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# Infinite Dilution Activity Coefficients of Hydrocarbons in Triethylene Glycol and Tetraethylene Glycol

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The infinite dilution activity coefficients for benzene, toluene, ethylbenzene, *n*-heptane, *n*-octane, *n*-nonane, and *n*-decane in triethylene glycol and tetraethylene glycol were experimentally measured by gas chromatography at (50 to 130) °C. The experimental data were correlated with the modified UNIFAC (Dortmund) method, and the group interaction parameters were obtained. The experimental data were compared with the calculated results, and a good agreement between experimental data and calculated values was obtained.

## Introduction

In petrochemical engineering, solvent extraction is one of the most important methods to produce high-purity aromatic extracts from catalytic reformates. In recent years, triethylene glycol and tetraethylene glycol have been employed as good-quality extraction solvents more and more in new or improved extraction processes. Therefore, it is necessary to have complete thermodynamic data for hydrocarbon + triethylene glycol or tetraethylene glycol systems. In previous work, we have determined the liquid−liquid equilibria for the ternary system *n*-heptane + water + tetraethylene glycol[1] and the vapor−liquid equilibria for three aromatic hydrocarbon + tetraethylene glycol binary systems[2] and for the binary system water + tetraethylene glycol.[3] Herskowitz and Gottlieb[4] have also reported the activity coefficients of the solvent in the water + tetraethylene glycol system by an isopiestic method at 298.15 K.

In this work, the infinite dilution activity coefficients of benzene, toluene, ethylbenzene, *n*-heptane, *n*-octane, *n*-nonane, and *n*-decane in the solvents triethylene glycol and tetraethylene glycol are measured at (50 to 130) °C. The data are correlated with the modified UNIFAC model (Dortmund) and compared with the correlation results.

## Experimental Section

***Chemicals.*** Pure benzene, toluene, ethylbenzene, *n*-heptane, *n*-octane, *n*-nonane, and *n*-decane were obtained from the Beijing Chemical Engineering Plant. Triethylene glycol and tetraethylene glycol were procured from Beijing Yanshan Petrochemical Company. All the chemicals were purified by distillation (triethylene glycol and tetraethylene glycol distilled under vacuum), and their middle fractions were collected. Then they were dried using type 0.5 nm molecular sieves, and the water content was found to be <0.01 mass %, as determined with a Mitsubishi moisture meter (model CA-05). To minimize the contact of these deliquescent reagents with moist air, all the purified chemicals were kept in sealed bottles in desiccators.

The purity was tested by gas liquid chromatography (GLC), which indicated a minimum purity of 99.8 mol %, and no appreciable peaks of impurities were detected. The densities and refractive indices of the purified chemicals are reported in Table 1 in comparison with the literature data[5] at 293.15 K and atmospheric pressure. The results in Table 1 showed that the purities of all of the chemicals satisfied the requirements of the experiment.

**Table 1. Densities $\rho$ and Refractive Indices $n_D$ of Pure Components and Comparison with Literature[5] Values at 293.15 K**

| | $\rho$/g·cm$^{-3}$ | | $n_D$ | |
|---|---|---|---|---|
| component | exptl | lit. | exptl | lit. |
| *n*-heptane | 0.6835 | 0.6838 | 1.3878 | 1.3877 |
| *n*-octane | 0.7026 | 0.7028 | 1.3975 | 1.3974 |
| *n*-nonane | 0.7178 | 0.7176 | 1.4057 | 1.4054 |
| *n*-decane | 0.7302 | 0.7301 | 1.4113 | 1.4110 |
| benzene | 0.8783 | 0.8787 | 1.5015 | 1.5011 |
| toluene | 0.8667 | 0.8660 | 1.4962 | 1.4960 |
| ethylbenzene | 0.8674 | 0.8670 | 1.4955 | 1.4959 |
| triethylene glycol | 1.1278 | 1.1274[a] | 1.4556 | 1.4550 |
| tetraethylene glycol | 0.1256 | 1.125 | 1.4571 | 1.4577 |

[a] Data at 288.15 K.

**Table 2. Constants of the Antoine Equation for *T*/°C and *P*/mmHg**

| | *A* | *B* | *C* |
|---|---|---|---|
| benzene | 6.905 65 | 1211.033 | 220.790 |
| toluene | 6.954 64 | 1344.800 | 219.48 |
| ethylbenzene | 6.957 19 | 1424.255 | 213.21 |
| *n*-heptane | 6.896 00 | 1264.90 | 216.54 |
| *n*-octane | 6.918 68 | 1351.99 | 209.15 |
| *n*-nonane | 6.938 93 | 1431.82 | 202.01 |
| *n*-decane | 6.943 65 | 1495.17 | 193.86 |

***Procedures.*** The experimental work was carried out by using gas−liquid chromatography to determine the infinite dilution activity coefficients of solutes with low boiling points in a solvent with a high boiling point. The apparatus used in this experiment is a SHIMADZU GC-14B type gas chromatograph. The solid support is 80−100 mesh chromosorb W acid-washed and silanized. As stationary phase, pure triethylene glycol and tetraethylene glycol were exactly weighed by an electronic balance with the accuracy ±0.0001 g and then attached uniformly on the solid support which was loaded with approximately 30% solvent by mass. The solid support with stationary phase was filled in a stainless steel column with a 3 mm inner diameter and a 2 m length, and it was finally heated under nitrogen for 6 h at the column temperature 60 °C. To avoid the loss of the stationary phase in the column, a saturation vessel that contains the same liquid as the stationary phase was placed

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**Table 3. Infinite Dilution Activity Coefficients of Hydrocarbons in Triethylene Glycol**

| | infinite dilution activity coefficients at the following $T$/°C | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| solute | 50 | 60 | 70 | 80 | 90 | 100 | 110 | 120 |
| benzene | 4.6238 | 4.3759 | 4.2634 | 4.1021 | 3.9713 | 3.9159 | 3.8227 | 3.7550 |
| toluene | 7.1078 | 6.7965 | 6.5103 | 6.2512 | 5.9922 | 5.8481 | 5.5627 | 5.5120 |
| ethylbenzene | 10.8636 | 10.2807 | 9.7303 | 9.1046 | 8.7188 | 8.3906 | 7.9420 | 7.7208 |
| *n*-heptane | 93.2555 | 82.7251 | 71.9152 | 62.7220 | 55.3420 | 50.1877 | 44.3104 | 40.6484 |
| *n*-octane | 129.3399 | 113.0827 | 99.4520 | 86.8640 | 75.8312 | 68.7312 | 60.5370 | 56.6890 |
| *n*-nonane | 182.6414 | 155.9893 | 139.8330 | 119.0435 | 103.0471 | 92.9946 | 81.4029 | 73.9146 |
| *n*-decane | 252.0811 | 219.4850 | 196.3944 | 161.9120 | 140.5329 | 125.2050 | 107.3318 | 95.5871 |

**Table 4. Infinite Dilution Activity Coefficients of Hydrocarbons in Tetraethylene Glycol**

| | infinite dilution activity coefficients at the following $T$/°C | | | | | | |
|---|---|---|---|---|---|---|---|
| solute | 60 | 80 | 90 | 100 | 110 | 120 | 130 |
| benzene | 2.9879 | 2.7258 | 2.6546 | 2.5004 | 2.4147 | 2.3738 | 2.2750 |
| toluene | 4.4984 | 4.0183 | 3.8479 | 3.6163 | 3.4624 | 3.3673 | 3.2120 |
| ethylbenzene | 6.3899 | 5.6277 | 5.3088 | 4.9950 | 4.7324 | 4.5773 | 4.3538 |
| *n*-heptane | 50.1970 | 37.6276 | 32.1486 | 29.7898 | 26.0853 | 23.0581 | 20.8123 |
| *n*-octane | 68.0508 | 49.5303 | 43.2492 | 37.5451 | 32.4140 | 31.4054 | 25.8207 |
| *n*-nonane | 92.3330 | 64.6860 | 57.4205 | 49.2577 | 42.9453 | 39.7168 | 34.1370 |
| *n*-decane | 122.9813 | 87.7984 | 75.1279 | 64.3745 | 55.2339 | 51.3082 | 42.9478 |

in front of the column. The microamounts of benzene, toluene, ethylbenzene, *n*-heptane, *n*-octane, *n*-nonane, and *n*-decane, sequentially, were injected into the chromatograph in amounts of <1 $\mu$L to ensure that the solutes are infinitely diluted in the stationary phase. The column temperatures are kept between 50 °C and 130 °C by a programmable controller, and the temperature of the thermal conductivity detector was 150 °C. The temperature was controlled to within ±0.1 °C and measured by means of an electronic thermometer. Hydrogen was used as a carrier gas, and its flow rate was 60 mL·min$^{-1}$. In the experiment, the retention time for the air peak and the solute peak was recorded. In this study, the losses of stationary phases with high boiling point were within 2% even at the higher column temperature, and the precision of the determination of the infinite dilution activity coefficient was <3% by averaging results for five chromatographic injections.

## Results and Discussion

The infinite dilution activity coefficient has been determined for volatile solute from[6]

$$\gamma_{\mathrm{i}}^{\infty} = \frac{RT}{M_{\mathrm{L}} P_i^{\circ} V_{\mathrm{g}}} \tag{1}$$

where $R$ is the gas constant, $T$ is the absolute temperature of the column, $M_{\mathrm{L}}$ is the molecular mass of the solvent, and $P_i^{\circ}$ is the saturated vapor pressure of the solute at the column temperature. Strictly speaking, vapor pressure in eq 1 must be substituted by fugacity, but the fugacity coefficient for solutes is close to unity under these experimental conditions. $V_{\mathrm{g}}$ represents the specific retention volume at 0 °C; $V_{\mathrm{g}}$ is calculated with

$$V_{\mathrm{g}} = \frac{V_{\mathrm{R}} - V_{\mathrm{R}}^{\circ}}{W_{\mathrm{L}}} = \frac{(t_{\mathrm{R}} - t_{\mathrm{R}}^{\circ})\overline{F_{\mathrm{C}}}}{W_{\mathrm{L}}} \tag{2}$$

where $W_{\mathrm{L}}$ is the mass of the stationary phase, $V_{\mathrm{R}}$ is the retention volume of the solute, $V_{\mathrm{R}}^{\circ}$ is the retention volume of air, and $t_{\mathrm{R}}$ and $t_{\mathrm{R}}^{\circ}$ are the retention times for the solute and air, respectively. $\overline{F_{\mathrm{C}}}$ is the average flow rate of the carrier gas, which is obtained by the following formula

**Table 5. Volume Parameters $R_k$ and Area Parameters $Q_k$ of Groups, Triethylene Glycol (TEG), and Tetraethylene Glycol (TeEG)**

| | ACH | $ACCH_3$ | $ACCH_2$ | $CH_3$ | $CH_2$ | TEG | TeEG |
|---|---|---|---|---|---|---|---|
| no. | 1 | 2 | 3 | 4 | 5 | 6 | 7 |
| $R_k$ | 03763 | 0.9100 | 0.9100 | 0.6325 | 0.6325 | 7.2772 | 9.0531 |
| $Q_k$ | 0.4321 | 0.9490 | 0.7962 | 1.0608 | 0.7081 | 7.1168 | 9.0744 |

$$\overline{F_{\mathrm{C}}} = 1.5\frac{\left(\dfrac{P_{\mathrm{b}}}{P_0}\right)^2 - 1}{\left(\dfrac{P_{\mathrm{b}}}{P_0}\right)^3 - 1}\,\frac{P_0 - P_{\mathrm{w}}^{\circ}}{P_0}\,\frac{T}{T_{\mathrm{a}}}F_{\mathrm{C}} \tag{3}$$

where $P_{\mathrm{b}}$ is the pressure in front of the column, $P_0$ is the atmospheric pressure, $P_{\mathrm{w}}^{\circ}$ is the saturated pressure of water at the environment temperature, $T$ is the absolute temperature of the column, $T_{\mathrm{a}}$ is the environment temperature, and $F_{\mathrm{C}}$ is the actual flow rate determined for the carrier gas.

The saturated vapor pressures of the solutes are calculated by the Antoine equation,[5] $\log P = A - B/(T + C)$. The constants of the Antoine equation of the solute are listed in Table 2.

The infinite dilution activity coefficients of hydrocarbon in triethylene glycol and tetraethylene glycol which are evaluated by eqs 1−3 using the experimental data for $t_{\mathrm{R}}$, $t_{\mathrm{R}}^{\circ}$, $\overline{F_{\mathrm{C}}}$, and the mass of the stationary phase are listed in Tables 3 and 4.

Gmehling et al.[7] have proposed a modified UNIFAC (universal quasichemical functional group activity coefficient) model (Dortmund). Compared to the original UNIFAC model, the modified model uses a large amount of experimental data for excess enthalpy $h^{\mathrm{E}}$ and infinite dilution activity coefficient $\gamma^{\infty}$ to obtain the group interaction parameters except for vapor−liquid equilibrium (VLE) and liquid−liquid equilibrium (LLE) experimental data, but it is only valid for the binary system with $\gamma^{\infty} < 100$. In this study, the molecules of triethylene glycol and tetraethylene glycol have to be treated as a special group. Their group interaction parameters with other groups are obtained from experimental data of infinite dilution activity coefficients.

The modified UNIFAC model (Dortmund) is represented by

**Table 6. Group Interaction Parameters of Triethylene Glycol (TEG), Tetraethylene Glycol (TeEG), and Other Groups**

| $n$ | $m$ | $a_{\mathrm{nm}}$/K | $b_{\mathrm{nm}}$ | $c_{\mathrm{nm}}$/K$^{-1}$ | $a_{\mathrm{mn}}$/K | $b_{\mathrm{mn}}$ | $c_{\mathrm{mn}}$/K$^{-1}$ |
|---|---|---|---|---|---|---|---|
| 1 | 6 | 89.5227 | −0.0862 | 0 | 133.5285 | 0.0516 | 0 |
| 2 | 6 | 153.2716 | −0.0480 | 0 | −223.9503 | −0.1624 | 0 |
| 3 | 6 | −197.9750 | −0.0363 | 0 | 98.7302 | 0.1843 | 0 |
| 4 | 6 | 171.1970 | −0.2138 | 0 | 64.9992 | 0.1640 | 0 |
| 5 | 6 | 132.1588 | −0.0126 | 0 | 89.3041 | −0.0349 | 0 |
| 1 | 7 | −82.3770 | 0.2500 | $0.2283 \times 10^{-4}$ | 240.4717 | −0.2567 | $0.1703 \times 10^{-4}$ |
| 2 | 7 | −32.8133 | −0.1604 | $-0.0502 \times 10^{-4}$ | −22.8083 | −0.0668 | $0.2237 \times 10^{-4}$ |
| 3 | 7 | −70.5925 | 0.1132 | $0.1325 \times 10^{-4}$ | −53.7005 | −0.2880 | $0.0796 \times 10^{-4}$ |
| 4 | 7 | 28.2857 | −0.1527 | $-0.1432 \times 10^{-4}$ | 195.0936 | 0.1307 | $0.1621 \times 10^{-4}$ |
| 5 | 7 | 104.7435 | −0.2615 | $-0.0665 \times 10^{-4}$ | 58.7107 | 0.1955 | $0.1457 \times 10^{-4}$ |

$$\ln \gamma_i = \ln \gamma_i^{\mathrm{C}} + \ln \gamma_i^{\mathrm{R}} \tag{4}$$

where the activity coefficient of combinatorial part $\gamma_i^{\mathrm{C}}$ is

$$\ln \gamma_i^{\mathrm{C}} = 1 - V_i' + \ln V_i' - 5q_i\left[1 - \frac{V_i}{F_i} + \ln\left(\frac{V_i}{F_i}\right)\right] \tag{5}$$

and where

$$V_i' = \frac{r_i^{3/4}}{\sum_j x_j r_j^{3/4}} \tag{6}$$

$$V_i = \frac{r_i}{\sum_j x_j r_j} \tag{7}$$

$$r_i = \sum \nu_k^{(i)} R_k \tag{7a}$$

$$F_i = \frac{q_i}{\sum_j x_j q_j} \tag{8}$$

$$q_j = \sum \nu_k{}^{(i)} Q_k \tag{8a}$$

and where the activity coefficient of the residual part $\gamma_i^{\mathrm{R}}$ is

$$\ln \gamma_i^{\mathrm{R}} = \sum_k \nu_k^{(i)} (\ln \Gamma_k - \ln \Gamma_k^{(i)}) \tag{9}$$

where

$$\ln \Gamma_k = Q_k\left[1 - \ln\left(\sum_m \Theta_m \Psi_{mk}\right) - \sum_m \frac{\Theta_m \Psi_{km}}{\sum_n \Theta_n \Psi_{nm}}\right] \tag{10}$$

$$\Theta_m = \frac{Q_m X_m}{\sum_n Q_n X_n} \tag{11}$$

$$X_m = \frac{\sum_j \nu_m^{(j)} x_j}{\sum_j \sum_n \nu_n^{(j)} x_j} \tag{12}$$

$$\Psi_{nm} = \exp\left(-\frac{a_{nm} + b_{nm}T + c_{nm}T^2}{T}\right) \tag{13}$$

**Table 7. Average Absolute Deviation between $\gamma_{exp}^{\infty}$ and $\gamma_{cal}^{\infty}$**

| | TEG | | | TeEG | | |
|---|---|---|---|---|---|---|
| | $T$/°C | $N$ | AAD[a] (%) | $T$/°C | $N$ | AAD[a] (%) |
| benzene | 50−120 | 8 | 4.53 | 50−130 | 8 | 9.17 |
| toluene | 50−120 | 8 | 3.81 | 50−130 | 8 | 9.10 |
| ethylbenzene | 50−120 | 8 | 3.09 | 50−130 | 8 | 1.60 |
| *n*-heptane | 50−120 | 8 | 5.75 | 50−130 | 8 | 5.53 |
| *n*-octane | 50−120 | 8 | 3.36 | 50−130 | 8 | 5.94 |
| *n*-nonane | 50−120 | 8 | 3.37 | 50−130 | 8 | 5.05 |
| *n*-decane | 50−120 | 8 | 4.09 | 50−130 | 8 | 5.39 |

[a] AAD = $(100/N)\sum_i^N|(\gamma - \gamma_{\mathrm{cal}}^{\infty})/\gamma_{\mathrm{exp}}^{\infty}|$, where $N$ is the number of experimental points.

In eqs 5−13, $V_i$ is the volume fraction for component $i$, $V_i'$ is the empirically modified $V_i$ value, $F_i$ is the surface fraction for component $i$, $r_i$ is the relative van der Waals volume of component $i$, $x_i$ is the mole fraction of component $i$ in the liquid phase, $R_k$ is the relative van der Waals volume of subgroup $k$, $Q_k$ is the relative van der Waals surface area of subgroup $k$, $q_i$ is the relative van der Waals surface area of component $i$, $\nu_k^{(i)}$ is the number of structural groups of type $k$ in molecule $i$, $\Gamma_k$ is the group activity coefficient of group $k$ in the mixture, $\Gamma_k^{(i)}$ is the group activity coefficient of group $k$ in the pure substance, $\Theta_m$ is the surface fraction of group $m$ in the liquid phase, $X_m$ is the group mole fraction of group $m$ in the liquid phase, and $a_{nm}$, $b_{nm}$, and $c_{nm}$ are the UNIFAC group interaction parameters between groups $n$ and $m$.

In a calculation, the volume and area parameters of triethylene glycol and tetraethylene glycol are the sums of the group parameters from eqs 7a and 8a, which are listed in Table 5.

The group interaction parameters $a_{nm}$, $b_{nm}$, $c_{nm}$, $a_{mn}$, $b_{mn}$, and $c_{mn}$ in eq 13 between triethylene glycol, or tetraethylene glycol, and other groups, which are calculated from experimentally determined $\gamma_i^{\infty}$ using regression analysis, are shown in Table 6.

The infinite dilution activity coefficients of benzene, toluene, ethylbenzene, *n*-heptane, *n*-octane, *n*-nonane, and *n*-decane are calculated using the modified UNIFAC model with group interaction parameters. Table 7 lists the average absolute deviation between the experimental data and calculated values for infinite dilution activity coefficients. As shown in Table 7, most of the average absolute deviations are <5%.

## Conclusion

The infinite dilution activity coefficients of benzene, toluene, ethylbenzene, *n*-heptane, *n*-octane, *n*-nonane, and *n*-decane in triethylene glycol and tetraethylene glycol at temperatures (50 to 130) °C were measured by gas chromatography and correlated with the modified UNIFAC model (Dortmund). The group interaction parameters between triethylene glycol or tetraethylene glycol and some other groups are presented in this study. Most of the average absolute deviations between the experimental data and calculated values are <5%, with those of benzene and toluene in tetraethylene glycol a bit higher, but they are still applicable for engineering design.

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