

Experimental and Theoretical Thermodynamic Study of Distillable Ionic Liquid 1,5-Diazabicyclo[4.3.0]non-5-enium Acetate:

Supporting Information

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Table S1. Provenance and Purity of Samples Used

| Chemical name | Source | Initial mass fraction purity | Final mass fraction purity | Mass fraction water content | Mole fraction of APP/APPH ^a | Analysis method | Purification method |
|---------------|---------------|------------------------------|----------------------------|-----------------------------|--|-------------------------|---------------------|
| Acetic acid | Sigma-Aldrich | - | ≥ 0.998 | - | - | - | - |
| DBN | Fluorochem | ≥ 0.990 | ≥ 0.997 | ≤ 0.0028 | ≤ 0.0001 | ¹ H NMR, K-F | Distillation |
| [DBNH][OAc] | - | - | ≥ 0.989 | ≤ 0.0003 | ≤ 0.0095 | ¹ H NMR, K-F | - |

| Chemical name | Source | Initial mass fraction purity | Final mass fraction purity | Mass fraction water content | Mole fraction of APP/APPH ^a | Analysis method ^{a,b} | Purification method |
|----------------------|---------------|------------------------------|----------------------------|-----------------------------|--|--------------------------------|---------------------|
| Acetic acid | Sigma-Aldrich | - | ≥ 0.998 | - | - | - | - |
| DBN | Fluorochem | ≥ 0.990 | ≥ 0.997 | ≤ 0.0028 | ≤ 0.0001 | ¹ H NMR, K-F | Distillation |
| [DBNH][OAc] | - | - | ≥ 0.989 | ≤ 0.0003 | ≤ 0.0095 | ¹ H NMR, K-F | - |
| n-Octane | Sigma-Aldrich | ≥ 0.980 | ≥ 0.980 | ≤ 0.0002 | - | GC, K-F | - |
| n-Nonane | Sigma-Aldrich | ≥ 0.980 | ≥ 0.980 | ≤ 0.0002 | - | GC, K-F | - |
| n-Decane | Sigma-Aldrich | ≥ 0.980 | ≥ 0.980 | ≤ 0.0002 | - | GC, K-F | - |
| n-Undecane | Sigma-Aldrich | ≥ 0.980 | ≥ 0.980 | ≤ 0.0002 | - | GC, K-F | - |
| n-Dodecane | Sigma-Aldrich | ≥ 0.980 | ≥ 0.980 | ≤ 0.0002 | - | GC, K-F | - |
| Benzene | Sigma-Aldrich | ≥ 0.990 | ≥ 0.996 | ≤ 0.0003 | - | GC, K-F | Distillation |
| Toluene | Sigma-Aldrich | ≥ 0.980 | ≥ 0.985 | ≤ 0.0003 | - | GC, K-F | Distillation |
| Butylbenzene | Sigma-Aldrich | ≥ 0.980 | ≥ 0.988 | ≤ 0.0002 | - | GC, K-F | Distillation |
| Pentylbenzene | Sigma-Aldrich | ≥ 0.980 | ≥ 0.989 | ≤ 0.0002 | - | GC, K-F | Distillation |
| Methanol | Sigma-Aldrich | ≥ 0.980 | ≥ 0.984 | ≤ 0.0003 | - | GC, K-F | Distillation |
| Ethanol | Sigma-Aldrich | ≥ 0.980 | ≥ 0.986 | ≤ 0.0004 | - | GC, K-F | Distillation |
| 1-Propanol | Sigma-Aldrich | ≥ 0.980 | ≥ 0.985 | ≤ 0.0004 | - | GC, K-F | Distillation |
| 1-Butanol | Sigma-Aldrich | ≥ 0.980 | ≥ 0.989 | ≤ 0.0004 | - | GC, K-F | Distillation |
| 1-Pentanol | Sigma-Aldrich | ≥ 0.980 | ≥ 0.985 | ≤ 0.0004 | - | GC, K-F | Distillation |
| Acetone | Sigma-Aldrich | ≥ 0.990 | ≥ 0.994 | ≤ 0.0002 | - | GC, K-F | Distillation |
| Acetonitrile | Sigma-Aldrich | ≥ 0.990 | ≥ 0.997 | ≤ 0.0002 | - | GC, K-F | Distillation |
| Tetrahydrofuran | Sigma-Aldrich | ≥ 0.980 | ≥ 0.987 | ≤ 0.0002 | - | GC, K-F | Distillation |
| Dichloromethane | Sigma-Aldrich | ≥ 0.980 | ≥ 0.988 | ≤ 0.0002 | - | GC, K-F | Distillation |
| Trichloromethane | Sigma-Aldrich | ≥ 0.980 | ≥ 0.989 | ≤ 0.0002 | - | GC, K-F | Distillation |
| 2,6-Dimethoxyphenol | Sigma-Aldrich | ≥ 0.980 | ≥ 0.989 | ≤ 0.0002 | - | GC, K-F | Recrystallization |
| 1,2-Dihydroxybenzene | Sigma-Aldrich | ≥ 0.980 | ≥ 0.987 | ≤ 0.0002 | - | GC, K-F | Recrystallization |
| 3-Methoxyphenol | Sigma-Aldrich | ≥ 0.980 | ≥ 0.988 | ≤ 0.0003 | - | GC, K-F | Distillation |
| 4-Ethylphenol | Sigma-Aldrich | ≥ 0.980 | ≥ 0.989 | ≤ 0.0003 | - | GC, K-F | Recrystallization |

^a GC-Gas chromatography analysis of compounds purity.

^b K-F – Karl-Fisher titration technic for determination of water content.

Table S2. Measured Heat Capacities of DBN^a

| $C_p(\text{DBN, liq})$ | | | $C_p(\text{DBN, liq})$ | | |
|------------------------|--|--|------------------------|--|--|
| T / K | $\text{J}\cdot\text{K}^{-1}\cdot\text{g}^{-1}$ | $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ | T / K | $\text{J}\cdot\text{K}^{-1}\cdot\text{g}^{-1}$ | $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ |
| 227.0 | 1.524 | 189.3 | 272.2 | 1.653 | 205.2 |
| 227.0 | 1.523 | 189.2 | 278.0 | 1.668 | 207.1 |
| 228.0 | 1.532 | 190.2 | 278.0 | 1.670 | 207.4 |
| 228.1 | 1.535 | 190.6 | 279.0 | 1.667 | 207.0 |
| 229.0 | 1.533 | 190.3 | 279.0 | 1.670 | 207.4 |
| 229.0 | 1.545 | 191.9 | 280.0 | 1.672 | 207.6 |
| 230.0 | 1.548 | 192.2 | 280.0 | 1.674 | 207.8 |
| 230.0 | 1.536 | 190.7 | 281.0 | 1.679 | 208.5 |
| 231.0 | 1.550 | 192.4 | 281.0 | 1.679 | 208.5 |
| 231.0 | 1.539 | 191.1 | 282.0 | 1.685 | 209.2 |
| 232.0 | 1.552 | 192.8 | 282.0 | 1.683 | 209.0 |
| 232.0 | 1.545 | 191.8 | 283.0 | 1.684 | 209.1 |
| 233.0 | 1.550 | 192.5 | 283.0 | 1.688 | 209.6 |
| 233.0 | 1.552 | 192.8 | 284.0 | 1.694 | 210.4 |
| 234.0 | 1.553 | 192.8 | 284.0 | 1.685 | 209.3 |
| 234.0 | 1.556 | 193.2 | 285.0 | 1.688 | 209.6 |
| 235.0 | 1.554 | 193.0 | 285.0 | 1.697 | 210.7 |
| 235.0 | 1.557 | 193.3 | 286.0 | 1.690 | 209.8 |
| 236.0 | 1.560 | 193.8 | 286.0 | 1.699 | 210.9 |
| 236.1 | 1.555 | 193.1 | 287.0 | 1.691 | 210.0 |
| 237.0 | 1.567 | 194.5 | 287.1 | 1.710 | 212.4 |
| 237.0 | 1.562 | 194.0 | 288.0 | 1.713 | 212.8 |
| 238.0 | 1.570 | 195.0 | 288.0 | 1.690 | 209.9 |
| 238.0 | 1.570 | 195.0 | 289.0 | 1.718 | 213.4 |
| 239.0 | 1.574 | 195.5 | 289.0 | 1.698 | 210.9 |
| 239.0 | 1.568 | 194.7 | 290.0 | 1.724 | 214.1 |
| 240.0 | 1.576 | 195.7 | 290.0 | 1.703 | 211.5 |
| 240.0 | 1.583 | 196.6 | 291.0 | 1.730 | 214.9 |
| 241.0 | 1.583 | 196.6 | 291.0 | 1.707 | 212.0 |
| 241.0 | 1.576 | 195.7 | 292.0 | 1.732 | 215.1 |
| 242.0 | 1.581 | 196.3 | 292.0 | 1.711 | 212.5 |
| 242.0 | 1.581 | 196.3 | 293.0 | 1.735 | 215.5 |
| 243.0 | 1.582 | 196.5 | 293.0 | 1.715 | 213.0 |
| 243.0 | 1.583 | 196.6 | 294.0 | 1.740 | 216.1 |
| 244.0 | 1.581 | 196.3 | 294.0 | 1.717 | 213.2 |
| 244.0 | 1.585 | 196.8 | 295.0 | 1.745 | 216.7 |
| 245.0 | 1.581 | 196.4 | 295.0 | 1.718 | 213.3 |
| 245.0 | 1.589 | 197.3 | 296.0 | 1.747 | 217.0 |
| 246.0 | 1.579 | 196.1 | 296.0 | 1.721 | 213.7 |
| 246.0 | 1.589 | 197.3 | 297.0 | 1.752 | 217.6 |
| 247.0 | 1.596 | 198.2 | 297.0 | 1.721 | 213.7 |
| 247.1 | 1.597 | 198.3 | 298.0 | 1.758 | 218.3 |
| 248.0 | 1.590 | 197.5 | 298.1 | 1.726 | 214.3 |
| 248.0 | 1.590 | 197.4 | 299.0 | 1.730 | 214.8 |
| 249.0 | 1.590 | 197.4 | 299.0 | 1.759 | 218.4 |
| 249.0 | 1.601 | 198.8 | 300.0 | 1.733 | 215.2 |
| 250.0 | 1.595 | 198.1 | 300.0 | 1.765 | 219.2 |

| | | | | | |
|-------|-------|-------|-------|-------|-------|
| 250.0 | 1.599 | 198.6 | 301.0 | 1.734 | 215.3 |
| 251.0 | 1.600 | 198.7 | 301.0 | 1.765 | 219.2 |
| 251.0 | 1.598 | 198.4 | 302.0 | 1.733 | 215.2 |
| 252.0 | 1.601 | 198.9 | 302.0 | 1.768 | 219.6 |
| 252.0 | 1.596 | 198.2 | 303.0 | 1.734 | 215.4 |
| 253.0 | 1.607 | 199.6 | 303.0 | 1.777 | 220.7 |
| 253.0 | 1.597 | 198.3 | 304.0 | 1.741 | 216.1 |
| 254.0 | 1.614 | 200.5 | 304.0 | 1.780 | 221.1 |
| 254.0 | 1.596 | 198.2 | 305.0 | 1.780 | 221.1 |
| 255.0 | 1.608 | 199.7 | 305.0 | 1.750 | 217.3 |
| 255.1 | 1.597 | 198.3 | 306.0 | 1.778 | 220.8 |
| 256.0 | 1.606 | 199.4 | 306.0 | 1.758 | 218.3 |
| 256.0 | 1.601 | 198.8 | 307.0 | 1.778 | 220.8 |
| 257.0 | 1.613 | 200.2 | 307.0 | 1.761 | 218.7 |
| 257.0 | 1.606 | 199.4 | 308.0 | 1.782 | 221.3 |
| 258.0 | 1.616 | 200.7 | 308.0 | 1.762 | 218.8 |
| 258.0 | 1.610 | 199.9 | 309.0 | 1.786 | 221.8 |
| 259.0 | 1.619 | 201.1 | 309.0 | 1.764 | 219.0 |
| 259.0 | 1.612 | 200.2 | 310.0 | 1.790 | 222.3 |
| 260.0 | 1.623 | 201.5 | 310.0 | 1.763 | 219.0 |
| 260.0 | 1.620 | 201.1 | 311.0 | 1.797 | 223.1 |
| 261.0 | 1.623 | 201.5 | 311.1 | 1.770 | 219.8 |
| 261.0 | 1.621 | 201.3 | 312.0 | 1.804 | 224.0 |
| 262.0 | 1.625 | 201.8 | 312.1 | 1.776 | 220.5 |
| 262.0 | 1.624 | 201.7 | 313.0 | 1.804 | 224.0 |
| 263.0 | 1.631 | 202.6 | 313.1 | 1.781 | 221.2 |
| 263.0 | 1.626 | 201.9 | 314.0 | 1.784 | 221.5 |
| 264.0 | 1.637 | 203.3 | 314.0 | 1.807 | 224.4 |
| 264.0 | 1.626 | 201.9 | 315.0 | 1.812 | 225.0 |
| 265.0 | 1.641 | 203.8 | 315.0 | 1.782 | 221.3 |
| 265.0 | 1.628 | 202.1 | 316.0 | 1.814 | 225.3 |
| 266.0 | 1.640 | 203.6 | 316.0 | 1.782 | 221.2 |
| 266.0 | 1.629 | 202.3 | 317.0 | 1.814 | 225.3 |
| 267.0 | 1.634 | 203.0 | 317.0 | 1.784 | 221.5 |
| 267.0 | 1.644 | 204.1 | 318.0 | 1.819 | 225.8 |
| 268.0 | 1.646 | 204.4 | 318.0 | 1.790 | 222.3 |
| 268.0 | 1.639 | 203.5 | 319.0 | 1.816 | 225.6 |
| 269.0 | 1.637 | 203.3 | 319.1 | 1.797 | 223.1 |
| 269.0 | 1.646 | 204.4 | 320.0 | 1.796 | 223.0 |
| 270.0 | 1.637 | 203.3 | 320.0 | 1.812 | 225.1 |
| 270.0 | 1.646 | 204.4 | 321.0 | 1.813 | 225.1 |
| 271.0 | 1.644 | 204.2 | 321.0 | 1.795 | 222.9 |
| 271.0 | 1.650 | 204.9 | 322.0 | 1.813 | 225.1 |
| 272.0 | 1.644 | 204.2 | 322.0 | 1.793 | 222.7 |
| 272.0 | 1.653 | 205.2 | 322.4 | 1.813 | 225.2 |
| 272.1 | 1.643 | 204.0 | 322.4 | 1.793 | 222.6 |

^a T is the temperature, $C_p(\text{DBN, liq})$ is the measured heat capacity of liquid DBN.

Table S3. Measured Heat Capacities of [DBNH][OAc]^a

| $C_p(\text{IL, liq})$ | | | $C_p(\text{IL, liq})$ | | |
|-----------------------|--|--|-----------------------|--|--|
| T / K | $\text{J}\cdot\text{K}^{-1}\cdot\text{g}^{-1}$ | $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ | T / K | $\text{J}\cdot\text{K}^{-1}\cdot\text{g}^{-1}$ | $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ |
| 278.5 | 1.865 | 343.6 | 325.3 | 2.097 | 386.4 |
| 278.5 | 1.867 | 344.0 | 326.0 | 2.100 | 386.9 |
| 279.2 | 1.867 | 344.0 | 326.7 | 2.103 | 387.5 |
| 279.2 | 1.868 | 344.1 | 328.2 | 2.109 | 388.6 |
| 280.2 | 1.873 | 345.1 | 329.2 | 2.113 | 389.2 |
| 280.2 | 1.871 | 344.7 | 329.2 | 2.116 | 389.8 |
| 281.2 | 1.877 | 345.8 | 330.2 | 2.115 | 389.7 |
| 281.2 | 1.874 | 345.3 | 330.2 | 2.119 | 390.4 |
| 282.2 | 1.880 | 346.3 | 331.1 | 2.122 | 390.9 |
| 282.2 | 1.877 | 345.9 | 331.2 | 2.120 | 390.5 |
| 283.2 | 1.883 | 346.9 | 332.2 | 2.127 | 391.8 |
| 283.2 | 1.884 | 347.0 | 332.2 | 2.126 | 391.7 |
| 284.2 | 1.886 | 347.5 | 333.2 | 2.132 | 392.7 |
| 284.2 | 1.891 | 348.4 | 333.2 | 2.132 | 392.7 |
| 285.2 | 1.889 | 348.0 | 334.2 | 2.138 | 393.9 |
| 285.2 | 1.898 | 349.7 | 334.2 | 2.136 | 393.5 |
| 286.2 | 1.894 | 349.0 | 335.2 | 2.143 | 394.8 |
| 286.2 | 1.905 | 350.9 | 335.2 | 2.142 | 394.6 |
| 287.2 | 1.901 | 350.2 | 336.2 | 2.147 | 395.6 |
| 287.2 | 1.907 | 351.4 | 336.2 | 2.148 | 395.8 |
| 288.2 | 1.911 | 352.0 | 337.1 | 2.154 | 396.8 |
| 288.2 | 1.916 | 352.9 | 337.2 | 2.150 | 396.1 |
| 289.2 | 1.908 | 351.4 | 338.1 | 2.154 | 396.7 |
| 289.2 | 1.912 | 352.3 | 338.1 | 2.160 | 397.9 |
| 290.2 | 1.912 | 352.2 | 339.1 | 2.160 | 398.0 |
| 290.2 | 1.917 | 353.1 | 339.1 | 2.164 | 398.6 |
| 291.2 | 1.916 | 353.0 | 340.2 | 2.168 | 399.4 |
| 291.2 | 1.923 | 354.2 | 340.2 | 2.169 | 399.6 |
| 292.2 | 1.921 | 354.0 | 341.2 | 2.175 | 400.7 |
| 292.2 | 1.928 | 355.3 | 341.2 | 2.175 | 400.7 |
| 293.2 | 1.929 | 355.3 | 342.2 | 2.177 | 401.1 |
| 293.2 | 1.934 | 356.4 | 342.2 | 2.182 | 402.0 |
| 294.1 | 1.941 | 357.6 | 343.2 | 2.176 | 401.0 |
| 294.2 | 1.936 | 356.7 | 343.2 | 2.189 | 403.3 |
| 295.1 | 1.949 | 359.1 | 344.2 | 2.176 | 400.8 |
| 295.2 | 1.940 | 357.4 | 344.2 | 2.191 | 403.6 |
| 296.1 | 1.954 | 359.9 | 345.1 | 2.195 | 404.3 |
| 296.2 | 1.939 | 357.3 | 345.2 | 2.180 | 401.7 |
| 297.2 | 1.959 | 360.9 | 346.1 | 2.187 | 403.0 |
| 297.2 | 1.943 | 357.9 | 346.1 | 2.194 | 404.2 |
| 298.2 | 1.965 | 362.1 | 347.2 | 2.194 | 404.2 |
| 298.2 | 1.952 | 359.6 | 347.2 | 2.196 | 404.5 |
| 299.2 | 1.960 | 361.0 | 348.2 | 2.198 | 405.0 |
| 299.2 | 1.969 | 362.7 | 348.2 | 2.201 | 405.5 |
| 300.2 | 1.963 | 361.7 | 349.2 | 2.202 | 405.7 |
| 300.2 | 1.971 | 363.2 | 349.2 | 2.200 | 405.4 |

| | | | | | |
|-------|-------|-------|-------|-------|-------|
| 301.2 | 1.965 | 362.1 | 350.2 | 2.202 | 405.7 |
| 301.2 | 1.975 | 363.9 | 350.2 | 2.184 | 402.4 |
| 302.2 | 1.970 | 362.8 | 351.2 | 2.203 | 405.9 |
| 302.2 | 1.980 | 364.7 | 351.2 | 2.207 | 406.6 |
| 303.2 | 1.974 | 363.7 | 352.1 | 2.220 | 409.0 |
| 303.2 | 1.985 | 365.7 | 352.2 | 2.208 | 406.8 |
| 304.2 | 1.979 | 364.6 | 353.1 | 2.216 | 408.3 |
| 304.2 | 1.993 | 367.1 | 353.1 | 2.230 | 410.8 |
| 305.2 | 1.985 | 365.7 | 354.1 | 2.222 | 409.4 |
| 305.2 | 2.000 | 368.5 | 354.1 | 2.228 | 410.4 |
| 306.2 | 1.992 | 366.9 | 355.2 | 2.230 | 410.8 |
| 306.2 | 2.003 | 369.0 | 355.2 | 2.228 | 410.4 |
| 307.2 | 1.995 | 367.6 | 356.2 | 2.237 | 412.1 |
| 307.2 | 2.006 | 369.6 | 356.2 | 2.234 | 411.6 |
| 308.1 | 1.998 | 368.0 | 357.2 | 2.247 | 414.0 |
| 308.2 | 2.013 | 370.8 | 357.2 | 2.240 | 412.6 |
| 309.1 | 2.003 | 368.9 | 358.2 | 2.245 | 413.7 |
| 309.1 | 2.025 | 373.1 | 358.2 | 2.243 | 413.2 |
| 310.1 | 2.008 | 369.9 | 359.2 | 2.245 | 413.5 |
| 310.2 | 2.033 | 374.6 | 359.2 | 2.252 | 414.8 |
| 311.2 | 2.013 | 370.8 | 360.2 | 2.246 | 413.7 |
| 311.2 | 2.032 | 374.4 | 360.2 | 2.249 | 414.3 |
| 312.2 | 2.021 | 372.3 | 361.1 | 2.247 | 414.0 |
| 312.2 | 2.034 | 374.8 | 361.1 | 2.249 | 414.3 |
| 313.2 | 2.027 | 373.4 | 362.1 | 2.256 | 415.6 |
| 313.2 | 2.037 | 375.2 | 362.2 | 2.252 | 414.9 |
| 314.2 | 2.031 | 374.1 | 363.2 | 2.262 | 416.8 |
| 314.2 | 2.040 | 375.9 | 363.2 | 2.257 | 415.7 |
| 315.2 | 2.034 | 374.7 | 364.2 | 2.268 | 417.8 |
| 315.2 | 2.044 | 376.6 | 364.2 | 2.261 | 416.6 |
| 316.2 | 2.042 | 376.3 | 365.2 | 2.270 | 418.1 |
| 316.2 | 2.046 | 376.9 | 365.2 | 2.266 | 417.4 |
| 317.1 | 2.048 | 377.4 | 366.2 | 2.270 | 418.1 |
| 317.2 | 2.051 | 377.9 | 366.2 | 2.271 | 418.4 |
| 318.1 | 2.046 | 376.9 | 367.2 | 2.275 | 419.1 |
| 318.2 | 2.065 | 380.5 | 367.2 | 2.272 | 418.7 |
| 319.2 | 2.057 | 379.0 | 368.2 | 2.279 | 419.9 |
| 319.2 | 2.071 | 381.6 | 368.2 | 2.275 | 419.1 |
| 320.2 | 2.067 | 380.8 | 369.1 | 2.285 | 420.9 |
| 320.2 | 2.077 | 382.7 | 369.1 | 2.280 | 420.1 |
| 321.2 | 2.074 | 382.0 | 370.1 | 2.286 | 421.2 |
| 321.2 | 2.082 | 383.6 | 370.1 | 2.281 | 420.3 |
| 322.2 | 2.080 | 383.1 | 371.2 | 2.288 | 421.6 |
| 322.2 | 2.085 | 384.2 | 371.2 | 2.285 | 421.0 |
| 322.5 | 2.081 | 383.3 | 372.2 | 2.285 | 421.0 |
| 323.2 | 2.088 | 384.8 | 372.2 | 2.293 | 422.4 |
| 324.6 | 2.094 | 385.8 | 373.1 | 2.295 | 422.8 |

^a T is the temperature, $C_p(\text{IL, liq})$ is the measured heat capacity of liquid [DBNH][OAc].

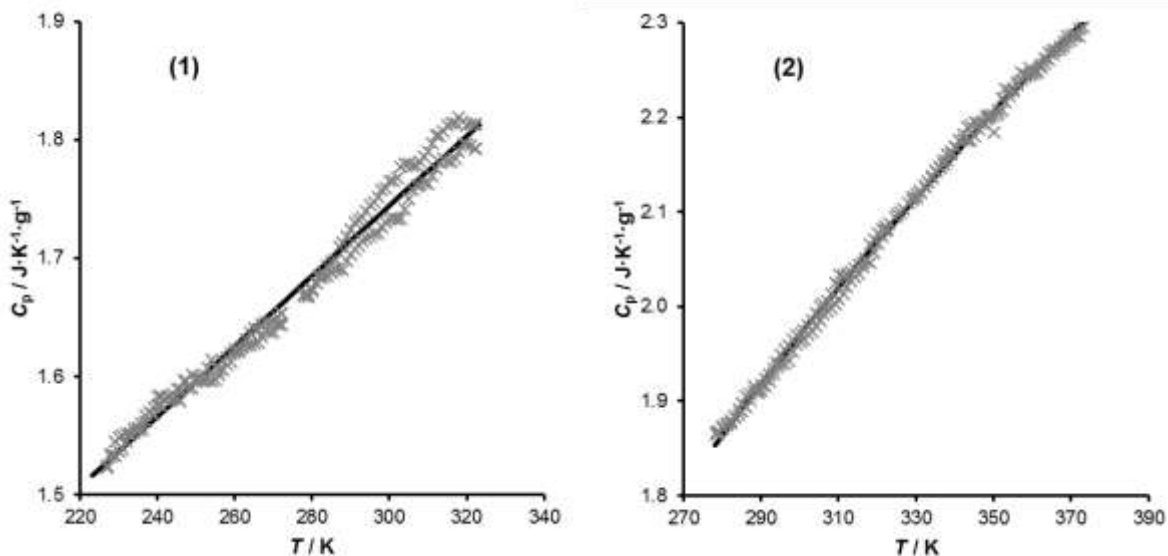


Figure S1. Experimental and smoothed heat capacities of DBN (1) and [DBNH][OAc] (2). Symbols: experimental data points; lines: correlation results.

Table S4. G4 Total Energies at 0 K and Enthalpies at 298.15 K (in Hartree) of the molecules Studied in This Work

| Compounds | G4 | | |
|-------------|-------------|-------------|-----------------------------------|
| | E_0 | H_{298} | $\Delta_f H_m^\circ$ ^a |
| DBN | -383.208629 | -383.199778 | 66.7±3.5 |
| Acetic acid | -228.982903 | -228.977339 | - |
| [DBNH][OAc] | -612.214166 | -612.199229 | -421.9±3.5 |

^a Calculated according to the atomization procedure and using the constant bias correction of 12.8 kJ·mol⁻¹, derived from the G4 calculations reported by Suntsova and Dorofeeva.¹

Table S5. Measured Enthalpies of Phase Transitions of [DBNH][OAc]^a

| Experiment | $T_{\text{trns}} / \text{K}$ | $\Delta_{\text{trns}} H_m^\circ / \text{kJ}\cdot\text{mol}^{-1}$ |
|------------------|------------------------------|--|
| 1 | 285.9 | 4.16 |
| | 317.5 | 11.50 |
| 2 | 285.8 | 7.59 |
| | 317.5 | 10.4 |
| 3-4 ^b | 261.4 | 0.15 |
| | 272.9 | 0.47 |
| | 282.6 | 1.94 |
| | 292.4 | 0.70 |
| | 320.9 | 11.40 |
| 5-12 | 277.0 | 2.4 |
| | 315.1 | 13.8 |

^a T_{trns} is the phase transition onset temperature, $\Delta_{\text{trns}} H_m^\circ$ is the enthalpy of the phase transition.

^b The reproducibility of the phase transition temperatures and the enthalpies of phase transition of experiments 3-4 were $\pm 1 \text{ K}$ and $\pm 0.1 \text{ kJ}\cdot\text{mol}^{-1}$, respectively.

DETAILS ON CALIBRATION AND MEASUREMENTS WITH THE PARR CALORIMETER

The Parr calorimeter was calibrated by dissolution of tris-(hydroxymethyl)-aminomethane (TRIS) (mass fraction purity ≥ 0.998) in 0.1 M HCl solution according to the recommendations provided by the manufacturer.² The energy equivalent of the calorimeter was calculated according to Eqs. S1 and S2.

$$\frac{e'}{\text{J}\cdot\text{K}^{-1}} = \left(\frac{Q_r/\text{J}}{\Delta T/\text{K}} - \frac{m(\text{HCl})}{\text{g}} \cdot \frac{C_p(\text{HCl})}{\text{J}\cdot(\text{K}\cdot\text{g})^{-1}} \right) \quad (\text{S1})$$

$$\frac{Q_r}{\text{J}} = \frac{m(\text{TRIS})}{\text{g}} \cdot \left[245.760 \frac{\text{J}}{\text{g}} + 1.4364 \frac{\text{J}}{\text{g}\cdot\text{K}} \cdot \left(298.15\text{K} - \frac{T(0.63)}{\text{K}} \right) \right] \quad (\text{S2})$$

where e' is the energy equivalent of the calorimeter, Q_r is the energy released from the reaction, ΔT is the net temperature rise due to the dissolution, $m(\text{HCl})$ is the mass of the 0.1 M HCl solution, $C_p(\text{HCl})$ is the heat capacity of the 0.1 M HCl solution at 298.15 K ($4.17956\text{J}\cdot\text{K}^{-1}\cdot\text{g}^{-1}$), $m(\text{TRIS})$ is the mass of the dissolved TRIS sample, $T(0.63)$ is the interpolated average reaction temperature at which the temperature has reached 63 % of its total rise resulted from the reaction.

The calculated energy equivalent at 298.15 K was $(112.1 \pm 5.1) \text{ J}\cdot\text{K}^{-1}$. The calibration was checked with the HCl + NaOH neutralization reaction. The obtained value was adjusted to the infinite dilution and 298.15 K temperature using values from refs 3 and 4, respectively. The adjusted value $-(55.75 \pm 0.54 \text{ kJ}\cdot\text{mol}^{-1})$ agreed within determination uncertainty with the value recommended by the National Bureau of Standards $(-55.836 \text{ kJ}\cdot\text{mol}^{-1})$.⁵ The results of the calibration experiments as well as the description of the adjustments are available in Table S6. A temperature profile of a typical calorimetric experiment is presented in Fig. S2.

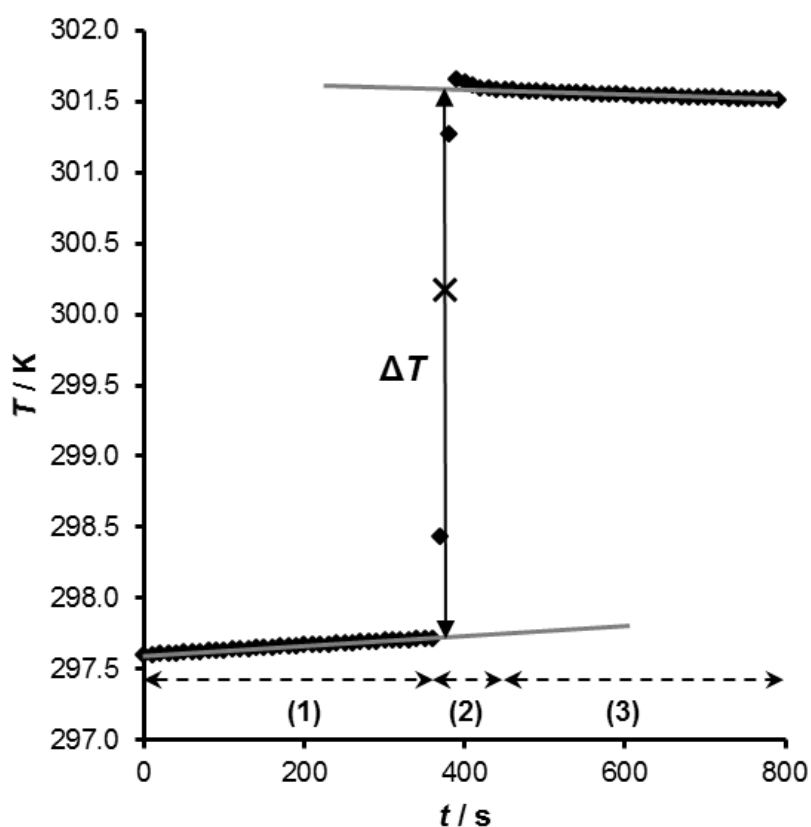


Figure S2. Temperature profile in a typical net [DBNH][OAc] synthesis reaction experiment. (1): initial period; (2): main period; (3): final period; (×): interpolated average reaction temperature at which the temperature has reached 63 % of its total rise; (◆): measured data points; Gray lines: extrapolations of the initial and final period points.

Table S6. Calibration Results of Parr 6755 Solution Calorimeter^a

| Dissolution of TRIS in 0.1 M HCl solution^e | | | | | |
|--|----------|----------|----------|----------|----------|
| Experiment | 1 | 2 | 3 | 4 | 5 |
| $m(\text{TRIS}) / \text{g}$ | 0.5009 | 0.5002 | 0.5010 | 0.5003 | 1.0002 |
| $m(0.1 \text{ M HCl}) / \text{g}$ | 100.0026 | 100.0010 | 100.0009 | 100.0026 | 100.0011 |
| $\Delta T / \text{K}$ | 0.2354 | 0.2340 | 0.2378 | 0.2340 | 0.4657 |
| $T(0.63) / \text{K}$ | 295.1695 | 294.9418 | 297.2860 | 296.3459 | 296.8235 |
| Q_r / J | 125.25 | 125.23 | 123.75 | 124.25 | 247.71 |
| $e' / \text{J}\cdot\text{K}^{-1}$ | 114.09 | 117.23 | 102.42 | 113.02 | 113.96 |

| Dissolution of 1 M NaOH in 0.1 M HCl^e | | | | |
|--|----------|----------|----------|----------|
| Experiment | 1 | 2 | 3 | 4 |
| $m(1 \text{ M NaOH}) / \text{g}$ | 0.9998 | 1.0010 | 2.0000 | 2.0001 |
| $n(\text{NaOH}) / \text{mmol}$ | 0.9595 | 0.9607 | 1.9194 | 1.9195 |
| $m(0.1 \text{ M HCl}) / \text{g}$ | 100.0005 | 100.0022 | 100.0007 | 100.0015 |
| $n(\text{HCl}) / \text{mmol}$ | 10.0201 | 10.0203 | 10.0201 | 10.0202 |
| $\Delta T / \text{K}$ | 0.1030 | 0.1017 | 0.2082 | 0.2081 |
| $T(0.63) / \text{K}$ | 295.5122 | 295.8784 | 296.1694 | 295.5217 |
| $\Delta_{\text{neut}}H_m(x, T(0.63)) / \text{kJ}\cdot\text{mol}^{-1\text{b}}$ | -56.90 | -56.12 | -57.50 | -57.47 |
| $\Delta_{\text{neut}}H_m(\text{inf}, T(0.63)) / \text{kJ}\cdot\text{mol}^{-1\text{c}}$ | -56.21 | -55.42 | -56.74 | -56.71 |
| $\Delta_{\text{neut}}H_m^\circ(\text{inf}) / \text{kJ}\cdot\text{mol}^{-1\text{d}}$ | -55.63 | -54.92 | -56.31 | -56.13 |

^a $m(i)$ and $n(i)$ are the mass and molar amounts of component i , ΔT is the temperature change resulted from the dissolution, $T(0.63)$ is the interpolated temperature value at which the temperature has reached 63 % of its total rise resulted from the reaction, Q_r is the energy released from the reaction, e' is the energy equivalent of the calorimeter, $\Delta_{\text{neut}}H_m$ is the enthalpy of neutralization reaction, inf is the infinite dilution.

$$\text{b } x(i) = n(\text{H}_2\text{O})/n(i)$$

$$\text{c } \Delta_{\text{neut}}H_m(\text{inf}, T(0.63)) = \Delta_{\text{neut}}H_m(x, T(0.63)) - \Delta_{\text{dil}}H_m(\text{HCl}) - \Delta_{\text{dil}}H_m(\text{NaOH}) + \Delta_{\text{dil}}H_m(\text{NaCl});$$

$$\Delta_{\text{dil}}H_m(i) = \Delta_f H_m^\circ(i, \text{inf}) - \Delta_f H_m^\circ(i, x(i))$$

$$\text{d } \Delta_{\text{neut}}H_m^\circ(\text{inf}) = \Delta_{\text{neut}}H_m(\text{inf}, T(0.63)) + \Delta_r C_p \cdot (298.15 - T(0.63))$$

^e sample information: tris(hydroxymethyl)aminomethane (TRIS, mass fraction purity ≥ 0.998), 0.1 M HCl and 1 M NaOH were purchased from Sigma-Aldrich.

The total duration of an experiment was approximately 30 minutes. Stable baselines before and after the sample mixing are required during the experiment to achieve reliable and repeatable results. Therefore, the calorimeter was placed in a constant temperature room in order to maintain stable conditions during the experiments despite the lack of a thermostat in the calorimeter. The room temperature was 294.5-299.5K over 60 days with ± 0.5 K deviation over 24 hours while the relative humidity was 44.5 ± 0.1 %. The stable room temperature was beneficial for keeping the baseline of the calorimeter stable during the experiments. In addition, the stirring was started 90 minutes prior to the beginning of each experiment to stabilize the baselines. The enthalpy of reaction 1 (Eq. 1) at temperature T was calculated according to Eq. S3:

$$\Delta_r H_m((1), \text{liq}, T) = \frac{(C_p^\circ(\text{DBN}) \cdot n(\text{DBN}) + e') \cdot \Delta T}{n(\text{HAc})} \quad (\text{S3})$$

and adjusted to 298.15 K according to Eq S4:

$$\Delta_r H_m^\circ(1) = \Delta_r H_m((1), \text{liq}, T) + \Delta_r C_{p,m}^\circ \cdot (298.15\text{K} - T) \quad (\text{S4})$$

The value $\Delta_r C_{p,m}^\circ(298.15\text{K}) = 22 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ was used in Eq S4. It was calculated from heat capacities of the reaction participants DBN ($216 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$), acetic acid ($123.1 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$)⁶ and [DBNH][OAc] ($361 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$) at 298.15 K. The resulting enthalpy of reaction was $\Delta_r H_m^\circ(1) = -(44.6 \pm 0.7) \text{ kJ}\cdot\text{mol}^{-1}$.

Table S7. Measured Enthalpies of the liquid phase [DBNH][OAc] Synthesis Reaction^a

| Experiment | 1 | 2 | 3 | 4 |
|--|-------------------|----------|----------|----------|
| $m(\text{DBN}) / \text{g}$ | 100.0061 | 100.0038 | 100.1612 | 100.0055 |
| $m(\text{HOAc}) / \text{g}$ | 1.0026 | 1.5002 | 1.5009 | 1.5001 |
| $\Delta T / \text{K}$ | 2.6469 | 3.9231 | 3.782 | 3.8922 |
| $T(0.63) / \text{K}$ | 301.0246 | 300.6459 | 302.3831 | 300.1791 |
| $\Delta_r H_m((1), \text{liq}, T(0.63)) / \text{kJ}\cdot\text{mol}^{-1}$ | -45.34 | -44.91 | -43.32 | -44.56 |
| $\Delta_r H_m^\circ(1), \text{liq}) / \text{kJ}\cdot\text{mol}^{-1}$ | -45.41 | -44.97 | -43.41 | -44.61 |
| $\Delta_r H_m^\circ(1), \text{liq}) / \text{kJ}\cdot\text{mol}^{-1}$ (average) | -44.60 \pm 0.74 | | | |

^a $m(i)$ is the mass of compound i , ΔT is the temperature rise resulted from the reaction, $T(0.63)$ is the interpolated average reaction temperature at which the temperature has reached 63 % of its total rise resulted from the reaction, $\Delta_r H_m(1)$ is the enthalpy of the net [DBNH][OAc] synthesis reaction.

ENTHALPIES OF SOLUTION OF DBN AND [DBNH][OAc] IN WATER

The results of the solution enthalpy measurements of [DBNH][OAc] DBN and in water or water + HOAc solutions are presented in Tables S8 and S9, respectively. Some details on solution calorimetry experiments are worth mentioning. By the dissolving of DBN in pure water, the measured value $\Delta_{\text{sol}}H_{\text{m}}^{\circ}(\text{IV}) = -39.5 \pm 0.3 \text{ kJ}\cdot\text{mol}^{-1}$ was significantly less negative than $\Delta_{\text{sol}}H_{\text{m}}^{\circ}(\text{V}) = -53.4 \pm 0.7 \text{ kJ}\cdot\text{mol}^{-1}$ which was measured in the water+acetic acid solutions. This difference is due to the additional chemical reaction. For comparison, an enthalpy of neutralization reaction between a strong base and acetic acid, of $-54.3 \text{ kJ}\cdot\text{mol}^{-1}$ for the system NaOH + acetic acid at 293.15 K^7 is in a good agreement with $\Delta_{\text{sol}}H_{\text{m}}^{\circ}(\text{V})$ determined in this work. As seen from Figure S3, the enthalpy of solution of DBN in water + HOAc solutions remains constant ($\Delta_{\text{sol}}H_{\text{m}}^{\circ}(\text{III}) = -92.9 \pm 0.7 \text{ kJ}\cdot\text{mol}^{-1}$) when the HOAc:DBN mole ratio is 1:1 or higher. Therefore, the complexes of [DBNH][OAc] observed in the liquid phase experiments are not formed in the aqueous solution. Moreover, this observation suggests that the complexes are formed due to dimerization of acetic acid, not by the second protonation of DBN.

Table S8. Measured Enthalpies of Solution of Crystalline [DBNH][OAc] in Water^a

| Solid [DBNH][OAc] dissolution in water | | | | |
|--|----------------------------|------------------------------|------------------------------------|---|
| experiment # | $m(\text{IL}) / \text{mg}$ | $n(\text{IL}) / \text{mmol}$ | $m(\text{H}_2\text{O}) / \text{g}$ | $\Delta_{\text{sol}}H_{\text{m}}^{\circ}(\text{I}) / \text{kJ}\cdot\text{mol}^{-1}$ |
| 1 | 39.80 | 0.2160 | 25.5492 | -41.25 |
| 2 | 29.83 | 0.1619 | 25.2320 | -41.62 |
| 3 | 88.09 | 0.4782 | 25.2868 | -41.45 |
| 4 | 38.53 | 0.2091 | 25.1852 | -40.90 |
| 5 | 57.48 | 0.3120 | 25.1546 | -40.13 |
| Average | | | | -41.07 ± 0.53 |

^a $m(\text{IL})$ is the mass of the [DBNH][OAc] sample, $n(\text{IL})$ is the molar amount of the [DBNH][OAc] sample, $m(\text{H}_2\text{O})$ is the mass of water in the cell, $\Delta_{\text{sol}}H_{\text{m}}^{\circ}(\text{I})$ is the enthalpy of solution of crystalline [DBNH][OAc] in water.

Table S9. Measured Enthalpies of Solution of DBN in Water and Water + Acetic Acid Solutions^a

| DBN dissolution in water + acetic acid solutions | | | | | | | |
|--|-------------------------|---------------------------|--------------------------|----------------------------|--------------------------------|--------------------------------|---|
| experiment # | $m(\text{DBN})$ / mg | $n(\text{DBN})$ / mmol | $m(\text{HOAc})$ / mg | $n(\text{HOAc})$ / mmol | $m(\text{H}_2\text{O})$ / g | $n(\text{HOAc})/n(\text{DBN})$ | $\Delta_{\text{sol}}H_m^\circ$ (III) / $\text{kJ}\cdot\text{mol}^{-1}$ |
| 1 | 32.67 | 0.2631 | 5.27 | 0.0877 | 24.7836 | 0.33 | -58.24 |
| 2 | 33.81 | 0.2723 | 8.18 | 0.1362 | 24.8544 | 0.50 | -67.53 |
| 3 | 57.91 | 0.4663 | 25.46 | 0.4239 | 25.2339 | 0.91 | -89.39 |
| 4 | 62.50 | 0.5033 | 29.75 | 0.4954 | 24.9206 | 0.98 | -93.04 |
| 5 | 60.59 | 0.4879 | 30.08 | 0.5010 | 25.1986 | 1.03 | -92.72 |
| 6 | 62.53 | 0.5035 | 30.27 | 0.5041 | 25.3576 | 1.00 | -92.20 |
| 7 | 63.50 | 0.5114 | 30.26 | 0.5038 | 25.3425 | 0.99 | -94.22 |
| 8 | 48.61 | 0.3914 | 25.86 | 0.4306 | 24.9031 | 1.10 | -93.87 |
| 9 | 30.84 | 0.2483 | 29.82 | 0.4966 | 24.9785 | 2.00 | -92.23 |
| 10 | 31.88 | 0.2567 | 30.84 | 0.5135 | 25.8311 | 2.00 | -92.29 |
| 11 | 19.45 | 0.1566 | 28.21 | 0.4698 | 24.9879 | 3.00 | -92.83 |
| | | | | | | Average | -92.92 ± 0.71 |
| DBN dissolution in water | | | | | | | |
| experiment # | $m(\text{DBN})$ / mg | $n(\text{DBN})$ / mmol | | | | $m(\text{H}_2\text{O})$ / g | $\Delta_{\text{sol}}H_m^\circ$ (IV) / $\text{kJ}\cdot\text{mol}^{-1}$ |
| 1 | 148.50 | 1.1958 | | | | 25.7292 | -39.07 |
| 2 | 76.75 | 0.6181 | | | | 25.0536 | -39.65 |
| 3 | 69.75 | 0.5617 | | | | 25.2523 | -39.35 |
| 4 | 34.77 | 0.2800 | | | | 24.9978 | -39.89 |
| | | | | | | Average | -39.49 ± 0.31 |

^a $m(i)$ is the mass of component i , $n(i)$ is the molar amount of component i , $n(\text{HOAc})/n(\text{DBN})$ is the mole ratio of acetic acid and DBN, $\Delta_{\text{sol}}H_m^\circ$ (III) is the enthalpy of solution of liquid DBN in water + acetic acid solution, $\Delta_{\text{sol}}H_m^\circ$ (IV) is the enthalpy of solution of liquid DBN in water.

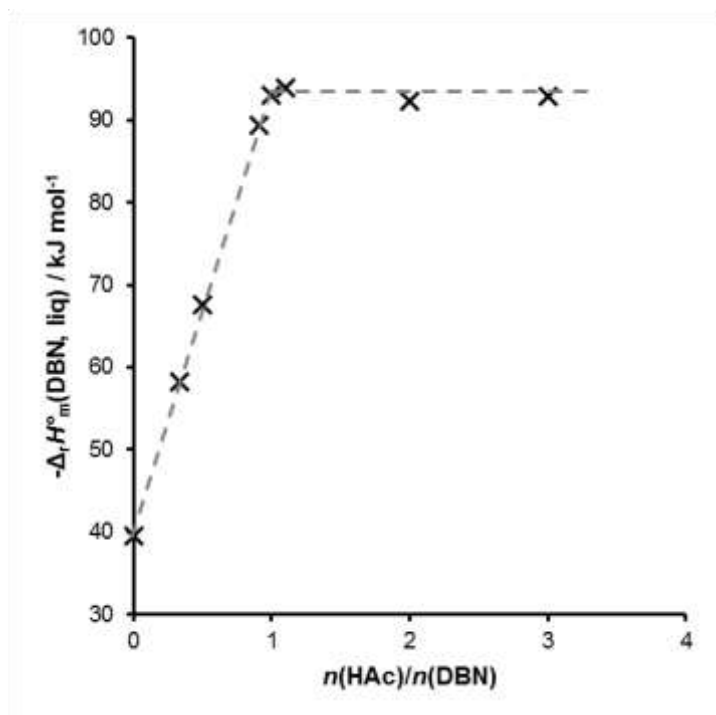


Figure S3. Enthalpy of solution of DBN in water and water + acetic acid solutions.

Table S10. GC Results for Infinite Dilution Activity Coefficients (298.15 K), Solution Enthalpies (298.15 K) and Regressed Parameters of Organic Solvents in [DBNH][OAc]^a

| Solute <i>i</i> | Temperature interval (K) | <i>a</i> | <i>b</i> (K) | γ_i^∞ | $\Delta_{\text{sol}}H_m^{\text{A/L}} / \text{kJ}\cdot\text{mol}^{-1}$ |
|------------------------------|--------------------------|----------|--------------|-------------------|---|
| <i>alkanes</i> | | | | | |
| decane | 303-323 | 3.1751 | 890.8 | 474.85 | 7.40 |
| undecane | 303-323 | 3.4312 | 1084.6 | 1174.93 | 9.02 |
| dodecane | 303-323 | 3.4211 | 1239.2 | 1953.54 | 10.30 |
| <i>alkenes</i> | | | | | |
| 1-decene | 303-323 | 3.6065 | 740.73 | 441.83 | 6.16 |
| 1-dodecene | 303-323 | 3.9653 | 919.77 | 1153.12 | 7.65 |
| <i>alkylbenzene</i> | | | | | |
| butylbenzene | 303-323 | 2.3952 | 194.87 | 21.09 | 1.62 |
| pentylbenzene | 303-323 | 3.5131 | 227.88 | 72.05 | 1.89 |
| <i>alcohols</i> | | | | | |
| methanol | 303-323 | -0.8708 | 156.3 | 0.71 | 1.30 |
| ethanol | 303-323 | -1.0409 | 356.65 | 1.17 | 2.97 |
| 1-propanol | 303-323 | -0.5926 | 409.89 | 2.19 | 3.41 |
| 1-butanol | 303-323 | -0.7076 | 596.65 | 3.63 | 4.96 |
| 1-pentanol | 303-323 | -0.4374 | 760.75 | 8.28 | 6.32 |
| <i>polar solvents</i> | | | | | |
| Acetone | 303-323 | -0.3357 | 108.62 | 1.03 | 0.90 |
| Acetonitrile | 303-323 | -0.073 | -272.08 | 0.43 | -2.26 |
| Tetrahydrofuran | 303-323 | 0.296 | -617.07 | 0.17 | -5.13 |
| Dichloromethane | 303-323 | 6.0302 | -1848 | 0.85 | -15.36 |
| Trichloromethane | 303-323 | 8.607 | -2313.4 | 0.84 | -19.23 |

^a *a-b* are the regressed parameters for Eq. 17, γ_i^∞ is the infinite dilution activity coefficient of compound *i*, $\Delta_{\text{sol}}H_m^{\text{A/L}}$ is the enthalpy of partial molar excess enthalpy at infinite dilution of compound *i*.

DETAILS ON GC MEASUREMENTS OF ACTIVITY COEFFICIENTS

Chromosorb W/AW-DMCS 100/120 mesh was used as solid support for the ionic liquid in the GC column. The chromosorb has been subjected to vacuum treatment with heating in order to remove traces of adsorbed moisture.

Coating the solid support material with the ionic liquid was performed by dispersing a certain portion of chromosorb in a solution of the ionic liquid in dichloromethane followed by evaporation of the solvent using a rotating evaporator. The chromosorb was weighed before and after the coating process. The experiments were performed with a Hewlett Packard gas-chromatograph equipped with a flame ionization detector. Nitrogen was used as carrier gas. GC column (stainless steel) with length 45 cm with an inside diameter of 0.40 cm was used. The amount of stationary phase (ionic liquid) was around 5.4 mmol. The mass of the stationary phase was determined with a precision of ± 0.0003 g. In order to avoid possible residual adsorption effects of the solutes on chromosorb, the amount of ionic liquid was about 35 mass per cent of the support material.

According to Cruickshank et al.⁸ the following equation for the data treatment was used:

$$\ln \gamma_{i,3}^{\infty} = \ln \left(\frac{n_3 \cdot R \cdot T}{V_N \cdot p_1^0} \right) - \frac{B_{11} - V_1^0}{RT} \cdot p_1^0 + \frac{2 \cdot B_{12} - V_1^{\infty}}{RT} \cdot J \cdot p_0 \quad (\text{S5})$$

where $\gamma_{i,3}^{\infty}$ is the activity coefficient of component i at infinite dilution in the stationary phase (index 3), p_1^0 is the vapor pressure of the pure liquid solute, n_3 is the number of moles of the stationary phase component (ionic liquid) on the column and V_N is the standardized retention volume obtained by:

$$V_N = J \cdot U_0 \cdot (t_r - t_G) \cdot \frac{T_{col}}{T_f} \cdot \left[1 - \frac{p_{ow}}{p_o} \right] \quad (\text{S6})$$

where t_r is the retention time, t_G is the dead time, and U_0 is the flow rate, measured by a soap bubble flowmeter, T_{col} is the column temperature, T_f is flowmeter temperature, p_{ow} is saturation pressure of water at T_f , p_o is the pressure at the column outlet.

The second and third term in Eq. S5 are correction terms which arise from the non-ideality of mobile gaseous phase. B_{11} is the second virial coefficient of the solute, B_{12} the mixed

virial coefficient of the solute (1) with the carrier gas nitrogen (2). V_1^0 is the liquid molar volume of pure solute and V_1^∞ is the partial molar volume of solute in the ionic liquid at infinite dilution.

The factor J appearing in Eqs. S5 and S6 corrects for the influence of the pressure drop along the column given by⁹:

$$J = \frac{3}{2} \cdot \frac{(p_i / p_o)^2 - 1}{(p_i / p_o)^3 - 1} \quad (S7)$$

where p_i and p_o are the inlet and the outlet pressure of the GC column respectively.

The outlet pressure p_o was kept equal to the atmospheric pressure. The pressure drop ($p_i - p_o$) was varied between (20.3 and 101.3 kPa), providing suitable retention times with sharp peaks. The pressure drop and the outlet pressure were measured using a membrane manometer with an uncertainty of ± 0.2 kPa.

Volumes of the samples injected into the GC probes were (0.5 to 2 μ l). No differences in retention times t_r were found by injecting individual pure components or their mixtures. This fact indicates that different concentrations of the solute in the stationary phase caused by different ratios of the injected amounts of solute and the amount of stationary phase do not affect the results and it can be concluded that in all cases the state of infinite dilution was realised to a high degree of approximation. Experiments were carried out at 4 to 5 temperatures between 303 K and 353 K. The temperature of the GC column was maintained constant to within ± 0.01 K. At a given temperature each experiment was repeated at least twice to check the reproducibility. Retention times were generally reproducible within (0.01 to 0.03) min. Absolute values of retention times varied between (3 to 30) min depending on the individual solute. At each temperature values of the dead time t_G identical to the retention time of a non-retainable component were measured. While our GC was equipped with a flame-ionization detector, methane⁸ was used as non-retainable component under the assumption that the effect of solubility of methane in ionic liquid is negligible. This assumption has been justified by attestation of our experimental procedure with the reliable data on γ_i^∞ of hexane, heptane and benzene in hexadecane.¹⁰

In order to check the stability of the experimental conditions, such as the possible elution of the stationary phase by the nitrogen stream, the measurements of retention times were repeated systematically every (2 to 3) hours for tridecane. No changes of the retention times were observed during 2-3 days of continuous operation.

Data needed for calculating the correction terms in Eq. S5 have been obtained in the following way. Molar volumes of solutes V_1^0 were estimated using experimental values of their densities, partial molar volumes of solute at infinite dilution V_1^∞ have been assumed to be equal of V_1^0 . Values of B_{11} have been estimated according to Tsonopolous' method.¹¹ Critical parameters needed for the calculations were available from the literature.¹² If these data were not available, values of the critical pressure P_c , the critical temperature T_c , and the critical volume V_c were estimated using Lydersen's method.¹³ Acentric factors ω_i were calculated by Edmister equation.⁹ Values of B_{12} have also been estimated according to Tsonopolous' method. The mixed critical properties P_{cij} , T_{cij} , V_{cij} , Z_{cij} and mixed acentric factor ω_{ij} were calculated by equations given in the literature.^{11,14}

Values of vapor pressures p_1^0 of pure solutes are of a crucial importance for the reliability of γ_i^∞ . For alkanes these values were calculated using parameters of the Cox equation recommended by Ruzicka and Majer.¹⁵ For alkenes values of p_1^0 were calculated using parameters of the Cox equation recommended by Steele and Chirico.¹⁶ Vapor pressures of pure alcohols were calculated using coefficients of Wagner's equation recommended by Ambrose and Walton¹⁷. Specification of the sources of vapor pressures of other solutes was given in the previous papers of this series.¹⁸⁻¹⁹

The validity of the experimental procedure has been checked by comparison of our measured values of γ_i^∞ for hexane in hexadecane with those available in the literature.¹⁰ The procedure of the experimental error estimation was described in our previous work.¹⁰ Values of γ_i^∞ are estimated to be accurate within to ± 3 %.

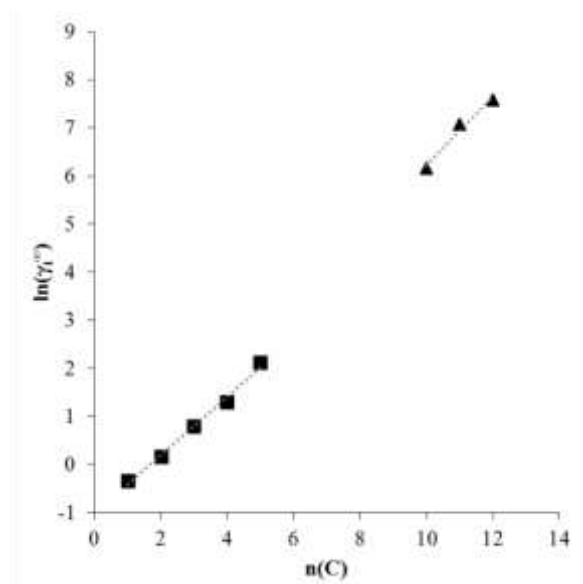


Figure S4. Values of $\ln \gamma_i^\infty$ of alkanes and alcohols in [DBNH][OAc] at 298 K as a function of carbon atoms number (▲ – alkanes, ■ – alcohols).

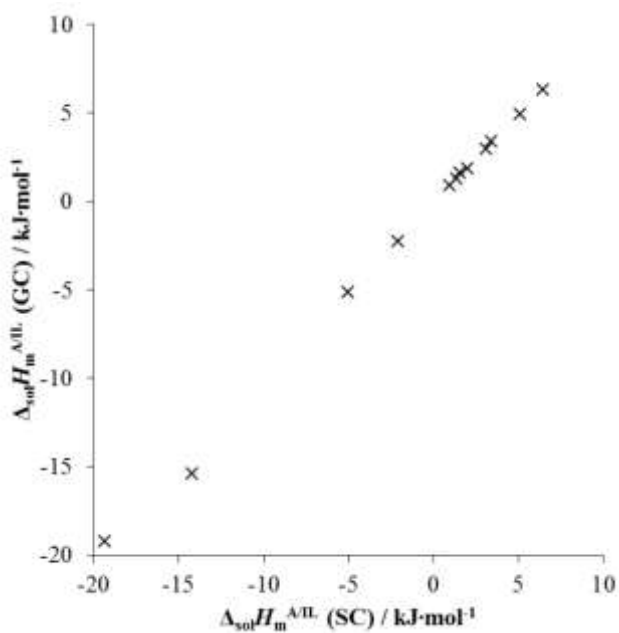


Figure S5. Comparison of solution enthalpies at infinite dilution of organic solutes in [DBNH][OAc] determined by solution calorimetry (SC) and by gas-liquid chromatography (GC) methods.

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