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Activity coefficients at infinite dilution and physicochemical properties for organic solutes and water in the ionic liquid 1-(2-hydroxyethyl)-3-methylimidazolium trifluorotris(perfluoroethyl)phosphate

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ABSTRACT

This work presents new data of activity coefficients at infinite dilution, γ^{∞} of different organic solutes and water in the 1-(2-hydroxyethyl)-3-methylimidazolium trifluorotris(perfluoroethyl)phosphate, [C_2OHmim][FAP] ionic liquid. Values of γ^{∞} were determined for 65 organic solutes, including alkanes, alkenes, alkynes, cycloalkanes, aromatic hydrocarbons, alcohols, thiophene, ethers, ketones, esters, 1-nitropropane, aldehydes, acetonitrile and water by inverse gas chromatography within the temperature range from (318.15 to 368.15) K. The basic thermodynamic functions, such as partial molar excess Gibbs energies, $\Delta G_1^{E,\infty}$, enthalpies, $\Delta H_1^{E,\infty}$ and entropies, $\Delta S_1^{E,\infty}$ at infinite dilution were calculated from the experimental γ^{∞} values obtained over the temperature range. Additionally the gas–liquid partition coefficients, K_L were determined. Experimental values of gas–liquid partition coefficients were used to determine the coefficients in the Abraham solvation parameter model (LFER). Results are compared to previously investigated ionic liquids with the same $[C_2OHmim]^+$ cation and $[FAP]^-$ anion. The selectivity and capacity at infinite dilution for alkanes/thiophene extraction problems were calculated from experimental γ^{∞} values to verify the possibility of investigated ionic liquid as an entrainer in liquid–liquid extraction.

1. Introduction

Over 20 years, ionic liquids (ILs) have been the subject of intensive studies. Generally speaking, ionic liquids are salts, which are liquid at room temperature or their melting point is lower than 100 °C. An important feature of ILs is that their physicochemical properties can be simply adjusted by modification of the structure of both the cation as well as the anion. One of the most important features of ionic liquids is their negligible vapor pressure. This is very important property especially for solvents in liquid extraction. Actually used solvents in separation processes are often toxic and volatile what makes them environmentally unfriendly. Therefore there is a need for looking for better environmentally friendly solvents for new and existing industrial processes. To use an IL in a particular industrial process, knowledge is needed about the interaction of the IL with different solvents. Activity coefficients at infinite dilution, γ^{∞} provide such a basic knowledge. From these measurements the selectivity ($S_{ij}^{\infty} = \gamma_i^{\infty}/\gamma_j^{\infty}$) and capacity ($k_j^{\infty} = 1/\gamma_j^{\infty}$) can be directly calculated for different separation problems.

In this work, which is a continuation of our systematic study on interactions between ionic liquid and different solutes, the activity coefficients at infinite dilution for organic solutes and water in the ionic liquid 1-(2-hydroxyethyl)-3-methylimidazolium trifluorotris(perfluoroethyl)phosphate, [C_2OHmim][FAP] were determined within the temperature range from (318.15 to 368.15) K using inverse gas chromatography (IGC). Based on these results the gas–liquid partition coefficients, K_L, and basic thermodynamic functions such as partial molar excess Gibbs energy $\Delta G_1^{E,\infty}$, enthalpies $\Delta H_1^{E,\infty}$ and entropies $\Delta S_1^{E,\infty}$ at infinite dilution were determined.

Ionic liquids are considered as extractants in separation of sulfur compounds from fuels [1–3], therefore the selectivities and capacities at infinite dilution for alkanes/thiophene extraction problems were calculated and compared to other ILs based on the same $[FAP]^-$ anion [4–9]. Additionally results were compared to ionic liquid based on the same cation with bis(trifluoromethylsulfonyl)-amide, $[NTf_2]^-$ anion [10].

2. Experimental

2.1. Materials

The ionic liquid [C_2OHmim][FAP] had a purity of >0.995 mass fraction and was supplied by Merck. To remove any volatile chemicals and water from the ionic liquid this compound was maintained at a very low pressure of about $5 \cdot 10^{-3}$ Pa at temperature

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TABLE 1
Density, ρ as a function of temperature for ionic liquid [C_2OHmim][FAP].

T/K	ρ/g · cm^{-3}
298.15	1.76454
308.15	1.75293
318.15	1.74127
328.15	1.72961
338.15	1.71797
348.15	1.70638
358.15	1.69472
368.15	1.68308

of about 363 K for approximately 5 h. The water content was analyzed by Karl–Fischer titration technique (method TitroLine KF). The sample of IL was dissolved in methanol and titrated with steps of 0.0025 cm^3. The results obtained have shown the water content to be less than $150 \cdot 10^{-6}$. The titrant CombiTitrant 5 No. 1.8805.1000 Merck one-component reagent for volumetric Karl Fischer titration was used. The lower determination limit of this technique is approximately (50 to 100) · 10^{-6} H_2O. Density as a function of temperature, necessary to calculate K_L, was measured using an Anton Paar GmbH 4500 vibrating-tube densimeter (Graz, Austria) with uncertainty of 10^{-5} g · cm^{-3} and are presented in table 1. The list of solutes including source and purities are

TABLE 2
The experimental activity coefficients at infinite dilution γ_{13}^{∞} for the solutes in ionic liquid [C_2OHmim][FAP] at different temperatures.[a]

Solute	T/K					
	318.15	328.15	338.15	348.15	358.15	368.15
Pentane	21.3	19.9	18.5	17.4	16.5	15.6
Hexane	32.6	30.0	27.9	25.8	24.5	22.9
3-Methylpentane	28.3	25.8	24.1	22.3	21.0	19.6
2,2-Dimethylbutane	24.3	22.6	21.0	19.6	18.6	17.6
Heptane	51.4	46.6	42.3	38.8	35.9	33.2
Octane	79.1	70.9	63.9	58.0	53.9	48.8
2,2,4-Trimethylpentane	45.6	41.7	38.1	35.5	33.3	31.0
Nonane	121	106	96.0	85.5	78.8	71.0
Decane	184	161	143	128	115	103
Cyclopentane	12.5	11.6	10.8	10.2	9.71	9.18
Cyclohexane	19.3	17.8	16.5	15.3	14.5	13.5
Methylcyclohexane	27.3	25.0	22.9	21.3	19.8	18.5
Cycloheptane	29.0	26.2	24.1	22.0	20.3	18.9
Cyclooctane	41.8	37.4	33.7	30.8	28.3	25.9
Pent-1-ene	8.95	8.67	8.39	8.18	8.00	7.80
Hex-1-ene	14.2	13.4	12.8	12.3	11.8	11.3
Cyclohexene	9.58	9.18	8.72	8.37	8.10	7.82
Hept-1-ene	22.0	20.9	19.7	18.7	17.8	17.1
Oct-1-ene	34.7	32.5	30.1	28.3	26.7	25.2
Dec-1-ene	81.4	75.1	68.8	63.2	58.7	54.6
Pent-1-yne	3.11	3.13	3.15	3.17	3.20	3.22
Hex-1-yne	4.87	4.84	4.82	4.80	4.78	4.76
Hept-1-yne	7.56	7.44	7.30	7.20	7.08	6.99
Oct-1-yne	11.8	11.5	11.1	10.8	10.5	10.2
Benzene	1.08	1.13	1.18	1.23	1.28	1.33
Toluene	1.65	1.72	1.80	1.86	1.93	1.99
Ethylbenzene	2.72	2.79	2.86	2.93	3.00	3.06
o-Xylene	2.37	2.44	2.52	2.59	2.65	2.72
m-Xylene	2.57	2.66	2.76	2.85	2.93	3.03
p-Xylene	2.68	2.77	2.88	2.95	3.05	3.14
Styrene	1.62	1.69	1.76	1.83	1.90	1.97
α-Methylstyrene	2.66	2.79	2.90	3.03	3.13	3.25
Thiophene	1.11	1.14	1.18	1.22	1.26	1.30
Pyridine		0.0694	0.0854	0.104	0.126	0.149
Methanol	0.689	0.701	0.710	0.719	0.729	0.735
Ethanol	0.789	0.801	0.811	0.821	0.829	0.838
Propan-1-ol	1.11	1.12	1.12	1.13	1.13	1.13
Propan-2-ol	0.811	0.821	0.834	0.841	0.853	0.864
Butan-1-ol	1.57	1.55	1.54	1.52	1.51	1.50
Butan-2-ol	1.06	1.07	1.09	1.10	1.11	1.13
2-Methyl-propan-1-ol	1.55	1.52	1.50	1.47	1.45	1.43
tert-Butanol	0.709	0.735	0.767	0.789	0.818	0.845
Pentan-1-ol	2.04	2.02	2.00	1.98	1.97	1.96
Water	2.22	2.10	2.01	1.92	1.85	1.77
Methyl acetate	0.176	0.198	0.225	0.251	0.279	0.308
Methyl propanoate	0.260	0.293	0.330	0.365	0.404	0.445
Methyl butanoate	0.404	0.451	0.502	0.548	0.601	0.657
Ethyl acetate	0.235	0.265	0.300	0.333	0.370	0.410
Vinyl acetate	0.485	0.520	0.561	0.596	0.634	0.673
Tetrahydrofuran	0.172	0.202	0.234	0.266	0.302	0.342
1,4-Dioxane	0.127	0.151	0.175	0.204	0.234	0.266
tert-Butyl methyl ether	0.583	0.684	0.787	0.907	1.03	1.16
tert-Butyl ethyl ether	1.37	1.58	1.79	2.04	2.27	2.52
tert-Amyl methyl ether	0.995	1.15	1.30	1.48	1.66	1.84
Diethyl ether	0.668	0.765	0.861	0.970	1.08	1.20

(*continued on next page*)