J. Chem. Thermodynamics 54 (2012) 90–96

Contents lists available at SciVerse ScienceDirect

J. Chem. Thermodynamics

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

Activity coefficients at infinite dilution and physicochemical properties for organic solutes and water in the ionic liquid 1-(2-methoxyethyl)-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)-amide

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ARTICLE INFO

Article history:
Received 13 February 2012
Received in revised form 12 March 2012
Accepted 14 March 2012
Available online 23 March 2012

Keywords:
Activity coefficient at infinite dilution
Ionic liquid
1-(2-Methoxyethyl)-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)-amide
[COC_2mPYR][NTf_2]
Selectivity
Extraction
LFER

ABSTRACT

The activity coefficients at infinite dilution, γ^{∞}, gas–liquid partition coefficients, K_L, 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 for 61 organic solutes and water in the ionic liquid 1-(2-methoxyethyl)-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)-amide were determined by inverse gas chromatography at the temperatures from (318.15 to 368.15) K. The values of the selectivity for selected compounds which form azeotropic mixtures were calculated from the γ^{∞} and compared to the literature values for other ionic liquids based on bis(trifluoromethylsulfonyl)-amide anion.

1. Introduction

This paper presents new data on activity coefficients at infinite dilution, γ^{∞}, gas–liquid partition coefficients, K_L, 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 for 61 solutes: alkanes, alkenes, alkynes, cycloalkanes, aromatic hydrocarbons, alcohols, thiophene, ethers, ketones, esters, 1-nitropropane, butanol, acetonitrile, and water in the ionic liquid 1-(2-methoxyethyl)-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)-amide, [COC_2mPYR][NTf_2], determined by inverse gas chromatography (IGC) at the temperatures from (318.15 to 368.15) K.

This is continuation of our previous studies which concern separation of aromatic hydrocarbons from aromatic/aliphatic mixtures [1] and separation of compounds which form azeotropic mixtures [2–4]. Previously studied ionic liquids 1-(3-hydroxypropyl)pyridinium bis(trifluoromethylsulfonyl)-amide, [*N*-C_3OHPY][NTf_2] [2] and two ILs with 2-methoxyethyl substituents in the cation, namely 4-(2-methoxyethyl)-4-methylmorpholinium bis(trifluoromethylsulfonyl)amide, [COC_2mMOR][NTf_2] [3] and 1-(2-methoxyethyl)-1-methylpiperidinium bis(trifluoromethylsulfonyl)-amide, [COC_2mPIP][NTf_2] [4] reveal good properties as extractants especially for separation of polar/non-polar azeotropic mixtures. To show the influence of cation structure on γ^{∞} values, the ionic liquid [COC_2mPYR][NTf_2] was chosen. This enables a comparison of the results with two previously studied ILs with 2-methoxyethyl group in the cation structure.

2. Experimental

2.1. Materials

The ionic liquid [COC_2mPYR][NTf_2] had a mass fraction purity > 0.995 and was supplied by Merck. The ionic liquid was further purified by subjecting the liquid to a very low pressure of about $5 \cdot 10^{-3}$ Pa at temperature of about 363 K for approximately 5 h. This procedure removed any volatile chemicals and water from the ionic liquid. The water content was analysed 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 $160 \cdot 10^{-6}$. The solutes, purchased from Aldrich and Fluka, were used without further purification because the IGC technique separated any impurities on the column. The list of materials with purities are presented in table 1S. Structure of investigated IL is presented below:

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http://dx.doi.org/10.1016/j.jct.2012.03.015

TABLE 1
The experimental activity coefficients at infinite dilution γ_{13}^{∞} for the solutes in ionic liquid [COC_2mPYR][NTf_2] at different temperatures.[a]

Solute	T/K					
	318.15	328.15	338.15	348.15	358.15	368.15
Pentane	13.4	12.7	12.1	11.5	11.0	10.5
Hexane	19.0	17.8	16.7	15.9	15.0	14.3
3-Methylpentane	16.6	15.6	14.8	14.1	13.5	12.8
2,2-Dimethylbutane	15.1	14.4	13.7	13.1	12.6	12.0
Heptane	28.0	25.9	24.2	22.6	21.1	19.7
Octane	40.5	36.9	33.9	31.4	29.0	27.0
2,2,4-Trimethylpentane	26.9	25.1	23.7	22.3	21.2	20.0
Nonane	58.1	52.9	48.4	44.3	41.0	37.8
Decane	83.1	75.5	68.1	61.8	56.1	51.3
Cyclopentane	7.52	7.19	6.85	6.54	6.26	5.98
Cyclohexane	11.1	10.4	9.69	9.22	8.65	8.23
Methylcyclohexane	15.4	14.4	13.5	12.7	12.0	11.2
Cycloheptane	15.3	14.1	13.1	12.3	11.5	10.8
Cyclooctane	20.7	19.0	17.4	16.2	15.0	14.0
Pent-1-ene	6.65	6.50	6.35	6.17	6.07	5.91
Hex-1-ene	9.74	9.34	8.92	8.61	8.24	7.96
Cyclohexene	6.04	5.82	5.63	5.44	5.27	5.10
Hept-1-ene	14.1	13.4	12.9	12.3	11.8	11.4
Oct-1-ene	20.8	19.5	18.2	17.3	16.3	15.6
Dec-1-ene	41.7	39.0	36.4	33.8	31.7	29.8
Hex-1-yne	3.29	3.29	3.28	3.28	3.28	3.27
Hept-1-yne	4.75	4.71	4.66	4.62	4.58	4.55
Oct-1-yne	6.85	6.73	6.58	6.48	6.37	6.27
Benzene	1.03	1.04	1.06	1.07	1.08	1.09
Toluene	1.48	1.50	1.51	1.53	1.55	1.56
Ethylbenzene	2.23	2.24	2.24	2.25	2.25	2.26
o-Xylene	1.94	1.96	1.97	1.98	1.99	2.00
m-Xylene	2.14	2.16	2.17	2.19	2.20	2.22
p-Xylene	2.15	2.17	2.18	2.20	2.21	2.23
Styrene	1.29	1.32	1.33	1.36	1.37	1.39
α-Methylstyrene	1.87	1.93	1.98	2.03	2.08	2.12
Thiophene	0.885	0.897	0.909	0.918	0.929	0.938
Pyridine	0.602	0.610	0.618	0.625	0.633	0.639
Methanol	1.37	1.27	1.18	1.10	1.03	0.972
Ethanol	1.77	1.63	1.48	1.38	1.28	1.20
Propan-1-ol	2.20	2.02	1.86	1.71	1.58	1.48
Propan-2-ol	2.00	1.83	1.67	1.54	1.43	1.34
Butan-1-ol	2.87	2.60	2.35	2.16	1.98	1.84
Butan-2-ol	2.40	2.19	2.00	1.85	1.72	1.61
2-Methyl-propan-1-ol	2.76	2.46	2.20	2.01	1.84	1.70
tert-Butanol	1.92	1.79	1.67	1.56	1.48	1.40
Water	3.15	2.81	2.51	2.26	2.05	1.85
Methyl acetate	0.714	0.730	0.742	0.756	0.769	0.783
Methyl propanoate	0.922	0.944	0.959	0.978	0.992	1.01
Methyl butanoate	1.29	1.31	1.33	1.35	1.36	1.38
Ethyl acetate	0.950	0.968	0.983	1.00	1.02	1.03
Tetrahydrofuran	0.813	0.827	0.843	0.855	0.870	0.880
1,4-Dioxane	0.656	0.679	0.699	0.719	0.737	0.756
tert-Butyl methyl ether	2.76	2.79	2.81	2.84	2.86	2.89
tert-Butyl ethyl ether	6.31	6.19	6.12	6.03	5.94	5.85
tert-Amyl methyl ether	4.08	4.06	4.05	4.03	4.01	4.00
Diethyl ether	2.79	2.79	2.78	2.78	2.78	2.78
Di-*n*-propyl ether	7.22	7.03	6.82	6.64	6.47	6.32
Di-*iso*-propyl ether	6.63	6.55	6.46	6.39	6.31	6.23
Di-*n*-butyl ether	15.8	15.0	14.2	13.4	12.8	12.2
Acetone	0.468	0.478	0.489	0.499	0.508	0.517
Pentan-2-one	0.826	0.844	0.857	0.874	0.887	0.900
Pentan-3-one	0.831	0.851	0.871	0.887	0.905	0.919
Butanal	0.808	0.823	0.838	0.851	0.864	0.876
Acetonitrile	0.467	0.469	0.472	0.474	0.477	0.479
1-Nitropropane	0.74	0.742	0.743	0.744	0.746	0.747

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

TABLE 2
The experimental gas–liquid partition coefficients K_L for the solutes in ionic liquid [COC_2mPYR][NTf_2] at different temperatures.[a]

Solute	T/K					
	318.15	328.15	338.15	348.15	358.15	368.15
Pentane	5.21	4.20	3.44	2.87	2.43	2.1
Hexane	10.7	8.30	6.56	5.23	4.30	3.56
3-Methylpentane	10.2	7.89	6.23	5.04	4.11	3.45
2,2-Dimethylbutane	7.16	5.68	4.59	3.78	3.16	2.69
Heptane	21.3	15.7	11.8	9.13	7.23	5.84
Octane	42.0	29.9	21.7	16.2	12.4	9.64
2,2,4-Trimethylpentane	21.2	15.7	11.9	9.23	7.25	5.86
Nonane	83.2	55.9	38.8	27.8	20.4	15.4
Decane	165	105	70.6	48.8	34.9	25.5
Cyclopentane	14.0	10.9	8.73	7.10	5.87	4.94
Cyclohexane	27.3	20.8	16.2	12.7	10.3	8.42
Methylcyclohexane	39.0	28.8	21.7	16.8	13.3	10.8
Cycloheptane	77.1	55.6	41.3	31.1	24.1	18.9
Cyclooctane	194	133	94.4	68.1	50.9	38.6
Pent-1-ene	8.67	6.83	5.49	4.53	3.75	3.19
Hex-1-ene	17.7	13.4	10.4	8.19	6.63	5.43
Cyclohexene	54.3	39.8	29.8	23.0	18.0	14.4
Hept-1-ene	35.0	25.3	18.7	14.3	11.1	8.84
Oct-1-ene	68.3	47.6	34.3	25.0	19.0	14.6
Dec-1-ene	261	165	109	75.0	52.7	37.9
Hex-1-yne	68.8	49.1	36.1	27.0	20.7	16.2
Hept-1-yne	135	92.4	65.3	47.1	34.9	26.4
Oct-1-yne	263	172	117	81.6	58.4	42.7
Benzene	297	206	147	108	80.6	61.7
Toluene	619	410	280	197	142	104
Ethylbenzene	1093	697	460	312	218	156
o-Xylene	1743	1090	705	471	324	228
m-Xylene	1290	814	532	358	248	176
p-Xylene	1234	780	511	345	239	170
Styrene	2779	1704	1088	716	486	339
α-Methylstyrene	4219	2502	1543	981	643	434
Thiophene	403	277	195	142	105	79.9
Pyridine	1963	1268	845	580	408	295
Methanol	150	108	80.0	60.2	46.6	36.5
Ethanol	222	154	111	81.1	61.0	46.7
Propan-1-ol	444	292	200	142	103	76.7
Propan-2-ol	247	168	118	85.1	63.1	47.6
Butan-1-ol	926	584	387	261	184	132
Butan-2-ol	462	301	204	143	103	76.2
2-Methyl-propan-1-ol	625	403	272	187	133	97.9
tert-Butanol	260	172	119	84.8	61.9	46.9
Water	297	208	150	111	83.6	65.0
Methyl acetate	199	139	101	74.5	56.4	43.5
Methyl propanoate	351	236	164	117	86.3	64.8
Methyl butanoate	603	393	265	183	130	95.2
Ethyl acetate	314	213	149	107	78.5	58.9
Tetrahydrofuran	231	162	117	86.7	65.4	50.6
1,4-Dioxane	1063	694	468	324	230	167
tert-Butyl methyl ether	47.0	34.2	25.6	19.5	15.2	12.1
tert-Butyl ethyl ether	37.5	27.2	20.2	15.3	11.9	9.49
tert-Amyl methyl ether	93.1	65.3	47.1	34.8	26.4	20.4
Diethyl ether	23.4	17.8	13.8	10.9	8.77	7.18
Di-*n*-propyl ether	61.6	43.6	31.9	23.8	18.2	14.2
Di-*iso*-propyl ether	31.1	22.7	16.9	12.8	9.99	7.92
Di-*n*-butyl ether	219	143	97.0	67.8	48.7	35.6
Acetone	292	207	150	112	84.7	65.7
Pentan-2-one	882	578	392	273	195	143
Pentan-3-one	856	563	382	266	190	139
Butanal	324	224	160	117	87.5	66.9
Acetonitrile	713	501	361	266	200	153
1-Nitropropane	3079	1950	1278	863	599	427

[a] Standard uncertainties u are $u(K_L) < 3\%$, $u(T) = 0.02$ K.