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Ionic liquids as amphiphile self-assembly media

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Table S1 Transfer of nonpolar gases to EAN or water, where ΔG^o is the free energy of transfer, ΔH^o is the enthalpy change, T the temperature and ΔS^o the change in entropy. (Reproduced from ref. 17, with permission. Copyright 1982, Elsevier)

		ΔG (Kcal)	ΔH (Kcal)	ΔS (cal/K)
Kr	EAN	1.6	-0.9	-9
	water	2.8	-2.9	-19
CH_4	EAN	1.6	-0.5	-4
	water	2.9	-2.7	-18
C_2H_6	EAN	2.0	-1.0	-10
	water	3.9	-2.1	-20
C_4H_{10} [a]	EAN	(3.61)	(-5.71)	(-31.3)
	water	(6.35)	(-6.21)	(-42.1)

[a] Transfer from butane gas phase to EAN or water.

Table S2 Aggregation numbers and hydrodynamic radii for micelles of amphiphiles in ILs, water or formamide.

Surfactant	Solvent	Aggregation No.	Hydrodynamic Radii (nm)
C_{14}PyrB	EAN	17±1 [a 18]	1.4±3 [18]
	water	81 [b 75]	
C_{16}PyrB	EAN	26±2 [a 18]	2.2±3 [18]
	water	111 [b 75]	
C_{16}MImCl	EAN		119.2 [c 82]
	water		87.6 [c 82]
C_{16}MImBF$_4$	EAN		105.2 [c 82]
	water		55.4 [c 82]
$C_{16}E_8$	BMIm BF$_4$	~145 [a 83]	3.2±0.4 [a 83]
	Water	150±15 [a,d 83]	3.7 [a,d 83]
	formamide	~4 [d,e 83]	
$C_{14}E_8$	BMIm BF$_4$	~75 [a 83]	2.5±0.3 [a 83]
	BMIm PF$_6$	~15 [a 83]	1.4±0.1 [a 83]
	BMIm Tf$_2$N	No aggregation [a 83]	No aggregation [a 83]
$C_{12}E_8$	BMIm BF$_4$	~20 [a 83]	1.6±0.1 [a 83]
	Water	95±5 [a,d 83]	~3.1 [a,d 83]
$C_{12}E_6$	BMIm BF$_4$	~75 [a 83]	2.3±0.1 [a,d 83]
	Water	140±15 [a,d 83]	~3.2 [a,d 83]
	formamide	~30 [a,d 83]	~2 [a,c 83]
$C_{12}E_4$	BMIm BF$_4$	No aggregation [a,f 83]	No aggregation [a,f 83]
	Water	165±62 [d,g 83]	
	formamide		~2 [a,d 83]

[a] 25°C
[b] 30°C
[c] These reported values seem unrealistically large.
[d] From references within the reference.
[e] 40°C
[f] Cloud point reached at 25°C.
[g] 0°C

Table S3 Phospholipid aggregate structure formation in ionic liquids. Temperatures in °C.

Lipid	Solvent	Phospholipid concentration	Phase 1	Transition Temp. 1 (°C)	Phase 2	Transition Temp. 2 (°C)	Phase 3	Transition Temp. 3 (°C)	Phase 4	Ref
DSPC	EAN	1:1 by wt.	$L_{\beta'}$, 5.9 nm	56.7	$P_{\beta'}$	57.3	L_α, 6.3nm			85
DSPC	Water		$L_{\beta'}$, 6.4 nm	51.5		54.9	L_α			176,177
DSPC[a]	EAN	20% w/v	L_c	68.9	L_α					57
DSPC[a]	Water	20% w/v	L_c	26.7	$L_{\beta'}$	50.2	$P_{\beta'}$	53.9	L_α	57
DPPC	EAN	29 wt%	L_α	59.5	Micellar					56
DPPC[a]	EAN	20% w/v	L_c	58	H_2					94

DPPC[b]	EAN	20% w/v	L_c	~45	L_α	~55	H_2			94
DPPC[a]	EAN	20% w/v	L_c	53.8	L_α	58.6	H_2			57
DPPC[a]	Water	20% w/v	L_c	20.7	$L_{\beta'}$	35.0	$P_{\beta'}$	41.0	L_α	57
DPPE[a]	Water	20% w/v	sub-gel	36	gel	63	L_β	123	H_2	95
DPPE[a]	EAN	20% w/v	sub-gel	39	gel	67	L_β	73-77	H_2	95
DPPE[a]	EAN	20% w/v			pregel	38.9	gel	56.7	L_β	57
DPPE[a]	Water	20% w/v	subgel	25.9	pregel	38.2	gel	63.8	L_β	57
DPPG[a]	EAN	20% w/v	L_c	46.9	L_β					57
DPPG[a]	Water	20% w/v	subgel	23.2	gel	38.5	L_β	41.2	L_α	57
DPPA[a]	EAN	20% w/v	L_c	91.7	H_2					57
DPPA[a]	Water	20% w/v	L_c	63.4	L_α					57
DLPC[a]	EAN	20% w/v	L_c	27.2	[c]					57
DLPC[a]	Water	20% w/v	L_c	-3.2	gel state	0.6				57
DMPC[a]	EAN	20% w/v	L_c	42.5	[c]					57
DMPC[a]	Water	20% w/v	L_c	15.6	$L_{\beta'}$	24.0	$P_{\beta'}$			57

[a] Initial heating, after sample equilibrated at 0 °C for 4-7 days.
[b] Reheating sample, after previously cycled above main transition.
[c] Nonlamellar phase, including H_2 and micellar.

Table S4 Summary of microemulsion systems involving ILs. IL/O, O/IL refer to IL-in-oil and oil-in-IL respectively.

Solvent phase 1: IL	Solvent phase 2	Amphiphile	Microemulsion	Liquid Crystal Phases	Ref
EAN	Various alkanes [a]	Various C_nE_m surfactants [b]			129
TMGA	Supercritical CO_2	*N*-EtFOSA	IL/supercritical CO_2		130
TMGL	Supercritical CO_2	*N*-EtFOSA	IL/supercritical CO_2		130
TMGTFA	Supercritical CO_2	*N*-EtFOSA	IL/supercritical CO_2		130
BMIm BF_4	cyclohexane	Tx-100	IL/oil	Homogeneous ellipsoid particles	120
BMIm BF_4	cyclohexane	TX-100	IL/O, bicontinuous and O/IL [c]	Droplets from 15-80nm for IL/O	111
BMIm BF_4	cyclohexane	TX-100	IL/O		121
BMIm BF_4	toluene	TX-100	IL/O, bicontinuous and O/IL [c]		114,119
BMIm PF_6	toluene	TX-100	IL/O, bicontinuous and O/IL [c]		113
BMIm BF_4	benzene	TX-100	IL/O, bicontinuous and O/IL [c]		117,118
BMIm BF_4	p-xylene	TX-100	IL/O, bicontinuous and O/IL [c]		115
BMIm PF_6	ethylene glycol	TX-100	IL/O, bicontinuous and O/IL [c]		123
BMIm PF_6	water	TX-100	Water/IL, for water <33%, IL/water for water >65%. [c]	33%<water<65% bicontinuous microemulsion. Spherical droplets	112
BMIm PF_6	water	TX-100	IL/water		126
BMIm PF_6	water	TX-100	water/IL		135
BMIm PF_6	water	Tween 20	IL/water, bicontinuous and water/IL [c]		116
C_6MIm PF_6	perfluorohexane	$(CF_2)_5CF_3$MIm PF_6 (IL)	O/IL		137
C_6MIm PF_6	perfluorohexane	$(CF_2)_5CF_3$BIm PF_6 (IL)	O/IL		137
C_6MIm PF_6	perfluorohexane	$(CF_2)_7CF_3$MIm PF_6 (IL)	O/IL		137
C_6MIm PF_6	perfluorohexane	$(CF_2)_7CF_3$BIm PF_6 (IL)	O/IL		137
BMIm PF_6	PAN	AOT	IL/IL		128
ethylenediamine/ ammonia/ potassium [d]	decane	SDS			122
[e]	[f]				132
Water, oil and IL [g]					138

[a] octane, decane, dodecane or tetradecane.
[b] C_8E_2, $C_{12}E_3$ or $C_{14}E_4$.
[c] phase diagram in paper.
[d] molten salt.
[e] Solvent phase 1: IL in water microemulsion stabilised by a non-ionic surfactant.
[f] Solvent phase 2: lamellar liquid crystal of the same IL and surfactant in water.
[g] Emulsions were prepared with the IL present as either the continuous or non-continuous phase. Coated silica nanoparticles were used to stabilise the emulsions.