

Building Blocks for Ionic Liquids: A Study of Alkyl Chain Length Dependence of Vaporization Enthalpies of 1-(*n*-Alkyl)-2-methylimidazolesVladimir N. Emel'yanenko, Svetlana V. Portnova,[†] and Sergey P. Verevkin^{*,‡}

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ABSTRACT: The transpiration method has been used to measure temperature dependence of vapor pressures for the 1-(*n*-alkyl)-2-methylimidazoles with the linear alkyl chain C₂–C₁₀. The molar enthalpies of vaporization at 298.15 K of this homologues series were correlated with the number of carbon atoms in the alkyl chain, as well as with the Kovat's indices on the low-polar gas chromatography (GC) columns. In both cases linear correlations have been found.

1. INTRODUCTION

Ionic liquids (ILs) in contrast to molecular compounds are typically composed solely of organic cations and inorganic anions and exhibit interesting and sometimes unusual physical properties. The high thermal stability, vanishing vapor pressure up to 300 °C, and variable miscibility contrast favorably with the characteristics of traditional volatile organic solvents. This has resulted in ILs being perceived as more environmentally friendly solvents for use in the industrial manufacturing of chemicals.¹ Alkylimidazoles are the building blocks for ILs. ILs are usually thermally stable, and their decomposition begins approximately above (200 to 250) °C. Also upon decomposition ILs release alkylimidazoles. The fate of alkylimidazoles released in an environment to a large extent depends on their vapor pressure and vaporization enthalpy. This work was initiated to investigate the relationship between vaporization enthalpy and the alkyl chain length as well as with Kovat's indices of a series of linear 1-(*n*-alkyl)-2-methylimidazoles with the chain length C₂–C₁₀. The enthalpies of vaporization, Δ_f^gH_m(298.15 K), have been obtained from the temperature dependence of the vapor pressures measured by the transpiration method.

2. EXPERIMENTAL SECTION

2.1. Materials. Samples of 1-(*n*-alkyl)-2-methylimidazoles with the linear alkyl chains C₂–C₁₀ were synthesized at the Poznań University of Technology (see Figure 1).

A typical synthetic procedure was performed as follows. 2-Methylimidazole (0.1 mol) and 0.1 mol of sodium were dissolved in 75 mL of anhydrous methanol. After adding an appropriate bromoalkane C₂–C₁₀ (0.1 mol), the mixture was stirred at 338 K for 6 h. The sodium bromide was filtered, and the solvent was evaporated. Liquid 1-(*n*-alkyl)-2-methylimidazoles samples were purified using the fractional distillation at reduced pressure [(1 to 10) Torr]. The conversion of the starting materials was sufficient with yields of (38 to 67) %.

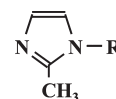


Figure 1. 1-Alkyl-2-methylimidazoles studied in this work with R = ethyl to decyl.

We used a Hewlett-Packard gas chromatograph 5890 Series II equipped with a capillary column HP-5 and a flame ionization detector to check the purity of samples under study. All samples were with the purity of 99.9 %.

2.2. Vapor Pressure Measurements on 1-(*n*-Alkyl)-2-methylimidazoles. The enthalpies of vaporization and vapor pressures of liquid 1-(*n*-alkyl)-2-methylimidazoles were determined by using the method of transference in a saturated N₂-stream. The method has been described before^{2,3} and has proved to give results being in excellent agreement with other established techniques for determining vapor pressures of pure substances and enthalpies of vaporization from the temperature dependence of the vapor pressure. The sample was mixed with glass beads (to provide surface which is sufficient enough for the vapor–liquid equilibration) and placed in a glass saturator having a length of 20 cm and a diameter of 0.5 cm. A stream of an inert gas (N₂) was passed through the U-tube at constant temperature (± 0.1 K) under saturation conditions at each temperature. The transported material was collected in a cold trap at 243 K and quantified chromatographically using the method of an external standard. We used in this work the hydrocarbons *n*-C_{*n*}H_{2*n*+2} as standards. Saturation vapor pressures *p*_{*i*} were calculated according to the ideal gas law from the amount of product *m*_{*i*} collected

Received: April 5, 2011

Accepted: August 3, 2011

Published: August 15, 2011

Table 1. Vapor Pressures p and Vaporization Enthalpies $\Delta^{\text{f}}H_{\text{m}}(T)$ Measured Using the Transpiration Method

T^{a}	m^{b}	$V_{(\text{N}_2)}^{\text{c}}$	gas flow	p^{d}	$(p_{\text{exp}} - p_{\text{calc}})$	$\Delta^{\text{f}}H_{\text{m}}(T)$
K	mg	dm ³	dm ³ · h ⁻¹	Pa	Pa	kJ · mol ⁻¹
1-Ethyl-2-methylimidazole, $\Delta^{\text{f}}H_{\text{m}}(298.15 \text{ K}) = 60.37 \pm 0.27 \text{ kJ} \cdot \text{mol}^{-1}$						
$\ln(p/\text{Pa}) = (296.32/R) - \{81057.5/[R \cdot (T, \text{K})]\} - (69.4/R)\ln[(T, \text{K})/298.15]$						
293.5	0.70	1.24	3.73	12.7	-0.2	60.69
294.3	2.49	3.90	7.09	14.2	0.5	60.64
295.8	0.86	1.24	3.73	15.5	0.0	60.53
297.4	1.95	2.44	6.97	17.9	0.1	60.42
298.4	1.38	1.57	3.78	19.8	0.6	60.35
300.8	0.86	0.840	3.73	22.9	-0.4	60.19
301.4	2.37	2.22	4.03	23.9	-0.6	60.14
303.3	1.13	0.944	3.78	26.9	-1.7	60.01
304.2	2.04	1.48	4.03	30.6	0.0	59.95
307.2	3.06	1.81	4.02	37.7	-0.8	59.74
308.3	1.72	0.944	3.78	40.9	-1.0	59.66
310.3	2.76	1.24	3.92	49.4	0.7	59.53
313.2	3.25	1.14	4.04	63.1	2.9	59.32
313.3	1.60	0.609	1.83	59.0	-1.6	59.32
317.2	2.94	0.807	4.03	80.6	0.4	59.05
318.2	1.68	0.431	1.85	87.4	1.4	58.98
321.2	3.13	0.629	1.08	110.3	4.4	58.77
323.2	2.22	0.431	1.85	115.5	-5.8	58.63
324.3	2.98	0.510	1.61	129.8	-0.8	58.55
328.2	3.51	0.462	1.85	170.7	1.7	58.28
329.2	3.03	0.356	1.07	188.9	8.5	58.21
333.2	4.17	0.400	1.85	234.0	1.3	57.94
333.3	3.50	0.317	1.06	244.1	10.0	57.93
335.5	2.00	0.173	1.09	260.0	-8.4	57.78
338.1	5.81	0.429	1.84	303.8	-10.9	57.60
338.2	2.88	0.197	1.08	323.4	6.7	57.59
340.6	2.38	0.142	1.06	376.4	10.6	57.42
343.1	7.62	0.398	1.84	429.6	5.7	57.25
343.3	3.40	0.176	1.06	427.4	-1.6	57.24
348.1	10.70	0.423	1.88	567.4	2.3	56.90
353.1	14.18	0.439	1.88	725.2	-20.8	56.56
363.0	24.04	0.439	1.88	1229.4	-28.4	55.87
1-Propyl-2-methylimidazole, $\Delta^{\text{f}}H_{\text{m}}(298.15 \text{ K}) = 63.67 \pm 0.15 \text{ kJ} \cdot \text{mol}^{-1}$						
$\ln(p/\text{Pa}) = (309.37/R) - \{86652.67/[R \cdot (T, \text{K})]\} - (77.1/R)\ln[(T, \text{K})/298.15]$						
288.6	1.88	9.47	6.11	4.00	-0.03	64.41
288.6	1.97	9.78	6.11	4.05	0.02	64.41
289.6	2.12	9.81	4.12	4.34	-0.08	64.33
289.6	2.06	9.47	4.12	4.38	-0.04	64.33
291.5	1.70	6.33	6.13	5.38	0.12	64.18
294.7	1.88	5.47	4.10	6.92	-0.09	63.94
294.7	2.23	6.22	4.10	7.20	0.19	63.94
295.4	1.88	5.05	4.04	7.38	-0.08	63.88
295.4	2.22	5.92	4.04	7.48	0.02	63.88
297.3	1.98	4.55	6.07	8.72	-0.08	63.73
298.4	1.00	1.96	3.10	10.02	0.34	63.65
298.4	1.87	3.72	4.06	9.97	0.29	63.65
298.4	2.21	4.39	4.06	10.02	0.34	63.65
300.3	1.81	3.17	4.05	11.33	-0.06	63.50

Table 1. Continued

T^a	m^b	$V_{(N_2)}^c$	gas flow	p^d	$(p_{\text{exp}} - p_{\text{calc}})$	$\Delta_f H_m(T)$
K	mg	dm ³	dm ³ ·h ⁻¹	Pa	Pa	kJ·mol ⁻¹
300.3	2.14	3.71	4.05	11.46	0.07	63.50
300.8	0.73	1.19	3.57	12.04	0.16	63.46
301.1	1.93	3.18	3.74	11.97	-0.21	63.44
303.3	0.63	0.827	3.10	14.90	0.25	63.27
303.7	1.76	2.35	6.13	14.94	-0.19	63.24
305.7	0.65	0.724	3.10	17.60	-0.23	63.09
305.9	2.00	2.32	2.04	17.24	-0.88	63.07
306.6	0.90	0.951	3.57	18.67	-0.58	63.01
308.5	0.85	0.750	3.10	22.17	-0.15	62.87
308.6	2.65	2.33	2.09	22.54	0.04	62.86
309.5	1.92	1.53	2.08	25.06	0.80	62.79
310.6	1.06	0.803	3.57	25.98	-0.37	62.71
311.2	1.99	1.46	2.04	27.42	-0.19	62.66
313.4	1.26	0.776	3.10	31.81	-0.91	62.49
314.0	1.97	1.13	2.06	35.05	0.67	62.44
316.0	1.98	0.975	2.09	40.35	0.51	62.29
316.5	1.68	0.803	3.57	41.10	-0.42	62.25
318.3	1.60	0.672	3.10	46.71	-0.78	62.11
318.5	1.76	0.757	2.06	46.74	-1.24	62.10
320.3	2.40	0.886	2.04	53.80	-0.93	61.96
320.6	2.18	0.776	3.10	55.14	-0.80	61.94
321.4	1.96	0.697	2.09	56.84	-2.43	61.88
322.5	1.23	0.374	1.12	64.43	0.29	61.79
323.3	1.51	0.429	1.03	69.17	1.27	61.73
324.0	2.25	0.619	2.06	73.43	2.07	61.68
325.4	2.37	0.588	2.08	80.08	1.35	61.57
325.5	2.44	0.621	3.10	77.27	-2.02	61.56
327.1	2.03	0.463	1.03	88.65	0.03	61.44
327.5	1.58	0.336	1.12	92.01	0.92	61.41
328.3	1.26	0.257	1.03	95.93	-0.31	61.34
330.5	1.82	0.319	1.37	111.78	0.04	61.17
331.0	1.52	0.263	1.02	114.00	-1.57	61.14
331.5	1.69	0.280	1.12	118.02	-1.49	61.10
333.3	1.58	0.226	1.05	137.20	2.51	60.96
334.0	1.52	0.214	1.03	139.89	-1.15	60.91
335.4	1.95	0.243	1.12	157.77	2.80	60.79
335.8	2.23	0.275	1.03	164.48	5.86	60.77
337.7	2.39	0.281	1.02	172.26	-7.01	60.62
338.2	2.17	0.226	1.05	188.57	3.49	60.58
338.8	2.68	0.273	1.03	193.40	0.51	60.53
343.2	2.97	0.226	1.05	257.18	4.08	60.20
1-Butyl-2-methylimidazole, $\Delta_f H_m(298.15 \text{ K}) = 67.76 \pm 0.18 \text{ kJ} \cdot \text{mol}^{-1}$						
$\ln(p/\text{Pa}) = (323.75/R) - \{93400.40/[R \cdot (T, \text{K})]\} - (86.0/R) \ln[(T, \text{K})/298.15]$						
293.6	2.13	16.1	7.71	2.35	0.05	68.15
296.2	2.06	12.4	7.85	2.92	-0.02	67.93
298.2	2.03	10.4	7.81	3.44	-0.09	67.76
300.1	2.13	8.76	7.85	4.30	0.07	67.59
303.1	2.04	6.57	7.88	5.47	-0.02	67.34
305.1	1.97	5.36	8.04	6.51	-0.06	67.16
307.2	2.28	5.21	8.02	7.72	-0.10	66.99
310.2	1.69	3.00	3.00	10.00	-0.11	66.72
311.1	2.09	3.33	3.03	11.02	0.08	66.64

Table 1. Continued

T^a	m^b	$V_{(N_2)}^c$	gas flow	p^d	$(p_{\text{exp}} - p_{\text{calc}})$	$\Delta_f H_m(T)$
K	mg	dm ³	dm ³ ·h ⁻¹	Pa	Pa	kJ·mol ⁻¹
313.2	1.17	1.61	3.12	12.98	0.05	66.47
313.2	2.33	3.17	3.12	13.01	0.10	66.47
314.1	2.13	2.70	3.06	14.05	0.07	66.39
316.1	1.66	1.83	3.06	16.24	-0.18	66.21
317.1	2.21	2.21	3.09	17.87	0.12	66.13
319.1	2.34	2.02	2.89	20.34	-0.42	65.96
322.1	2.03	1.38	3.06	26.50	0.35	65.70
325.1	2.36	1.24	2.86	33.51	0.82	65.44
328.1	2.17	0.959	3.03	40.49	-0.28	65.19
330.1	2.13	0.815	3.06	46.12	-0.95	65.02
331.1	1.37	0.479	2.87	50.86	0.26	64.93
334.0	2.21	0.621	0.98	62.90	0.61	64.67
337.0	0.98	0.231	0.99	75.70	-0.91	64.42
337.0	2.02	0.473	1.01	76.53	-0.08	64.42
340.0	2.08	0.393	0.98	93.51	-0.17	64.16
342.0	2.03	0.334	0.95	107.36	0.26	63.99
343.0	2.15	0.336	1.01	114.61	0.33	63.90
1-Pentyl-2-methylimidazole, $\Delta_f H_m(298.15 \text{ K}) = 71.35 \pm 0.33 \text{ kJ} \cdot \text{mol}^{-1}$						
$\ln(p/\text{Pa}) = (346.85/R) - \{102198.0/[R \cdot (T, \text{K})]\} - (102.6/R)\ln[(T, \text{K})/298.15]$						
303.3	2.05	12.4	8.00	2.66	0.00	70.87
305.3	2.03	10.4	8.03	3.15	-0.04	70.68
307.4	2.11	8.97	8.03	3.81	-0.05	70.49
310.4	2.31	7.60	8.00	4.94	-0.10	70.20
314.2	2.20	5.05	4.04	7.00	0.01	69.85
317.2	2.21	3.83	4.04	9.29	0.29	69.56
321.2	1.71	2.16	4.05	12.66	0.17	69.19
324.3	2.27	2.23	4.06	16.58	0.59	68.89
326.1	2.41	2.10	4.07	18.50	0.09	68.72
327.2	2.31	1.82	4.04	20.45	0.40	68.62
328.2	2.37	1.70	4.08	22.48	0.84	68.53
331.3	2.51	1.48	4.04	27.19	-0.18	68.23
332.2	2.47	1.42	4.05	28.22	-1.05	68.15
334.2	2.37	1.16	4.08	32.96	-0.97	67.96
335.3	1.70	0.744	4.06	37.08	0.33	67.86
339.1	2.15	0.730	1.04	47.40	-0.85	67.50
339.2	2.12	0.708	1.06	48.45	-0.14	67.49
343.2	1.90	0.490	1.05	62.53	-1.65	67.11
346.2	2.14	0.466	1.08	74.66	-3.99	66.83
348.2	2.45	0.432	1.04	92.19	2.33	66.64
349.1	2.06	0.363	1.04	92.14	-3.21	66.55
350.1	2.25	0.347	1.04	104.93	3.13	66.46
351.1	1.91	0.280	1.05	109.77	1.13	66.37
352.1	1.88	0.250	1.07	120.92	5.03	66.27
353.2	2.52	0.328	1.04	124.98	0.64	66.17
354.2	3.83	0.469	1.04	131.22	-1.28	66.07
1-Hexyl-2-methylimidazole, $\Delta_f H_m(298.15 \text{ K}) = 74.72 \pm 0.35 \text{ kJ} \cdot \text{mol}^{-1}$						
$\ln(p/\text{Pa}) = (347.79/R) - \{105308.39/[R \cdot (T, \text{K})]\} - (102.6/R)\ln[(T, \text{K})/298.15]$						
313.0	1.82	12.5	8.69	2.16	0.02	73.20
314.2	2.51	15.3	8.53	2.43	0.04	73.07
317.0	1.77	8.61	8.76	3.04	-0.03	72.78
320.1	1.85	6.80	8.69	4.04	0.04	72.47

Table 1. Continued

T^a	m^b	$V_{(N_2)}^c$	gas flow	p^d	$(p_{\text{exp}} - p_{\text{calc}})$	$\Delta_f H_m(T)$
K	mg	dm ³	dm ³ ·h ⁻¹	Pa	Pa	kJ·mol ⁻¹
321.1	2.43	8.03	8.31	4.45	0.10	72.36
324.1	1.68	4.65	9.00	5.35	-0.23	72.06
327.1	1.78	3.69	8.53	7.19	0.07	71.75
328.1	3.75	7.08	4.13	7.82	0.07	71.64
331.1	1.75	2.66	8.39	9.72	-0.06	71.34
335.1	1.79	2.08	4.03	12.67	-0.63	70.93
339.0	1.84	1.50	4.10	18.04	0.14	70.52
342.0	1.48	1.02	4.08	21.57	-0.69	70.22
345.0	1.88	1.00	4.00	27.86	0.26	69.91
349.0	2.49	0.997	1.00	36.76	0.40	69.50
353.0	1.80	0.552	1.00	48.75	1.05	69.09
358.0	1.77	0.383	1.05	68.77	2.76	68.58
360.9	1.67	0.314	1.05	79.37	-0.44	68.28
362.9	1.76	0.296	1.05	88.19	-2.21	68.07
1-Heptyl-2-methylimidazole, $\Delta_f H_m(298.15 \text{ K}) = 79.40 \pm 0.18 \text{ kJ} \cdot \text{mol}^{-1}$						
$\ln(p/\text{Pa}) = (3364.73/R) - \{112464.27/[R \cdot (T, \text{K})]\} - (110.9/R) \ln[(T, \text{K})/298.15]$						
312.2	1.09	15.8	4.04	0.94	0.01	77.85
312.3	1.29	18.5	9.03	0.96	0.02	77.84
313.2	2.07	26.9	9.03	1.05	0.03	77.74
314.3	1.14	13.5	9.03	1.16	0.03	77.61
314.3	1.34	16.2	4.04	1.13	0.00	77.61
316.2	1.14	11.7	9.03	1.34	-0.01	77.40
319.3	1.06	8.37	4.08	1.73	-0.07	77.06
322.2	1.23	7.22	9.03	2.34	0.01	76.74
323.2	0.88	4.70	4.08	2.59	0.04	76.63
323.5	0.93	4.65	3.49	2.70	0.09	76.59
326.2	1.17	4.81	9.03	3.34	0.03	76.29
328.5	0.83	2.73	3.49	4.09	0.06	76.04
329.3	1.20	3.91	4.05	4.21	-0.10	75.95
332.1	1.22	3.09	4.03	5.42	-0.03	75.64
333.3	0.83	1.97	4.08	5.76	-0.25	75.51
333.5	0.64	1.45	3.49	5.92	-0.19	75.48
336.1	1.23	2.22	4.03	7.61	0.07	75.20
338.5	0.88	1.34	3.49	8.87	-0.25	74.93
339.2	1.15	1.68	4.03	9.42	-0.21	74.85
342.2	1.21	1.42	4.05	11.76	-0.39	74.52
343.2	0.86	0.921	4.09	12.84	-0.27	74.41
343.4	1.07	1.10	3.49	13.15	-0.16	74.39
345.2	1.19	1.07	4.03	15.27	0.02	74.19
348.4	1.62	1.16	3.49	18.87	-0.45	73.83
349.1	1.07	0.721	1.55	20.34	-0.01	73.75
353.2	2.00	1.01	4.05	27.26	-0.04	73.30
353.4	0.91	0.454	1.51	27.03	-0.66	73.28
356.3	1.31	0.540	1.54	33.72	-0.19	72.96
358.4	1.28	0.454	1.51	38.23	-0.93	72.72
359.0	1.13	0.364	1.56	42.23	1.44	72.66
361.2	1.15	0.323	1.55	49.57	2.27	72.41
363.3	1.49	0.359	1.54	55.95	1.48	72.18
363.3	1.40	0.347	1.54	55.76	1.39	72.18
368.4	1.91	0.333	1.54	77.69	1.86	71.61

Table 1. Continued

T^a	m^b	$V_{(N_2)}^c$	gas flow	p^d	$(p_{\text{exp}} - p_{\text{calc}})$	$\Delta_f H_m(T)$
K	mg	dm ³	dm ³ ·h ⁻¹	Pa	Pa	kJ·mol ⁻¹
1-Octyl-2-methylimidazole, $\Delta_f H_m(298.15 \text{ K}) = 83.84 \pm 0.22 \text{ kJ} \cdot \text{mol}^{-1}$						
$\ln(p/\text{Pa}) = (378.85/R) - \{119376.90/[R \cdot (T, \text{K})]\} - (119.2/R)\ln[(T, \text{K})/298.15]$						
323.1	0.87	11.2	7.90	0.99	0.02	80.86
325.1	0.89	9.6	7.92	1.17	0.00	80.63
325.1	0.83	8.90	3.81	1.19	0.02	80.62
327.0	0.88	8.02	8.02	1.37	-0.03	80.39
330.1	0.97	6.57	8.05	1.87	0.03	80.03
330.1	0.87	6.07	3.84	1.82	-0.02	80.03
333.0	0.99	5.23	5.23	2.44	0.06	79.68
335.0	0.93	4.18	5.02	2.84	0.02	79.44
337.0	0.89	3.46	5.18	3.30	-0.04	79.21
341.0	0.97	2.76	5.18	4.48	-0.16	78.73
344.0	0.91	1.97	5.14	5.88	-0.03	78.37
347.0	1.04	1.80	5.40	7.38	-0.08	78.02
348.9	0.97	1.39	5.23	8.87	0.18	77.78
351.9	1.24	1.49	1.31	10.64	-0.28	77.43
353.9	0.90	0.921	1.38	12.48	-0.18	77.19
356.9	1.10	0.900	1.35	15.52	-0.20	76.84
360.9	0.84	0.508	1.33	21.12	0.19	76.36
363.9	0.81	0.403	1.34	25.85	0.05	76.00
366.8	0.92	0.374	1.40	31.59	0.03	75.65
369.8	0.98	0.322	1.38	39.19	0.62	75.30
372.8	0.99	0.266	1.33	47.52	0.72	74.94
1-Nonyl-2-methylimidazole, $\Delta_f H_m(298.15 \text{ K}) = 87.40 \pm 0.27 \text{ kJ} \cdot \text{mol}^{-1}$						
$\ln(p/\text{Pa}) = (389.94/R) - \{125413.72/[R \cdot (T, \text{K})]\} - (127.5/R)\ln[(T, \text{K})/298.15]$						
328.2	0.27	5.41	5.90	0.59	0.01	83.57
328.2	0.25	4.83	4.91	0.61	0.02	83.56
328.2	1.22	25.1	7.41	0.58	0.00	83.57
330.2	1.24	21.3	7.53	0.69	-0.01	83.32
330.6	0.34	5.24	5.24	0.75	0.02	83.26
333.2	0.36	4.72	4.88	0.88	-0.04	82.94
333.2	0.20	2.54	4.91	0.92	-0.01	82.93
333.2	1.37	17.5	7.50	0.93	0.01	82.94
335.6	0.30	3.03	5.20	1.16	0.01	82.62
337.2	1.48	13.2	7.47	1.34	0.02	82.43
338.2	0.31	2.44	4.88	1.47	0.03	82.29
338.2	0.25	2.04	4.91	1.44	0.00	82.29
340.7	0.23	1.58	3.79	1.73	-0.05	81.98
341.1	1.42	9.41	7.53	1.80	-0.04	81.93
343.2	0.23	1.23	4.91	2.17	-0.03	81.66
344.2	1.38	6.97	7.47	2.36	-0.03	81.53
345.6	0.52	2.21	3.79	2.74	0.04	81.35
347.2	1.34	5.45	4.03	2.93	-0.12	81.15
348.2	0.36	1.22	3.67	3.40	0.10	81.02
348.2	0.60	2.04	4.91	3.45	0.14	81.02
350.2	1.34	4.33	4.06	3.69	-0.18	80.77
350.6	0.96	2.72	3.79	4.14	0.12	80.71
352.1	0.67	1.72	4.91	4.57	0.04	80.52
353.1	0.54	1.32	3.77	4.78	-0.09	80.40
353.2	1.58	3.79	4.07	5.00	0.09	80.39
355.6	0.51	1.02	2.05	5.81	-0.12	80.07

Table 1. Continued

T^a	m^b	$V_{(N_2)}^c$	gas flow	p^d	$(p_{\text{exp}} - p_{\text{calc}})$	$\Delta_f H_m(T)$
K	mg	dm ³	dm ³ ·h ⁻¹	Pa	Pa	kJ·mol ⁻¹
356.2	1.72	3.36	4.04	6.08	-0.10	80.00
357.3	0.44	0.750	2.14	6.81	0.10	79.86
359.3	1.44	2.24	4.07	7.69	-0.10	79.61
360.6	0.49	0.682	2.05	8.37	-0.25	79.44
362.1	1.64	2.02	4.03	9.68	0.11	79.25
362.2	0.54	0.638	2.13	9.94	0.23	79.23
362.3	0.59	0.697	2.20	9.86	0.15	79.23
365.2	1.63	1.62	4.05	12.0	0.03	78.86
365.6	0.53	0.512	2.05	12.01	-0.37	78.80
367.2	0.65	0.551	2.20	13.72	-0.12	78.60
367.3	0.60	0.507	2.17	13.82	-0.05	78.59
368.2	1.13	0.875	1.05	15.35	0.58	78.47
368.2	1.50	1.18	2.02	15.06	0.29	78.47
370.2	1.40	1.02	2.04	16.38	-0.59	78.22
370.6	0.77	0.512	2.05	17.67	0.17	78.16
372.2	0.82	0.474	2.03	20.22	0.69	77.96
372.2	0.93	0.551	2.20	19.78	0.32	77.96
372.2	1.57	0.981	2.03	18.92	-0.53	77.96
373.2	1.36	0.815	2.04	19.92	-0.89	77.84
374.1	1.50	0.778	2.03	22.83	0.73	77.72
1-Decyl-2-methylimidazole, $\Delta_f H_m(298.15 \text{ K}) = 91.84 \pm 0.27 \text{ kJ} \cdot \text{mol}^{-1}$						
$\ln(p/\text{Pa}) = (404.19/R) - \{132297.46/[R \cdot (T, \text{K})]\} - (135.7/R) \ln[(T, \text{K})/298.15]$						
343.0	1.62	19.6	7.36	0.92	-0.01	85.76
344.0	0.95	10.4	7.36	1.02	-0.01	85.62
346.0	1.87	17.3	7.31	1.20	-0.01	85.35
349.0	1.93	13.3	7.20	1.60	0.04	84.94
351.9	1.50	8.51	7.29	1.96	-0.05	84.54
354.9	1.50	6.57	5.12	2.52	-0.03	84.13
356.9	1.64	6.00	5.14	3.02	0.03	83.87
359.9	1.59	4.65	4.90	3.80	0.02	83.46
363.9	1.51	3.19	5.04	5.22	0.11	82.92
367.8	1.62	2.53	4.90	7.09	0.23	82.38
369.8	1.59	2.26	5.03	7.79	-0.11	82.12
372.8	1.47	1.60	1.01	10.14	0.32	81.71
375.8	1.36	1.26	1.01	11.97	-0.14	81.30
378.7	1.54	1.14	1.02	15.00	0.19	80.90
380.7	1.52	1.02	1.02	16.41	-0.52	80.63
382.7	1.54	0.906	1.05	18.86	-0.43	80.37

^a Saturation temperature ($\pm 0.1 \text{ K}$). ^b Mass of transferred sample ($\pm 0.0001 \text{ g}$) trapped at 243 K. ^c Volume of nitrogen measured ($\pm 0.01 \text{ dm}^3 \cdot \text{h}^{-1}$) by transfer of the mass m . ^d Experimental vapor pressure obtained from the m and the small amount of the residual vapor pressure at $T = 243 \text{ K}$ calculated by iteration.

within a definite period of time:

$$p_i = m_i \cdot R \cdot T_a / V \cdot M_i \quad (1)$$

where M_i is the molar mass of the compound i . The total volume of the system $V = V_{N_2} + V_i$ consists from the volume V_{N_2} of transporting gas and the volume contribution V_i to the gaseous phase of the compound i under study. It is apparent that $V_{N_2} \gg V_i$. The volume V_{N_2} was calculated from the flow rate and time measurements. The flow rate is measured with the soap bubble meter at ambient temperature T_a . R is the universal gas constant. The decomposition of samples during vapor pressures studies was not observed.

3. RESULTS AND DISCUSSION

To the best of our knowledge, these compounds are studied for the first time. Vapor pressures of 1-(n -alkyl)-2-methylimidazoles measured in this work and enthalpies of vaporization (Table 1) were treated with eqs 2 and 3, respectively

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

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

Table 2. Temperature Range of the Transpiration Studies, Heat Capacities, and Enthalpies of Vaporization of 1-(*n*-Alkyl)-2-methylimidazoles

compound	<i>T</i> range	C_p^1 ($\Delta_f^f C_m$) ^a	$\Delta_f^f H_m T_{av}$	$\Delta_f^f H_m$ (298.15 K)
	K	J · mol ⁻¹ · K ⁻¹	kJ · mol ⁻¹	
1-ethyl-2-methylimidazole	293.5–363.0	226.2 (–69.4)	58.7	60.4 ± 0.3
1-propyl-2-methylimidazole	288.6–343.2	258.1 (–77.1)	62.5	63.7 ± 0.2
1-butyl-2-methylimidazole	293.6–343.0	290.0 (–86.0)	66.0	67.8 ± 0.2
1-pentyl-2-methylimidazole	303.3–354.2	321.9 (–94.3)	68.5	71.4 ± 0.3
1-hexyl-2-methylimidazole	313.0–362.9	353.8 (–102.6)	70.8	74.7 ± 0.4
1-heptyl-2-methylimidazole	312.2–368.4	385.7 (–110.9)	75.1	79.4 ± 0.2
1-octyl-2-methylimidazole	323.1–372.8	417.6 (–119.2)	78.2	83.8 ± 0.2
1-nonyl-2-methylimidazole	328.2–374.1	449.5 (–127.5)	80.8	87.4 ± 0.3
1-decyl-2-methylimidazole	343.0–382.7	481.4 (–135.7)	83.2	91.8 ± 0.6

^a Values of C_p^1 and $\Delta_f^f C_p$ have been calculated by group-contribution method.⁴

Values of $\Delta_f^f C_p$ were calculated using a procedure suggested by Chickos and Acree.⁴ Experimental values of the isobaric molar heat capacities of liquid, C_p^1 , of 1-(*n*-alkyl)-2-methylimidazoles required for $\Delta_f^f C_p$ calculations were not found in the literature. Values of C_p^1 were assessed using the group contribution method.⁴ Vapor pressures obtained by the transpiration method are reliable within (1 to 3) % according to test measurements with the alkanols.² The accuracy of vapor pressures is mostly governed by reproducibility of the analytical procedure used for the determination of the transported mass m_i , and a contribution due to uncertainties of other experimental parameters given in eq 1 is negligible.²

The quality of the experimental data is presented by differences ($p_{exp} - p_{calc}$) in Table 1, column 6. It has turned out that for 2-methyl-(*n*-alkyl)imidazoles the reproducibility of the experimental vapor pressures was mostly within (1 to 3) %; however, some points deviate up to (5 to 6) %, and this is typical for the low vapor pressures measured in the current work.

3.1. Correlation of $\Delta_f^f H_m$ (298.15 K) of 1-(*n*-Alkyl)-2-methylimidazoles with the Chain Length. Molar vaporization enthalpies $\Delta_f^f H_m$ (298.15 K) of the aliphatic aldehydes,⁵ nitriles,⁶ esters,⁷ and alkylbenzenes⁸ appear to be a linear function of the number of carbon atoms in the alkyl chain. The approximation of $\Delta_f^f H_m$ (298.15 K) with the number of C-atoms in the alkyl chain of 1-(*n*-alkyl)-2-methylimidazoles (N_C) fit very well in the linear correlation. The chain length dependence of vaporization enthalpy (see Table 2) is expressed by the following equation:

$$\Delta_f^f H_m(298.15 \text{ K}) / (\text{kJ} \cdot \text{mol}^{-1}) = 51.9 + 4.0N_C \quad \text{with} \quad (R^2 = 0.998) \quad (4)$$

Using this equation, enthalpies of vaporization of alkyl-2-methylimidazoles with the longer alkyl chain where experimental data are absent could be derived. Also, a good linear correlation is an evidence of the internal consistency of the data measured in this work.

3.2. Correlation of $\Delta_f^f H_m$ (298.15 K) of 1-(*n*-Alkyl)-2-methylimidazoles with Kovat's Indices. The correlation of the enthalpies of vaporization with the Kovat's indices of the organic compounds is a valuable method to study the systematic behavior in a homologous series. The vaporization enthalpy $\Delta_f^f H_m$ also appears to be a function of the Kovat's indices in a homologous series of alkanes, alcohols, and aliphatic ethers⁹ as

Table 3. Kovat's Indices of Alkylimidazoles on the HP-101 Phase at Different Temperatures

compound	Kovat's indices, J_x					
	T , K	393	403	413	423	433
1-ethyl-2-methylimidazole		1046	1049	1052	1055	1058
1-propyl-2-methylimidazole		1129	1132	1136	1139	1143
1-butyl-2-methylimidazole		1225	1228	1232	1235	1239
	T , K	443	453	463	473	483
1-pentyl-2-methylimidazole		1337	1340	1344	1345	1354
1-hexyl-2-methylimidazole		1435	1438	1443	1447	1452
1-heptyl-2-methylimidazole		1534	1537	1542	1546	1552
1-octyl-2-methylimidazole		1634	1637	1642	1647	1652
	T , K	483	493	503	513	523
1-nonyl-2-methylimidazole		1752	1756	1760	1765	1768
1-decyl-2-methylimidazole		1852	1856	1860	1865	1868

well as of alkylbenzenes.⁸ However, for the alkylimidazoles this aspect needs further investigation.

Although coupled techniques of GC with mass spectrometry have made tremendous progress in the last decades, measurements of GC retention values, especially the retention indices, are still widely used as a simple, effective, inexpensive, and sensitive means of identification. In the Kovat's index or Kovat's retention index, J_x , used in gas chromatography, *n*-alkanes serve as the standards, and logarithmic interpolation is utilized as defined by

$$J_x = \frac{\log(t_x) - \log(t_N)}{\log(t_{N+1}) - \log(t_N)} \cdot 100 + 100N \quad (5)$$

where *x* refers to the adjusted retention time *t*, *N* is the number of carbon atoms of the *n*-alkane eluting before, and (*N* + 1) is the number of carbon atoms of the *n*-alkane eluting after the peak of interest. According to the established GC procedure, all retention times are corrected for the “dead” retention time adjusted from the retention times of the homologues of linear aliphatic hydrocarbons.¹⁰ Thus, the retention time t_x of the compound of interest *x* is bounded by retention times of the two *n*-alkanes. Kovat's index is the characteristic retention index acknowledged among analytical chemists for the identification of the individual compounds in diverse mixtures. The Kovat's indices are generally

Table 4. Coefficients of the Temperature Dependences of Kovat's Indices $J_x = a + b \cdot T$

compound	<i>a</i>	<i>b</i>	<i>R</i> ²	<i>J_x</i> 373 K	<i>J_x</i> 373 K ¹¹
1-ethyl-2-methylimidazole	923	0.312	0.9973	1064	1050
1-propyl-2-methylimidazole	993	0.346	0.9986	1150	1131
1-butyl-2-methylimidazole	1081	0.365	0.9987	1246	1226
1-pentyl-2-methylimidazole	1162	0.392	0.9086	1340	1320
1-hexyl-2-methylimidazole	1242	0.435	0.9943	1439	
1-heptyl-2-methylimidazole	1336	0.446	0.9942	1538	
1-octyl-2-methylimidazole	1430	0.459	0.9956	1638	
1-nonyl-2-methylimidazole	1557	0.403	0.9981	1740	
1-decyl-2-methylimidazole	1654	0.410	0.9974	1840	

standardized for the common stationary phase of a GC column. As a rule, Kovat's indices are only slightly dependent on the GC-oven temperature.¹⁰

In this work we have measured Kovat's indices for in the temperature range (393 to 523) K using the low polarity column HP-101 (see Table 3). In the studied temperature range Kovat's indices have been approximated with linear equations $J_x = a + b \cdot T$ (see Table 4), and indices at the reference temperature 373 K have been calculated for comparisons with the literature data.¹¹ As can be seen in Table 4, Kovat's indices on the low polar stationary phase OV-101 reported in ref 11 are very close to our results, and they show the same trend with the chain length.

We consider how the vaporization enthalpy $\Delta_f^g H_m$ correlates with Kovat's indices within a homologous series of 1-(*n*-alkyl)-2-methylimidazoles. It has turned out that the data for $\Delta_f^g H_m$ - (298.15 K) fit very well in the linear correlation. The following empirical equations for the enthalpy of vaporization have been obtained:

$$\Delta_f^g H_m(298.15 \text{ K}) / (\text{kJ} \cdot \text{mol}^{-1}) = 17.2 + 0.042 J_x \quad \text{with} \\ (R^2 = 0.999) \quad \text{for HP-101} \quad (6)$$

$$\Delta_f^g H_m(298.15 \text{ K}) / (\text{kJ} \cdot \text{mol}^{-1}) = 16.7 + 0.042 J_x \quad \text{with} \\ (R^2 = 0.999) \quad \text{for OV-101/KF} \quad (7)$$

where J_x is the Kovat's index of a alkylbenzene and R^2 is the correlation coefficient. On the one hand, these relationships can be used as evidence of internal consistency of our experimental results for vaporization enthalpies. On another hand, these relationships can be used to predict enthalpies of vaporization of the parent alkyl-2-methylimidazoles provided that their retention indices are known.

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Funding Sources

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.

Notes

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