



Activity coefficients at infinite dilution of organic solutes in the ionic liquid 1-ethyl-3-methylimidazolium trifluoromethanesulfonate using gas–liquid chromatography at $T = (313.15, 323.15, \text{ and } 333.15) \text{ K}$

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ABSTRACT

Activity coefficients at infinite dilution were determined for 24 solutes (n-alkanes, alk-1-enes, alk-1-yne, cycloalkanes, alkylbenzenes, and alcohols) in the ionic liquid 1-ethyl-3-methylimidazolium trifluoromethanesulfonate by gas–liquid chromatography at three different temperatures $T = (313.15, 323.15, 333.15) \text{ K}$. The partial molar excess enthalpy values at infinite dilution were calculated from the experimental results over the same temperature range. Selectivities and capacities at infinite dilution for the hexane/benzene and methanol/benzene separation problems were calculated from experimental infinite dilution activity coefficient values. The activity coefficients, enthalpies, selectivities, and capacities are discussed and compared to literature values for other ionic liquids, as well as industrial molecular solvents.

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1. Introduction

Activity coefficients at infinite dilution have a wide range of applications in the field of chemical engineering [1] and can be used for the pre-screening of solvents to be used in unit operations such as extractive distillation and liquid–liquid extraction. Ionic liquids (ILs) are considered to be environmentally friendly, possess a large *liquidus* range, have a very low vapour pressure and can be tuned to possess certain properties [2,3]. As a result, ionic liquids are deemed to be alternatives to many volatile organic solvents used in industrial processes. Ionic liquids have the potential to separate effectively organic liquids [4–6] through liquid–liquid extraction as well as extractive distillation.

As a continuation of our studies on the solvent properties of ionic liquids [7–19], experimental measurements of infinite dilution activity coefficients of selected organic solutes are reported in 1-ethyl-3-methylimidazolium trifluoromethanesulfonate ([EMIM][CF₃SO₃]) whose the structure is shown in figure 1. The temperature range is between (313.15 and 333.15) K. This work is the first part of a project aimed at understanding the role of the anion of an IL in the interactions of organic liquids and ILs. The work is also aimed at providing data with the view of extending the application of thermodynamic models such as Group Contribution Methods [20,21] as well as contributing to the understanding of how struc-

ture influences ionic liquids selectivity and capacity in different separation problems.

2. Experimental

2.1. Materials

The ionic liquid, 1-ethyl-3-methylimidazolium trifluoromethanesulfonate (purchased from Capital Lab Supplies), with a quoted mass fraction purity >0.98 was subjected to a very low pressure of about $4 \cdot 10^{-3} \text{ Pa}$ at $T = 343.15 \text{ K}$ for 6 h to remove any traces of volatile impurities and moisture. The density of the ionic liquid was determined at $T = 298.15 \text{ K}$ and 1 atm using an Anton Paar DMA 5000 densitometer. The experimental value of $1.38707 \text{ g} \cdot \text{cm}^{-3}$ is in excellent agreement with literature [22,23]. Solutes samples (obtained from DLD Scientific), with mass fraction purity >0.98 were used without further purification since the GLC technique separates the solutes from impurities. Celite (Chromosorb W HP 80/100 mesh) was used as the solid support and dry helium was used as the carrier gas.

2.2. Experimental procedure

The detailed experimental procedure used in his work can be found in previous published works [7,8,14]. The column used in the experiment was constructed of stainless steel with a length of 1 m and an inside diameter of 4.1 mm. Two different loadings were used for each temperature. Before being packed the columns

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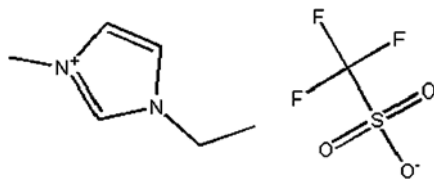


FIGURE 1. Structure of the ionic liquid 1-ethyl-3-methylimidazolium trifluoromethanesulfonate.

were washed with hot soapy water, rinsed with cold water, and flushed with acetone to reduce the drying time. Dichloromethane was used as solvent to aid uniform coating of the ionic liquid onto the inert solid support and removed afterwards by evaporation. The masses of the ionic liquid and Chromosorb in the stationary phase mixture, determined from measurements taken before the addition and after the evaporation of dichloromethane, were in agreement to within 0.005 g. The column packing contained 29.30 (8.01 mmol) and 32.88 (6.23 mmol) mass percent of ionic liquid, large enough to avoid residual adsorption effects. Experiments were performed on a Shimadzu GC-2014 gas chromatograph apparatus, equipped with a thermal conductivity detector, an auto-sampler, and an auto-injector. The carrier gas flow rate was determined with the aid of a calibrated soap bubble flow meter placed at the outlet of the detector. The measured flow rates were corrected for water vapour pressure and varied from $(0.6 \text{ to } 0.75) \mu\text{m}^3 \cdot \text{s}^{-1}$. The carrier gas flow rate was allowed to stabilize for at least 15 min prior to any series of runs. The pressure drop through the column varied from (25 to 50) kPa, providing conducive retention times and sharp peaks. Solute injection volumes ranged between $(0.1 \cdot 10^{-6} \text{ and } 0.5 \cdot 10^{-6}) \text{ dm}^3$ and were considered small enough to comply with the condition of infinite dilution of the solutes in the solvent packing. The injector and the detector temperatures were both set at 523.15 K. The equipment was able to achieve a temperature control of better than 0.01 K. The GLC technique and equipment was tested for systems of selected hydrocarbons in hexadecane as the stationary phase at various temperatures. The results were within 2.5% of literature values [24,25]. The overall errors in γ_{13}^{∞} and $\Delta H_1^{E,\infty}$ were estimated to be less than 4% and 10% respectively.

3. Theory

In this work, the equation developed by Everett [26] and Cruickshank *et al.* [27] was used to calculate γ_{13}^{∞} of solutes in the ionic liquid

$$\ln \gamma_{13}^{\infty} = \ln \left(\frac{n_3 RT}{V_n P_1^*} \right) - \frac{(B_{11} - V_1^*) P_1^*}{RT} + \frac{(2B_{12} - V_1^{\infty}) J_2^3 P_0}{RT}, \quad (1)$$

where n_3 is the number of moles of the stationary phase, T the column temperature, V_n the net retention volume, P_0 the outlet pressure which is equal to atmospheric pressure, P_1^* the saturated vapour pressure of the solute at temperature T , B_{11} the second virial coefficient of the pure solute, V_1^* the molar volume of the solute, V_1^{∞} the partial molar volume of the solute at infinite dilution (here taken to be equal to V_1^*), B_{12} the cross second virial coefficient of the solute (1) and the carrier gas (2), and $P_0 J_2^3$, the mean column pressure. B_{11} and B_{12} were determined using the McGlashan and Potter equation [28]:

$$B/V_C = 0.43 - 0.886(T_C/T) - 0.694(T_C/T)^2 - 0.0375(n-1) \times (T_C/T)^{4.5}, \quad (2)$$

where n refers to the number of carbon atoms of the solute. The Hudson and McCoubrey combining rules [29,30] allowed the calcu-

TABLE 1

The vapour pressure values, P_1^* , molar volumes, V_1^* , and virial coefficients B_{11} and B_{12} used in the calculation of γ_{13}^{∞} at temperatures $T = (313.15, 323.15, \text{ and } 333.15) \text{ K}$.

T/K	P_1^*/kPa	$V_1^*/(\text{cm}^3 \cdot \text{mol}^{-1})$	$B_{11}/(\text{cm}^3 \cdot \text{mol}^{-1})$	$B_{12}/(\text{cm}^3 \cdot \text{mol}^{-1})$
<i>n-Pentane</i>				
313.15	115.14	116.34	-1030.52	47.31
323.15	158.78	118.44	-951.88	47.85
333.15	214.28	120.70	-882.32	48.37
<i>n-Hexane</i>				
313.15	37.15	134.63	-1654.91	54.11
323.15	53.86	136.69	-1517.10	54.72
333.15	76.12	138.86	-1396.5	55.29
<i>n-Heptane</i>				
313.15	12.33	151.03	-2498.59	60.36
323.15	18.85	153.07	-2274.52	61.02
333.15	27.97	155.21	-2079.88	61.63
<i>n-Octane</i>				
313.15	4.15	166.37	-3601.38	66.28
323.15	6.72	168.42	-3258.33	66.98
333.15	10.5	170.57	-2961.96	67.64
<i>Hex-1-ene</i>				
313.15	44.9	128.19	-1536.41	52.24
323.15	64.59	130.17	-1408.94	52.82
333.15	90.49	132.26	-1297.34	53.37
<i>Hept-1-ene</i>				
313.15	14.93	142.45	-2302.18	57.70
323.15	22.6	144.39	-2096.39	58.34
333.15	33.22	146.43	-1917.57	58.93
<i>Oct-1-ene</i>				
313.15	5.04	157.47	-3354.45	63.54
323.15	8.07	159.43	-3035.58	64.22
333.15	12.46	161.47	-2760.05	64.85
<i>Non-1-ene</i>				
313.15	1.71	173.20	-4721.68	69.52
323.15	2.90	175.21	-4250.28	70.25
333.15	4.71	177.29	-3844.68	70.92
<i>Dec-1-ene</i>				
313.15	0.67	186.87	-6437.29	75.23
323.15	1.15	188.92	-5768.59	75.99
333.15	1.93	191.04	-5195.10	76.70
<i>Undec-1-ene</i>				
313.15	0.20	196.45	-8389.25	79.13
323.15	0.38	198.49	-7488.64	79.92
333.15	0.68	200.60	-6718.26	80.66
<i>Pent-1-yne</i>				
313.15	100.73	105.91	-1070.09	43.98
323.15	141.48	107.58	-986.34	44.53
333.15	194.06	109.34	-912.57	45.05
<i>Hex-1-yne</i>				
313.15	32.54	121.85	-1760.38	49.23
323.15	48.06	123.42	-1608.74	49.84
333.15	69.15	125.07	-1476.53	50.40
<i>Hept-1-yne</i>				
313.15	11.69	129.03	-2319.21	54.07
323.15	18.20	130.73	-2108.81	54.71
333.15	27.3	132.49	-1926.25	55.30
<i>Oct-1-yne</i>				
313.15	3.87	151.74	-3809.60	60.20
323.15	6.32	153.39	-3436.80	60.90
333.15	9.95	155.16	-3115.52	61.55
<i>Non-1-yne</i>				
313.15	1.49	168.27	-5140.18	67.66
323.15	2.49	170.11	-4618.88	68.40
333.15	4.02	172.01	-4170.95	69.09
<i>Cyclopentane</i>				
313.15	73.95	96.37	-1097.60	41.30
323.15	103.81	97.78	-1010.05	41.84
333.15	142.35	99.26	-933.10	42.36
<i>Cyclohexane</i>				
313.15	24.63	110.35	-1769.87	46.42

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