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

3 Stella K. Papadopoulou<sup>a,\*</sup>, Nicolas Papaiconomou<sup>a,b</sup>, Stéphane Baup<sup>c</sup>,  
4 Cristina Iojoiu<sup>a</sup>, Lenka Svecova<sup>a</sup>, Pierre-Xavier Thivel<sup>a</sup>

5  
6 <sup>a</sup> *Université Grenoble Alpes, Université Savoie Mont Blanc, CNRS, Grenoble INP, LEPMI,*  
7 *38000 Grenoble, France*

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

10 <sup>c</sup> *Université Grenoble Alpes, CNRS, Grenoble INP, LRP, 38000 Grenoble, France*

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21 \* Corresponding author e-mail address: [papadopoulou.styliani@gmail.com](mailto: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, [C<sub>2</sub>C<sub>4</sub>PIP]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 [C<sub>2</sub>C<sub>4</sub>PIP]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 [C<sub>2</sub>C<sub>4</sub>PIP]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 [C<sub>2</sub>C<sub>4</sub>PIP]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 [C<sub>2</sub>C<sub>4</sub>PIP]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 [C<sub>2</sub>C<sub>4</sub>PIP]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 [C<sub>2</sub>C<sub>4</sub>PIP]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,  $\gamma_s^d$ , 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  $\Delta G^{CH_2}$  is the adsorption free energy of one methylene group,  $N$  is the Avogadro's  
148 number,  $\alpha_{CH_2}$  is the cross-sectional area of an adsorbed methylene group ( $6 \text{ \AA}^2$ ) and  $\gamma_{CH_2}$  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,  $\Delta G^{CH_2}$ .

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  $\alpha$  is the surface area of the probe molecules,  $\gamma_s^d$  and  $\gamma_l^d$  are the dispersive components  
 162 of the surface energy of the solid and the liquid probe, respectively and  $C$  is a constant.  
 163  $\gamma_s^d$  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  $\Delta G^{sp}$ , can be considered as the difference between the total free energy of adsorption,  $\Delta G^{ads}$ ,  
 174 and the dispersive contribution to the free energy of adsorption  $\Delta G^d$ . Several methods have  
 175 been proposed for the determination of the  $\Delta G^{sp}$  [17]. In the present study,  $\Delta G^{sp}$  was  
 176 calculated through the use of the Flour and Papirer approach [43] and the Brookman and  
 177 Sawyer method [44]. The estimation of  $\Delta G^{sp}$  is based on a plot of  $\Delta G$  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,  $\Delta G^{sp}$ , 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,  $\Delta H^{sp}$ , can be determined after the calculation of the specific  
189 component of the free energy of adsorption at various temperatures. When plotting the  $\Delta G^{sp}$   
190 values as a function of the reciprocal temperature,  $T^{-1}$ ,  $\Delta H^{sp}$  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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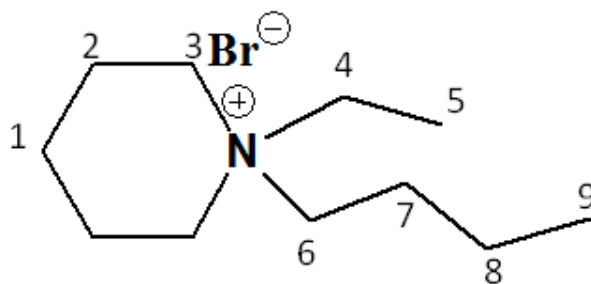
218 **Table 1.** Physical and chemical properties of the probes used for the IGC analysis [27, 47-52]

Probe	Boiling point (°C)	Saturated vapor pressure (kPa)	$\alpha$ ( $10^{-19} \text{ m}^2$ )	$\gamma_i^d$ ( $\text{mJ}/\text{m}^2$ )	$DN$ ( $\text{kJ mol}^{-1}$ )	$AN^*$ ( $\text{kJ mol}^{-1}$ )	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 ( $\sim 0.1$  mbar) for 24 hours. The final product was obtained as a white solid.  
227 Purity was checked by Nuclear Magnetic Resonance Spectroscopy ( $^1\text{H}$  NMR). The  $^1\text{H}$  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  $\text{CH}_2$ , 2), 1.58-1.53 (4H, m,  
232  $\text{CH}_2$ , 1,7), 1.37-1.28 (2H, m,  $\text{CH}_2$ , 8), 1.19-1.15 (3H, t,  $\text{CH}_3$ , 5), 0.95-0.92 (3H, t,  $\text{CH}_3$ , 9).



233  
 234 **Figure 1.** Structure of [C<sub>2</sub>C<sub>4</sub>PIP]Br. The protons observed in the NMR spectrum were  
 235 identified.

236  
 237 The melting point of [C<sub>2</sub>C<sub>4</sub>PIP]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 [C<sub>2</sub>C<sub>4</sub>PIP]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]. [C<sub>2</sub>C<sub>4</sub>PIP]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

<b>1-butyl-1-ethylpiperidinium bromide</b>	
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 <sub>2</sub> C <sub>4</sub> PIP]Br loading (%)	20.7
Flow rate (mL/min)	10

265

## 266 **4 Results**

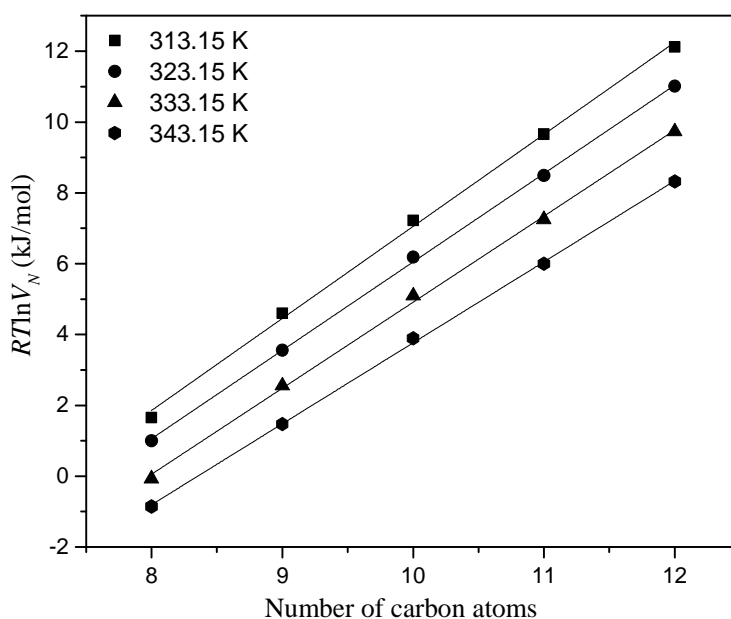
### 267 **4.1 Dispersive component of the surface energy**

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,  $\Delta G^{CH_2}$  as  
275 indicated by Eq. (4). The corresponding plot is illustrated in Figure 2. The dispersive  
276 component of the surface energy of [C<sub>2</sub>C<sub>4</sub>PIP]Br was calculated via Eq. (3) according to the  
277 Dorris-Gray method. The values of  $\gamma_s^d$  together with their maximum errors are presented in  
278 Table 3.

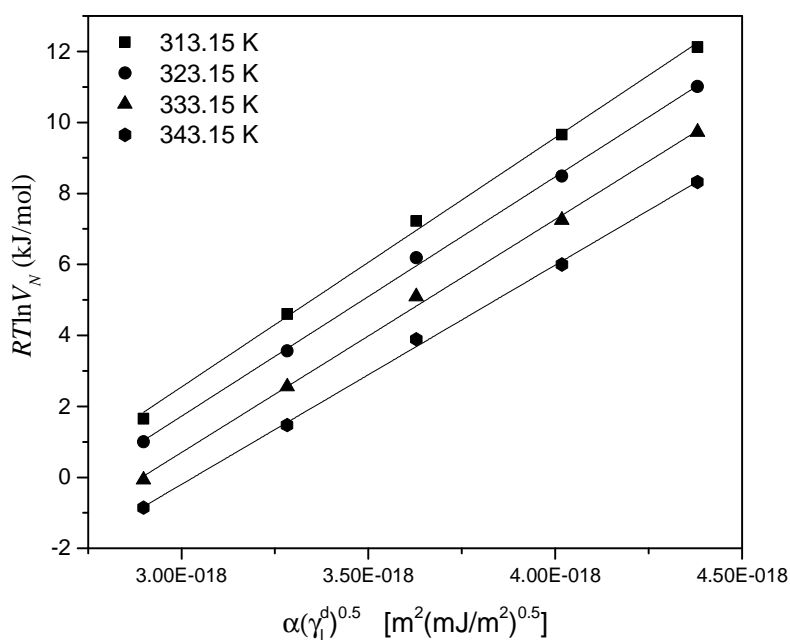


279  
 280 **Figure 2.** Surface free energy of adsorption of *n*-alkanes  $RT \ln V_N$  on  $[C_2C_4PIP]Br$  versus  
 281 their number of carbon atoms, measured at the temperature range 313.15-343.15 K.

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.

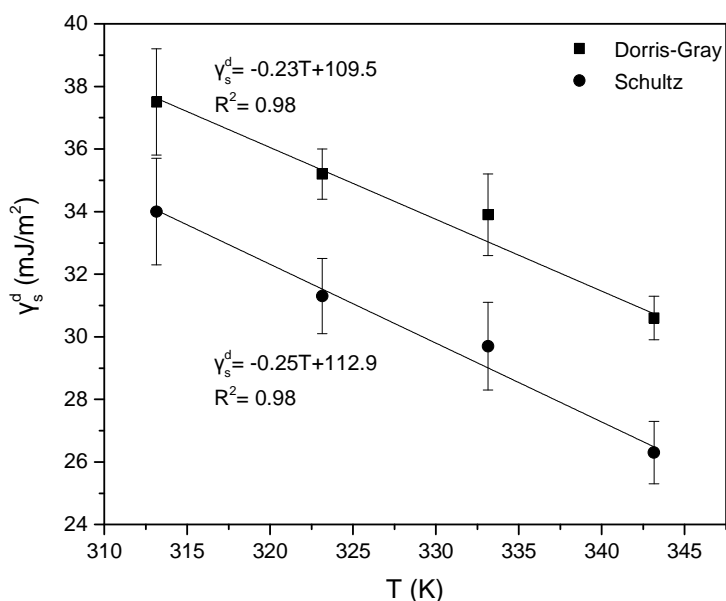
289  
 290



291  
 292 **Figure 3.** Surface free energy of adsorption of *n*-alkanes  $RT \ln V_N$ , on  $[C_2C_4PIP]Br$  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  $[C_2C_4PIP]Br$  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	
	$\gamma_s^d$ (mJ/m <sup>2</sup> )	$R^2$	$\gamma_s^d$ (mJ/m <sup>2</sup> )	$R^2$
313.15	$37.5 \pm 1.7$	0.998	$34.0 \pm 1.7$	0.998
323.15	$35.2 \pm 0.8$	0.999	$31.3 \pm 1.2$	0.999
333.15	$33.9 \pm 1.3$	0.999	$29.7 \pm 1.4$	0.998
343.15	$30.6 \pm 0.7$	0.999	$26.3 \pm 1.0$	0.999



297  
 298 **Figure 4.** Variation of the dispersive component of the surface energy of [C<sub>2</sub>C<sub>4</sub>PIP]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  $\alpha \sqrt{\gamma_l^d}$  term (Schultz method). The dispersive component of  
 305 the surface energy of [C<sub>2</sub>C<sub>4</sub>PIP]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 R<sup>2</sup> values were found. It appears that the  
 308 dispersive component of the surface energy of [C<sub>2</sub>C<sub>4</sub>PIP]Br presents a decreasing trend with  
 309 the increase of temperature [57]. Moreover, based on Figure 4 we notice that the dependence  
 310 of  $\gamma_s^d$  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  $\gamma_s^d$  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 [C<sub>2</sub>C<sub>4</sub>PIP]Br of the present study

T (K)	$\gamma$ (mJ/m <sup>2</sup> )		$\gamma_s^d$ (mJ/m <sup>2</sup> )
	[C <sub>3</sub> C <sub>1</sub> PIP][NTf <sub>2</sub> ]	[C <sub>4</sub> C <sub>1</sub> PIP][NTf <sub>2</sub> ] [68]	[C <sub>2</sub> C <sub>4</sub> PIP]Br (this work)
298	35.2 <sup>[69]</sup> / 35.3 <sup>[68]</sup>	34.2	-
303.2	34.5 <sup>[67]</sup> / 35.1 <sup>[68]</sup>	34.0	-
313.2	34.5 <sup>[68]</sup>	33.5	34.0 - 37.5
323.2	34.0 <sup>[68]</sup>	33.0	31.3 - 35.2
333.2	33.5 <sup>[68]</sup>	32.5	29.7 - 34.0
343.2	33.0 <sup>[68]</sup>	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 ([C<sub>3</sub>C<sub>1</sub>PIP][NTf<sub>2</sub>]) measured with the Dynamic Light  
326 Scattering (DLS) technique. Bhattacharjee et al. [68] assessed the surface energy of  
327 [C<sub>3</sub>C<sub>1</sub>PIP][NTf<sub>2</sub>] and [C<sub>4</sub>C<sub>1</sub>PIP][NTf<sub>2</sub>] (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  $\gamma$  [16, 68]. Moreover, the  
333 anion [NTf<sub>2</sub>]<sup>-</sup> ((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  $\gamma$  and is  $\gamma_s^d$  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.

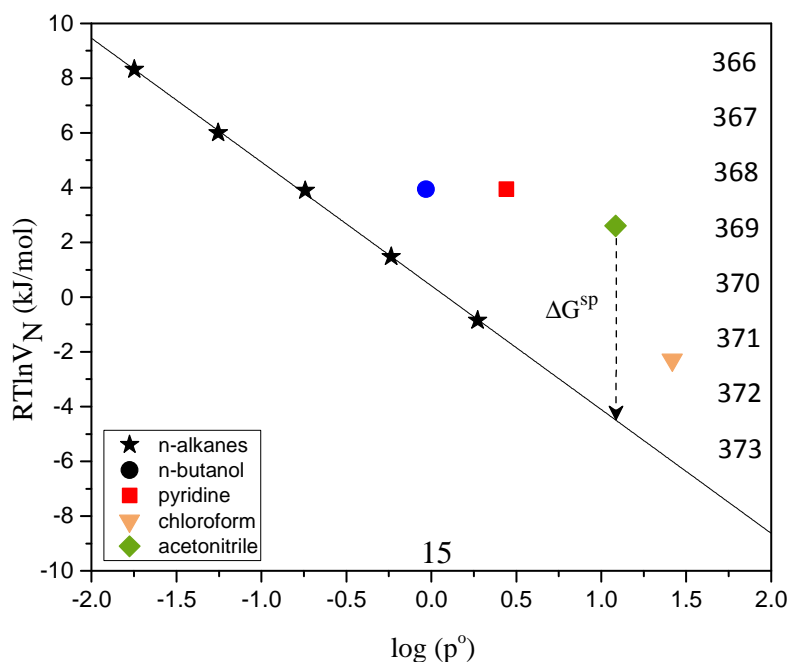
346 The assessment of the acid-base interactions of a surface includes the calculation of the  
347 specific component of the free energy of adsorption of a probe,  $\Delta G^{sp}$ , the specific component  
348 of the free enthalpy of adsorption of a probe,  $\Delta H^{sp}$  and the ratio  $K_B/K_A$  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  $\Delta G^{sp}$  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  $\gamma_s^d$  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.



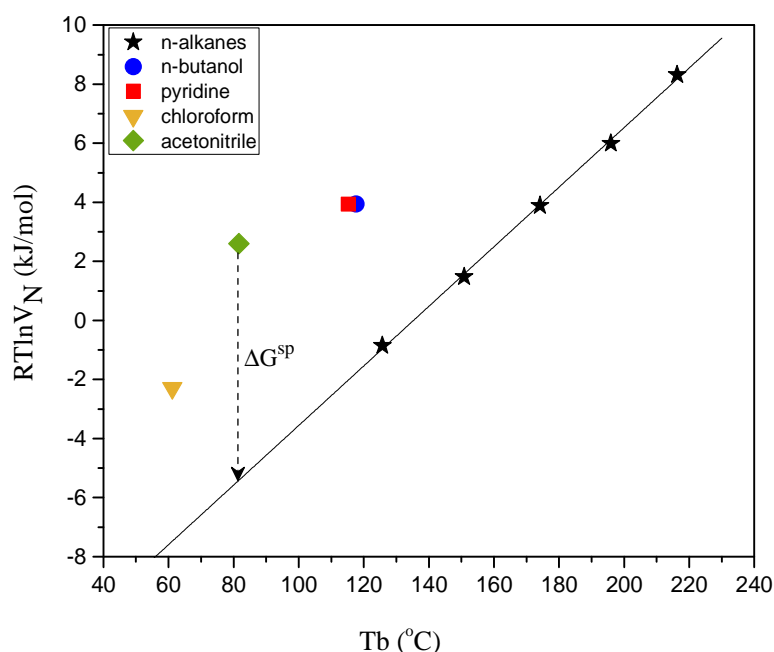


374 **Figure 5.** Energy of adsorption of *n*-alkanes and polar probes on the surface of [C<sub>2</sub>C<sub>4</sub>PIP]Br  
375 versus the logarithm of their saturated vapour pressure, at 343.15 K.

376  
377 The values of the specific component of the free energy of adsorption  $\Delta G^{sp}$  of the polar  
378 probes used in this study are high. The fact that the  $\Delta G^{sp}$  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 [C<sub>2</sub>C<sub>4</sub>PIP]Br [71]. The highest  $\Delta G^{sp}$  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  $\Delta G^{sp}$  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 [C<sub>2</sub>C<sub>4</sub>PIP]Br  
387 versus their boiling temperatures, at 343.15 K.

388  
389 The  $\Delta G^{sp}$  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 [C<sub>2</sub>C<sub>4</sub>PIP]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 [C<sub>2</sub>C<sub>4</sub>PIP]Br were calculated by the aid of Eq. (7) and via a plot of  $\Delta G^{sp}$

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 [C<sub>2</sub>C<sub>4</sub>PIP]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

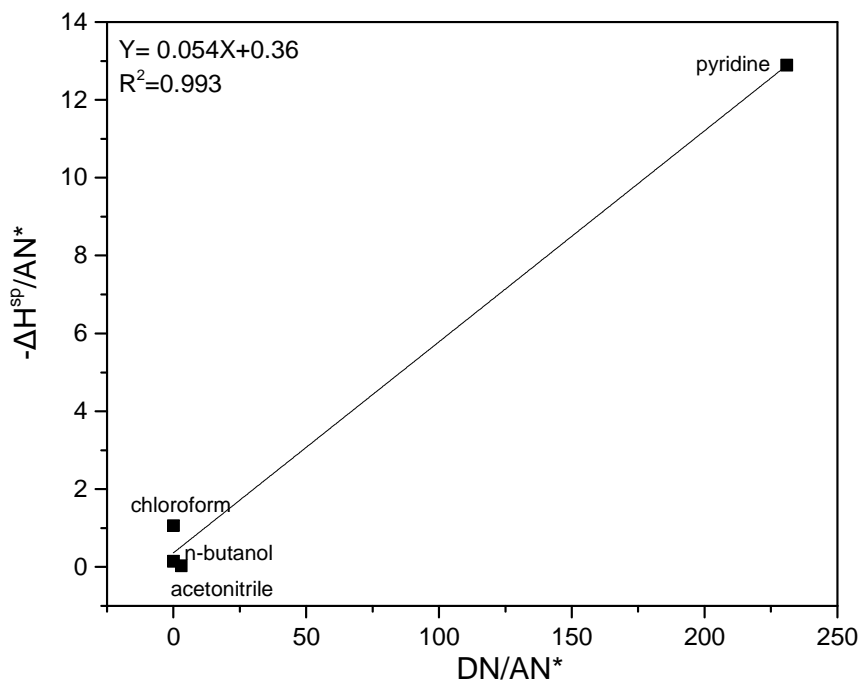
399 The enthalpies and entropies of adsorption of polar probes on the surface of [C<sub>2</sub>C<sub>4</sub>PIP]Br  
 400 estimated with the Flour and the Brookman methods are comparable, with the exception of n-  
 401 butanol. The enthalpy of adsorption of all probes was found to be exothermic in all cases.  
 402 Acetonitrile which is an amphoteric probe presents the highest enthalpy of adsorption whereas  
 403 chloroform which is acidic has the lowest  $\Delta H^{sp}$  implying that [C<sub>2</sub>C<sub>4</sub>PIP]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 [C<sub>2</sub>C<sub>4</sub>PIP]Br follow the same trend as discussed above. Acetonitrile  
 406 has the highest  $\Delta S^{sp}$  values, indicating that the surface is amphoteric. Moreover, we notice  
 407 that all  $\Delta S^{sp}$  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

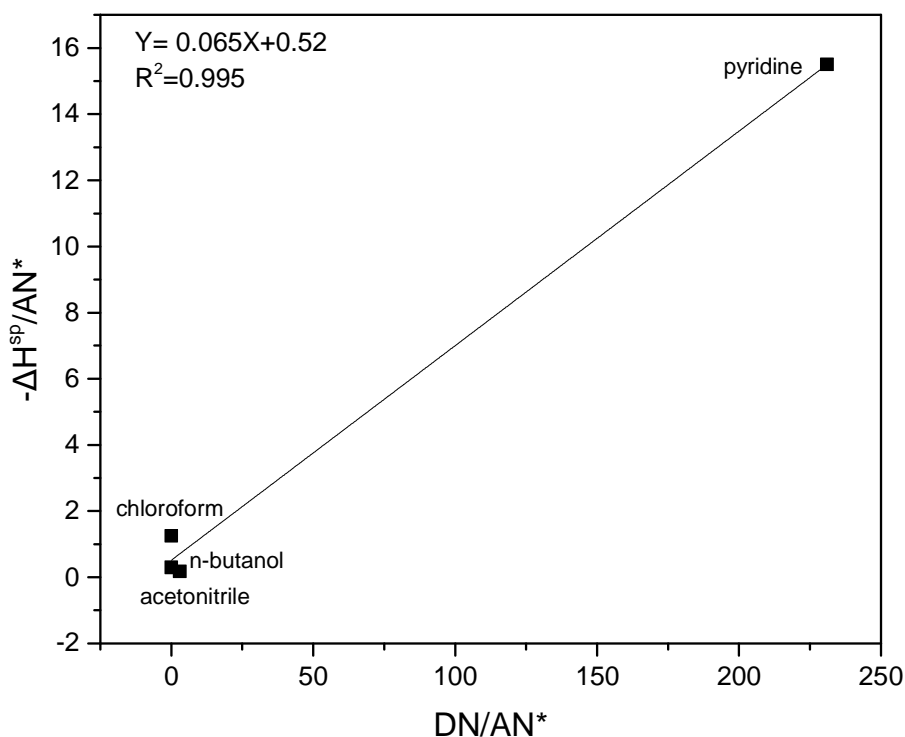
### 413 4.2.3 Acidity and basicity constants

414 The values for the specific enthalpies of polar probes were employed in order to evaluate the  
 415 acidity and basicity constants of [C<sub>2</sub>C<sub>4</sub>PIP]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  $\Delta H^{sp}$  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 [C<sub>2</sub>C<sub>4</sub>PIP]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<sup>-</sup> anion. As reported previously in IGC studies dealing with polymers, CH<sub>2</sub> and CH<sub>3</sub>  
448 groups are known to be weak Lewis acidic sites [50, 72, 73]. On the other hand, Br<sup>-</sup>, as F<sup>-</sup> or  
449 Cl<sup>-</sup> 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 [C<sub>2</sub>C<sub>4</sub>PIP]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 [C<sub>2</sub>C<sub>4</sub>PIP]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  $\gamma_s^d$   
462 decreases with temperature. Moreover, the comparison of the dispersive component of the  
463 surface energy of [C<sub>2</sub>C<sub>4</sub>PIP]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 [C<sub>2</sub>C<sub>4</sub>PIP]Br is amphoteric  
468 with a predominantly basic character, a conclusion which is further supported by taking into  
469 account the molecular structure of [C<sub>2</sub>C<sub>4</sub>PIP]Br bearing, both, weak Lewis acidic and basic  
470 sites.

471

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475

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