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Electronic Supplementary Information for "Poly(vinylbenzyl chloride)-based poly(ionic liquids) as membranes for CO_2 capture from flue gas".

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Introduction

1 On the role of CO_2 affinity

Although, the role of CO_2 affinity towards PILs has been widely acknowledged, the underlying fundamentals have never been systematically studied. For polymerized ILs, a study on the CO_2 sorption revealed a clear influence of the chemical composition of cationic pendants and anions.[1] The reported results suggest that CO_2 sorption in studied PILs with identical cationic species decreases in the row of anions as follows: $[PF_6]^-$>$[BF_4]^-$>$[Tf_2N]^-$. Moreover, the capability of IL-based materials to absorb CO_2 decreases in the following order $P[VBTMA]^+$>$P[MATMA]^+$>$[DTEA]^+$>$[bmim]^+$>$[VBTMA]^+$>$[MATMA]^+$ for the identical anion $[BF_4]$. The DMM parameters derived in this study were based on the sorption experiments up to 1 bar.[1] Even though, the sorption isotherms have been successfully fitted into DMM, the pressure range can be considered insufficient for that kind of approximation.[2] Additionally, the influence of the material history was demonstrated on the PILs synthesized from the neutral polymers.[3-4] The post-modified P[VBTMA][Ac] and P[VBTMA]$[BF_4]$ were prepared from commercially available PVBC via anion metathesis. Remarkable, the Langmuir saturation constant increased in 7 times when compared to pristine material.[3] The comparison of CO_2 sorption isotherms reported for P[VBTMA]$[BF_4]$ demonstrated a strong disagreement between the measurements (Fig.1). This clearly signifies the variability in the synthesized PILs, that is often observed when obtained in batches on the lab-scale.

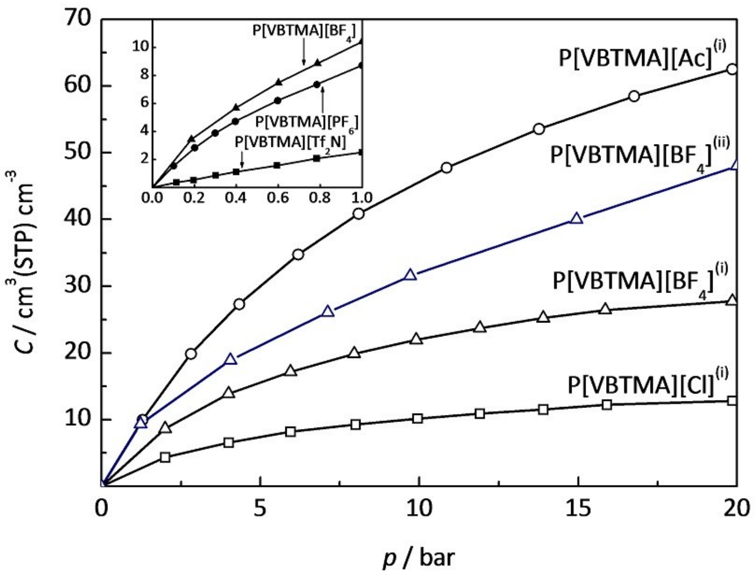

Fig. 1 Overview of CO_2 sorption isotherms reported for PILs based on the $P[VBTMA]^+$ polycation. The data adopted from (i)[3], (ii)[4], (inlet)[1].

2 Separation performance of PILs-based membranes reported in the literature

Table 1 Summary of physicochemical properties and separation performance of PILs.

Precursor[a]	Treatment	PILs	Membrane		Performance		Comments	Reference
			Sample[b]	δ^c_{AL} [µm]	$\alpha^d_{CO2/N2}$	P^e_{CO2} [Barrer]		
MMA	Synthesis of diblock-copolymers	p[MEBEm-TFSI]; p[MMA-b-MUBIm-TFSI	T	70 - 240	28.5	22.8	ideal permselectivity	5
Styrene/ acrylate-based RTIL monomers	Photoinitiated polymerisation		T	145	28 - 32	7 - 32	ideal permselectivity	6
OEG1, OEG2, $(CH_2)_3CH$,$(CH_2)_5CN$	Photoinitiated polymerisation	PILs with polar substituents	T	145	37 - 44	4.1 - 22	ideal permselectivity	7
Styrene/Imim-based RTIL	Photoinitiated polymerisation in presence of IL		T	200	39	44	ideal permselectivity	8
P[DADMA]Cl	Anion methathesis		-	-	114.3	-	sorption selectivity	3
PBI	Polycondensation		-	-	2.66 - 12.60	-	sorption selectivity	9
[EMIM][BF_4]; PVDF-HFP	Polymer conditioning with IL	Polymer gel membranes	T	100 - 200	50 - 60	45 - 400	mixed-gas selectivity; CO_2/N_2=50/50 2 atm; 35 - 45 °C	10

[a] Precursor material abbreviation as used in the reference.

[b] Morphology of the selective layer abbreviated as 'T' and 'TFC' for thick dense and thin film composite membranes, respectively. '-' marks the materials which were to brittle to obtain a membrane sample.

[c] Thickness of the selective layer.

[d] Selectivity for CO_2

[e] Permeability for CO_2

AAIL	Photoinitiated polymerisation in presence of IL	Polymer gel membranes	T	300	60 - 230	1000 - 10000	mixed-gas selectivity; CO_2/N_2=2.5:97.5 2.5 kPa; 373K	11
DAB; Bul	Polycondensation	Diff. degree of N-quaternisation	T	100	11 - 21	15 - 40	ideal permselectivity 20 atm; 30 °C	12
[ViEhIm][NTf_2]; [ViEtPy][NTf_2]; [Pyrr11][NTf_2]; [EMTMA][NTf_2]; [EMCh][NTf_2]	Free radical polymerisation; conditioning with ILs		T	145 - 190	20 - 34	3 - 20	ideal permselectivity 20 °C	13
P[DADMA]Cl	Anion metathesis; conditioning with IL		T	120 - 150	40 - 65	3 - 440	ideal permselectivity 20 °C	14
imidazolium-based poly(RTIL) and an alkyl non-ionic polymer.	Living polymerisation		TFC	13 - 18	9 - 27	30 - 9300	ideal permselectivity	15
PTAUDMA	Removal of the protective group and simultaneous thio-Michael reaction		T	-	24	71	ideal permselectivity	16
Pebax® 1657, 2533; [BMIM][Tf_2N]	Polymer conditioning with IL	Polymer gel membranes	T	-	40	300	ideal permselectivity	17
[EMIM][Tf_2N]; p(VDF-HFP)	Polymer conditioning with IL	Polymer gel membranes	T	-	30	533	ideal permselectivity	18
[EMIM][TFSI]; [HdMIM][TFSI]; p(VDF-HFP)	Polymer conditioning with IL	Polymer gel membranes	T	-	27	14	ideal permselectivity	19
Poly(diphenylacetylene)s imidazolium salts			T	50 - 60	11 - 16	1.5 - 250	ideal permselectivity	20
PVC	Atom transfer radical polymerisation		T	80	20 - 25	7.5 - 137	ideal permselectivity	21

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