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

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ABSTRACT

This work is continuation of our systematic study of activity coefficients at infinite dilution, γ^{∞} of different organic solutes and water in the ionic liquids. New data of γ^{∞} were determined for 62 solutes, including alkanes, alkenes, alkynes, cycloalkanes, aromatic hydrocarbons, alcohols, thiophene, ethers, ketones, esters, 1-nitropropane, butanal, acetonitrile, and water in the ionic liquid 1-(2-methoxyethyl)-1-methylpiperidinium trifluorotris(perfluoroethyl)phosphate by inverse gas chromatography at the temperature range from (318.15 to 368.15) K. The basic thermodynamic functions, namely partial molar excess Gibbs free 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. Results are compared to previously investigated ionic liquids with the same cations or anions. Values of the selectivity and capacity at infinite dilution for heptane/benzene, heptane/thiophene, and heptane/methanol extraction problems were calculated from experimental γ^{∞} values to verify the possibility of investigated ionic liquid as an entrainer in liquid–liquid extraction.

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1. Introduction

Ionic liquids, ILs, are salts usually melting at low temperatures as a result of asymmetry in structure. They have very important property which makes them suitable media in extraction, namely negligible vapor pressure. Additionally they have wide liquid range, high thermal, and chemical stability. These unique properties make them potential, environmental friendly replacements for conventional, usually volatile, and toxic organic solvents used as entrainers in separation processes. An additional advantage is that physicochemical properties of ILs can be simply adjusted by modification of the cation or anion structure. Nonetheless to use an ionic liquid in chemical industry the determination of interaction with different compounds is needed. Activity coefficients at infinite dilution, γ^{∞}, are very helpful in the characterization of interactions between the solvent (IL) and solutes. Due to low volatility of ionic liquids, inverse gas chromatography (IGC) is a useful method to determine activity coefficients at infinite dilution, gas–liquid partition coefficients, K_L, and basic thermodynamic functions such as 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. Additionally from the experimental activity coefficients at infinite dilution, 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, the ionic liquid 1-(2-methoxyethyl)-1-methylpiperidinium trifluorotris(perfluoroethyl)phosphate, [COC_2mPIP][FAP] was examined. This work is a continuation of our systematic study of γ^{∞} of organic solutes and water in the ionic liquids. The results obtained are related to the previously investigated IL, namely 1-(2-methoxyethyl)-1-methylpiperidinium bis(trifluoromethylsulfonyl)-amide, [COC_2mPIP][NTf_2] [1] based on the same cation and other ILs with the same $[FAP]^-$ anion [2–6].

2. Experimental

2.1. Materials

The ionic liquid [COC_2mPIP][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 5×10^{-3} Pa at a temperature of about 363 K for approximately 5 h. The characterization of the IL investigated, including water content, density and viscosity as a function of temperature, glass transition temperature, change of heat capacity at the glass transition temperature and decomposition temperature, was presented previously [1]. The list of solutes including source and purities are presented in

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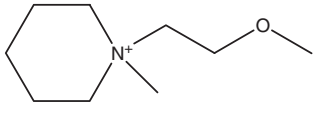
TABLE 1
The experimental activity coefficients at infinite dilution γ_{13}^{∞} for the solutes in ionic liquid [COC_2mPIP][FAP] at different temperatures.[a]

Solute	T/K					
	318.15	328.15	338.15	348.15	358.15	368.15
Pentane	7.05	6.86	6.72	6.56	6.42	6.32
Hexane	9.84	9.53	9.20	8.98	8.73	8.50
3-Methylpentane	8.61	8.35	8.13	7.92	7.72	7.55
2,2-Dimethylbutane	7.76	7.55	7.41	7.25	7.10	6.98
Heptane	13.8	13.2	12.6	12.2	11.6	11.2
Octane	19.3	18.2	17.2	16.4	15.6	15.0
2,2,4-Trimethylpentane	12.5	12.0	11.6	11.2	10.9	10.5
Nonane	26.7	25.0	23.4	22.1	20.9	19.9
Decane	37.1	34.5	32.1	30.0	28.3	26.6
Cyclopentane	4.56	4.44	4.34	4.25	4.16	4.08
Cyclohexane	6.65	6.37	6.12	5.88	5.68	5.51
Methylcyclohexane	8.6	8.26	7.97	7.66	7.40	7.22
Cycloheptane	9.08	8.67	8.27	7.89	7.56	7.24
Cyclooctane	12.4	11.7	11.1	10.5	10.1	9.64
Pent-1-ene	3.57	3.57	3.58	3.58	3.58	3.59
Hex-1-ene	5.03	5.00	4.97	4.95	4.93	4.90
Cyclohexene	3.80	3.77	3.73	3.70	3.68	3.66
Hept-1-ene	6.97	6.89	6.82	6.75	6.67	6.62
Oct-1-ene	9.81	9.60	9.39	9.19	9.01	8.86
Dec-1-ene	18.6	17.9	17.3	16.8	16.2	15.7
Pent-1-yne	1.62	1.69	1.76	1.81	1.87	1.93
Hex-1-yne	2.27	2.33	2.41	2.46	2.53	2.58
Hept-1-yne	3.10	3.18	3.23	3.30	3.35	3.41
Oct-1-yne	4.32	4.36	4.39	4.43	4.47	4.50
Benzene	0.546	0.582	0.617	0.659	0.693	0.732
Toluene	0.727	0.775	0.824	0.881	0.926	0.978
Ethylbenzene	1.04	1.10	1.16	1.23	1.29	1.35
o-Xylene	0.932	0.985	1.04	1.11	1.16	1.22
m-Xylene	0.961	1.02	1.09	1.16	1.23	1.29
p-Xylene	0.998	1.06	1.12	1.20	1.26	1.33
Styrene	0.660	0.706	0.752	0.805	0.849	0.901
α-Methylstyrene	0.951	1.03	1.12	1.20	1.27	1.35
Thiophene	0.573	0.605	0.637	0.676	0.707	0.742
Pyridine	0.373	0.397	0.417	0.443	0.462	0.488
Methanol	2.11	1.95	1.83	1.70	1.57	1.49
Ethanol	2.50	2.30	2.10	1.95	1.81	1.69
Propan-1-ol	3.06	2.80	2.52	2.34	2.16	2.02
Propan-2-ol	2.50	2.28	2.09	1.92	1.78	1.68
Butan-1-ol	3.75	3.44	3.09	2.84	2.61	2.41
Butan-2-ol	2.79	2.58	2.34	2.18	2.03	1.91
2-Methyl-propan-1-ol	3.61	3.21	2.91	2.63	2.40	2.24
tert-Butanol	2.09	1.95	1.82	1.71	1.62	1.54
Water	7.06	6.10	5.37	4.71	4.10	3.70
Methyl acetate	0.347	0.370	0.395	0.423	0.452	0.478
Methyl propanoate	0.420	0.452	0.482	0.519	0.554	0.587
Methyl butanoate	0.561	0.598	0.638	0.683	0.721	0.760
Ethyl acetate	0.426	0.456	0.486	0.521	0.554	0.586
Tetrahydrofuran	0.425	0.454	0.478	0.512	0.540	0.567
1,4-Dioxane	0.355	0.388	0.418	0.453	0.485	0.519
tert-Butyl methyl ether	1.28	1.35	1.43	1.50	1.57	1.65
tert-Butyl ethyl ether	2.90	2.97	3.05	3.11	3.18	3.25
tert-Amyl methyl ether	1.84	1.92	2.01	2.08	2.15	2.23
Diethyl ether	1.32	1.38	1.45	1.51	1.57	1.63
Di-*n*-propyl ether	3.21	3.26	3.33	3.37	3.42	3.48
Di-*iso*-propyl ether	2.90	2.99	3.08	3.16	3.23	3.30
Di-*n*-butyl ether	6.55	6.50	6.45	6.39	6.34	6.30
Acetone	0.233	0.250	0.269	0.286	0.303	0.325
Pentan-2-one	0.363	0.389	0.416	0.446	0.472	0.503
Pentan-3-one	0.361	0.392	0.421	0.453	0.482	0.516
Butanal	0.430	0.456	0.482	0.514	0.540	0.566
Acetonitrile	0.300	0.315	0.327	0.344	0.356	0.371
1-Nitropropane	0.495	0.512	0.530	0.548	0.566	0.582

[a] Standard uncertainties u are $u(\gamma_{13}^{\infty}) < 3\%$, $u(T) = 0.02$ K.

table 1S. Due to the high purity of solutes and in fact that the IGC technique separated any impurities on the column, solutes were used without further purification. The structure of the ILs investigated is presented below:



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