COMPARATIVE STUDY OF THE RETENTION OF PYRIDINIUM AND IMIDAZOLIUM BASED IONIC LIQUIDS ON OCTADECYLSILICA STATIONARY PHASE UNDER ION PAIRING MECHANISM WITH ALKYLSULPHONATE ANIONS

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Retention data for several pyridinium and imidazolium ionic liquids in presence of alkylsulphonates (C6, C7 and C8) were used in studying the retention of these cations on the octadecylsilica surface. This study showed that ionic liquids can be adsorbed on octadecylsilica surface, due to the polar interactions with the residual silanols from surface of stationary phase and hydrophobic interactions between hydrophobic moiety of these cations and octadecyl chains from the surface of the stationary phase. An unusual chromatographic retention behavior has been observed: the functional dependencies between the logarithm of the retention factor (k) and the methanol content in the mobile phase followed a binomial pattern (U-shaped), with a minimum positioned within the interval 60-75% methanol.

INTRODUCTION

Room temperature ionic liquids (RTILs) are a group of organic salts whose melting points range within the interval -81°C-125°C.[1,2] Unlike classical liquids, which are made of neutral molecules, this special group of compounds contains an equal number of positive and negative ions so that the whole liquid is electrically neutral. The most commonly RTILs are nitrogen-containing organic cations, such as imidazole, pyridine or pyrrolidine.[3] The innorganic counterpart of these salts is represented by a halogen-based anion (e.g. Cl^-, Br^-, BF_4^-, $AlCl_4^-$) or some less common anions, such as bis(trifluoromethanesulfonyl)imide, $[(CF_3SO_2)_2N]^-$, trifluoroacetate $[CF_3CO_2]^-$ and trifluoromethanesulfonate $[CF_3SO_3]^-$. Hundreds of combinations of such cations and anions have been synthesized and reported, leading to a large number of different RTILs with unique physic-chemical properties like: wide temperature range as a liquid phase, high ionic conductivity, a wide window of electrochemical stability, negligible vapor pressure, good extractabilities for various organic compound and metal ions.[4] Due to these particular characteristics, a large number of ILs chemical applications were reported. These salts have been used to improve the selectivity in chromatographic techniques as stationary phases in gas-chromatography, electroosmotic flow modifiers for CE, mobile phase additives in LC, matrices for MALDI,[5] as well as solvents for spectral analysis[6] and electrochemistry.[7]

During the last decade ILs became an interesting subject for the analysts in terms of improvement of their knowledge about their special properties. Chromatographic processes are suitable tools for determining physical characteristics, like liquid-liquid partition coefficients, activity coefficients, thermodynamic

constants, retention mechanisms, or separation methods of these salts on various stationary phases.[8] Due to their positive charge, these ionic species can form ion pairs with opposite charged species, e.g. alkylsulphonate anion, which can be adsorbed on hydrophobic surface,[9] such as pentafluorophenylpropyl silica-based stationary phase that is used as stationary phase in liquid chromatography.[10] In this case, the adsorption can be explained by interactions between aromatic ring from stationary phase and imidazolium moiety from ionic liquids. Their adsorption on octadecylsilica surface in the absence of ion pairing agents has revealed strong interactions between imidazolium-based cations and stationary phase, which can be used in their separation from mixtures.[11] It is aim of this paper to report some interesting results related to the retention of some pyridinium and imidazolium ionic liquids as ion pairs with alkylsulphonate anions on octadecylsilica silica surface, and to study the influence of alkylsulphonate and mobile phase composition on this process.

EXPERIMENTAL

Instrumentation: All experiments were performed on an Agilent 1100 liquid chromatograph (Agilent Technologies, Waldbronn, Germany), consisting in the following modules: degasser (G1379A), binary pump (G1312A), autosampler (G1313A), column thermostat (G1316A) and diode array detector (G1315A). The chromatographic system was operationally qualified before the study. Chromatographic data were acquired by means of Agilent Chemstation software rev. B.01.03.

Reagents: All solvents were HPLC (gradient) grade from Merck (Darmstadt, Germany). Water (resistivity minimum 18.2 MΩ and TOC maximum 30 ppb) was produced within the laboratory with a TKA Lab HP 6UV/UF instrument. Reagents were p.a. grade (phosphoric acid) or ion-pair grade (alkylsulphonates) from Merck. The six studied ionic liquids containing imidazolium or pyridinium cations (with their structures given in Fig. 1) are commercially available compounds, having purities higher than 99%, from Fluka and Sigma-Aldrich.

Chromatographic conditions: A Zorbax ODS column, packed with extra densely bonded doubled end-capped octadecyl silicagel, 150 mm length, 4.6 mm i.d. and 5 μm particle size was used under isocratic elution conditions. All experiments were performed at 25°C, using a flow-rate of 1 mL/min. UV detection was achieved by monitoring 220 or 254 nm wavelength, according to the spectral characteristics of the tested compounds.

The aqueous component of the mobile phase contained 0.1% H_3PO_4 (pH = 2.5) and 15 mmoles/L of the ion pairing agent. Methanol (MeOH) was used as organic modifier in the mobile phase. The two components were mixed in different volume ratios by means of the binary HPLC pump, as further described in the text. Sodium hexane- (C6), heptane- (C7) and octane-sulphonates (C8) were used as ion pairing agents.

Retention factors were computed according to the well-known relationship $k = (t_R - t_0)/t_0$. Absolute retention time values (t_R) are considered as mean resulting for experiments carried out in triplicate (the maximum allowed relative standard deviation calculated for the experimental values is 1%). Injection peak was used as the dead time (t_0) indicator. The working solutions of each tested compound were prepared in methanol at 200 μg/mL concentration level and injected as a volume of 5 μL.
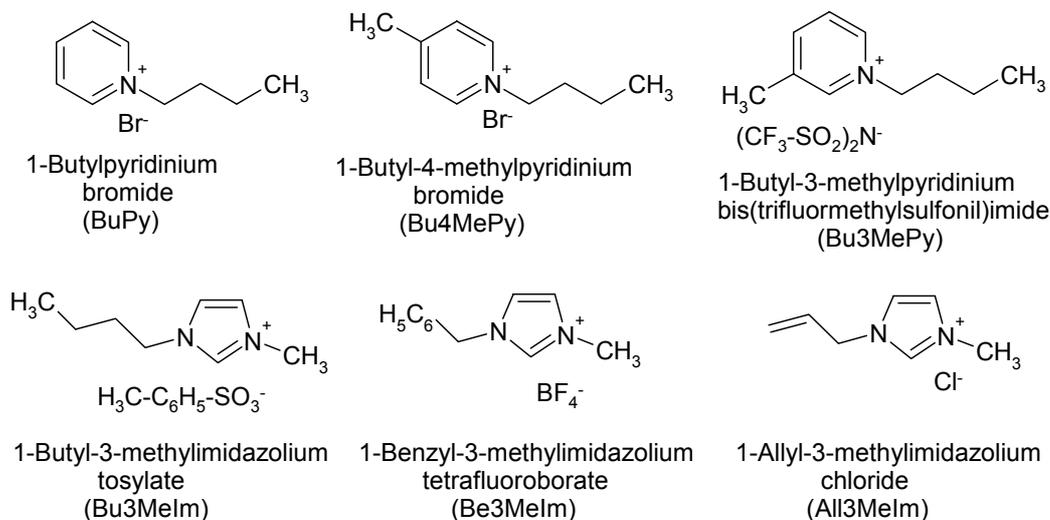

1-Butylpyridinium bromide (BuPy)

1-Butyl-4-methylpyridinium bromide (Bu4MePy)

1-Butyl-3-methylpyridinium bis(trifluormethylsulfonil)imide (Bu3MePy)

1-Butyl-3-methylimidazolium tosylate (Bu3MeIm)

1-Benzyl-3-methylimidazolium tetrafluoroborate (Be3MeIm)

1-Allyl-3-methylimidazolium chloride (All3MeIm)

Fig. 1 – Chemical structure and denomination of studied compounds belonging to the ionic liquids class.

RESULTS AND DISCUSSION

Experimental values for the retention factor (k) of studied ionic liquids were acquired for the nine compositions of mobile phase on a wide interval (50 – 80% MeOH, v/v). The dependence between k and percentage of methanol in mobile phase (C_{om}, as volume percentage) is usually used in quantitative structure-retention relationship (QSRR) studies,[12] with applications in method developing a liquid chromatographic or a deep insight of the retention mechanism.[13] In this cases, the graphical representations between the ten base logarithm of the retention factor (lg k) for each ionic liquid and the volume percentage of methanol in mobile phase (C_{om}) showed a characteristic "U" shape with a minimum value within studied interval of mobile phase composition (Fig. 2). This unusual shape can be described by a second order polynomial regression, which is applied to the dependence between lg k and C_{om}, according to the following equation:

$$\lg k = \alpha_0 + \alpha_1 C_{om} + \alpha_2 C_{om}^2 \qquad (1)$$

where α_0 is the intercept and it represents the extrapolated value of the retention factor corresponding to a hypothetical mobile phase containing only the aqueous component ($\alpha_0 = \lg k_w$ for $C_{om} = 0$), while α_1 and α_2 are the upper regression parameters of the given functional dependence. Mathematically, this dependence has a minimum (min lg k), which can be obtained from relationship $\partial \lg k / \partial C_{om} = 0$. This minimum of the plot is characterized by the value of C_{om}, denoted by C_0, and min lg k, according to these relationships:

$$C_0 = -\frac{\alpha_1}{2 \times \alpha_2} \qquad (2)$$

$$\min \lg k = \alpha_0 - \frac{\alpha_1^2}{4 \times \alpha_2} \qquad (3)$$

This minimum corresponds to the mobile phase composition that allows the lowest affinity of the ion pairs between studied ionic liquids and alkylsulphonate for the octadecylsilica surface. The values of the polynomial regression parameters and calculated minimum value of lg k are given in Table 1, where good correlations can be observed for the data fitting, excepting one case when r^2 was closed to 0.99.

Extrapolation of dependences (1) to a mobile phase consisting in organic modifier (MeOH) only (lg k for $C_{om} = 100$ is denoted by lg k_o) corresponds to an adsorption of simple ionic compound from methanol to C18 hydrophobic sites from stationary phase.[14] This adsorption proved to be significant as can be seen from the values of lg k_o. As can be observed from Table 1 the values of lg k_o are practically the same for the three alkylsulphonates used as ion pairing agents. Thus, the values of lg k_o for Bu3MePy are 1.482, 1.483, and 1.410, resulted from extrapolations for C6, C7 and C8 ion paring agents, respectively. An opposite situation is given by the extrapolated values lg k_o for BuPy: 1.362, 1.407, and 1.354, respectively.

These results suggest that the studied ionic compounds can be adsorbed strongly on the surface of the C18 modified silica surface. Although the interactions of these cations with C18 chains are not likely to occur, we may assume that this can be explained by strong interactions with residual silanols from silica surface as well as hydrophobic interaction between the hydrophobic moiety of the cations and the bonded chains of the stationary phase.

The opposite situation is the extrapolation of the retention to a mobile phase consisting in aqueous component only (lg k for $C_{om} = 0$ is denoted by lg k_w, which is α_0). This time the adsorption corresponds to the pair between ionic liquid and alkylsulphonate anion. Therefore the extrapolated value lg k_w describes the adsorption of the pair between the ionic pair of ionic liquid and R-SO$_3^-$. The hydrophobicity of these pairs depends now on the length of R, which is in agreement with calculated data of lg k_w (Table 1). On the other hand, these results are in a better agreement with theoretical prediction of hydrophobicity of methylimidazolium-based cations: allyl < butyl < benzyl.
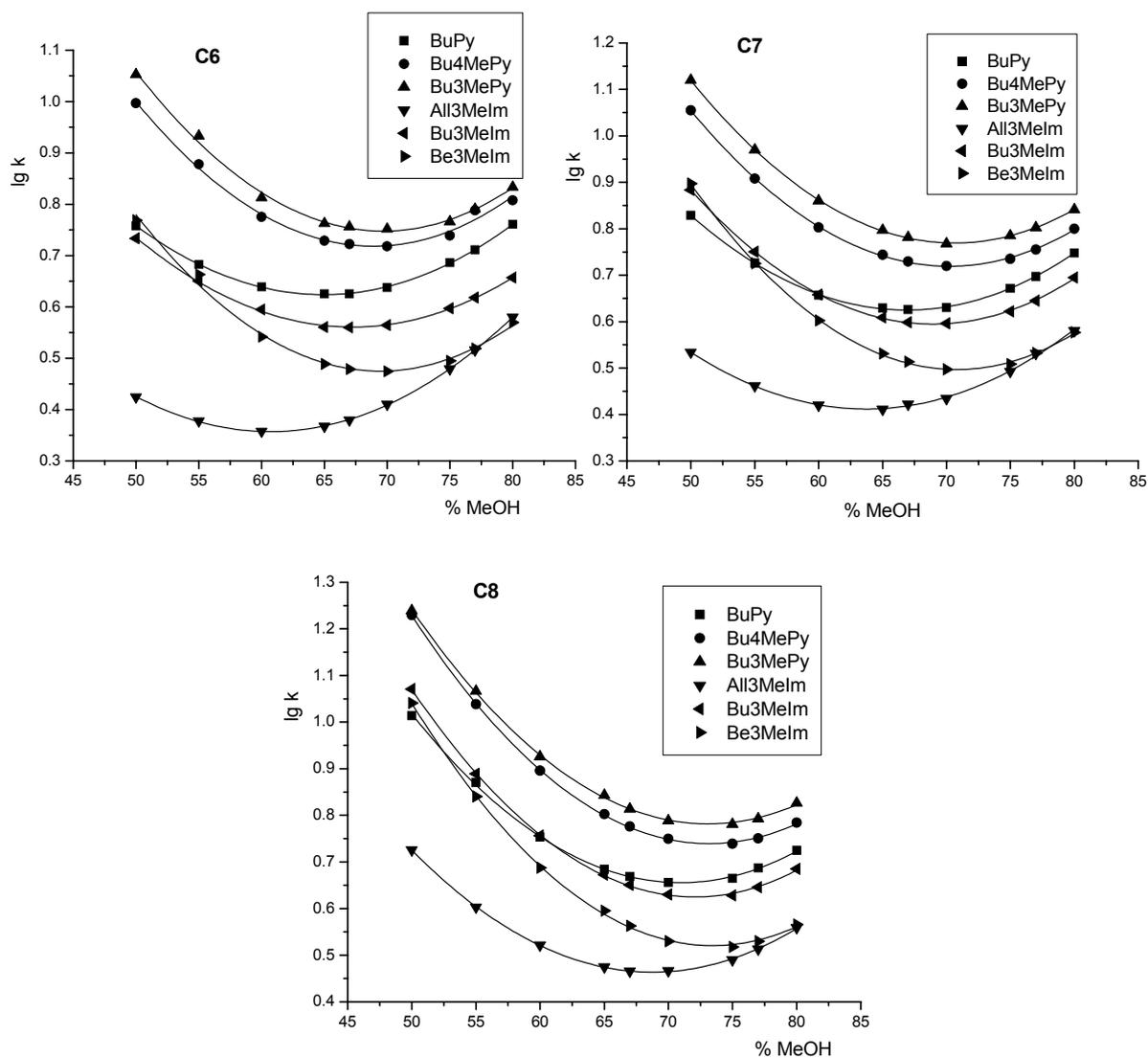
Fig. 2 – Dependences between lg k and C_o for studied ionic liquids and the three ion pairing agents (C6, C7 and C8).

Table 1

Regression parameters for data fitting by eq. 1 for the experimental retention data of the six studied ionic liquids, and some calculated parameters which are characteristic to these dependences

Analyte	$\alpha_0 = \log k_w$	α_1	α_2	r^2	C_{om} for min lg k	lg k_o
Ion pairing agent: sodium hexanesulphonate (C6)						
BuPy	3.161	-0.0782	6.021×10^{-4}	0.9996	64.9	1.362
Bu4MePy	4.458	-0.1086	7.879×10^{-4}	0.9890	68.9	1.477
Bu3MePy	4.627	-0.1113	7.985×10^{-4}	0.9948	69.7	1.482
All3MeIm	2.559	-0.0726	5.978×10^{-4}	0.9998	60.7	1.277
Bu3MeIm	3.221	-0.0792	5.889×10^{-4}	0.9983	67.2	1.190
Be3MeIm	4.359	-0.1118	8.052×10^{-4}	0.9900	69.4	1.231

Ion pairing agent: sodium heptanesulphonate (C7)					
BuPy	3.819	-0.0955	7.138×10^{-4}	0.9996	66.9	1.407
Bu4MePy	4.762	-0.1151	8.199×10^{-4}	0.9995	70.2	1.451
Bu3MePy	4.871	-0.1161	8.222×10^{-4}	0.9998	70.6	1.483
All3MeIm	3.045	-0.0826	6.483×10^{-4}	0.9971	63.7	1.268
Bu3MeIm	4.413	-0.1107	8.032×10^{-4}	0.9997	68.9	1.375
Be3MeIm	5.118	-0.1305	9.216×10^{-4}	0.9994	70.8	1.284
Ion pairing agent: sodium octanesulphonate (C8)					
BuPy	4.806	-0.1170	8.248×10^{-4}	0.9992	70.9	1.354
Bu4MePy	5.619	-0.1334	9.115×10^{-4}	0.9997	73.2	1.394
Bu3MePy	5.387	-0.1260	8.623×10^{-4}	0.9994	73.1	1.410
All3MeIm	3.977	-0.1022	7.431×10^{-4}	0.9996	68.8	1.188
Bu3MeIm	5.367	-0.1316	9.129×10^{-4}	0.9996	72.1	1.336
Be3MeIm	5.621	-0.1389	9.457×10^{-4}	0.9993	73.4	1.188
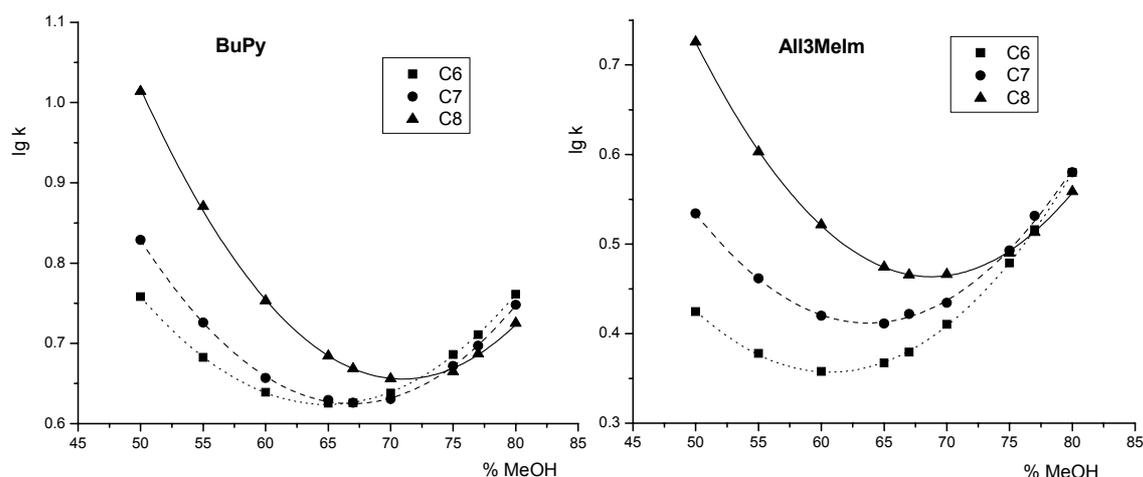
Fig. 3 – Comparative graphs for lg k versus C_o, for the three alkylsulphonates as ion pairing agents, depicted for BuPy and All3MeIm.

The U-shape of the curve describing the relationship between lg k and C_{om} has been reported previously for similar situations, where the studied solutes were ionic species.[10,15-17] One explanation of this unusual behavior relies on the variable content of the ion pairing agent in mobile phase. Because the ion pairing agent is added at a constant concentration only in the aqueous component, it results that its concentration in mobile phase decreases with the increase of methanol content in mobile phase. Therefore, the formation of ion pairs is less and less favored as

the value of C_{om} approaches to 100%. However, the experiments carried out at constant concentration of ion pairing in aqueous component and methanol as well (*i.e.*, 15 mmoles/L) showed a similar U-shaped curves, with the minimum shifted to the higher value of C_{om}. An example is illustrated in Fig. 4, where the retention behavior of All3MeIm at constant concentration of C6 ion pairing agent in aqueous component versus constant concentration in mobile phase is depicted. As can be seen the effect of adding hexanesulphonate anion in aqueous component and

also in methanol at a constant concentration (15 mmoles/L) was the shift of minimum point towards higher content of methanol in mobile phase. Thus, the minimum value of lg k shifted from 60.7% to 68.5% MeOH, while the extrapolated values for C_{om} = 100% MeOH decreased to lg k_o = 0.662, in comparison to 1.277 obtained in the absence of C6 in organic modifier. This result may indicate that the ion pair between

ionic liquid cation and alkylsulphonate anion is less adsorbed on the stationary phase surface than the ionic cation solely.

According to the curves given in Fig. 2, the separation selectivities of these cations are maximum within the shortest elution time at around 70% MeOH (for C6 and C7 as ion pairing agents) and 72.5% MeOH for C8 as ion pairing agent.
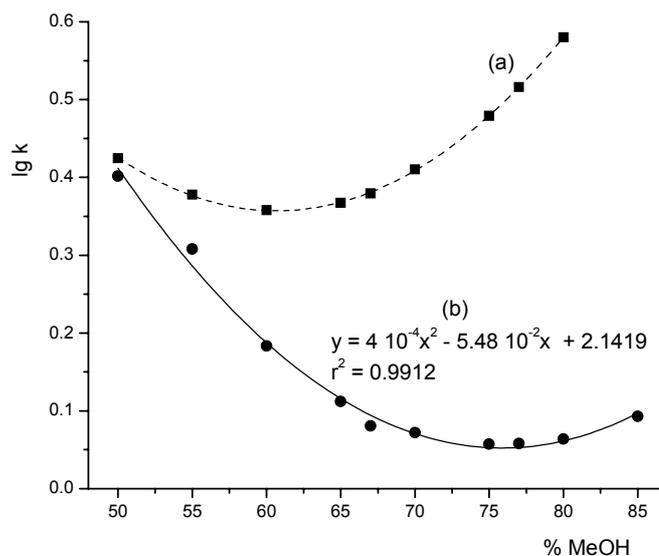

Fig. 4 – Comparative retention curves for All3MeIm for mobile phase containing:
a) 15 mmoles/L $C_6H_{13}SO_3Na$ in aqueous component + methanol; b) 15 mmoles/L $C_6H_{13}SO_3Na$
in aqueous component + 15 mmoles/L $C_6H_{13}SO_3Na$ in methanol.

CONCLUSIONS

Retention study by ion pairing reversed-phase liquid chromatography, achieved on octadecylsilica stationary phase, showed a strong interaction between some pyridinium and imidazolium ionic liquids and this surface, in presence or the absence of alkylsulphonate ion in mobile phase. An unusual chromatographic retention behavior has been observed: the functional dependencies between the logarithm of the retention factor and the methanol content in the mobile phase followed a binomial pattern (U-shaped), with a minimum positioned within the interval 60-75% methanol. This may be explained by ion-dipole interactions occurring between pyridinium and imidazolium cations and residual silanols on the surface of stationary phase. This interaction can be weakened by the presence of ion pairing agent in the composition of mobile phase. Hydrophobic interactions between the hydrophobic moiety of the cations and the bonded chains of the

stationary phase contribute also to the adsorption of these species on octadecylsilica surface.

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