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Activity Coefficients at Infinite Dilution of Alkanes, Alkenes, and Alkyl Benzenes in 1-(2-Hydroxyethyl)-3-methylimidazolium Tetrafluoroborate Using Gas−Liquid Chromatography

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Activity coefficients at infinite dilution of 14 organic solutes, alkanes, alkenes, and alkyl benzenes, in 1-(2-hydroxyethyl)-3-methylimidazolium tetrafluoroborate, have been determined using gas−liquid chromatography over a temperature range of (303.15 to 363.15) K with the ionic liquid as the stationary phase. The partial molar excess enthalpies at infinite dilution were also determined for the solutes from the temperature dependence of the experimental activity values.

Introduction

This work is a continuation of our studies on the determination of activity coefficients at infinite dilution by the gas−liquid chromatographic (GLC) method for ionic liquids.[1−4]

Experimental Section

The ionic liquid 1-(2-hydroxyethyl)-3-methylimidazolium tetrafluoroborate ([Hydemim][BF$_4$]) (Figure 1) was purchased from Lanzhou Institute of Chemical Physics of the Chinese Academy of Science. Its certified mass fraction purity was above 0.95, and impurities: [Cl$^-$] < 500 ppm. Water mass fractions analyzed by Karl Fischer analysis were less than 400 ppm. The chemical shifts for the ^{1}H NMR spectrum (parts per million, D$_2$O$_3$) appeared as follows: δ8.774 [s, 1H, CHN], 7.573 [d, 1H, H(2)], 7.519 [d, 1H, H(2)], 3.978 [s, 3H, NCH$_3$], 4.373−4.398 [t, 2H, CH$_2$], 3.990−4.025 [dd, 6H, CH$_2$O], and 4.799 [s, 1H, OH].

The hydrocarbons provided by Beijing Chemical Reagents Company were analytical reagents. The solutes were used without further purification.

The GLC apparatus, column preparation, packing method, and experimental process in this work are the same as described by Zhou.[1,2] In this work, the GC columns with length of 130 cm and inner diameter of 0.40 cm have been used. Dry helium was used as the carrier gas, and ethanol was used as solvent to coat the ionic liquid onto the solid support. The mass of the stationary phase (ionic liquid) was 4.2100 g with an uncertainty of ± 0.008 %. According to the literature,[4] the mass fraction of the ionic liquid coating was chosen as 60 % of the stationary phase. The column was filled uniformly with the help of an ultrasonic vibrator.

Cruickshank et al.[5] and Everett[6] developed the following equation for obtaining the $\gamma^\infty_{i,3}$ for a volatile solute (i) in an involatile solvent (3) from GC results

$$\ln \gamma^\infty_{i,3} = \ln\left(\frac{n_3RT}{V_N P_i^0}\right) - \frac{B_{11} - V_i^0}{RT}P_i^0 + \frac{2B_{12} - V_i^\infty}{RT}JP_0 \tag{1}$$

where $\gamma^\infty_{i,3}$ is the activity coefficient of solute i at infinite dilution in the stationary phase 3; P_i^0(kPa) is the vapor pressure of the pure liquid solute i; n_3 is the number of moles of the stationary phase component on the column; and V_N is the standardized retention volume obtained by

$$V_N = JU_0(t_r - t_G)\frac{T_{col}}{T_f}\left[1 - \frac{P_w^0}{P_o}\right] \tag{2}$$

where t_r (min) is the etention time; t_G (min) is the dead time; U_0 (mL·min^{-1}) is the flow rate, measured by a soap bubble

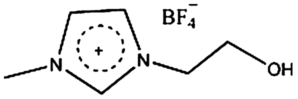

Figure 1. Structure of 1-(2-hydroxyethyl)-3-methylimidazolium tetrafluoroborate.

Table 1. Critical Constants Z_c, T_c, P_c, and V_c and Acentric Factors ω of the Solutes Used in the Calculation of the Virial Coefficients

solutes (i)	Z_c	T_c/K	P_c/bar	V_c/cm^3·mol^{-1}	ω
Alkanes					
heptane	0.261	540	27.4	428	0.350
octane	0.259	569	24.9	492	0.399
nonane	0.252	595	22.9	555	0.445
2,2,4-trimethylpentane	0.273	554	40.7	308	0.211
cyclohexane	0.268	572	34.7	368	0.235
methylcyclohexane	0.266	544	25.7	470	0.304
Alkenes					
cyclohexene	0.27	560	42.9	292	0.210
styrene	0.274	647	39.4	374	0.257
Alkyl Benzenes					
benzene	0.268	562	49.0	256	0.210
toluene	0.264	592	41.1	316	0.264
ethylbenzene	0.263	617	36.1	374	0.304
o-xylene	0.263	630	37.3	370	0.312
m-xylene	0.259	617	35.4	375	0.327
p-xylene	0.259	616	35.1	378	0.322

Table 2. Uncertainties in the Measured and Derived Quantities

parameters	uncertainty
$t_r - t_G$	± 2.6 %
U_0	± 0.4 %
P_i	± 0.7 %
P_o	± 0.02 %
J	± 1 %
P_i^0	0.25 %
n_3	± 0.6 %
$\gamma^\infty_{i,3}$	± 5.2 %

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Table 3. Experimental Activity Coefficients at Infinite Dilution for Various Solutes in the Ionic Liquid 1-(2-Hydroxyethyl)-3-methylimidazolium Tetrafluoroborate as the Stationary Phase at Temperatures of (303.15 to 363.15) K

solutes (i)	T/K = 303.15	T/K = 313.15	T/K = 323.15	T/K = 333.15	T/K = 343.15	T/K = 353.15	T/K = 363.15
			Alkanes				
heptane	620.379	849.867	1196.302	1609.196	2191.584	2977.502	4222.320
octane	497.517	532.333	574.000	614.581	658.840	708.911	760.092
nonane	546.427	564.500	582.139	598.951	615.725	632.816	651.215
cyclohexane	339.159	417.912	488.085	592.790	689.144	803.390	933.957
methylcyclohexane	328.133	372.583	421.386	485.942	545.968	610.977	676.837
2,2,4-trimethylpentane	412.431	523.282	730.895	962.352	1297.741	1702.478	2309.485
			Alkenes				
cyclohexene	122.523	118.021	113.722	109.844	105.722	103.420	100.404
styrene	15.302	15.092	14.810	14.635	14.434	14.224	14.047
			Alkyl				
benzene	9.132	9.114	9.097	9.076	9.062	9.049	9.037
toluene	18.265	17.992	17.728	17.477	17.274	17.154	16.918
ethylbenzene	42.059	40.631	39.000	37.920	36.690	35.859	35.011
o-xylene	28.950	28.241	27.728	27.025	26.522	25.881	25.402
m-xylene	37.216	36.317	35.508	34.691	34.002	33.202	32.529
p-xylene	35.438	34.669	33.949	33.157	32.473	31.958	31.405

Table 4. Coefficients of Equation 1, *a* and *b*, Correlation Coefficient R^2, Calculated (at 298.15 K) Activity Coefficients at Infinite Dilution ($\gamma^{\infty}_{\mathrm{i298.15K}}$) Using Equation 1, Values of $H_{\mathrm{i}}^{\mathrm{E},\infty}$ Derived from Equation 1, and Standard Deviation σ

solutes i	a	$\frac{b}{\mathrm{K}}$	R^2	$\gamma^{\infty}_{\mathrm{i298.15K}}$ [a]	$\frac{H_{\mathrm{i}}^{\mathrm{E},\infty b}}{\mathrm{kJ \cdot mol^{-1}}}$	σ
			Alkanes			
heptane	17.875	−3482.7	0.9968	489.9	−28.96	0.04208
cctane	8.7667	−778.6	0.9971	536.1	−2.652	0.009
nonane	7.3543	−319.0	0.9992	529.5	−2.577	0.00188
cyclohexane	11.922	−1847.3	0.9994	306.9	−15.36	0.00974
methylcyclohexane	10.224	−1346.2	0.9991	301.5	−11.19	0.00845
2,2,4-trimethylpentane	16.46	−3181.6	0.9960	325.3	−26.45	0.04341
			Alkenes			
cyclohexene	3.604	364.7	0.9868	124.9	3.032	0.00906
styrene	2.150	174.9	0.9538	15.44	1.454	0.00827
			Alkyl Benzenes			
benzene	2.147	19.62	0.9976	9.142	0.1631	$2.0651 \cdot 10^{-4}$
toluene	2.447	138.6	0.9963	18.39	1.152	0.0018
ethylbenzene	2.601	345.5	0.9916	42.96	2.873	0.00683
o-xylene	2.620	225.5	0.9939	29.25	1.875	0.00378
m-xylene	2.858	230.9	0.9842	37.80	1.920	0.00629
p-xylene	2.829	224.4	0.9706	35.92	1.866	0.00840

[a] Range of uncertainties is within ± 4 %. [b] Range of uncertainties is within ± 6 %.

flow meter; T_{col} (K) is the column temperature; T_{f} (K) is the flow meter temperature; P_{w}^{0} (kPa) is the vapor pressure of water at T_{f} (K); and P_{o} (kPa) is the pressure at the column outlet.

The second and third terms in eq 1 are correction terms that arise from the nonideality of the mobile gaseous phase. B_{11} (mL·mol^{-1}) is the second virial coefficient of the solute, and B_{12} (mL·mol^{-1}) is the cross second virial coefficient of the solute (1) with the carrier gas (2). V_{i}^{0} (mL·mol^{-1}) is the liquid molar volume of pure solute, and V_{i}^{∞} (mL·mol^{-1}) is the partial molar volume of the solute in the ionic liquid at infinite dilution.

The data for calculating the correction terms have been obtained in the following way. For all solutes, values of P_i^0 were calculated from the Antoine equation, with Antoine coefficients given by Boublik et al.[7] The calculated results of vapor pressure of these solutes from T = (303.15 to 363.15) K have been reported in our previous paper.[8]

Molar volumes of solutes V_{i}^{0} were estimated using experimental values of their densities; partial molar volumes of solute at infinite dilution V_{i}^{∞} have been assumed to be equal to V_{i}^{0}. Values of B_{11} and B_{12} have been estimated according to the equations suitable for nonpolar liquids by Tsonopolous's method[9] with an uncertainty of < ± 10 mL·mol^{-1}. The critical parameters needed for the calculations are given in Table 1. The cross critical properties P_{cij}, T_{cij}, V_{cij}, and Z_{cij} and mixed acentric factor ω_{ij} were calculated by using equations given in the literature.[9,10]

The factor J appearing in eqs 1 and 2 corrects for the influence of the pressure drop along the column given by[11]

$$J = \frac{3}{2}\frac{(P_{\mathrm{i}}/P_{\mathrm{o}})^2 - 1}{(P_{\mathrm{i}}/P_{\mathrm{o}})^3 - 1} \tag{3}$$

where P_{i} and P_{o} are the inlet and outlet pressures of the GC column, respectively.

The outlet pressure P_{o} was kept equal to the atmospheric pressure. The specified pressure drop ($P_{\mathrm{i}} - P_{\mathrm{o}}$) was varied between (20.3 and 101.3) kPa, providing suitable retention time with sharp peaks. The pressure drop was recorded by GC automatically measured by a self-equipped membrane manometer with an uncertainty of ± 0.2 kPa.

Retention time, dead time, column temperature, flow rate, input and output pressure, and the mass of the stationary phase all have experimental errors. According to the error propagation law, $\gamma_{\mathrm{i},3}^{\infty}$ is estimated to have a relative uncertainty within ± 0.04. The uncertainties in the measured and derived quantities are listed in Table 2.

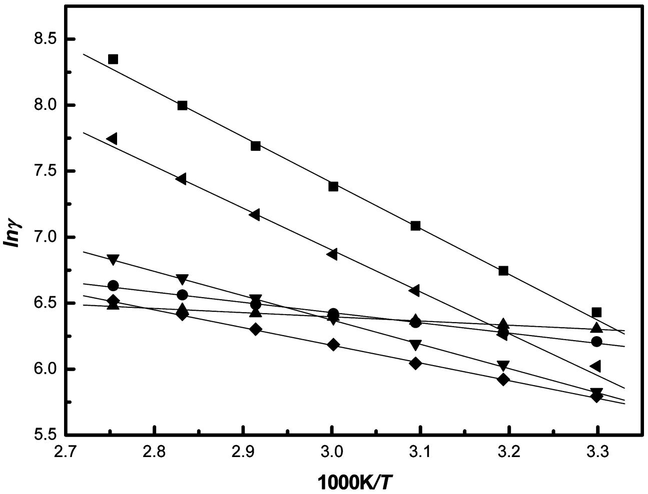

Figure 2. Plot of ln $\gamma_{i,3}^{\infty}$ vs 1/*T* for the solutes: ■, heptane; ●, octane; ▲, nonane; ▼, cyclohexane; ♦, methylcyclohexane; solid triangle pointing left,2,2,4-trimethylpentane; —, linear correlation.

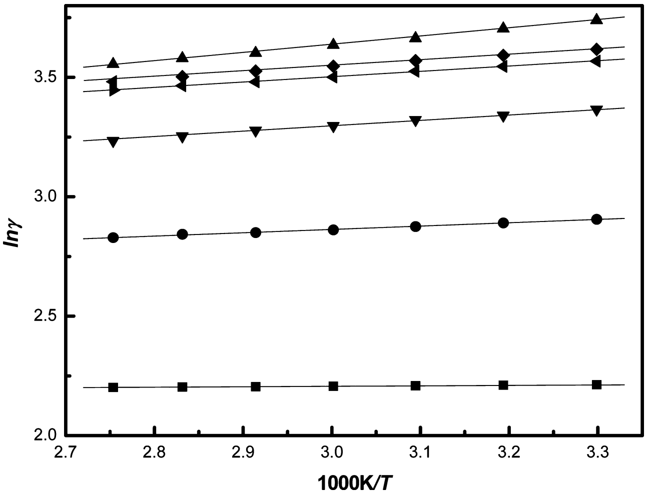

Figure 3. Plot of ln $\gamma_{i,3}^{\infty}$ vs 1/*T* for the solutes: ■, benzene; ●, toluene; ▲, ethyl benzene; ▼, *m*-xylene; ♦, *p*-xylene; solid triangle pointing left, *o*-xylene; —, linear correlation.

Results and Discussion

The values of $\gamma_{i,3}^{\infty}$ of different solutes in [Hydemim][BF$_4$] obtained over a temperature range of (303.15 to 363.15) K were listed in Table 3. The results of $\gamma_{i,3}^{\infty}$ were correlated with temperature by the following equation.

$$\ln \gamma_{i,3}^{\infty} = a + \frac{b}{(T/\mathrm{K})} \qquad (4)$$

According to the Gibbs−Helmholtz equation, the value for the partial molar excess enthalpy at infinite dilution, $H_i^{E,\infty}$, can be obtained from the slope of a straight line derived from eq 4.

The coefficients *a* and *b*, the correlation coefficient R^2, the standard deviation σ of the fitted equation, $\gamma_{i,3}^{\infty}$ at the standard condition ($T = 298.15$ K) calculated using eq 1, and values of $H_i^{E,\infty}$ derived from eq 1 are listed in Table 4. The plots of measured ln $\gamma_{i,3}^{\infty}$ vs 1/*T* values are given in Figures 2 to 4 which showed a fairly good fitting quality of eq 1.

The selectivity S_{ij}^{∞} is defined below[12]

$$S_{ij}^{\infty} = \frac{\gamma_{i3}^{\infty}}{\gamma_{j3}^{\infty}} \qquad (5)$$

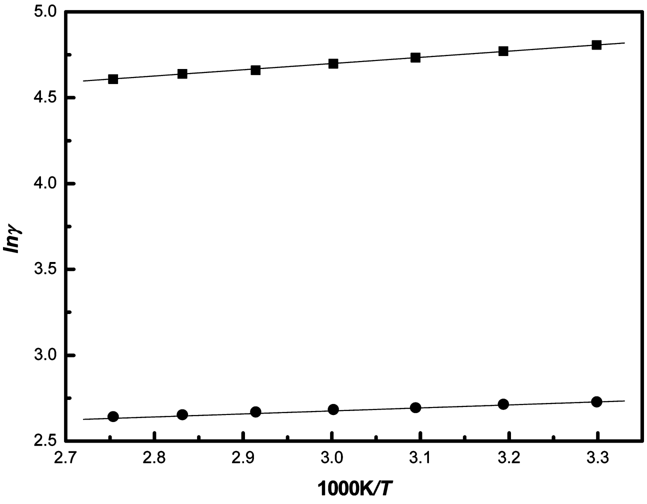

Figure 4. Plot of ln $\gamma_{i,3}^{\infty}$ vs 1/*T* for the solutes: ■, cyclohexene; ●, styrene; —, linear correlation.

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

solutes	S_{ij}^{∞}
[HMIM][CF$_3$SO$_3$][a]	7.82
[PDMIM][BF$_4$][b]	37.6
[BMIM][BF$_4$][c]	19.7
[BMIM][CF$_3$SO$_3$][d]	12.8
[BMIM][MDEGSO$_4$][e]	16.9
[BMIM][PF$_6$][e]	16.7
[HMIM][Tf$_2$N][e]	10.2
[Hydemim][BF$_4$] (this work)	33.6

[a] Ref 3. [b] Ref 16. [c] Ref 1. [d] Ref 17. [e] Ref 15.

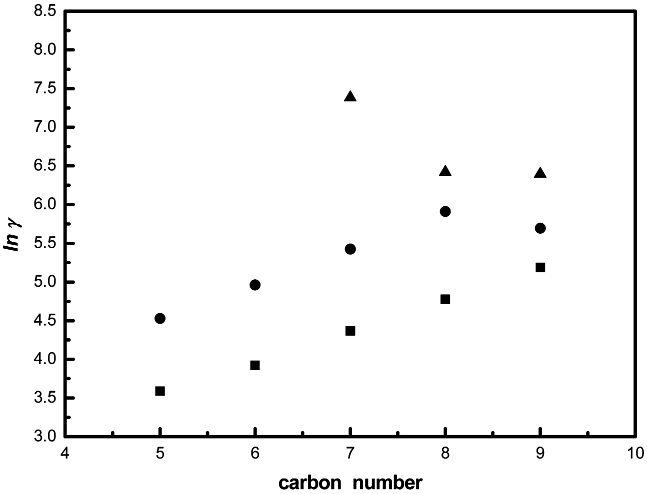

Figure 5. Plot of ln $\gamma_{i,3}^{\infty}$ vs carbon number of normal alkanes in different ILs at 333.15 K: ▲, 1-(2-hydroxyethyl)-3-methylimidazolium tetrafluoroborate (this work); ●, 1-propyl-2,3-dimethylimidazolium tetrafluoroborate;[16] ■, 1-butyl-3-methylimidazolium tetrafluoroborate.[1]

The values of selectivity, S_{ij}^{∞}, for the separation of a cyclohexane (i)/benzene (j) mixture at $T = 298.15$ K using different ILs, and some very polar solvents obtained from the literature[13,14] and from this work are compared in Table 5. The results indicated that [Hydemim][BF$_4$] is an ideal extraction solvent for separation of the cyclohexane and benzene binary system.

A large activity coefficient of a solute in a solvent usually means that they have small mutual solubilities and weak molecular interaction. Figure 5 shows a comparison of the activity coefficients at infinite dilution of normal alkanes in 1-butyl-3-methylimidazolium tetrafluoroborate,[1] 1-propyl-2, 3-dimethylimidazolium tetrafluoroborate,[16] and [Hydemim][BF$_4$]. It can be predicted that with an increase of polarity of an ionic liquid the mutual solubilities of an alkane with the ionic liquid will be decreased. A measurement to show this conclusion is undergoing.

Literature Cited

(1) Zhou, Q.; Wang, L.-S. Activity coefficients at infinite dilution of alkanes, alkenes and alkyl benzenes in 1-butyl-3-methylimidazolium tetrafluoroborate using gas-liquid chromatography. *J. Chem. Eng. Data* **2006**, *51*, 1698–1701.

(2) Zhou, Q.; Wang, L.-S.; Wu, J.-S.; Li, M.-Y. Activity coefficients at infinite dilution of polar solutes in 1-butyl-3-methylimidazolium tetrafluoroborate using gas-liquid chromatography. *J. Chem. Eng. Data* **2007**, *52*, 131–134.

(3) Yang, X.-J.; Wu, J.-S.; Ge, M.-L.; Wang, L.-S.; Li, M.-Y. Activity coefficients at infinite dilution of alkanes, alkenes, and alkyl benzenes in 1-hexyl-3-methylimidazolium trifluoromethanesulfonate using gas-liquid chromatography. *J. Chem. Eng. Data* **2008**, *53*, 1220–1222.

(4) Ge, M.-L.; Wang, L.-S.; Wu, J.-S.; Zhou, Q. Activity coefficients at infinite dilution of organic solutes in 1-ethyl-3-methylimidazolium tetrafluoroborate using gas-liquid chromatography. *J. Chem. Eng. Data* **2008**, *53*, 1970–1974.

(5) Cruickshank, A. J. B.; Windsor, M. L.; Young, C. L. The use of gas-liquid chromatography to determine activity coefficients and second virial coefficients of mixtures. *Proc. R. Soc. London* **1966**, *295*, 259–270.

(6) Everett, D. H. Effect of gas imperfection of G. L. C. measurements: A refined method for determining activity coefficients and second virial coefficients. *Trans. Faraday Soc.* **1965**, *61*, 1637–1645.

(7) Boublik, T.; Fried, V.; Hala, E. The vapor pressure of pure substances. *Physical science data 17*; Elsevier: Amsterdam, The Netherlands, 1984.

(8) Yang, X.-J.; Wu, J.-S.; Ge, M.-L.; Wang, L.-S.; Li, M.-Y. Activity coefficients at infinite dilution of alkanes, alkenes, and alkyl benzenes in 1-hexyl-3-methylimidazolium trifluoromethanesulfonate using gas-liquid chromatography. *J. Chem. Eng. Data* **2008**, *53*, 1220–1222.

(9) Reid, R. C.; Prausnitz, J. M.; Sherwood, T. K. *The Properties of Gases and Liquids*, 3rd ed.; McGraw-Hill Chemical Engineering Series: New York, 1977.

(10) Prausnitz, J. M.; Lichtenthaler, R. N.; Azevedo, E. G. *Molecular Thermodynamics of Fluid Phase Eqilibria*, 2nd ed.; Prentice Hall: New York, 1986.

(11) Grant, D. W. *Gas-Liquid Chromatography*; van Nostrand Reinhold: London, U. K., 1971.

(12) Tiegs, D.; Gmehling, J.; Medina, A.; Soares, M.; Bastos, J.; Alessi, P.; Kikic, I. *DECHEMA Chemistry Data Series IX, Part 1.* DECHEMA: Frankfurt/Main, 1986.

(13) Letcher, T. M.; Marciniak, A.; Marciniak, M.; Domańska, U. Activity coefficients at infinite dilution measurements for organic solutes in the ionic liquid 1-hexyl-3-methyl-imidazolium bis(trifluoromethylsulfonyl)-imide using g.l.c. at $T = (298.15, 313.15, \text{and } 333.15)$ K. *J. Chem. Thermodyn.* **2005**, *37*, 1327–1331.

(14) Deenadayalu, N.; Thango, S. H.; Letcher, T. M.; Ramjugernath, D. Measurement of activity coefficients at infinite dilution using polar and non-polar solutes in the ionic liquid 1-methyl-3-octyl-imidazolium diethyleneglycolmonomethylethersulfate at $T = (288.15, 298.15, \text{and } 313.15)$ K. *J. Chem. Thermodyn.* **2006**, *38*, 542–546.

(15) Domańska, U.; Marciniak, A. Activity coefficients at infinite dilution measurements for organic solutes and water in the ionic liquid 1-butyl-3-methylimidazolium trifluoromethanesulfonate. *J. Phys. Chem. B* **2008**, *112*, 11100−11105.

(16) Wang, M.-H.; Wu, J.-S.; Wang, L.-S.; Li, M.-Y. Activity coefficients at infinite dilution of alkanes, alkenes and alkyl benzenes in1-propyl-2,3-dimethylimidazolium tetrafluoroborate using gas-liquid chromatography. *J. Chem. Eng. Data* **2007**, *52*, 1488–1491.

(17) Ge, M.-L.; Wang, L.-S.; Li, M.-Y.; Wu, J.-S. Activity coefficients at infinite dilution of alkanes, alkenes, and alkyl benzenes in 1-butyl-3-methylimidazolium trifluoromethanesulfonate using gas-liquid chromatography. *J. Chem. Eng. Data* **2007**, *52*, 2257–2260.

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