, we obtain

$$S_T^{\text{lib}} = -\frac{1}{3} \sum_{i=1}^3 \gamma_{2,i} \xi_{2,i}^2 (I_{2,i}/I_{1,i} - 1) \left[\alpha(2\gamma_{2,i} + 1) - (\partial \ln \gamma_{2,i}/\partial T)_p + T^{-1} \right]. \quad (12)$$

The further simplifications will be done with the assumptions that the values of the Grüneisen parameter are equal for all libration modes, $\gamma_{2,i} \equiv \gamma_2$, and that the ‘elasticity’ K in eqn (8) has the same order of magnitude for all non-polar fluids.²⁸ It will be approximated by its value for benzene $K = \nu_b^2 \bar{I}_b$, where ν_b is the libration frequency of pure benzene and \bar{I}_b is the characteristic value of the moment of inertia of a benzene molecule. It is connected with the eigenvalues $I_{b,i}$ by

$$\bar{I}_b^{-1} = \frac{1}{3} \sum_{i=1}^3 I_{b,i}^{-1}. \quad (13)$$

Finally, we find

$$S_T^{\text{lib}} = -b \bar{I}_b (\bar{I}_1^{-1} - \bar{I}_2^{-1}),$$

$$b = \left(\frac{h\nu_b}{2k_{\text{B}}T} \right)^2 \gamma_2 \left[\alpha(2\gamma_2 + 1) - (\partial \ln \gamma_2/\partial T)_p + T^{-1} \right]. \quad (14)$$

The contribution of translational degrees of freedom, S_T^{tr} , can be found in complete analogy to that for librational movement. Obviously, the moments of inertia in eqn (14) should be exchanged by the corresponding molecular masses and instead of the librational frequency and its Grüneisen parameter the analogous quantities for translational motion should be used. Thus the thermodynamic contribution of six external degrees of freedom to the Soret effect, $S_T^{\text{iso}} = S_T^{\text{tr}} + S_T^{\text{lib}}$, reads

$$S_T^{\text{iso}} = -a M_b (M_1^{-1} - M_2^{-1}) - b \bar{I}_b (\bar{I}_1^{-1} - \bar{I}_2^{-1}), \quad (15)$$

where M_b and \bar{I}_b are the molecular mass and characteristic moment of inertia of a benzene molecule. Note that internal vibrations are hardly sensitive to the state of matter and do not contribute due to their very small Grüneisen parameter, which is only of the order of $\gamma_{\text{vib}} \leq 10^{-3}$.³²

Table 1 Properties of the pure substances. $I_{s,i}$ are the eigenvalues of moments of inertia and $\bar{I}_s = [(I_{s,1}^{-1} + I_{s,2}^{-1})/2]^{-1}$ the characteristic moment of inertia of substance s

Substance, s	M/u	$I_{s,1}/u\text{\AA}^2$	$I_{s,2}/u\text{\AA}^2$	$I_{s,3}/u\text{\AA}^2$	$\bar{I}_s/u\text{\AA}^2$
Benzene (C ₆ H ₆)	78.11	88.9	88.9	177.8	88.9
Bromobenzene (C ₆ H ₅ Br)	157.01	88.9	512.1	601	151.5
Chlorobenzene (C ₆ H ₅ Cl)	112.56	88.9	323	411.9	139.4
Fluorobenzene (C ₆ H ₅ F)	96.10	88.9	197.6	286.5	122.6
Toluene (C ₇ H ₈)	92.14	91.9	201.2	289.8	126.2
Cyclohexane (C ₆ H ₁₂)	84.16	116.8	116.8	204.1	116.8

Let us estimate the typical value of the coefficients a and b . According to eqn (14) they are determined correspondingly by the values of Grüneisen parameters γ^{tr} and γ^{lib} for translational and rotational movements. The separate determination of both values is very rare in the literature. In practice both values prove to be close to each other and can be approximated by the common averaged value as expressed by the thermodynamic properties of the solvent: $\gamma^{\text{tr}} \approx \gamma^{\text{lib}} \approx \bar{\gamma} = V_0 \alpha / (6R\beta)$. $V_0 = 8.99 \times 10^{-5} \text{ m}^3 \text{ mol}^{-1}$ is the molar volume of the liquid, $\beta = 0.962 \times 10^{-9} \text{ Pa}^{-1}$ its isothermal compressibility, $\alpha = 1.22 \times 10^{-3} \text{ K}^{-1}$ its thermal expansibility.^{33–35} R is the gas constant. $(\partial \ln \beta / \partial T)_p = 7.87 \times 10^{-3} \text{ K}^{-1}$ ²² and $(\partial \ln \alpha / \partial T)_p = 1.18 \times 10^{-3} \text{ K}^{-1}$.³³ Using these data we find for benzene $\bar{\gamma}_b \approx 2.3$ and $(\partial \gamma_2 / \partial T)_p \approx (\partial \bar{\gamma} / \partial T)_p = \bar{\gamma} [\alpha + (\partial \ln \alpha / \partial T)_p - (\partial \ln \beta / \partial T)_p] = -0.013 \text{ K}^{-1}$. Since the characteristic values of the translational and librational frequencies of benzene molecules roughly take the close values $\bar{\nu}^{\text{tr}} \approx \bar{\nu}^{\text{lib}} \approx 100 \text{ cm}^{-1}$,^{28,36} we conclude that according to the thermodynamic mechanism the coefficients a and b in eqn (15) should be of similar order $a \approx b \approx 0.0021 \text{ K}^{-1}$.

We have used eqn (15) for the ISE to fit our experimental data. Due to the cage effect,³⁷ the highest frequencies are expected for librations around axes lying within the plane of plate-like molecules like benzene. The motion around the third axes, which corresponds to the highest eigenvalue of the inertia tensor, does not rotate the molecular plane and experiences weaker restoring forces. It is of lower frequency and, hence, only a minor contribution is expected from this mode. Therefore, only the two smaller eigenvalues have been considered for the computation of the average values of the moments of inertia \bar{I}_b , \bar{I}_1 and \bar{I}_2 .²⁸

5 Experimental test of the theory

Measurements of the Soret coefficients have been performed by means of a transient holographic grating technique as described in³⁸ at a temperature of 25 °C (see ESI†). The following pure substances were employed for the experiments: bromobenzene (Fluka 16350, $\geq 99.5\%$), chlorobenzene (Aldrich 284513, anhydrous, 99.8%), fluorobenzene (Fluka 46660, $\geq 99.5\%$), toluene (Acros Organics 326981000, 99.8%), cyclohexane (Acros Organics 326831000, extra dry).

For a proper test of our theory we were looking for molecules where the Soret coefficient is almost exclusively determined by the ISE with negligible chemical contribution. The homologous series of the halobenzenes (fluoro-, chloro- and bromobenzene) provides suitable candidates of chemically similar rigid molecules with a gradual increase of molecular mass and moment of inertia. Additionally, this series has been complemented by the very

similar toluene, where the substituent is a methyl group instead of a halogen atom. In particular, toluene and fluorobenzene are virtually identical with respect to their masses and moments of inertia (Tab. 1).

The Soret coefficients of all three binary mixtures of the three halogenated benzenes are plotted as a function of concentration of the heavier component in Fig. 1a. As for true isotopes,¹⁴ the measured values are constant and essentially independent of concentration. The two coefficients $a = 0.0108 \text{ K}^{-1}$ and $b = 0.0023 \text{ K}^{-1}$ have been determined by fitting eqn (15) to the chloro-/fluorobenzene and the bromo-/fluorobenzene mixtures (lower and upper curve). The three horizontal lines in Fig. 1a have been calculated from eqn (15) using these parameters a and b and the masses and moments of inertia from Table 1. Besides the chloro-/fluorobenzene and the bromo-/fluorobenzene values, also the data for the bromo-/chlorobenzene mixtures are rather well reproduced, although no results for this system had been incorporated into the fit.

As in case of the halobenzene mixtures, the Soret coefficient of the halobenzenes in toluene (Fig. 1b) changes only very little with concentration, which is a strong indication that also here the ISE is the dominating mechanism. In particular, the Soret coefficient of the mixture of the two molecules of almost identical mass and moment of inertia, fluorobenzene and toluene, is only very small.

We attribute the slight deviation from a horizontal line, which is identical for all three halobenzene/toluene mixtures, to a small chemical contribution, which might be linked to the cross-interaction terms between unlike molecules.¹⁸ As expected from the chemical similarity of the molecules, it is negligible for the halobenzene mixtures in Fig. 1a and small for all halobenzene/toluene mixtures in Fig. 1b.

Subtraction of the ISE from every data set using the *identical* a and b values as determined from the binary halobenzene mixtures yields nearly indistinguishable chemical contributions (open symbols in Fig. 1b). These almost entirely account for the Soret coefficient of fluorobenzene/toluene, two molecules of very similar mass and moments of inertia.

In Fig. 1c toluene has been replaced by the chemically different cyclohexane. As expected, the chemical contribution is much more pronounced and its sign is even negative. Most remarkably, the ISE can be extracted with the same set of parameters a and b as above, corresponding to identical sequencing and vertical spacing of the data in Fig. 1b and c. Furthermore, the distance between any two mixtures from Fig. 1b and c is identical to the Soret coefficient of the respective halobenzene mixture in Fig. 1a.

The Soret coefficients of chloro- and fluorobenzene in cyclohexane show an interesting sign change at a mole fraction around

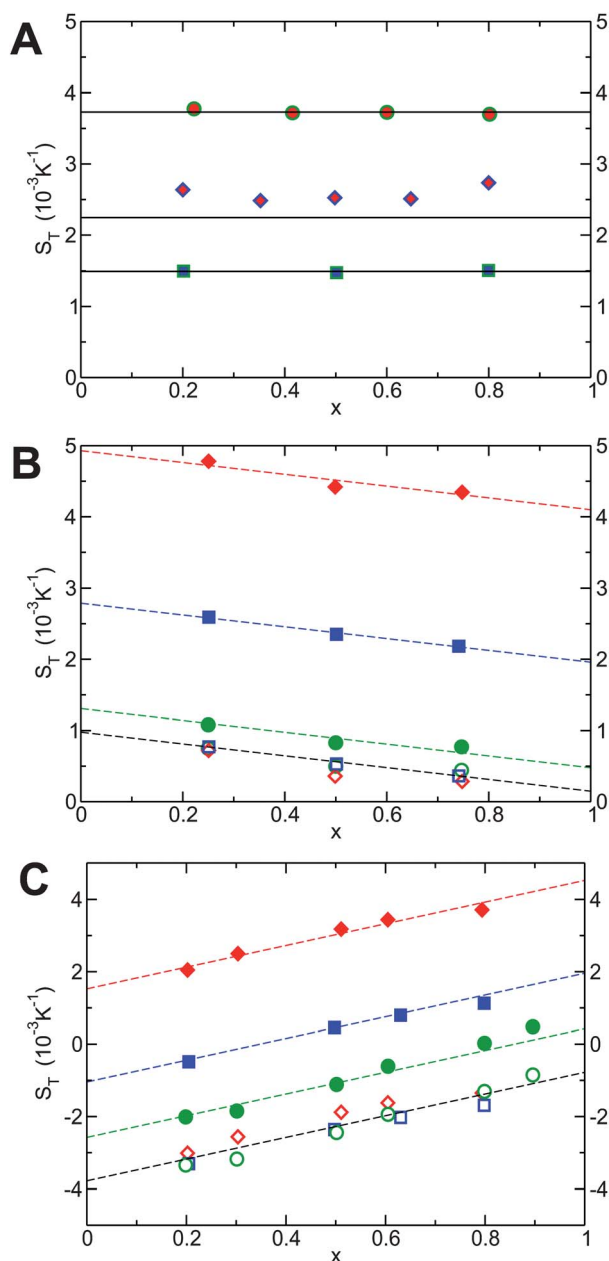


Fig. 1 Soret coefficients as function of the mole fraction x of the first component. $T = 25$ °C. (A) binary mixtures bromo-/fluoro-, bromo-/chloro- and chloro-/fluorobenzene (top to bottom). (B) and (C): the three halobenzenes (filled symbols, top to bottom: bromo-, chloro-, fluoro-benzene) in toluene (B) and cyclohexane (C); x is the halobenzene mole fraction. The open symbols are the respective chemical contributions after subtraction of the ISE. The four guiding lines in every plot have identical slopes. The error bars are approximately the size of the symbols. They are estimated from error propagation of measured concentration amplitudes and contrast factors and from variations between repeated measurements.

0.33 and 0.8, respectively. For lower concentrations the halobenzenes are thermophilic and for higher concentrations are thermophobic. Such a sign change is sometimes considered as something peculiar in the literature,³⁹ but our analysis shows that, at least in the systems considered here, it is merely

a consequence of a negative and concentration dependent chemical contribution and a concentration independent positive ISE. Nothing special happens at the location of the sign change.

In the literature there exists data for binary mixtures of tetrachloromethane, cyclohexane and benzene,⁴⁰ which are virtually the same with respect to their size and Lennard-Jones parameters.^{22,41} Benzene/cyclohexane shows a large change of volume on mixing and a strong chemical contribution. The other two mixtures, tetrachloromethane/benzene and tetrachloromethane/cyclohexane, show volume additivity and behave almost as ideal ‘isotopic’ mixtures with respect to S_T . Their nearly constant Soret coefficients can well be described using the above a and b values, resulting in $S_T = 0.0069$ and 0.0056 K⁻¹, respectively. The deviation from the experimental values does not exceed 10%.

6 Summary and outlook

The Soret effect in binary liquid mixtures is caused by a number of different mechanisms that could, so far, hardly be separated for most systems. In this work, we have shown that the so-called ‘isotopic’ contribution, which is caused by differences in the molecular masses and moments of inertia, is not limited to truly isotopic systems or isotopic substitutions in non-isotopic mixtures. It can be understood in a much more general framework and contributes significantly to the Soret coefficient of many molecular mixtures. In case of chemically like molecules it can be the dominating or even sole contribution.

In order to account quantitatively for the ISE, we have developed a theoretical model that is based on a recently developed statistical theory.²² The main objective of this model is the calculation of the contribution of the external degrees of freedom connected with the translational and librational movement of the molecules.

The homologous series of the halobenzenes contains chemically similar molecules. Their binary mixtures have been used as promising candidates for a test of our theory, and experiments have shown that their Soret coefficients are, indeed, dominated by the ISE. Even more, the identical set of parameters could be used to separate the ‘isotopic’ and the chemical contribution to S_T for mixtures of the halobenzene with the similar toluene and with cyclohexane.

Besides to our own measurements the concept can also be applied to literature data for tetrachloromethane in benzene and cyclohexane. The amount of suitable literature data is, however, rather limited. For a further development and quantitative refinement of our model systematic studies of *e.g.* the temperature dependence of the Soret coefficient on both truly isotopic or chemically similar systems would be desirable.

Although the agreement between experiment and theory is quite convincing, there is one issue that requires closer consideration. As mentioned above, the kinetic contribution cannot be found in closed form and has been neglected. By fitting eqn (15) it is implicitly contained in the parameters a and b determined from the experiment. While the experimental value of the librational coefficient b agrees perfectly with the theoretical prediction ($a \approx b \approx 0.0021$ K⁻¹), the experimental value for the translational coefficient a is five times larger. Magro *et al.* have determined the vibrational and librational amplitudes of benzene in the cage to $\langle x^2 \rangle^{1/2} \sim 0.16$ Å and $\langle \varphi^2 \rangle^{1/2} \sim 11^\circ$.³⁷ Based on these numbers

a rough estimation leads to a value of a that indeed exceeds b , however only by somewhat less than a factor of two. One might speculate, whether the remaining unaccounted-for amplitude of a is due to the neglected kinetic contribution, which shows up in e.g. classical non-equilibrium molecular dynamics simulations. Given the approximations we had to make, such as the assumptions of one common Grüneisen constant, such considerations are, however, still beyond the scope of our theory in its present state, and further research will have to clarify this important issue.

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