Thermophysical Properties of Tricyanomethide- and Tetracyanoborate-Based Ionic Liquids by Using Dynamic Light Scattering and Conventional Methods

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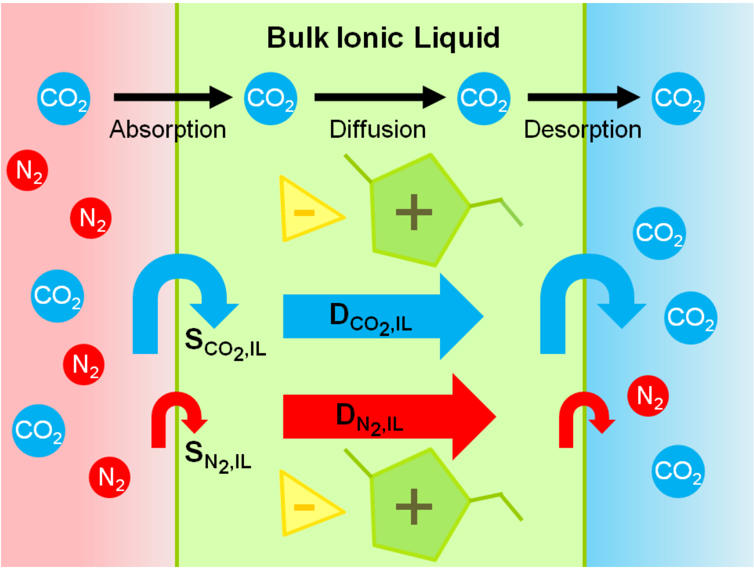
    Mutual Diffusivity D_{12} and Thermal Diffusivity a of Binary Mixtures of ILs with Dissolved Carbon Dioxide

- **Conclusions**

Potential of ionic liquids (ILs) in various technical applications such as …

… Supported Ionic Liquid Membranes (SILMs) for the separation of carbon dioxide (CO_2) from nitrogen (N_2)



Selectivity of separation α

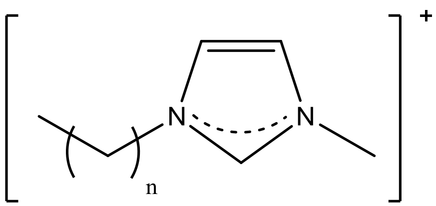
$$\alpha_{CO_2,N_2} = \frac{S_{CO_2,IL}}{S_{N_2,IL}} \cdot \frac{D_{CO_2,IL}}{D_{N_2,IL}}$$

$S_{gas,IL}$: Solubility of gas in IL

$D_{gas,IL}$: Mutual diffusivity of gas and IL

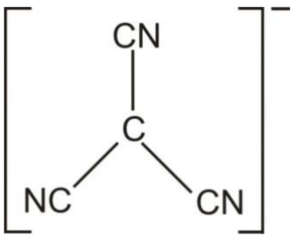
⇒ Reliable and accurate thermophysical data for ILs and their mixtures with dissolved gases are of economic and practical importance

Homologous series of **1-alkyl-3-methylimidazolium** cations combined with **tricyanomethide** or **tetracyanoborate** anions

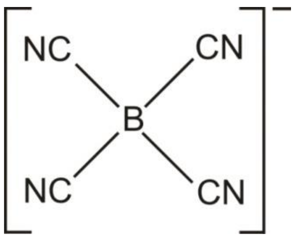


[XMIM]+

n = 1: [EMIM]+
n = 3: [BMIM]+
n = 5: [HMIM]+
n = 7: [OMIM]+
n = 9: [DMIM]+



[TCM]−



[TCB]−

[TCB]−-based ILs: transparent samples by own synthesis or from Merck KGaA, Germany (sample purity > 99%)

[BMIM][TCB]
by own synthesis

[TCM]−-based ILs:
semitransparent samples from IoLiTec Ionic Liquids Technologies GmbH, Germany (sample purity > 98%)
⇒ *laser heating effects due to light absorption*

transparent [BMIM][TCM] by own synthesis (sample purity > 99%)
⇒ *applicable for light scattering experiments*

[BMIM][TCM] …

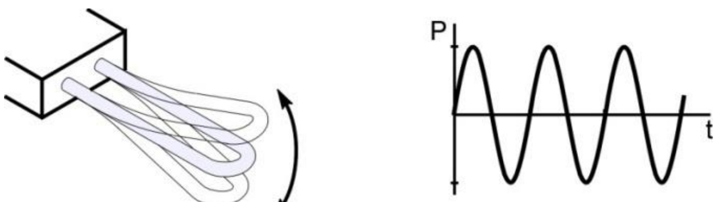
…from IoLiTec

…by own synthesis

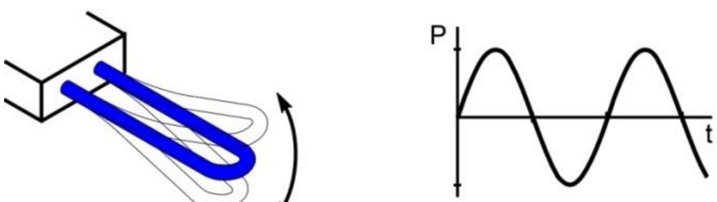
Sample preparation:
Filtration with syringe filter (pore size 250 nm), degassing with vacuum pump (4 h, 0.5 mbar, 50°C), water content by Karl Fischer titration before and after experiments (typically < 1000 ppm)

U-Tube Densimeter – Density

Measurement principle:
Change of natural frequency of system tube and fluid



low density → high tone



high density → low tone

Oscillating U-tube Density Sensor DMA 5000 from Anton Paar GmbH

measures true density
no influence of buoyancy in air
no influence of gravity

minimum amount of sample
approx. 1 ml

measuring range
0 to 3 $g \cdot cm^{-3}$

accuracy
density: ±5 x 10^{-6} $g \cdot cm^{-3}$
temperature: ±10 mK

repeatability s.d.
density: 1 x 10^{-6} $g \cdot cm^{-3}$
temperature: 1 mK

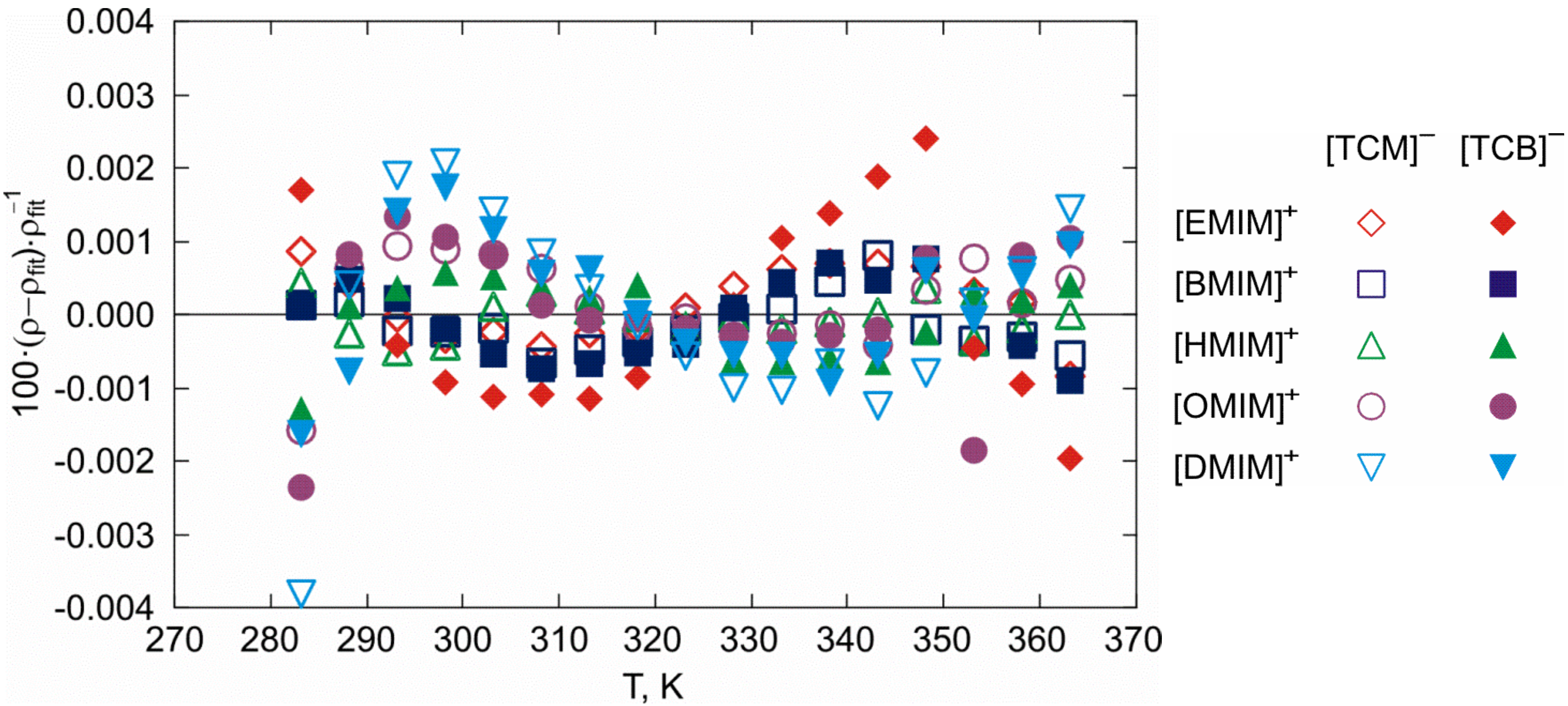
measuring temperature
273 to 363 K

pressure range
<1 to 10 bars

extremely fast
1 to 5 minutes/measurement

Density of [TCM]⁻- and [TCB]⁻-Based ILs at Atmospheric Pressure as a Function of Temperature

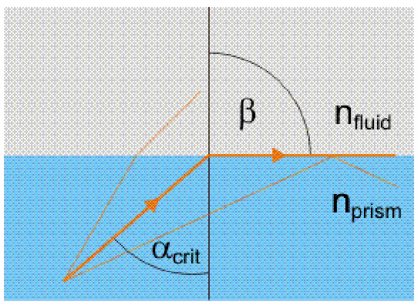
Representation of experimental data by fit $\rho_{fit} = \rho_0 + \rho_1 T + \rho_2 T^2$



Experimental uncertainty Δρ/ρ (k = 2) 0.02%

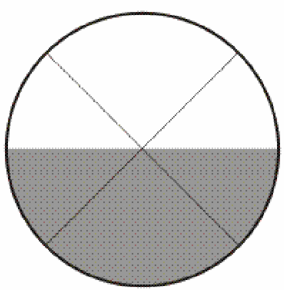
Abbe Refractometer – Refractive Index

Measurement principle:
Determination of angle of total reflection (critical angle α_{crit}) between prism and fluid



Snell's law:

$$n_{fluid} = n_{prism} \sin \alpha_{crit}$$



shadow boundary
seen through the telescope

Abbe refractometer R 6000 G from Leo Kuebler GmbH

direct access to refractive index of fluid n_D at sodium vapor line λ_D = 589.3 nm

no conversion necessary

minimum amount of sample

approx. 1 ml

measuring temperature

273 to 363 K

extremely fast

about 5 minutes/measurement

access to wavelength dependence of refractive index

mean dispersion obtained from

$$\frac{\Delta n}{\Delta \lambda} = \frac{n_F - n_C}{\lambda_F - \lambda_C}$$

with Fraunhofer lines F (λ_F = 486.1 nm) and C (λ_C = 656.3 nm)

Refractive Index of $[TCM]^-$- and $[TCB]^-$-Based ILs at Atmospheric Pressure as a Function of Temperature

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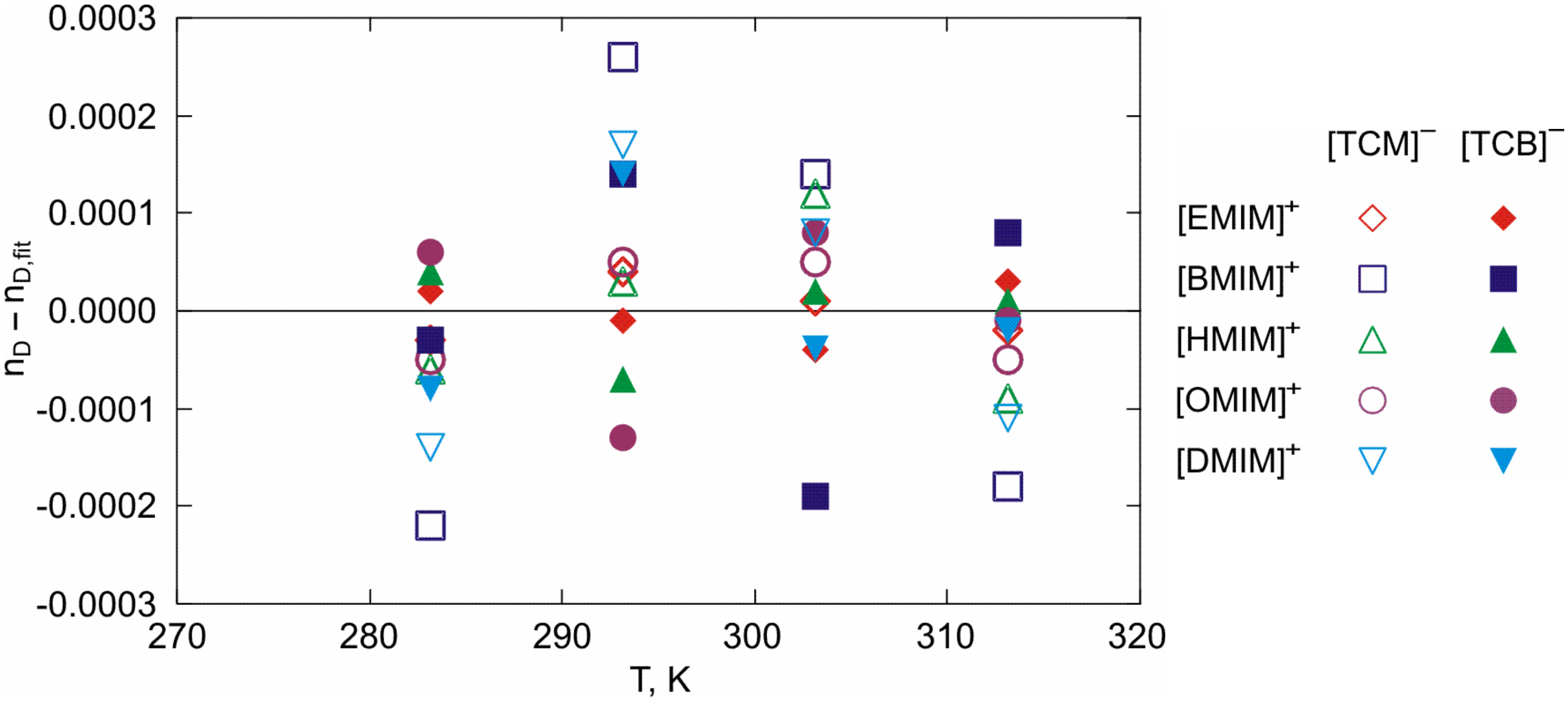
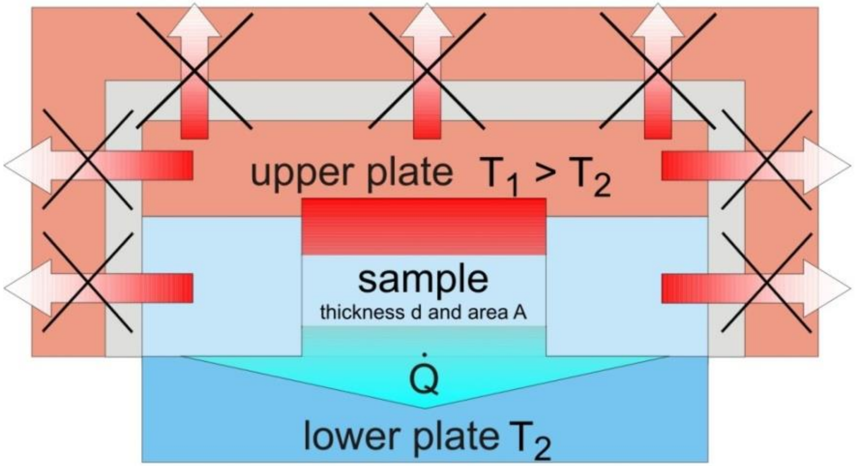
Representation of experimental data by fit $n_{D,fit} = n_0 + n_1 T$



Experimental uncertainty Δn_D (k = 2) 0.0005

Measuring principle based on the ideal form of the Fourier-law of heat conduction



apparatus is designed to fulfill as close as possible the ideal one-dimensional form of the Fourier-law

$$\dot{Q} = -\lambda \frac{A}{d}(T_2 - T_1)$$

Specifications

measuring range:
0.01 - 10 $W \cdot m^{-1} \cdot K^{-1}$

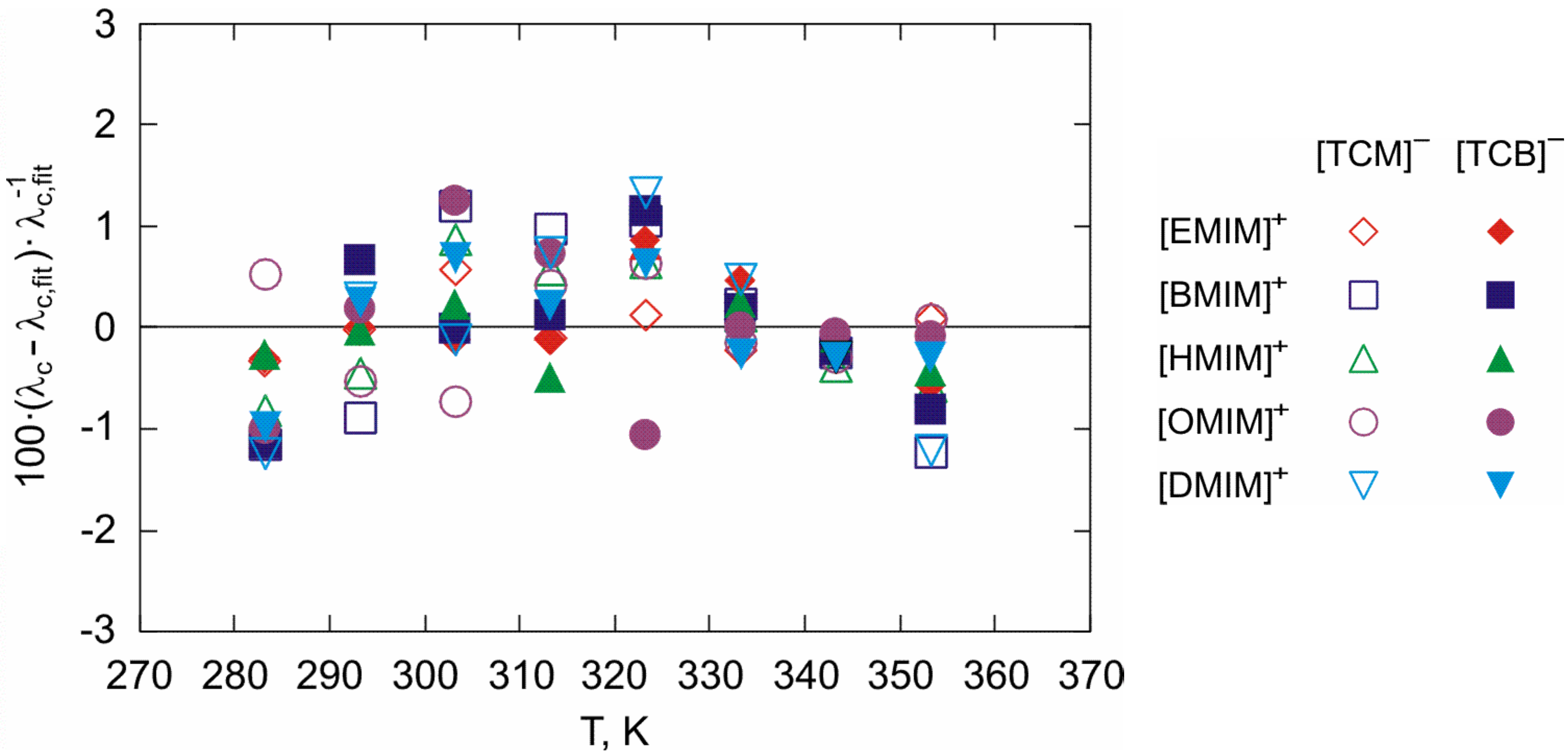
temperature range:
250 to 400 K

pressure range:
up to 10 bar

sample size:
∅ 85 mm, d = 0.5 to 5 mm

uncertainty:
smaller than 3% achievable

Representation of experimental data by fit $\lambda_{c,fit} = \lambda_0 + \lambda_1 T$

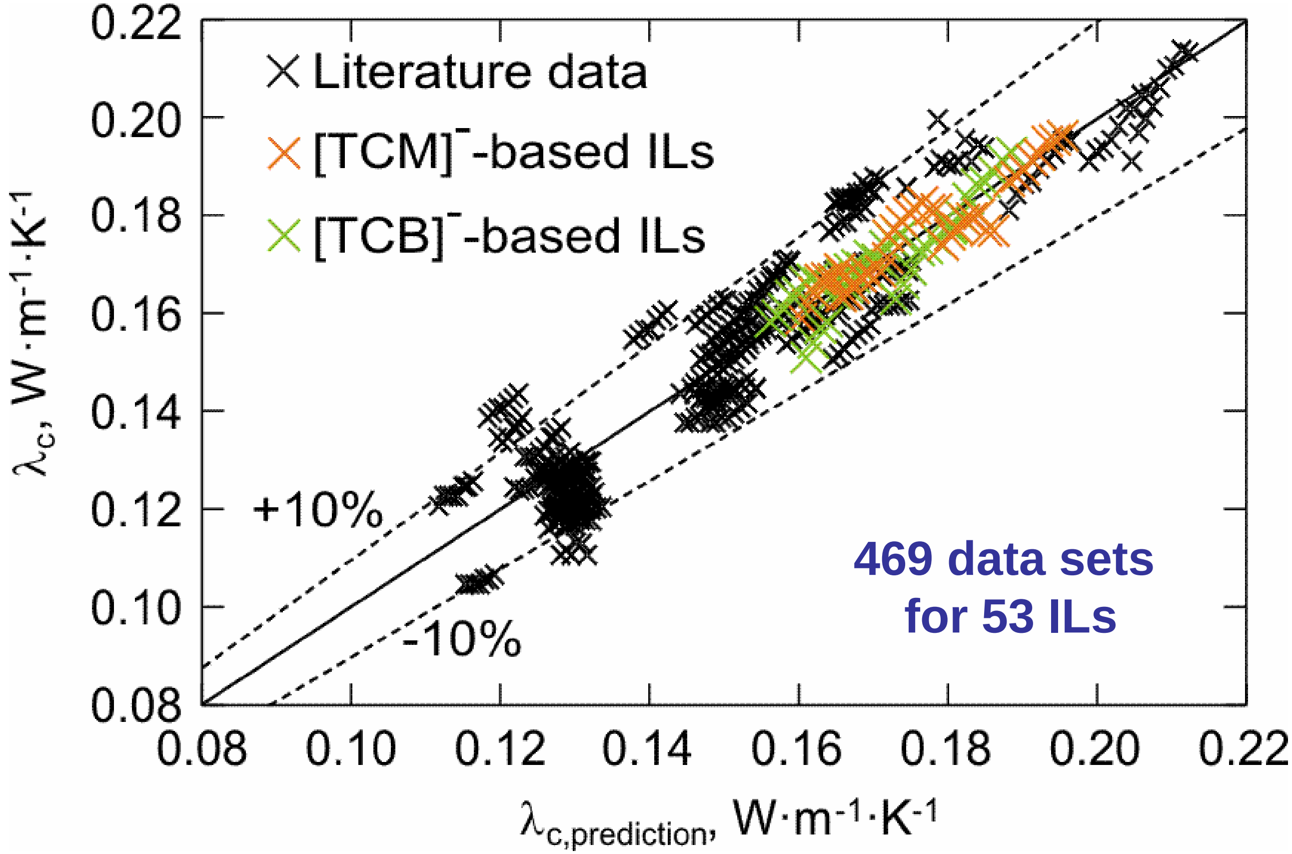


Experimental uncertainty $\Delta\lambda_c/\lambda_c$ (k = 2) 5%

Prediction of the Thermal Conductivity of ILs as a Function of Temperature

$$\lambda_{c,prediction}(T) = \left(A + \frac{B}{M\rho_{293.15\,K}}\right) \cdot \left(\frac{\rho(T)}{\rho_{293.15\,K}}\right)^{C}$$

M: molar mass of IL
$A = 0.0960\ W \cdot m^{-1} \cdot K^{-1}$
$B = 21.43\ g^2 \cdot cm^{-3} \cdot W \cdot m^{-1} \cdot K^{-1} \cdot mol^{-1}$
$C = 0.826$

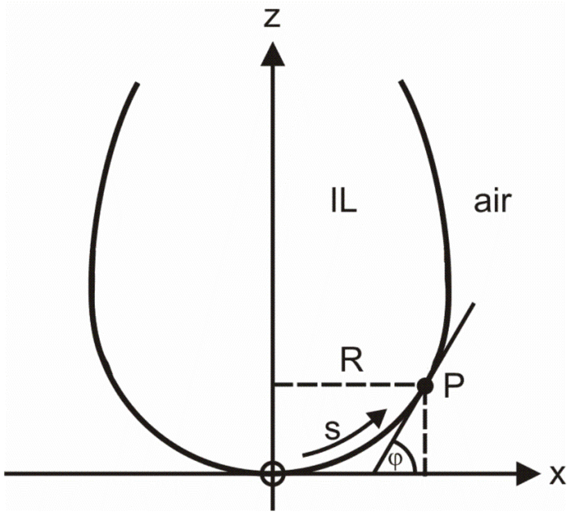


Root mean square (rms) deviation between experiment and prediction 6.32%

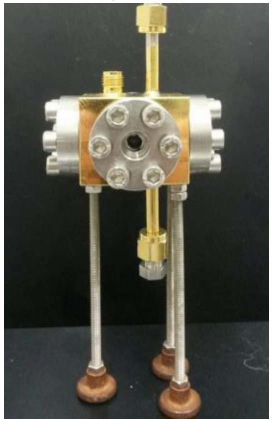
Laplace's equation for curved interfaces (exposed to a gravitational field)

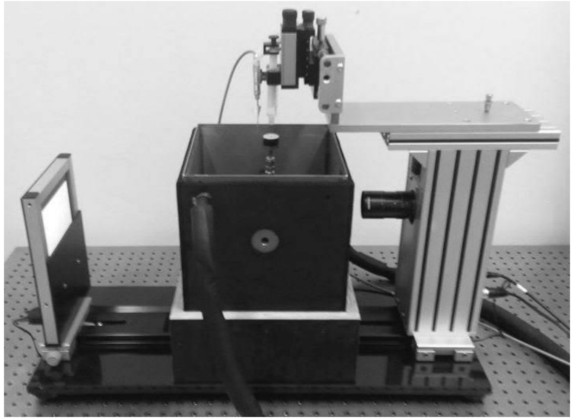
$$\frac{\partial\varphi}{\partial s} = \frac{2}{R} - \frac{\Delta\rho\, g\, z}{\sigma} - \frac{\sin\varphi}{z}$$

φ ... angle
$\Delta\rho$ ... difference of the densities of the drop and air
σ ... interfacial or surface tension
g ... acceleration of gravity
R ... radius of curvature at a point P (φ, z)
s ... shape line
x, z ... axes



Temperature-dependent measurements in cell with optical accesses





Data evaluation by solving the Laplace's equation numerically - σ has to be adjusted to match the measured and calculated shape of the drop

Surface Tension of [TCM]⁻- and [TCB]⁻-Based ILs at Atmospheric Pressure as a Function of Temperature

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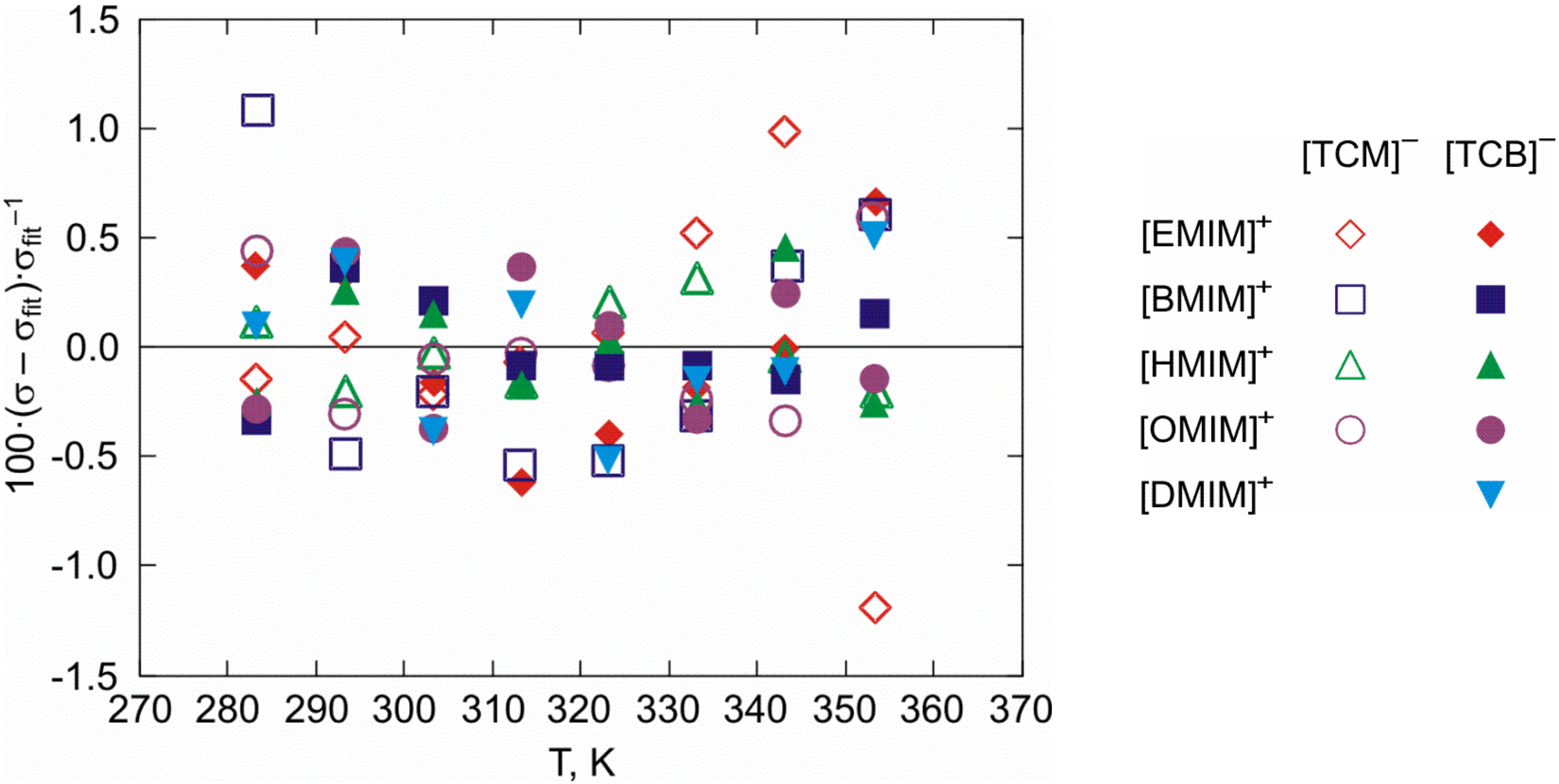
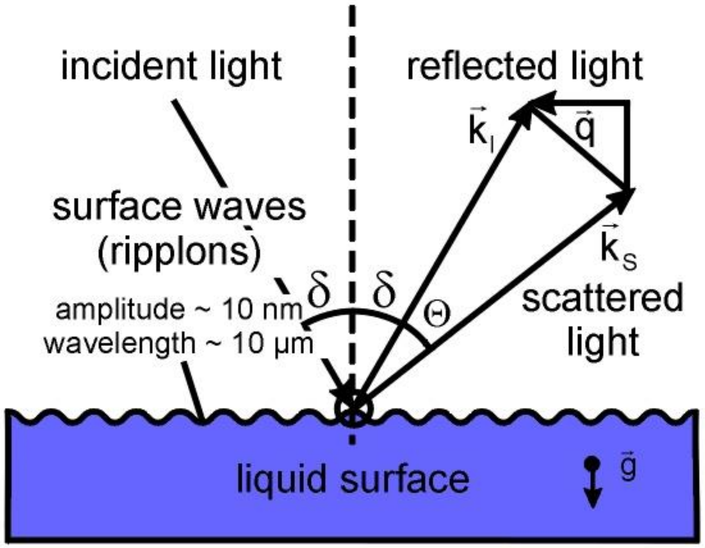
Representation of experimental data by fit $\sigma_{fit} = \sigma_0 + \sigma_1 T$



Experimental uncertainty $\Delta\sigma/\sigma$ (k = 2) 2%

Light Scattering by Surface Waves – Viscosity and Surface Tension

Scattering Geometry



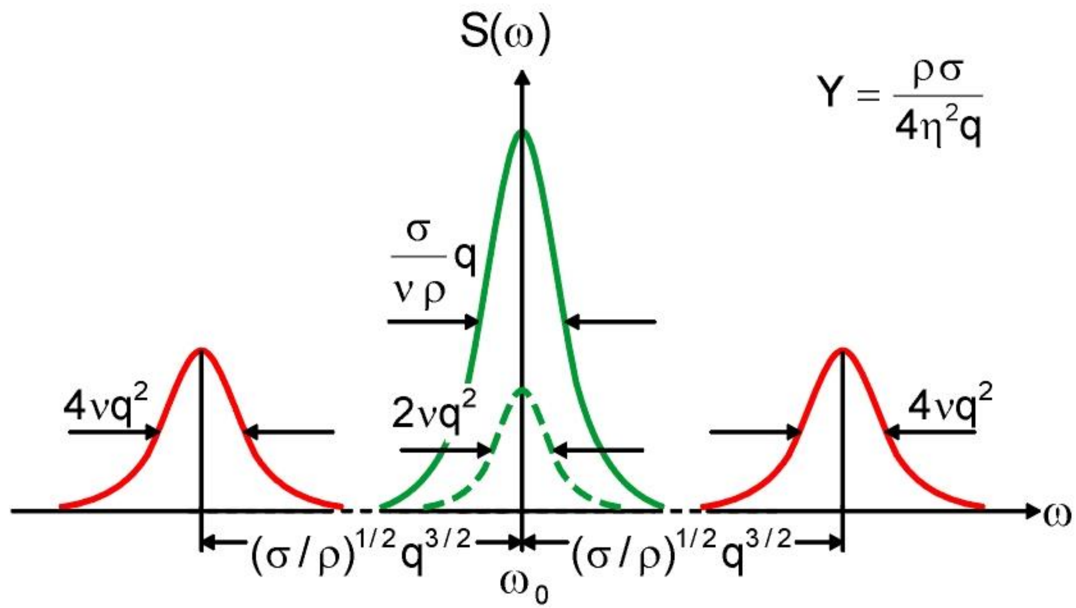
scattering vector

$$q = \left|\vec{k}'_I - \vec{k}'_S\right| \cong \frac{4\pi n}{\lambda_0}\sin(\Theta/2)\cos(\delta + \Theta/2)$$

Spectrum of Scattered Light

large viscosity ($Y \leq 0.145$) - two frequency unshifted lines

small viscosity ($Y > 0.145$) - Brillouin doublet

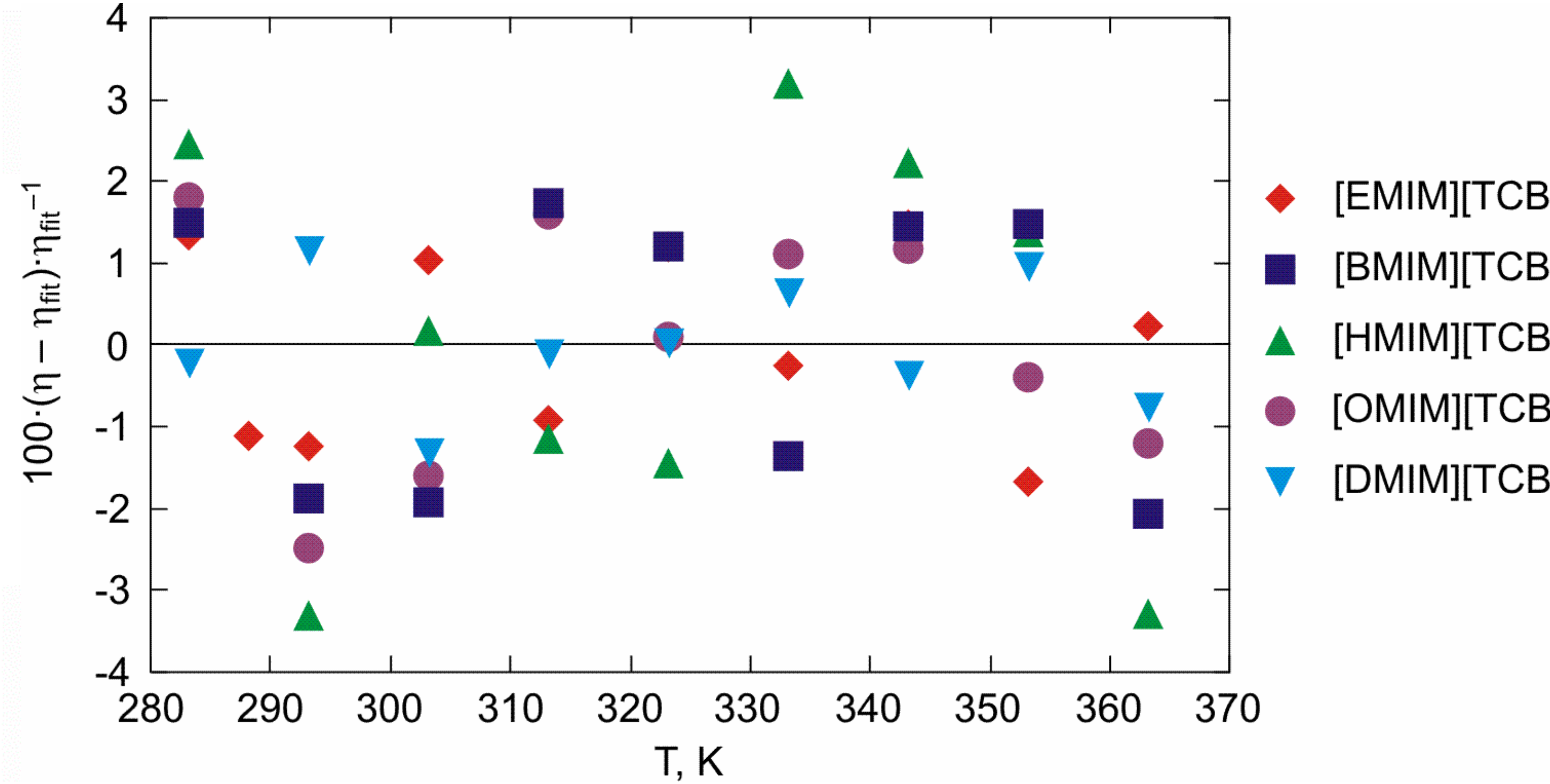


ν: kinematic viscosity; σ: surface tension; ρ: density

(first order approximation)

Dynamic Viscosity of [TCB]$^-$-Based ILs at Atmospheric Pressure as a Function of Temperature

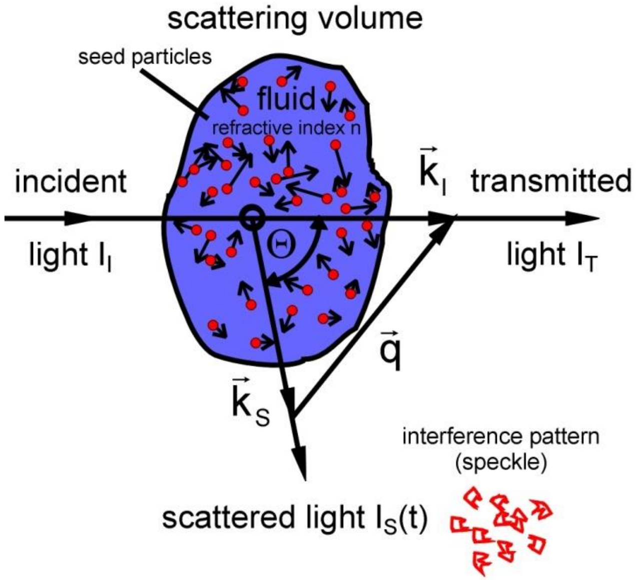
Representation of experimental data by Vogel type equation $\eta_{fit} = \eta_0 \exp\left(B/(T - C)\right)$



[TCB]$^-$-
ıples
CB]
power
mW

Experimental uncertainty $\Delta\eta/\eta$ (k = 2) typically less than 3%

Scattering Geometry

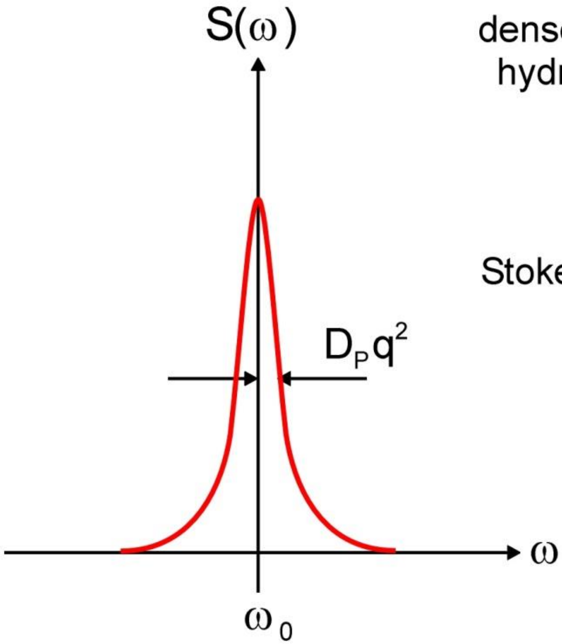


scattering vector $q = \left| \vec{k}_I - \vec{k}_S \right|$

$$q = \frac{4 \cdot \pi \cdot n}{\lambda_0} \sin \frac{\Theta}{2}$$

Spectrum of Scattered Light

caused by local statistical fluctuations in the particle concentration



dense fluid phase in the hydrodynamic regime

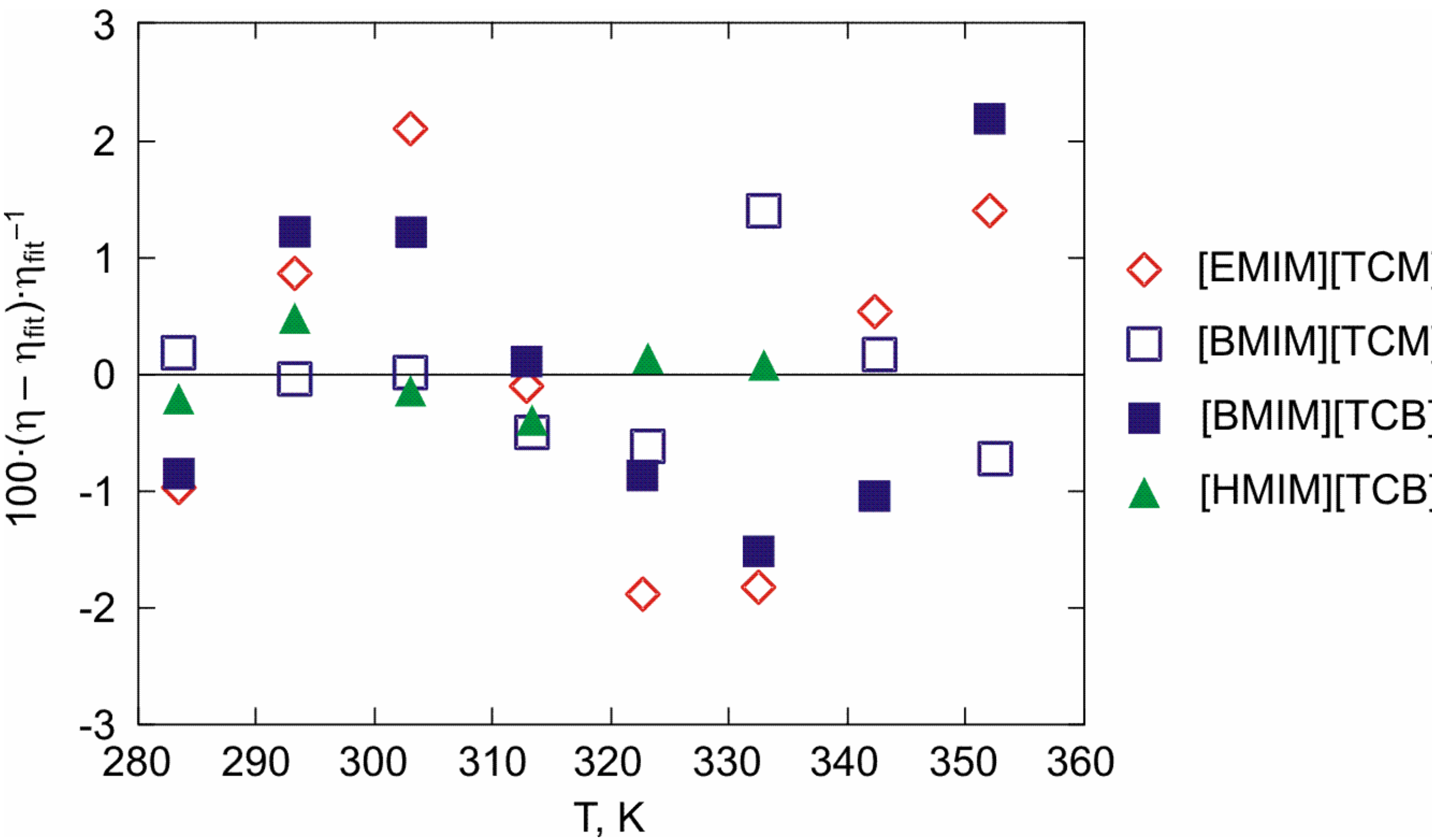
$$D_P = \frac{k_B T}{3 \pi \eta d}$$

Stokes-Einstein relation

$$D_P = \frac{1}{\tau_C q^2}$$

(D_P: particle diffusion coefficient, η: dynamic viscosity; d: hydrodynamic particle diameter; k_B: Boltzmann's constant; T: temperature; τ_c: decay time)

Representation of experimental data by Vogel type equation $\eta_{fit} = \eta_0 \exp(B/(T - C))$



orated particles:

l-%	d / nm
5-0.01	220.8±5.5
05	493.5±14.4

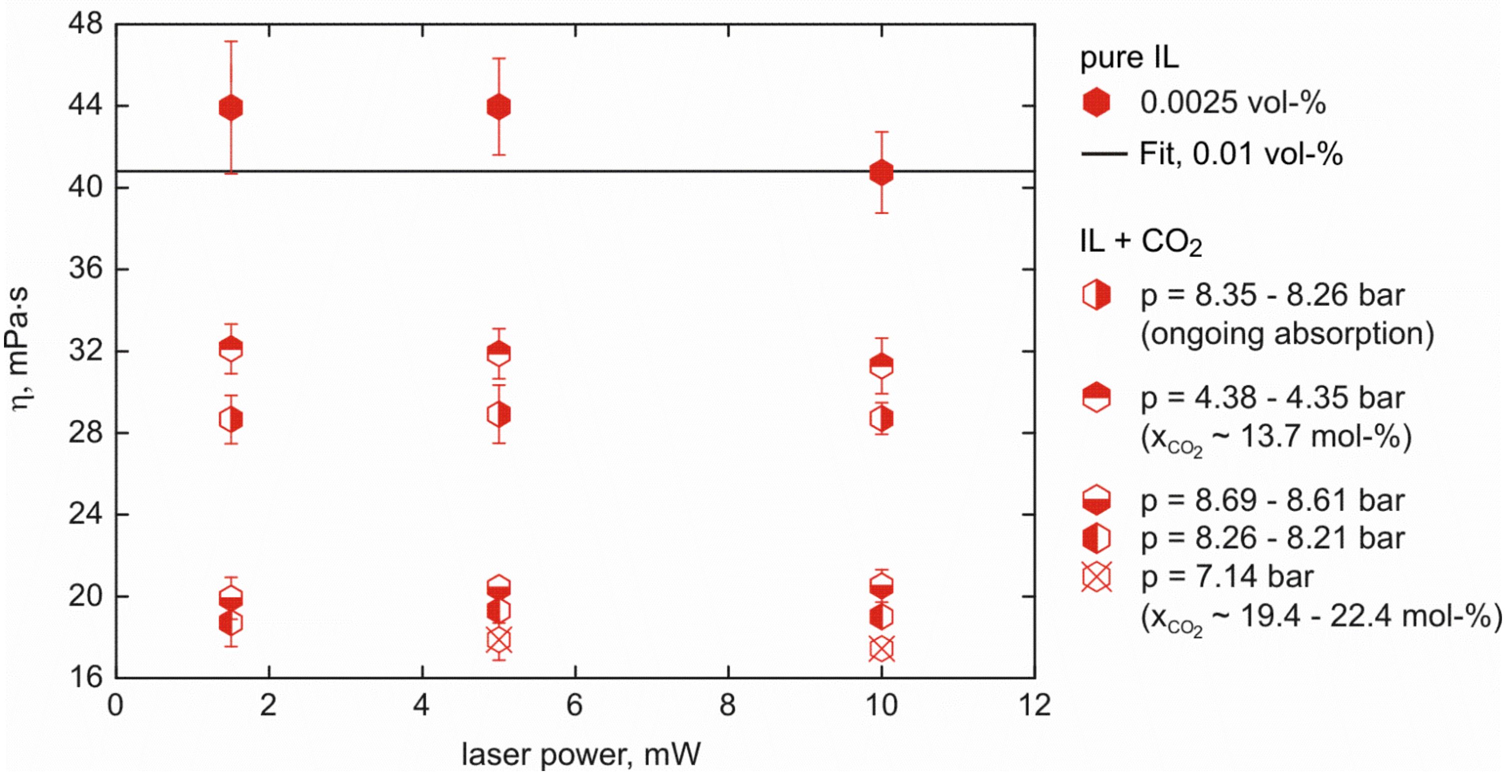
aser power
and 10.8 mW

Experimental uncertainty $\Delta\eta/\eta$ (k = 2) less than 5%

Silica particles dispersed by 0.0025 vol-% in IL

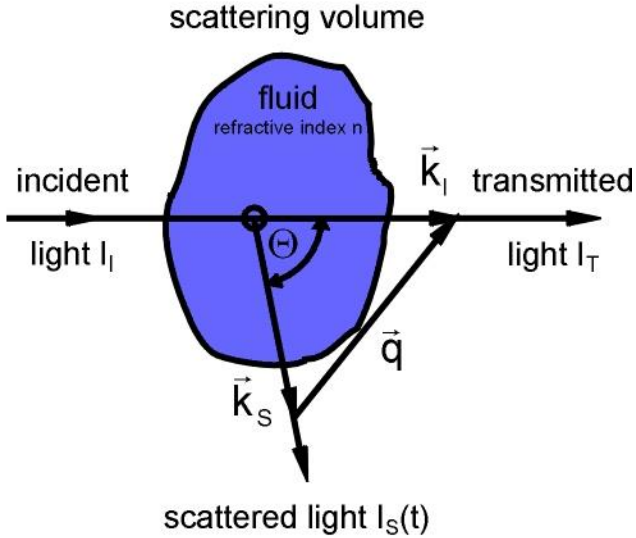
Mole fraction of dissolved CO_2, x_{CO_2}, calculated from solubility data in literature

measurement cell



Light Scattering from Bulk Fluids – Mutual and Thermal Diffusivity

Scattering Geometry

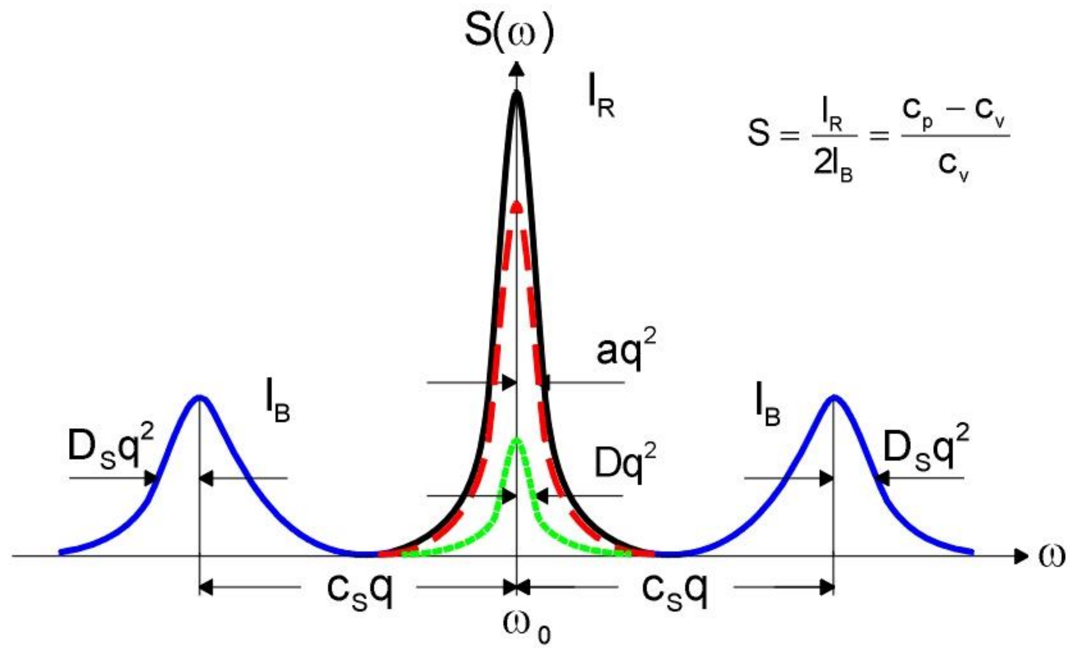


scattering vector $q = \left|\vec{k}_I - \vec{k}_S\right|$

$$q = \frac{4 \cdot \pi \cdot n}{\lambda_0} \sin\frac{\Theta}{2}$$

Spectrum of Scattered Light

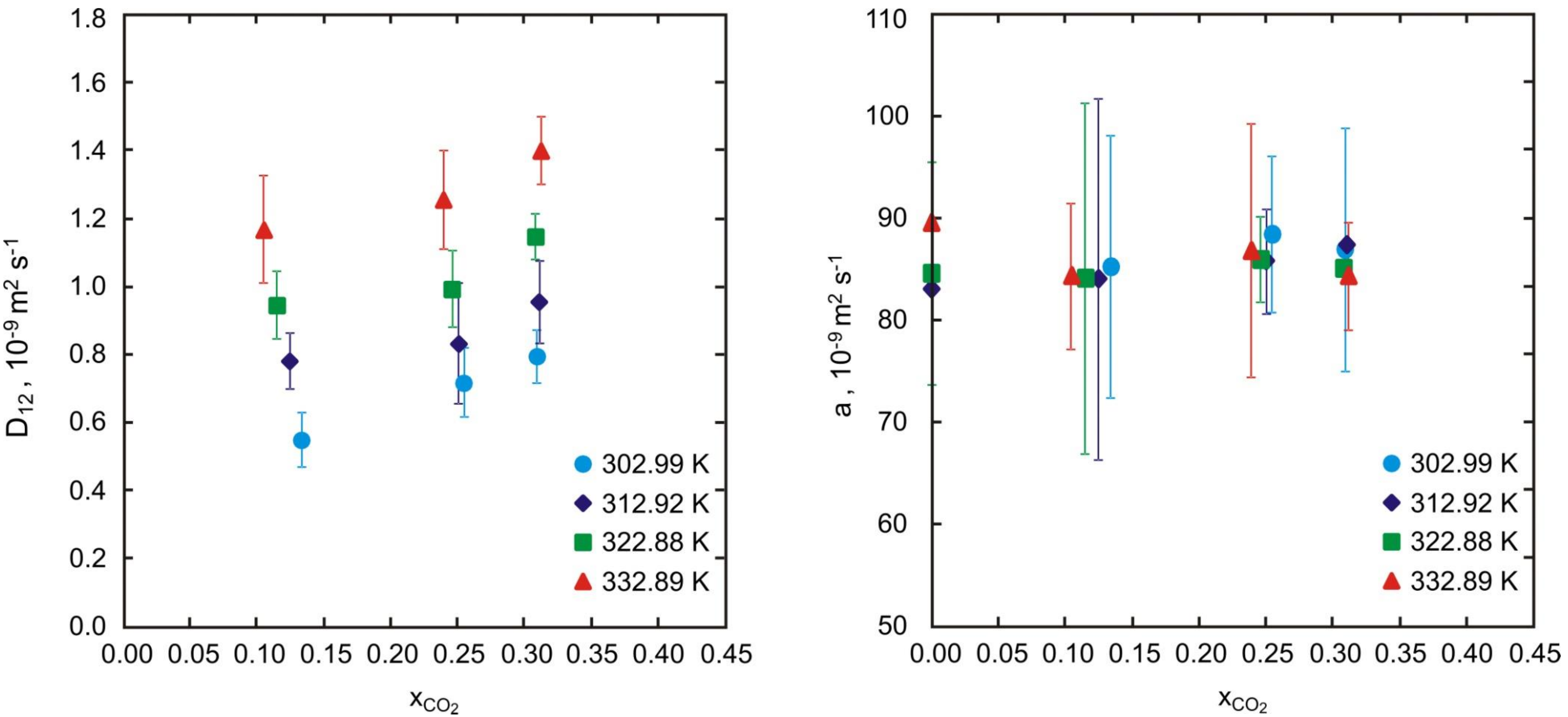
caused by local statistical fluctuations of temperature, concentration, and pressure in thermodynamic equilibrium



(a: thermal diffusivity; D: diffusion coefficient; c_S: sound velocity; D_S: sound attenuation; S: Landau-Placzek ratio)

Mutual and Thermal Diffusivity of Binary Mixtures of [BMIM][TCB] with Dissolved CO_2

Mole fraction of dissolved CO_2, x_{CO_2}, calculated from solubility data in literature



Experimental uncertainties $\Delta D_{12} / D_{12}$ and $\Delta a/a$ (k = 2) typically less than 10%

Conclusions

- **Reliable determination of a large variety of thermophysical properties of pure [TCM]⁻- and [TCB]⁻-based ILs as well as their binary mixtures with dissolved carbon dioxide by DLS and conventional methods**

- *Measurement of **thermal conductivity of pure ILs** (283 to 353 K, $\Delta\lambda_c/\lambda_c < \pm 5\%$) at atmospheric pressure with a **steady-state parallel plate instrument** and development of a **simple prediction method** for the **thermal conductivity of arbitrary ILs** as a function of temperature*

- *Determination of **surface tension of pure ILs** (283 to 353 K, $\Delta\sigma/\sigma < \pm 2\%$) at atmospheric pressure by **pendant drop method***

- *Determination of **dynamic viscosity of transparent [TCB]⁻-based ILs** (283 to 353 K, $\Delta\eta/\eta$ typically $< \pm 3\%$) at atmospheric pressure **by light scattering from surface waves***

- *Access to **dynamic viscosity of transparent [TCB]⁻-based ILs and semitransparent [TCM]⁻-based ILs** (283 to 353 K, $\Delta\eta/\eta < \pm 5\%$) via the determination of the **particle diffusion coefficient by light scattering from dispersed particles***

- ***Mutual and thermal diffusivity of binary mixtures of ILs with carbon dioxide** (303 to 333 K, $\Delta D_{12}/D_{12}$ and $\Delta a/a$ typically $< \pm 10\%$) **accessible by light scattering from bulk fluids** over a wide concentration range with low experimental uncertainties*


Thank you for
your attention

IoLiCAP

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