

Low-temperature heat capacity and the thermodynamic functions of a novel ether-based ionic liquid 1-(2-ethoxyethyl)-3-ethylimidazolium thiocyanate

Donglu Fu,^a Zongren Song,^{*a} Jiankang Liu,^a Jie Yang,^a Shilong Suo,^a Kunhao Liang,^{*b} Xiaoxue Ma,^{*a} Dawei Fang^a

^a Institute of Rare and Scattered Elements, College of Chemistry, Liaoning University, Shenyang, Liaoning 110036, China. E-mail: zongrensong@lnu.edu.cn.

^b School of Opto-Electronic Engineering, Zaozhuang University, Zaozhuang, Shandong 277160, China

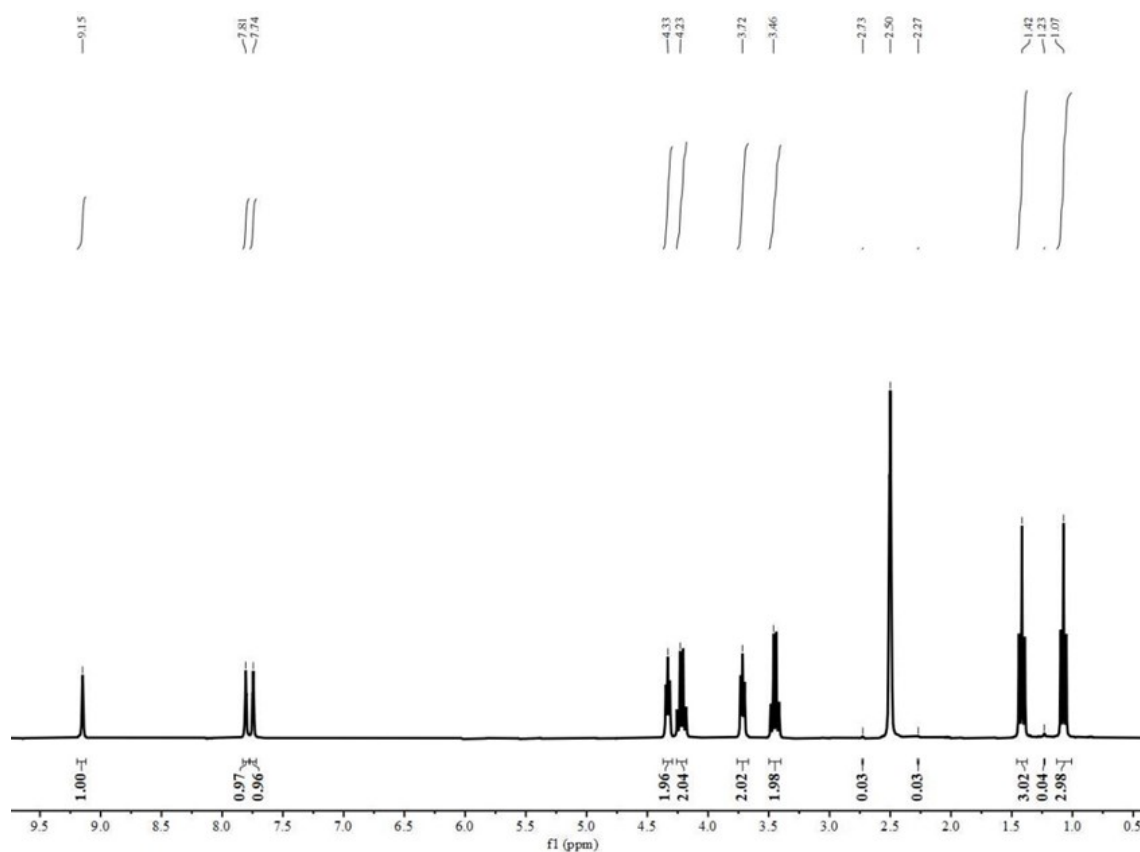


Figure S1. The ¹H-NMR spectroscopy of [C₂2O₂Im][SCN]

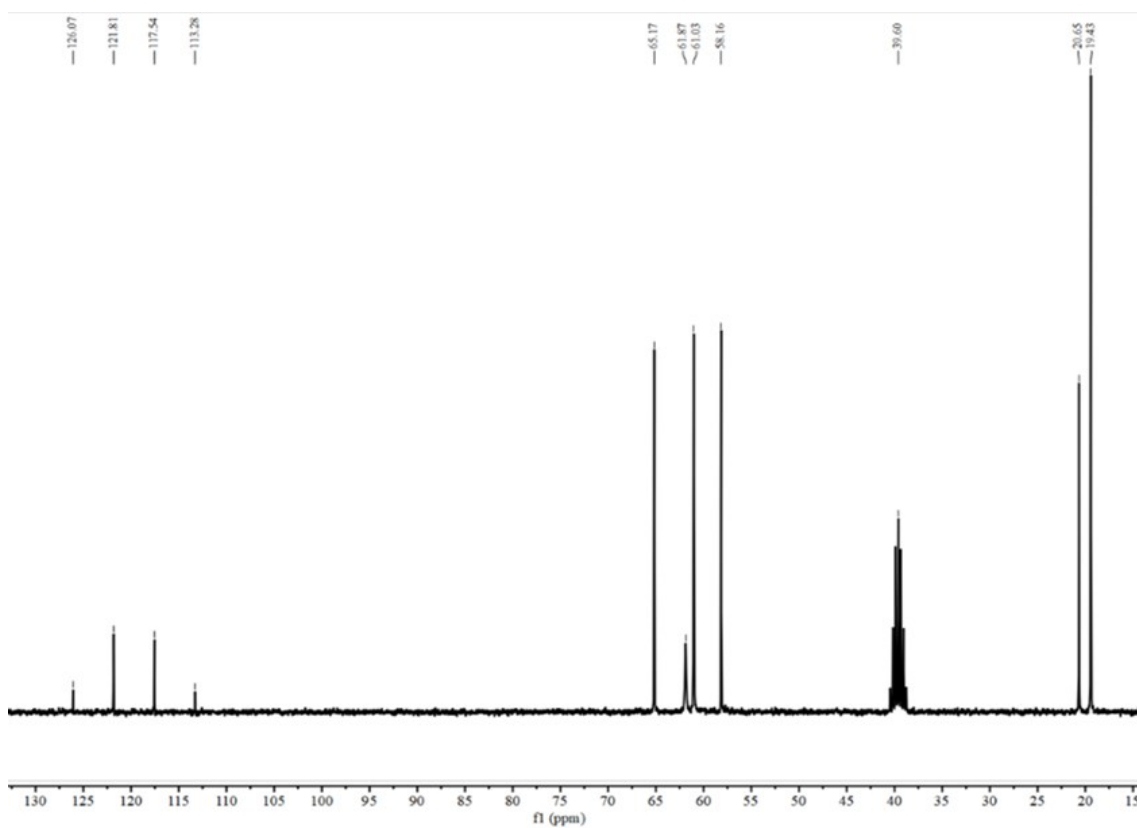


Figure S2. The ^{13}C -NMR spectroscopy of $[\text{C}_2\text{O}_2\text{Im}][\text{SCN}]$

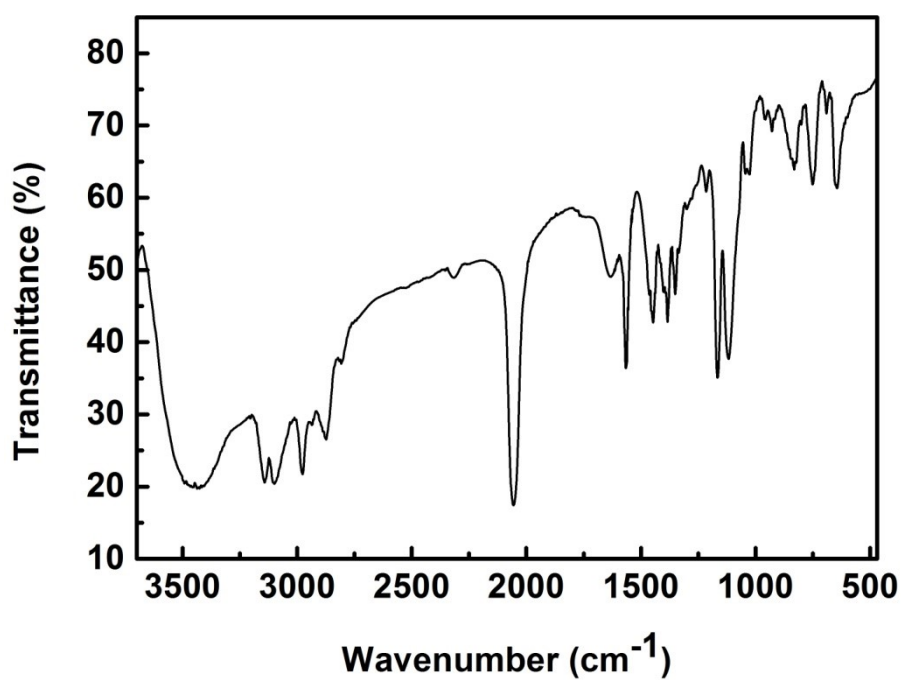


Figure S3. The FT-IR spectroscopy of $[\text{C}_2\text{O}_2\text{Im}][\text{SCN}]$

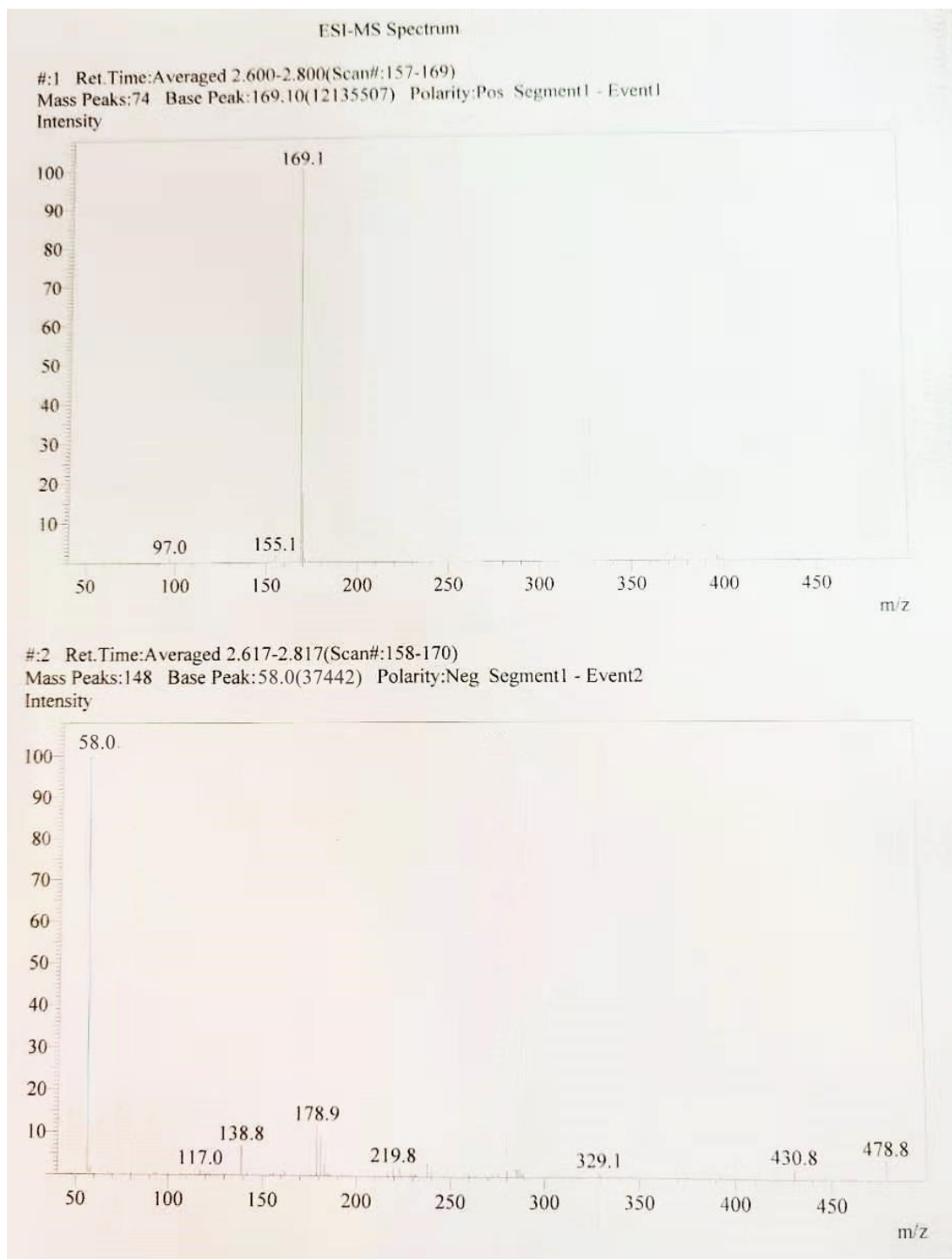


Figure S4. ESI-MS spectrum of $[C_{22}O_2Im][SCN]$

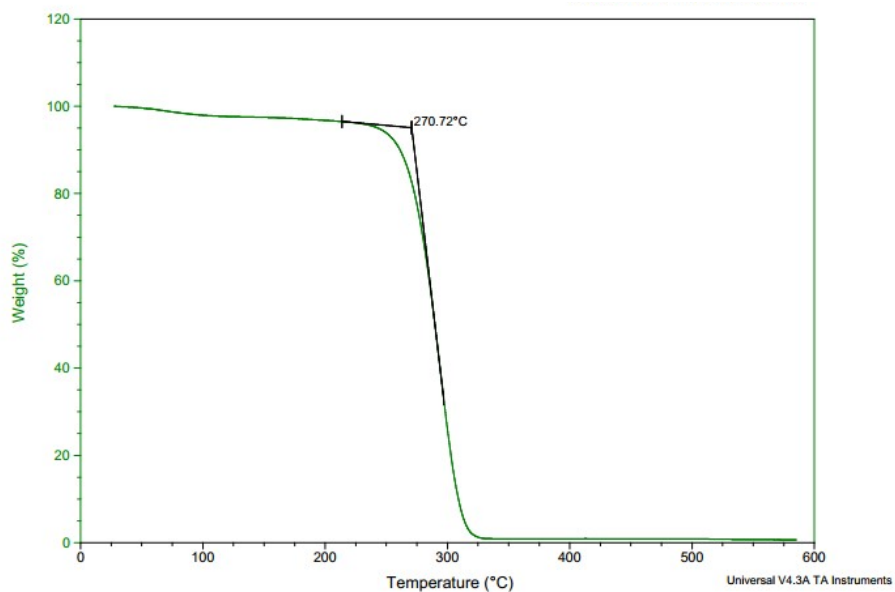


Figure S5. The TG spectroscopy of $[C_22O_2Im][SCN]$

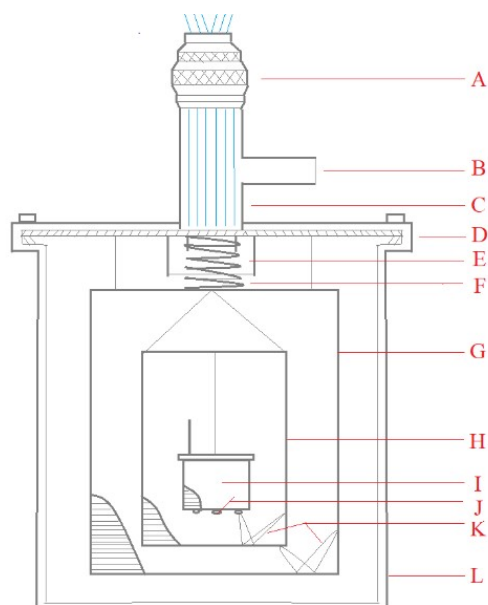


Figure S6. Cross-sectional diagram of adiabatic calorimetric cryostat: A is the sealing junction unit; B is the high vacuum system; C is the vacuum tube; D is the fuse gasket; E is the wire temperature control ring; F is the wire bundle; G and H are respectively the outer and inner adiabatic shields; I is the sample cell; J is the miniature platinum resistance thermometer; K are the chromel–copper thermocouples; L is a vacuum can.^{1,2}

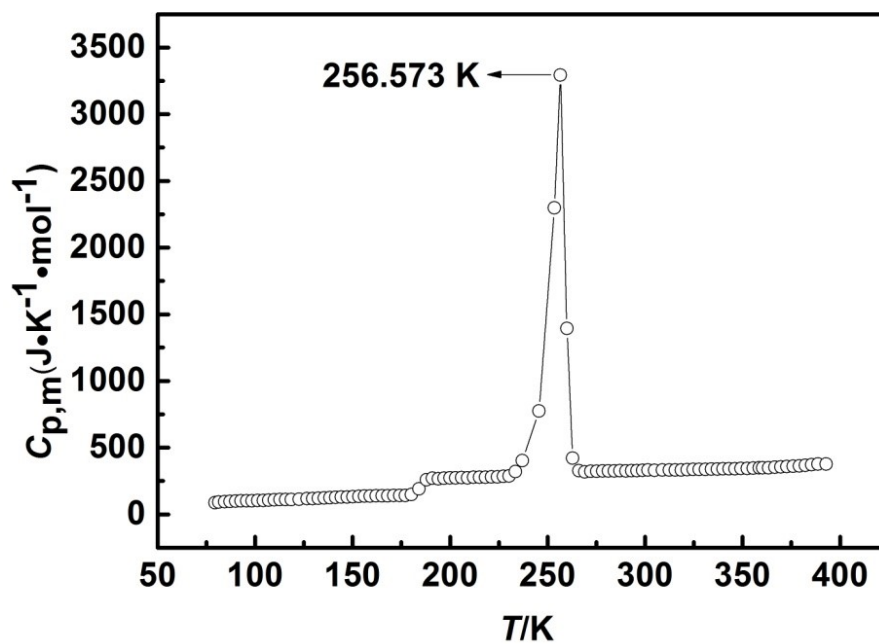


Figure S7. The experimental molar heat capacities in Table S6 of $[\text{C}_2\text{O}_2\text{IM}][\text{SCN}]$ in the temperature range from 79 K to 393 K.

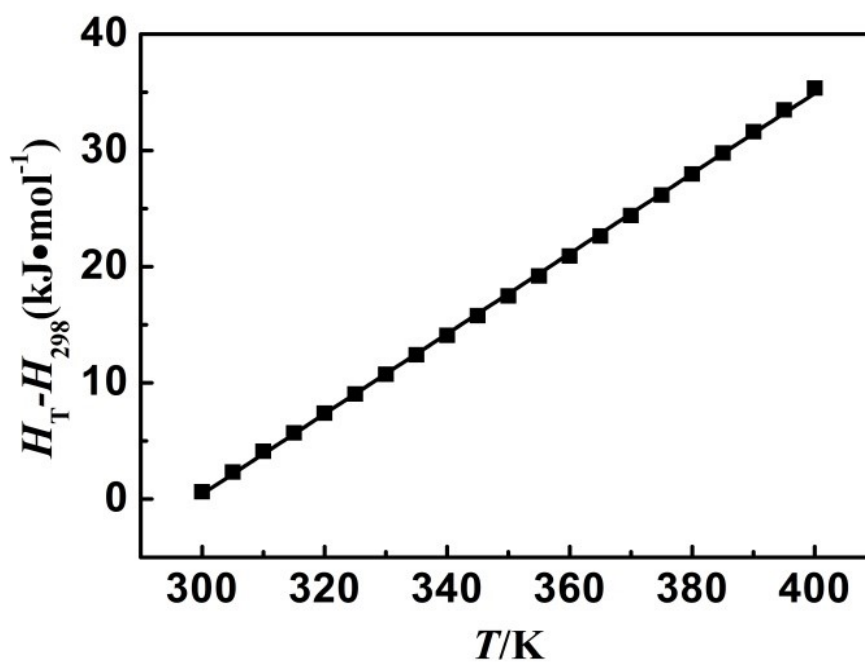


Figure S8. Plot of $H_T - H_{298}$ vs. T of $[\text{C}_2\text{O}_2\text{IM}][\text{SCN}]$.

$$(H_T - H_{298} = -103.0038 + 0.3448T, R^2 = 0.9997)$$

Table S1

The heat capacities of empty equivalent in the temperature range from (78.254 – 400.134) K.

T/K	$H_0/J\cdot K^{-1}$	T/K	$H_0/J\cdot K^{-1}$	T/K	$H_0/J\cdot K^{-1}$	T/K	$H_0/J\cdot K^{-1}$
78.254	5.22	158.346	8.57	242.690	9.88	326.245	10.34
80.542	5.40	161.498	8.60	246.459	9.89	329.205	10.34
83.156	5.57	164.498	8.69	249.309	9.91	332.654	10.36
85.870	5.69	167.289	8.76	252.298	9.93	335.701	10.37
88.854	5.90	170.534	8.81	255.475	9.94	338.546	10.39
91.654	6.08	173.865	8.89	258.596	9.96	341.400	10.39
94.569	6.26	176.198	8.92	261.455	9.98	344.654	10.41
97.438	6.37	179.536	8.99	264.506	10.02	347.790	10.41
100.286	6.57	183.265	9.04	267.670	10.03	350.865	10.42
103.256	6.70	186.897	9.11	270.617	10.04	354.450	10.42
106.574	6.83	189.888	9.17	273.581	10.09	357.241	10.42
108.899	6.96	192.756	9.24	276.512	10.12	360.341	10.42
111.901	7.09	195.856	9.30	279.654	10.16	363.457	10.42
114.849	7.19	198.712	9.35	282.759	10.18	366.579	10.43
117.759	7.32	201.805	9.41	285.798	10.20	369.798	10.43
120.780	7.48	204.709	9.46	288.651	10.25	372.475	10.44
124.802	7.60	207.886	9.51	291.852	10.25	375.789	10.44
128.799	7.71	211.178	9.58	295.235	10.24	378.423	10.44
131.805	7.78	214.262	9.65	298.175	10.26	381.897	10.45
134.612	7.89	217.355	9.68	301.275	10.26	385.245	10.45
137.603	7.99	220.133	9.79	304.361	10.27	388.103	10.45
140.700	8.09	223.480	9.95	307.257	10.28	391.324	10.46
143.260	8.18	226.649	10.19	310.578	10.30	394.245	10.44
146.390	8.26	229.690	9.78	313.678	10.31	397.312	10.46
149.450	8.31	232.750	9.77	316.865	10.31	400.134	10.46

152.378	8.39	235.638	9.81	319.745	10.32
155.539	8.46	238.780	9.84	322.896	10.33

The standard uncertainty (0.68 level of confidence): $u(T) = 0.001$ K. $u(p) = \pm 0.001$ MPa.

Table S2

The experimental molar heat capacities of α -Al₂O₃ in the temperature range from (79.432 – 400.854) K.

<i>T</i> /K	<i>C</i> _{p,m}	<i>T</i> /K	<i>C</i> _{p,m}	<i>T</i> /K	<i>C</i> _{p,m}	<i>T</i> /K	<i>C</i> _{p,m}
79.432	6.584	158.465	35.952	239.562	64.301	322.54	83.653
82.160	7.326	161.543	36.369	243.145	65.154	325.845	84.845
84.529	8.375	164.482	37.901	246.857	66.246	328.652	85.145
88.156	9.652	167.803	38.850	249.665	67.653	331.854	85.596
91.312	10.452	170.489	40.232	253.852	67.952	335.740	86.652
94.843	11.295	173.800	41.859	256.251	68.603	338.453	86.528
97.456	11.832	176.693	42.952	259.456	69.635	341.647	87.354
100.320	12.990	179.752	43.539	262.852	70.125	345.045	87.748
103.168	13.695	183.852	45.002	265.542	71.352	348.653	88.465
105.375	14.643	187.256	46.198	268.154	72.562	351.543	89.248
108.984	15.746	190.805	47.439	271.950	72.852	354.548	89.469
111.562	17.135	193.653	48.496	274.742	73.642	358.485	90.254
114.802	18.210	196.601	49.798	278.125	74.352	361.528	90.542
117.524	19.350	199.685	50.852	281.542	75.782	364.432	91.301
120.952	20.580	202.693	52.159	284.746	75.746	367.685	91.654
124.625	21.639	205.798	53.253	287.425	76.526	370.568	91.875
128.952	23.693	208.982	54.203	290.268	77.201	374.654	92.594
131.596	24.456	211.695	55.502	293.460	77.558	377.413	93.265
134.693	25.853	215.120	56.327	296.685	78.624	380.580	93.452
137.695	27.285	218.146	57.258	299.524	79.526	383.758	93.748

140.546	28.23	221.650	58.653	302.532	80.001	387.263	94.254
143.592	29.479	224.523	59.496	306.112	80.652	390.245	94.548
146.593	30.850	227.205	60.163	309.450	81.650	393.498	95.361
149.324	31.958	230.116	61.041	312.521	82.116	396.845	95.956
152.752	33.201	233.245	62.885	315.743	82.589	400.854	96.364
155.502	34.302	236.452	62.745	318.798	83.654		

The standard uncertainty (0.68 level of confidence): $u(T) = 0.001$ K. $u(p) = \pm 0.001$ MPa. The maximum permissible error of high precision automatic adiabatic calorimeter is ± 0.130 %.

Table S3

The experimental and fitted heat capacity values of empty equivalent and relative deviation in the temperature range of 78.245 K – 400.134 K.

T/K	$H_0/J \cdot K^{-1}$	$H_{0(f)}/J \cdot K^{-1}$	$A/\%$	T/K	$H_0/J \cdot K^{-1}$	$H_{0(f)}/J \cdot K^{-1}$	$A/\%$
78.254	5.22	5.241	-0.397	238.780	9.84	9.833	0.076
80.542	5.40	5.382	0.327	242.690	9.88	9.863	0.169
83.156	5.57	5.546	0.440	246.459	9.89	9.896	-0.060
85.870	5.69	5.715	-0.433	249.309	9.91	9.916	-0.059
88.854	5.90	5.898	0.030	252.298	9.93	9.932	-0.020
91.654	6.08	6.066	0.223	255.475	9.94	9.946	-0.063
94.569	6.26	6.236	0.381	258.596	9.96	9.961	-0.009
97.438	6.37	6.397	-0.424	261.455	9.98	9.977	0.026
100.286	6.57	6.550	0.304	264.506	10.02	10.000	0.201
103.256	6.70	6.702	-0.032	267.670	10.03	10.029	0.012
106.574	6.83	6.863	-0.478	270.617	10.04	10.059	-0.192
108.899	6.96	6.970	-0.139	273.581	10.09	10.091	-0.012
111.901	7.09	7.101	-0.153	276.512	10.12	10.122	-0.015
114.849	7.19	7.223	-0.453	279.654	10.16	10.151	0.091
117.759	7.32	7.337	-0.226	282.759	10.18	10.177	0.027
120.780	7.48	7.449	0.422	285.798	10.20	10.207	-0.064

124.802	7.60	7.589	0.144	288.651	10.25	10.248	0.018
128.799	7.71	7.720	-0.132	291.852	10.25	10.216	0.335
131.805	7.78	7.814	-0.437	295.235	10.24	10.238	0.022
134.612	7.89	7.899	-0.112	298.175	10.26	10.252	0.078
137.603	7.99	7.986	0.047	301.275	10.26	10.264	-0.036
140.700	8.09	8.074	0.195	304.361	10.27	10.273	-0.034
143.260	8.18	8.145	0.427	307.257	10.28	10.282	-0.018
146.390	8.26	8.230	0.361	310.578	10.30	10.291	0.087
149.450	8.31	8.312	-0.020	313.678	10.31	10.300	0.097
152.378	8.39	8.388	0.023	316.865	10.31	10.310	0.004
155.539	8.46	8.469	-0.106	319.745	10.32	10.319	0.011
158.346	8.57	8.539	0.359	322.896	10.33	10.329	0.006
161.498	8.60	8.617	-0.193	326.245	10.34	10.341	-0.010
164.498	8.69	8.688	0.021	329.205	10.34	10.351	-0.111
167.289	8.76	8.753	0.081	332.654	10.36	10.363	-0.034
170.534	8.81	8.826	-0.177	335.701	10.37	10.374	-0.036
173.865	8.89	8.897	-0.079	338.546	10.39	10.383	0.069
176.198	8.92	8.945	-0.279	341.400	10.39	10.391	-0.012
179.536	8.99	9.010	-0.226	344.654	10.41	10.400	0.097
183.265	9.04	9.079	-0.428	347.790	10.41	10.407	0.027
186.897	9.11	9.141	-0.339	350.865	10.42	10.413	0.064
189.888	9.17	9.189	-0.209	354.450	10.42	10.419	0.008
192.756	9.24	9.233	0.073	357.241	10.42	10.423	-0.026
195.856	9.30	9.279	0.224	360.341	10.42	10.426	-0.057
198.712	9.35	9.321	0.310	363.457	10.42	10.429	-0.082
201.805	9.41	9.367	0.455	366.579	10.43	10.431	-0.007

204.709	9.46	9.413	0.495	369.798	10.43	10.433	-0.027
207.886	9.51	9.469	0.431	372.475	10.44	10.435	0.052
211.178	9.58	9.536	0.457	375.789	10.44	10.437	0.029
214.262	9.65	9.612	0.394	378.423	10.44	10.439	0.007
217.355	9.68	9.705	-0.259	381.897	10.45	10.443	0.069
220.133	9.79	9.808	-0.180	385.245	10.45	10.447	0.031
223.480	9.95	9.962	-0.120	388.103	10.45	10.450	-0.004
226.649	10.19	10.147	0.425	391.324	10.46	10.454	0.053
229.690	9.78	9.762	0.188	394.245	10.4499	10.457	-0.071
232.750	9.77	9.727	0.442	397.312	10.461	10.459	0.020
235.638	9.81	9.830	-0.204	400.134	10.464	10.458	0.059

$H_{0(f)}$ is the fitted heat capacity value, A is the relative deviation.

Table S4

The experimental and fitted heat capacity values of $\alpha\text{-Al}_2\text{O}_3$ and relative deviation in the temperature range of 79.432 K – 400.854 K.

T/K	$C_{p,m}$	$C_{p,m(f)}$	$A/\%$	T/K	$C_{p,m}$	$C_{p,m(f)}$	$A/\%$
79.432	6.684	6.713	-0.430	239.562	64.301	64.046	0.399
82.160	7.486	7.516	-0.399	243.145	65.154	65.193	-0.059
84.529	8.225	8.210	0.185	246.857	66.246	66.398	-0.229
88.156	9.320	9.277	0.464	249.665	67.653	67.146	0.755
91.312	10.252	10.220	0.317	253.852	67.952	68.179	-0.333
94.843	11.295	11.299	-0.036	256.251	68.603	68.774	-0.248
97.456	12.102	12.119	-0.138	259.456	69.635	69.596	0.056
100.320	12.990	13.040	-0.385	262.852	70.225	70.505	-0.397
103.168	13.915	13.982	-0.478	265.542	71.352	71.243	0.153
105.375	14.693	14.730	-0.248	268.154	72.162	71.964	0.276
108.984	15.926	15.986	-0.376	271.950	72.852	72.993	-0.193

111.562	16.935	16.909	0.155	274.742	73.642	73.720	-0.105
114.802	18.021	18.097	-0.418	278.125	74.352	74.554	-0.271
117.524	19.135	19.117	0.093	281.542	75.582	75.340	0.321
120.952	20.458	20.429	0.141	284.746	75.746	76.033	-0.377
124.625	21.839	21.864	-0.113	287.425	76.526	76.589	-0.083
128.952	23.693	23.585	0.460	290.268	77.201	77.172	0.038
131.596	24.556	24.649	-0.376	293.460	77.558	77.836	-0.357
134.693	25.853	25.904	-0.197	296.685	78.624	78.539	0.108
137.695	27.225	27.127	0.361	299.524	79.526	79.196	0.416
140.546	28.230	28.291	-0.216	302.532	80.001	79.932	0.086
143.592	29.479	29.535	-0.190	306.112	80.652	80.833	-0.224
146.593	30.850	30.758	0.297	309.45	81.650	81.629	0.025
149.324	31.958	31.868	0.283	312.521	82.116	82.218	-0.124
152.752	33.201	33.252	-0.154	315.743	82.589	82.518	0.086
155.502	34.302	34.355	-0.155	318.798	83.654	83.488	0.199
158.465	35.552	35.534	0.050	322.54	83.853	84.091	-0.283
161.543	36.669	36.748	-0.214	325.845	84.845	84.630	0.254
164.482	37.901	37.895	0.015	328.652	85.145	85.095	0.058
167.803	39.185	39.178	0.018	331.854	85.596	85.635	-0.045
170.489	40.232	40.205	0.068	335.74	86.652	86.300	0.408
173.800	41.459	41.457	0.005	338.453	86.528	86.770	-0.279
176.693	42.652	42.540	0.263	341.647	87.354	87.327	0.031
179.752	43.539	43.675	-0.311	345.045	87.748	87.920	-0.196
183.852	45.002	45.180	-0.394	348.653	88.465	88.546	-0.091
187.256	46.198	46.418	-0.475	351.543	89.248	89.042	0.232
190.805	47.539	47.700	-0.338	354.548	89.469	89.549	-0.089
193.653	48.496	48.723	-0.466	358.485	90.254	90.197	0.063

196.601	49.798	49.778	0.040	361.528	90.542	90.683	-0.156
199.685	50.852	50.878	-0.051	364.432	91.301	91.134	0.183
202.693	52.159	51.947	0.407	367.685	91.654	91.623	0.034
205.798	53.253	53.049	0.385	370.568	91.875	92.043	-0.183
208.982	54.203	54.174	0.053	374.654	92.594	92.619	-0.028
211.695	55.402	55.130	0.494	377.413	93.265	92.998	0.287
215.120	56.327	56.329	-0.004	380.58	93.452	93.427	0.027
218.146	57.258	57.380	-0.212	383.758	93.748	93.855	-0.114
221.650	58.653	58.580	0.125	387.263	94.254	94.334	-0.085
224.523	59.496	59.545	-0.083	390.245	94.548	94.753	-0.217
227.205	60.163	60.426	-0.436	393.498	95.361	95.234	0.134
230.116	61.141	61.354	-0.348	396.845	95.956	95.764	0.200
233.245	62.885	62.309	0.925	400.854	96.364	96.467	-0.106
236.452	62.745	63.227	-0.763				

$C_{p,m(f)}$ is the fitted heat capacity value, A is the relative deviation.

Table S5

The experimental and recommended NIST heat capacity values of α -Al₂O₃, and relative deviation in the temperature range of 80 K - 395 K.

T/K	$C_{p,m(r)}$	$C_{p,m(e)}$	$A/\%$	T/K	$C_{p,m(r)}$	$C_{p,m(e)}$	$A/\%$
80	6.901	6.875	-0.378	240	64.184	64.493	0.482
85	8.234	8.262	0.345	245	65.649	65.542	-0.163
90	9.678	9.639	-0.405	250	67.076	67.346	0.403
95	11.221	11.223	0.017	255	68.466	68.191	-0.401
100	12.855	12.880	0.191	260	69.82	69.722	-0.141
105	14.567	14.530	-0.253	265	71.137	71.055	-0.115
110	16.347	16.275	-0.438	270	72.419	72.751	0.458
115	18.184	18.250	0.364	275	73.656	73.702	0.062

120	20.069	20.092	0.115	280	74.871	75.225	0.473
125	21.993	21.898	-0.432	285	76.053	75.778	-0.361
130	23.951	24.013	0.258	290	77.204	77.164	-0.052
135	25.935	26.012	0.296	295	78.324	77.997	-0.418
140	27.935	28.050	0.411	300	79.415	79.628	0.268
145	29.943	30.009	0.220	305	80.476	80.391	-0.105
150	31.952	32.005	0.166	310	81.509	81.774	0.325
155	33.957	34.045	0.260	315	82.514	82.398	-0.140
160	35.953	36.060	0.298	320	83.493	83.698	0.246
165	37.934	38.104	0.447	325	84.445	84.546	0.120
170	39.896	39.956	0.151	330	85.373	85.246	-0.148
175	41.836	42.006	0.406	335	86.276	86.560	0.329
180	43.752	43.601	-0.345	340	87.155	86.858	-0.340
185	45.640	45.424	-0.474	345	88.011	87.744	-0.304
190	47.499	47.357	-0.299	350	88.844	88.876	0.036
195	49.326	49.102	-0.454	355	89.656	89.533	-0.137
200	51.121	50.975	-0.285	360	90.447	90.380	-0.074
205	52.881	53.017	0.257	365	91.217	91.411	0.213
210	54.606	54.689	0.152	370	91.967	91.819	-0.161
215	56.295	56.301	0.011	375	92.698	92.685	-0.015
220	57.948	58.012	0.110	380	93.411	93.434	0.025
225	59.564	59.623	0.099	385	94.105	93.939	-0.177
230	61.141	60.979	-0.265	390	94.782	94.509	-0.288
235	62.682	62.817	0.215	395	95.441	95.680	0.250

$C_{p,m(r)}$ is recommended NIST values, $C_{p,m(e)}$ is the experimental heat capacity, A is the relative deviation.

Table S6

The second set of molar heat capacity experimental values of $[C_2O_2Im][SCN]$ in the temperature

range from 79.373 K to 392.829 K with 3 K intervals.

T/K	$C_{p,m}/J\cdot K^{-1}\cdot mol^{-1}$	T/K	$C_{p,m}/J\cdot K^{-1}\cdot mol^{-1}$	T/K	$C_{p,m}/J\cdot K^{-1}\cdot mol^{-1}$
79.373	85.950	180.100	147.560	295.937	327.875
81.458	90.763	183.966	191.268	298.713	328.520
84.370	94.461	187.875	259.495	301.481	330.723
87.200	96.423	190.944	270.757	304.881	330.494
90.045	97.921	194.000	266.897	308.898	330.880
92.866	100.040	196.997	270.144	312.513	331.909
95.668	100.931	199.912	272.855	315.582	332.493
98.490	102.022	202.899	273.833	318.643	332.866
101.336	103.216	205.954	275.517	321.706	334.283
104.208	104.284	209.008	273.494	324.768	335.541
107.071	106.978	212.060	276.478	327.839	336.313
109.925	108.696	215.114	277.911	330.932	337.175
112.816	109.457	218.170	278.282	334.021	337.812
115.701	110.331	221.251	279.435	337.071	339.396
118.588	111.325	224.357	280.011	340.108	340.462
122.642	114.088	227.415	285.635	343.119	340.821
126.689	116.942	230.360	287.588	346.187	340.865
129.598	118.578	233.540	321.055	349.271	342.488
132.539	120.870	237.123	401.630	352.363	343.880
135.514	123.203	245.532	775.114	355.464	345.987
138.467	124.869	253.422	2296.900	358.566	347.449
141.394	126.571	256.573	3292.554	360.291	347.396
144.306	128.621	259.870	1393.508	363.419	349.326
147.255	130.010	262.921	421.739	366.556	353.292
150.243	131.891	266.054	327.408	369.690	355.008

153.213	133.822	269.158	317.989	372.825	358.212
156.167	135.316	272.238	322.196	375.965	360.314
159.112	136.865	275.269	322.761	379.119	361.359
162.099	137.912	278.236	323.757	382.281	366.896
165.124	138.944	281.251	324.581	385.454	372.556
168.135	139.620	284.297	324.990	388.638	375.818
171.137	140.817	287.249	326.329	392.829	375.492
174.133	141.570	290.168	325.812		
177.120	141.950	293.090	327.169		

Notes: The standard uncertainty (0.68 level of confidence): $u(T) = 0.001$ K, $u(p) = 0.001$ MPa. The expanded uncertainties $U(C_{p,m})$ is at 0.95 confidence level, ($k \approx 2$), $U_c(C_{p,m}) = 0.002 \cdot C_{p,m}$.

Notes and references

- [1] Z.C. Tan, Q. Shi, B.P. Liu, H.T. Zhang, A Fully Automated Adiabatic Calorimeter For Heat Capacity Measurement Between 80 And 400 K, *J. Therm. Anal. Calorim.* 2008, **92**, 367-374.
- [2] K.H. Liang, Z.W. Lu, C.X. Ren, J. Wei, D. W. Fang, Feasibility of 1-Ethyl-4-butyl-1,2,4-triazolium Acetyl Amino Acid Ionic Liquids as Sustainable Heat-Transfer Fluids, *ACS Sustainable Chem. Eng.* 2022, **10**, 3417–3429.