SUPPORTING INFORMATION

Tris(dialkylamino)cyclopropenium dialkylphosphate ionic liquids as lubricants

Owen J. Curnow,*[a] Rathiga Senthooran[a] and Anthony E. Somers*[b]

[a] *School of Physical and Chemical Sciences, University of Canterbury, Private Bag 4800, Christchurch 8140, New Zealand*

[b] *Institute for Frontier Materials, Deakin University, Geelong, Victoria 3220, Australia*

Corresponding Author's email: owen.curnow@canterbury.ac.nz

Contents **Page**

Table S1. Uncorrected density data for TDAC BEHP ionic liquids. $u(\rho)$ = 0.00005 g·cm^{-3}.

Compound	Density (g·cm^{-3})								
	20 °C	25 °C	30 °C	40 °C	50 °C	60 °C	70 °C	80 °C	90 °C
[C$_3$(NEt$_2$)$_3$]BEHP	0.979692	0.976001	0.973055	0.96641	0.959869	0.95340	0.946925	0.940459	0.934012
[C$_3$(NBuMe)$_3$]BEHP	0.963887	0.960549	0.957208	0.950525	0.944023	0.937523	0.931013	0.924505	0.917955
[C$_3$(NPr$_2$)$_3$]BEHP	0.960237	0.956924	0.953622	0.947041	0.940477	0.933810	0.927600	0.921199	0.914814
[C$_3$(NBu$_2$)$_3$]BEHP	0.943743	0.940050	0.937008	0.930291	0.923573	0.917054	0.910504	0.903976	0.897466
[C$_3$(NHex$_2$)$_3$]BEHP	0.919530	0.916203	0.912881	0.906244	0.89967	0.893045	0.886403	0.879765	0.873327
[C$_3$(NDec$_2$)$_3$]BEHP	0.903770	0.900476	0.897202	0.890694	0.884296	0.877989	0.871677	0.865410	0.859146

Table S2. Corrected density data for TDAC BEHP ionic liquids. $u(\rho)$ = 0.00010 g·cm^{-3}.

Compound	Density (g·cm^{-3})								
	20 °C	25 °C	30 °C	40 °C	50 °C	60 °C	70 °C	80 °C	90 °C
[C$_3$(NEt$_2$)$_3$]BEHP	0.97900	0.97536	0.97248	0.96606	0.95974	0.95337	0.94692	0.94046	0.93401
[C$_3$(NBuMe)$_3$]BEHP	0.96318	0.95987	0.95658	0.95007	0.94378	0.93744	0.93100	0.92450	0.91795
[C$_3$(NPr$_2$)$_3$]BEHP	0.95950	0.95620	0.95291	0.94640	0.93999	0.93355	0.92751	0.92118	0.91481
[C$_3$(NBu$_2$)$_3$]BEHP	0.94301	0.93933	0.93630	0.92966	0.92311	0.91681	0.91042	0.90396	0.89747
[C$_3$(NHex$_2$)$_3$]BEHP	0.91879	0.91547	0.91216	0.90558	0.89914	0.89273	0.88627	0.87973	0.87332
[C$_3$(NDec$_2$)$_3$]BEHP	0.90306	0.89978	0.89654	0.89016	0.88396	0.87783	0.87162	0.86540	0.85915

Table S3. Density fitting parameters for the corrected data for TDAC BEHP ionic liquids.[a]

Compound	b × 10^4	a
[C$_3$(NEt$_2$)$_3$]BEHP	6.39	1.1662
[C$_3$(NBuMe)$_3$]BEHP	6.43	1.1516
[C$_3$(NPr$_2$)$_3$]BEHP	6.37	1.1460
[C$_3$(NBu$_2$)$_3$]BEHP	6.47	1.1323
[C$_3$(NHex$_2$)$_3$]BEHP	6.49	1.1088
[C$_3$(NDec$_2$)$_3$]BEHP	6.25	1.0860

[a] density is fit to $\rho = a - bT$.

Table S4. Molar volumes (cm^3·mol^{-1}) for TDAC BEHP ILs

Compound	MW	293 K	298 K	303 K	313 K	323 K	333 K	343 K	353 K	363 K
[C$_3$(NEt$_2$)$_3$]BEHP	573.84	586	588	590	594	598	602	606	610	614
[C$_3$(NBuMe)$_3$]BEHP	615.92	638	640	643	647	652	656	661	665	670
[C$_3$(NPr$_2$)$_3$]BEHP	658.00	685	688	690	695	700	705	709	714	719
[C$_3$(NBu$_2$)$_3$]BEHP	742.16	786	790	792	798	804	809	815	821	827
[C$_3$(NHex$_2$)$_3$]BEHP	910.48	990	994	997	1005	1012	1020	1027	1035	1043
[C$_3$(NDec$_2$)$_3$]BEHP	1247.12	1380	1385	1390	1400	1410	1420	1431	1441	1452

Table S5. Viscosity data for TDAC BEHP ILs.

Compound	Viscosity/mPa·s								
	293 K	298 K	303 K	313 K	323 K	333 K	343 K	353 K	363 K
[C$_3$(NEt$_2$)$_3$]BEHP	739	494	338	173	94	56.7	36.5	24.7	17.9
[C$_3$(NBuMe)$_3$]BEHP	950	645	450	227	130	77.4	49.7	33.3	23.4
[C$_3$(NPr$_2$)$_3$]BEHP	2517	1560	1017	479	247	138	83.1	52.0	34.2
[C$_3$(NBu$_2$)$_3$]BEHP	2238	1427	939	446	231	131	78.1	51.0	34.7
[C$_3$(NHex$_2$)$_3$]BEHP	3088	2041	1255	558	281	158	95.8	60.4	43.0
[C$_3$(NDec$_2$)$_3$]BEHP	1086	757	540	285	164	104	68.4	47.3	33.9

Table S6. VFT and Arrhenius viscosity fit parameters for TDAC BEHP ILs.[a]

Compound	Parameter						
	$\eta_0 \times 10^2$ (mPa·s)	B (K)	T_0 (K)	D^b	δ (mPa·s)	$A \times 10^6$ (mPa·s)	E_a (kJ·mol^{-1})
$[C_3(NEt_2)_3]$BEHP	2.90	1210	174	6.96	1.2	2.34	47
$[C_3(NBuMe)_3]$BEHP	2.74	1329	166	8.00	2.6	3.60	47
$[C_3(NPr_2)_3]$BEHP	2.39	1376	174	7.90	6.1	4.87	54
$[C_3(NBu_2)_3]$BEHP	2.30	1403	171	8.21	1.1	7.32	53
$[C_3(NHex_2)_3]$BEHP	3.19	1327	178	7.47	10.1	4.53	55
$[C_3(NDec_2)_3]$BEHP	6.82	1202	169	7.13	3.9	8.63	44

[a] Data was fit to the VFT ($\eta = \eta_0 \cdot \exp(B/(T - T_0))$ and Arrhenius ($\eta = A \cdot \exp(E_a/RT)$) equations. [b] $D = B/T_0$.

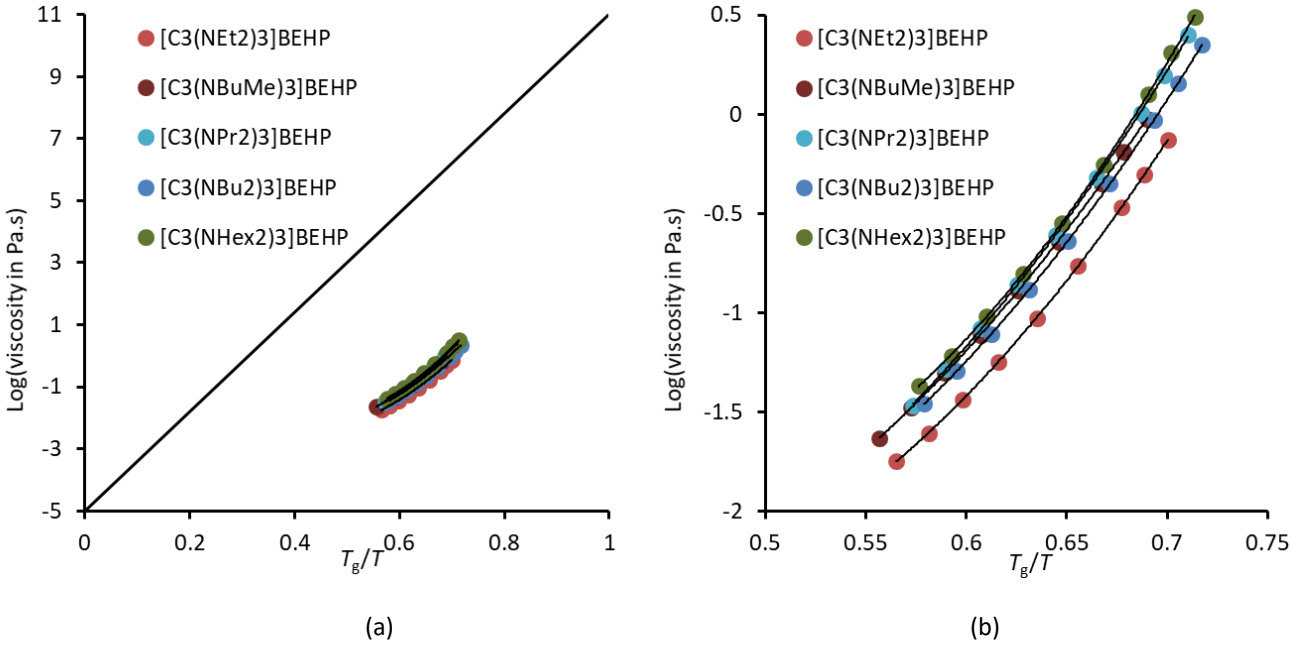

Figure S1. (a) Fragility plot for TDAC BEHP ILs; (b) Expanded view.

Table S7. Conductivity data for TDAC BEHP ILs.

Compound	Conductivity/mS·cm^{-1} × 10^2								
	293 K	298 K	303 K	313 K	323 K	333 K	343 K	353 K	363 K
$[C_3(NEt_2)_3]$BEHP	8.92	12.4	16.9	29	45.8	67.1	92	121	152
$[C_3(NBuMe)_3]$BEHP	5.24	7.4	10.1	17.5	27.8	41.1	57.9	77.2	98.1
$[C_3(NPr_2)_3]$BEHP	8.5	11.8	15.8	26.7	41.5	59.4	80.2	103	127
$[C_3(NBu_2)_3]$BEHP	0.95	1.4	2.02	3.91	6.85	11.1	16.8	23.8	32.4
$[C_3(NHex_2)_3]$BEHP	0.7	0.99	1.37	2.43	3.97	6.06	8.76	12.2	15.8
$[C_3(NDec_2)_3]$BEHP	0.22	0.32	0.44	0.78	1.29	1.98	2.89	4.01	5.34

Table S8. VFT and Arrhenius conductivity fit parameters for TDAC BEHP ILs.[a]

Compound	Parameter						
	σ_∞ (mS·cm^{-1})	B (K)	T_0 (K)	D^b	$\Delta \times 10^3$	A × 10^4 (mS·cm^{-1})	E_a (kJ·mol^{-1})
$[C_3(NEt_2)_3]$BEHP	44.4	514	211	2.4	3.2	24	36
$[C_3(NBuMe)_3]$BEHP	44.2	610	203	3.0	3.4	23	37
$[C_3(NPr_2)_3]$BEHP	24.9	434	217	2.0	4.7	12	34
$[C_3(NBu_2)_3]$BEHP	40.3	795	198	4.0	0.62	95	45
$[C_3(NHex_2)_3]$BEHP	14.8	776	192	4.0	0.71	8.2	39
$[C_3(NDec_2)_3]$BEHP	6.80	872	183	4.8	0.29	3.3	40

[a] Data was fit to the VFT ($\sigma = \sigma_\infty \cdot \exp(-B/(T - T_0))$ and Arrhenius ($\sigma = A \cdot \exp(-E_a/RT)$) equations. [b] $D = B/T_0$.

Table S9. Molar conductivity data for TDAC BEHP ILs.

Compound	Molar conductivity/mS·cm^2·mol^{-1}								
	293 K	298 K	303 K	313 K	323 K	333 K	343 K	353 K	363 K
$[C_3(NEt_2)_3]$BEHP	52.2	73.1	99.8	172	274	404	558	736	934
$[C_3(NBuMe)_3]$BEHP	33.4	47.4	64.8	113	181	270	382	514	657
$[C_3(NPr_2)_3]$BEHP	58.2	81.1	109	186	290	418	569	737	912
$[C_3(NBu_2)_3]$BEHP	7.47	11.1	16	31.2	55	89.8	137	195	268
$[C_3(NHex_2)_3]$BEHP	6.93	9.84	13.7	24.4	40.2	61.8	90	126	165
$[C_3(NDec_2)_3]$BEHP	3.09	4.4	6.14	11	18.2	28.1	41.3	57.8	77.5