

# Measurement of Activity Coefficient at Infinite Dilution of Hydrocarbons in Sulfolane Using Gas–Liquid Chromatography

Yang-Xin Yu,\* Qiang Gong, and Li-Li Huang

Department of Chemical Engineering, Tsinghua University, Beijing 100084, People's Republic of China, and State Key Laboratory of Chemical Engineering, Tsinghua University, Beijing 100084, People's Republic of China

Activity coefficients at infinite dilution are reported for ten solutes (heptane, octane, nonane, decane, benzene, toluene, ethylbenzene, *o*-xylene, *m*-xylene, and *p*-xylene) in sulfolane at temperatures  $T = (333.15 \text{ to } 373.15) \text{ K}$ . These data were measured with the help of gas–liquid chromatography (GC) in which sulfolane was used as the stationary phase. The results show good agreement with the activity coefficients at infinite dilution obtained from various methods in the literature. The temperature dependence of the activity coefficients found in the GC experiments could be confirmed using the excess enthalpy data. The present data can be used to determine and compare the selective effect caused by the addition of sulfolane to a given binary mixture in the separation processes such as extractive distillation and solvent extraction. The calculated selectivity suggests that both sulfolane and ionic liquid  $[\text{HMIM}^+][\text{BF}_4^-]$  can act as a good solvent in separating aromatic and aliphatic compounds.

## Introduction

Sulfolane is a common solvent used in liquid–liquid extraction or extractive distillation to separate aromatic compounds from other hydrocarbons.<sup>1</sup> The liquid–liquid equilibrium data needed for the process engineering calculations are conveniently predicted using a group contribution method such as the modified UNIFAC (Dortmund) method.<sup>2</sup> As only five groups are involved and  $\text{CH}_3$  and  $\text{CH}_2$  are classified under the same main group, there are six possible pairs of groups, and only six group interaction parameters,  $\psi_{nm}$ , are required for the prediction of liquid–liquid equilibria. The activity coefficients at infinite dilution are considered to be an excellent data source for evaluation of the group interaction parameters.<sup>3</sup> Besides, the activity coefficients at infinite dilution with sulfolane can be used to determine the parameters in other activity coefficient equations such as NRTL and UNIQUAC at different temperatures to predict vapor–liquid equilibria for the systems containing sulfolane. In the design of the separation process, the activity coefficients at infinite dilution can provide the selective effect caused by the addition of solvent to a given binary mixture. The other properties of the systems involving sulfolane such as viscosity and density have been studied in different temperatures in the literature.<sup>4</sup>

The activity coefficients at infinite dilution for benzene, toluene, and ethylbenzene in sulfolane have been determined by different experimental methods<sup>5–9</sup> at temperatures not higher than 333.15 K, but little work<sup>3,7</sup> has been done for normal alkanes with a carbon number larger than six. In this work, we report the activity coefficients at infinite dilution for six aromatic hydrocarbons and four linear alkanes in sulfolane at several temperatures between (333.15 and 373.15) K. From the temperature dependence of the limiting activity coefficients, partial molar excess enthalpies at infinite dilution of hydrocarbons in sulfolane have been derived and compared with those measured using a calorimeter.

\* Corresponding author. Tel.: +86 10 62782558. Fax: +86 10 62770304. E-mail: yangxyu@mail.tsinghua.edu.cn.

**Table 1. Critical Constants, Pitzer's Acentric Factors, and Empirical Constants in the Modified Racket Equation<sup>16,18</sup>**

substance	$p_c$	$T_c$	$V_c$	$\omega$	$Z_{RA}$
	atm	K	$\text{cm}^3 \cdot \text{mol}^{-1}$		
benzene	48.3	562.1	259	0.212	0.2698
toluene	40.6	591.7	316	0.257	0.2644
ethylbenzene	35.6	617.1	374	0.301	0.2620
<i>o</i> -xylene	36.8	630.2	369	0.314	0.2625
<i>m</i> -xylene	35.0	617.0	376	0.331	0.2592
<i>p</i> -xylene	34.7	616.2	379	0.324	0.2592
heptane	27.0	540.2	432	0.351	0.2604
octane	24.5	568.8	492	0.394	0.2571
nonane	22.8	594.6	548	0.444	0.2543
decane	20.8	617.6	603	0.490	0.2507
hydrogen <sup>a</sup>			51.5	0	0.3060

<sup>a</sup> For quantum gas  $\text{H}_2$ , the modified critical constants are recommended;<sup>17</sup> i.e.,  $Z_c = 0.305$ ,  $T_c/\text{K} = 43.6/(1 + 10.9 \text{ K}/T)$  and  $p_c/\text{atm} = 20.2/(1 + 22.1 \text{ K}/T)$ .

## Experimental Section

**Materials.** All hydrocarbons provided by the Beijing Chemical Reagent Company were of analytical grade, and sulfolane was supplied by Beijing Chemical Engineering Plant (chemical reagent). All compounds were purified and kept using the methods described previously,<sup>10,11</sup> and the purity was tested by gas–liquid chromatography (GLC) along with the measurements of densities and refractive indices of the purified chemicals.<sup>12</sup>

**Apparatus and Procedure.** The experiments were carried out with gas–liquid chromatography (Shimadzu GC-14B) with a thermal conductivity detector (TCD). The diatomaceous earth Chromosorb W-HP (80/100 mesh) was used as solid support for sulfolane in the gas–liquid chromatography (GC) column. As the stationary phase, pure sulfolane was exactly weighed by an electronic balance with an accuracy of  $\pm 0.0001 \text{ g}$ . Coating the solid support material with sulfolane was performed by dispersing a certain portion of Chromosorb in sulfolane–acetone solution followed by evaporation of the solvent. The solid support material with the stationary phase was filled in a stainless steel column with an inner diameter of 3 mm and a length of 2 m, and it was heated under flowing nitrogen for

Table 2. Vapor Pressures, Liquid Molar Volumes, and Virial Coefficients at  $T = (333.15 \text{ to } 373.15) \text{ K}$ 

$T$ K	$p_i^{\text{sat}}$ kPa	$V_i^L$ $\text{cm}^3 \cdot \text{mol}^{-1}$	$B_{ii}$ $\text{cm}^3 \cdot \text{mol}^{-1}$	$B_{i3}$ $\text{cm}^3 \cdot \text{mol}^{-1}$	$T$ K	$p_i^{\text{sat}}$ kPa	$V_i^L$ $\text{cm}^3 \cdot \text{mol}^{-1}$	$B_{ii}$ $\text{cm}^3 \cdot \text{mol}^{-1}$	$B_{i3}$ $\text{cm}^3 \cdot \text{mol}^{-1}$
benzene					<i>p</i> -xylene				
333.15	52.19	93.5	-1147.52	-4.34	333.15	6.86	128.12	-2710.16	-1.68
343.15	73.43	94.71	-1059.09	-1.96	343.15	10.5	129.54	-2449.16	1.37
353.15	101.01	95.98	-981.97	0.27	353.15	15.62	131.02	-2228.41	4.22
363.15	136.11	97.31	-914.13	2.36	363.15	22.64	132.56	-2039.70	6.89
373.15	180.04	98.7	-853.98	4.33	373.15	32.06	134.16	-1876.79	9.40
toluene					heptane				
333.15	18.53	110.64	-1773.21	-3.76	333.15	27.98	153.68	-2057.9	8.49
343.15	27.16	111.94	-1620.90	-1.03	343.15	40.41	155.90	-1884.56	11.43
353.15	38.82	113.31	-1490.14	1.52	353.15	56.93	158.24	-1734.38	14.18
363.15	54.23	114.73	-1376.75	3.91	363.15	78.44	160.71	-1603.09	16.76
373.15	74.17	116.22	-1277.53	6.16	373.15	105.9	163.32	-1487.39	19.19
ethylbenzene					octane				
333.15	7.39	127.44	-2574.08	-2.55	333.15	10.49	170.37	-2939.27	10.31
343.15	11.3	128.84	-2330.46	0.47	343.15	15.87	172.60	-2669.72	13.54
353.15	16.77	130.30	-2124.08	3.29	353.15	23.34	174.93	-2439.10	16.57
363.15	24.25	131.81	-1947.37	5.94	363.15	33.45	177.37	-2239.86	19.40
373.15	34.25	133.38	-1794.57	8.43	373.15	46.83	179.94	-2066.20	22.07
<i>o</i> -xylene					nonane				
333.15	5.44	125.40	-2789.81	-3.53	333.15	5.83	184.29	-4066.12	12.43
343.15	8.43	126.73	-2514.93	-0.49	343.15	9.13	186.51	-3660.79	15.90
353.15	12.67	128.10	-2283.39	2.36	353.15	13.84	188.83	-3318.09	19.15
363.15	18.53	129.52	-2086.21	5.02	363.15	20.40	191.25	-3025.31	22.19
373.15	26.47	131.00	-1916.60	7.53	373.15	29.31	193.77	-2772.79	25.06
<i>m</i> -xylene					decane				
333.15	6.59	127.13	-2728.94	-1.69	333.15	1.51	206.82	-5623.12	15.15
343.15	10.12	128.54	-2464.19	1.35	343.15	2.52	209.14	-5020.67	18.94
353.15	15.10	130.00	-2240.46	4.19	353.15	4.07	211.55	-4516.37	22.48
363.15	21.95	131.52	-2049.35	6.85	363.15	6.33	214.05	-4089.68	25.80
373.15	31.15	133.10	-1884.51	9.35	373.15	9.56	216.66	-3725.04	28.92

6 h at the column temperature 333.15 K. To avoid the loss of the stationary phase in the column, a saturated vessel that contained liquid sulfolane was placed at the inlet of the GC column. Two columns were used for each temperature to check for the reliability of the results. The column temperature was maintained within  $\pm 0.05$  K using a programmable controller and measured using an electronic thermometer. The temperature of the thermal conductivity detector was 423.15 K. Dry hydrogen was used as a carrier gas, and the flow rate of carrier gas,  $U$ , was measured using a soap bubble flow meter, which had been placed at the outlet of the detector. Volumes of the samples injected into the GC probes were  $< 1 \mu\text{L}$  to ensure that the solutes underwent infinite dilution in the stationary phase.

The equation proposed by Cruickshank et al.<sup>13</sup> and Everett<sup>14</sup> can be used to obtain the activity coefficient at infinite dilution,  $\gamma_i^\infty$ , for the solute  $i$  eluting in a carrier gas (3) in a liquid solvent (2)

$$\ln \gamma_i^\infty = \ln \left( \frac{n_2 RT}{V_N p_i^{\text{sat}}} \right) - \frac{B_{ii} - V_i^L}{RT} p_i^{\text{sat}} + \frac{2B_{i3} - V_i^\infty}{RT} J p_0 \quad (1)$$

where  $n_2$  is the number of moles of the stationary phase component on the column;  $p_i^{\text{sat}}$  is the vapor pressure of the pure liquid solute at column temperature  $T$ ;  $R$  is the gas constant ( $R = 8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ );  $V_N$  is the standardized retention volume;  $V_i^L$  is the saturated molar volume;  $V_i^\infty$  is the partial molar volume of solute  $i$  in the solvent at infinite dilution;  $p_0$  is the outlet pressure of the column;  $B_{ii}$  is the second virial coefficient of solute  $i$ ; and  $B_{i3}$  is the cross second virial coefficient of solute  $i$  with the carrier gas (3). The values of  $B_{ii}$  were evaluated using a correlation modified by Tsonopolous.<sup>15</sup> Critical parameters needed were taken from Reid et al.<sup>16</sup> and listed in Table 1. Because hydrogen is a quantum gas, modified critical constants recommended by Prausnitz and Chueh<sup>17</sup> were used. To evaluate

the cross second virial coefficient, the mixed critical parameters,  $p_{cij}$ ,  $T_{cij}$ ,  $V_{cij}$ , and  $Z_{cij}$ , and mixed acentric factor,  $\omega_{ij}$ , were calculated according to Reid et al.<sup>18</sup> The saturated molar volume  $V_i^L$  is calculated using the modified Racket equation in which empirical constants  $Z_{RA}$  were taken from Reid et al.<sup>18</sup> In the calculation,  $V_i^\infty$  is assumed to be equal to  $V_i^L$ . The vapor pressures  $p_i^{\text{sat}}$  were calculated from the Antoine equation, and the corresponding constants were obtained from the literature.<sup>16</sup> The values of  $p_i^{\text{sat}}$ ,  $V_i^L$ ,  $B_{ii}$ , and  $B_{i3}$  used in eq 1 at different temperatures are presented in Table 2.

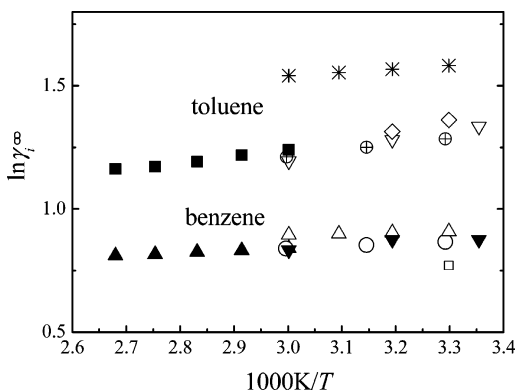
The standardized retention volume in eq 1 is given by

$$V_N = JU(t_R - t_G) \frac{T}{T_F} \left( 1 - \frac{p_w^{\text{sat}}}{p_0} \right) \quad (2)$$

where  $U$  is the flow rate of the carrier gas;  $t_R$  is the retention time and  $t_G$  is the dead time;  $T_F$  is the flow temperature; and  $p_w^{\text{sat}}$  is the saturation pressure of water at temperature  $T_F$ . The factor  $J$  in eqs 1 and 2 corrects the influence of pressure drop along the column given by

$$J = \frac{3(p_i/p_0)^2 - 1}{2(p_i/p_0)^3 - 1} \quad (3)$$

where  $p_i$  and  $p_0$  are the inlet and outlet pressures of the GC column, respectively. The outlet pressure was kept equal to atmospheric pressure, and the pressure drop ( $p_i - p_0$ ) was varied in the range (50 to 101.3) kPa, providing suitable retention times with sharp peaks. The process which is clearly the most liable to error is the determination of the mass of the stationary phase. At a given temperature, each solute was injected at least three times to check the reproducibility. In this work, the losses of stationary phases were within 2 % even at a higher column



**Figure 1.** Activity coefficients at infinite dilution,  $\gamma_i^\infty$ , in sulfolane as a function of temperature  $T$  for benzene:  $\blacktriangle$ , this work;  $\blacktriangledown$ , Rawat et al.;<sup>6</sup>  $\circ$ , Mollmann and Gmehling;<sup>7</sup>  $\square$ , Letcher and Moollan;<sup>8</sup>  $\triangle$ , data of Karvo calculated from vapor–liquid equilibria.<sup>5</sup> Activity coefficients for toluene:  $\blacksquare$ , this work;  $\nabla$ , Rawat et al.;<sup>6</sup>  $\oplus$ , Mollmann and Gmehling;<sup>7</sup>  $*$ , data of Karvo calculated from vapor–liquid equilibria;<sup>5</sup>  $\diamond$ , data of Ashcroft et al.<sup>9</sup> calculated from vapor–liquid equilibria.

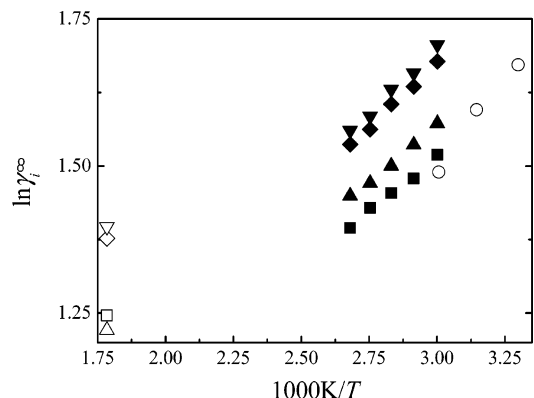
**Table 3. Experimental Activity Coefficients at Infinite Coefficients,  $\gamma_i^\infty$ , of Ten Hydrocarbons in Sulfolane as a Function of Temperature  $T$**

solute $i$	$T/K$				
	333.15	343.15	353.15	363.15	373.15
benzene	2.316	2.297	2.281	2.260	2.249
toluene	3.457	3.382	3.291	3.228	3.197
ethylbenzene	4.819	4.646	4.483	4.353	4.260
<i>o</i> -xylene	4.568	4.388	4.281	4.174	4.035
<i>m</i> -xylene	5.354	5.130	4.978	4.769	4.650
<i>p</i> -xylene	5.508	5.249	5.105	4.877	4.761
heptane	60.256	53.102	47.647	41.204	38.543
octane	80.699	70.450	61.712	54.252	48.632
nonane	108.963	93.118	81.136	71.593	62.608
decane	147.362	125.839	106.628	92.151	79.825

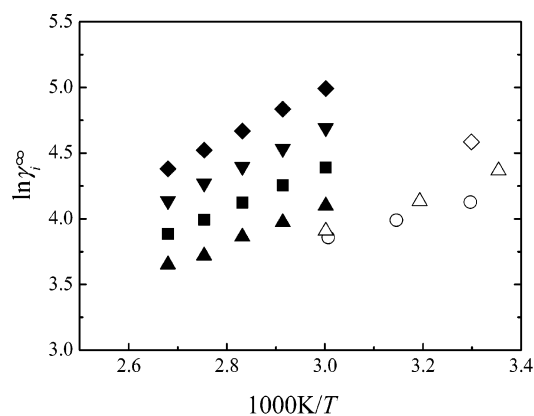
temperature, and the overall uncertainty in the measurement of activity coefficients at infinite dilution is  $\pm 3\%$ .

## Results and Discussion

The measured activity coefficients at infinite dilution for six aromatics and four linear alkanes in sulfolane at different temperatures were listed in Table 3. Figure 1 shows the linear relationship between the natural logarithm of the activity coefficients at infinite dilution,  $\ln \gamma_i^\infty$ , and the inverse of the absolute temperature for benzene and toluene in sulfolane. Apart from the values determined in this work, the data for the corresponding systems obtained by other authors<sup>5–9</sup> are also shown. The comparison demonstrates that there is good agreement between the present data and those in the literature except for that of Karvo,<sup>5</sup> in which the activity coefficients in infinite dilution for toluene were overestimated. Figures 2 and 3 depict  $\ln \gamma_i^\infty$  as a function of temperature  $T$ , respectively, for xylenes (including ethylbenzene) and normal alkanes in sulfolane. Introducing methyl or ethyl to the ring of benzene will result in the increase of the activity coefficients at infinite dilution. This is the reason  $\gamma_i^\infty$  values for xylenes and alkanes (the number of carbon atoms is larger than six) are higher than those for benzene and toluene. The activity coefficients of the linear alkanes increase with increasing chain length. For xylenes and ethylbenzene, the values of  $\gamma_i^\infty$  are in the order of *p*-xylene > *m*-xylene > ethylbenzene > *o*-xylene, in accordance with the results determined by vapor–liquid equilibria.<sup>10</sup> The selectivity at infinite dilution for sulfolane, which indicates suitability of sulfolane for separating mixtures of components 1 and 2 by extraction, can be calculated through



**Figure 2.** Activity coefficients at infinite dilution,  $\gamma_i^\infty$ , for ethylbenzene and xylenes in sulfolane as a function of temperature  $T$ :  $\blacktriangle$ , ethylbenzene this work;  $\blacksquare$ , *o*-xylene this work;  $\blacklozenge$ , *m*-xylene this work;  $\blacktriangledown$ , *p*-xylene this work;  $\triangle$ , ethylbenzene;  $\square$ , *o*-xylene;  $\diamond$ , *m*-xylene;  $\nabla$ , *p*-xylene from vapor–liquid equilibria using NRTL parameters of Yu et al.;<sup>10</sup>  $\circ$ , ethylbenzene from Mollmann and Gmehling.<sup>7</sup>



**Figure 3.** Activity coefficients at infinite dilution,  $\gamma_i^\infty$ , for linear alkanes in sulfolane as a function of temperature  $T$ :  $\blacktriangle$ , heptane;  $\blacksquare$ , octane;  $\blacktriangledown$ , nonane;  $\blacklozenge$ , decane;  $\triangle$ , heptane from Rawat et al.;<sup>6</sup>  $\circ$ , heptane from Mollmann and Gmehling;<sup>7</sup>  $\diamond$ , heptane from Letcher and Moollan.<sup>8</sup>

$$S_{12}^\infty = \gamma_1^\infty / \gamma_2^\infty \quad (4)$$

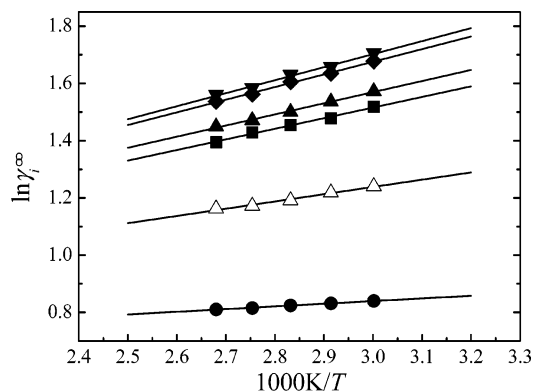
The selectivity data at infinite dilution were listed in Table 4 together with the literature values<sup>19,20</sup> for solvents that are used in industry for the separation of aromatic and aliphatic compounds. The selectivity,  $S_{12}^\infty$ , for sulfolane and the ionic liquid 1-hexyl-3-methylimidazolium tetrafluoroborate ([HMIM<sup>+</sup>][BF<sub>4</sub><sup>−</sup>]) is large. This result suggests that sulfolane and ionic liquid [HMIM<sup>+</sup>][BF<sub>4</sub><sup>−</sup>] can play an important role in separating aromatic and aliphatic compounds by an extractive distillation process or solvent extraction process.

From Figures 1–3, a good linear relationship is obtained between the natural logarithm of the activity coefficients at infinite dilution,  $\ln \gamma_i^\infty$ , and the inverse of the absolute temperature; i.e.,  $\ln \gamma_i^\infty$  can be expressed as

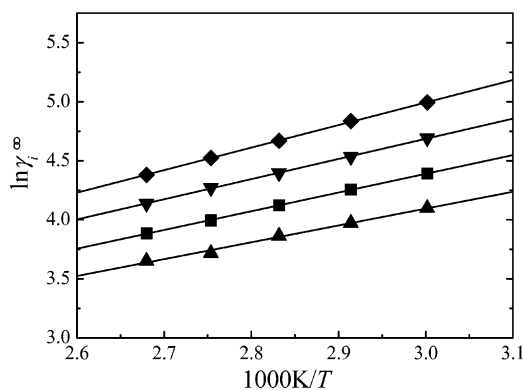
$$\ln \gamma_i^\infty = a + b/(T/K) \quad (5)$$

where  $a$  and  $b$  are constants. Figures 4 and 5 show the activity coefficients at infinite dilution as deviations from the linear fit of eq 5. According to the Gibbs–Helmholtz equation, the value for the partial molar excess enthalpy at infinite dilution,  $\bar{H}_i^{E,\infty}$ , can be directly obtained from

$$\frac{\partial \ln \gamma_i^\infty}{\partial (1/T)} = \frac{\bar{H}_i^{E,\infty}}{R} \quad (6)$$



**Figure 4.** Linear plots for activity coefficients at infinite dilution,  $\ln \gamma_i^\infty$ , vs the inverse of absolute temperature  $T$ : ●, benzene; △, toluene; ▲, ethylbenzene; ■, *o*-xylene; ◆, *m*-xylene; ▼, *p*-xylene.



**Figure 5.** Linear plots for activity coefficients at infinite dilution,  $\ln \gamma_i^\infty$ , vs the inverse of absolute temperature  $T$ : ▲, heptane; ■, octane; ▼, nonane; ◆, decane.

**Table 4.** Selectivity Values,  $S_{12}^\infty$ , at Infinite Dilution of Various Solvents for the Heptane (1) and Benzene (2) Separation at  $T = (323.15 \text{ and } 333.15) \text{ K}$

solvent	$S_{12}^\infty$	
	$T/K = 323.15$	$T/K = 333.15$
sulfolane		26.0
triethylene glycol <sup>a</sup>	20.2	18.9
tetraethylene glycol <sup>a</sup>		16.8
<i>N</i> -methylacetamide <sup>b</sup>		5.4
<i>N,N</i> -dimethylacetamide <sup>b</sup>		7.0
<i>N,N</i> -dibutylformamide <sup>b</sup>		3.1
[HMIM <sup>+</sup> ][BF <sub>4</sub> <sup>-</sup> ] <sup>c</sup>	26.9	

<sup>a</sup> Data from Sun et al.<sup>19</sup> <sup>b</sup> Data from Mollmann and Gmehling.<sup>7</sup> <sup>c</sup> Data from Letcher et al.<sup>20</sup>

The values of  $\bar{H}_i^{E,\infty}$  with their uncertainties for the compounds studied were listed in Table 5. The available values of  $\bar{H}_i^{E,\infty}$  measured with an LKB flow calorimeter<sup>21–23</sup> were also listed in Table 5 for comparison. All the values of  $\bar{H}_i^{E,\infty}$  are positive and increase with increasing chain length of the linear alkanes. Excess enthalpies measured with the calorimeter show that the temperature dependence determined from the direct measurement of the limiting activity coefficients ( $\bar{H}_i^{E,\infty}$ ) is in good agreement with the data obtained from excess enthalpy measurements of Pansini and Jannelli<sup>23</sup> for benzene considering that the excess enthalpy data were obtained at lower temperatures. However, the partial molar excess enthalpies for toluene and *p*-xylene from the Gibbs–Helmholtz equation are about  $1000 \text{ J}\cdot\text{mol}^{-1}$  more than that from Karvo<sup>21,22</sup> using the calorimeter.

**Table 5.** Partial Molar Excess Enthalpies at Infinite Dilution,  $\bar{H}_i^{E,\infty}$ , of Hydrocarbons in Sulfolane at  $T = (333.15 \text{ to } 373.15) \text{ K}$

solute $i$	$\bar{H}_i^{E,\infty}/(\text{J}\cdot\text{mol}^{-1})$	
	calculated from eq 5	measured from calorimeter
benzene	$775.4 \pm 30.7$	$509.5 \pm 3.7$ ; <sup>a</sup> $258.3 \pm 3.4$ <sup>b</sup>
toluene	$2105 \pm 155$	$982.9 \pm 8.0$ <sup>b</sup>
ethylbenzene	$3230 \pm 128$	
<i>o</i> -xylene	$3083 \pm 143$	
<i>m</i> -xylene	$3672 \pm 136$	
<i>p</i> -xylene	$3779 \pm 192$	$2866.1 \pm 6.1$ <sup>b</sup>
heptane	$11874 \pm 563$	
octane	$13177 \pm 113$	
nonane	$14188 \pm 157$	
decane	$15896 \pm 138$	

<sup>a</sup> Data at 303.16 K from Pansini and Jannelli.<sup>23</sup> <sup>b</sup> Data at 323.15 K from Karvo.<sup>21,22</sup>

## Conclusions

The activity coefficients at infinite dilution,  $\gamma_i^\infty$ , of ten hydrocarbons in sulfolane at several temperatures, (333.15 to 373.15) K, were measured using gas chromatography. The data are useful to the distillation processes commonly encountered in the chemical industry where a high boiling solvent is added near the top of the column to separate a binary mixture by means of extractive distillation. By application of a thermodynamic relationship, the reliability of the data measured in this work has been checked using excess enthalpy data in the literature. The calculated selectivity suggests that sulfolane and ionic liquid [HMIM<sup>+</sup>][BF<sub>4</sub><sup>-</sup>] can act as a good solvent in separating aromatic and aliphatic compounds by extractive distillation and solvent extraction. The data measured in this work can be used to extend the range of applications of existing group contribution methods (e.g., modified UNIFAC (Dortmund) model) for the synthesis and design of separation processes.<sup>2</sup>

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