# Fluorine-Free Imidazolium-Based Ionic Liquids with a Phosphorous-Containing Anion as Potential $CO_2$ Absorbents

**Jelliarko Palgunadi, Je Eun Kang, Sung Yeup Chung, Ki-Chun Lee, Hyunjoo Lee, Honggon Kim, Hoon Sik Kim, Minserk Cheong**

*Department of Chemistry and Research Institute of Basic Science, Kyung Hee University, Seoul 130-701, Korea*
**E-mail: khs2004@khu.ac.kr*
*†Environment and Energy Research Team, Central Advanced Research & Engineering Institute, Hyundai Kia Motors Corporation, 460-30, Gyeonggi 437-040, Korea*
*‡Clean Energy Research Center, Korea Institute of Science and Technology, Seoul 136-791, Korea*
**E-mail: hjlee@kist.re.kr*
*Received May 25, 2009, Accepted June 19, 2009*

**Key Words**: $CO_2$ solubility, Room temperature ionic liquids, Dialkylimidazolium dialylphosphate, Dialkylimidazolium alkylphosphite

## General Synthesis of Ionic Liquids

**Synthesis of dialkylimidazolium dialkylphosphates.** 1,3-Dimethylimidazolium dimethylphosphate ([DMIM][$Me_2PO_4$]). In a typical synthesis, 0.1 mol of 1-methylimidazole was charged in a 100 mL two-necked round bottomed flask equipped with a magnet bar, a reflux condenser, and an equalizing pressure dropping funnel filled with 0.1 mol of trialkylphosphate. The flask was heated to 333 K with vigorous stirring, and then trimethylphosphate was slowly added drop-wise over a period of 1 h. After the addition of trimethylphosphate was completed, the resulting solution was heated to 413 K and reacted further for 7 h to complete the reaction. After cooling, a slightly viscous ionic liquid was washed four times with ether and dried under vacuum (<1 mbar) at 348 K for 8 h to remove the residual volatiles and moisture.

1,3-Dimethylimidazolium dimethylphosphate [DMIM][$Me_2PO_4$] (95% of yield). $^1$H-NMR (400 MHz, $d_6$-DMSO, [ppm]) δ 3.29 (6H, d, P(OC$H_3$)$_2$, $J$ = 10.0 Hz), 3.88 (6H, s, $H_3$CNCHNC$H_3$), 7.82 (2H, s, NC$H$C$H$N), 9.60 (1H, s, NC$H$N).

Other dialkylimidazolium dialkylphosphates were synthesized analogously.

1-Ethyl-3-methylimidazolium diethylphosphate [EMIM][$Et_2PO_4$] (92 % of yield). $^1$H-NMR (400 MHz, $d_6$-DMSO, [ppm]) δ 1.08 (6H, t, P(OCH$_2$C$H_3$)$_2$, $J$ = 7.2 Hz), 1.43 (3H, t, NCH$_2$C$H_3$, $J$ = 7.6 Hz), 3.65 (4H, p, P(OC$H_2$CH$_3$)$_2$, $J$ = 7.2 Hz), 3.91 (3H, s, NC$H_3$), 4.25 (2H, q, NC$H_2$CH$_3$, $J$ = 7.2 Hz), 7.86 (1H, s, NC$H$CHN) 7.96 (1H, s, NCHC$H$N), 9.83 (1H, s, NC$H$N).

1-*n*-Butyl-3-methylimidazolium dibutylphosphate [BMIM][$Bu_2PO_4$] (92 % of yield). $^1$H-NMR (400 MHz, $d_6$-DMSO, [ppm]) δ 0.87 (9H, m, NCH$_2$CH$_2$CH$_2$C$H_3$, P(OCH$_2$CH$_2$CH$_2$C$H_3$)$_2$), 1.31 (6H, m, NCH$_2$CH$_2$C$H_2$CH$_3$, P(OCH$_2$CH$_2$C$H_2$CH$_3$)$_2$), 1.41 (4H, m, P(OCH$_2$C$H_2$CH$_2$CH$_3$)$_2$), 1.76 (2H, m, NCH$_2$C$H_2$CH$_2$CH$_3$), 3.56 (4H, q, P(OC$H_2$CH$_2$CH$_2$CH$_3$)$_2$), 3.86 (1H, s, NC$H3$), 4.18 (2H, t, CH$_3$CH$_2$CH$_2$C$H_2$N, $J$ = 7.2 Hz), 7.75 (1H, t, NC$H$CHN, $J$ = 1.6 Hz), 7.82 (1H, t, NCHC$H$N, $J$ = 2.0 Hz), 9.46 (1H, s, NC$H$N).

**Synthesis of dialkylimidazolium alkylphosphites.** 1,3-Dimethylimidazolium methylphosphite ([DMIM][$MeHPO_3$]). 1-Methylimidazole was charged in a 100 mL two-necked round bottomed flask equipped with a magnet bar, a reflux condenser, and an equalizing pressure dropping funnel filled with 0.1 mol of trialkylphosphate dimethylphosphite. The flask was heated to 333 K with vigorous stirring, and then dimethylphosphate was slowly added drop-wise over a period of 1 h. After the addition of dimethylphosphate was completed, the resulting solution was heated to 413 K and reacted further for 7 h to complete the reaction. After cooling, a slightly viscous ionic liquid was washed four times with ethyl acetate and dried under vacuum (<1 mbar) at 348 K for 12 h to remove the residual volatiles and moisture. Yield: 87.15 g (92%). $^1$H-NMR (400 MHz, $d_6$-DMSO, [ppm]) δ 3.28 (3H, d, HPOC$H_3$, $J$ = 6.0 Hz), 3.88 (6H, s, $H_3$CNCHNC$H_3$), 6.54 (1H, d, $H$POCH$_3$, $J$ = 563.8 Hz), 7.80 (2H, s, NC$H$C$H$N), 9.53 (1H, s, NC$H$N).

Other dialkylimidazolium alkylphosphites were synthesized analogously.

1-Ethyl-3-methylimidazolium ethylphosphite [EMIM][$EtHPO_3$] (93% of yield). $^1$H-NMR (400 MHz, $d_6$-DMSO, [ppm]) δ 1.11 (3H, t, HPOCH$_2$C$H_3$, $J$ = 7.2 Hz), 1.44 (3H, t, NCH$_2$C$H_3$, $J$ = 7.6 Hz), 3.67 (2H, o, POC$H_2$CH$_3$, $J$ = 6.0 Hz), 3.94 (3H, s, NC$H_3$), 4.28 (2H, q, NC$H_2$CH$_3$, $J$ = 7.2 Hz), 6.67 (1H, d, $H$POCH$_2$CH$_3$, $J$ = 563.0 Hz), 7.96 (1H, s, NC$H$CHN), 8.07 (1H, s, NCHC$H$N), 9.94 (1H,s, NC$H$N).

1-*n*-Butyl-3-methylimidazolium butylphosphite, [BMIM][$BuHPO_3$] (85% of yield). $^1$H-NMR (400 MHz, $d_6$-DMSO, [ppm]) δ 0.88 (6H, m, N(CH$_2$)$_3$C$H_3$ and HPO(CH$_2$)$_3$C$H_3$), 1,28 (4H, m, N(CH$_2$)$_2$C$H_2$CH$_3$ and HP(CH$_2$)$_2$C$H_2$CH$_3$), 1.45 (2H, m, HPOCH$_2$C$H_2$CH$_2$CH$_3$), 1.78 (2H, m, NCH$_2$C$H_2$CH$_2$CH$_3$), 3.58 (2H, q, HPC$H_2$(CH$_2$)$_2$CH$_3$, $J$ = 6.8 Hz), 3.91 (3H, s, NC$H_3$), 4.21 (2H, t, NC$H_2$(CH$_2$)$_2$CH$_3$, $J$ = 7.2 Hz), 6.62 (1H, d, $H$PO(CH$_2$)$_3$CH$_3$, $J$ = 562.2 Hz), 7.94 (1H, s, NC$H$CHN), 7.86 (1H, s, NCHC$H$N), 9.78 (1H, s, NC$H$N).

1-*n*-Butyl-3-methylimidazolium methylphosphite, [BMIM][$MeHPO_3$] (89% of yield). $^1$H-NMR (400 MHz, $d_6$-DMSO, [ppm]) δ 0.90 (3H, t, N(CH$_2$)$_3$C$H_3$), 1,25 (2H, m, N(CH$_2$)$_2$ C$H_2$CH$_3$),

1.76 (2H, m, $NCH_2CH_2CH_2CH_3$), 3.25 (3H, d, $HPOCH_3$, $J$ = 11.6 Hz), 3.87 (3H, s, $NCH_3$), 4.19 (2H, t, $NCH_2(CH_2)_2CH_3$, $J$ = 7.2 Hz), 6.51 (1H, d, $HPOCH_3$, $J$ = 565.4 Hz), 7.85 (1H, s, NCHCHN), 7.77 (1H, s, NCHCHN), 9.48 (1H, s, NCHN).

**Table S-1.** Experimental data of equilibrium pressure ($p$), mole fraction ($x_2$), and molarity ($c$) of the solutes ($CO_2$) in the liquid phase at three different temperatures.

| $T$ = 313.15 K | | | $T$ = 323.15 K | | | $T$ = 333.15 K | | |
|---|---|---|---|---|---|---|---|---|
| $p$/MPa | $10^2x_2$ | 10 $c$/mol·L$^{-1}$ | $p$/MPa | $10^2x_2$ | 10 $c$/mol·L$^{-1}$ | $p$/MPa | $10^2x_2$ | 10 $c$/mol·L$^{-1}$ |
| | | | | [DMIM][$Me_2PO_4$] + $CO_2$ | | | | |
| 0.049 | 0.459 | 0.260 | 0.052 | 0.400 | 0.225 | 0.056 | 0.346 | 0.193 |
| 0.093 | 0.913 | 0.519 | 0.095 | 0.741 | 0.418 | 0.098 | 0.629 | 0.353 |
| 0.145 | 1.347 | 0.769 | 0.146 | 1.142 | 0.647 | 0.148 | 0.977 | 0.550 |
| 0.173 | 1.597 | 0.914 | 0.174 | 1.361 | 0.773 | 0.175 | 1.148 | 0.647 |
| 0.259 | 2.380 | 1.430 | 0.291 | 2.283 | 1.371 | 0.305 | 1.978 | 1.184 |
| 0.675 | 5.848 | 3.644 | 0.583 | 4.194 | 2.568 | 0.738 | 4.334 | 2.657 |
| 1.452 | 11.399 | 7.547 | 1.043 | 6.933 | 4.370 | 1.173 | 6.536 | 4.102 |
| 2.228 | 15.827 | 11.030 | 1.652 | 10.410 | 6.816 | 1.740 | 9.190 | 5.937 |
| 3.198 | 20.724 | 15.335 | 2.505 | 14.359 | 9.835 | 2.483 | 12.314 | 8.238 |
| | | | 3.405 | 17.941 | 12.826 | 4.057 | 17.741 | 12.651 |
| | | | 4.682 | 22.103 | 16.645 | 4.821 | 19.964 | 14.632 |
| | | | | [EMIM][$Et_2PO_4$] + $CO_2$ | | | | |
| 0.024 | 0.328 | 0.142 | 0.026 | 0.307 | 0.132 | 0.041 | 0.422 | 0.180 |
| 0.045 | 0.631 | 0.273 | 0.046 | 0.563 | 0.242 | 0.086 | 0.896 | 0.385 |
| 0.072 | 1.025 | 0.446 | 0.073 | 0.865 | 0.374 | 0.111 | 1.156 | 0.498 |
| 0.103 | 1.457 | 0.637 | 0.104 | 1.241 | 0.538 | 0.131 | 1.370 | 0.592 |
| 0.148 | 2.138 | 0.941 | 0.149 | 1.833 | 0.800 | 0.158 | 1.619 | 0.701 |
| 0.175 | 2.475 | 1.094 | 0.175 | 2.130 | 0.932 | 0.180 | 1.852 | 0.804 |
| 0.189 | 2.666 | 1.180 | 0.189 | 2.340 | 1.026 | 0.192 | 1.962 | 0.853 |
| 0.834 | 11.044 | 5.455 | 1.035 | 11.505 | 5.713 | 0.199 | 2.041 | 0.888 |
| 1.429 | 17.172 | 9.109 | 1.404 | 14.619 | 7.523 | 0.738 | 7.438 | 3.531 |
| 2.119 | 22.947 | 13.085 | 2.001 | 19.590 | 10.704 | 1.012 | 9.686 | 4.713 |
| 2.777 | 27.989 | 17.078 | 2.417 | 22.332 | 12.634 | 1.384 | 12.478 | 6.264 |
| 3.488 | 32.314 | 20.977 | 3.511 | 29.370 | 18.271 | 1.779 | 14.991 | 7.749 |
| 4.205 | 36.020 | 24.737 | | | | 2.154 | 17.316 | 9.202 |
| | | | | | | 2.851 | 21.442 | 11.992 |
| | | | | | | 3.182 | 23.776 | 13.705 |
| | | | | | | 4.396 | 28.617 | 17.614 |
| | | | | [BMIM][$Bu_2PO_4$] + $CO_2$ | | | | |
| 0.022 | 0.426 | 0.128 | 0.022 | 0.372 | 0.111 | 0.023 | 0.317 | 0.094 |
| 0.044 | 0.849 | 0.256 | 0.045 | 0.773 | 0.231 | 0.044 | 0.619 | 0.184 |
| 0.072 | 1.412 | 0.427 | 0.073 | 1.255 | 0.377 | 0.072 | 1.049 | 0.313 |
| 0.103 | 2.056 | 0.627 | 0.104 | 1.782 | 0.538 | 0.103 | 1.497 | 0.448 |
| 0.150 | 2.979 | 0.917 | 0.145 | 2.519 | 0.767 | 0.136 | 1.965 | 0.591 |
| 0.175 | 3.529 | 1.092 | 0.173 | 2.984 | 0.912 | 0.169 | 2.471 | 0.747 |
| 0.707 | 12.622 | 4.436 | 0.809 | 12.939 | 4.564 | 0.776 | 11.039 | 3.811 |
| 1.391 | 21.548 | 8.435 | 1.383 | 19.451 | 7.415 | 1.425 | 17.803 | 6.651 |
| 2.054 | 28.782 | 12.411 | 2.063 | 26.063 | 10.825 | 2.071 | 23.304 | 9.331 |
| 2.761 | 35.172 | 16.661 | 2.745 | 31.832 | 14.340 | 2.755 | 28.494 | 12.237 |
| 3.618 | 41.744 | 22.005 | 3.540 | 37.285 | 18.257 | 3.496 | 33.733 | 15.632 |
| | | | | [DMIM][$MeHPO_3$] + $CO_2$ | | | | |
| 0.055 | 0.451 | 0.291 | 0.054 | 0.375 | 0.240 | 0.055 | 0.314 | 0.200 |
| 0.972 | 0.841 | 0.544 | 0.096 | 0.692 | 0.446 | 0.103 | 0.605 | 0.387 |
| 0.147 | 1.272 | 0.827 | 0.147 | 1.078 | 0.697 | 0.151 | 0.923 | 0.592 |
| 0.175 | 1.521 | 0.991 | 0.174 | 1.284 | 0.831 | 0.177 | 1.088 | 0.700 |
| 0.223 | 2.010 | 1.365 | 0.255 | 1.951 | 1.324 | 0.255 | 1.663 | 1.125 |
| 0.477 | 3.822 | 2.645 | 0.505 | 3.445 | 2.375 | 0.507 | 2.812 | 1.926 |
| 1.047 | 7.484 | 5.384 | 1.046 | 6.320 | 4.490 | 1.049 | 5.351 | 3.762 |
| 1.756 | 11.796 | 8.901 | 1.804 | 10.007 | 7.401 | 1.793 | 8.473 | 6.161 |
| 2.757 | 16.461 | 13.115 | 2.645 | 13.621 | 10.495 | 2.661 | 11.791 | 8.896 |
| 4.140 | 21.854 | 18.613 | 4.033 | 18.289 | 14.898 | 4.353 | 17.209 | 13.835 |
| 4.781 | 24.316 | 21.384 | 4.722 | 20.405 | 17.063 | 5.035 | 19.496 | 16.119 |

**Table S-1.** Continued

| $T$ = 313.15 K | | | $T$ = 323.15 K | | | $T$ = 333.15 K | | |
|---|---|---|---|---|---|---|---|---|
| $p$/MPa | $10^2x_2$ | 10 $c$/mol·L$^{-1}$ | $p$/MPa | $10^2x_2$ | 10 $c$/mol·L$^{-1}$ | $p$/MPa | $10^2x_2$ | 10 $c$/mol·L$^{-1}$ |
| | | | | [EMIM][$EtHPO_3$] + $CO_2$ | | | | |
| 0.054 | 0.566 | 0.297 | 0.055 | 0.504 | 0.263 | 0.056 | 0.446 | 0.231 |
| 0.093 | 1.002 | 0.528 | 0.093 | 0.860 | 0.450 | 0.090 | 0.718 | 0.373 |
| 0.145 | 1.571 | 0.833 | 0.145 | 1.351 | 0.711 | 0.144 | 1.160 | 0.605 |
| 0.173 | 1.869 | 0.994 | 0.174 | 1.609 | 0.849 | 0.173 | 1.391 | 0.728 |
| 0.288 | 3.017 | 1.691 | 0.288 | 2.787 | 1.558 | 0.788 | 6.241 | 3.617 |
| 0.767 | 7.397 | 4.341 | 0.752 | 6.496 | 3.776 | 1.565 | 10.953 | 6.685 |
| 1.259 | 11.508 | 7.067 | 1.575 | 12.238 | 7.578 | 2.209 | 14.508 | 9.222 |
| 1.932 | 16.555 | 10.781 | 2.203 | 16.141 | 10.459 | 2.901 | 17.963 | 11.899 |
| 2.715 | 21.919 | 15.255 | 2.999 | 20.493 | 14.007 | 4.320 | 23.783 | 16.957 |
| 3.740 | 27.901 | 21.030 | 4.375 | 26.760 | 19.855 | | | |
| 4.766 | 32.653 | 26.348 | | | | | | |
| | | | | [BMIM][$BuHPO_3$] + $CO_2$ | | | | |
| 0.055 | 0.838 | 0.326 | 0.054 | 0.707 | 0.273 | 0.055 | 0.622 | 0.239 |
| 0.093 | 1.481 | 0.580 | 0.096 | 1.256 | 0.488 | 0.094 | 1.101 | 0.425 |
| 0.145 | 2.254 | 0.890 | 0.147 | 1.955 | 0.765 | 0.146 | 1.697 | 0.658 |
| 0.173 | 2.728 | 1.082 | 0.174 | 2.316 | 0.909 | 0.174 | 2.029 | 0.790 |
| 0.675 | 10.100 | 4.499 | 0.665 | 8.577 | 3.757 | 1.361 | 14.313 | 6.690 |
| 1.389 | 17.869 | 8.714 | 1.402 | 15.665 | 7.439 | 2.106 | 19.760 | 9.863 |
| 2.180 | 25.010 | 13.357 | 2.113 | 21.610 | 11.041 | 2.871 | 24.433 | 12.949 |
| 2.845 | 30.414 | 17.505 | 3.181 | 29.250 | 16.558 | 3.518 | 28.160 | 15.699 |
| 4.184 | 39.092 | 25.705 | | | | | | |
| | | | | [BMIM][$MeHPO_3$] + $CO_2$ | | | | |
| 0.055 | 0.599 | 0.292 | 0.054 | 0.525 | 0.254 | 0.055 | 0.448 | 0.216 |
| 0.093 | 1.052 | 0.515 | 0.097 | 0.964 | 0.469 | 0.098 | 0.846 | 0.409 |
| 0.145 | 1.662 | 0.819 | 0.148 | 1.483 | 0.726 | 0.148 | 1.316 | 0.639 |
| 0.173 | 2.004 | 0.991 | 0.175 | 1.741 | 0.854 | 0.175 | 1.553 | 0.756 |

**Table S-2.** Coefficients of Eq. (13) and the percent of average absolute deviation (AAD) of the fit.

| Compound | $B_0$ | $B_1$ | $B_2$ | AAD% |
|---|---|---|---|---|
| [DMIM][$Me_2PO_4$] | +16.57 | $-5.712 \times 10^3$ | $+6.205 \times 10^5$ | 0.34 |
| [EMIM][$Et_2PO_4$] | +26.84 | $-1.281 \times 10^4$ | $+1.796 \times 10^6$ | 1.36 |
| [BMIM][$Bu_2PO_4$] | +28.87 | $-1.438 \times 10^4$ | $+2.053 \times 10^6$ | 1.02 |
| [DMIM][$MeHPO_3$] | +23.85 | $-1.039 \times 10^4$ | $+1.38 \times 10^6$ | 1.32 |
| [EMIM][$EtHPO_3$] | +7.169 | −70.47 | $-2.39 \times 10^5$ | 0.01 |
| [BMIM][$BuHPO_3$] | −11.13 | $+1.154 \times 10^4$ | $-2.117 \times 10^6$ | 0.30 |
| [BMIM][$MeHPO_3$] | +5.705 | +650.2 | $-3.267 \times 10^5$ | 0.04 |

**Table S-3.** Experimental solubility measurements of [BMIM][$BF_4$] and [BMIM][$Tf_2N$] at 313.15 K.

| $T$ = 313.15 K | | $T$ = 313.15 K | |
|---|---|---|---|
| $p$/MPa | $10^2x_2$ | $p$/MPa | $10^2x_2$ |
| [BMIM][$BF_4$] + $CO_2$ | | [BMIM][$Tf_2N$] + $CO_2$ | |
| 0.497 | 6.039 | 0.283 | 6.705 |
| 0.741 | 8.741 | 0.701 | 15.584 |
| 1.004 | 11.267 | 1.333 | 26.301 |
| 1.254 | 13.539 | 2.086 | 36.061 |
| 1.362 | 14.657 | 2.823 | 42.959 |