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Thermodynamics and activity coefficients at infinite dilution measurements for organic solutes and water in the ionic liquid 1-butyl-1-methylpyrrolidinium tetracyanoborate

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ABSTRACT

The activity coefficients at infinite dilution, γ_{13}^{∞}, for 45 solutes, including alkanes, cycloalkanes, alkenes, alkynes, aromatic hydrocarbons, alcohols, thiophene, tetrahydrofuran, ethers, acetone, and water, in the ionic liquid 1-butyl-1-methylpyrrolidinium tetracyanoborate, [BMPYR][TCB], were determined by gas–liquid chromatography at temperatures from 318.15 K to 368.15 K. The values of the partial molar excess Gibbs free energy $\Delta G_1^{E,\infty}$, enthalpy $\Delta H_1^{E,\infty}$, and entropy $\Delta S_1^{E,\infty}$ at infinite dilution were calculated from the experimental γ_{13}^{∞} values obtained over the temperature range. The gas–liquid partition coefficients, K_L were calculated for all solutes and the Abraham solvation parameter model was discussed. The values of the selectivity for different separation problems were calculated from γ_{13}^{∞} and compared to literature values for *N*-methyl-2-pyrrolidinone (NMP), sulfolane, 1-ethyl-3-methylimidazolium tetracyanoborate, [EMIM][TCB], 1-decyl-3-methylimidazolium tetracyanoborate, [DMIM][TCB], and similar ionic liquids. The densities of [BMPYR][TCB] in temperatures range from 318.15 K to 368.15 K, the temperature of fusion and the enthalpy of fusion were measured.

1. Introduction

The new development of ionic liquids (ILs) is closely linked to their applications for extraction and separation processes. Ionic liquids show the set of favourable properties for extraction processes due to their unique properties that can be tailored to suit the application, such as strong solvation within three dimensional polar networks and in general non-flammability and negligible volatility. In particular, they are expected to play a growing role as replacements for conventional volatile organic solvents for biphasic catalysis, solvent extraction, synthesis, and electrochemical investigations [1–4]. In their various manifestations, ILs are capable of dissolving a diverse range of inorganic, organic, or biomaterials to a useful extent. The solute–solvent interactions in solution are controlled by the nature and interplay of the cation and anion pair comprising the IL. Furthermore, the range of extraction of robust cations and anions has been extended in recent rears, allowing the preparation of new ionic liquids with enhanced applicability. In this regard, perfluorinated anions (*e.g.* trifluorotris(perfluoroethyl)phosphate, [FAP] [5]), or cyano-based anions (tricyanomethanide, $[C(CN)_3]$ [6]; tetracyanoborate, $[B(CN)_4]$; [TCB] [7–9] created a break-through concerning extraction properties. Related investigations showed that ionic liquids containing pyrrolidinium cations can surpass the performance of imidazolium ones, increasing the selectivity and capacity of separation processes [10]. Recently, the phase equilibria [11–13] and the activity coefficients at infinite dilution, γ_{13}^{∞} of the pyrrolidinium-based ILs [14] were measured in our laboratory. Also the solubility parameters of pyrrolidinium-based ILs were described between many others [15].

The fundamental properties describing the extraction processes include selectivity and capacity, which can be directly calculated from the activity coefficients at infinite dilution, γ_{13}^{∞} [16]. In the literature, there are three studies on γ_{13}^{∞} for different organic solutes, such as alcohols, hydrocarbons, ethers, ketones, and water in tetracyanoborate, $[B(CN)_4]$, [TCB]-based ILs [7,8,17], namely, a recent publications from our group on 1-decyl-3-methylimidazolium tetracyanoborate, [DMIM][TCB] [7], and on 1-ethyl-3-methylimidazolium tetracyanoborate, [EMIM][TCB] [8], and the second paper on [EMIM][TCB] [17].

Recently, the cyano-containing ILs were tested in extraction in ternary systems for the separation of benzene/*n*-hexane, or toluene/*n*-heptane with maximum average values of selectivity from 20 to 30 [6,9]. Mahurin *et al.* [18] used membranes based on

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[EMIM][TCB] yielded the highest known permeability whilst exhibiting excellent CO_2/N_2 separation selectivities over 50. In our previous work, the [DMIM][TCB] [7] and [EMIM][TCB] [17] revealed selectivities calculated from the activity coefficients at infinite dilution on the average level with better values for shorter *n*-alkane chain, [EMIM][TCB].

Many results suggested that cyano-containing ILs deserve further consideration in chemical separations. The data coming from the activity coefficients measurements for 1-ethyl-3-methylimidazolium dicyanamide, [EMIM][$N(CN)_2$] [19], or for 1-(3-cyanopropyl)-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, [CN-C_3MIM][NTf_2] [20], or for 1-(3-cyanopropyl)-2,3-dimethylimidazolium bis(trifluoromethylsulfonyl)imide, [CN-C_3MMIM][NTf_2] [20]), or for 1-(3-cyanopropyl)-3-methylimidazolium dicyanamide, [CN-C_3MIM][$N(CN)_2$] [20], and 1-(3-cyanopropyl)-2,3-dimethyl imidazolium dicyanamide, [CN-C_3MMIM][$N(CN)_2$] [20] show interesting values of selectivity in the aliphatic hydrocarbons/aromatic hydrocarbons separation process.

Here, we report the activity coefficients at infinite dilution, γ_{13}^{∞}, for 45 solutes, including saturated and unsaturated alkanes, cycloalkanes, aromatic hydrocarbons, alcohols, thiophene, tetrahydrofuran (THF), ethers, acetone, ketones, and water, in the IL 1-butyl-1-methylpyrrolidinium tetracyanoborate, [BMPYR][TCB]. Values of γ_{13}^{∞} were determined by gas–liquid chromatography at 10 K intervals at temperature from 338.15 K to 368.15 K. This work also provides an opportunity to make comparisons with previously-published tetracyanoborate-based ILs. The densities of the IL as a function of temperature and the thermophysical data (temperature of fusion and enthalpy of melting) were also determined. The values of density, viscosity, surface tension, thermal decomposition, and heat capacity of [BMPYR][TCB] were submitted for publication during the preparation of the current manuscript [9].

2. Experimental

2.1. Materials

The ionic liquid [BMPYR][TCB] had a purity of >0.99 by mass fraction and was supplied by Merck, KGaA. The sample was dried for several days at T = 350 K under reduced pressure to remove volatile impurities and trace water. The water content was <0.0004 mass fraction purity, as determined by Karl Fisher titration. The different solutes, purchased from Aldrich or Fluka, had mass fraction purities better than 0.99 and were used without further

TABLE 1
Average experimental activity coefficients at infinite dilution, γ_{13}^{∞}, for various solutes in [BMPYR][TCB] at different temperatures.

Solute	T/K					
	318.15	328.15	338.15	348.15	358.15	368.15
n-Pentane	12.1	11.2	10.5	10.2	9.56	9.09
n-Hexane	16.4	15.3	14.3	13.8	12.9	12.3
3-Methylpentane	14.9	13.8	13.0	12.6	11.8	11.2
2,2-Dimethylbutane	15.7	14.0	13.2	12.9	12.1	11.2
n-Heptane	23.0	21.5	19.8	19.0	17.5	16.6
n-Octane	32.6	30.2	27.5	26.2	23.8	22.5
2,2,4-Trimethylpentane	27.5	25.4	23.5	22.5	20.9	20.0
n-Nonane	46.2	42.5	38.2	36.3	32.6	30.3
n-Decane	65.7	59.5	53.8	50.4	44.9	42.1
Cyclopentane	5.87	5.47	5.27	5.18	4.88	4.72
Cyclohexane	8.42	7.80	7.45	7.23	6.75	6.47
Methylcyclohexane	11.9	11.0	10.5	10.1	9.38	8.94
Cycloheptane	10.4	9.70	9.18	8.85	8.21	7.78
Cyclooctane	13.5	12.5	11.6	11.2	10.3	9.76
1-Pentene	5.58	5.32	5.30	5.24	5.01	5.02
1-Hexene	7.68	7.31	7.16	7.03	6.57	6.57
Cyclohexene	4.09	3.97	3.93	3.88	3.73	3.71
1-Heptene	10.7	10.2	10.0	9.72	9.09	8.93
1-Octene	15.4	14.6	14.1	13.4	12.6	12.5
1-Decene	29.7	28.3	27.1	26.1	23.5	22.8
1-Hexyne	2.53	2.56	2.58	2.63	2.63	2.68
1-Heptyne	3.49	3.50	3.51	3.53	3.54	3.56
1-Octyne	4.93	4.90	4.88	4.85	4.81	4.78
Benzene	0.810	0.816	0.836	0.855	0.870	0.887
Toluene	1.09	1.11	1.14	1.16	1.18	1.20
Ethylbenzene	1.56	1.58	1.60	1.64	1.66	1.69
o-Xylene	1.34	1.36	1.39	1.41	1.43	1.46
m-Xylene	1.54	1.56	1.59	1.62	1.64	1.66
p-Xylene	1.46	1.49	1.54	1.58	1.59	1.62
Methanol	0.991	0.912	0.861	0.812	0.753	0.723
Ethanol	1.29	1.17	1.09	1.02	0.950	0.894
1-Propanol	1.50	1.36	1.27	1.18	1.10	1.04
1-Butanol	1.88	1.67	1.55	1.44	1.33	1.23
Water	2.15	1.87	1.73	1.58	1.39	1.28
Thiophene	0.659	0.663	0.684	0.702	0.711	0.734
Tetrahydrofuran	0.610	0.611	0.639	0.652	0.661	0.679
Methyl *tert*-butyl ether	2.37	2.39	2.46	2.48	2.52	2.55
Methyl *tert*-pentyl ether	3.32	3.34	3.35	3.36	3.37	3.39
Diethyl ether	2.32	2.33	2.34	2.36	2.37	2.39
Di-*n*-propyl ether	5.78	5.65	5.51	5.42	5.33	5.26
Di-*iso*-propyl ether	6.08	5.94	5.91	5.82	5.75	5.68
Di-*n*-butyl ether	11.6	10.9	10.6	10.2	9.7	9.41
Acetone	0.439	0.441	0.454	0.464	0.468	0.485
2-Pentanone	0.692	0.701	0.721	0.735	0.738	0.755
3-Pentanone	0.650	0.664	0.688	0.710	0.719	0.732