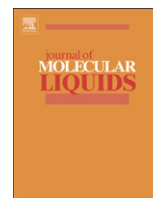




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Contents lists available at ScienceDirect

Journal of Molecular Liquids

journal homepage: www.elsevier.com/locate/molliq

An effect of cation's cyano group on interactions between organic solutes and ionic liquids elucidated by thermodynamic data at infinite dilution



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ARTICLE INFO

Article history:

Received 12 July 2017

Received in revised form 20 August 2017

Accepted 22 August 2017

Available online 25 August 2017

Keywords:

Ionic liquids

Infinite dilution

LSER

Solubility parameter

COSMO-RS

ABSTRACT

New measurements on infinite dilution activity coefficients (γ^∞) of 48 molecular solutes (including: alkanes, alkenes, alkynes, aromatics, ethers, alcohols, ketones, pyridine, thiophene, acetonitrile and 1-nitropropane) in 1-(3-cyanopropyl)-3-methylimidazolium dicyanamide ionic liquid (IL) are reported in temperature range from $T = (308.15 \text{ to } 368.15) \text{ K}$ and addressed to previously published data. Relationships between the chemical structure of the solute and the observed value of γ^∞ , closely related to relative strength and nature of molecular interactions, are elucidated by the data and discussed. An effect of substitution of methyl group by cyano functional group in the cation's side chain is analyzed based on a comparison of the measurements with the data published previously for a "plain" counterpart of the studied IL, namely, 1-butyl-3-methylimidazolium dicyanamide. Besides, infinite dilution selectivity is adopted to evaluate the IL under study as an entrainer for common separation problems. Three modeling approaches are demonstrated to be capable of capturing the substitution effects observed experimentally. First, representation of the investigated systems by linear solvation-energy relationship (LSER) is shown and an effect of cyano group is confirmed in terms of the coefficients of the obtained correlation. Hildebrand solubility parameters of pure IL are calculated by regressing the γ^∞ data with regular solution theory in order to check an influence on enthalpy of vaporization. Finally, conductor-like screening model for real solvents (COSMO-RS) calculations is demonstrated along with a discussion of an impact of molecular geometry of cation and solute on the accuracy of predicted γ^∞ data.

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1. Introduction

Due to their peculiar physical and chemical properties, low melting organic salts named as ionic liquids (ILs) have been recently considered by various scientific communities as chemicals interesting from the point of view of both academic and industrial applications [1,2]. In particular, a vast amount of effort has been devoted to utilization of ILs as novel entrainers for various processes of separating liquid mixtures, mainly in liquid-liquid extraction, or extractive distillation [3,4]. The properties, which are the most important from the point of view of possible application of ILs in these processes are liquid-liquid and vapor-liquid phase equilibria (LLE and VLE, respectively), as they allow to evaluate performance of the tested extractant or entrainer directly in terms of such measures like distribution ratio, or selectivity, or relative volatility. Nevertheless, high quality LLE and

VLE data are usually not so easy to measure, but also their determination requires specialized and experienced staff, is time and cost consuming. A rough, but still thermodynamically solid, estimation of performance of a potential IL in a given separation process can be carried out by using another thermodynamic property, namely, infinite dilution activity coefficient (γ^∞) of molecular compound involved in the separation [5]. In fact, the value of γ^∞ for a given solute in an IL is strictly related with the deviations from ideal phase behavior. Therefore, γ^∞ data can be seen as interesting quantitative information on intermolecular interactions and mutual affinity between the studied IL and solute. Furthermore, the ratio of γ^∞ obtained for two solutes, so-called infinite dilution selectivity, expresses somewhat the capability of IL of separating one from the other – higher the ratio, potentially better performance of IL acting as separating agent [3,6]. The IL-based separations most intensively evaluated on the basis of γ^∞ are: aromatic from aliphatic hydrocarbons [7–9], alkenes from alkanes [10,11], thiophene from aliphatic hydrocarbons (model systems for extractive desulfurization of fuels) [12–14], butanol from water [15–17]; very recently, γ^∞ data of terpenoids were used to estimate the performance of several ILs in separating mixtures of

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these natural compounds [18]. Finally, from the purely utilitarian point of view, γ^∞ data are much easier and cheaper to measure compared to LLE/VLE phase diagrams, or estimate using various computational methods, for example empirical tools employing machine learning or sophisticated thermodynamic models like conductor-like screening model for real solvents (COSMO-RS) [19–21]. This is a reason for which why γ^∞ was used as a benchmark property in computer-aided (i.e. *in silico*) molecular design of task-specific ILs suitable for diverse purposes [22–26].

ILs based on dicyanamide anion, $[\text{N}(\text{CN})_2]$ abbreviated by [DCA], have been found particularly interesting and worth of being considered in separations for a number of research groups [10,27–34]. This was mainly because these ILs disclose significantly lower viscosity compared to ILs incorporating some “standard” anions like, bistriflamide [35]. This makes these ILs particularly attractive from many applications in chemical engineering. Having the anion fixed as [DCA], one can try to “tune” new ILs by modifying the cation’s structure and study an impact of the imposed changes on γ^∞ . The list of the cations, for which γ^∞ data in [DCA]-based ILs are available covers 15 distinct chemical structures: 1-ethyl-3-methylimidazolium [27], 1-butyl-3-methylimidazolium [10], 1-benzyl-3-methylimidazolium [28], 1-methyl-3-(propoxymethyl)imidazolium [29], 1-benzyl-3-(propoxymethyl)imidazolium [29], 2-methyl-1-octyl-3-(propoxymethyl)imidazolium [29], 1-(3-cyanopropyl)-3-methylimidazolium [32,33], 1-(3-cyano propyl)-2,3-dimethylimidazolium [33], 1-butyl-4-methylpyridinium [30], 1-butyl-1-methylpyrrolidinium [31], tris (diethylamino) cyclopropenylum [36] and four different di- and trications [29,34].

This work presents a new set of experimental γ^∞ data of 48 different molecular compounds in 1-(3-cyanopropyl)-3-methylimidazolium dicyanamide, abbreviated henceforth as $[\text{C}_3\text{CN}_1\text{Im}][\text{DCA}]$, in temperature range from $T = (308.15 \text{ to } 368.15)$ K, measured by using gas-liquid chromatography. We decided to consider this IL for two main reasons: first, to continue our systematic investigations on an impact of the cation’s structure on performance of [DCA]-based ILs in representative separation problems – commonly studied in literature separations like alkenes/aromatics from aliphatic hydrocarbons [37,38] and extractive desulfurization of fuels [39] were selected; second, to compare our results with the data published previously for the same IL by Revelli et al. [32] and Zhang et al. [33] and discuss/explain the observed differences and discrepancies. Besides, regression of the measured γ^∞ data in terms of linear solvation-energy relationship (LSER) is presented along with the data reduction by using regular solution theory, applied to obtain an estimate of the Hildebrand solubility parameter of pure IL. Finally, COSMO-RS predictions of γ^∞ in the investigated systems are demonstrated.

2. Experimental methods

2.1. Materials

Chemical structure of the investigated IL 1-(3-cyanopropyl)-3-methylimidazolium dicyanamide, henceforth abbreviated by $[\text{C}_3\text{CN}_1\text{Im}][\text{DCA}]$, is shown in Fig. 1. The sample of IL was purchased from IoLiTec. Mass fraction purity of the used sample was 0.95, as certified by the supplier. Drying under vacuum at temperature 353 K for 48 h was applied prior to the final measurements to remove any volatile chemicals and water. This process resulted in mass of the sample reduced by approximately 5%, thus we assumed that all the volatile components present in the IL were evaporated. Water content of the dried sample was determined with Karl-Fischer method by using Schott Instruments Titro-Line KF apparatus and CombiTitrant 2 supplied by Merck. The final mass fraction of water in the sample of IL was $500 \cdot 10^{-6}$.

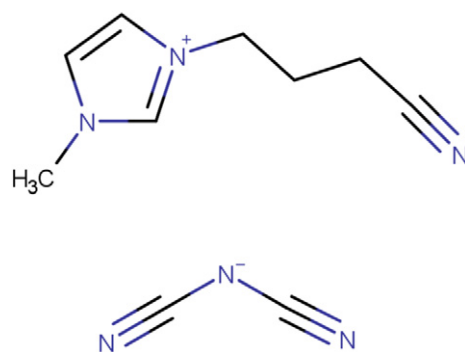


Fig. 1. Chemical structure of the investigated ionic liquid, 1-(3-cyanopropyl)-3-methylimidazolium dicyanamide, $[\text{C}_3\text{CN}_1\text{Im}][\text{DCA}]$.

All the molecular compounds employed in retention measurements (henceforth referred to as solutes) were purchased from Sigma-Aldrich or Fluka and used as received without further purification, because the gas-liquid chromatography technique used in this work to determine γ^∞ separates any impurities in the column. A complete list of the solutes, including their sources and mass fraction purities is given in the Supplementary Material, Table S1.

2.2. Determination of γ^∞

The values of γ^∞ presented in this work were calculated from gas-liquid chromatographic retention data, following the standard procedures based on the equations proposed and developed by Everett and Cruickshank [40,41]. Computational details as well as all the information on the apparatus used and the experimental procedures, including preparation of IL-coated packed column and the retention parameters/conditions, can be found in our previous paper [42]. The only relevant parameters that should be mentioned when reporting the new data are the molar amounts of IL used to prepare the packed columns and the corresponding mass percents IL packing. Two packed columns with IL mass-percent loading of 50% and 55% were prepared. These values were established based on our previous experience with chromatographic determinations of γ^∞ in ionic liquid systems. We checked that above 55%, non-uniform, i.e. heterogeneous and “lumpy” coating were obtained, that results in inaccurate and irreproducible values of γ^∞ . The data for a given column were obtained by repeating the measurement at least three times. The differences in the obtained values of infinite dilution activity coefficients were random and relatively small, in a great majority of cases lower than 1%, regardless of packing of the column. The finally reported data are the arithmetic means of the two values, obtained from two different columns, differing in each case by approximately 1%. Any loss of IL during measurements was not observed. Prior to the final determinations, the columns were conditioned until constant mass. Finally accepted column filled with coated support was weighted before and after the measurements and the difference in mass higher than accuracy of analytic balance, i.e. 0.0005 g, was not observed.

Uncertainty of γ^∞ data calculated using Everett-Cruickshank equations was carefully analyzed by Bahadur et al. [43,44]. Based on the standard uncertainties of all the input data required in γ^∞ calculation, the combined relative uncertainty of calculated γ^∞ was judged by these authors to be 5%, regardless of a chemical family of solute. Since, our experimental setup as well as methodology for γ^∞ determination are basically the same as those described in this literature [43,44], one can expect that uncertainty of the data reported in this work is of the same order of magnitude.

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