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1 **Surface characterization of 1-butyl-1-ethylpiperidinium bromide**
2 **by inverse gas chromatography**

3 Stella K. Papadopoulou^{a,*}, Nicolas Papaiconomou^{a,b}, Stéphane Baup^c,
4 Cristina Iojoiu^a, Lenka Svecova^a, Pierre-Xavier Thivel^a

5
6 ^a *Université Grenoble Alpes, Université Savoie Mont Blanc, CNRS, Grenoble INP, LEPMI,*
7 *38000 Grenoble, France*

8 ^b *Institut de Chimie de Nice, Université Côte d'Azur, UMR CNRS 7272, Parc Valrose, F-*
9 *06108 Nice Cedex 2, France*

10 ^c *Université Grenoble Alpes, CNRS, Grenoble INP, LRP, 38000 Grenoble, France*

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21 * Corresponding author e-mail address: papadopoulou.styliani@gmail.com (S.K.
22 Papadopoulou)

23 **Abstract**

24 This work addresses the surface characterization of an organic salt based on a piperidinium
25 cation and a halide anion, similar to a first generation ionic liquid, using the Inverse Gas
26 Chromatography (IGC) technique. IGC was employed in order to assess the dispersive surface
27 energy and the acid/base character of 1-butyl-1-ethylpiperidinium bromide, [C₂C₄PIP]Br at a
28 temperature range (313.15-343.15 K) well below its melting point, where the retention
29 mechanism is governed by the surface adsorption of the probes. This type of characterization
30 was possible due to the high melting point of [C₂C₄PIP]Br, namely 413.15 K. The dispersive
31 component of the surface energy was estimated with the aid of the Schultz method and the
32 Dorris-Gray method. Results obtained using the first method were higher than the ones
33 obtained by the latter. The discrepancy between the two methods was found to increase with
34 the increase of temperature. The acid/base characterization was implemented by using the
35 Flour and Papirer approach as well as the Brookman and Sawyer method. The acidity and
36 basicity constants of the surface of [C₂C₄PIP]Br revealed that it is amphoteric with a
37 predominantly basic character.

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55 **Keywords:** Ionic liquids; Inverse gas chromatography; 1-butyl-1-ethylpiperidinium bromide;
56 Surface energy; Acid-base interactions

57 **1 Introduction**

58 Ionic liquids (ILs) are salts exhibiting low melting points, typically below 100°C, composed
59 of anions and large organic cations, such as imidazolium, pyridinium, pyrrolidinium and less
60 commonly piperidinium [1-6]. ILs have a number of interesting properties such as non-
61 volatility, non-flammability, high thermal and ionic conductivity and an enhanced solvation
62 ability for a wide range of materials [1, 4, 5, 7]. On these grounds, ILs have been widely
63 explored as ‘green’ media in chemical and catalytic reactions, distillations, liquid-liquid
64 extractions and solvent-aided crystallizations [1, 4, 5]. Other studies report the utilization of
65 ILs as lubricants, in gas separation processes and as gas storage media [7]. ILs were also
66 employed as electrolytes in batteries, electrochemical capacitors [3] and as catalysts [8].

67 Piperidinium based ILs are of special interest for electrochemical applications due to their
68 water immiscibility, high conductivities and wide electrochemical windows [9, 10]. As
69 piperidinium based ionic liquids contain only saturated carbons, Shukla demonstrated that for
70 a given anion, these ILs exhibit higher melting points and are thermally more stable than the
71 respective imidazolium ILs having the same alkyl chains appended on the cation [9, 10]. In
72 particular, piperidinium bromide salts exhibit very high melting points (in the vicinity of
73 200°C) whereas their homologous imidazolium bromide salts are either liquids or present low
74 melting points [9, 10]. When ionic liquids are involved in applications such as extraction and
75 catalysis, the presence of a second phase (liquid or gas) other than the ionic liquid is required.
76 Reactions, interactions and chemical exchanges that take place at the interface of the two-
77 phase systems strongly depend on the surface properties of each fluid [11]. Therefore, the
78 understanding of surface related properties of ionic liquids, such as their surface energy and
79 acid-base character is necessary for the elucidation of the mechanisms that govern these
80 reactions [7, 12-15].

81 Although there is a plethora of experimental studies investigating the surface tension of ionic
82 liquids with various techniques [16], only a restricted number of publications address the
83 estimation of the dispersive surface energy of ionic liquids with the use of inverse gas
84 chromatography (IGC). Over the past years, inverse gas chromatography has proved to be a
85 valuable tool towards the characterization of the surface and thermodynamic properties of
86 various inorganic and organic materials such as polymers, fillers and pharmaceuticals [17]. It
87 should be outlined that the choice of the measurement temperature range is crucial in IGC as

88 it determines the state (melt or solid) of the material under study, governing thus the retention
89 mechanism of the probes (surface adsorption in the case of solids or mixing with bulk of the
90 melt) [17].

91 Although during the last decade IGC appears to be very popular for the thermodynamic
92 characterization of ionic liquids [8, 18-26], it has rarely been utilized for their surface
93 characterization. This is due to the fact that such characterization should be conducted at a
94 temperature range below the melting point of the IL in order to ensure that the interaction
95 mechanism between the probes and IL is surface adsorption [17]. On these grounds, as ILs
96 exhibit low melting points, IGC is rather appropriate for the surface analysis of high melting
97 point salts or for the thermodynamic characterization of ionic liquids.

98 The group of Wang has published a series of papers on the surface [27-29] and
99 thermodynamic characterization [8, 18, 30-33] of methyl imidazolium ILs by means of IGC.
100 To our knowledge, these are the only IGC studies addressing the surface characterization of
101 ionic liquids [27-29]. It has to be stressed that the authors conducted both the surface and the
102 thermodynamic characterizations at the same experimental temperature range, which is well
103 above the melting point of the studied ILs [34]. Given the fact that the studied substances
104 were in all cases in the liquid state and thus the probes' interaction mechanism was bulk
105 absorption, the measurement temperatures used in these three studies were not appropriate for
106 the surface characterization of the methyl imidazolium ILs.

107 In the current contribution, we present the results of the IGC surface characterization of 1-
108 butyl-1-ethylpiperidinium bromide [C₂C₄PIP]Br. Piperidinium based ILs is a family of ionic
109 liquids much less studied than those based on imidazolium or pyridinium cations for example
110 [35]. Concerning their IGC characterizations, only a limited number of studies have reported
111 the estimation of the thermodynamic properties of piperidinium-based ILs bearing anions
112 other than the bromide anion, or with different alkyl chain appended onto the cation, as those
113 present in [C₂C₄PIP]Br [36-38]. 1-butyl-1-ethylpiperidinium bromide is an organic salt being
114 by all aspects similar to halide-based ionic liquid, with the exception that its melting point is
115 above 373 K. Hence, IGC measurements were performed at 313.15-343.15 K, a temperature
116 range which is below the melting point of [C₂C₄PIP]Br. The energy, enthalpy and entropy of
117 adsorption of polar probes on the surface of the salt, the dispersive component of the surface
118 energy and the Lewis acidity and basicity constants of [C₂C₄PIP]Br were determined. The
119 dispersive interactions were investigated with the aid of well-known methods proposed by
120 Dorris and Gray and by Schultz, whereas the specific interactions of the polar probes were
121 calculated using the Brookman and Sawyer approach and the Flour and Papirer method.

122 In this article, after the theoretical background section and a section dedicated to detailing the
123 procedure used for carrying out the IGC analysis, results will be presented and discussed.

124

125 **2 Theoretical background**

126 Contrary to the conventional gas chromatography, in IGC, the material under study is packed
127 into the column where injections of carefully selected probes with known physicochemical
128 properties are made [17, 39, 40]. The probes can be injected onto the column either at infinite
129 dilution or at finite concentration. In the case of infinite dilution, the injection of minor
130 amounts of the tested solvent makes sure that the retention is governed by the stationary
131 phase-probe interactions and the probe-probe interactions are avoided [17].

132 The key measurement in IGC experiments is the net retention volume of the probes, V_N . It is
133 expressed as the volume of the carrier gas necessary to elute the solute from the column and is
134 calculated by the following equation [41]:

$$135 \quad V_N = jF_M(t_R - t_M)\frac{T}{T_F}\left(1 - \frac{p_W}{p_0}\right) \quad (1)$$

136 where t_R, t_M are the probe's and marker's retention times, respectively, F_M is the carrier gas
137 flow rate measured at the column outlet at ambient pressure, p_0 and at room temperature, T_F .
138 Also, T is the column temperature, p_W is the vapor pressure of water at T_F and j is the James
139 and Martin factor used to correct the gas carrier compressibility, defined as [41]:

$$140 \quad j = \frac{3}{2} \left[\frac{\left(\frac{p_i}{p_0}\right)^2 - 1}{\left(\frac{p_i}{p_0}\right)^3 - 1} \right] \quad (2)$$

141 where p_i and p_0 are the column inlet and outlet pressures, respectively.

142

143 **2.1 Dispersive interactions**

144 The dispersive component of the surface energy of a solid, γ_s^d , can be determined, using the
145 Dorris-Gray method [36], as described by the following equation:

$$146 \quad \gamma_s^d = \left(\frac{1}{4\gamma_{CH_2}}\right) \left(\frac{-\Delta G^{CH_2}}{N\alpha_{CH_2}}\right)^2 \quad (3)$$

147 where ΔG^{CH_2} is the adsorption free energy of one methylene group, N is the Avogadro's
148 number, α_{CH_2} is the cross-sectional area of an adsorbed methylene group (6 \AA^2) and γ_{CH_2} is the
149 surface free energy of a solid material constituted by methylene groups only, such as linear

150 polyethylene [$\gamma_{CH_2} = 35.6 - 0.058t$, with t being the working temperature, in °C)]. The
 151 adsorption free energy of one methylene group is calculated by the following equation:

$$152 \quad \Delta G^{CH_2} = -RT \ln \left(\frac{V_{N(n+1)}}{V_{N(n)}} \right) \quad (4)$$

153 where $V_{N(n+1)}$ and $V_{N(n)}$ are the retention volumes of n -alkanes with $n + 1$ and n carbon
 154 atoms, respectively, T is the column temperature and R is the ideal gas constant. The slope of
 155 the straight line obtained by a plot of the surface free energy of adsorption
 156 of n -alkanes $RT \ln V_N$ versus the number of their carbon atoms is equal to the free energy of
 157 adsorption of a methylene group, ΔG^{CH_2} .

158 Another method used for the calculation of the dispersive component of the surface free
 159 energy, is the one proposed by Schultz et al. [42] and is based on the following equation:

$$160 \quad -\Delta G_a = RT \ln V_N = 2N\alpha \sqrt{\gamma_s^d \gamma_l^d} + C \quad (5)$$

161 where α is the surface area of the probe molecules, γ_s^d and γ_l^d are the dispersive components
 162 of the surface energy of the solid and the liquid probe, respectively and C is a constant.
 163 γ_s^d can be extracted from the slope of the linear plot of the $RT \ln V_N$ values of n -alkanes
 164 versus the term $\alpha \sqrt{\gamma_l^d}$.

165

166 **2.2 Specific interactions**

167 The non-dispersive character of the stationary phase is studied by the employment of probes
 168 that can also interact through specific intermolecular forces with the stationary phase. When a
 169 polar probe is injected in the column, it interacts with the material under study by both
 170 dispersive and specific interactions. The term specific includes all types of interactions, i.e.
 171 polar, hydrogen bonding, metallic or magnetic, apart from the dispersive ones (London
 172 forces) [17]. Hence, the contribution of specific interactions to the free energy of adsorption,
 173 ΔG^{sp} , can be considered as the difference between the total free energy of adsorption, ΔG^{ads} ,
 174 and the dispersive contribution to the free energy of adsorption ΔG^d . Several methods have
 175 been proposed for the determination of the ΔG^{sp} [17]. In the present study, ΔG^{sp} was
 176 calculated through the use of the Flour and Papirer approach [43] and the Brookman and
 177 Sawyer method [44]. The estimation of ΔG^{sp} is based on a plot of ΔG or simply $RT \ln V_n$
 178 values of both polar and apolar probes versus their boiling temperatures (t_b , in °C) according
 179 to the Brookman and Sawyer method, or the $\log p^0$, logarithm of their saturated vapor
 180 pressure, according to the Flour and Papirer method. The n -alkane series leads to a linear plot,

181 which constitutes a reference straight line for the dispersive interactions. The contribution of
182 specific interactions to the free energy of adsorption, ΔG^{sp} , corresponds to the vertical
183 distance between the $-\Delta G^{ads}$ value and the reference line according to the equation:

$$184 \quad (-\Delta G^{sp}) = (-\Delta G^{ads}) - (-\Delta G^{ref}) = RT \ln(V_N/V_{N,ref}) \quad (6)$$

185 where V_N is the net retention volume of the polar probe and $V_{N,ref}$ the net retention volume of
186 a hypothetical alkane with the same boiling point or saturated vapor pressure as that of the
187 polar probe.

188 The specific enthalpy, ΔH^{sp} , can be determined after the calculation of the specific
189 component of the free energy of adsorption at various temperatures. When plotting the ΔG^{sp}
190 values as a function of the reciprocal temperature, T^{-1} , ΔH^{sp} is calculated from the slope of
191 the straight line corresponding to the following relation:

$$192 \quad \Delta G^{sp}/T = \Delta H^{sp} \cdot 1/T - \Delta S^{sp} \quad (7)$$

193 The enthalpies of specific interactions between the examined surface and the polar probe can
194 be used for the estimation of the K_A and K_B indices reflecting the acidity (electron acceptor)
195 and basicity (electron donor) of a solid surface, respectively [17, 45-47] and are related to the
196 acidic or basic character through the equation:

$$197 \quad -\Delta H^{sp}/AN^* = K_A \cdot DN/AN^* + K_B \quad (8)$$

198 where DN [45] and AN^* [47] are Gutmann's donor and modified acceptor numbers of the
199 polar probes, respectively. Hence, K_A and K_B can be determined by the slope and intercept,
200 respectively, of the straight line obtained when plotting $\Delta H^{sp}/AN^*$ versus DN/AN^* . The
201 K_B/K_A ratio provides an empirical basis for the classification of a surface with respect to
202 acidity-basicity. At $K_B/K_A > 1$ the surface is considered to be basic, while for $K_B/K_A < 1$
203 the surface is considered to be acidic [17].

204

205 **3 Experimental**

206 **3.1 Materials**

207 For the synthesis of the ionic liquid, 1-bromobutane (99%), 1-ethylpiperidine (99%) and
208 acetonitrile were used and were purchased from Sigma Aldrich.

209 For the IGC analysis, the following solvents were used as probes: n-octane, n-nonane, n-
210 decane, n-undecane, n-dodecane, acetonitrile, n-butanol, pyridine and chloroform. The
211 characteristics of the solvents used for the IGC analysis are presented in Table 1. All solvents
212 were of the highest available purity and were purchased from Sigma Aldrich. Chromosorb W

213 HP (100/120) mesh was used as the solid support (Antelia, France). All the gases used were
214 purchased from Air Liquide and were of high purity.

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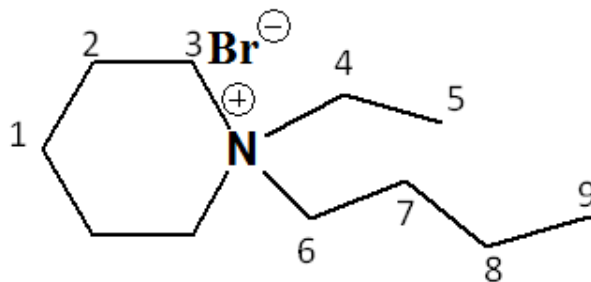
218 **Table 1.** Physical and chemical properties of the probes used for the IGC analysis [27, 47-52]

Probe	Boiling point (°C)	Saturated vapor pressure (kPa)	α (10^{-19} m^2)	γ_i^d (mJ/m^2)	DN (kJ mol^{-1})	AN^* (kJ mol^{-1})	Character
n-Octane	125.7	1.871	6.29	21.3	n/a	n/a	Neutral
n-Nonane	150.8	0.580	6.89	22.7	n/a	n/a	Neutral
n-Decane	174.2	0.181	7.5	23.4	n/a	n/a	Neutral
n-Undecane	195.9	0.056	8.1	24.6	n/a	n/a	Neutral
n-Dodecane	216.3	0.018	8.7	25.4	n/a	n/a	Neutral
n-Butanol	117.7	0.930	-	-	0	38.1	Acidic
Pyridine	115.3	2.772	-	-	138.6	0.6	Basic
Chloroform	61.2	26.165	-	-	0	22.6	Acidic
Acetonitrile	81.6	12.147	-	-	59	19.7	Amphoteric

219

220 3.2 Synthesis and characterization of 1-butyl-1-ethyl piperidinium bromide

221 1-butyl-1-ethylpiperidinium bromide (Figure 1) was synthesized as previously reported [53].
222 Briefly, 1-bromobutane was mixed with 1-ethylpiperidine in 100 mL acetonitrile at reflux for
223 2 days. The solvent was then evaporated using a rotary evaporator. The resulting product
224 appearing as a white solid was washed several times with ethyl acetate. After filtering, the
225 product was initially dried on a rotary evaporator to remove the remaining solvent and then
226 dried under vacuum (~ 0.1 mbar) for 24 hours. The final product was obtained as a white solid.
227 Purity was checked by Nuclear Magnetic Resonance Spectroscopy (^1H NMR). The ^1H NMR
228 spectrum was collected on a Bruker WM 400 MHz spectrometer in Dimethylsulfoxide
229 (DMSO- d_6) as solvent. The spectrum is given in the Supplementary Material section (Figure
230 S1). The chemical shift of different protons from $[\text{C}_2\text{C}_4\text{PIP}]\text{Br}$ are at: 3.36-3.30, (6H, m,
231 $(\text{CH}_2)_3\text{-N}^+$, 3,6), 3.25-3.21, (2H, t, $\text{CH}_2\text{-N}^+$, 4), 1.77 (4H, m, 2 CH_2 , 2), 1.58-1.53 (4H, m,
232 CH_2 , 1,7), 1.37-1.28 (2H, m, CH_2 , 8), 1.19-1.15 (3H, t, CH_3 , 5), 0.95-0.92 (3H, t, CH_3 , 9).



233
234 **Figure 1.** Structure of [C₂C₄PIP]Br. The protons observed in the NMR spectrum were
235 identified.

236
237 The melting point of [C₂C₄PIP]Br was assessed by Differential Scanning Calorimetry using a
238 TA Instruments DSC 2920 modulated DSC device. The sample was heated from 25 °C to
239 250 °C at a heating rate of 5K/min. The DSC thermogram is presented in the Supplementary
240 Material section (Figure S2). The melting point of the [C₂C₄PIP]Br was found to be 140 °C.

241 242 **3.3 Column preparation and IGC setup**

243 The IGC experiments were performed using a Perkin Elmer Clarus 480 gas chromatograph,
244 equipped with a flame ionization detector (FID). The data acquisition was made with the
245 AZUR software. The retention times of the probes were determined after the calculation of
246 the first-order moment of the concentration distribution. This was necessary due to the slight
247 “tailing” observed at the elution profile of the probes [41]. High purity helium was used as the
248 carrier gas and methane was used as a marker. The flow rate of helium was measured with a
249 soap bubble flowmeter connected to the end of the column, at room temperature. The
250 experiments were performed at infinite dilution, by injecting manually 0.1 μL of each probe
251 with a 1 μL Hamilton syringe. At least three injections of each probe were made and the
252 retention time was taken as the average of the three measurements. The standard deviation
253 was less than 2% in all cases.

254 The IGC experimental conditions and the column characteristics are presented in Table 2. A
255 stainless steel column was used for the measurements and was washed with acetone prior to
256 use. The stationary phase of the column was prepared via the coating method proposed by Al-
257 Saigh and Munk in order to better control the amount of the salt coated on the solid support
258 [54]. [C₂C₄PIP]Br was coated onto Chromosorb W HP at a loading of 20.7% w/w. The
259 column was preconditioned overnight to the working conditions (temperature and helium flow
260 rate) in order to remove any possible contaminants that could be eluted during measurements.

261 The protocol regarding the preparation of the column was described in detail elsewhere [50,
262 55, 56].

263

264 **Table 2.** Chromatographic conditions and column specifications

1-butyl-1-ethylpiperidinium bromide	
Injector temperature (K)	473.15
Detector temperature (K)	473.15
Column temperatures (K)	313.15, 323.15, 333.15, 343.15
Column type of material	SS 316 ASTM A-269
Column length (cm)	70
Column O.D (inch)	1/8
[C ₂ C ₄ PIP]Br loading (%)	20.7
Flow rate (mL/min)	10

265

266 **4 Results**

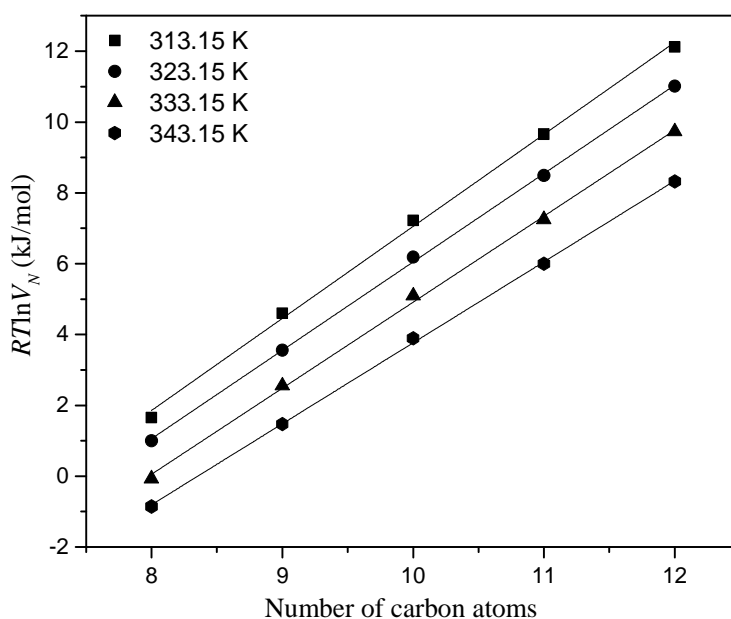
267 **4.1 Dispersive component of the surface energy**

268 The dispersive component of the surface energy of 1-butyl-1-ethylpiperidinium bromide was
269 calculated at the temperature range 313.15-343.15 K, using the Dorris-Gray method and the
270 approach proposed by Schultz.

271

272 **4.1.1 Dorris-Gray method**

273 The slope of the line obtained when plotting the $RT \ln V_N$ values of *n*-alkanes versus their
274 number of carbon atoms yields the free energy of adsorption of a methylene group, ΔG^{CH_2} as
275 indicated by Eq. (4). The corresponding plot is illustrated in Figure 2. The dispersive
276 component of the surface energy of [C₂C₄PIP]Br was calculated via Eq. (3) according to the
277 Dorris-Gray method. The values of γ_s^d together with their maximum errors are presented in
278 Table 3.

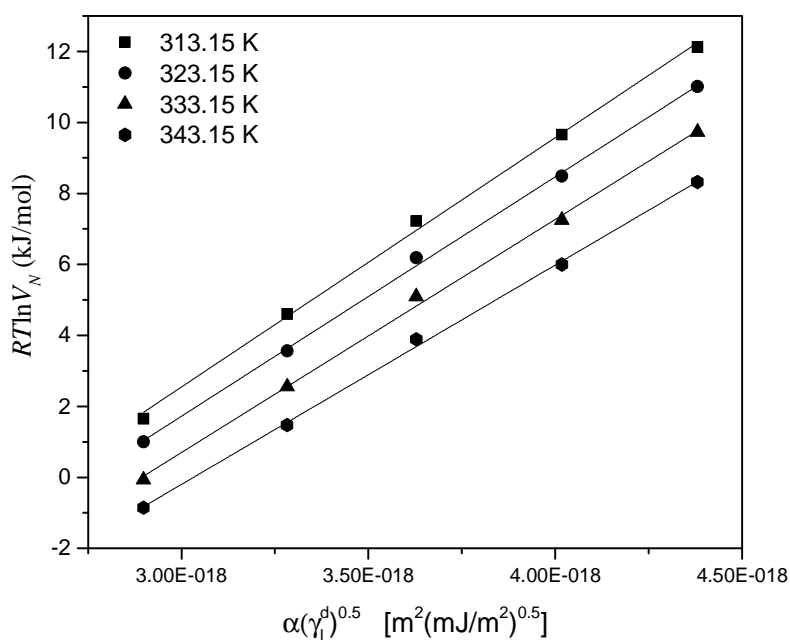


279
 280 **Figure 2.** Surface free energy of adsorption of *n*-alkanes $RT \ln V_N$ on $[C_2C_4PIP]Br$ versus
 281 their number of carbon atoms, measured at the temperature range 313.15-343.15 K.

282
 283 **4.1.2 Schultz method**

284 Figure 3 illustrates the surface free energy of adsorption of *n*-alkanes $RT \ln V_N$, on
 285 $[C_2C_4PIP]Br$ as a function of the term $a \sqrt{\gamma_l^d}$, measured between 313.15 and 343.15 K,
 286 according to the Schultz method. The values of the surface area of *n*-alkanes and the values of
 287 their dispersive surface energies listed in Table 1 in combination with Eq. (5) were used for
 288 this purpose. Results are listed in Table 3.

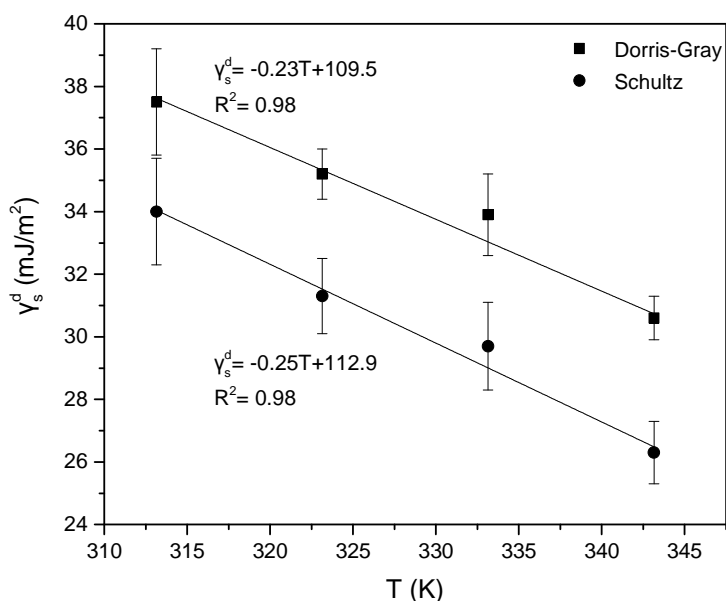
289
 290



291
 292 **Figure 3.** Surface free energy of adsorption of *n*-alkanes $RT \ln V_N$, on $[\text{C}_2\text{C}_4\text{PIP}]\text{Br}$ versus
 293 $a\sqrt{\gamma_i^d}$ measured at the temperature range 313.15-343.15 K.

294
 295 **Table 3.** Dispersive component of the surface energy of $[\text{C}_2\text{C}_4\text{PIP}]\text{Br}$ at the temperature range
 296 313.15-343.15 K, obtained by the Dorris-Gray and the Schultz methods

T (K)	Dorris-Gray method		Schultz method	
	γ_s^d (mJ/m^2)	R^2	γ_s^d (mJ/m^2)	R^2
313.15	37.5 ± 1.7	0.998	34.0 ± 1.7	0.998
323.15	35.2 ± 0.8	0.999	31.3 ± 1.2	0.999
333.15	33.9 ± 1.3	0.999	29.7 ± 1.4	0.998
343.15	30.6 ± 0.7	0.999	26.3 ± 1.0	0.999



297
 298 **Figure 4.** Variation of the dispersive component of the surface energy of [C₂C₄PIP]Br with
 299 temperature, at the temperature range 313.15-343.15 K, obtained by the Dorris-Gray and the
 300 Schultz methods

301
 302 Focusing on Figure 2 and Figure 3 we notice that good linearity was achieved for the
 303 dependence of the free energy of adsorption with the increasing number of aliphatic carbons
 304 (Dorris-Gray method) or with the $\alpha \sqrt{\gamma_i^d}$ term (Schultz method). The dispersive component of
 305 the surface energy of [C₂C₄PIP]Br obtained by the Dorris-Gray and the Schultz methods was
 306 plotted as a function of temperature (Figure 4) and the values are given in Table 3. For all
 307 studied temperatures, high correlation coefficients R² values were found. It appears that the
 308 dispersive component of the surface energy of [C₂C₄PIP]Br presents a decreasing trend with
 309 the increase of temperature [57]. Moreover, based on Figure 4 we notice that the dependence
 310 of γ_s^d with temperature is almost linear, and when comparing the slopes corresponding at the
 311 descending trend obtained by both methods, we observe that they are similar.

312 In addition, we notice that the γ_s^d values calculated with the aid of the Dorris-Gray method are
 313 higher with respect to those obtained with the Schultz method. The discrepancy between the
 314 results calculated by these methods increases with temperature. This trend is in line with the
 315 results presented in pertinent literature [58-66].

316 As it was mentioned in the introduction, there is no study in literature addressing the
 317 estimation of the dispersive surface energy of piperidinium or bromide based ILs. However,

318 the surface tension of piperidinium ILs has been assessed by techniques other than IGC (see
319 Table 4).

320

321 **Table 4.** Surface tension values of piperidinium based ILs taken from literature and dispersive
322 component of the surface energy results of [C₂C₄PIP]Br of the present study

T (K)	γ (mJ/m ²)		γ_s^d (mJ/m ²)
	[C ₃ C ₁ PIP][NTf ₂]	[C ₄ C ₁ PIP][NTf ₂] [68]	[C ₂ C ₄ PIP]Br (this work)
298	35.2 ^[69] / 35.3 ^[68]	34.2	-
303.2	34.5 ^[67] / 35.1 ^[68]	34.0	-
313.2	34.5 ^[68]	33.5	34.0 - 37.5
323.2	34.0 ^[68]	33.0	31.3 - 35.2
333.2	33.5 ^[68]	32.5	29.7 - 34.0
343.2	33.0 ^[68]	32.1	26.3 - 30.6

323

324 Osada et al. [67] reported the surface energy of 1-methyl-1-propylpiperidinium
325 bis(trifluoromethanesulfonyl)imide ([C₃C₁PIP][NTf₂]) measured with the Dynamic Light
326 Scattering (DLS) technique. Bhattacharjee et al. [68] assessed the surface energy of
327 [C₃C₁PIP][NTf₂] and [C₄C₁PIP][NTf₂] (1-Butyl-1-methylpiperidinium bis (trifluoromethyl
328 sulfonyl)imide) by using the contact angle method. The comparison between our results (last
329 column in Table 4) with literature data is not straightforward for several reasons; firstly, the
330 latter concern surface energy values contrary to the former which concern values of dispersive
331 surface energy. Furthermore, as it has been shown, the measuring techniques of the surface
332 energy as well as the sample purity have an impact on the values of γ [16, 68]. Moreover, the
333 anion [NTf₂]⁻ ((bistrifluoromethanesulfonyl)imide) reported in the literature is a polyatomic,
334 bulky and very weakly coordinating anion. It is thus very different from the small and
335 coordinating bromide ion studied here. On these grounds, only a rough comparison between
336 literature data and the results of this study can be made. As a first remark, the same
337 temperature dependence of γ and is γ_s^d observed for all ILs, all values decrease with
338 increasing temperature. It is well known that the surface tension depends on the contribution
339 of the groups which are exposed at the surface [16, 68]. In the case of ionic liquids, when the
340 cation bears long alkyl side chains and is thus bulkier than the anion, the surface tension is
341 affected primarily by the nature of the cation [16, 68].

342

343 4.2 Acid-base interactions

344 The ability of the ionic liquid to intermolecular specific interactions with other substances is
345 strongly dependent on the presence of acidic and basic sites on its surface.

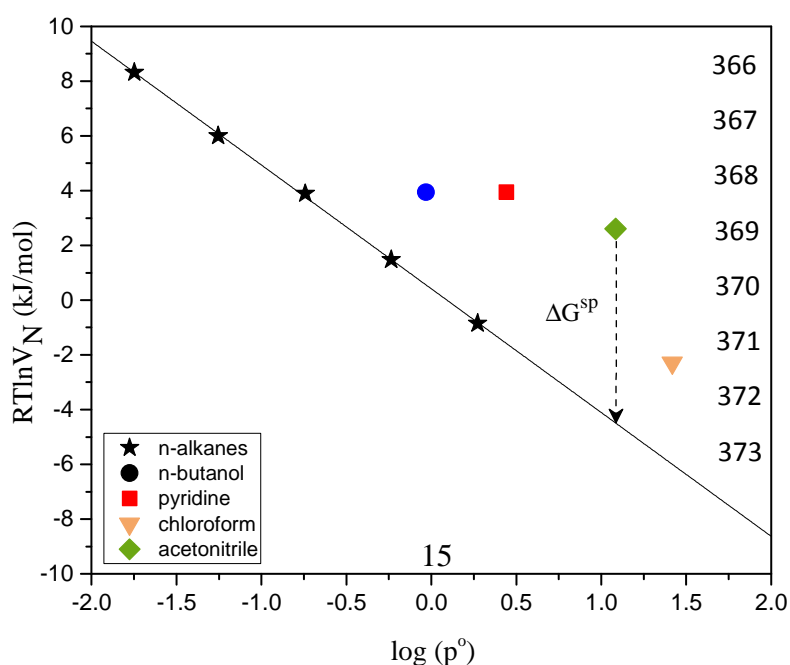
346 The assessment of the acid-base interactions of a surface includes the calculation of the
347 specific component of the free energy of adsorption of a probe, ΔG^{sp} , the specific component
348 of the free enthalpy of adsorption of a probe, ΔH^{sp} and the ratio K_B/K_A of the examined
349 surface [17]. As it has been mentioned in Section 2.2, several methods have been developed
350 for the acid-base characterisation of a material through the use of the IGC technique. The

351 Schultz method allows the estimation of ΔG^{sp} through the use of the term $\sqrt{\gamma_i^d}$, whereas the
352 Papirer method and the Brookman and Sawyer method are based on the saturated vapor
353 pressures and the boiling points of the probes, respectively. The latter two properties are
354 readily available in literature, contrary to the molecular area and the dispersive component of
355 the surface tension of polar probes. The discrepancy between the values of γ_s^d and a of polar
356 probes appearing in literature [65, 70] is due to the presence of one or more functional groups
357 [59]. For the above reasons, although in the present study the Schultz method was employed
358 for the dispersive surface energy calculation of $[C_2C_4PIP]Br$, the acid-base interactions were
359 studied with the aid of the Flour and Papirer method and the Brookman and Sawyer method.

360

361 4.2.1 Flour and Papirer method

362 Figure 5 presents the results of the energies of adsorption of *n*-alkanes and polar probes on the
363 surface of $[C_2C_4PIP]Br$ versus the logarithm of their saturated vapour pressure, according to
364 the Flour and Papirer method. The straight reference line defines the London dispersive
365 interactions, while the energies of adsorption polar probes lie above this line.

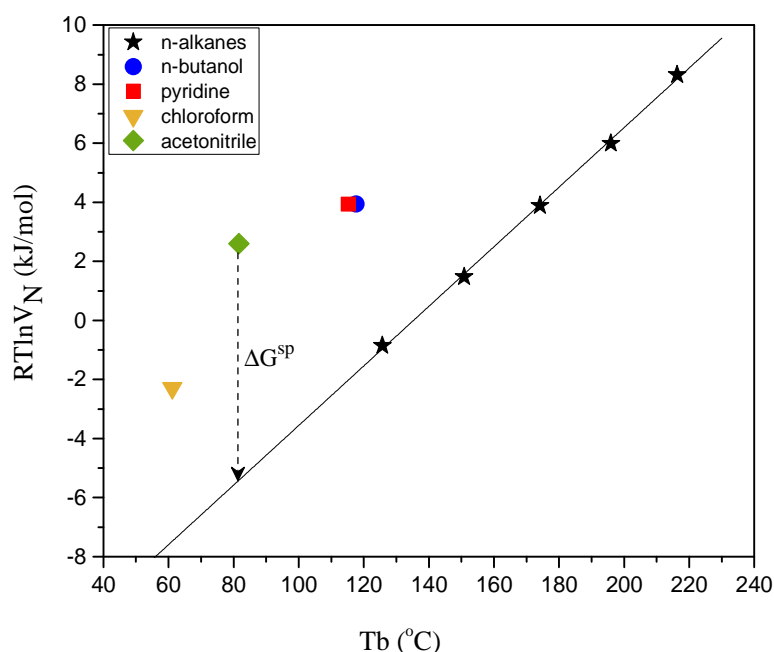


374 **Figure 5.** Energy of adsorption of *n*-alkanes and polar probes on the surface of [C₂C₄PIP]Br
375 versus the logarithm of their saturated vapour pressure, at 343.15 K.

376
377 The values of the specific component of the free energy of adsorption ΔG^{sp} of the polar
378 probes used in this study are high. The fact that the ΔG^{sp} values of the Lewis acidic, basic,
379 and amphoteric probes lie above the reference line of *n*-alkanes suggests that all types of
380 active sites are present on the surface of [C₂C₄PIP]Br [71]. The highest ΔG^{sp} values,
381 correspond to acetonitrile, which has an amphoteric character.

382 4.2.2 Brookman and Sawyer method

383 The contribution of specific interactions to the free energy of adsorption ΔG^{sp} of polar
384 probes, was calculated by the aid of the Brookman and Sawyer method, as shown in Figure 6.



385
386 **Figure 6.** Energy of adsorption of *n*-alkanes and polar probes on the surface of [C₂C₄PIP]Br
387 versus their boiling temperatures, at 343.15 K.

388
389 The ΔG^{sp} values obtained by both methods exhibit the same trend. Similarly to the conclusion
390 extracted by the Flour and Papirer analysis, results show that both acidic and basic sites exist
391 on the surface of [C₂C₄PIP]Br. However, the dominant character of the surface is determined
392 by means of the K_B/K_A ratio.

393 For such an estimation, the values of the enthalpy and entropy of adsorption of polar probes
394 on the surface of [C₂C₄PIP]Br were calculated by the aid of Eq. (7) and via a plot of ΔG^{sp}

395 values versus the reciprocal temperature, T^{-1} . The results obtained by both methods
 396 employed are reported in Table 5.

397 **Table 5.** Specific components of the enthalpy and entropy of adsorption of polar probes on
 398 the surface of [C₂C₄PIP]Br at the temperature range 313.15-343.15 K

Probe	Flour and Papirer method		Brookman and Sawyer method	
	$-\Delta H^{sp}$	$-\Delta S^{sp}$	$-\Delta H^{sp}$	$-\Delta S^{sp}$
	(kJ/mol)	(J/mol K)	(kJ/mol)	(kJ/mol K)
n-Butanol	5.59	6.48	11.31	15.56
Pyridine	7.74	6.51	9.30	8.99
Chloroform	24.07	59.58	28.73	66.41
Acetonitrile	0.63	-18.48	3.55	-13.84

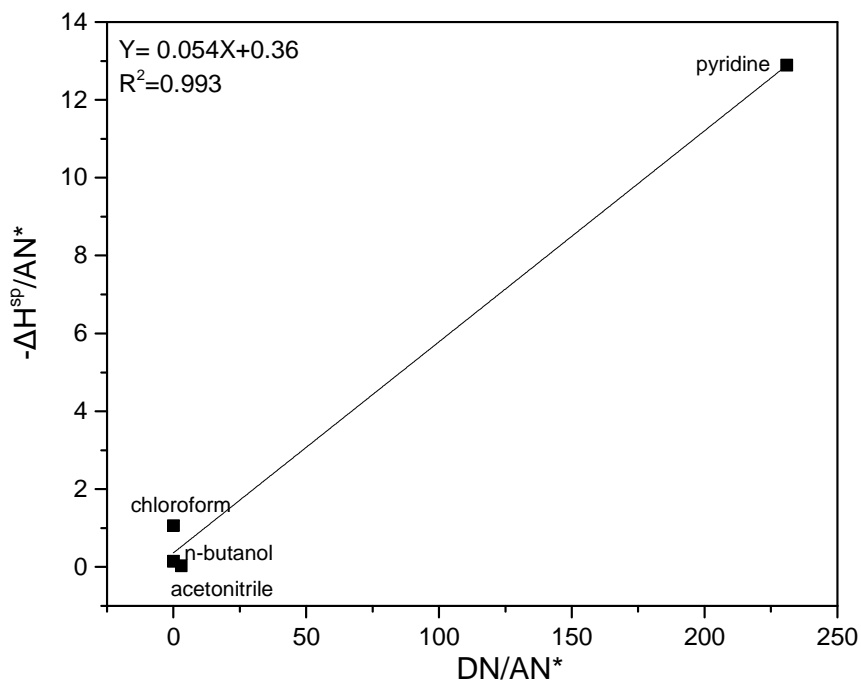
399 The enthalpies and entropies of adsorption of polar probes on the surface of [C₂C₄PIP]Br
 400 estimated with the Flour and the Brookman methods are comparable, with the exception of n-
 401 butanol. The enthalpy of adsorption of all probes was found to be exothermic in all cases.
 402 Acetonitrile which is an amphoteric probe presents the highest enthalpy of adsorption whereas
 403 chloroform which is acidic has the lowest ΔH^{sp} implying that [C₂C₄PIP]Br is amphoteric with
 404 a basic character. The values of the specific components of the entropy of adsorption of polar
 405 probes on the surface of [C₂C₄PIP]Br follow the same trend as discussed above. Acetonitrile
 406 has the highest ΔS^{sp} values, indicating that the surface is amphoteric. Moreover, we notice
 407 that all ΔS^{sp} values are negative, with the exception of acetonitrile. The adsorption of a probe
 408 from a surface is usually accompanied by an entropy loss as the probe passes from the less
 409 ordered vapor phase to the more ordered adsorbed phase. In the case of acetonitrile, the
 410 entropy increase implies an increase in the degrees of freedom which could be attributed to
 411 the rearrangement of the surface [72].

412

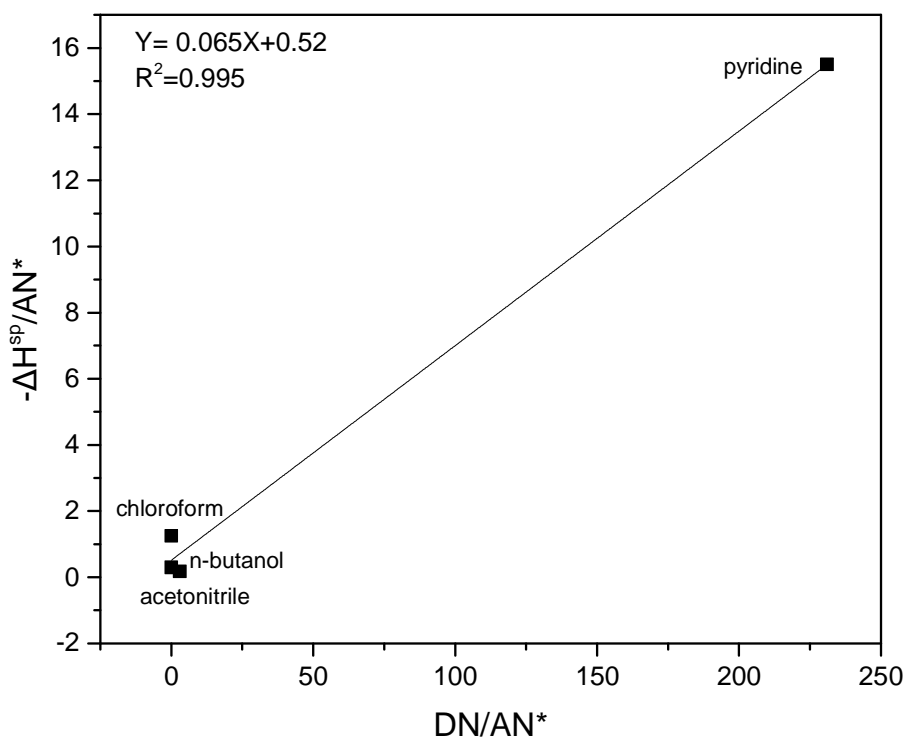
413 4.2.3 Acidity and basicity constants

414 The values for the specific enthalpies of polar probes were employed in order to evaluate the
 415 acidity and basicity constants of [C₂C₄PIP]Br. According to Eq. (8) the K_A and K_B constants
 416 can be assessed by the slope and the intercept, respectively, of a plot of $\Delta H^{sp}/AN^*$ versus
 417 DN/AN^* . Based on the values of the Gutmann's donor and modified acceptor numbers of the
 418 polar probes presented in Table 1 as well as the values of ΔH^{sp} obtained by the two methods
 419 used, K_A and K_B constants were evaluated (Figures 7 and 8). Examining the two plots we can

420 deduce that, in both cases, linear dependencies of $\Delta H^{sp}/AN^*$ versus DN/AN^* were achieved,
421 based on the high values of the regression coefficients. Similar plots for the estimation of the
422 K_A and K_B constants appear in literature [27, 51, 62, 68]. The results of the acidity and
423 basicity constants of the surface of $[C_2C_4PIP]Br$ are reported in Table 6.



424
425 **Figure 7.** Determination of the K_A and K_B values of the of $[C_2C_4PIP]Br$ based on the Flour
426 and Papirer approach.



427
 428 **Figure 8.** Determination of the K_A and K_B values of the of $[C_2C_4PIP]Br$ based on the
 429 Brookman and Sawyer method.

430

431

432 **Table 6.** Acidity and basicity constants of the surface of $[C_2C_4PIP]Br$

Method	K_A	K_B	K_B/K_A
Flour and Papirer	0.054	0.36	6.67
Brookman and Sawyer	0.065	0.52	8.00

433

434 The K_B/K_A ratios calculated by the Flour and Papirer method and the Brookman and Sawyer
 435 method suggest that the surface of 1-butyl-1-ethylpiperidinium bromide has a predominantly
 436 Lewis basic character. This conclusion is in line with the findings of the analysis based on the
 437 values of the energy and enthalpy of polar probes, presented in paragraphs 4.2.1 and 4.2.2.
 438 Despite the fact that the K_B/K_A ratios are not similar, we can safely conclude that
 439 $[C_2C_4PIP]Br$ is a Lewis base, since in both cases the K_B/K_A ratio is greater than 1.

440 Bearing in mind the structure of 1-butyl-1-ethylpiperidinium bromide, we notice that both
 441 acidic and basic moieties are present in the molecule. As no comparable work has been
 442 carried out previously for solid organic salts or ionic liquids below their melting point, neither
 443 the comparison with literature nor the interpretation of our results are straightforward.

444 Nevertheless, a tentative explanation can be given as following. Since in our case, the ions of
445 the salt are relatively small and bound together, the overall basicity of [C₂C₄PIP]Br is due to
446 an average of all of its parts, i.e. the alkyl groups, the positive charge on the nitrogen atom
447 and the Br⁻ anion. As reported previously in IGC studies dealing with polymers, CH₂ and CH₃
448 groups are known to be weak Lewis acidic sites [50, 72, 73]. On the other hand, Br⁻, as F⁻ or
449 Cl⁻ anions, is a dense, monoatomic and relatively electronegative anion, and is known to be
450 basic [50, 74]. The positive charge on the nitrogen is acidic, but is expected to be hidden and
451 to be sterically hindered by the alkyl groups bound to it. Therefore, we can surmise that the
452 general basic character of [C₂C₄PIP]Br is due to the relatively dense and monoatomic bromide
453 anion.

454

455 **Conclusions**

456 This contribution reports for the first time on the surface characterization of a piperidinium
457 based organic salt, 1-butyl-1-ethylpiperidinium bromide, by means of IGC. Measurements
458 were conducted at a temperature range (313.15-343.15 K), well below the melting point of
459 [C₂C₄PIP]Br (413.15 K) to ensure that the dominant retention mechanism of the probes is
460 adsorption onto the surface. The Schultz and the Dorris-Gray methods were used for the
461 calculation of the dispersive component of the surface energy. Results showed that γ_s^d
462 decreases with temperature. Moreover, the comparison of the dispersive component of the
463 surface energy of [C₂C₄PIP]Br with that of two piperidinium based ILs revealed that the
464 results of this study are comparable with literature values. The anion does therefore not appear
465 to play a crucial role in the surface energy of the piperidinium-based organic salts studied here
466 and in the literature. The acid/base characterization based on the Flour and Papirer approach
467 and the Brookman and Sawyer method showed that the surface of [C₂C₄PIP]Br is amphoteric
468 with a predominantly basic character, a conclusion which is further supported by taking into
469 account the molecular structure of [C₂C₄PIP]Br bearing, both, weak Lewis acidic and basic
470 sites.

471

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476 **References**

- 477 [1] S. Genand-Pinaz, N. Papaiconomou, J.-M. Leveque, Removal of platinum from water
478 by precipitation or liquid-liquid extraction and separation from gold using ionic liquids,
479 Green Chem. 15 (2013) 2493-2501.
- 480 [2] T.M. Koller, C. Steininger, M.H. Rausch, A.P. Fröba, A Simple Prediction Method for
481 the Surface Tension of Ionic Liquids as a Function of Temperature, Int. J. Thermophys.
482 38 (2017) 167.
- 483 [3] T. Mandai, K. Yoshida, K. Ueno, K. Dokko, M. Watanabe, Criteria for solvate ionic
484 liquids, Phys. Chem. Chem. Phys. 16 (2014) 8761-8772.
- 485 [4] V. Mazan, I. Billard, N. Papaiconomou, Experimental connections between aqueous-
486 aqueous and aqueous-ionic liquid biphasic systems, RSC Adv. 4 (2014) 13371-13384.
- 487 [5] P. Pollet, E.A. Davey, E.E. Urena-Benavides, C.A. Eckert, C.L. Liotta, Solvents for
488 sustainable chemical processes, Green Chem. 16 (2014) 1034-1055.
- 489 [6] F. Pena-Pereira, A. Kloskowski, J. Namiesnik, Perspectives on the replacement of
490 harmful organic solvents in analytical methodologies: a framework toward the
491 implementation of a generation of eco-friendly alternatives, Green Chem. 17 (2015)
492 3687-3705.
- 493 [7] H.F. Almeida, A.R.R. Teles, J.A. Lopes-da-Silva, M.G. Freire, J.A. Coutinho, Influence
494 of the anion on the surface tension of 1-ethyl-3-methylimidazolium-based ionic liquids,
495 J. Chem. Thermodyn. 54 (2012) 49-54.
- 496 [8] L. Deng, Q. Wang, Y. Chen, Z. Zhang, J. Tang, Determination of the solubility
497 parameter of ionic liquid 1-octyl-3-methylimidazolium hexafluorophosphate by inverse
498 gas chromatography, J. Mol. Liq. 187 (2013) 246-251.
- 499 [9] M. Shukla, S. Saha, A Comparative Study of Piperidinium and Imidazolium Based
500 Ionic Liquids: Thermal, Spectroscopic and Theoretical Studies, in: Ionic Liquids-New
501 Aspects for the Future INTECH Open Access Publisher, 2013.
- 502 [10] M. Shukla, H. Noothalapati, S. Shigeto, S. Saha, Importance of weak interactions and
503 conformational equilibrium in N-butyl-N-methylpiperidinium bis (trifluoro-
504 methanesulfonyl) imide room temperature ionic liquids: Vibrational and theoretical
505 studies, Vib. Spectrosc. 75 (2014) 107-117.
- 506 [11] G. Járvas, J. Kontos, G. Babics, A. Dallos, A novel method for the surface tension
507 estimation of ionic liquids based on COSMO-RS theory, Fluid Phase Equilib. 468
508 (2018) 9-17.

- 509 [12] T.M. Koller, M.H. Rausch, K. Pohako-Esko, P. Wasserscheid, A.P. Fröba, Surface
510 tension of tricyanomethanide-and tetracyanoborate-based imidazolium ionic liquids by
511 using the pendant drop method, *J. Chem. Eng. Data* 60 (2015) 2665-2673.
- 512 [13] G. Law, P.R. Watson, Surface tension measurements of N-alkylimidazolium ionic
513 liquids, *Langmuir*, 17 (2001) 6138-6141.
- 514 [14] S.A. Mirkhani, F. Gharagheizi, N. Farahani, K. Tumba, Prediction of surface tension of
515 ionic liquids by molecular approach, *J. Mol. Liq.* 179 (2013) 78-87.
- 516 [15] J. Restolho, J.L. Mata, B. Saramago, On the interfacial behavior of ionic liquids:
517 Surface tensions and contact angles, *J. Colloid Interf. Sci.* 340 (2009) 82-86.
- 518 [16] M. Tariq, M.G. Freire, B. Saramago, J.A. Coutinho, J.N.C. Lopes, L.P.N. Rebelo,
519 Surface tension of ionic liquids and ionic liquid solutions, *Chem. Soc. Rev.* 41 (2012)
520 829-868.
- 521 [17] A. Voelkel, B. Strzemieska, K. Adamska, K. Milczewska, Inverse gas chromatography
522 as a source of physicochemical data, *J. Chromatogr. A* 1216 (2009) 1551-1566.
- 523 [18] Y. Chen, Q. Wang, Z. Zhang, J. Tang, Determination of the Solubility Parameter of
524 Ionic Liquid 1-Hexyl-3-methylimidazolium Hexafluorophosphate by Inverse Gas
525 Chromatography, *Ind. Eng. Chem. Res.* 51 (2012) 15293-15298.
- 526 [19] U. Domańska, A. Marciniak, Measurements of activity coefficients at infinite dilution
527 of aromatic and aliphatic hydrocarbons, alcohols, and water in the new ionic liquid
528 [EMIM][SCN] using GLC, *J. Chem. Thermodyn.* 40 (2008) 860-866.
- 529 [20] K. Heydar, M. Nazifi, A. Sharifi, M. Mirzaei, H. Gharavi, S. Ahmadi, Determination of
530 Activity Coefficients at Infinite Dilution of Solutes in New Dicationic Ionic Liquids
531 Based on Morpholine Using Gas-Liquid Chromatography, *Chromatographia*, 76 (2013)
532 165-175.
- 533 [21] M. Królikowski, M. Królikowska, The study of activity coefficients at infinite dilution
534 for organic solutes and water in 1-butyl-4-methylpyridinium dicyanamide,
535 [B4MPy][DCA] using GLC, *J. Chem. Thermodyn.* 68 (2014) 138-144.
- 536 [22] A. Marciniak, M. Wlazło, Activity Coefficients at Infinite Dilution Measurements for
537 Organic Solutes and Water in the Ionic Liquid 1-(3-Hydroxypropyl)pyridinium
538 Trifluorotris(perfluoroethyl)phosphate, *J. Phys. Chem. B* 114 (2010) 6990-6994.
- 539 [23] A. Marciniak, M. Wlazło, Activity coefficients at infinite dilution and physicochemical
540 properties for organic solutes and water in the ionic liquid 1-(2-methoxyethyl)-1-
541 methylpiperidinium bis(trifluoromethylsulfonyl)-amide, *J. Chem. Thermodyn.* 49
542 (2012) 137-145.

- 543 [24] F. Mutelet, J.-N. Jaubert, Accurate measurements of thermodynamic properties of
544 solutes in ionic liquids using inverse gas chromatography, *J. Chromatogr. A* 1102
545 (2006) 256-267.
- 546 [25] F. Mutelet, J.-N. Jaubert, Measurement of activity coefficients at infinite dilution in 1-
547 hexadecyl-3-methylimidazolium tetrafluoroborate ionic liquid, *J. Chem. Thermodyn.* 39
548 (2007) 1144-1150.
- 549 [26] Q. Wang, Y. Chen, L. Deng, J. Tang, Z. Zhang, Determination of the solubility
550 parameter of ionic liquid 1-allyl-3-methylimidazolium chloride by inverse gas
551 chromatography, *J. Mol. Liq.* 180 (2013) 135-138.
- 552 [27] Q. Wang, Y. Chen, Z. Zhang, J. Tang, Determination of Surface Characteristics of Ionic
553 Liquid [1-Hexyl-3-methylimidazolium Hexafluorophosphate] by Inverse Gas
554 Chromatography, *J. Chem. Eng. Data* 58 (2013) 2142-2146.
- 555 [28] Y. Chen, Q. Wang, L. Deng, Z. Zhang, J. Tang, Characterization of surface properties
556 of 1-allyl-3-methylimidazolium chloride ionic liquid by inverse gas chromatography,
557 *Chin. J. Chromatogr.* 31 (2013) 147-150.
- 558 [29] T. Ban, X.-P. Li, C.-L. Li, Q. Wang, Surface Characterization of a Series of 1-Alkyl-3-
559 methylimidazolium-Based Ionic Liquids by Inverse Gas Chromatography, *Ind. Eng.*
560 *Chem. Res.* 57 (2018) 12249-12253.
- 561 [30] X. Li, Q. Wang, L. Li, Y. Ding, Determination of the thermodynamic parameters of
562 ionic liquid 1-hexyl-3-methylimidazolium tetrafluoroborate by inverse gas
563 chromatography, *Chin. J. Chromatogr.* 33 (2015) 58-64.
- 564 [31] X. Li, Q. Wang, L. Li, L. Deng, Z. Zhang, L. Tian, Determination of the
565 thermodynamic parameters of ionic liquid 1-hexyl-3-methylimidazolium chloride by
566 inverse gas chromatography, *J. Mol. Liq.* 200 (2014) 139-144.
- 567 [32] L. Deng, Q. Wang, Z. Zhang, J. Tang, Determination of thermodynamic parameters for
568 ionic liquid 1-hexyl-3-methylimidazolium trifluoromethanesulfonate by inverse gas
569 chromatography, *Chin. J. Chromatogr.* 32 (2014) 169-173.
- 570 [33] L. Tian, Y. Chen, Q. Wang, *Chin. J. Appl. Chem.* 34 (2017) 824-832.
- 571 [34] S. Zhang, X. Lu, Q. Zhou, X. Li, X. Zhang, S. Li, *Ionic Liquids: Physicochemical*
572 *Properties*, Elsevier, Amsterdam, 2009.
- 573 [35] U. Domańska, M. Królikowska, K. Padaszyński, Physico-chemical properties and phase
574 behaviour of piperidinium-based ionic liquids, *Fluid Phase Equilib.* 303 (2011) 1-9.

- 575 [36] U. Domańska, K. Padaszyński, Measurements of activity coefficients at infinite dilution
576 of organic solutes and water in 1-propyl-1-methylpiperidinium bis {(trifluoromethyl)
577 sulfonyl}imide ionic liquid using g.l.c, *J. Chem. Thermodyn.* 42 (2010) 1361-1366.
- 578 [37] A. Marciniak, M. Wlazło, Activity coefficients at infinite dilution and physicochemical
579 properties for organic solutes and water in the ionic liquid 1-(2-methoxyethyl)-1-
580 methylpiperidinium trifluorotris(perfluoroethyl)phosphate, *J. Chem. Thermodyn.* 57
581 (2013) 197-202.
- 582 [38] K. Padaszyński, U. Domańska, Limiting Activity Coefficients and Gas-Liquid Partition
583 Coefficients of Various Solutes in Piperidinium Ionic Liquids: Measurements and
584 LSER Calculations, *J. Phys. Chem. B* 115 (2011) 8207-8215.
- 585 [39] M.N. Belgacem, G. Czeremuszkin, S. Sapieha, A. Gandini, Surface characterization of
586 cellulose fibres by XPS and inverse gas chromatography, *Cellulose*, 2 (1995) 145-157.
- 587 [40] J. Kolodziejek, A. Voelkel, K. Heberger, Characterization of hybrid materials by means
588 of inverse gas chromatography and chemometrics, *J. Pharm. Sci.* 102 (2013) 1524-1531.
- 589 [41] J.R. Conder, C.L. Young, *Physicochemical Measurement by Gas Chromatography*,
590 Wiley, New York, 1979.
- 591 [42] J. Schultz, L. Lavielle, C. Martin, The role of the interface in carbon fibre-epoxy
592 composites, *J. Adhesion*, 23 (1987) 45-60.
- 593 [43] C. Saint Flour, E. Papirer, Gas-solid chromatography: a quick method of estimating
594 surface free energy variations induced by the treatment of short glass fibers, *J. Colloid
595 Interf. Sci.* 91 (1983) 69-75.
- 596 [44] D.J. Brookman, D.T. Sawyer, Specific Interactions Affecting Gas Chromatographic
597 Retention for Modified Alumina Columns, *Anal. Chem.* 40 (1968) 106-110.
- 598 [45] V. Gutmann, *The Donor-Acceptor Approach to Molecular Interactions*, Plenum Press,
599 New York, 1978.
- 600 [46] D.P. Kamdem, S.K. Bose, P. Luner, Inverse Gas-Chromatography Characterization of
601 Birch Wood Meal, *Langmuir*, 9 (1993) 3039-3044.
- 602 [47] F.L. Riddle, F.M. Fowkes, Spectral Shifts in Acid-Base Chemistry .1. Vanderwaals
603 Contributions to Acceptor Numbers, *J. Am. Chem. Soc.* 112 (1990) 3259-3264.
- 604 [48] D. Cava, R. Gavara, J. Lagaron, A. Voelkel, Surface characterization of poly (lactic
605 acid) and polycaprolactone by inverse gas chromatography, *J. Chromatogr. A* 1148
606 (2007) 86-91.
- 607 [49] T.E. Daubert, R.P. Danner, *Physical and Thermodynamic Properties of Pure Chemicals:*
608 *Data Compilation*, Hemisphere, New York, 2001.

- 609 [50] S.K. Papadopoulou, G. Dritsas, I. Karapanagiotis, I. Zuburtikudis, C. Panayiotou,
610 Surface characterization of poly (2, 2, 3, 3, 3-pentafluoropropyl methacrylate) by
611 inverse gas chromatography and contact angle measurements, *Eur. Polym. J.* 46 (2010)
612 202-208.
- 613 [51] J.M.R.C.A. Santos, J.T. Guthrie, Lewis acid/base character and crystallisation properties
614 of poly(butylene terephthalate), *J. Chromatogr. A* 1379 (2015) 92-99.
- 615 [52] K. Vasanth Kumar, F. Rocha, On the effect of a non-ionic surfactant on the surface of
616 sucrose crystals and on the crystal growth process by inverse gas chromatography, *J.*
617 *Chromatogr. A* 1216 (2009) 8528-8534.
- 618 [53] N. Papaiconomou, J. Estager, Y. Traore, P. Bauduin, C. Bas, S. Legeai, S. Viboud, M.
619 Draye, Synthesis, Physicochemical Properties, and Toxicity Data of New Hydrophobic
620 Ionic Liquids Containing Dimethylpyridinium and Trimethylpyridinium Cations[†], *J.*
621 *Chem. Eng. Data* 55 (2010) 1971-1979.
- 622 [54] Z.Y. Al-Saigh, P. Munk, Study of polymer-polymer interaction coefficients in polymer
623 blends using inverse gas chromatography, *Macromolecules*, 17 (1984) 803-809.
- 624 [55] S.K. Papadopoulou, C. Panayiotou, Assessment of the thermodynamic properties of
625 poly(2,2,2-trifluoroethyl methacrylate) by inverse gas chromatography, *J. Chromatogr.*
626 *A* 1324 (2014) 207-214.
- 627 [56] S.K. Papadopoulou, I. Karapanagiotis, I. Zuburtikudis, C. Panayiotou, Thermodynamic
628 characterization of poly(2,2,3,3,3-pentafluoropropyl methacrylate), *J. Polym. Sci. Pol.*
629 *Phys.* 48 (2010) 1826-1833.
- 630 [57] S. Ramanaiiah, V. Karde, P. Venkateswarlu, C. Ghoroi, Effect of temperature on the
631 surface free energy and acid–base properties of Gabapentin and Pregabalin drugs – a
632 comparative study, *RSC Adv.* 5 (2015) 48712-48719.
- 633 [58] A. Voelkel, K. Batko, K. Adamska, B. Strzemiecka, Determination of Hansen solubility
634 parameters by means of gas-solid inverse gas chromatography, *Adsorpt. Sci. Technol.*
635 26 (2008) 93-102.
- 636 [59] A. van Asten, N. van Veenendaal, S. Koster, Surface characterization of industrial fibers
637 with inverse gas chromatography, *J. Chromatogr. A* 888 (2000) 175-196.
- 638 [60] B. Shi, Y. Wang, L. Jia, Comparison of Dorris–Gray and Schultz methods for the
639 calculation of surface dispersive free energy by inverse gas chromatography, *J.*
640 *Chromatogr. A* 1218 (2011) 860-862.

- 641 [61] L.H.G.J. Segeren, M.E.L. Wouters, M. Bos, J.W.A. van den Berg, G.J. Vancso, Surface
642 energy characteristics of toner particles by automated inverse gas chromatography, *J.*
643 *Chromatogr. A* 969 (2002) 215-227.
- 644 [62] H. Ocak, S. Mutlu-Yanic, F. Cakar, B. Bilgin-Eran, D. Guzeller, F. Karaman, O.
645 Cankurtaran, A study of the thermodynamical interactions with solvents and surface
646 characterisation of liquid crystalline 5-((S)-3,7-dimethyloctyloxy)-2-[[[4-
647 (dodecyloxy)phenyl]imino]-methyl]phenol by inverse gas chromatography, *J. Mol. Liq.*
648 223 (2016) 861-867.
- 649 [63] M.A. Mohammad, Chromatographic adhesion law to simplify surface energy
650 calculation, *J. Chromatogr. A* 1318 (2013) 270-275.
- 651 [64] L. Lapčík, M. Otyepka, E. Otyepková, B. Lapčíková, R. Gabriel, A. Gavenda, B.
652 Prudilová, Surface heterogeneity: Information from inverse gas chromatography and
653 application to model pharmaceutical substances, *Curr. Opin. Colloid In.* 24 (2016) 64-
654 71.
- 655 [65] J.A.F. Gamelas, E. Ferraz, F. Rocha, An insight into the surface properties of calcined
656 kaolinitic clays: The grinding effect, *Colloid. Surface. A* 455 (2014) 49-57.
- 657 [66] C. Bilgiç, F. Tımsek, Determination of the acid/base properties of MgY and NH₄Y
658 molecular sieves by inverse gas chromatography, *J. Chromatogr. A* 1162 (2007) 83-89.
- 659 [67] R. Osada, T. Hoshino, K. Okada, Y. Ohmasa, M. Yao, Surface tension of room
660 temperature ionic liquids measured by dynamic light scattering, *J. Chem. Phys.* 130
661 (2009) 184705.
- 662 [68] A. Bhattacharjee, P.J. Carvalho, J.A. Coutinho, The effect of the cation aromaticity
663 upon the thermophysical properties of piperidinium-and pyridinium-based ionic liquids,
664 *Fluid Phase Equilib.* 375 (2014) 80-88.
- 665 [69] M. Oliveira, M. Dominguez-Perez, O. Cabeza, J. Lopes-da-Silva, M. Freire, J.
666 Coutinho, Surface tensions of binary mixtures of ionic liquids with bis
667 (trifluoromethylsulfonyl) imide as the common anion, *J. Chem. Thermodyn.* 64 (2013)
668 22-27.
- 669 [70] M.N. Belgacem, A. Gandini, in: E. Pefferkorn (Ed.), *Interfacial Phenomena*
670 *in Chromatography*, Marcel Dekker Inc., New York, 1999.
- 671 [71] A.B. Nastasović, A.E. Onjia, S.K. Milonjić, S.M. Jovanović, Surface characterization of
672 macroporous glycidyl methacrylate based copolymers by inverse gas chromatography,
673 *Eur. Polym. J.* 41 (2005) 1234-1242.

- 674 [72] J. Santos, K. Fagelman, J. Guthrie, Characterisation of the surface Lewis acid–base
675 properties of the components of pigmented, impact-modified, bisphenol A
676 polycarbonate–poly (butylene terephthalate) blends by inverse gas chromatography–
677 phase separation and phase preferences, *J. Chromatogr. A* 969 (2002) 119-132.
- 678 [73] J.M.R.C.A. Santos, J.T. Guthrie, Study of a core-shell type impact modifier by inverse
679 gas chromatography, *J. Chromatogr. A* 1070 (2005) 147-154.
- 680 [74] M.-L. Abel, M.M. Chehimi, F. Fricker, M. Delamar, A.M. Brown, J.F. Watts,
681 Adsorption of poly(methyl methacrylate) and poly(vinyl chloride) blends onto
682 polypyrrole: Study by X-ray photoelectron spectroscopy, time-of-flight static secondary
683 ion mass spectroscopy, and inverse gas chromatography, *J. Chromatogr. A* 969 (2002)
684 273-285.
- 685