Liquid Ion Pairs

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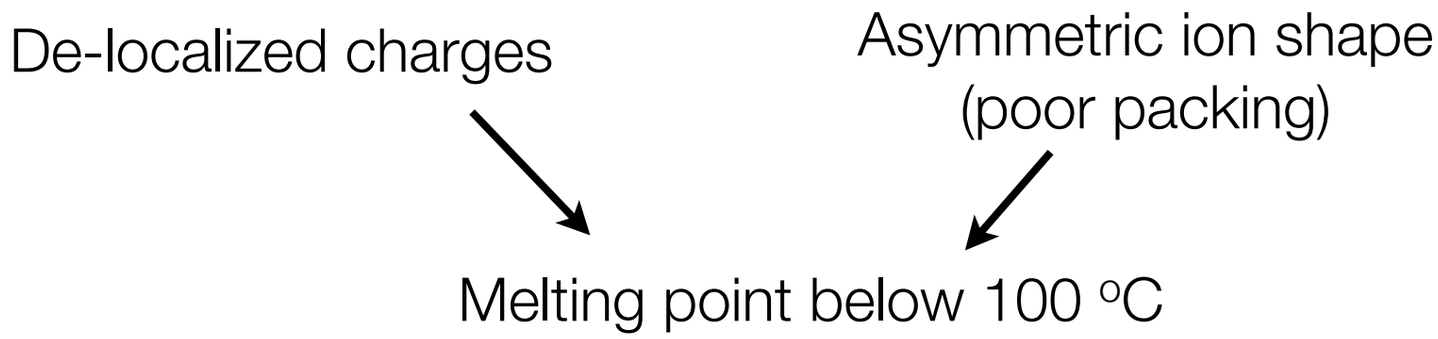
CRC Smartprint

MONASH University Science

Ionic liquids: A brief introduction

A liquid that is composed entirely of ions



Ionic liquids: A brief introduction

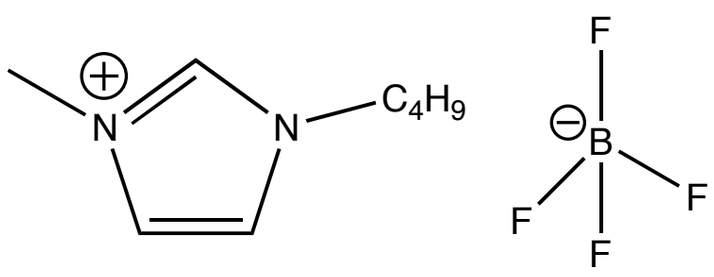
A liquid that is composed entirely of ions

De-localized charges

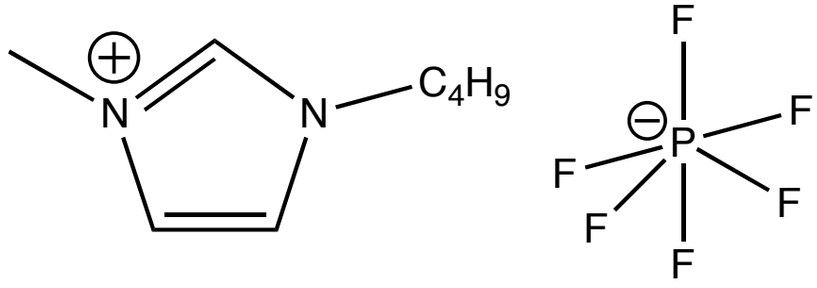
Asymmetric ion shape
(poor packing)

Melting point below 100 ^{o}C

Typical ions to form ionic liquids



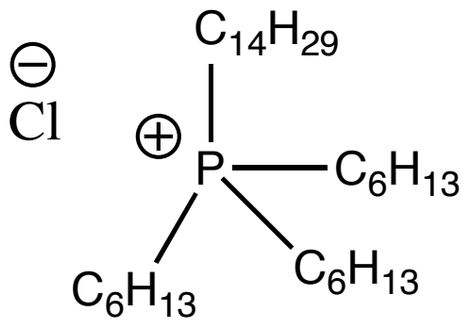
Hydrophilic
Tg -81^{o}C only



Hydrophobic
M.P. of 6.4^{o}C

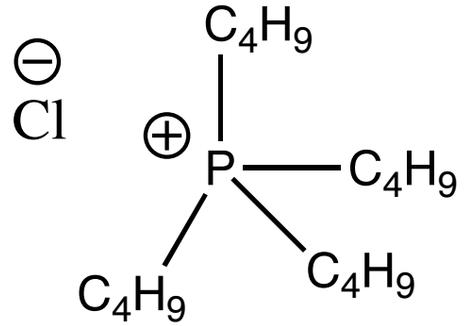
Ionic liquids: Compounds synthesised

Cytec^{R} routinely produces tetraalkylphosphonium halides such as the ionic liquid trihexyl-tetradecyl phosphonium chloride



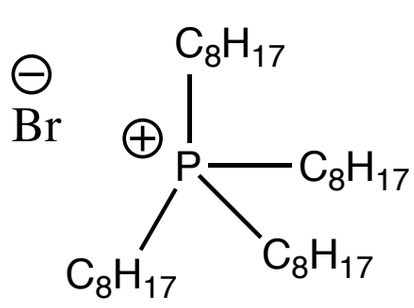
Trihexyl-tetradecyl phosphonium chloride

Liquid at room temperature



Tetrabutyl phosphonium chloride

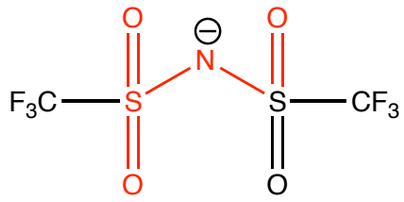
M.P 67^{o}C



Tetraoctyl phosphonium bromide

M.P 45^{o}C

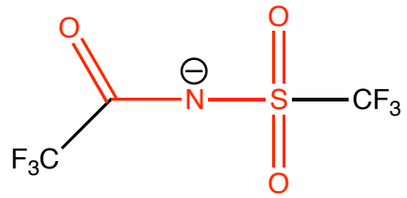
Ionic liquids: Compounds synthesised

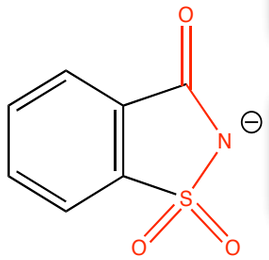


Commonly used anion
TFSA

Exploring alternative analoges

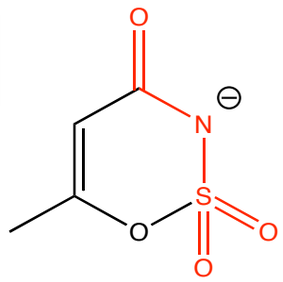
2,2,2-trifluoro-*N*-(trifluoromethylsulfonyl)acetamide (TSAC)





Saccharinate
(Sacc)

Acesulfamate
(Ace)



LD_{50} NaSacc: 14,200 mg/kg

LD_{50} KAce: N/A

N-acyl-N-sulfonyl imides

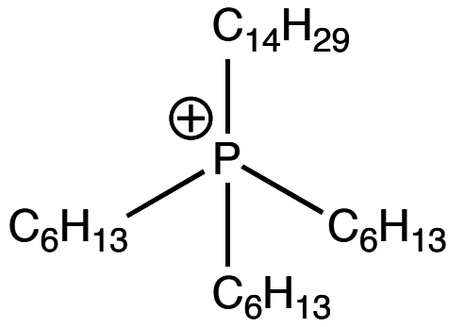
Sacc and Ace are non fluorous and have well established toxicological profiles

Used as non nutritive sweeteners

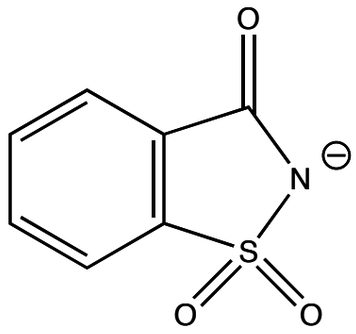
E. B. Carter, S. L. Culver, P. A. Fox, R. D. Goode, I. Ntai, M. D. Tickell, R. K. Traylor, N. W. Hoffman and J. H. Davis, Jr., *Chem. Commun.*, 2004, 630-631.

ILs Studied

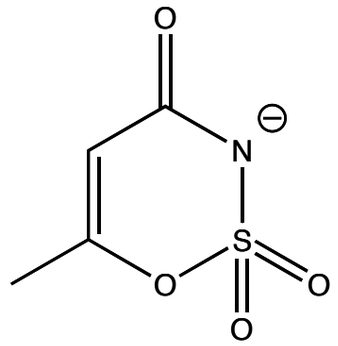
6 new ILs.



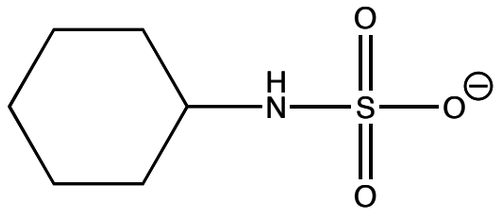
$[P_{6,6,6,14}]^+$



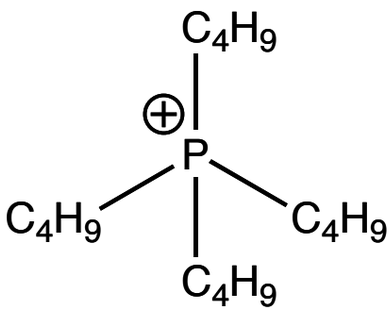
$[Sacc]^-$



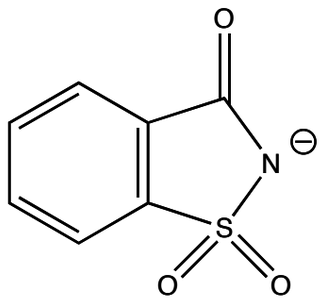
$[Ace]^-$



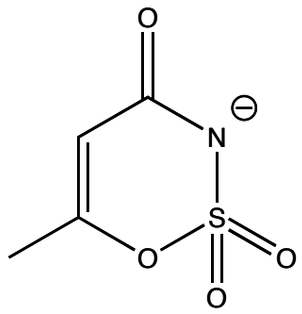
$[Cyc]^-$



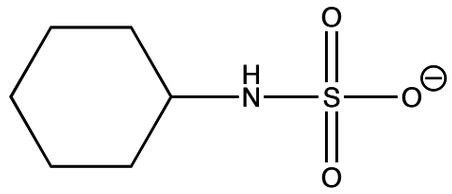
$[P_{4,4,4,4}]^+$



$[Sacc]^-$



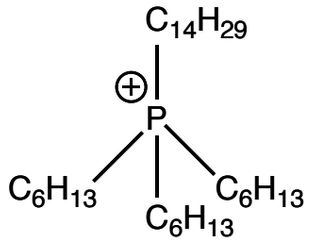
$[Ace]^-$



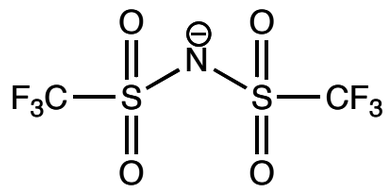
$[Cyc]^-$

ILs Studied

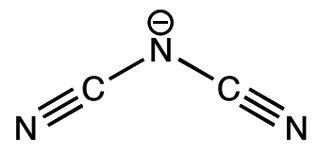
Purchased ILs



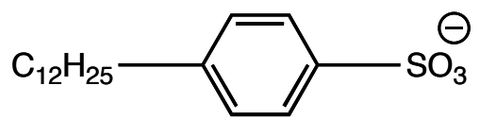
$[P_{6,6,6,14}]^+$



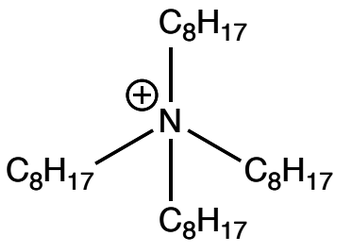
$[NTf_2]^-$



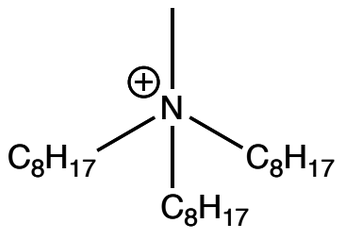
$[dca]^-$



$[dbsa]^-$



$[N_{8,8,8,8}]^+$



$[N_{1,8,8,8}]^+$

$Cl^\ominus$

$[Cl]^-$

Thermal analysis

IL	T_g / °C	T_{dec} / °C
$[P_{6,6,6,14}][Sacc]$	-56	197
$[P_{6,6,6,14}][Ace]$	-61*	196
$[P_{6,6,6,14}][Cyc]$	-53	194
$[P_{6,6,6,14}][NTf_2]$**	-76	400
$[P_{6,6,6,14}][dca]$**	-67	395
$[P_{6,6,6,14}][Cl]$	-61	373
$[P_{4,4,4,4}][Sacc]$	-34	300
$[P_{4,4,4,4}][Ace]$	-47 (T_g) 5 (crystallisation) 42 (melt, $\overline{\Delta}S_f$ = 43(10) $JK^{-1}mol^{-1}$)	280
$[P_{4,4,4,4}][Cyc]$	-32	280
$[N_{1,8,8,8}][Cl]$		202
$[N_{8,8,8,8}][Cl]$	33 (S_{III} - S_{II} $\overline{\Delta}S_f$ = 12(10) $JK^{-1}mol^{-1}$) 44 (S_{II} - S_I $\overline{\Delta}S_f$ = 68(10) $JK^{-1}mol^{-1}$) 54 (T_{melt} $\overline{\Delta}S_f$ = 59(10) $JK^{-1}mol^{-1}$)	196

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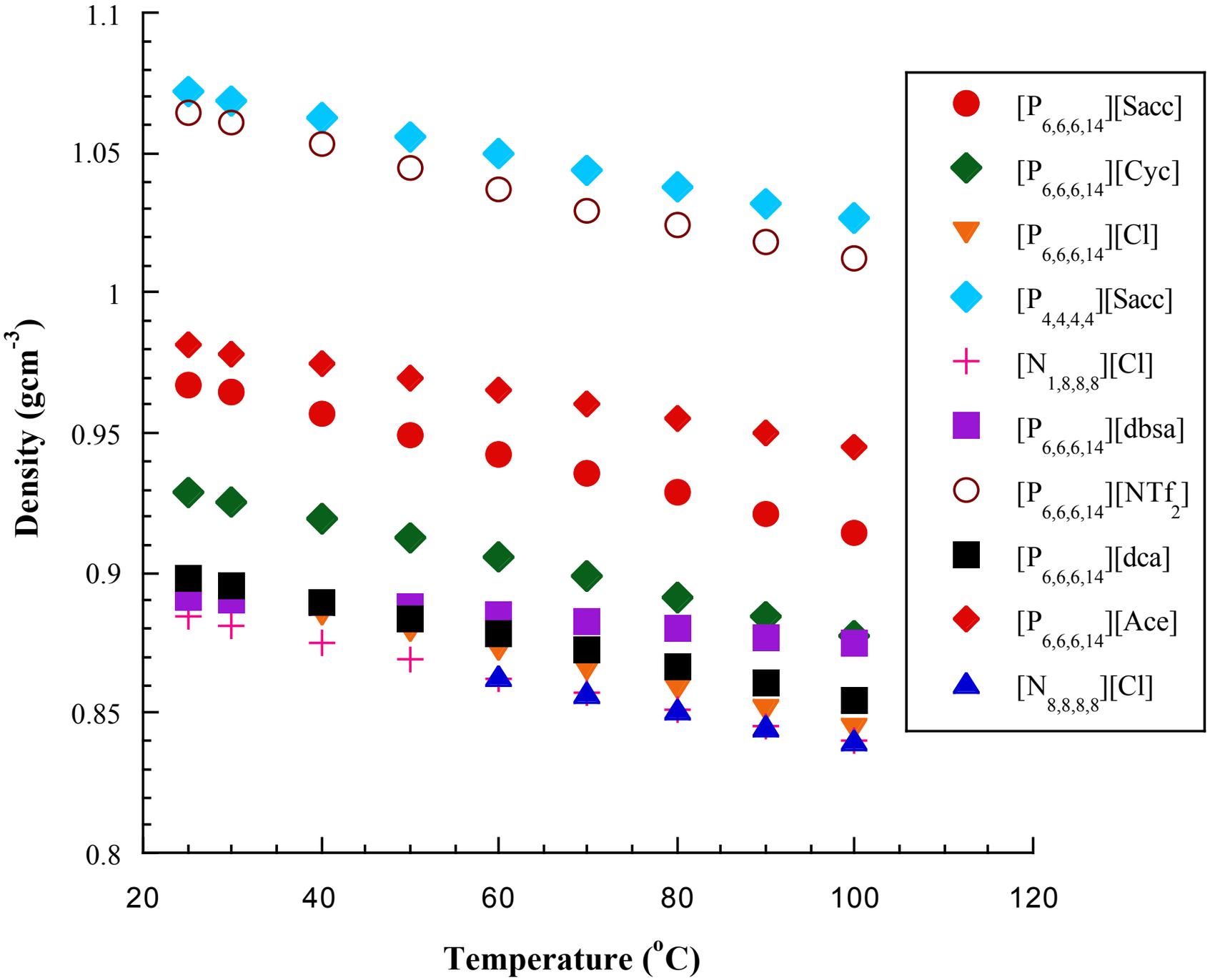
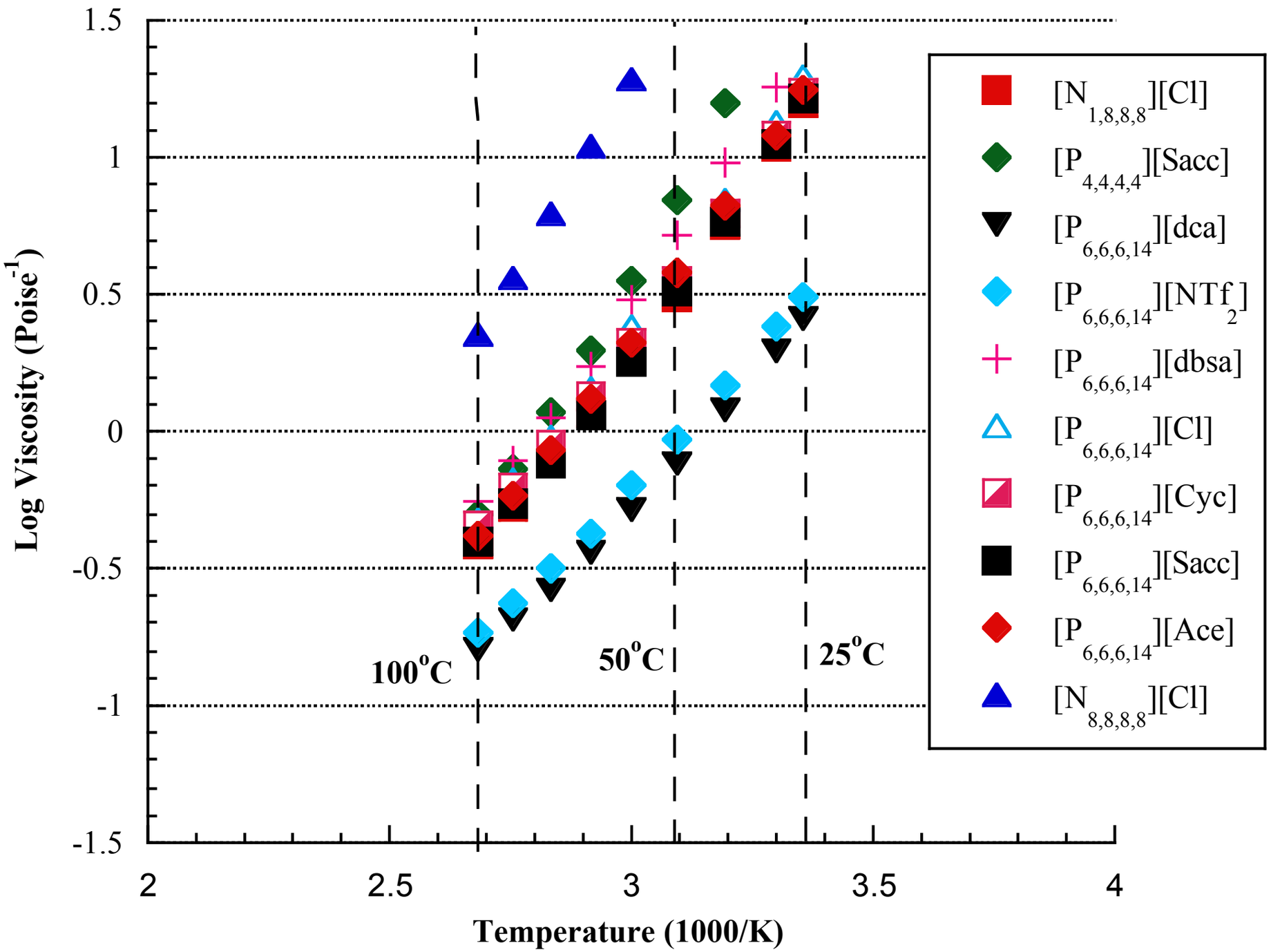
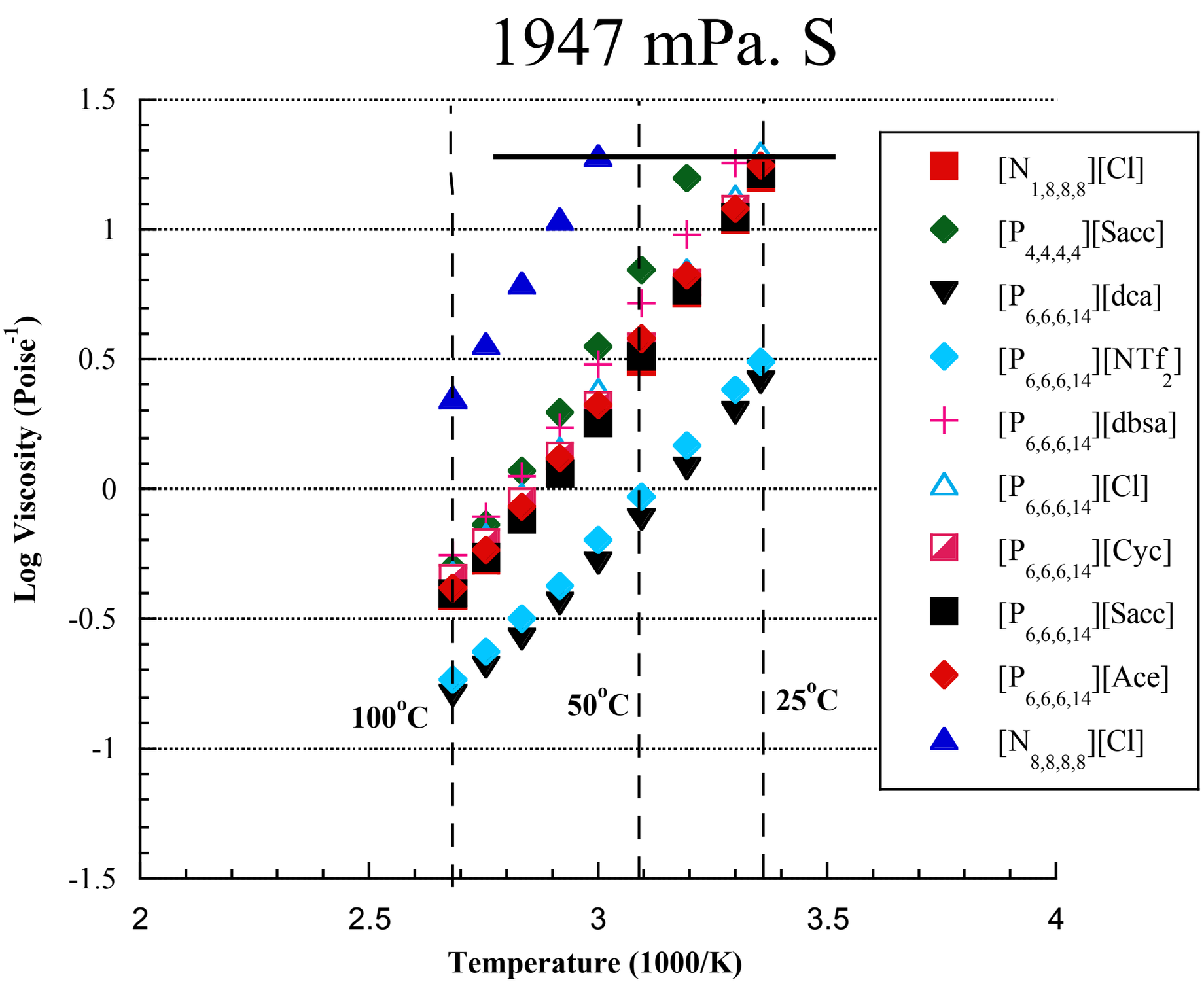
Density


1.1
1.05
1
0.95
0.9
0.85
0.8
20
40
60
80
100
120
Density (gcm-3)
Temperature (°C)
[P6,6,6,14][Sacc]
[P6,6,6,14][Cyc]
[P6,6,6,14][Cl]
[P4,4,4,4][Sacc]
[N1,8,8,8][Cl]
[P6,6,6,14][dbsa]
[P6,6,6,14][NTf2]
[P6,6,6,14][dca]
[P6,6,6,14][Ace]
[N8,8,8,8][Cl]

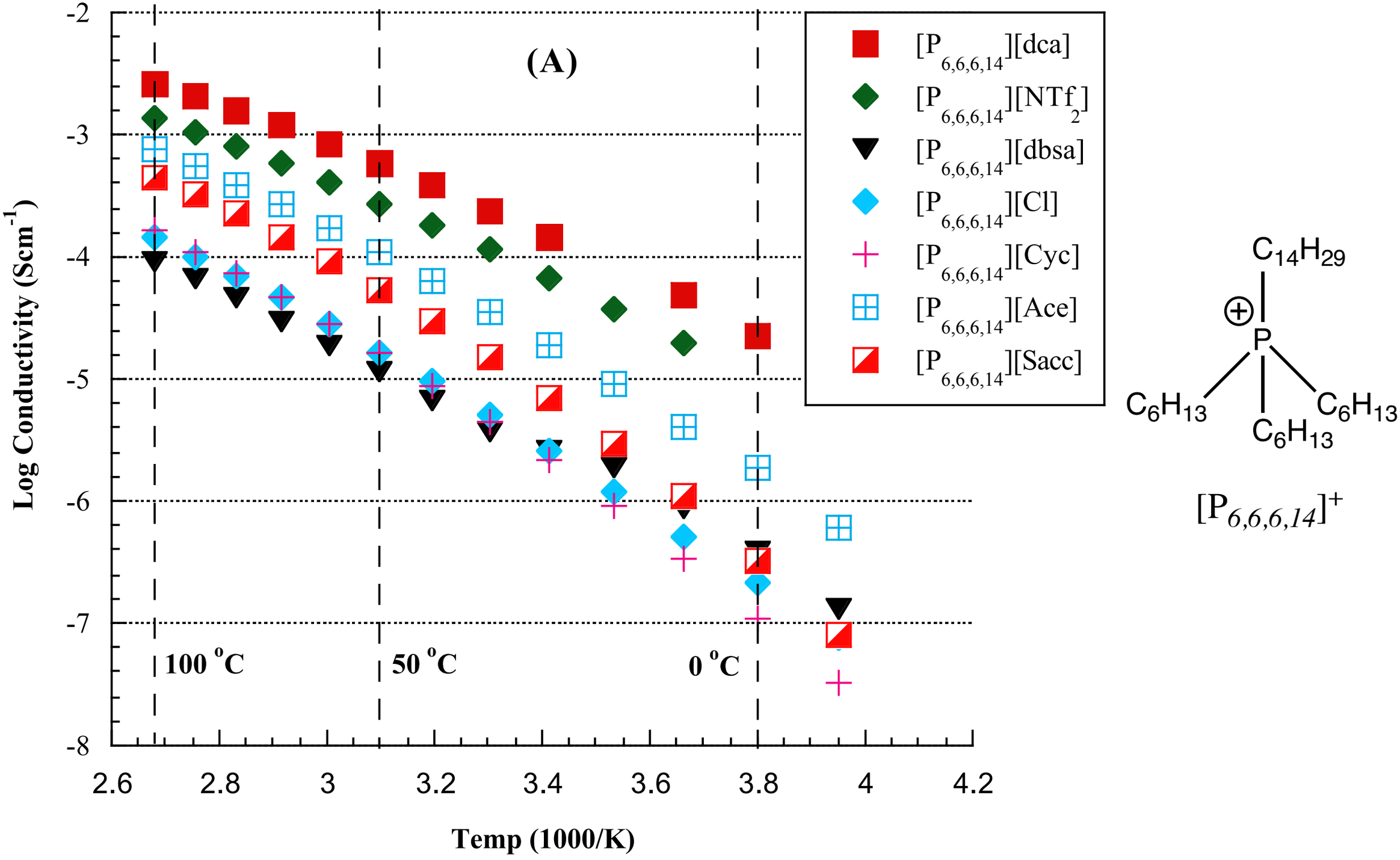
Viscosity


1.5
1
0.5
0
-0.5
-1
-1.5
2
2.5
3
3.5
4
Log Viscosity (Poise-1)
Temperature (1000/K)
100°C
50°C
25°C
[N1,8,8,8][Cl]
[P4,4,4,4][Sacc]
[P6,6,6,14][dca]
[P6,6,6,14][NTf2]
[P6,6,6,14][dbsa]
[P6,6,6,14][Cl]
[P6,6,6,14][Cyc]
[P6,6,6,14][Sacc]
[P6,6,6,14][Ace]
[N8,8,8,8][Cl]

Viscosity

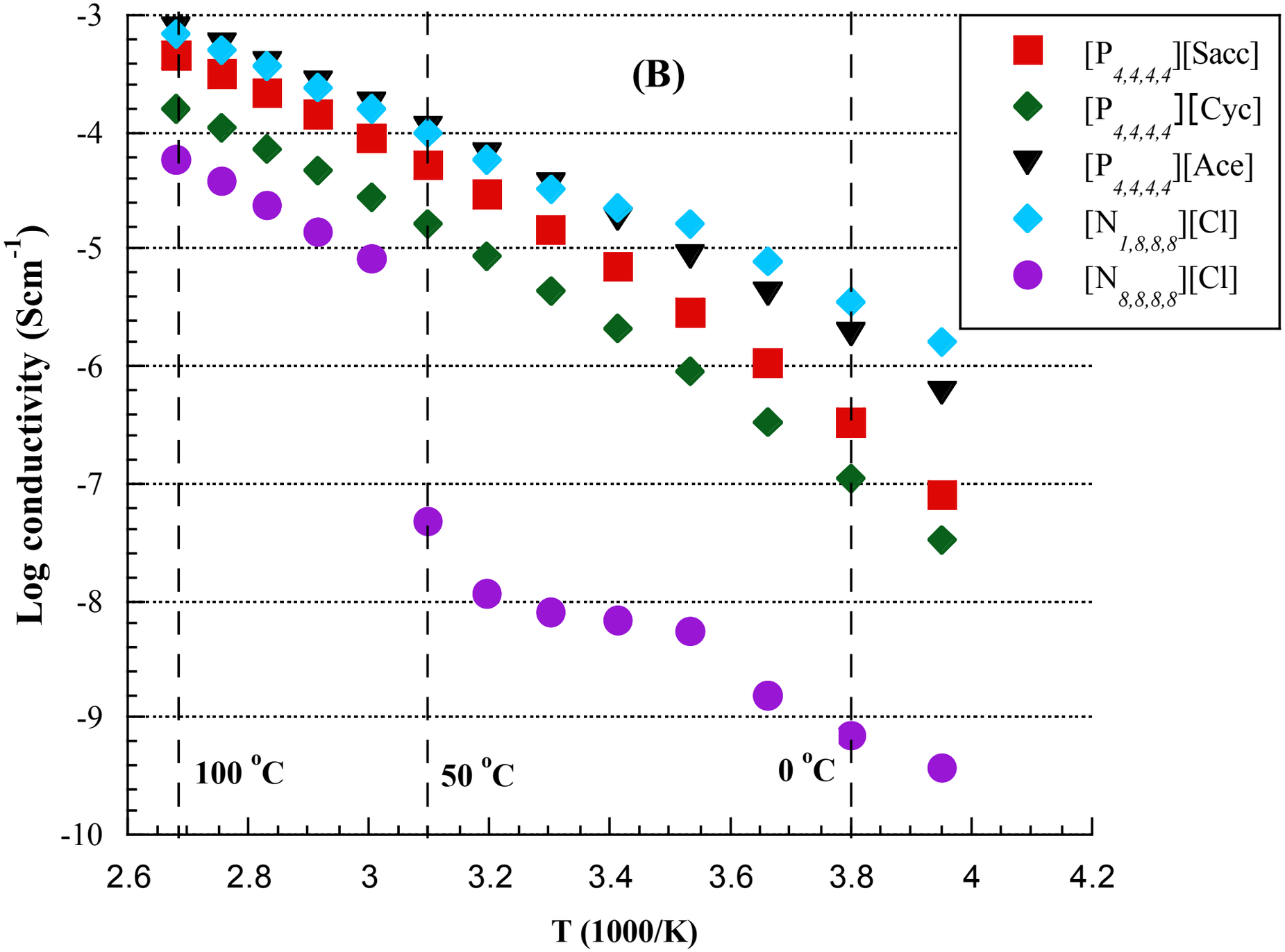

1947 mPa. S
1.5
1
0.5
0
-0.5
-1
-1.5
2
2.5
3
3.5
4
Log Viscosity (Poise-1)
Temperature (1000/K)
100°C
50°C
25°C
[N1,8,8,8][Cl]
[P4,4,4,4][Sacc]
[P6,6,6,14][dca]
[P6,6,6,14][NTf2]
[P6,6,6,14][dbsa]
[P6,6,6,14][Cl]
[P6,6,6,14][Cyc]
[P6,6,6,14][Sacc]
[P6,6,6,14][Ace]
[N8,8,8,8][Cl]

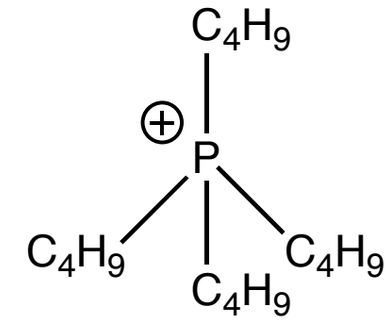
Conductivity



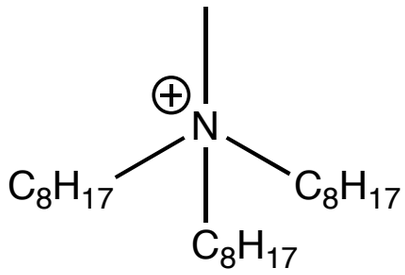
$[P_{6,6,6,14}]^+$

Conductivity

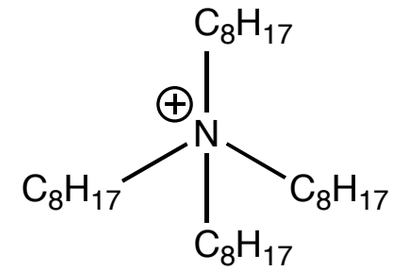




$[P_{4,4,4,4}]^+$



$[N_{1,8,8,8}]^+$



$[N_{8,8,8,8}]^+$

Interesting points about the data

IL	Conductivity (S cm^{-1}) (40 °C)	Viscosity (Pa.s) (40 °C)
$[P_{6.6.6.14}][Cl]$	9.5×10^{-6}	0.70
$[P_{6.6.6.14}][Cyc]$	8.9×10^{-6}	0.62
$[P_{6.6.6.14}][dbsa]$	6.7×10^{-6}	0.95
$[P_{6.6.6.14}][Ace]$	6.4×10^{-5}	0.67
$[P_{6.6.6.14}][Sacc]$	3.0×10^{-5}	0.58
$[P_{6.6.6.14}][NTf_2]$	1.8×10^{-4}	0.15
$[P_{6.6.6.14}][dca]$	3.8×10^{-4}	0.12
$[P_{4.4.4.4}][Sacc]$	4.0×10^{-5}	1.58
$[P_{4.4.4.4}][Ace]$*	1.5×10^{-4}	--
$[P_{4.4.4.4}][Cyc]$*	8.7×10^{-5}	--
$[N_{1.8.8.8}][Cl]$	5.4×10^{-5}	0.57
$[N_{8.8.8.8}][Cl]$**	1.2×10^{-8}	--

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$[N_{8.8.8.8}][Cl]$**	1.2×10^{-8}	--

Interesting points about the data

As an example of these effects, [$P_{4,4,4,4}$][Sacc], although being almost three times more viscous (1.58 Pa.s at 40 ^{o}C) than [$P_{6,6,6,14}$][Sacc] (0.58 Pa.s at 40 ^{o}C) nonetheless has similar conductivity,

Interesting points about the data

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- Consider the low conductivity, one realises that it is not behaving as a true ionic liquid and is better thought of as reflecting the properties of a liquid ion paired compound.

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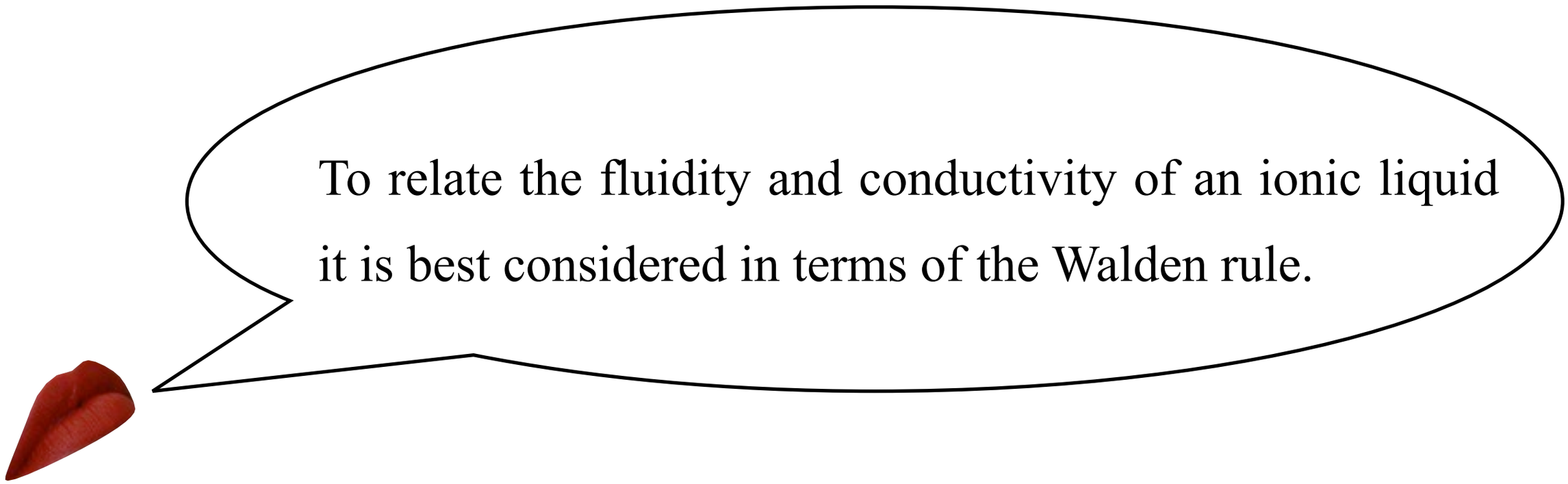
- Presumably because the degree of ion correlation and association is lower in the former case.

COIL-3
3rd Congress on Ionic Liquids
May 31 - June 4 2009

Ionicity: A qualitative analysis (quantitative is another talk)



Ionicity: A qualitative analysis (quantitative is another talk)

To relate the fluidity and conductivity of an ionic liquid it is best considered in terms of the Walden rule.

States that the equivalent conductivity, is directly proportional to the fluidity of the medium through which the ions move.

$$\Lambda\eta = \text{constant}$$

Ionicity: A qualitative analysis (quantitative is another talk)

The Walden rule is temperature independent,

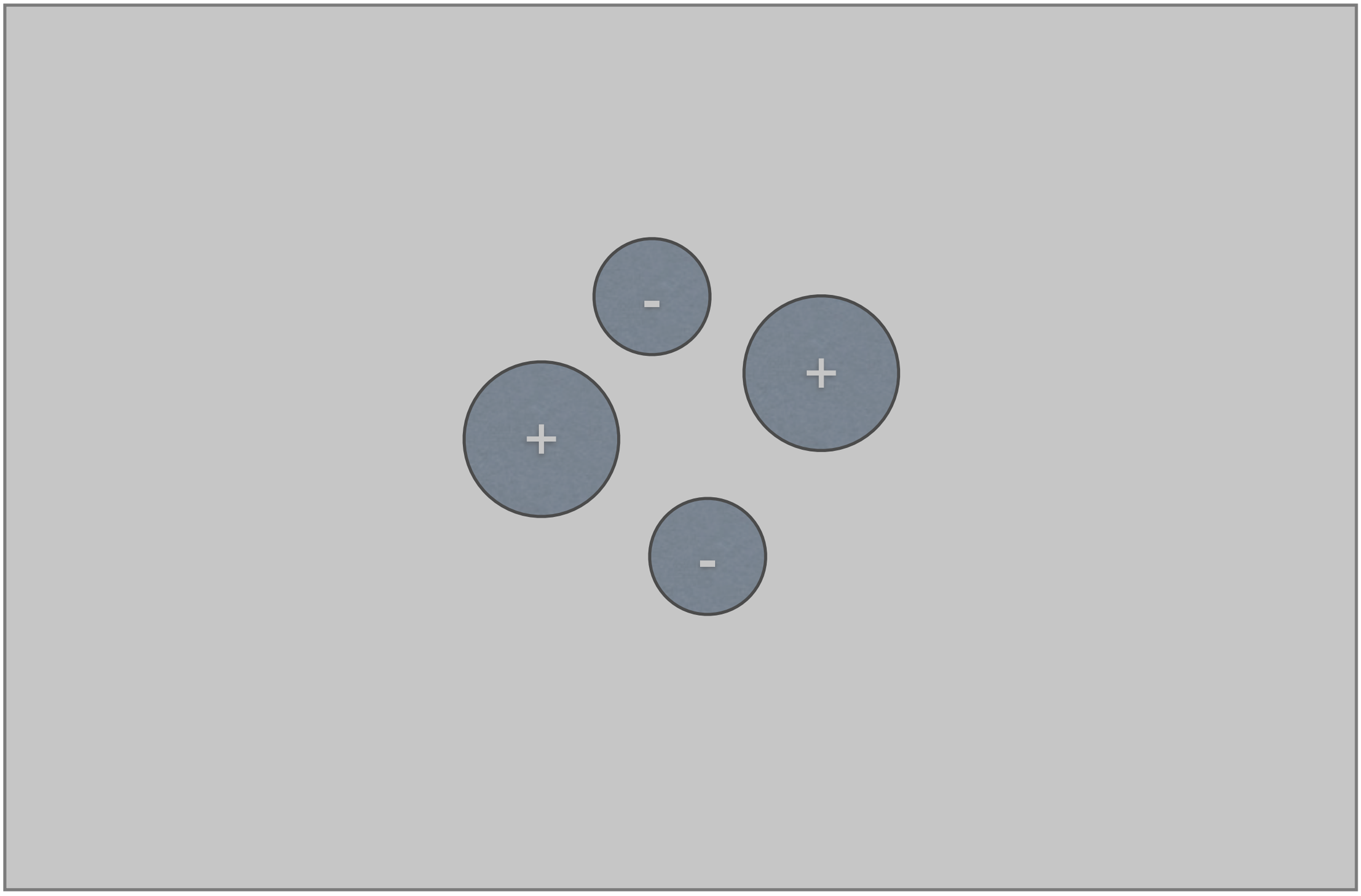
The change in equivalent conductivity is the same

rate as the inverse viscosity.

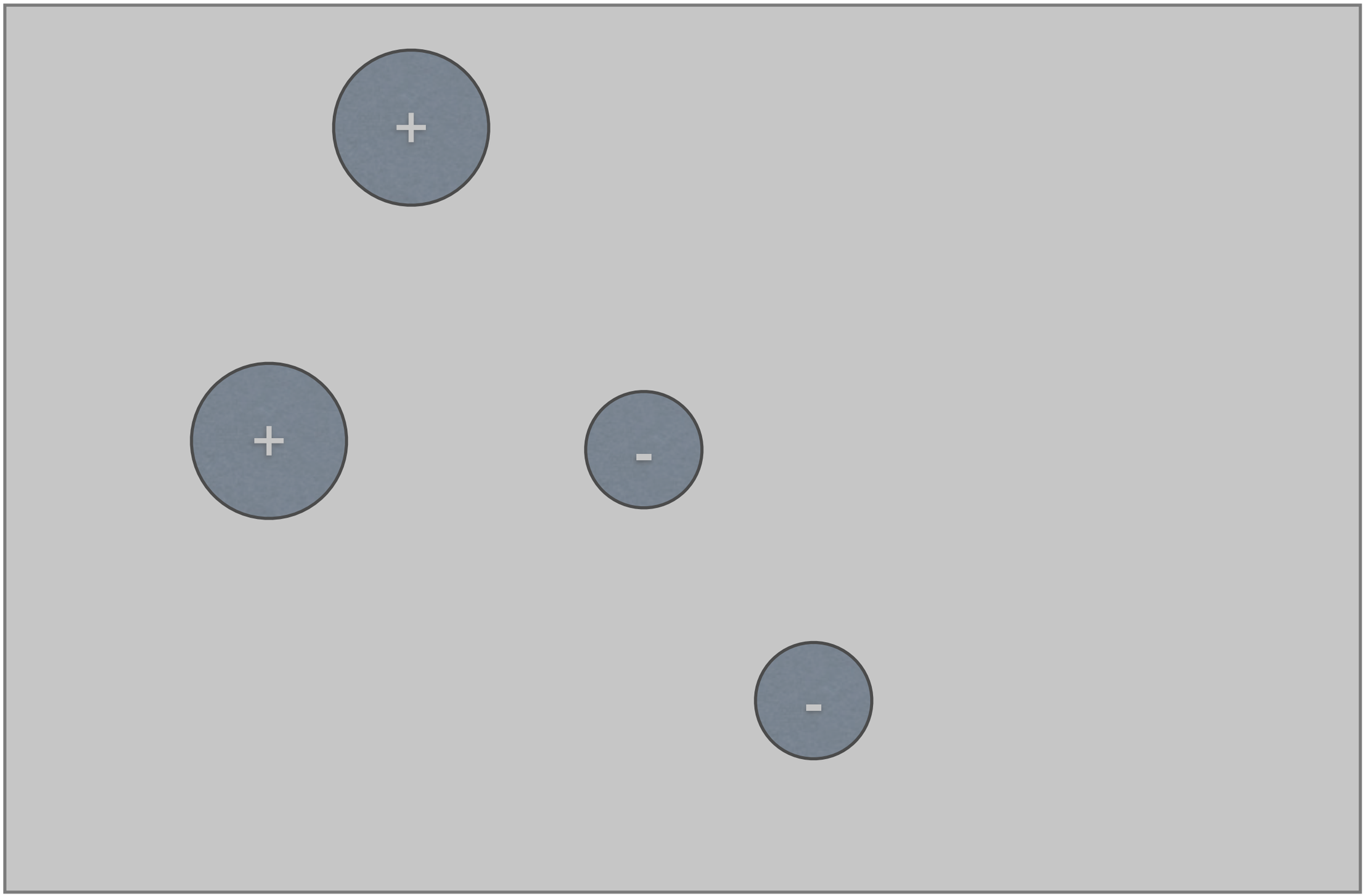
States that the equivalent conductivity, is directly proportional to the fluidity of the medium through which the ions move.

$$\Lambda\eta = \text{constant}$$

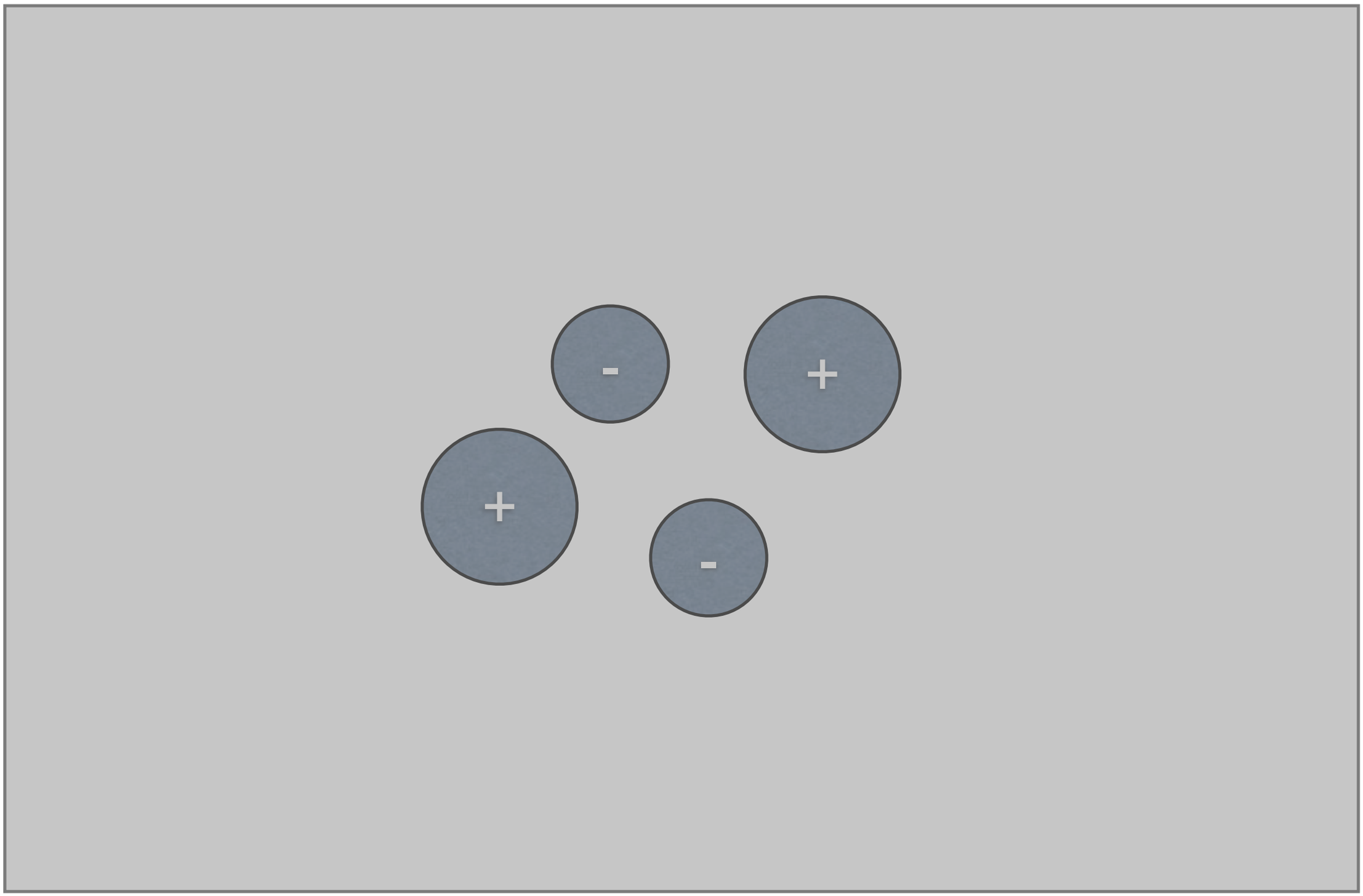
“Ideal” Walden behavior



“Ideal” Walden behavior

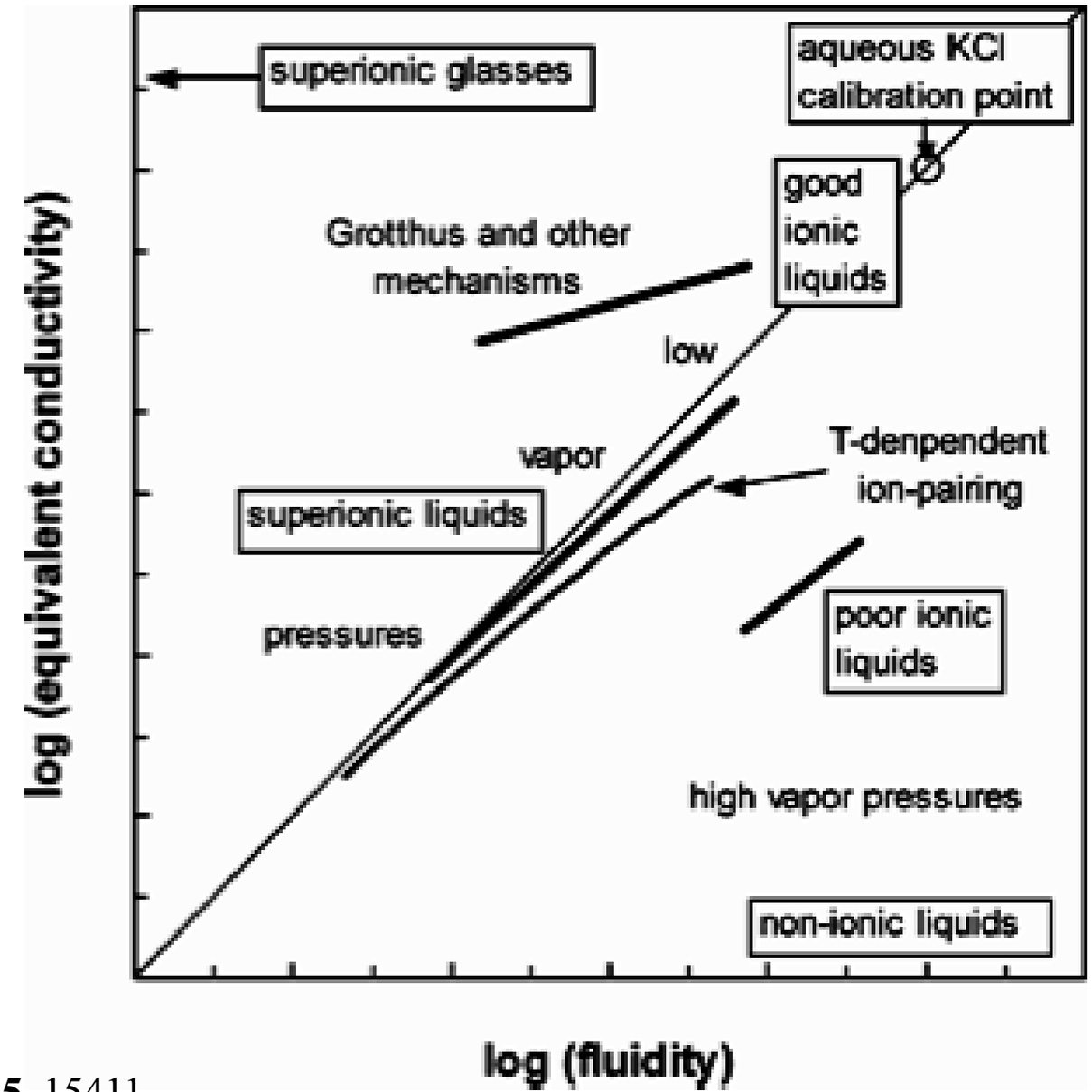


Non ideal behavior



Ionicity: A qualitative analysis

Show is a classification system of the Walden plot and deviations from the Walden rule as proposed by Angell et al.

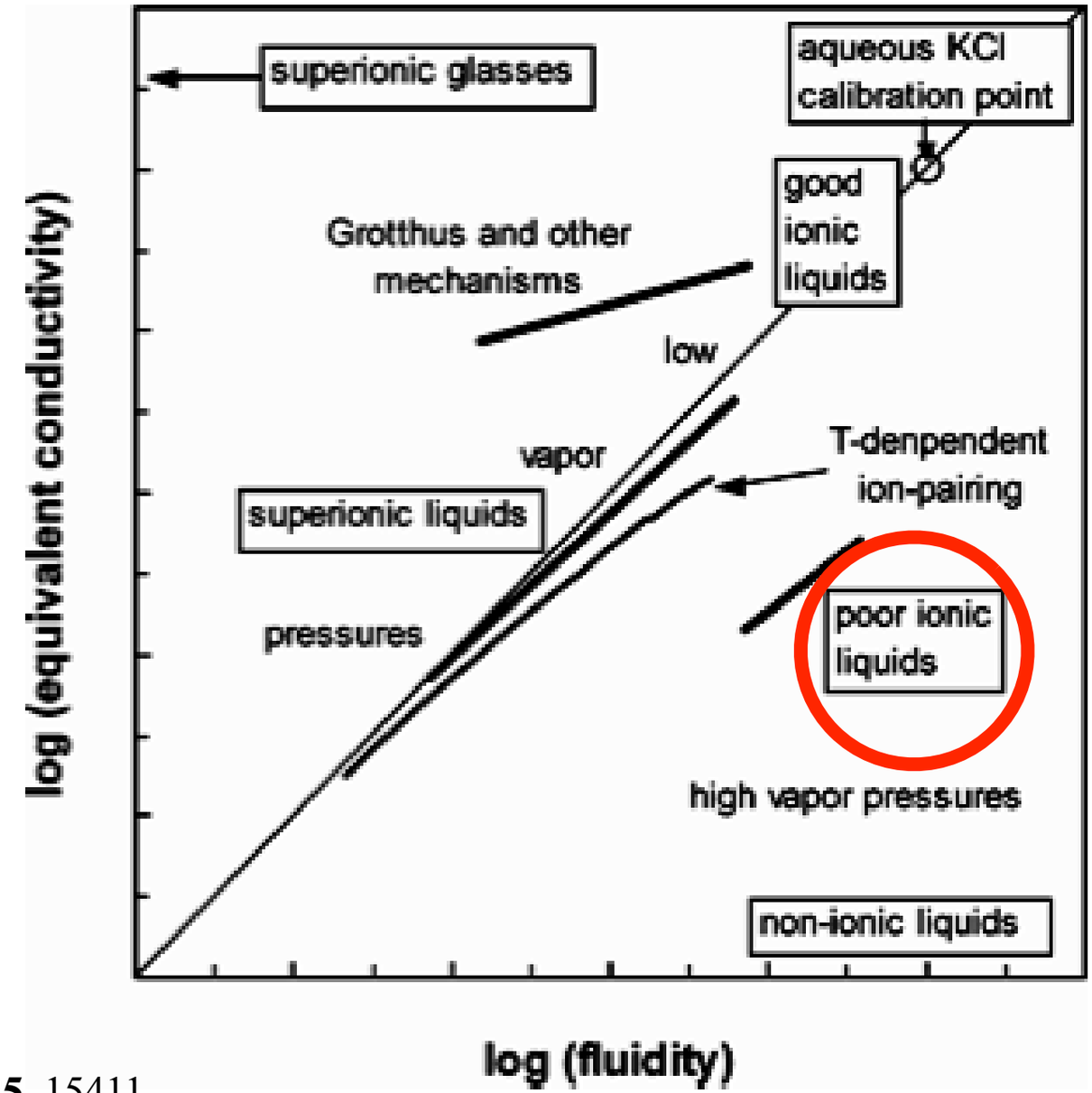


M. Yoshizawa, W. Xu and C. A. Angell, *J. Am. Chem. Soc.*, 2003, **125**, 15411.

Ionicity: A qualitative analysis

Show is a classification system of the Walden plot and deviations from the Walden rule as proposed by Angell et al.

"Poor Ionic Liquids" are ionic liquids that exhibit only 10% of the "Ideal" molar conductivity for a given viscosity.



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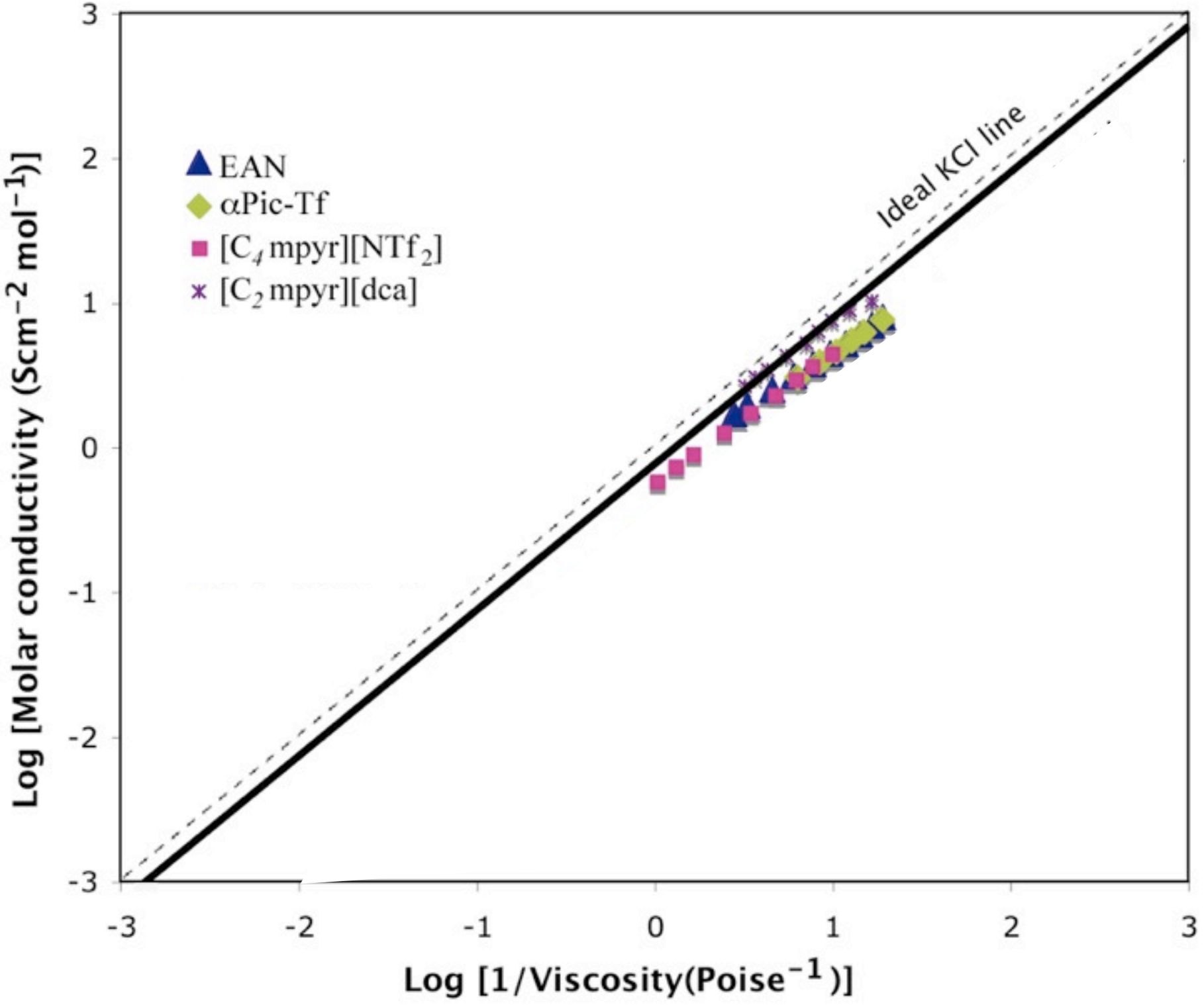
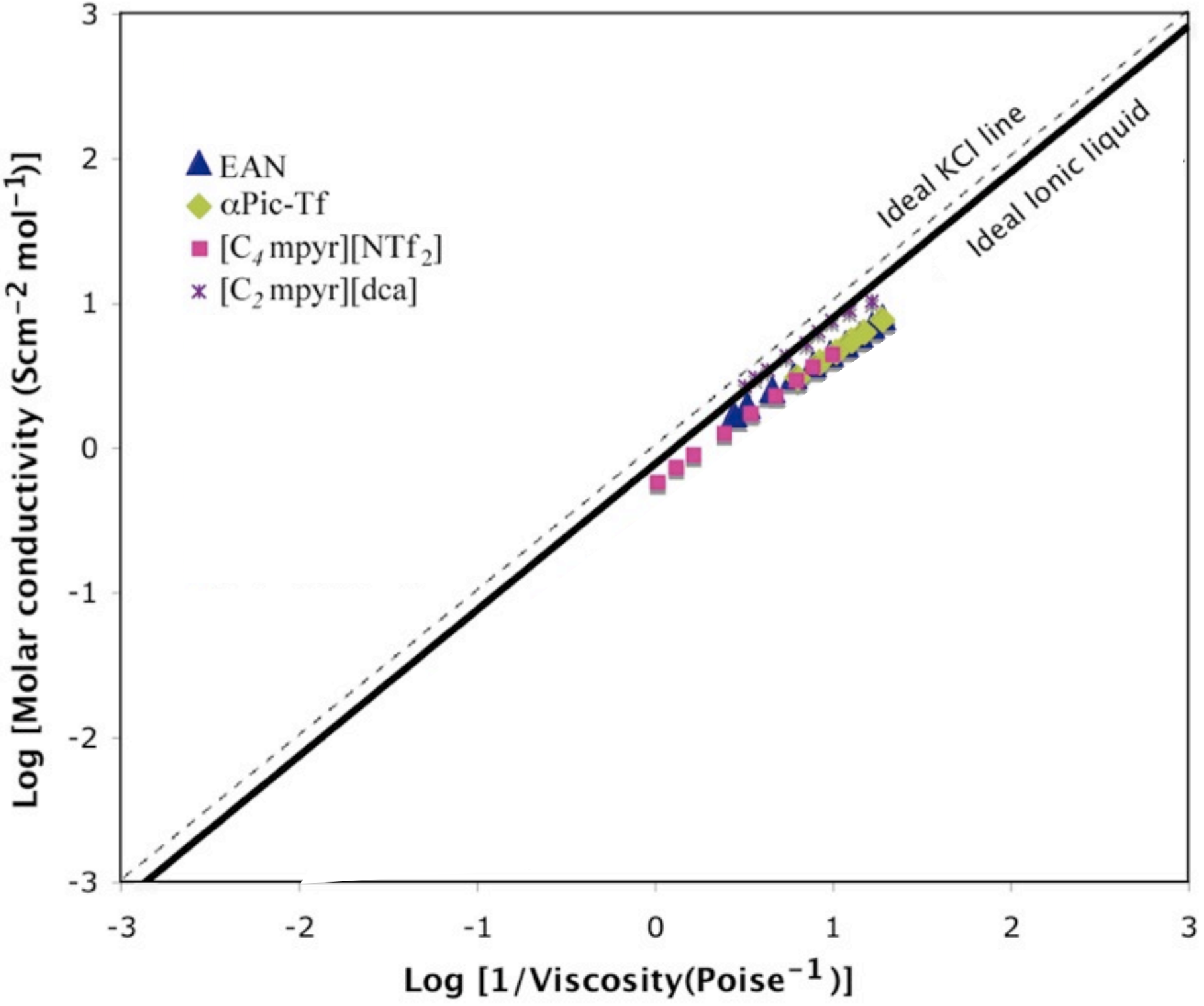
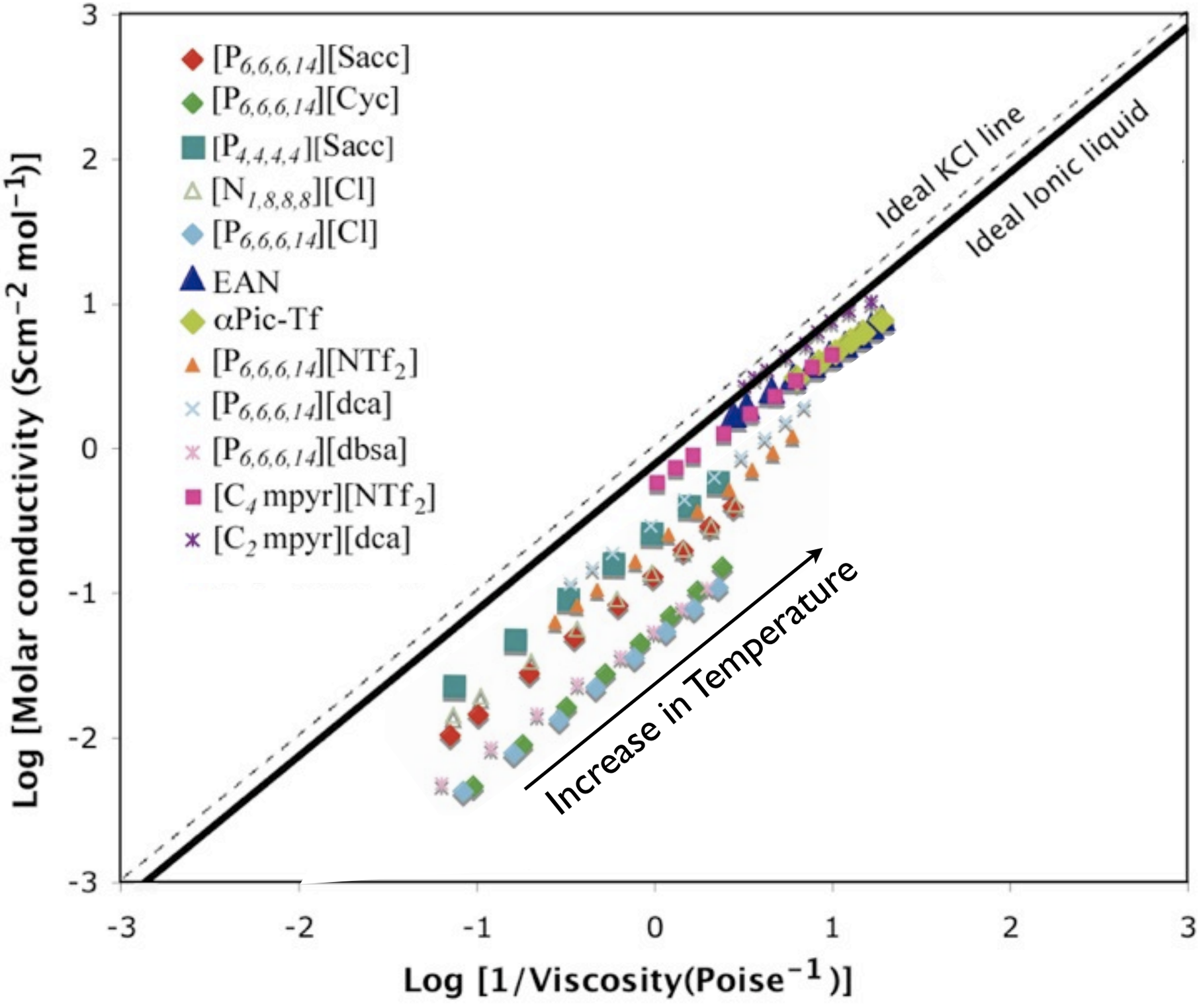
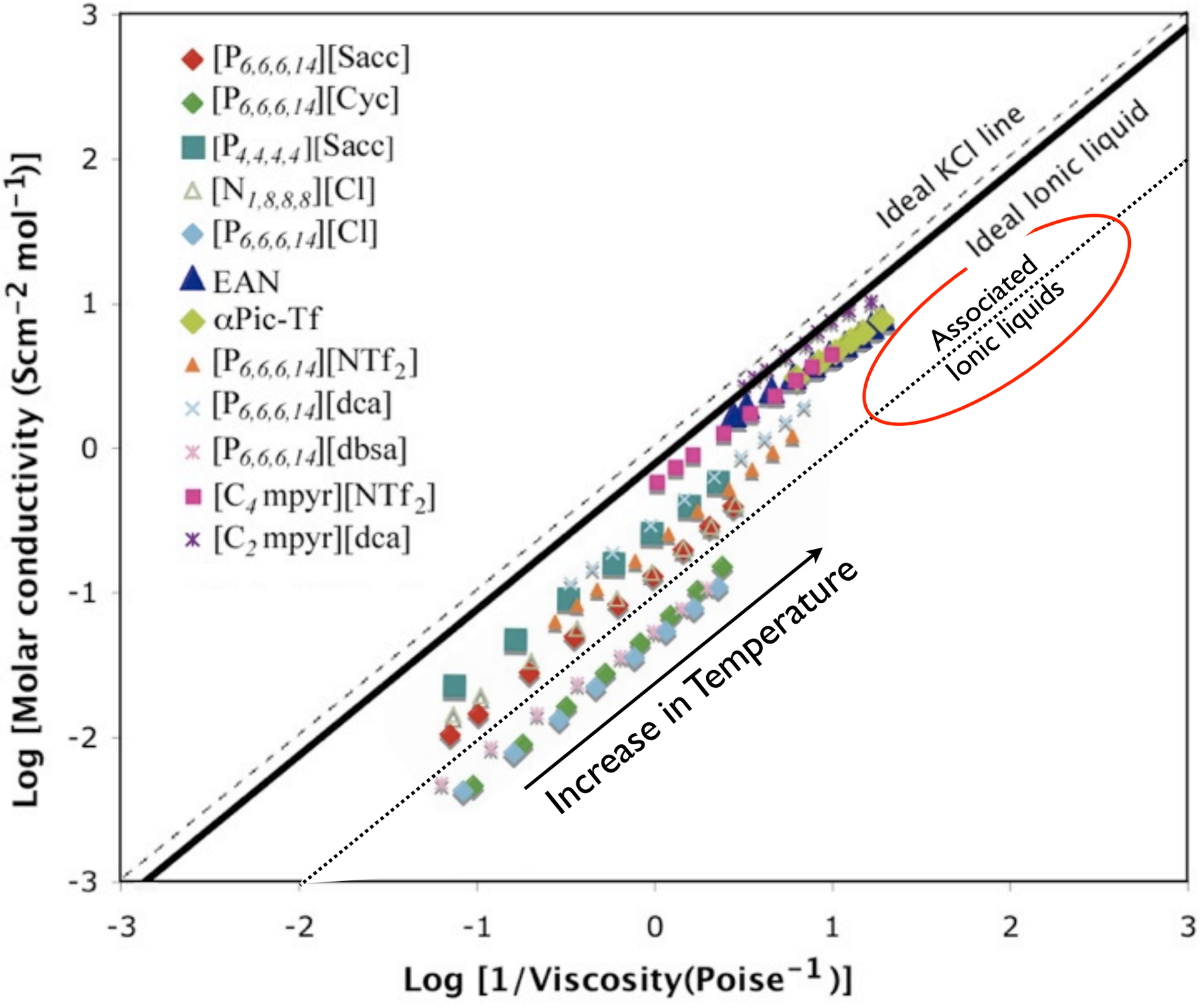
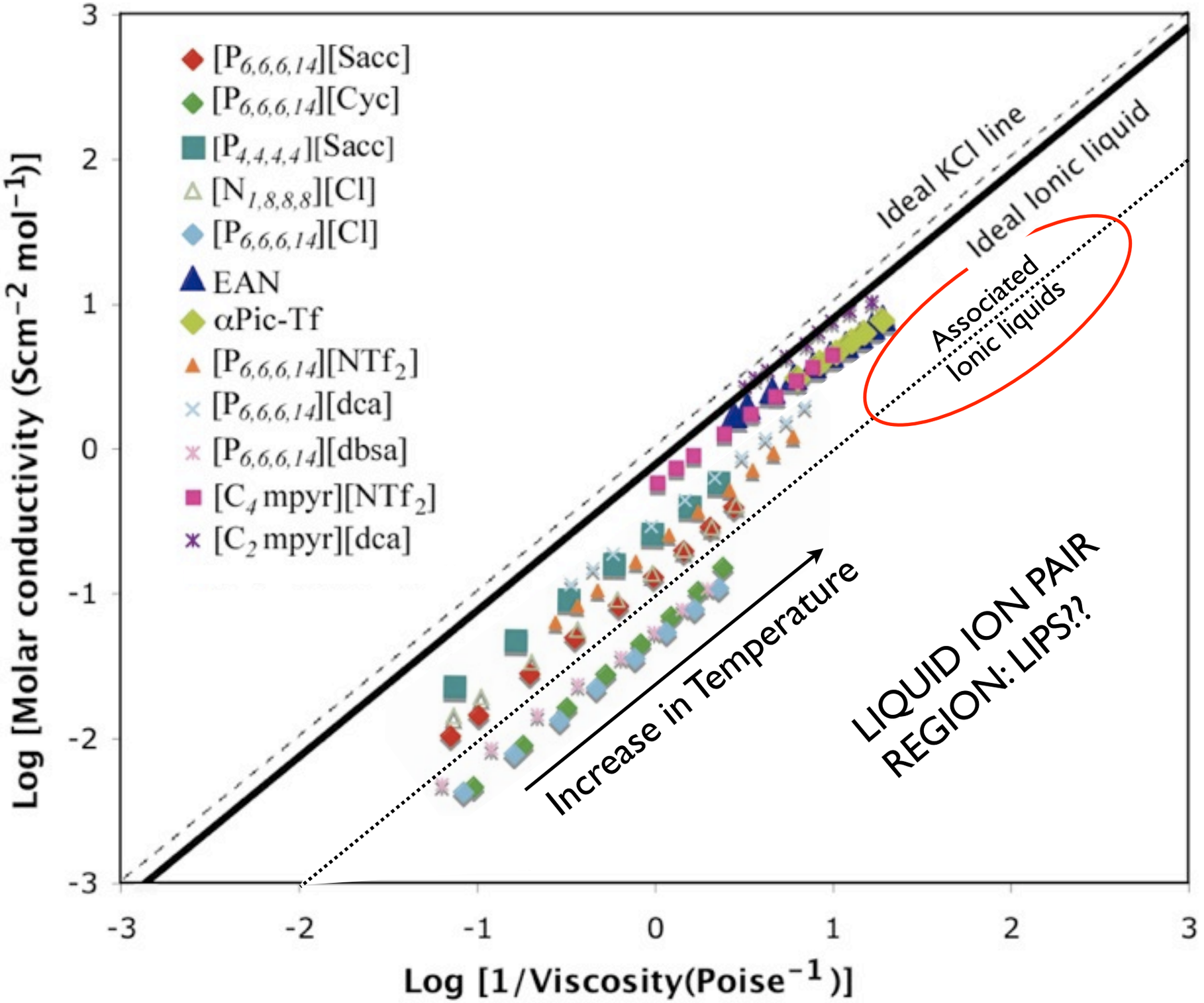

EAN
αPic-Tf
[C4mpyr][NTf2]
[C2mpyr][dca]
Ideal KCl line
Log [Molar conductivity (Scm−2 mol−1)]
Log [1/Viscosity(Poise−1)]
3
2
1
0
-1
-2
-3
-3
-2
-1
0
1
2
3

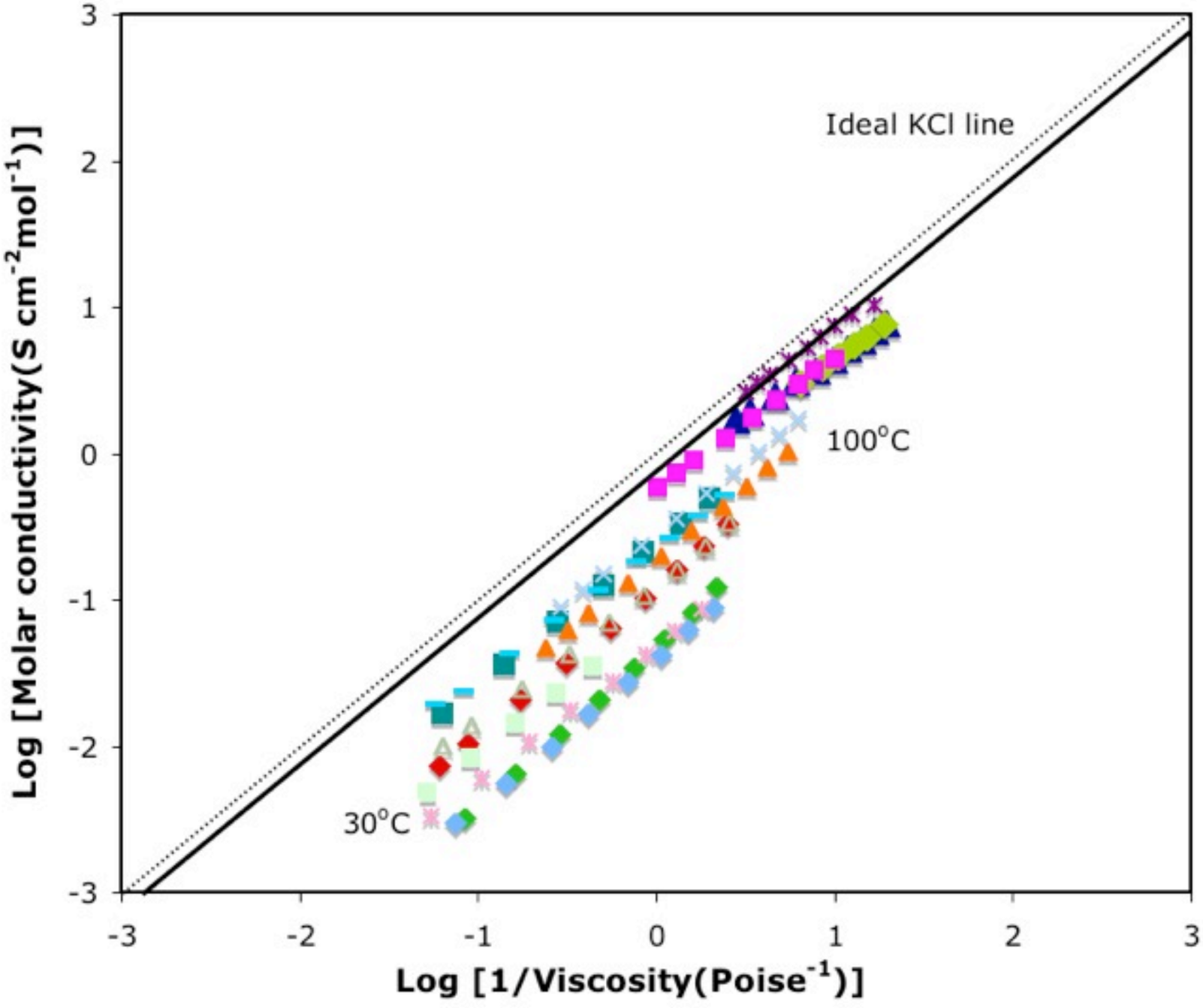

EAN
αPic-Tf
[C4mpyr][NTf2]
[C2mpyr][dca]
Ideal KCl line
Ideal Ionic liquid
Log [Molar conductivity (Scm−2 mol−1)]
Log [1/Viscosity(Poise−1)]
3
2
1
0
-1
-2
-3
-3
-2
-1
0
1
2
3


[P6,6,6,14][Sacc]
[P6,6,6,14][Cyc]
[P4,4,4,4][Sacc]
[N1,8,8,8][Cl]
[P6,6,6,14][Cl]
EAN
αPic-Tf
[P6,6,6,14][NTf2]
[P6,6,6,14][dca]
[P6,6,6,14][dbsa]
[C4 mpyr][NTf2]
[C2 mpyr][dca]
Ideal KCl line
Ideal Ionic liquid
Increase in Temperature
Log [Molar conductivity (Scm−2 mol−1)]
Log [1/Viscosity(Poise−1)]
3
2
1
0
-1
-2
-3
-3
-2
-1
0
1
2
3

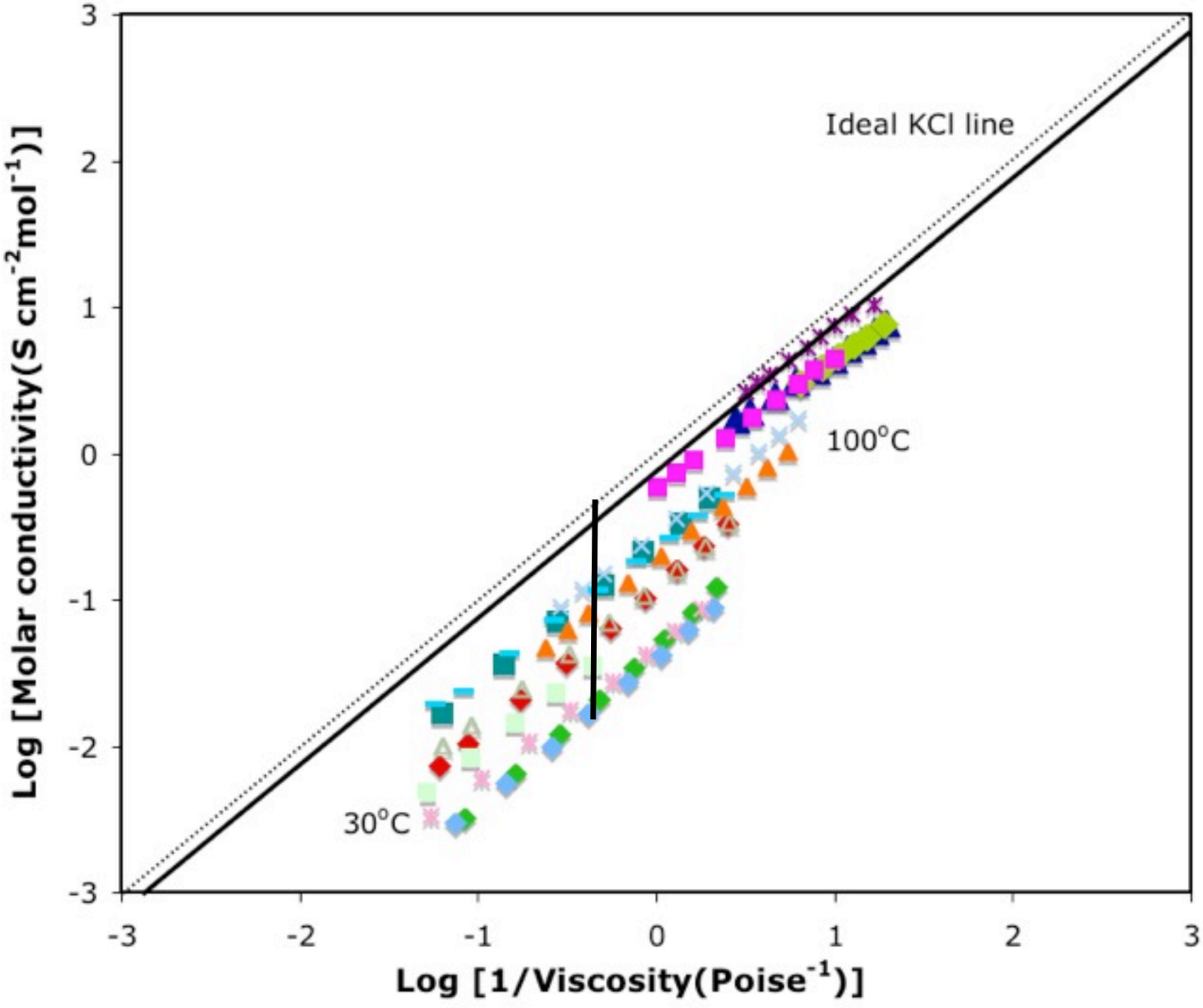

[P6,6,6,14][Sacc]
[P6,6,6,14][Cyc]
[P4,4,4,4][Sacc]
[N1,8,8,8][Cl]
[P6,6,6,14][Cl]
EAN
αPic-Tf
[P6,6,6,14][NTf2]
[P6,6,6,14][dca]
[P6,6,6,14][dbsa]
[C4 mpyr][NTf2]
[C2 mpyr][dca]
Ideal KCl line
Ideal Ionic liquid
Associated Ionic liquids
Increase in Temperature
Log [Molar conductivity (Scm−2 mol−1)]
Log [1/Viscosity(Poise−1)]
3
2
1
0
-1
-2
-3
-3
-2
-1
0
1
2
3


[P6,6,6,14][Sacc]
[P6,6,6,14][Cyc]
[P4,4,4,4][Sacc]
[N1,8,8,8][Cl]
[P6,6,6,14][Cl]
EAN
αPic-Tf
[P6,6,6,14][NTf2]
[P6,6,6,14][dca]
[P6,6,6,14][dbsa]
[C4 mpyr][NTf2]
[C2 mpyr][dca]
Ideal KCl line
Ideal Ionic liquid
Associated Ionic liquids
Increase in Temperature
LIQUID ION PAIR REGION: LIPS??
Log [Molar conductivity (Scm−2 mol−1)]
Log [1/Viscosity(Poise−1)]
3
2
1
0
-1
-2
-3
-3
-2
-1
0
1
2
3

Extraction of data



Extraction of data

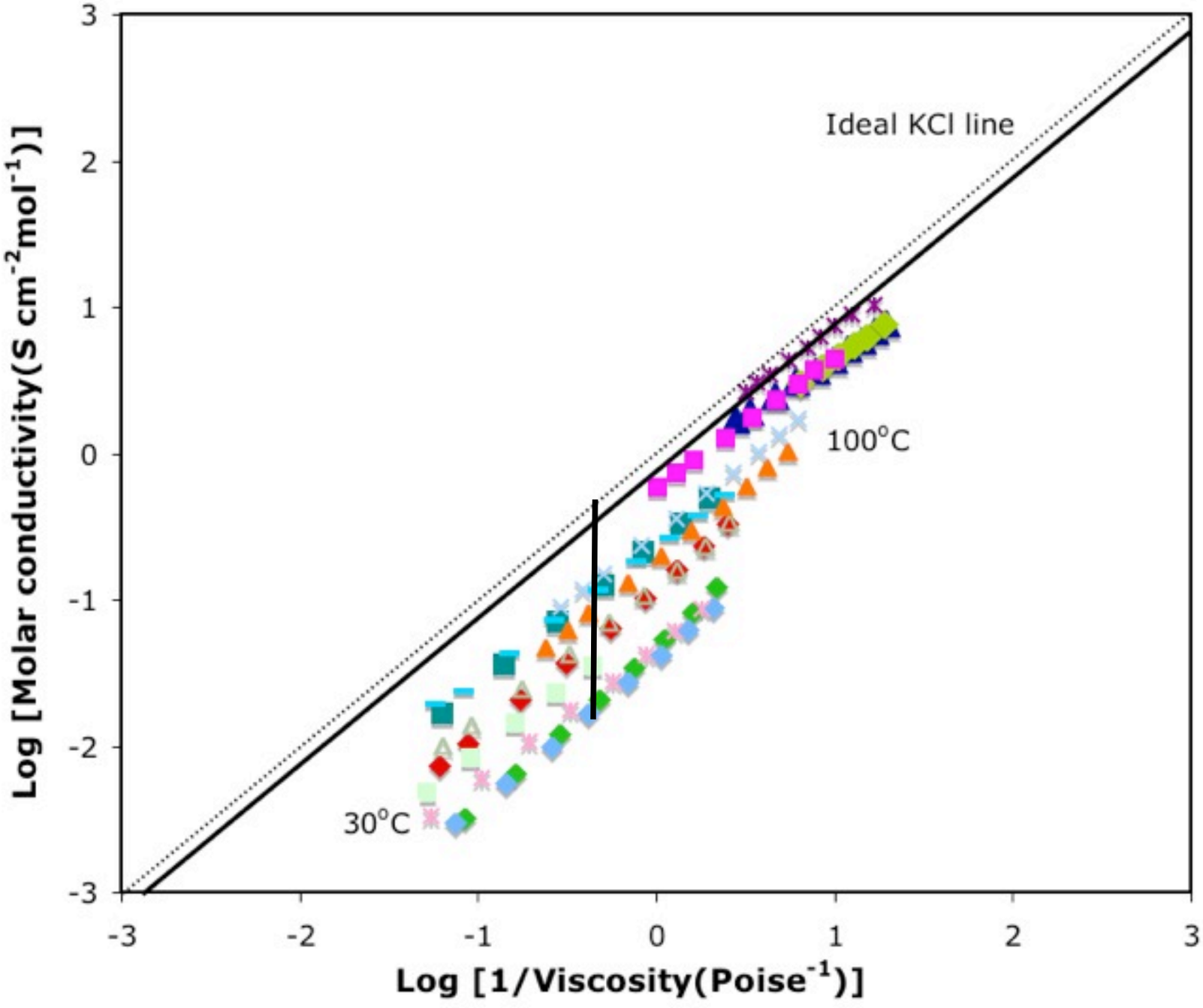


ΔW

Between 0 - 1

Associated IL

Extraction of data



ΔW

Between 0 - 1

Associated IL

ΔW

< 1

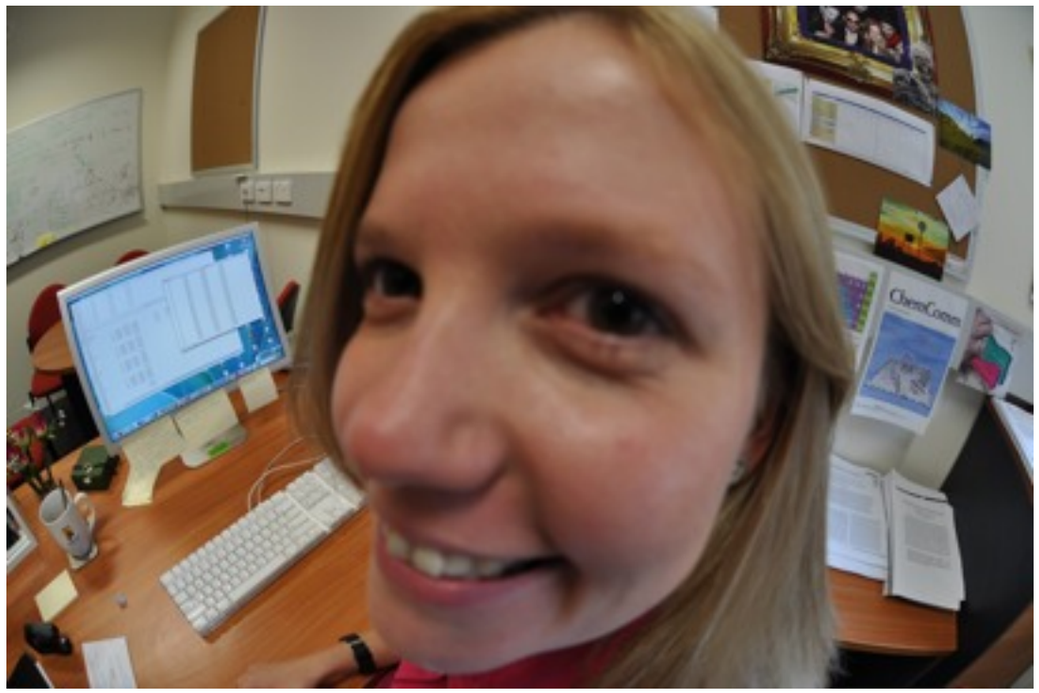
Poor IL: Angell

LIPs: Fraser

Extraction of data

IL	**ΔW (± 0.1)**
$[P_{6,6,6,14}][Cl]$	1.4
$[P_{6,6,6,14}][Cyc]$	1.4
$[P_{6,6,6,14}][dbsa]$	1.3
$[P_{6,6,6,14}][Sacc]$	0.9
$[P_{4,4,4,4}][Sacc]$	0.6
$[N_{8,8,8,8}][Cl]$	1.0
$[N_{1,8,8,8}][Cl]$	0.9
$[P_{6,6,6,14}][dca]$	0.6
$[P_{6,6,6,14}][NTf_2]$	0.7

Ab initio



To further investigate the role of ion pairs (and by implication larger ion aggregates) in the large ΔW observed for some of the salts, *ab initio* calculations of the corresponding ion pairs were carried out

Ab initio

IL	**ΔW (± 0.1)**	**ΔE_{disp}**
$[P_{6,6,6,14}][Cl]$	1.4	-46.0
$[P_{6,6,6,14}][Cyc]$	1.4	-48.5
$[P_{6,6,6,14}][dbsa]$	1.3	-44.7
$[P_{6,6,6,14}][Sacc]$	0.9	-32.4
$[P_{4,4,4,4}][Sacc]$	0.6	-
$[N_{8,8,8,8}][Cl]$	1.0	-
$[N_{1,8,8,8}][Cl]$	0.9	-
$[P_{6,6,6,14}][dca]$	0.6	-14.2
$[P_{6,6,6,14}][NTf_2]$	0.7	0.0

A negative ΔE_{disp} indicates a more tightly bound ion pair.

Ab initio

IL	ΔW (± 0.1)	ΔE_{disp}
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$[N_{1,8,8,8}][Cl]$	0.9	-
$[P_{6,6,6,14}][dca]$	0.6	-14.2
$[P_{6,6,6,14}][NTf_2]$	0.7	0.0

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$[P_{4,4,4,4}][Cyc]$ and $[P_{4,4,4,4}][Cl]$ are more strongly bound $[P_{4,4,4,4}][NTf_2]$ by almost 50 kJ mol^{-1},

Ab initio

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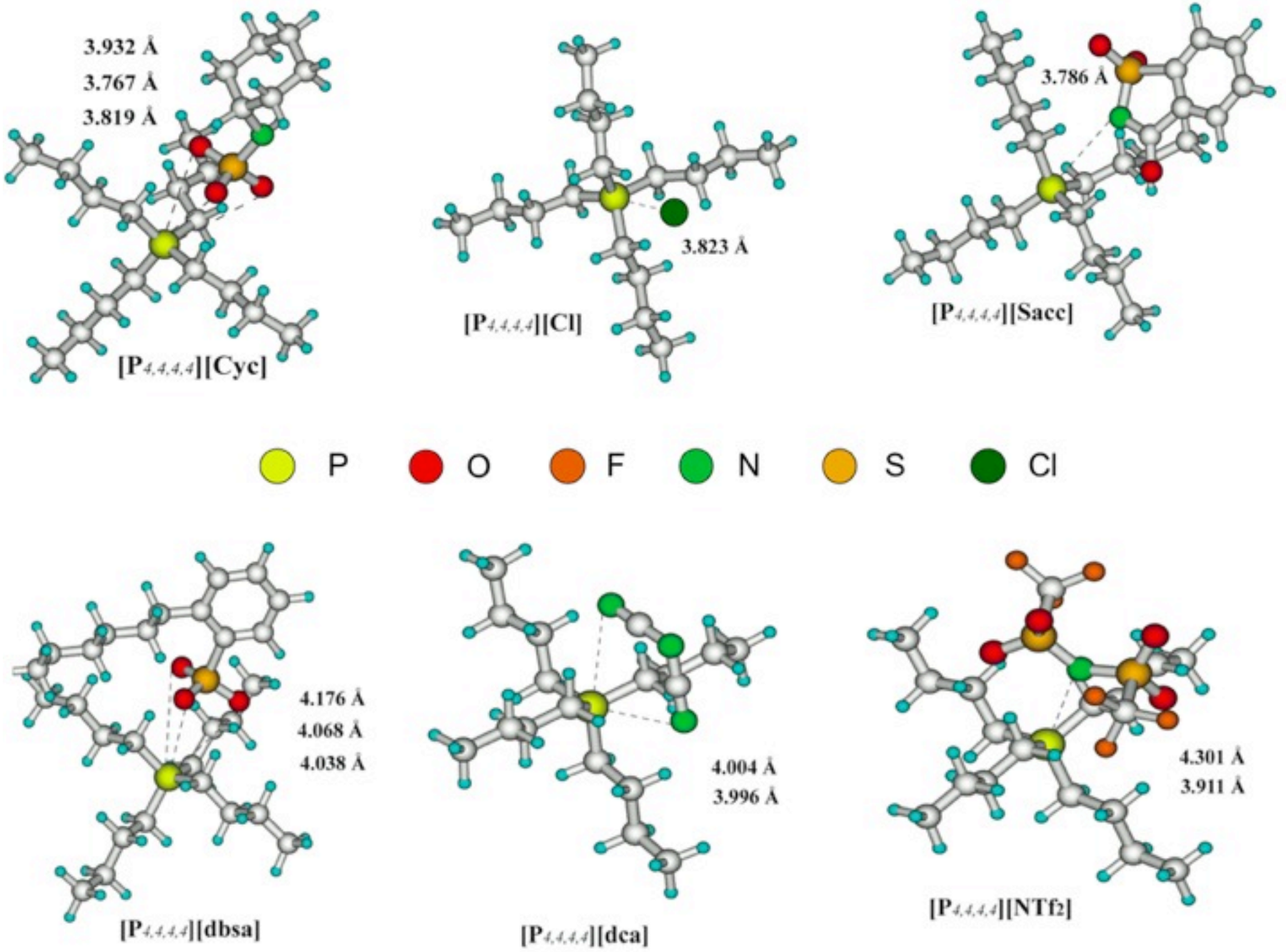
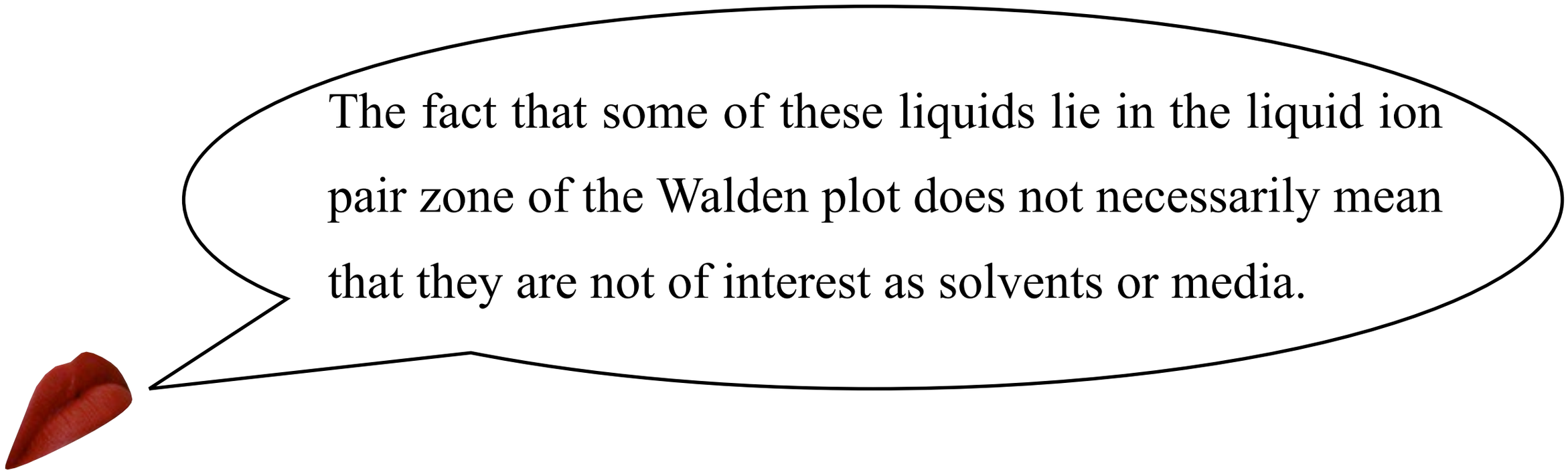
Indicating a tendency for very strong ion pairing in the former two ILs.

Ab initio



Optimised structures for the calculated ion pairs.

Conclusions

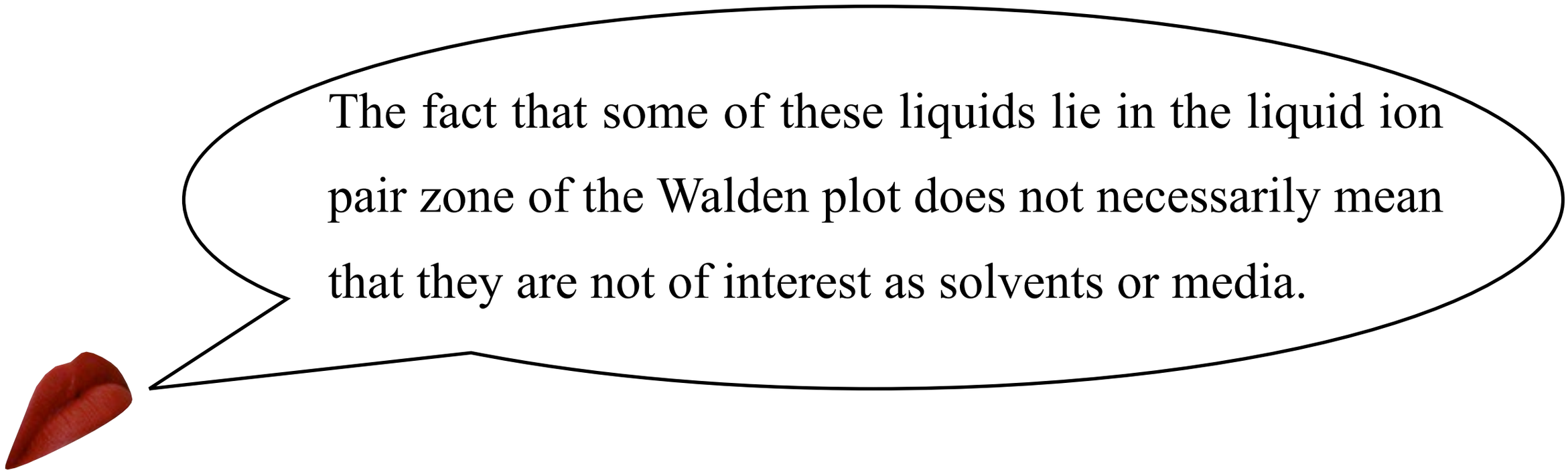


Conclusions

The fact that some of these liquids lie in the liquid ion pair zone of the Walden plot does not necessarily mean that they are not of interest as solvents or media.

For example, if ion pairing is significant, it may be predicted that such compounds would exhibit higher vapour pressures.

Conclusions



For example, if ion pairing is significant, it may be predicted that such compounds would exhibit higher vapour pressures.

Conclusions

The concept of ionicity does not necessarily describe the chemical availability of individual ions, which may depend more strongly on the associated nature of the ionic liquid.

Such chemical reflections of the state of ions will be described by much needed thermodynamic activity measurements in ionic liquids

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