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Contents lists available at ScienceDirect

J. Chem. Thermodynamics

journal homepage: [www.elsevier.com/locate/jct](http://www.elsevier.com/locate/jct)

# Building blocks for ionic liquids: Vapor pressures and vaporization enthalpies of 1-(*n*-alkyl)-imidazoles

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## ARTICLE INFO

### Article history:

Received 5 April 2011

Received in revised form 26 April 2011

Accepted 2 May 2011

Available online 10 May 2011

### Keywords:

Alkyl-imidazoles

Transpiration method

Vapor pressure

Enthalpy of vaporization

## ABSTRACT

Vapor pressures of the linear 1-(*n*-alkyl)-imidazoles with the alkyl chain C<sub>3</sub>, C<sub>5</sub>–C<sub>7</sub>, and C<sub>9</sub>–C<sub>10</sub> have been measured by the transpiration method. The molar enthalpies of vaporization  $\Delta_f^{\text{H}}H_m$  of these compounds were derived from the temperature dependencies of vapor pressures. A linear correlation of enthalpies of vaporization  $\Delta_f^{\text{H}}H_m$  (298.15 K) of the 1-(*n*-alkyl)-imidazoles with the chain length has been found.

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## 1. Introduction

Ionic liquids (ILs) have gained a large and increasing interest over the past years. Since they have no significant vapor pressure a number of interesting applications such as solvents for new catalytic reactions and other chemical production processes as well as separation processes with respect to a “green chemistry”. Striking types of reactions are Friedel–Crafts alkylations or Diels–Alder reactions [1]. Many ILs are thermally stable, and their decomposition begins often at temperatures above 200 °C. The main decomposition products of imidazolium based ionic liquids are the appropriate 1-alkyl-imidazoles, which are one of the most common building blocks in the synthesis of ionic liquids. Processes in which ILs release 1-alkyl-imidazoles under certain conditions are not properly studied yet. The fate and transport of released 1-alkyl-imidazoles in environment as well as biodegradation to a large extent depends on their vapor pressure and vaporization enthalpy. In the current work we have performed a systematic determination of the vapor pressures and

vaporization enthalpies of a series of 1-alkyl-imidazoles with the chain length C<sub>3</sub>, C<sub>5</sub>–C<sub>7</sub>, and C<sub>9</sub>–C<sub>10</sub> (see figure 1).

## 2. Experimental

### 2.1. Materials

Samples of 1-alkyl-imidazoles with the chain length C<sub>3</sub>, C<sub>5</sub>, C<sub>7</sub>, C<sub>9</sub>, and C<sub>11</sub> were prepared and purified at the Poznań University of Technology.

Sodium (2.3 g/0.1 mol) was added to 75 mL of anhydrous methanol and the imidazole (0.1 mol) was dissolved. The appropriate amount (0.11 mol) of one of the bromoalkane (bromopropane, bromopentane, bromoheptane, bromononane, or bromoundecane) was added and the mixture was stirred for 6 h at 338 K. Precipitated sodium bromide was filtered and the methanol was removed. The final product: 1-propyl-, 1-pentyl-, 1-heptyl-, 1-nonyl-, or 1-undecyl-imidazole was twice distilled under reduced pressure (1 Torr). The yields were between 68% and 91%.

Samples of 1-alkyl-imidazoles with the chain length C<sub>6</sub>, and C<sub>10</sub> were prepared and purified at IoLiTec. The degree of purity was controlled before measurements using a Hewlett Packard gas chromatograph 5890 Series II equipped with a flame ionization detector and a Hewlett Packard 3390A integrator. The carrier gas (nitrogen) flow was 12.1 cm<sup>3</sup> · s<sup>−1</sup>. A capillary column HP-5 (station-

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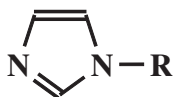


FIGURE 1. 1-Alkyl-imidazoles studied in this work with R = C<sub>3</sub>, C<sub>5</sub>–C<sub>7</sub>, and C<sub>9</sub>–C<sub>10</sub>.

ary phase crosslinked 5% PH ME silicone) was used with a column length of 30 m, an inside diameter of 0.32 mm, and a film thickness of 0.25 μm. The standard temperature program of the GC was T = 333 K for 180 s followed by a heating rate of 0.167 K · s<sup>−1</sup> to T = 523 K. No impurities (greater than mass fraction 0.003) could

TABLE 1

Results from measurements of the vapor pressure *p* of the liquid 1-(*n*-alkyl)-imidazoles using the transpiration method.

<i>T</i> <sup>a</sup> /K	<i>m</i> <sup>b</sup> /mg	<i>V</i> <sub>(N<sub>2</sub>)</sub> <sup>c</sup> /dm <sup>3</sup>	Gas-flow/(dm <sup>3</sup> /h)	<i>p</i> <sup>d</sup> /Pa	( <i>p</i> <sub>exp</sub> − <i>p</i> <sub>calc</sub> )/Pa	Δ <sub>f</sub> <sup>g</sup> <i>H</i> <sub>m</sub> /(kJ · mol <sup>−1</sup> )
1-Propylimidazole Δ <sub>f</sub> <sup>g</sup> <i>H</i> <sub>m</sub> (298.15 K) = 61.05 ± 0.18 kJ · mol <sup>−1</sup>						
$\ln(p/\text{Pa}) = \frac{296.7}{R} - \frac{82095.3}{R(T/K)} - \frac{70.3}{R} \ln\left(\frac{T/K}{298.15}\right)$						
279.1	1.22	10.71	5.54	2.59	0.11	62.39
283.4	0.97	5.69	5.51	3.83	0.10	62.09
288.3	0.75	2.85	5.51	5.89	0.06	61.74
290.4	0.84	2.70	3.60	7.00	−0.02	61.59
293.3	0.67	1.73	4.96	8.81	−0.22	61.39
296.3	0.85	1.70	3.65	11.16	−0.50	61.18
298.5	0.79	1.29	5.51	13.85	−0.14	61.02
301.6	0.92	1.14	3.61	18.16	0.15	60.81
304.1	0.86	0.885	2.31	21.65	−0.33	60.63
305.5	0.89	0.802	0.80	24.59	0.06	60.53
307.5	1.99	1.57	3.63	28.32	−0.31	60.39
312.6	0.86	0.450	0.79	43.02	0.96	60.03
313.4	1.18	0.597	2.37	44.31	−0.31	59.98
316.6	2.34	0.904	3.62	57.94	1.66	59.75
319.7	1.10	0.371	0.79	67.24	−2.87	59.53
323.2	1.09	0.280	1.12	87.18	−2.14	59.29
325.2	0.96	0.212	0.79	102.53	0.24	59.15
328.5	2.96	0.512	1.02	128.90	1.52	58.92
332.3	3.43	0.480	0.80	160.63	−2.31	58.65
333.5	2.17	0.279	1.12	173.97	−1.90	58.56
337.0	1.99	0.201	0.80	222.87	3.95	58.32
339.5	3.31	0.281	1.12	264.14	9.01	58.14
341.0	2.72	0.213	0.80	286.06	5.92	58.03
1-Pentylimidazole Δ <sub>f</sub> <sup>g</sup> <i>H</i> <sub>m</sub> (298.15 K) = 69.05 ± 0.51 kJ · mol <sup>−1</sup>						
$\ln(p/\text{Pa}) = \frac{324.43}{R} - \frac{94959.72}{R(T/K)} - \frac{86.9}{R} \ln\left(\frac{T/K}{298.15}\right)$						
308.2	2.42	8.44	4.65	5.10	0.09	68.18
313.3	2.67	6.31	4.86	7.75	0.03	67.74
318.3	3.16	4.72	4.65	11.81	0.21	67.30
323.7	2.66	2.83	4.86	16.86	−0.84	66.83
328.3	2.84	1.94	4.65	26.13	1.08	66.43
333.7	1.52	0.800	1.41	34.11	−2.99	65.97
338.5	3.17	1.11	1.85	52.29	0.36	65.55
345.8	2.33	0.484	0.97	85.73	1.02	64.91
348.3	3.06	0.585	1.85	95.16	−4.43	64.70
350.7	2.35	0.339	0.97	124.64	8.62	64.49
353.2	2.52	0.329	1.41	136.95	1.31	64.27
355.9	2.22	0.242	0.97	165.32	5.22	64.04
358.1	5.64	0.558	2.09	178.16	−4.68	63.85
360.8	2.89	0.242	0.97	214.73	0.12	63.61
363.1	4.99	0.377	1.41	237.70	−7.72	63.41
366.3	3.76	0.226	0.97	299.29	4.55	63.13
1-Hexylimidazole Δ <sub>f</sub> <sup>g</sup> <i>H</i> <sub>m</sub> (298.15 K) = 73.06 ± 0.23 kJ · mol <sup>−1</sup>						
$\ln(p/\text{Pa}) = \frac{338.66}{R} - \frac{101447.3}{R(T/K)} - \frac{95.2}{R} \ln\left(\frac{T/K}{298.15}\right)$						
309.2	1.388	9.55	6.71	2.34	0.00	72.02
311.2	1.465	8.17	6.92	2.86	0.07	71.83
314.2	1.424	6.27	6.53	3.64	−0.01	71.54
317.2	1.574	5.16	7.00	4.87	0.14	71.25
318.4	1.510	4.54	4.78	5.45	0.22	71.14
320.2	1.421	3.78	6.50	6.01	−0.09	70.96
323.2	0.917	2.02	4.05	7.33	−0.45	70.68
323.2	2.066	4.38	4.78	7.71	−0.08	70.68
326.1	1.585	2.55	3.90	9.90	0.07	70.41
328.5	1.902	2.55	4.78	12.19	0.31	70.18
329.2	1.636	2.16	3.81	12.33	−0.22	70.11
332.1	1.384	1.45	3.88	15.31	−0.38	69.84
333.2	2.209	2.15	4.78	16.82	−0.23	69.73
335.2	1.468	1.21	4.03	19.83	0.01	69.54
338.2	1.534	1.04	3.85	23.80	−0.91	69.26
338.4	2.094	1.35	4.78	25.27	0.20	69.24

(continued on next page)

TABLE 1 (continued)

$T^a/\text{K}$	$m^b/\text{mg}$	$V_{(\text{N}_2)}^c/\text{dm}^3$	Gas-flow/(dm <sup>3</sup> /h)	$p^d/\text{Pa}$	$(p_{\text{exp}} - p_{\text{calc}})/\text{Pa}$	$\Delta_f^g H_m/(\text{kJ} \cdot \text{mol}^{-1})$
341.1	1.355	0.705	1.06	31.11	0.65	68.98
343.1	0.634	0.294	1.36	35.23	0.13	68.79
344.1	1.446	0.633	1.03	36.84	−0.94	68.69
347.1	1.505	0.531	1.06	45.79	−0.52	68.41
348.1	1.923	0.634	1.36	49.59	−0.15	68.31
350.0	1.468	0.426	1.02	55.65	−0.87	68.13
353.0	1.873	0.453	1.36	67.62	−1.09	67.85
353.2	1.384	0.321	1.07	69.49	−0.13	67.83
355.1	1.578	0.322	1.02	78.97	0.21	67.65
355.8	2.672	0.518	1.07	84.84	2.44	67.58
357.1	1.625	0.293	1.03	89.70	0.16	67.46
358.2	6.043	0.996	4.78	98.58	2.57	67.35
359.2	1.662	0.266	1.06	101.39	−0.85	67.26
360.1	2.005	0.295	1.07	111.50	3.34	67.17
363.2	2.344	0.294	1.36	130.16	−0.78	66.88
1-Heptylimidazole $\Delta_f^g H_m (298.15 \text{ K}) = 76.78 \pm 0.27 \text{ kJ} \cdot \text{mol}^{-1}$						
$\ln(p/\text{Pa}) = \frac{350.64}{R} - \frac{107638.6}{R(T/\text{K})} - \frac{103.5}{R} \ln\left(\frac{T/\text{K}}{298.15}\right)$						
298.5	0.521	23.84	8.08	0.30	0.00	76.75
300.5	0.475	18.18	8.08	0.36	−0.01	76.54
303.5	0.532	14.70	8.02	0.49	0.00	76.23
303.5	0.504	14.06	7.96	0.48	−0.01	76.23
305.5	0.475	11.45	8.08	0.56	−0.04	76.02
306.5	0.704	14.11	8.06	0.68	0.02	75.92
307.5	0.504	9.40	8.06	0.72	−0.01	75.82
309.5	0.749	11.58	8.08	0.88	0.00	75.61
312.5	0.749	8.70	8.03	1.17	0.00	75.30
314.7	0.531	5.46	4.55	1.44	0.01	75.07
318.5	0.746	4.89	4.19	2.06	0.05	74.68
319.6	0.512	3.34	4.55	2.27	0.04	74.56
321.5	0.787	4.09	4.09	2.61	−0.01	74.37
321.6	0.606	3.06	4.08	2.69	0.05	74.36
322.2	0.535	2.77	4.49	2.86	0.08	74.30
324.5	0.715	2.85	4.07	3.41	0.03	74.06
324.6	0.633	2.73	4.55	3.42	0.01	74.05
327.5	0.778	2.39	4.10	4.41	0.06	73.75
329.6	0.615	1.75	4.55	5.21	0.05	73.53
329.9	0.850	2.17	4.07	5.32	0.03	73.50
332.3	0.593	1.35	4.49	6.50	0.08	73.25
332.9	0.371	0.750	1.00	6.72	−0.02	73.19
333.4	0.789	1.50	4.09	7.14	0.13	73.14
334.6	0.595	1.14	4.55	7.72	0.02	73.01
335.8	0.666	1.08	1.01	8.36	−0.10	72.89
339.4	0.783	0.945	2.03	11.24	0.08	72.52
341.7	0.721	0.762	1.02	12.82	−0.44	72.28
342.3	1.048	1.12	4.49	13.79	−0.07	72.22
344.3	0.836	0.685	1.00	16.54	0.48	72.01
344.5	1.127	1.06	4.55	15.68	−0.67	71.98
346.9	0.702	0.499	1.00	19.06	−0.33	71.74
347.0	0.808	0.559	0.99	19.60	0.07	71.73
349.8	0.764	0.430	0.99	24.09	0.27	71.44
352.2	0.581	0.301	1.29	28.57	0.42	71.19
352.8	0.787	0.350	1.05	30.51	1.17	71.13
354.6	2.479	1.14	4.55	32.19	−0.98	70.94
359.6	2.952	0.987	4.55	44.23	−2.07	70.43
362.2	1.026	0.279	1.29	54.37	−0.45	70.16
366.2	1.127	0.236	1.29	70.55	−0.11	69.74
1-Nonylimidazole $\Delta_f^g H_m (298.15 \text{ K}) = 85.55 \pm 0.23 \text{ kJ} \cdot \text{mol}^{-1}$						
$\ln(p/\text{Pa}) = \frac{382.43}{R} - \frac{121355.5}{R(T/\text{K})} - \frac{120.1}{R} \ln\left(\frac{T/\text{K}}{298.15}\right)$						
318.2	0.729	20.50	7.88	0.45	0.01	83.15
320.1	0.737	16.99	7.85	0.55	0.02	82.91
323.1	0.724	12.69	8.02	0.72	0.01	82.55
326.1	0.708	9.28	7.85	0.96	0.02	82.19
329.1	0.636	6.48	7.78	1.24	0.00	81.84
330.0	0.820	7.73	4.83	1.34	0.00	81.73
332.0	0.739	5.77	7.86	1.62	0.01	81.49
335.1	0.961	5.77	7.86	2.12	0.01	81.12
335.4	0.702	4.11	4.83	2.16	0.00	81.08
337.9	1.314	6.29	7.86	2.62	−0.07	80.78
338.6	0.569	2.57	4.83	2.80	−0.05	80.70
341.0	1.228	4.64	7.95	3.33	−0.16	80.41
341.5	1.283	4.51	4.83	3.60	−0.03	80.35
343.9	1.334	3.90	3.96	4.32	−0.14	80.05
344.6	0.648	1.77	4.83	4.63	−0.06	79.98

347.0	1.314	3.00	4.00	5.57	−0.15	79.68
347.5	1.199	2.49	4.83	6.08	0.17	79.63
349.9	1.264	2.32	3.98	6.89	−0.31	79.33
351.2	1.126	1.77	4.83	8.05	0.15	79.18
352.9	1.241	1.79	3.98	8.71	−0.31	78.97
353.7	0.190	0.252	1.01	9.54	−0.03	78.88
355.7	1.213	1.37	4.83	11.22	0.10	78.64
355.9	1.284	1.47	1.96	10.98	−0.34	78.61
359.0	1.251	1.14	1.95	13.98	−0.21	78.25
359.7	0.372	0.302	1.01	15.56	0.63	78.16
359.7	1.420	1.21	4.83	14.88	−0.06	78.16
361.8	1.281	0.943	1.95	17.10	−0.39	77.90
363.2	1.096	0.701	2.47	19.80	0.60	77.74
364.8	1.208	0.716	1.95	21.27	−0.31	77.54
365.2	0.673	0.386	1.01	22.05	−0.06	77.50
366.7	1.410	0.701	2.47	25.45	0.91	77.32
366.8	1.261	0.651	1.95	24.41	−0.38	77.30
369.6	1.541	0.618	2.47	31.53	1.52	76.97
371.2	0.957	0.353	1.01	34.31	0.98	76.78

1-Decylimidazole  $\Delta_f^g H_m$  (298.15 K) = 89.63 ± 0.34 kJ · mol<sup>−1</sup>

$$\ln(p/\text{Pa}) = \frac{394.17}{R} - \frac{127913.4}{R(T/K)} - \frac{128.4}{R} \ln\left(\frac{T/K}{298.15}\right)$$

324.1	0.246	10.90	4.95	0.27	0.01	86.31
326.2	0.213	7.60	4.95	0.33	0.01	86.04
328.2	0.226	6.52	4.89	0.41	0.03	85.78
329.7	2.391	64.63	4.56	0.44	−0.01	85.59
332.1	0.787	16.94	4.33	0.55	−0.01	85.28
334.2	0.767	12.84	7.01	0.71	0.03	85.01
334.4	0.665	11.67	4.49	0.67	−0.02	84.98
335.8	0.353	5.62	4.56	0.74	−0.04	84.80
337.1	0.657	8.73	6.98	0.90	0.02	84.64
338.6	0.934	11.56	4.48	0.95	−0.05	84.44
340.1	0.717	7.48	6.91	1.15	0.01	84.25
340.7	0.861	8.49	4.51	1.20	−0.01	84.17
341.2	0.553	4.96	4.03	1.31	0.05	84.11
343.1	0.426	3.57	4.56	1.41	−0.08	83.87
343.1	0.657	5.24	4.03	1.49	0.01	83.87
343.2	0.495	4.02	4.02	1.47	−0.03	83.85
345.2	0.525	3.58	4.48	1.73	−0.04	83.60
346.1	0.657	3.98	3.98	1.96	0.05	83.48
348.3	1.208	6.38	4.56	2.24	−0.06	83.20
349.1	0.713	3.49	4.03	2.41	−0.05	83.10
349.2	0.550	2.63	4.04	2.46	−0.02	83.08
350.7	0.788	3.36	4.48	2.77	−0.03	82.89
352.1	0.810	2.95	4.03	3.27	0.14	82.71
353.5	1.164	4.02	4.56	3.41	−0.09	82.53
355.2	0.691	2.05	3.97	4.01	0.01	82.31
355.6	0.547	1.55	2.02	4.17	0.02	82.25
355.7	0.538	1.57	4.48	4.05	−0.11	82.25
358.0	0.679	1.59	3.97	5.06	0.07	81.95
358.5	0.737	1.75	4.56	4.98	−0.20	81.89
360.7	0.543	1.04	2.01	6.17	0.05	81.61
361.0	0.552	1.06	4.00	6.10	−0.15	81.57
363.1	0.682	1.14	4.56	7.07	−0.26	81.30
364.2	0.720	1.09	4.10	7.90	−0.04	81.16
364.7	0.566	0.804	2.01	8.31	0.07	81.09
366.7	0.815	1.07	4.00	9.02	−0.51	80.84
367.1	0.699	0.813	1.08	10.13	0.32	80.78
370.1	0.514	0.488	1.08	12.45	0.30	80.40
371.3	0.738	0.644	1.05	13.80	0.58	80.24
373.1	0.503	0.377	1.08	15.75	0.76	80.01
374.3	0.599	0.425	1.02	16.96	0.68	79.86

1-Undecylimidazole  $\Delta_f^g H_m$  (298.15 K) = 93.88 ± 0.34 kJ · mol<sup>−1</sup>

$$\ln(p/\text{Pa}) = \frac{408.20}{R} - \frac{134633.7}{R(T/K)} - \frac{136.7}{R} \ln\left(\frac{T/K}{298.15}\right)$$

334.0	0.276	10.35	5.18	0.30	0.01	88.97
336.1	0.270	8.31	5.19	0.36	0.01	88.70
338.0	0.260	6.66	7.99	0.43	0.01	88.42
341.0	0.590	11.91	8.12	0.54	−0.01	88.01
343.0	0.304	5.06	5.06	0.67	0.01	87.75
344.0	0.565	8.54	7.88	0.73	0.01	87.61
347.0	0.633	7.39	8.06	0.94	0.00	87.20
350.0	0.580	5.48	8.22	1.17	−0.05	86.79
353.0	0.551	4.12	8.24	1.47	−0.10	86.38
356.0	0.605	3.44	4.13	1.94	−0.06	85.97
358.0	0.535	2.71	4.07	2.21	−0.13	85.70
358.9	0.692	2.97	4.05	2.56	0.02	85.57
360.9	0.610	2.37	4.06	2.83	−0.14	85.29

(continued on next page)

TABLE 1 (continued)

$T^a/\text{K}$	$m^b/\text{mg}$	$V_{(\text{N}_2)}^c/\text{dm}^3$	Gas-flow/(dm <sup>3</sup> /h)	$p^d/\text{Pa}$	$(p_{\text{exp}} - p_{\text{calc}})/\text{Pa}$	$\Delta_f^g H_m/(\text{kJ} \cdot \text{mol}^{-1})$
361.9	0.627	2.19	4.10	3.15	−0.06	85.16
364.9	0.773	2.09	4.04	4.07	0.02	84.75
367.9	0.633	1.41	4.04	4.91	−0.15	84.35
369.9	0.664	1.22	2.09	6.08	0.21	84.07
370.9	0.590	1.08	4.05	6.01	−0.31	83.94
371.9	0.621	0.975	2.09	7.08	0.28	83.80
373.8	0.641	0.869	2.01	8.10	0.25	83.53
374.8	0.608	0.836	2.09	8.16	−0.26	83.40
376.8	0.544	0.604	2.01	9.93	0.24	83.13
377.8	0.557	0.570	2.01	10.77	0.36	82.99
378.8	0.546	0.571	1.07	10.63	−0.52	82.85
380.8	0.599	0.514	1.10	13.02	0.25	82.58
1-Dodecylimidazole $\Delta_f^g H_m(298.15 \text{ K}) = 97.55 \pm 0.42 \text{ kJ} \cdot \text{mol}^{-1}$						
$\ln(p/\text{Pa}) = \frac{420.49}{\text{K}} - \frac{140755.1}{\text{K}^2(T/\text{K})} - \frac{144.9}{\text{K}} \ln\left(\frac{T/\text{K}}{298.15}\right)$						
319.1	0.476	203.1	4.51	0.02	0.00	94.52
324.8	0.285	66.06	4.51	0.05	0.00	93.70
327.2	0.374	63.52	4.26	0.06	0.00	93.35
329.7	0.215	30.36	4.51	0.07	0.00	92.99
331.9	1.021	102.2	4.26	0.11	0.01	92.67
333.7	0.245	21.24	4.26	0.12	0.00	92.41
335.7	1.130	83.94	4.51	0.14	0.00	92.12
335.9	1.109	78.40	5.21	0.15	0.00	92.09
337.7	1.383	80.86	4.26	0.18	0.00	91.83
340.0	0.377	17.28	5.21	0.23	0.01	91.50
340.2	0.245	10.66	4.26	0.24	0.02	91.47
342.9	0.407	14.85	5.21	0.29	0.00	91.08
342.9	0.295	10.48	4.19	0.30	0.01	91.08
344.6	0.438	13.22	4.26	0.35	0.01	90.83
346.1	0.297	8.03	4.26	0.39	0.00	90.61
347.7	3.505	85.75	4.51	0.43	−0.02	90.38
350.0	0.407	7.82	4.26	0.55	0.00	90.05
350.3	0.530	9.78	4.19	0.57	0.01	90.00
352.6	0.276	4.43	4.51	0.66	−0.04	89.67
354.0	0.671	9.03	5.21	0.79	0.00	89.47
355.9	0.378	4.58	4.51	0.87	−0.05	89.19
358.0	0.766	7.21	5.21	1.12	0.03	88.89
359.3	0.809	6.98	4.19	1.22	0.00	88.70
359.5	0.643	5.64	4.51	1.20	−0.04	88.67
361.9	0.581	3.99	5.21	1.54	0.02	88.32
363.0	0.662	4.19	4.26	1.67	0.02	88.16
364.8	0.478	2.65	4.55	1.90	−0.01	87.90
365.9	0.790	3.99	5.21	2.09	0.01	87.74
365.9	0.894	4.55	4.26	2.08	−0.01	87.74
368.8	0.540	2.13	4.26	2.68	0.06	87.32
369.9	0.539	1.99	5.21	2.85	0.01	87.16
370.9	0.487	1.74	4.55	2.95	−0.12	87.02
372.8	0.558	1.70	4.26	3.46	−0.09	86.74
373.1	0.631	1.78	2.98	3.74	0.11	86.70
376.1	1.019	2.33	2.98	4.62	0.09	86.27
379.1	0.605	1.14	2.98	5.61	−0.02	85.83

<sup>a</sup> Temperature of saturation.<sup>b</sup> Mass of transferred sample, condensed at  $T = 243 \text{ K}$ .<sup>c</sup> Volume of nitrogen, used to transfer mass  $m$  of sample.<sup>d</sup> Vapor pressure at temperature, calculated from  $m$  and the residual vapor pressure at  $T = 243 \text{ K}$ .

be detected in the samples used for the vapor pressure measurements.

## 2.2. Vapor pressure measurements on 1-alkyl-imidazoles

Vapor pressures and enthalpies of vaporization of 1-alkyl-imidazoles were determined using the method of transpiration in a saturated  $\text{N}_2$ -stream and applying the Clausius–Clapeyron equation [2,3]. About 0.5 g of the sample was mixed with glass beads and placed in a thermostatted U-shaped tube having a length of 20 cm and a diameter of 0.5 cm. Glass beads with diameter of 1 mm provide surface which is sufficient enough for the (vapor-liquid) equilibration. At constant temperature ( $\pm 0.1 \text{ K}$ ), a nitrogen stream was passed through the U-tube and the transported amount of gaseous material was collected in a cooling trap. The

flow rate of the nitrogen stream was measured using a soap bubble flow meter and optimized in order to reach the saturation equilibrium of the transporting gas at each temperature under study. On the one hand, flow rate of nitrogen stream in the saturation tube should be not too slow in order to avoid the transport of material from U-tube due to diffusion. On the other hand the flow rate should be not too fast in order to reach the saturation of the nitrogen stream with a compound. We tested our apparatus at different flow rates of the carrier gas in order to check the lower boundary of the flow below which the contribution of the vapor condensed in the trap by diffusion becomes comparable to the transpired one. In our apparatus the contribution due to diffusion was negligible at a flow rate up to  $0.45 \text{ dm}^3 \cdot \text{h}^{-1}$ . The upper limit for our apparatus where the speed of nitrogen could already disturb the equilibration was at a flow rate of  $9.0 \text{ dm}^3 \cdot \text{h}^{-1}$ . Thus, we carried out

TABLE 2

Compilation of data on enthalpies of vaporization  $\Delta_1^g H_m$  (298.15 K) of 1-alkyl-imidazoles.

Compounds	T-range/K	$C_p^l$ ( $\Delta_1^g C_p$ )/(J · mol <sup>-1</sup> · K <sup>-1</sup> )	$\Delta_1^g H_m$ $T_{av}/(kJ · mol^{-1})$	$\Delta_1^g H_m/(298.15 K)/(kJ · mol^{-1})$
1-Propyl-imidazole	279.1 to 341.0	229.7(–70.3)	60.2	61.1 ± 0.2
1-Pentyl-imidazole	308.2 to 366.3	293.5(–86.9)	65.7	69.1 ± 0.5
1-Hexyl-imidazole	309.2 to 363.2	325.4(–95.2)	69.5	73.1 ± 0.2
1-Heptyl-imidazole	298.5 to 366.2	357.3(–103.5)	73.6	76.8 ± 0.3
1-Nonyl-imidazole	318.2 to 371.2	421.1(–120.1)	80.0	85.6 ± 0.2
1-Decyl-imidazole	324.1 to 374.3	453.0(–128.4)	83.1	89.6 ± 0.3

<sup>a</sup> Values of  $\Delta_1^g C_p$  have been calculated from the estimated isobaric molar heat capacity of the liquid 1-alkyl-imidazoles  $C_p^l$  according to procedure developed by Chickos [4].

the experiments in the flow rate interval of (0.8 to 8) dm<sup>3</sup> · h<sup>-1</sup> which has ensured that transporting gas was in saturated equilibrium with the coexisting liquid phase in the saturation tube. The amount of condensed substance was determined by GC analysis using an external standard (hydrocarbon  $n\text{-C}_n\text{H}_{2n+2}$ ). The saturation vapor pressure  $p_i^{sat}$  at each temperature  $T_i$  was calculated from the amount of product collected within a definite period of time. Assuming that Dalton's law of partial pressures applied to the nitrogen stream saturated with the substance  $i$  of interest is valid, values of  $p_i^{sat}$  were calculated:

$$p_i^{sat} = m_i \cdot R \cdot T_a / V \cdot M_i; \quad V = V_{N_2} + V_i; \quad (V_{N_2} \gg V_i), \quad (1)$$

where  $R = 8.31447 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ ;  $m_i$  is the mass of transported compound,  $M_i$  is the molar mass of the compound, and  $V_i$  its volume contribution to the gaseous phase.  $V_{N_2}$  is the volume of transporting gas and  $T_a$  is the temperature of the soap bubble meter. The volume of transporting gas  $V_{N_2}$  was determined from the flow rate and time measurements. Data of  $p_i^{sat}$  have been obtained as a function of temperature and were fitted using following equation (2):

$$R \cdot \ln p_i^{sat} = a + \frac{b}{T} + \Delta_1^g C_p \cdot \ln \left( \frac{T}{T_0} \right), \quad (2)$$

where  $a$  and  $b$  are adjustable parameters and  $\Delta_1^g C_p$  is the difference of the molar heat capacities of the gaseous and the liquid phase respectively. The  $T_0$  appearing in equation (2) is an arbitrarily chosen reference temperature (which has been chosen to be 298.15 K). Consequently, from equation (2) the expression for the vaporization enthalpy at temperature  $T$  is derived:

$$\Delta_1^g H_m(T) = -b + \Delta_1^g C_p \cdot T. \quad (3)$$

Values of  $\Delta_1^g C_p$  have been calculated from the estimated isobaric molar heat capacities of liquid,  $C_p^l$ , of 1-alkyl-imidazoles according to a procedure developed by Chickos [4]. We have checked experimental and calculation procedure with measurements of vapor pressures of  $n$ -alcohols [2]. It turned out, that vapor pressures derived from the transpiration method were reliable within (1 to 3)% and their accuracy was governed by reproducibility of the GC analysis. In order to assess the uncertainty of the vaporization enthalpy, the experimental data were approximated with the linear equation  $\ln(p_i^{sat}) = f(T^{-1})$  using the method of least squares. The uncertainty in the enthalpy of vaporization was assumed to be identical with the as average deviation of experimental  $\ln(p_i^{sat})$  values from this linear correlation. Experimental results, parameters  $a$  and  $b$  are listed in tables 1 and 2.

### 3. Results and discussion

A summary of vapor pressures and vaporization enthalpy measurements of 1-alkyl-imidazoles is presented in table 2. To the best of our knowledge these compounds have been studied for the first time.

The correlation of the enthalpies of vaporization with the number of C-atoms within the series of homologs is well documented. Vaporization enthalpies  $\Delta_1^g H_m$  (298.15 K) appear to be a linear function of the number of carbon atoms of the aldehydes [5], nitriles [6], esters [7], and alkylbenzenes [8]. The dependence of vaporization enthalpy (from table 2) on the number of C-atoms  $N_C = 3$  to 10 is expressed by the following linear equation:

$$\Delta_1^g H_m (298.15 \text{ K}) / (kJ \cdot mol^{-1}) = 48.7 + 4.08 N_C \text{ with } (R^2 = 0.9995) \quad (4)$$

from which the enthalpy of vaporization of the longer 1-alkyl-imidazoles where experimental data are absent could be derived. Additionally, such a good correlation is an evidence of the internal consistency of the data measured in this work.

### Acknowledgements

This work has been supported by the German Science Foundation (DFG) in the frame of the priority program SPP 1191 "Ionic Liquids". One of us (S.V.P.) acknowledges gratefully a research scholarship from the DAAD (Deutscher Akademischer Austauschdienst). Another one (A.S.) is grateful for financial support from the Polish Ministry of Science and Higher Education NN 209437639.

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