

Characteristic of Morpholinium Ionic Liquids as Gas Chromatography Stationary Phases With McReynolds Constants and Activity Coefficients at Infinite Dilution

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Keywords

activity coefficients at infinite dilution
gas-liquid chromatography
ionic liquids
McReynolds constants

Abstract

Four ionic liquids based on *N*-alkyl-*N*-methylmorpholinium cation ([Mor_{1,R}] where *R* = 2, 4, 8, 10) and bis(trifluoromethanesulfonyl)imide anion [TFSI] were synthesized. Using gas-liquid chromatography a number of parameters describing the sorption properties of the investigated ionic liquids were determined. The values of Kovats indices, McReynolds constants, and activity coefficients at infinite dilution were the basis for the evaluation of intermolecular interactions. The effect of the chain length of the alkyl substituent in the cation, which was used for modification of their polarity has been discussed.

1. Introduction

Ionic liquids (ILs), known as molten organic salts. A typical ionic liquid consists of a large non-symmetrical organic cation and a smaller organic/inorganic anion. ILs are characterized by a unique set of physicochemical properties which include: negligibly low vapor pressure, broad temperature range in the liquid state, thermal stability, high viscosity and density, and affinity to organic or inorganic compounds. Additionally, it is possible to control their physicochemical properties, and thus, to obtain an IL for specific application. This is why they are called “designer solvents” [3]. These properties make their application in many fields of science and technology more attractive [4–6]. Due to the unique properties inherent to ILs, they have been widely applied in various analytical applications including gas chromatography [5]. ILs became very attractive subject in GC development, mostly due to their liquid state, high thermal stability and low vapor pressure. Several studies have been carried out on new ILs and their retention

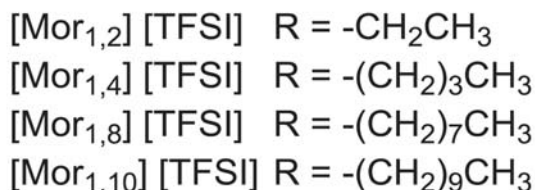
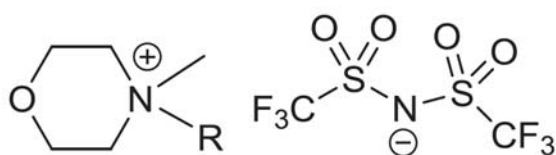


Fig. 1 Molecular structures of studied ionic liquids.

mechanism [8–11]. Selectivity is the main object of interest, since it makes their separation capability slightly different from that of conventional and popular stationary phases. The polarity and/or selectivity of IL-based GC stationary phase can be estimated using some empirical measures: e.g., the McReynolds' method [12], the solvatochromic effect of Reinhardt's dye [13], and Nile Red [14]. These polarity methods has not been definitive for ILs because they all seem to fall within the same narrow range values [15–17]. Considering the limitation of the "polarity" methods classification system, the solvation parameter model was developed by Abraham and co-workers by utilizing a large number of test probes that are capable of undergoing multiple interactions with stationary phase [18–20]. Similar qualitative information can be obtained from activity coefficients at infinite dilution. This parameter provide a useful tool for solvent selection in separation process.

The main goal of this work was to evaluate four ionic liquids (Fig. 1), namely: *N*-ethyl-*N*-methylmorpholinium bis(trifluoromethanesulfonyl)imide [Mor_{1,2}][TFSI], *N*-butyl-*N*-methylmorpholinium bis(trifluoromethanesulfonyl)imide [Mor_{1,4}][TFSI], *N*-octyl-*N*-methylmorpholinium bis(trifluoromethanesulfonyl)imide [Mor_{1,8}][TFSI], and *N*-decyl-*N*-methylmorpholinium bis(trifluoromethanesulfonyl)imide [Mor_{1,10}][TFSI] as potential stationary phases for gas chromatography. In order to estimate the polarity of investigated ionic liquids, the values of such parameters as Kovats indices, McReynolds constants were determined. For detailed investigation of the specific intermolecular interactions between the solutes and the ionic liquid-based stationary phase, activity coefficients at infinite dilution were determined in temperature range from 313.15 K up to 363.15 K.



2. Experimental

2.1 Reagents and chemicals

All four of the tested ionic liquids were synthesized by our team according to the procedure described in previous paper [21]. The solvents used, i.e., acetonitrile (purity > 99.9% and mass fraction of water $<2 \times 10^{-4}\%$), dichloromethane (> 99.9%), acetone (> 99.9%), and methanol (> 99.9%) were purchased from POCH (Poland). The Chromosorb W HP-DMCS, 80/100 mesh was purchased from Sigma-Aldrich (Germany). The squalane (>99%) used to prepare the reference column was purchased from Sigma-Aldrich, (Germany). The McReynolds test solutes and *n*-alkanes (C₅–C₁₄) were of analytical grade purity and were purchased from Sigma-Aldrich (Germany). Nitrogen (99.999%), as a carrier gas, was purchased from Linde (Poland).

2.2 Instrumentation

Chromatographic analyzes were performed using an Agilent 7890 A chromatograph equipped with a flame ionization detector (Agilent USA). Data was collected and processed using Agilent software. Both the injector port and the detector had a temperature of 523.15 K. Nitrogen (99.999%) was used as carrier gas. Solute samples with a volume of 1 μL were injected using the microsyringe. To provide infinite dilution conditions of a sample the injector port worked in split mode in the range of 1:50 to 1:100. The column was thermostated at a given temperature for at least 20 minutes. All measurements were made three times to determine the repeatability of the obtained results. Dead retention time was determined using methane. The volume flow of the carrier gas was measured using an automatic soap bubble flow meter. The flow rate was maintained between 0.0050 and 0.0200 $\text{dm}^3\text{min}^{-1}$ depending on temperature and type of compound.

Tested columns were made of stainless steel tubing (304 grade) purchased from Supelco (USA). The columns had a length of 1 m and an internal diameter of 2.1 mm. The detailed description of the experimental procedure of GC-columns preparation used in this work can be found in the literature [22]. The values of McReynolds constants were determined for the temperature of 393.15 K. The values of activity coefficients at infinite dilution were determined for temperatures in range 313.15–363.15 K.

3. Results and discussion

3.1 McReynolds compounds

The studied ionic liquids are based on the bis(trifluoromethanesulfonyl)imide anion [TFSI]⁻, well-defined in the literature, which, as a component of ionic liquids, increases their hydrophobic properties. The morpholinium ring



Table 1

McReynolds constants determined at 393.15 K.

Stationary phase	Benzene	1-Butanol	2-Pentanone	Nitropropane	Pyridine	ΔI_{av}
	X	Y	Z	U	S	
[Mor _{1,2}][TFSI]	777	923	984	1210	1133	1005
[Mor _{1,4}][TFSI]	599	755	807	1087	1005	851
[Mor _{1,8}][TFSI]	366	538	601	744	711	592
[Mor _{1,10}][TFSI]	311	398	509	657	609	497
SLB-IL111 ^a	766	930	957	1192	1093	988
SLB-IL100 ^b	602	853	884	1017	1081	887
SLB-IL59 ^c	338	505	549	649	583	525

^a 1.5-Di(2,3-dimethylimidazolium)pentane bis(trifluoromethanesulfonyl)imide.^b 1.9-Di(3-vinylimidazolium)nonane bis(trifluoromethanesulfonyl)imide.^c 1.12-Di(tripropylphosphonium)dodecane bis(trifluoromethanesulfonyl)imide.

substituted with *n*-alkyl chain [Mor_{1,*R*}]⁺ (*R* = 2, 4, 8, 10) was used as the cation. The six-membered ring contains oppositely placed oxygen and nitrogen atoms in its structure. The structural formula of the studied ionic liquids is shown in Fig. 1.}

Table 1 presents the determined McReynolds constant values as well as their mean values for each of the four tested columns. Mean values are often used to visualize the overall stationary phase polarity, while the individual component give a valuable evaluation of character of the interactions of a given type. For comparison, McReynolds constant values for three commercially available gas chromatography columns [23] are shown in Table 1. Although these values have been determined for polymerized ionic liquids, they may be a reference point in evaluating the polarity of the tested ionic liquids.

According to the posited classification of stationary phase polarity, the average values of McReynolds constants ΔI_{av} above 400 indicate high polarity. In the described cases, these values are significantly higher. In the case of the ionic liquid with *n*-decyl cation substituent, the mean value of ΔI_{av} was 497, while the highest value determined for the column with the lowest length of the alkyl substituent was twice as high – 1005.

In the latter case, the stationary phase polarity is comparable to the value determined for the SLB-IL111 column, whose cation contains two imidazolium rings connected with an *n*-pentane bridge. The elongation of the cation substituent to *n* = 10 results in a decrease in polarity below the value of the least polar commercial phase based on ionic liquid with tripropylphosphonium cation with an *n*-dodecane “bridge” which ΔY_v value is 525. Thus, it can be stated that ionic liquids based on morpholinium cation are tunable in a wide range of their polarity. There is a nonlinear relationship between the McReynolds constants and the number of carbon atoms of the cation substituent – the increase in number of carbon atoms reduces the polarity to an ever lesser degree.



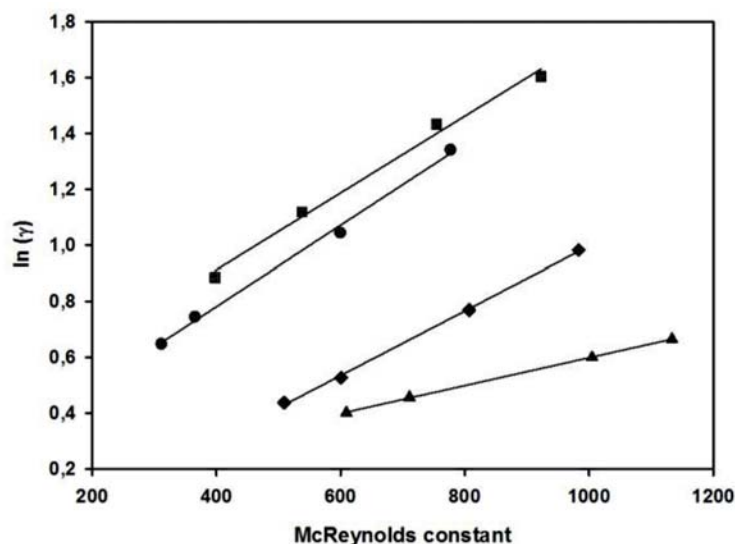


Fig. 2 Plot of dependence of $\ln(\gamma_{1,3}^{\infty})$ as a function of McReynolds constants for the tested compounds at 393.1 K (●) benzene, (■) 1-butanol, (◆) 2-pentanone, (▲) pyridine.

3.2 Activity coefficients at infinite dilution

The Kovats indices discussed in the previous section and the associated McReynolds constants provide only a brief overview of the specifics of intermolecular interactions between the solutes and the stationary phase of the chromatographic column. Their main advantage is the simplicity of both the experimental part and data processing. Nevertheless, for a better description, the values of activity coefficients at infinite dilution $\gamma_{1,3}^{\infty}$ for the four McReynolds compounds and hexane as the *n*-alkane representative were determined (due to the lack of critical values for nitropropane, the compound was omitted). The coefficient values for the tested ionic liquids were determined at seven temperatures: 313.15–363.15, and 393.15K.

The values of activity coefficients at infinite dilution determined for hexane are many times greater than those of McReynolds compounds. The low $\gamma_{1,3}^{\infty}$ values for the McReynolds compounds indicate their greater strength of interaction with the solvent, and thus higher mutual solubility. Comparison of $\gamma_{1,3}^{\infty}$ values of McReynolds compounds shows a slight difference when compared to the previously determined constants: $\gamma_{1,3}^{\infty}$ values decrease in the series 1-butanol > benzene > 2-pentanone > pyridine. Correlation of both parameters is shown in Figure 2.

For the tested compounds, the relationship between the two parameters is approximately linear. In the case of pyridine, which has a high dipole moment and a compact molecular structure, the effect of alkyl chain elongation significantly increases the value of McReynolds constants with relatively little effect on the value of the activity coefficients at infinite dilution. It can be concluded that in the



case of 1-butanol and 2-pentanone, the presence of a long carbon chain results in an increase in solute-ILs interactions, and thus a greater decrease in $\gamma_{1,3}^{\infty}$ value with the elongation of the alkyl substituent of the cation.

4. Conclusions

Based on the results of inverse gas chromatography, a number of parameters were determined describing the sorption properties of new class of ionic liquids based on N-alkyl-N-methylmorpholinium cation and bis(trifluoromethanesulfonyl)-imide anion. The determined values of Kovats indices, McReynolds constants, and activity coefficients at infinite dilution were the basis for the analysis of intermolecular interactions and the effect of the chain length of the alkyl substituent of the cation, which was used as a modulator of their polarity. The ionic liquids tested have a relatively high polarity, as evidenced by the high mean values of McReynolds constants. Correlation of the values of activity coefficients at infinite dilution with temperature inversion provided additional information on how the McReynolds compounds and hexane interact with the tested ionic liquids. Due to the ability of the test compounds to enter into specific intermolecular interactions, the dependence of the solute-ionic liquid interaction strength on the length of the alkyl chain substituent of the cation was determined.

Acknowledgments

The authors wish to thank the National Science Centre, Poland (2014/15/N/ST4/02732) for founding.

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