Thermophobicity of Liquids: Heats of Transport in Mixtures as Pure Component Properties

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We have measured the Soret coefficients of 41 out of 45 possible equimolar binary mixtures of 10 different organic solvents and found an additive rule for the heats of transport. These can, except for an undetermined offset, uniquely be assigned to the pure components. Based on their heats of transport, the fluids can be arranged according to their thermophobicity, similar to the standard electrode potential. A qualitative explanation of this unexpected additivity is based on the work of Morozov [Phys. Rev. E **79**, 031204 (2009)].

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The Soret effect describes mass diffusion in a multicomponent system that is driven by a temperature gradient. The corresponding motion of colloids is termed thermophoresis, and notable progress in understanding the dominating mechanisms has been obtained for charged [1–4] and magnetic [5–7] particles. In molecular mixtures, there is no distinction between large solute particles and a solvent continuum, and attempts have been made to relate specific contributions to the Soret effect to molecular properties. In particular, the Soret effect of isotopic mixtures has been attributed to differences in molecular mass M and moment of inertia I [8–14]:

$$S_T^{\mathrm{iso}} = (\tilde{a} M_2^{-1} + \tilde{b} I_2^{-1}) - (\tilde{a} M_1^{-1} + \tilde{b} I_1^{-1}). \tag{1}$$

$\tilde{a}$ and $\tilde{b}$ are universal constants. Computer simulations [15–17] have confirmed essential experimental trends like the tendency of heavier molecules to go to the cold side. Recently, the concept has been extended to pseudoisotopic mixtures of chemically similar molecules and explained as a quantum effect at room temperatures [14], but alternative theories are also discussed in the literature [18].

Denbigh [19] and Rutherford and Drickamer [20] have derived expressions for the Soret coefficient based on the heats of transport. Later, these ideas have been taken up by Shukla and Firoozabadi [21] and others. Eslamian and Saghir [22] distinguish between static and dynamic models. Static models, like that of Kempers [23], solely rely on equilibrium properties to derive an expression for the Soret coefficient. Dynamic models additionally require nonequilibrium transport properties, such as activation energies of self-diffusion or viscosity. In particular, the models based on an estimation of the heats of transport by certain activation energies have, with more or less success, been tested for a number of systems [21,22,24]. One of us (KM) [25] based his statistical mechanical theory on the temperature dependence of the partial pressure, as first formulated by Bearman and Kirkwood [26]. Besides a reasonable agreement for the benzene-cyclohexane system, this theory could also be extended to account for the isotope effect [14].

Since all models presently discussed are still rather phenomenological or contain unknown parameters, we have decided to address the question of to what extent the Soret coefficient can be traced back to properties of the pure components and, even more restrictive, whether simple additive rules are obeyed, from the experimental side. Our search for additivity has been motivated by the isotope Soret effect, which has been found to depend on differences of single molecule contributions of the pure compounds [Eq. (1)]. When trying to find empirical correlations from existing data, one is faced with the problem that experiments are usually conducted for a certain class of material, e.g., alkanes or isotopic systems. Within these classes, many physical parameters are very similar and correlations might be owed to this circumstance. In order to avoid such problems, our approach has been to select n (an expandable number) different fluids and to measure the Soret effect for all possible pairs, which is a very demanding task, since the experimental effort grows proportional to n^2.

General framework.—The phenomenological description of the Soret effect is based on the established theory of linear nonequilibrium thermodynamics [27,28]. Here, we only briefly summarize the main results in order to clearly define the relevant quantities. Following closely the notation of de Groot and Mazur [28] and ideas presented by Tichacek *et al.* [24], the reduced heat flow ($\vec{J}_q'$) and the mass flow ($\vec{J}_1$) in a binary mixture ($n = 2$ components) of temperature T without external forces and pressure gradients can be written in a barycentric reference system as [29]

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$$\vec{J}_q' = -L_{qq}\frac{\nabla T}{T^2} - L_{q1}\frac{(\partial\mu_1/\partial c_1)_{p,T}}{c_2 T}\nabla c_1, \qquad (2)$$

$$\vec{J}_1 = -L_{1q}\frac{\nabla T}{T^2} - L_{11}\frac{(\partial\mu_1/\partial c_1)_{p,T}}{c_2 T}\nabla c_1. \qquad (3)$$

L_{qq}, L_{11}, and $L_{1q} = L_{q1}$ are the Onsager coefficients, c_1 and $c_2 = 1 - c_1$ are the mass fractions of component 1 and 2, respectively, and μ_1 is the chemical potential per unit mass of component 1. The reduced heat flow $\vec{J}_q'$ and the total heat flow $\vec{J}_q$ are related by $\vec{J}_q = \vec{J}_q' + (h_1 - h_2)\vec{J}_1$, with h_k being the partial specific enthalpy of species k. Because of mass conservation, there is only one independent flow ($\vec{J}_1 = -\vec{J}_2$). The absolute flows in the lab system are

$$\vec{J}_k^{\text{abs}} = \rho_k\vec{v}_k = \vec{J}_k + \rho_k\vec{v} \qquad (k = 1\ldots n), \qquad (4)$$

$$\vec{J}_q^{\text{abs}} = \vec{J}_q' + \sum_{k=1}^{n} h_k\rho_k\vec{v}_k. \qquad (5)$$

$\vec{v}_k$ is the absolute velocity of component k in the laboratory system, ρ_k its density, and $\vec{v} = \sum_{k=1}^{n}(\rho_k\vec{v}_k)/\rho$ the barycentric velocity. $\vec{J}_q'$ is invariant for the change from relative to absolute flows [28].

Heats of transport are defined for isothermal systems by relating the isothermal heat flows ($\nabla T = 0$) to the respective mass flows:

$$\vec{J}_q' = \sum_{k=1}^{n} Q_{k,\text{abs}}'^{*}\vec{J}_k^{\text{abs}} = \sum_{k=1}^{n-1} Q_k'^{*}\vec{J}_k. \qquad (6)$$

$Q_{k,\text{abs}}'^{*}$ and $Q_k'^{*} = Q_{k,\text{abs}}'^{*} - Q_{n,\text{abs}}'^{*}$ are termed absolute reduced heat of transport and reduced heat of transport, respectively. Utilizing the symmetry relation $L_{q1} = L_{1q}$, the reduced heat of transport is expressed by the Onsager coefficients:

$$Q_1'^{*} = Q_{1,\text{abs}}'^{*} - Q_{2,\text{abs}}'^{*} = \frac{L_{1q}}{L_{11}}. \qquad (7)$$

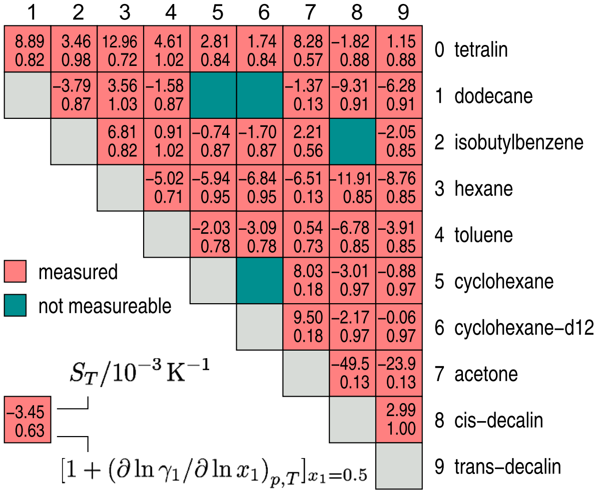
Diffusion (D) and thermal diffusion (D_T) coefficients are defined by writing the mass flow as $\vec{J}_1 = -\rho D\nabla c_1 - \rho c_1 c_2 D_T \nabla T$, and comparison with Eq. (3) yields

$$D = \frac{L_{11}}{\rho c_2 T}\left(\frac{\partial\mu_1}{\partial c_1}\right)_{p,T}, \qquad D_T = \frac{L_{1q}}{c_1 c_2 \rho T^2}. \qquad (8)$$

The Soret coefficient is the ratio between D_T and D:

$$S_T \equiv \frac{D_T}{D} = \frac{Q_1'^{*}}{c_1 T(\partial\mu_1/\partial c_1)_{p,T}}. \qquad (9)$$

Molar instead of specific quantities are introduced by defining the molar absolute reduced heat of transport $\tilde{Q}_{k,\text{abs}}'^{*} = Q_{k,\text{abs}}'^{*} M_k$, with M_k being the molar mass of component k. The transition from mass fractions c_k to mole fractions x_k is achieved by $c_k = x_k M_k (x_1 M_1 + x_2 M_2)^{-1}$.



	1	2	3	4	5	6	7	8	9	
	8.89 0.82	3.46 0.98	12.96 0.72	4.61 1.02	2.81 0.84	1.74 0.84	8.28 0.57	−1.82 0.88	1.15 0.88	0 tetralin
		−3.79 0.87	3.56 1.03	−1.58 0.87	🟩	🟩	−1.37 0.13	−9.31 0.91	−6.28 0.91	1 dodecane
			6.81 0.82	0.91 1.02	−0.74 0.87	−1.70 0.87	2.21 0.56	🟩	−2.05 0.85	2 isobutylbenzene
				−5.02 0.71	−5.94 0.95	−6.84 0.95	−6.51 0.13	−11.91 0.85	−8.76 0.85	3 hexane
					−2.03 0.78	−3.09 0.78	0.54 0.73	−6.78 0.85	−3.91 0.85	4 toluene
						🟩	8.03 0.18	−3.01 0.97	−0.88 0.97	5 cyclohexane
							9.50 0.18	−2.17 0.97	−0.06 0.97	6 cyclohexane−d12
								−49.5 0.13	−23.9 0.13	7 acetone
									2.99 1.00	8 cis−decalin
										9 trans−decalin

🟥 measured
🟩 not measureable

FIG. 1 (color online). Investigated binary equimolar mixtures of ten different solvents. The numbers are the Soret coefficients and the thermodynamic factors of the respective mixtures.

Using the molar chemical potential $\tilde{\mu}_1 = \mu_1 M_1$ and the Gibbs-Duhem relation [21] $x_1\tilde{Q}_{1,\text{abs}}'^{*} + x_2\tilde{Q}_{2,\text{abs}}'^{*} = 0$, the Soret coefficient can be expressed in terms of molar quantities:

$$S_T = \frac{\tilde{Q}_1'^{*}}{x_1 T(\partial\tilde{\mu}_1/\partial x_1)_{p,T}}. \qquad (10)$$

$\tilde{Q}_1'^{*} \equiv \tilde{Q}_{1,\text{abs}}'^{*} - \tilde{Q}_{2,\text{abs}}'^{*} = M_1 M_2 (x_1 M_1 + x_2 M_2)^{-1} Q_1'^{*}$ is the molar reduced heat of transport. Equation (10) is, except for the different sign convention, identical to the working equation used by Shukla and Firoozabadi [Eq. (16) in Ref. [21]]. Using $x_1(\partial\tilde{\mu}_1/\partial x_1)_{p,T} = RT[1 + (\partial\ln\gamma_1/\partial\ln x_1)_{p,T}]$ [30] and, for a simplified notation, the abbreviation $Q_k \equiv \tilde{Q}_{k,\text{abs}}'^{*}$ for the molar absolute reduced heats of transport, Eq. (10) becomes

$$S_T = \frac{Q_1 - Q_2}{RT^2[1 + (\partial\ln\gamma_1/\partial\ln x_1)_{p,T}]}. \qquad (11)$$

γ_1 is the activity coefficient of component 1 and R the gas constant. The denominator is a pure equilibrium quantity, but the situation is less clear for the heats of transport. Some nonequilibrium properties, like molecular friction coefficients, are factored out in Eq. (7), as has been shown for polymer solutions near the glass transition [31]. Nevertheless, the question of to what extent the Soret coefficient is an equilibrium or a nonequilibrium quantity is still a matter of debate.

Experiments and methods.—For a broad data base, we have measured the Soret coefficients of 41 out of the possible $n(n-1)/2 = 45$ equimolar binary mixtures of $n = 10$ solvents, numbered from 0 to 9, as shown in Fig. 1. Four systems have insufficient refractive index contrast. The temperature was always 25 °C. The experimental techniques employed were heterodyne thermal diffusion—forced Rayleigh scattering (TDFRS) [32] and, in some cases, a Soret cell with optical beam deflection (OBD) [33]. The numbering of the solvents does not follow a particular rule and reflects the sequence of how the data base has been built up. The Soret coefficients are always determined for the component with the lower index as the independent one, corresponding to mole fraction x_1 in Eq. (11). A positive sign of S_T means that the independent component migrates to the cold side. Since we only discuss equimolar mixtures, swapping of the two components merely reverses the sign of S_T.

The activity coefficients $\gamma_i(x_i)$ have been calculated by Modified UNIFAC (Dortmund) [34], which is a group contribution method. The activity coefficient is calculated using van der Waals volume and surface areas and group interaction parameters [34,35]. Some activity coefficients have additionally been calculated by the PC-SAFT equation of state [36,37]. This method is based on pure-component parameters (segment number, segment diameter, and the dispersion energy) and binary interaction parameters, which are determined from vapor pressure and liquid density data of the pure components [36] and from vapor-liquid equilibrium data, respectively. The agreement between PC-SAFT and UNIFAC (Dortmund) is within a few percentage points.

The thermodynamic factors $[1 + (\partial \ln\gamma_1/\partial \ln x_1)_{p,T}]$ of the mixtures are listed in Fig. 1. In the case of nonpolar systems, there is only a small deviation from unity, but for mixtures with the polar acetone the thermodynamic factor plays a decisive role in Eq. (11).

Results.—Inspired by the isotope Soret effect [Eq. (1)], the first idea for a simplified additive model is for the Soret coefficients directly, similar to the behavior observed for the hydrocarbon chain-aromatic compound mixtures in Ref. [38]. By assigning a single "Soret number" s_i to every component i, the Soret coefficient of the mixture of i and j would then be written as

$$S_T^{ij} = s_i - s_j. \tag{12}$$

Since there are 41 measured Soret coefficients for the 10 unknown s_i numbers, the problem is highly overdetermined, and the s_i numbers are obtained from a least squares fit such that

$$\sum_{i,j}(S_T^{(ij)} - (s_i - s_j))^2 = \text{minimum}. \tag{13}$$

$S_T^{(ij)}$ is the measured Soret coefficient of the mixture of components i and j. The result of this procedure is shown in Fig. 2, where the measured Soret coefficient $S_T = S_T^{(ij)}$ is plotted along the abscissa and the one recalculated from the Soret numbers s_i according to Eq. (12) along the ordinate.

There are two different data sets. One encompasses all ten compounds and the other one only nine, without the polar acetone. From all data, it is immediately clear that an assignment of unique Soret numbers is not possible. Without acetone the correlation is much better. The two dashed lines in Fig. 2 indicate a $\delta S_T = \pm[10^{-3}]\ \mathrm{K}^{-1}$ interval, which corresponds to an, albeit small, change of S_T that can safely be resolved in an experiment.

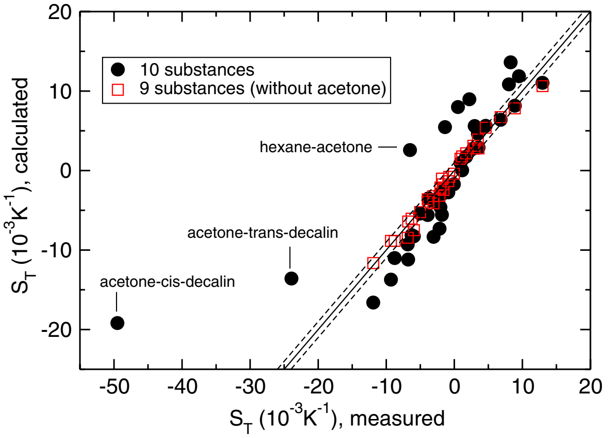


FIG. 2 (color online). Measured Soret coefficients (x-axis) and values recalculated from individual s_i numbers (y-axis) according to Eq. (12).

For polar compounds, the thermodynamic factor $[1 + (\partial \ln\gamma_1/\partial \ln x_1)_{p,T}]$ significantly deviates from unity. Thus, the next step is to factor out this nonideality and to consider the heats of transport

$$Q \equiv Q_1 - Q_2 = S_T RT^2[1 + (\partial \ln\gamma_1/\partial \ln x_1)_{p,T}] \tag{14}$$

instead of the Soret coefficients. The minimization, in analogy to Eq. (13), now directly yields the individual absolute molar reduced heats of transport $Q_i \equiv \tilde{Q}'^{*}_{i,\mathrm{abs}}$.

The result is plotted in Fig. 3. The correlation is convincing, and there is now a good agreement between the measured and the recalculated values. Obviously, the thermodynamic factor fully accounts for the strong deviation of the polar mixtures in Fig. 2. In particular, the

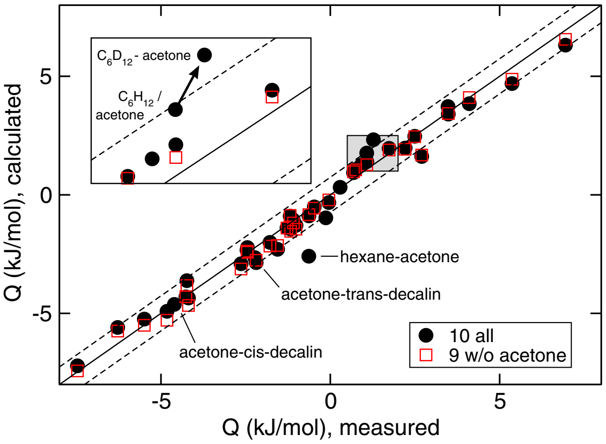


FIG. 3 (color online). Measured heats of transport (x-axis) and values recalculated from individual Q_i (y axis) according to Eq. (14). The insert, an enlargement of the shaded rectangle, shows the isotope effect of cyclohexane in acetone.

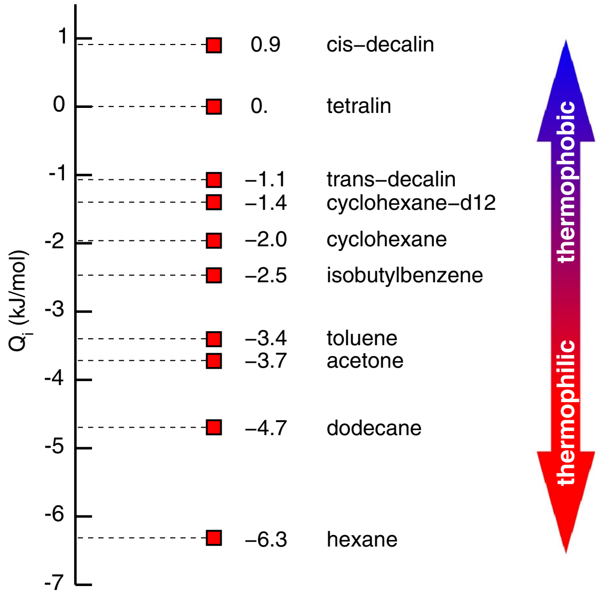


FIG. 4 (color online). Components sorted according to their thermophobicity based on the single-component heats of transport Q_i relative to tetralin.

mixtures of acetone with *cis*- and *trans*-decalin are nicely brought back onto the diagonal. The single apparent outlier is hexane-acetone, which might be caused by the very small thermodynamic factor. There is only a slight improvement for the subset without acetone. Again shown by dashed lines is the confidence interval that corresponds to $\delta S_T = \pm[10^{-3}]\ \mathrm{K}^{-1}$. It has been transformed (assuming ideal behavior) according to a $\delta Q = \delta S_T R T^2$ and now, other than in Fig. 2, contains almost all data points.

According to our results, it is possible to assign a single heat of transport Q_i to every pure substance that determines its thermophobicity, its tendency to migrate towards the cold side (Fig. 4). In an equimolar binary mixture, a competition takes place, and the substance with the larger value of Q_i will migrate towards the cold (thermophobic) and the one with the lower value towards the warm (thermophilic) side. The Soret coefficient of the mixture can be calculated from Eq. (11). The additionally required thermodynamic factor is obtained from equilibrium thermodynamics. Surprisingly, these absolute molar reduced heats of transport are properties of the pure compounds and do not depend on the mixing partner. As for the standard electrode potential, only differences of the heats of transport can be measured, and the zero point, here tetralin, can be chosen arbitrarily. From a careful consideration of all error sources, we estimate the uncertainties at $\delta Q_i \approx [0.2]$ kJ/mol.

Interpretation.—The additivity of the heats of transport and their assignment to the pure components is a very unexpected experimental result, which does not rely on a particular model for the Soret coefficient. In the remaining part of this work, we will give some qualitative arguments on how this surprising finding can be rationalized in terms of the theory given in Ref. [25]. We want to emphasize that even if this interpretation might be challenged, both the experimental observation and the underlying theory up to Eq. (11) remain unaffected.

According to Ref. [25], the Soret coefficient of dilute mixtures can be decomposed into two additive contributions, $S_T = S_T^{\mathrm{pur}} + S_T^{\mathrm{mix}}$, where S_T^{pur} is determined by properties of the pure liquids and describes a situation with a vanishing excess volume of mixing. S_T^{mix} accounts for mixing effects.

For a dilute mixture with a solute (component 1) and a solvent (component 2), the first contribution to the Soret coefficient $S_T^{\mathrm{pur}} = S_T^{\mathrm{pur}}(d_1, d_2, a_1, a_2, \eta)$ is determined by the characteristic diameters d_i of the particles, their interaction parameters a_i, and the solvent volume fraction η. The generic form of any contribution to the Soret coefficient has the form of a difference of some thermodynamic property F between the mixture and the pure solvent [25]:

$$S_T^{\mathrm{pur}} = F(d_1, d_2, a_1, a_2, \eta) - F(d_2, a_2, \eta). \tag{15}$$

Very often, the properties of the pure components are comparable, $d_1 \approx d_2$, $a_1 \approx a_2$, and Eq. (15) can be written as a Taylor series with the single nontrivial term

$$S_{T,1\mathrm{in}2}^{\mathrm{pur}} = A(d_1 - d_2) + B(a_1 - a_2). \tag{16}$$

The subscript explicitly indicates the type of mixture. The coefficients A and B depend only on solvent properties. Since the differences in Eq. (16) are assumed to be small, both coefficients can be considered as some averaged values for both components. Let us now exchange solute and solvent, with particle 2 now being solute and particle 1 solvent. Eq. (16) can then be rewritten as $S_{T,2\mathrm{in}1}^{\mathrm{pur}} = A(d_2 - d_1) + B(a_2 - a_1)$ with the same values of both coefficients A and B, according to the above reasoning. We now interpolate these results for the two limiting cases to arbitrary concentrations. Using the simplest linear approximation in mole fractions of both components, the contribution to the Soret coefficient of the first component is

$$S_{T,1}^{\mathrm{pur}} = A(d_1 - d_2) + B(a_1 - a_2) = f_1 - f_2 \tag{17}$$

with $f_i := A d_i + B a_i$.

Next, we consider the mixing term S_T^{mix}—which, for the first dilute mixture (1 in 2), is based on Ref. [25]:

$$S_{T,1\mathrm{in}2}^{\mathrm{mix}} \approx C \delta V_1. \tag{18}$$

Here, δV_1 is the defect of the molar volume of the solute. Similarly to A and B, coefficient C can be considered as some averaged property for both components. For the "inverse" mixture (2 in 1) we obviously have $S_{T,2\mathrm{in}1}^{\mathrm{mix}} \approx C \delta V_2$. As above, we interpolate to arbitrary concentrations, using the thermodynamic relation for both limiting volume defects: $\delta V_1 = (\partial V^E / \partial x_1)_{x_1 \to 0}$ and $\delta V_2 = -(\partial V^E / \partial x_1)_{x_1 \to 1}$ with $V^E(x_1)$ being the excess volume of mixing. The symmetrized form of the interpolation then is

$$S_{T,1}^{\mathrm{mix}} \approx C\frac{\partial V^E}{\partial x_1}, \qquad (19)$$

which, in contrast to $S_{T,1}^{\mathrm{pur}}$, has a nonadditive form.

Summarizing Eqs. (17) and (19) and taking into account the fact that the diffusion coefficient at finite concentrations additionally contains the thermodynamic factor $[1 + (\partial \ln\gamma_1/\partial \ln x_1)_{p,T}]$ [39], the most general relation for the Soret coefficient becomes

$$S_T \approx \frac{f_1 - f_2 + C(\partial V^E/\partial x_1)}{[1 + (\partial \ln\gamma_1/\partial \ln x_1)_{p,T}]}. \qquad (20)$$

For a large number of mixtures, including the acetone systems [40], the function $V^E(x)$ turns out to be highly symmetric around $x = 0.5$ [39], and the derivative $\partial V^E/\partial x_1$ is negligible for equimolar mixtures. Thus, the product $(S_T[1 + (\partial \ln\gamma_1/\partial \ln x_1)_{p,T}])_{x_1=0.5}$ is an additive property in the case of equimolar mixtures, in agreement with our observations. Because of the vanishing mixing term, the f_i in Eq. (20) can be identified with the heats of transport Q_i of Eq. (11): $f_i = Q_i/(RT^2)$. This may, however, not necessarily be true for arbitrary concentrations, which are beyond the scope of the present study.

Finally, we want to point to a still unsolved problem: the additivity of the heats of transport is, strictly speaking, not compatible with the additivity of the isotope effect. This is notable in cases where the thermodynamic factor becomes important. As shown in the insert of Fig. 3, the isotope effect of cyclohexane in acetone markedly deviates from the expected shift along the diagonal. The thermodynamic factor of these mixtures is only 0.18 (Fig. 1). For all other mixtures with cyclohexane and cyclohexane-d12, the isotopic shift of Q is additive within experimental resolution.

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