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Activity Coefficients at Infinite Dilution of Organic Solutes in 1-Ethyl-3-methylimidazolium Tris(pentafluoroethyl)trifluorophosphate [EMIM][FAP] Using Gas−Liquid Chromatography

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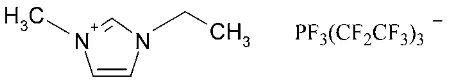
The activity coefficients at infinite dilution, γ_i^∞, for both polar and nonpolar solutes in the ionic liquid 1-ethyl-3-methylimidazolium tris(pentafluoroethyl)trifluorophosphate ([EMIM][FAP]) have been determined by gas−liquid chromatography using the ionic liquid as the stationary phase. The measurements were carried out in the temperature range of (313 to 364) K. The partial molar excess enthalpies at infinite dilution $H_i^{E,\infty}$ of the solutes in the ionic liquid were also derived from the temperature dependence of the γ_i^∞ values.

Introduction

Ionic liquids (ILs) are often called designer solvents or task specific ionic liquids (TSILs) because of their possibility to being tailored to fulfill technological demands of a variety of applications. IL properties can be significantly adjusted by tailoring their anion and/or cation structures.[1] Due to their unique properties such as nonflammability, wide liquid range, stability at high temperatures, and negligible vapor pressure, ionic liquids created interest to be used in separation processes as a potential greener replacement for conventional volatile, flammable, and toxic organic solvents. So, it is very important to know how they interact with different solutes. Activity coefficients at infinite dilution of a solute *i* (γ_i^∞) can be used to quantify the volatility of the solute as well as to provide information on the intermolecular energy between solvent and solute.[2,3]

Since ILs have a negligible vapor pressure, the gas−liquid chromatography (GLC) using the ionic liquid as the stationary phase is the most suitable method for measuring activity coefficients at infinite dilution γ_i^∞. Experimental γ_i^∞ data provide useful information about the interaction between the solvent (IL) and solute. Disubstituted imidazolium-based ionic liquids are a class of very promising extraction and separation reagents, being reported in various publications. Most of these research works used them with anions like $[BF_4]^-$,[4−8] $[PF_6]^-$,[9] $[N(CF_3SO_2)_2]^-$,[10−14] $[Br]^-$,[15] $[Cl]^-$,[16] $[CF_3SO_3]^-$,[17−19] $[SCN]^-$,[20,21] $[MDEGSO_4]^-$,[22] $[FeCl_4]^-$,[23] and $[CoBr_4]^-$.[24] To expand our knowledge about the nature of ILs, the influence of the anion on the thermodynamic properties of the disubstituted imidazolium-based ionic liquid with the tris(pentafluoroethyl)trifluorophosphate $[FAP]^-$ anion was studied in this work. ILs containing the tris(pentafluoroethyl)trifluorophosphate anion $[FAP]^-$ have attracted increased attention due to their unique properties including ultrahigh hydrophobicity, hydrolytic stability, and wide electrochemical window. Perfluoroalkylfluorophosphate $[FAP]^-$ anions are a promising means of overcoming the hydrolytic instability of the hexafluorophosphate anion $[PF_6]^-$.[25,26] In a recent study, the solvation parameter model was used via gas chromatography to characterize the solvation interactions of seven different ILs paired with $[FAP]^-$ anions.[27] Merck KGaA (Darmstadt, Germany) has developed a convenient method for the synthesis of ionic liquids with the tris(perfluoroalkyl)trifluorophosphate-anion $[FAP]^-$, as a replacement of $[PF_6]^-$.[28]

This paper presents γ_i^∞ values for 23 solutes (alkanes, cycloalkanes, 1-alkenes, 1-alkynes, benzene, alkylbenzenes, and alcohols) in the ionic liquid 1-ethyl-3-methylimidazolium tris(pentafluoroethyl)trifluorophosphate ([EMIM][FAP]) over the temperatures range (313 to 364) K. The partial molar excess enthalpies at infinite dilution, $H_i^{E,\infty}$, of these solutes in the ionic liquid were also derived from the temperature dependence of the γ_i^∞ values.



1-Ethyl-3-methylimidazolium tris(pentafluoroethyl)trifluorophosphate

Experimental Section

Materials. The hydrocarbons provided by Beijing Chemical Reagents Company were of analytical grade. Since the GLC process separated the solutes from any impurities, the solutes were used without further purification.

The ionic liquid [EMIM][FAP] possessed a purity of mass fraction > 0.999 and was supplied by Merck KGaA. The ionic liquid was further dried under vacuum for 1 day at 343 K. This procedure removed any volatile chemicals and water from the ionic liquid. A Karl Fischer titration showed that the water concentration in the ionic liquid was less than 0.0001 mass percent.

101 AW (the inert and white diatomite, 80/100 mesh) purchased from Shanghai Reagent Corporation was used as a solid support for the ionic liquid in the GC column. Before use, the support material was subjected to vacuum treatment with heating to remove traces of adsorbed moisture.

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Table 1. Critical Constants, V_c and T_c, and Ionization Energies, I, of the Solutes and the Carrier Gas Used in the Calculation of the Virial Coefficients

solute	V_c / $cm^3 \cdot mol^{-1}$	T_c / K	I / $kJ \cdot mol^{-1}$
pentane	304.0	469.7	998.6
hexane	370.0	507.5	977.4
heptane	432.0	540.3	957.1
octane	492.0	568.8	947.5
nonane	555.0	594.6	938.0
cyclohexane	308.0	553.5	951.3
methyl cyclohexane	369.0	572.1	930.0
1-hexene	350.0	504.0	910.8
1-octene	464.0	566.7	909.9
1-decene	584.0	616.6	909.1
1-pentyne	277.0	481.2	974.5
1-hexyne	332.0	516.2	960.0
1-heptyne	387.0	547.2	960.0
1-octyne	442.0	574.2	951.3
benzene	259.0	562.2	892.1
toluene	316.0	591.8	851.1
ethylbenzene	374.0	617.2	846.1
o-xylene	370.0	630.3	826.1
m-xylene	376.0	617.1	826.1
p-xylene	378.0	616.2	814.1
methanol	118.0	512.6	1047.1
ethanol	168.0	513.9	1010.2
n-propanol	219.0	536.8	986.3
nitrogen	89.2	126.2	1593.3

Apparatus and Procedure. A GC-7900 gas chromatograph was supplied by Shanghai Techcomp Limited Company in China equipped with a heated on-column injector and a flame ionization detector. The injector and detector temperatures were kept at 523 K during all experiments. The nitrogen flow rate was adjusted to obtain adequate retention times. The exit gas flow rate was determined using a GL-102B Digital bubble/liquid flowmeter with an uncertainty of ± 0.0017 $cm^3 \cdot s^{-1}$, which was placed at the outlet of the column. The temperature of the oven was measured with a Pt100 probe and controlled to within 0.1 K. A personal computer directly recorded detector signals, and corresponding chromatograms were obtained using N2000 software.

The solvent dichloromethane was used to coat IL onto the solid support 101 AW (80/100 mesh) by a rotary evaporator to ensure the homogeneous spread of the IL onto the surface of support. The solid support was weighed before and after the coating process. The GC column (stainless steel) with length of 200 cm and an inner diameter of 0.20 cm has been used. The amount of the stationary phase ([EMIM][FAP]) was 1.2698 mmol. The uncertainty of the mass of the stationary phase measurement was within ± 0.0001 g. To avoid possible residual adsorption effects of the solutes on solid support, the amount of ionic liquid was 31.11 mass percent of the support material. Before experiments, the column was conditioned by passing carrier gas at a high flow rate (about 2 $cm^3 \cdot s^{-1}$) and at the high temperature (about 373 K) over a period of about 8 h.

Volumes of the samples injected into the GC probes were from (0.1 to 0.3) μL. No differences in retention times t_r were found by injecting individual pure components or their mixtures. Experiments were carried out over the temperature range (313 to 364) K. At a given temperature, each experiment was repeated at least two times to check the reproducibility. The differences in the retention times of the two measurements were generally reproducible within (0.01 to 0.03) min. Absolute values of retention times varied between 0.5 and 30 min depending on the individual solute. At each temperature, values of the dead time t_G identical to the retention time of the nonretainable component were measured. While our GC was equipped with a flame ionization detector, methane[29] was used as nonretainable component under the assumption that the effect of solubility of methane in [EMIM][FAP] is negligible. The GLC technique was tested for the system hexane in hexadecane at 298 K, and the results were within 1.5 % of the literature values.[30]

The outlet pressure P_o was kept at atmospheric pressure. The pressure drop ($P_i - P_o$) varied between (50 and 150) kPa depending on the flow rate of the carrier gas. The pressure drop was measured by a pressure transducer implemented in the GC with an uncertainty of ± 0.1 kPa. The atmospheric pressure was measured using a membrane manometer with an uncertainty of ± 0.2 kPa.

To check the stability of the experimental conditions, such as the possible elution of the stationary phase by the carrier gas stream, the measurements of retention times were repeated systematically every day for hexane and benzene. No changes of the retention times were observed during months of continuous operation.

The uncertainty of γ_i^∞ values may be obtained from the law of propagation of errors. The following measured parameters exhibit uncertainties which must be taken into account in the error calculations with their corresponding standard deviations: the adjusted retention time t_r', ± 0.6 s; the flow rate of the carrier gas, ± 0.0017 $cm^3 \cdot s^{-1}$; mass of the stationary phase, ± 0.05 %; the inlet pressure, ± 0.1 kPa, outlet pressure, ± 0.2 kPa; the temperature of the oven, ± 0.1 K. The main source of uncertainty in the calculation of the net retention volume is the determination of the mass of the stationary phase. The estimated uncertainty in determining the net retention volume V_N is about ± 2 %. Taking into account that thermodynamic parameters are also subject to an error, the resulting uncertainty in the γ_i^∞ values is about ± 4 %.

The equation developed by Everett[31] and Cruickshank et al.[32] was used in this work to calculate the γ_i^∞ of solutes in the ionic liquid

$$\ln \gamma_{13}^\infty = \ln\left(\frac{n_3RT}{V_NP_1^*}\right) - \frac{P_1^*(B_{11} - V_1^*)}{RT} + \frac{P_oJ(2B_{12} - V_1^\infty)}{RT} \tag{1}$$

V_N is the standardized retention volume of the solute; P_o is the outlet pressure; n_3 is the number of moles of solvent on the column packing; T is the column temperature; P_1^* is the saturated vapor pressure of the solute at temperature T; B_{11} is the second virial coefficient of the pure solute; V_1^* is the molar volume of the solute; V_1^∞ is the partial molar volume of the solute at infinite dilution in the solvent (assumed as the same as V_1^*); and B_{12} (where 2 refers to the carrier gas, nitrogen) is the cross second virial coefficient of the solute and the carrier gas. The values of B_{11} and B_{12} were calculated using the McGlashan and Potter equation[33]

$$\frac{B}{V_c} = 0.430 - 0.886\left(\frac{T_c}{T}\right) - 0.694\left(\frac{T_c}{T}\right)^2 - 0.0375(n - 1)\left(\frac{T_c}{T}\right)^{4.5} \tag{2}$$

where n refers to the number of carbon atoms of the solute. Using the Hudson and McCoubrey combining rules,[34,35] $V_{c,12}$ and $T_{c,12}$ were calculated from the critical properties of the pure component.

Table 2. Vapor Pressure, P_1^*, Molar Volume, V_1^*, and Virial Coefficients B_{11} and B_{12} Used in the Calculation of γ_{13}^{∞} at Temperatures (313 to 364) K

T / K	V_1^* / $m^3 \cdot mol^{-1}$	P_1^* / kPa	B_{11} / $m^3 \cdot mol^{-1}$	B_{12} / $m^3 \cdot mol^{-1}$
		Pentane		
313.1	$1.2020 \cdot 10^{-4}$	115.53	$-1.031 \cdot 10^{-3}$	$-8.488 \cdot 10^{-5}$
322.9	$1.2232 \cdot 10^{-4}$	158.04	$-9.537 \cdot 10^{-4}$	$-7.821 \cdot 10^{-5}$
333.6	$1.2480 \cdot 10^{-4}$	217.27	$-8.794 \cdot 10^{-4}$	$-7.150 \cdot 10^{-5}$
343.5	$1.2727 \cdot 10^{-4}$	285.94	$-8.185 \cdot 10^{-4}$	$-6.578 \cdot 10^{-5}$
353.5	$1.2997 \cdot 10^{-4}$	370.91	$-7.635 \cdot 10^{-4}$	$-6.041 \cdot 10^{-5}$
		Hexane		
313.1	$1.3558 \cdot 10^{-4}$	37.37	$-1.657 \cdot 10^{-3}$	$-9.463 \cdot 10^{-5}$
322.9	$1.3760 \cdot 10^{-4}$	53.77	$-1.521 \cdot 10^{-3}$	$-8.712 \cdot 10^{-5}$
333.6	$1.3992 \cdot 10^{-4}$	77.67	$-1.392 \cdot 10^{-3}$	$-7.957 \cdot 10^{-5}$
343.5	$1.4221 \cdot 10^{-4}$	106.53	$-1.288 \cdot 10^{-3}$	$-7.313 \cdot 10^{-5}$
353.5	$1.4466 \cdot 10^{-4}$	143.49	$-1.194 \cdot 10^{-3}$	$-6.710 \cdot 10^{-5}$
		Heptane		
313.1	$1.4993 \cdot 10^{-4}$	12.25	$-2.500 \cdot 10^{-3}$	$-1.023 \cdot 10^{-4}$
322.9	$1.5191 \cdot 10^{-4}$	18.62	$-2.280 \cdot 10^{-3}$	$-9.408 \cdot 10^{-5}$
333.6	$1.5418 \cdot 10^{-4}$	28.44	$-2.072 \cdot 10^{-3}$	$-8.582 \cdot 10^{-5}$
343.5	$1.5639 \cdot 10^{-4}$	40.92	$-1.904 \cdot 10^{-3}$	$-7.878 \cdot 10^{-5}$
353.5	$1.5873 \cdot 10^{-4}$	57.66	$-1.755 \cdot 10^{-3}$	$-7.218 \cdot 10^{-5}$
		Octane		
313.1	$1.6440 \cdot 10^{-4}$	4.13	$-3.603 \cdot 10^{-3}$	$-1.087 \cdot 10^{-4}$
322.9	$1.6639 \cdot 10^{-4}$	6.62	$-3.266 \cdot 10^{-3}$	$-9.984 \cdot 10^{-5}$
333.6	$1.6866 \cdot 10^{-4}$	10.66	$-2.950 \cdot 10^{-3}$	$-9.094 \cdot 10^{-5}$
343.5	$1.7085 \cdot 10^{-4}$	16.05	$-2.696 \cdot 10^{-3}$	$-8.336 \cdot 10^{-5}$
353.5	$1.7317 \cdot 10^{-4}$	23.59	$-2.472 \cdot 10^{-3}$	$-7.626 \cdot 10^{-5}$
		Nonane		
313.1	$1.8257 \cdot 10^{-4}$	1.41	$-5.069 \cdot 10^{-3}$	$-1.138 \cdot 10^{-4}$
322.9	$1.8462 \cdot 10^{-4}$	2.39	$-4.571 \cdot 10^{-3}$	$-1.044 \cdot 10^{-4}$
333.6	$1.8693 \cdot 10^{-4}$	4.07	$-4.105 \cdot 10^{-3}$	$-9.489 \cdot 10^{-5}$
343.5	$1.8916 \cdot 10^{-4}$	6.42	$-3.733 \cdot 10^{-3}$	$-8.682 \cdot 10^{-5}$
353.5	$1.9151 \cdot 10^{-4}$	9.86	$-3.407 \cdot 10^{-3}$	$-7.927 \cdot 10^{-5}$
		Cyclohexane		
313.1	$1.1070 \cdot 10^{-4}$	24.55	$-1.768 \cdot 10^{-3}$	$-1.038 \cdot 10^{-4}$
322.9	$1.1204 \cdot 10^{-4}$	35.84	$-1.616 \cdot 10^{-3}$	$-9.612 \cdot 10^{-5}$
333.6	$1.1358 \cdot 10^{-4}$	52.60	$-1.472 \cdot 10^{-3}$	$-8.841 \cdot 10^{-5}$
343.5	$1.1507 \cdot 10^{-4}$	73.20	$-1.356 \cdot 10^{-3}$	$-8.184 \cdot 10^{-5}$
353.5	$1.1665 \cdot 10^{-4}$	100.01	$-1.253 \cdot 10^{-3}$	$-7.570 \cdot 10^{-5}$
		Methyl Cyclohexane		
313.1	$1.2991 \cdot 10^{-4}$	12.18	$-2.545 \cdot 10^{-3}$	$-1.094 \cdot 10^{-4}$
322.9	$1.3141 \cdot 10^{-4}$	18.30	$-2.313 \cdot 10^{-3}$	$-1.011 \cdot 10^{-4}$
333.6	$1.3311 \cdot 10^{-4}$	27.63	$-2.096 \cdot 10^{-3}$	$-9.278 \cdot 10^{-5}$
343.5	$1.3475 \cdot 10^{-4}$	39.35	$-1.921 \cdot 10^{-3}$	$-8.568 \cdot 10^{-5}$
353.5	$1.3649 \cdot 10^{-4}$	54.90	$-1.766 \cdot 10^{-3}$	$-7.905 \cdot 10^{-5}$
		1-Hexene		
312.8	$1.2808 \cdot 10^{-4}$	43.66	$-1.541 \cdot 10^{-3}$	$-9.174 \cdot 10^{-5}$
323.6	$1.3021 \cdot 10^{-4}$	65.10	$-1.404 \cdot 10^{-3}$	$-8.374 \cdot 10^{-5}$
333.5	$1.3228 \cdot 10^{-4}$	91.45	$-1.294 \cdot 10^{-3}$	$-7.700 \cdot 10^{-5}$
343.6	$1.3451 \cdot 10^{-4}$	126.36	$-1.195 \cdot 10^{-3}$	$-7.065 \cdot 10^{-5}$
353.6	$1.3687 \cdot 10^{-4}$	170.40	$-1.108 \cdot 10^{-3}$	$-6.483 \cdot 10^{-5}$
		1-Octene		
312.8	$1.6000 \cdot 10^{-4}$	4.91	$-3.368 \cdot 10^{-3}$	$-1.075 \cdot 10^{-4}$
323.6	$1.6212 \cdot 10^{-4}$	8.17	$-3.024 \cdot 10^{-3}$	$-9.798 \cdot 10^{-5}$
333.5	$1.6414 \cdot 10^{-4}$	12.59	$-2.753 \cdot 10^{-3}$	$-8.995 \cdot 10^{-5}$
343.6	$1.6630 \cdot 10^{-4}$	18.95	$-2.512 \cdot 10^{-3}$	$-8.239 \cdot 10^{-5}$
353.6	$1.6854 \cdot 10^{-4}$	27.62	$-2.304 \cdot 10^{-3}$	$-7.547 \cdot 10^{-5}$
		1-Decene		
312.8	$1.8985 \cdot 10^{-4}$	0.61	$-6.522 \cdot 10^{-3}$	$-1.182 \cdot 10^{-4}$
323.6	$1.9205 \cdot 10^{-4}$	1.12	$-5.793 \cdot 10^{-3}$	$-1.074 \cdot 10^{-4}$
333.5	$1.9415 \cdot 10^{-4}$	1.88	$-5.223 \cdot 10^{-3}$	$-9.831 \cdot 10^{-5}$
343.6	$1.9637 \cdot 10^{-4}$	3.08	$-4.721 \cdot 10^{-3}$	$-8.976 \cdot 10^{-5}$
353.6	$1.9865 \cdot 10^{-4}$	4.87	$-4.290 \cdot 10^{-3}$	$-8.192 \cdot 10^{-5}$
		1-Pentyne		
313.6	$1.1068 \cdot 10^{-4}$	102.15	$-9.954 \cdot 10^{-4}$	$-8.581 \cdot 10^{-5}$
322.7	$1.1230 \cdot 10^{-4}$	138.40	$-9.252 \cdot 10^{-4}$	$-7.968 \cdot 10^{-5}$
333.5	$1.1434 \cdot 10^{-4}$	193.71	$-8.515 \cdot 10^{-4}$	$-7.298 \cdot 10^{-5}$
343.4	$1.1635 \cdot 10^{-4}$	258.27	$-7.919 \cdot 10^{-4}$	$-6.732 \cdot 10^{-5}$
353.3	$1.1850 \cdot 10^{-4}$	338.34	$-7.387 \cdot 10^{-4}$	$-6.207 \cdot 10^{-5}$
		1-Hexyne		
313.6	$1.1903 \cdot 10^{-4}$	33.91	$-1.552 \cdot 10^{-3}$	$-9.552 \cdot 10^{-5}$
322.7	$1.2058 \cdot 10^{-4}$	48.02	$-1.433 \cdot 10^{-3}$	$-8.866 \cdot 10^{-5}$
333.5	$1.2253 \cdot 10^{-4}$	70.53	$-1.309 \cdot 10^{-3}$	$-8.115 \cdot 10^{-5}$
343.4	$1.2442 \cdot 10^{-4}$	97.88	$-1.210 \cdot 10^{-3}$	$-7.481 \cdot 10^{-5}$
353.3	$1.2641 \cdot 10^{-4}$	133.01	$-1.122 \cdot 10^{-3}$	$-6.893 \cdot 10^{-5}$

Table 2. Continued

T / K	V_1^* / $m^3 \cdot mol^{-1}$	P_1^* / kPa	B_{11} / $m^3 \cdot mol^{-1}$	B_{12} / $m^3 \cdot mol^{-1}$
		1-Heptyne		
313.6	$1.3980 \cdot 10^{-4}$	11.57	$-2.316 \cdot 10^{-3}$	$-1.041 \cdot 10^{-4}$
322.7	$1.4141 \cdot 10^{-4}$	17.14	$-2.125 \cdot 10^{-3}$	$-9.652 \cdot 10^{-5}$
333.5	$1.4342 \cdot 10^{-4}$	26.46	$-1.928 \cdot 10^{-3}$	$-8.827 \cdot 10^{-5}$
343.4	$1.4535 \cdot 10^{-4}$	38.31	$-1.771 \cdot 10^{-3}$	$-8.131 \cdot 10^{-5}$
353.3	$1.4737 \cdot 10^{-4}$	54.13	$-1.633 \cdot 10^{-3}$	$-7.486 \cdot 10^{-5}$
		1-Octyne		
313.6	$1.5430 \cdot 10^{-4}$	3.99	$-3.320 \cdot 10^{-3}$	$-1.108 \cdot 10^{-4}$
322.7	$1.5596 \cdot 10^{-4}$	6.21	$-3.029 \cdot 10^{-3}$	$-1.026 \cdot 10^{-4}$
333.5	$1.5800 \cdot 10^{-4}$	10.10	$-2.731 \cdot 10^{-3}$	$-9.373 \cdot 10^{-5}$
343.4	$1.5995 \cdot 10^{-4}$	15.29	$-2.495 \cdot 10^{-3}$	$-8.623 \cdot 10^{-5}$
353.3	$1.6199 \cdot 10^{-4}$	22.52	$-2.289 \cdot 10^{-3}$	$-7.928 \cdot 10^{-5}$
		Benzene		
313.1	$9.0133 \cdot 10^{-5}$	24.25	$-1.557 \cdot 10^{-3}$	$-1.013 \cdot 10^{-4}$
322.9	$9.1212 \cdot 10^{-5}$	35.75	$-1.422 \cdot 10^{-3}$	$-9.395 \cdot 10^{-5}$
333.1	$9.2383 \cdot 10^{-5}$	52.02	$-1.300 \cdot 10^{-3}$	$-8.693 \cdot 10^{-5}$
343.5	$9.3633 \cdot 10^{-5}$	74.21	$-1.191 \cdot 10^{-3}$	$-8.034 \cdot 10^{-5}$
353.3	$9.4866 \cdot 10^{-5}$	101.39	$-1.102 \cdot 10^{-3}$	$-7.461 \cdot 10^{-5}$
363.9	$9.6266 \cdot 10^{-5}$	138.98	$-1.016 \cdot 10^{-3}$	$-6.887 \cdot 10^{-5}$
		Toluene		
313.1	$1.0797 \cdot 10^{-4}$	7.87	$-2.424 \cdot 10^{-3}$	$-1.096 \cdot 10^{-4}$
322.9	$1.0916 \cdot 10^{-4}$	12.14	$-2.200 \cdot 10^{-3}$	$-1.015 \cdot 10^{-4}$
333.1	$1.1044 \cdot 10^{-4}$	18.46	$-1.998 \cdot 10^{-3}$	$-9.376 \cdot 10^{-5}$
343.5	$1.1180 \cdot 10^{-4}$	27.48	$-1.820 \cdot 10^{-3}$	$-8.651 \cdot 10^{-5}$
353.3	$1.1314 \cdot 10^{-4}$	38.98	$-1.673 \cdot 10^{-3}$	$-8.020 \cdot 10^{-5}$
363.9	$1.1465 \cdot 10^{-4}$	55.50	$-1.534 \cdot 10^{-3}$	$-7.388 \cdot 10^{-5}$
		Ethylbenzene		
313.1	$1.2559 \cdot 10^{-4}$	2.87	$-3.581 \cdot 10^{-3}$	$-1.172 \cdot 10^{-4}$
322.9	$1.2687 \cdot 10^{-4}$	4.64	$-3.232 \cdot 10^{-3}$	$-1.084 \cdot 10^{-4}$
333.1	$1.2825 \cdot 10^{-4}$	7.39	$-2.919 \cdot 10^{-3}$	$-1.000 \cdot 10^{-4}$
343.5	$1.2972 \cdot 10^{-4}$	11.47	$-2.644 \cdot 10^{-3}$	$-9.212 \cdot 10^{-5}$
353.3	$1.3115 \cdot 10^{-4}$	16.88	$-2.418 \cdot 10^{-3}$	$-8.526 \cdot 10^{-5}$
363.9	$1.3276 \cdot 10^{-4}$	24.94	$-2.205 \cdot 10^{-3}$	$-7.839 \cdot 10^{-5}$
		o-Xylene		
313.1	$1.2407 \cdot 10^{-4}$	2.04	$-3.805 \cdot 10^{-3}$	$-1.192 \cdot 10^{-4}$
322.9	$1.2529 \cdot 10^{-4}$	3.36	$-3.429 \cdot 10^{-3}$	$-1.103 \cdot 10^{-4}$
333.1	$1.2660 \cdot 10^{-4}$	5.43	$-3.093 \cdot 10^{-3}$	$-1.018 \cdot 10^{-4}$
343.5	$1.2798 \cdot 10^{-4}$	8.56	$-2.799 \cdot 10^{-3}$	$-9.384 \cdot 10^{-5}$
353.3	$1.2933 \cdot 10^{-4}$	12.76	$-2.557 \cdot 10^{-3}$	$-8.692 \cdot 10^{-5}$
363.9	$1.3085 \cdot 10^{-4}$	19.10	$-2.330 \cdot 10^{-3}$	$-7.999 \cdot 10^{-5}$
		m-Xylene		
313.1	$1.2448 \cdot 10^{-4}$	2.53	$-3.600 \cdot 10^{-3}$	$-1.161 \cdot 10^{-4}$
322.9	$1.2576 \cdot 10^{-4}$	4.11	$-3.248 \cdot 10^{-3}$	$-1.074 \cdot 10^{-4}$
333.1	$1.2715 \cdot 10^{-4}$	6.58	$-2.934 \cdot 10^{-3}$	$-9.901 \cdot 10^{-5}$
343.5	$1.2862 \cdot 10^{-4}$	10.28	$-2.657 \cdot 10^{-3}$	$-9.117 \cdot 10^{-5}$
353.3	$1.3005 \cdot 10^{-4}$	15.20	$-2.430 \cdot 10^{-3}$	$-8.434 \cdot 10^{-5}$
363.9	$1.3167 \cdot 10^{-4}$	22.56	$-2.217 \cdot 10^{-3}$	$-7.751 \cdot 10^{-5}$
		p-Xylene		
313.1	$1.2542 \cdot 10^{-4}$	2.64	$-3.601 \cdot 10^{-3}$	$-1.153 \cdot 10^{-4}$
322.9	$1.2672 \cdot 10^{-4}$	4.28	$-3.250 \cdot 10^{-3}$	$-1.065 \cdot 10^{-4}$
333.1	$1.2812 \cdot 10^{-4}$	6.83	$-2.935 \cdot 10^{-3}$	$-9.821 \cdot 10^{-5}$
343.5	$1.2960 \cdot 10^{-4}$	10.64	$-2.659 \cdot 10^{-3}$	$-9.039 \cdot 10^{-5}$
353.3	$1.3105 \cdot 10^{-4}$	15.69	$-2.432 \cdot 10^{-3}$	$-8.360 \cdot 10^{-5}$
363.9	$1.3268 \cdot 10^{-4}$	23.24	$-2.218 \cdot 10^{-3}$	$-7.679 \cdot 10^{-5}$
		Methanol		
313.6	$3.7111 \cdot 10^{-5}$	36.11	$-3.390 \cdot 10^{-4}$	$-7.203 \cdot 10^{-5}$
322.7	$3.7682 \cdot 10^{-5}$	54.45	$-3.220 \cdot 10^{-4}$	$-6.754 \cdot 10^{-5}$
333.5	$3.8397 \cdot 10^{-5}$	85.74	$-3.034 \cdot 10^{-4}$	$-6.260 \cdot 10^{-5}$
343.4	$3.9093 \cdot 10^{-5}$	126.34	$-2.878 \cdot 10^{-4}$	$-5.842 \cdot 10^{-5}$
353.3	$3.9832 \cdot 10^{-5}$	181.63	$-2.733 \cdot 10^{-4}$	$-5.454 \cdot 10^{-5}$
		Ethanol		
313.6	$5.6548 \cdot 10^{-5}$	18.42	$-5.430 \cdot 10^{-4}$	$-8.223 \cdot 10^{-5}$
322.7	$5.7365 \cdot 10^{-5}$	28.96	$-5.117 \cdot 10^{-4}$	$-7.695 \cdot 10^{-5}$
333.5	$5.8387 \cdot 10^{-5}$	47.76	$-4.781 \cdot 10^{-4}$	$-7.116 \cdot 10^{-5}$
343.4	$5.9381 \cdot 10^{-5}$	73.13	$-4.503 \cdot 10^{-4}$	$-6.626 \cdot 10^{-5}$
353.3	$6.0435 \cdot 10^{-5}$	108.89	$-4.250 \cdot 10^{-4}$	$-6.171 \cdot 10^{-5}$
		n-Propanol		
313.6	$7.5487 \cdot 10^{-5}$	7.20	$-8.678 \cdot 10^{-4}$	$-9.307 \cdot 10^{-5}$
322.7	$7.6445 \cdot 10^{-5}$	11.90	$-8.114 \cdot 10^{-4}$	$-8.699 \cdot 10^{-5}$
333.5	$7.7637 \cdot 10^{-5}$	20.69	$-7.518 \cdot 10^{-4}$	$-8.033 \cdot 10^{-5}$
343.4	$7.8787 \cdot 10^{-5}$	33.08	$-7.032 \cdot 10^{-4}$	$-7.470 \cdot 10^{-5}$
353.3	$7.9998 \cdot 10^{-5}$	51.18	$-6.594 \cdot 10^{-4}$	$-6.947 \cdot 10^{-5}$

Table 3. Experimental Activity Coefficients at Infinite Dilution, γ_i^∞, for Various Solutes in the Ionic Liquid 1-Ethyl-3-methylimidazolium Tris(pentafluoroethyl)trifluorophosphate at Temperatures (313 to 364) K[a]

solute (i)	313 K	323 K	333 K	343 K	353 K	364 K
pentane	4.44(313.1)	3.59(322.9)	2.87(333.6)	2.36(343.5)	2.01(353.5)	
hexane	10.14(313.1)	8.15(322.9)	6.47(333.6)	5.24(343.5)	4.38(353.5)	
heptane	19.72(313.1)	16.27(322.9)	13.00(333.6)	10.61(343.5)	8.75(353.5)	
octane	33.30(313.1)	28.33(322.9)	23.35(333.6)	19.47(343.5)	16.14(353.5)	
nonane	49.35(313.1)	42.85(322.9)	36.04(333.6)	31.80(343.5)	27.02(353.5)	
cyclohexane	9.47(313.1)	7.98(322.9)	6.58(333.6)	5.52(343.5)	4.71(353.5)	
methyl cyclohexane	13.71(313.1)	11.75(322.9)	9.91(333.6)	8.40(343.5)	7.21(353.5)	
1-hexene	6.66(312.8)	5.49(323.6)	4.64(333.5)	3.93(343.6)	3.34(353.6)	
1-octene	18.84(312.8)	16.39(323.6)	14.76(333.5)	12.89(343.6)	11.11(353.6)	
1-decene	37.62(312.8)	34.74(323.6)	32.40(333.5)	29.46(343.6)	26.71(353.6)	
1-pentyne	2.46(313.6)	2.26(322.7)	1.99(333.5)	1.82(343.4)	1.67(353.3)	
1-hexyne	4.18(313.6)	3.87(322.7)	3.52(333.5)	3.26(343.4)	2.94(353.3)	
1-heptyne	6.46(313.6)	6.11(322.7)	5.67(333.5)	5.29(343.4)	4.82(353.3)	
1-octyne	9.53(313.6)	9.12(322.7)	8.65(333.5)	8.08(343.4)	7.52(353.3)	
benzene[b]	1.06(313.1)	1.09(322.9)	1.15(333.1)	1.11(343.5)	1.10(353.3)	1.09(363.9)
toluene[b]	1.54(313.1)	1.59(322.9)	1.69(333.1)	1.66(343.5)	1.66(353.3)	1.66(363.9)
ethylbenzene[b]	2.40(313.1)	2.48(322.9)	2.63(333.1)	2.55(343.5)	2.54(353.3)	2.51(363.9)
o-xylene[b]	2.14(313.1)	2.20(322.9)	2.35(333.1)	2.30(343.5)	2.30(353.3)	2.29(363.9)
m-xylene[b]	2.29(313.1)	2.37(322.9)	2.53(333.1)	2.47(343.5)	2.47(353.3)	2.46(363.9)
p-xylene[b]	2.37(313.1)	2.44(322.9)	2.60(333.1)	2.55(343.5)	2.54(353.3)	2.53(363.9)
methanol	2.65(313.6)	2.29(322.7)	2.02(333.5)	1.73(343.4)	1.51(353.3)	
ethanol	3.29(313.6)	2.86(322.7)	2.44(333.5)	2.17(343.4)	1.88(353.3)	
n-propanol	4.46(313.6)	3.87(322.7)	3.35(333.5)	2.92(343.4)	2.59(353.3)	

[a] Measured experimental temperatures are given in parentheses. [b] Values are measured in the temperature interval (313 to 364) K.

Table 4. Coefficients *a* and *b* of Equation 5, γ_i^∞ at 298.15 K Calculated Using Equation 5, and Values of $H_i^{E,\infty}$ Derived from Equation 6

solute (i)	a	b/K	R^2	γ_i^∞(298.15 K)	$\frac{H_i^{E,\infty}}{\text{kJ}\cdot\text{mol}^{-1}}$
pentane	–5.507	2190.0	0.999	6.29	18.21
hexane	–5.076	2315.0	0.999	14.71	19.25
heptane	–4.155	2238.0	0.998	28.54	18.61
octane	–2.824	1987.0	0.996	46.55	16.52
nonane	–1.325	1638.0	0.997	64.64	13.62
cyclohexane	–3.902	1928.0	0.999	12.99	16.03
methyl cyclohexane	–3.012	1766.0	0.998	18.38	14.68
1-hexene	–4.060	1864.0	0.999	8.95	15.50
1-octene	–1.551	1407.0	0.992	23.76	11.70
1-decene	0.695	921.3	0.987	44.04	7.66
1-pentyne	–2.603	1100.0	0.998	2.96	9.15
1-hexyne	–1.637	964.1	0.995	4.94	8.02
1-heptyne	–0.694	806.6	0.986	7.47	6.71
1-octyne	0.173	656.3	0.982	10.74	5.46
benzene	1.405	–423.9	0.960	0.98	–3.52
toluene	2.067	–514.8	0.959	1.41	–4.28
ethylbenzene	2.376	–471.1	0.968	2.22	–3.92
o-xylene	2.345	–498.7	0.956	1.96	–4.15
m-xylene	2.460	–512.5	0.955	2.10	–4.26
p-xylene	2.413	–487.2	0.958	2.18	–4.05
methanol	–3.967	1550.0	0.997	3.43	12.89
ethanol	–3.727	1542.0	0.998	4.24	12.82
n-propanol	–3.328	1512.0	0.999	5.72	12.57

The standardized retention volume V_N was calculated with the following usual relationship

$$V_N = J \cdot U_0 \cdot (t_r - t_G) \cdot \frac{T_{col}}{T_f}\left(1 - \frac{P_{ow}}{P_o}\right) \tag{3}$$

where t_r is the retention time; t_G is the dead time; U_0 is the flow rate, measured by digital bubble/liquid flowmeter; T_{col} is the column temperature; T_f is flowmeter temperature; P_{ow} is saturation vapor pressure of water at T_f; and P_o is the pressure at the column outlet.

The factor J appearing in eqs 1 and 3 corrects for the influence of the pressure drop along the column given by[36]

$$J = \frac{3}{2} \cdot \frac{(P_i/P_o)^2 - 1}{(P_i/P_o)^2 - 1} \tag{4}$$

where P_i and P_o are the inlet and the outlet pressure of the GC column, respectively.

The vapor pressure values were calculated using the Antoine equation, and constants were taken from the literature.[37] Critical data and ionization energies used in the calculation of $V_{c,12}$ were obtained from the literature.[37−39] The critical data used to calculate B_{11} and B_{12}, and ionization energies used in the calculation of $T_{c,12}$, are given in Table 1, and the values of P_1^*, V_1^*, B_{11}, and B_{12} used in the calculation of γ_{13}^∞ are given in Table 2.

Results and Discussion

The values of γ_i^∞ of different solutes (alkanes, cycloalkanes, 1-alkenes, 1-alkynes, benzene, alkylbenzenes, and alcohols) in [EMIM][FAP] obtained at several temperatures were listed in Table 3. They have been approximated by the linear regression

$$\ln \gamma_i^\infty = a + \frac{b}{T} \tag{5}$$

T is the column temperature. The coefficients a and b, the correlation coefficients R^2, and the values of γ_i^∞(298.15 K)

Table 5. Selectivities, S_{ij}^∞, at Infinite Dilution of Various Solvents for the Hexane (*i*)/Benzene (*j*) and Cyclohexane (*i*)/Benzene (*j*) Separation at $T = 298.15$ K

ionic liquids	hexane (*i*)/benzene (*j*)	cyclohexane(*i*)/ benzene (*j*)
[EMIM][FAP](this work)	15.0	13.2
$[3C_6C_{14}P][FAP]$[a]	3.3	2.45
$[EMIM][N(CF_3SO_2)_2]$[b]	23.1	13.2
$[EMIM][CF_3CO_2]$[c]	30.7	14.4
$[EMIM][C_2H_5SO_4]$[d]	40.8[g]	21.7[g]
$[EMIM][BF_4]$[e]	49.5	38.9
[EMIM][SCN][f]	95.4	33.2

[a] Ref 41. [b] Ref 14. [c] Ref 40. [d] Ref 13. [e] Ref 4. [f] Ref 21. [g] Interpolated value.

calculated with these coefficients are given in Table 4. The quality of the linear regression was good because the correlation coefficients lie between 0.96 and 0.99.

The activity coefficients of the linear alkanes, 1-alkenes, 1-alkynes, alkylbenzenes, and alkanols increase with increasing chain length. This is also a typical behavior for other measured ionic liquids based on the methylimidazolium cation. The γ_i^∞ values obtained for alkanols, benzene, alkylbenzenes, and the 1-alkynes are lower than the values for the alkanes, alkenes, and cycloalkanes. The former group is reasonably associated with the ionic liquid because they are polar solutes or have delocalized electrons. The benzene and alkylbenzenes molecule, being an aromatic compound, has delocalized π electrons that can associate with the ionic liquid by $(n - \pi)$ iteration, which is stronger than the van der Waals interactions. For alkanes, cycloalkanes, 1-alkenes, 1-alkynes, and alkanols, values of γ_i^∞ decrease with increasing temperature. For the rest of the investigated solutes, benzene and alkylbenzene values of γ_i^∞ increase with increasing temperature (313 K to 333 K) and then change little with further increasing temperature (343 K to 364 K).

Table 4 also lists the partial molar excess enthalpies at infinite dilution, $H_i^{E,\infty}$, that were calculated from the Gibbs−Helmholtz eq 6

$$\left(\frac{\partial \ln \gamma_i^\infty}{\partial(1/T)}\right) = \frac{H_i^{E,\infty}}{R} \tag{6}$$

where R is the gas constant. $H_i^{E,\infty}$ was positive and decreases with increasing chain length of the linear alkanes, 1-alkenes, 1-alkynes, and alkanols. However, the $H_i^{E,\infty}$ value for pentane is smaller than that expected for the alkane series due to the greater error in the γ_i^∞ value, which is due to the smallest retention time for pentane. For benzene and alkylbenzenes, $H_i^{E,\infty}$ becomes negative.

The selectivity at infinite dilution for the ionic liquid, which indicated suitability of a solvent for separating mixtures of components i and j by extraction, was given by[30]

$$S_{ij}^\infty = \frac{\gamma_{i3}^\infty}{\gamma_{j3}^\infty} \tag{7}$$

The values of selectivity for the separation of hexane(*i*)/benzene(*j*) and cyclohexane(*i*)/benzene(*j*) mixtures at $T = 298.15$ K using different ILs with cation $[EMIM]^+$ and five anions are taken from the literature.[4,13,14,21,40] The results of the present work are listed in Table 5, which indicates that for a given cation, $[EMIM]^+$, γ_i^∞ values for the anions $[SCN]^-$, $[BF_4]^-$, $[C_2H_5SO_4]^-$, and $[CF_3CO_2]^-$ are higher than those for the anions $[N(CF_3SO_2)_2]^-$ and $[FAP]^-$, and in the case of a given anion $[FAP]^-$, γ_i^∞ values for the cation $[EMIM]^+$ are higher than those for trihexyl(tetradecyl)phosphonium $[3C_6C_{14}P]^+$. It means that the activity coefficients and intermolecular interactions of different solutes in ILs are very much dependent on the chemical structure of the cation and anion. The results indicate that [EMIM][FAP] is not an ideal extraction solvent for separation of hexane(*i*)/benzene(*j*) and cyclohexane(*i*)/benzene(*j*) binary systems.

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