

Liquid–Liquid Equilibria for Aromatics Extraction Systems with Tetraethylene Glycol

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Liquid–Liquid equilibria (LLE) have been measured for five ternary and two multicomponent mixtures containing cyclohexane, benzene, toluene, *p*-xylene, tetraethylene glycol (TTEG), and water at 60 °C and 140 °C. A new UNIFAC group was defined, and its parameters were determined from the experimental data. The calculated values are in good agreement with the experimental and literature data with sufficient accuracy for the engineering design.

Introduction

Tetraethylene glycol (TTEG) is one of the most widely used solvents in the extraction process of aromatic hydrocarbons from reformed naphtha and pyrolysis gasoline. The generation and the prediction of liquid–liquid equilibrium (LLE) data for such systems are therefore essential.

Ternary LLE data for heptane + benzene + (TTEG + water) (Rawat and Prasad, 1980) and heptane + toluene + (TTEG + water) (Wang et al., 1993) at different temperatures were compiled earlier. However, there are few data reported for the systems containing xylene, which is the most difficult substance to be extracted by the solvent, and for the multicomponent systems, which are close to the actual feed stock. In the present study, therefore, LLE data for the ternary systems of heptane + *p*-xylene + (TTEG + water) and multicomponent systems are determined at the temperature of 60 °C under atmospheric pressure and the temperature of 140 °C under 10 atm. This study also demonstrates the applicability of the UNIFAC model for the prediction of LLE in the aromatics extraction system with TTEG.

Experimental Section

Chemicals. TTEG was obtained from Beijing Yanshan Petrochemical Co. and was purified by distillation under reduced pressure. The water content and the refractive index were then measured for TTEG, which corresponds to minimum 99% purity. The other chemicals were obtained from Beijing Chemistry Plant with a stated minimum of 99.5% purity.

Measurement of the LLE. The liquid–liquid equilibria at atmospheric pressure were carried out in large tubes placed in a shaker at the temperature (60 ± 1 °C). The LLE experiment under high pressure at 140 °C was carried out in a high-pressure LLE bath with a magnetic agitator for mixing. The contents were mixed for about 120 min and then settled for at least 40 min until both phases became transparent. Approximately 5 mL samples of each phase were then taken off, and acetone was added to the sample in order to maintain a homogenous phase at normal temperature. The concentration of the components in each phase were analyzed by GC using octane as the internal standard.

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Table 1. Interaction Parameters a_{nm} (n/TETRA) and a_{mn} (TETRA/n) for the UNIFAC Model for TETRA

| | CH ₂ /TETRA | ACH/TETRA | ACCH ₂ /TETRA | H ₂ O/TETRA |
|--------------|------------------------|-----------|--------------------------|------------------------|
| a_{nm} (K) | 481.45 | 221.85 | 83.53 | 4567.1 |
| a_{mn} (K) | 14.68 | -19.94 | 102.7 | -371.49 |

Table 2. Experimental and Calculated Liquid–Liquid Equilibrium Compositions for the System Heptane (1) + *p*-Xylene (2) + TTEG (3) + 2 mass % or 5 mass % Water (4) at 60 °C

| no. | raffinate phase (α) | | | | extract phase (β) | | | | |
|-----|------------------------------|--------------|--------------|--------------|---------------------------|-------------|-------------|-------------|--------|
| | x_1^α | x_2^α | x_3^α | x_4^α | x_1^β | x_2^β | x_3^β | x_4^β | |
| 1 | exptl | 0.7325 | 0.2614 | 0.0037 | 0.0024 | 0.0119 | 0.0347 | 0.5817 | 0.3716 |
| | calcd | 0.7338 | 0.2584 | 0.0047 | 0.0031 | 0.0172 | 0.0379 | 0.5766 | 0.3683 |
| 2 | exptl | 0.4565 | 0.5268 | 0.0102 | 0.0065 | 0.0072 | 0.0531 | 0.5734 | 0.3663 |
| | calcd | 0.4815 | 0.4986 | 0.0154 | 0.0045 | 0.0166 | 0.0832 | 0.5481 | 0.3521 |
| 3 | exptl | 0.4593 | 0.5284 | 0.0075 | 0.0048 | 0.0103 | 0.0741 | 0.5587 | 0.3569 |
| | calcd | 0.4772 | 0.5010 | 0.0166 | 0.0052 | 0.0180 | 0.0993 | 0.5373 | 0.3453 |
| 4 | exptl | 0.6248 | 0.3692 | 0.0037 | 0.0024 | 0.0071 | 0.0473 | 0.5770 | 0.3686 |
| | calcd | 0.6267 | 0.3629 | 0.0080 | 0.0024 | 0.0173 | 0.0555 | 0.5651 | 0.3620 |
| 5 | exptl | 0.5492 | 0.4204 | 0.0185 | 0.0118 | 0.0102 | 0.0595 | 0.5677 | 0.3626 |
| | calcd | 0.5479 | 0.4244 | 0.0184 | 0.0093 | 0.0159 | 0.0614 | 0.5624 | 0.3603 |
| 6 | exptl | 0.1617 | 0.8177 | 0.0125 | 0.0080 | 0.0077 | 0.1255 | 0.5289 | 0.3379 |
| | calcd | 0.1628 | 0.8174 | 0.0196 | 0.0002 | 0.0072 | 0.1256 | 0.5259 | 0.3412 |
| 7 | exptl | 0.4299 | 0.5504 | 0.0160 | 0.0037 | 0.0172 | 0.1215 | 0.7014 | 0.1599 |
| | calcd | 0.4399 | 0.5338 | 0.0219 | 0.0045 | 0.0196 | 0.1350 | 0.6882 | 0.1572 |
| 8 | exptl | 0.6176 | 0.3729 | 0.0077 | 0.0018 | 0.0227 | 0.0852 | 0.7265 | 0.1657 |
| | calcd | 0.6176 | 0.3729 | 0.0089 | 0.0006 | 0.0227 | 0.0852 | 0.7260 | 0.1662 |
| 9 | exptl | 0.3121 | 0.6780 | 0.0081 | 0.0018 | 0.0291 | 0.1795 | 0.6444 | 0.1470 |
| | calcd | 0.3121 | 0.6780 | 0.0096 | 0.0003 | 0.0290 | 0.1795 | 0.6438 | 0.1476 |
| 10 | exptl | 0.5442 | 0.4120 | 0.0357 | 0.0081 | 0.0167 | 0.0877 | 0.7293 | 0.1663 |
| | calcd | 0.5313 | 0.4441 | 0.0204 | 0.0043 | 0.0184 | 0.0711 | 0.7413 | 0.1692 |
| 11 | exptl | 0.5408 | 0.4259 | 0.0271 | 0.0062 | 0.0205 | 0.0939 | 0.7212 | 0.1645 |
| | calcd | 0.5393 | 0.4293 | 0.0260 | 0.0054 | 0.0209 | 0.0924 | 0.7218 | 0.1649 |
| 12 | exptl | 0.4743 | 0.4911 | 0.0282 | 0.0064 | 0.0199 | 0.1071 | 0.7108 | 0.1621 |
| | calcd | 0.4741 | 0.4916 | 0.0289 | 0.0055 | 0.0199 | 0.1068 | 0.7107 | 0.1625 |
| 13 | exptl | 0.4627 | 0.4955 | 0.0340 | 0.0077 | 0.0199 | 0.0958 | 0.7201 | 0.1642 |
| | calcd | 0.4623 | 0.4964 | 0.0347 | 0.0067 | 0.0193 | 0.0947 | 0.7210 | 0.1649 |

Table 3. Experimental and Calculated Liquid–Liquid Equilibrium Compositions for the System Heptane (1) + *p*-Xylene (2) + TTEG (3) + 5 mass % Water (4) at 140 °C

| no. | exptl | raffinate phase (α) | | | | extract phase (β) | | | |
|-----|-------|------------------------------|--------------|--------------|--------------|---------------------------|-------------|-------------|-------------|
| | | x_1^α | x_2^α | x_3^α | x_4^α | x_1^β | x_2^β | x_3^β | x_4^β |
| 1 | exptl | 0.9839 | 0.0146 | 0.0010 | 0.0006 | 0.0516 | 0.0034 | 0.5831 | 0.3619 |
| | calcd | 0.9818 | 0.0142 | 0.0022 | 0.0018 | 0.0309 | 0.0034 | 0.5964 | 0.3693 |
| 2 | exptl | 0.7734 | 0.2223 | 0.0026 | 0.0016 | 0.0528 | 0.0655 | 0.5440 | 0.3377 |
| | calcd | 0.7738 | 0.2193 | 0.0039 | 0.0030 | 0.0394 | 0.0665 | 0.5518 | 0.3423 |
| 3 | exptl | 0.5811 | 0.4130 | 0.0037 | 0.0023 | 0.0685 | 0.1355 | 0.4912 | 0.3049 |
| | calcd | 0.5741 | 0.3900 | 0.0048 | 0.0021 | 0.0553 | 0.1376 | 0.4929 | 0.3142 |
| 4 | exptl | 0.4917 | 0.4978 | 0.0064 | 0.0040 | 0.0898 | 0.1879 | 0.4457 | 0.2766 |
| | calcd | 0.4864 | 0.4928 | 0.0140 | 0.0068 | 0.0703 | 0.1837 | 0.4654 | 0.2956 |
| 5 | exptl | 0.3262 | 0.6472 | 0.0164 | 0.0102 | 0.0730 | 0.2291 | 0.4306 | 0.2673 |
| | calcd | 0.3270 | 0.6465 | 0.0194 | 0.0071 | 0.0724 | 0.2296 | 0.4273 | 0.2707 |

Table 4. Experimental and Calculated Liquid–Liquid Equilibrium Compositions for the System Heptane (1) + Benzene (2) + Toluene (3) + *p*-Xylene (4) + TTEG (5) + 2 mass % Water (6) at 60 °C

| no. | phase | x_1 | | x_2 | | x_3 | | x_4 | | x_5 | | x_6 | |
|-----|-----------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|
| | | exptl | calcd | exptl | calcd | exptl | calcd | exptl | calcd | exptl | calcd | exptl | calcd |
| 1 | raffinate | 0.6890 | 0.6927 | 0.0554 | 0.0523 | 0.1272 | 0.1334 | 0.0925 | 0.0936 | 0.0293 | 0.0121 | 0.0067 | 0.0159 |
| | extract | 0.0140 | 0.0200 | 0.0208 | 0.0227 | 0.0338 | 0.0330 | 0.0183 | 0.0192 | 0.7435 | 0.7463 | 0.1696 | 0.1588 |
| 2 | raffinate | 0.6289 | 0.6222 | 0.0526 | 0.0532 | 0.1312 | 0.1451 | 0.1018 | 0.1085 | 0.0697 | 0.0660 | 0.0159 | 0.0082 |
| | extract | 0.0175 | 0.0207 | 0.0188 | 0.0151 | 0.0322 | 0.0263 | 0.0187 | 0.0115 | 0.7434 | 0.7489 | 0.1695 | 0.1762 |
| 3 | raffinate | 0.4850 | 0.4778 | 0.0926 | 0.0986 | 0.2094 | 0.2204 | 0.1399 | 0.1493 | 0.0596 | 0.0489 | 0.0136 | 0.0050 |
| | extract | 0.0163 | 0.0204 | 0.0334 | 0.0310 | 0.0503 | 0.0459 | 0.0224 | 0.0186 | 0.7147 | 0.7178 | 0.1630 | 0.1663 |
| 4 | raffinate | 0.4727 | 0.4583 | 0.0795 | 0.0864 | 0.1325 | 0.1367 | 0.1380 | 0.1472 | 0.1443 | 0.1505 | 0.0329 | 0.0209 |
| | extract | 0.0188 | 0.0274 | 0.0309 | 0.0283 | 0.0491 | 0.0436 | 0.0241 | 0.0209 | 0.7142 | 0.7084 | 0.1629 | 0.1714 |
| 5 | raffinate | 0.4332 | 0.4218 | 0.0777 | 0.0835 | 0.1885 | 0.1971 | 0.1394 | 0.1477 | 0.1313 | 0.1322 | 0.0299 | 0.0177 |
| | extract | 0.0181 | 0.0247 | 0.0313 | 0.0290 | 0.0530 | 0.0500 | 0.0264 | 0.0234 | 0.7094 | 0.7065 | 0.1618 | 0.1664 |
| 6 | raffinate | 0.6831 | 0.6807 | 0.0576 | 0.0563 | 0.1445 | 0.1291 | 0.1108 | 0.0976 | 0.0032 | 0.0030 | 0.0007 | 0.0332 |
| | extract | 0.0227 | 0.0242 | 0.0264 | 0.0270 | 0.0433 | 0.0499 | 0.0234 | 0.0291 | 0.7200 | 0.7196 | 0.1642 | 0.1502 |
| 7 | raffinate | 0.6967 | 0.7008 | 0.0489 | 0.0469 | 0.1218 | 0.1257 | 0.1009 | 0.0980 | 0.0258 | 0.0114 | 0.0059 | 0.0171 |
| | extract | 0.0228 | 0.0250 | 0.0200 | 0.0210 | 0.0339 | 0.0328 | 0.0193 | 0.0209 | 0.7361 | 0.7423 | 0.1679 | 0.1580 |
| 8 | raffinate | 0.6553 | 0.6517 | 0.0489 | 0.0559 | 0.1231 | 0.1324 | 0.0989 | 0.1100 | 0.0600 | 0.0508 | 0.0137 | 0.0083 |
| | extract | 0.0214 | 0.0213 | 0.0199 | 0.0169 | 0.0342 | 0.0300 | 0.0199 | 0.0149 | 0.7367 | 0.7446 | 0.1680 | 0.1725 |
| 9 | raffinate | 0.4507 | 0.4409 | 0.0902 | 0.0963 | 0.2098 | 0.2202 | 0.1435 | 0.1533 | 0.0861 | 0.0786 | 0.0196 | 0.0108 |
| | extract | 0.0191 | 0.0227 | 0.0339 | 0.0313 | 0.0540 | 0.0493 | 0.0252 | 0.0208 | 0.7067 | 0.7107 | 0.1612 | 0.1651 |
| 10 | raffinate | 0.6139 | 0.6053 | 0.0464 | 0.0547 | 0.1134 | 0.1254 | 0.0932 | 0.0973 | 0.1084 | 0.1133 | 0.0247 | 0.0102 |
| | extract | 0.0208 | 0.0237 | 0.0178 | 0.0141 | 0.0316 | 0.0263 | 0.0195 | 0.0133 | 0.7412 | 0.7400 | 0.1690 | 0.1798 |

Table 5. Experimental and Calculated Liquid–Liquid Equilibrium Compositions for the System Cyclohexane (1) + Benzene (2) + Toluene (3) + *p*-Xylene (4) + TTEG (5) + 2 mass % Water (6) at 60 °C

| no. | phase | x_1 | | x_2 | | x_3 | | x_4 | | x_5 | | x_6 | |
|-----|-----------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|
| | | exptl | calcd | exptl | calcd | exptl | calcd | exptl | calcd | exptl | calcd | exptl | calcd |
| 1 | raffinate | 0.3996 | 0.4050 | 0.1303 | 0.1264 | 0.2278 | 0.2289 | 0.1980 | 0.1891 | 0.0361 | 0.0431 | 0.0082 | 0.0075 |
| | extract | 0.0545 | 0.0511 | 0.0563 | 0.0586 | 0.0721 | 0.0730 | 0.0431 | 0.0482 | 0.6303 | 0.6221 | 0.1437 | 0.1459 |
| 2 | raffinate | 0.4195 | 0.4065 | 0.1029 | 0.1108 | 0.1953 | 0.2072 | 0.1656 | 0.1657 | 0.0950 | 0.0977 | 0.0217 | 0.0121 |
| | extract | 0.0605 | 0.0642 | 0.0490 | 0.0453 | 0.0659 | 0.0601 | 0.0407 | 0.0356 | 0.6383 | 0.6401 | 0.1456 | 0.1548 |
| 3 | raffinate | 0.4547 | 0.4483 | 0.0818 | 0.0854 | 0.1887 | 0.1942 | 0.1732 | 0.1779 | 0.0827 | 0.0843 | 0.0189 | 0.0099 |
| | extract | 0.0626 | 0.0638 | 0.0409 | 0.0361 | 0.0563 | 0.0534 | 0.0370 | 0.0344 | 0.6541 | 0.6557 | 0.1492 | 0.1567 |
| 4 | raffinate | 0.3649 | 0.3667 | 0.1381 | 0.1418 | 0.2357 | 0.2434 | 0.1831 | 0.1804 | 0.0636 | 0.0707 | 0.0145 | 0.0102 |
| | extract | 0.0530 | 0.0504 | 0.0610 | 0.0601 | 0.0734 | 0.0713 | 0.0402 | 0.0424 | 0.6290 | 0.6218 | 0.1434 | 0.1485 |
| 5 | raffinate | 0.3840 | 0.3944 | 0.1512 | 0.1524 | 0.2433 | 0.2447 | 0.1790 | 0.1700 | 0.0346 | 0.0357 | 0.0079 | 0.0028 |
| | extract | 0.0562 | 0.0529 | 0.0715 | 0.0712 | 0.0830 | 0.0831 | 0.0428 | 0.0471 | 0.6079 | 0.6028 | 0.1386 | 0.1414 |
| 6 | raffinate | 0.3684 | 0.3738 | 0.1539 | 0.1500 | 0.2297 | 0.2202 | 0.1892 | 0.1890 | 0.0480 | 0.0553 | 0.0109 | 0.0118 |
| | extract | 0.0531 | 0.0530 | 0.0667 | 0.0690 | 0.0799 | 0.0766 | 0.0416 | 0.0469 | 0.6178 | 0.6107 | 0.1409 | 0.1438 |
| 7 | raffinate | 0.2883 | 0.2957 | 0.1442 | 0.1373 | 0.2512 | 0.2406 | 0.2014 | 0.1943 | 0.0936 | 0.1082 | 0.0213 | 0.0289 |
| | extract | 0.0500 | 0.0510 | 0.0598 | 0.0661 | 0.0741 | 0.0861 | 0.0407 | 0.0525 | 0.6315 | 0.6014 | 0.1440 | 0.1429 |

Table 6. Average Absolute Deviation between the Experimental and Calculated Data

| system ^a | phase | δx_1 | δx_2 | δx_3 | δx_4 | δx_5 | δx_6 | δx_7 |
|---------------------|-----------|--------------|--------------|--------------|--------------|--------------|--------------|--------------|
| 1 | raffinate | 0.0057 | | | | 0.0115 | 0.0031 | 0.0024 |
| | extract | 0.0034 | | | | 0.0078 | 0.0077 | 0.0038 |
| 2 | raffinate | 0.0029 | | | | 0.0064 | 0.0028 | 0.0021 |
| | extract | 0.0134 | | | | 0.0016 | 0.0062 | 0.0087 |
| 3 | raffinate | 0.0089 | 0.0020 | | | | 0.0069 | 0.0023 |
| | extract | 0.0044 | 0.0018 | | | | 0.0027 | 0.0143 |
| 4 | raffinate | 0.0054 | | 0.0060 | | | 0.0047 | 0.0034 |
| | extract | 0.0030 | | 0.0093 | | | 0.0075 | 0.0035 |
| 5 | raffinate | 0.0072 | 0.0047 | 0.0095 | 0.0082 | 0.0075 | 0.0104 | |
| | extract | 0.0039 | 0.0024 | 0.0042 | 0.0038 | 0.0041 | 0.0077 | |
| 6 | raffinate | 0.0084 | 0.0044 | 0.0068 | 0.0047 | 0.0059 | 0.0053 | |
| | extract | 0.0022 | 0.0030 | 0.0036 | 0.0052 | 0.0087 | 0.0044 | |

^a System: 1. Heptane (1) + *p*-xylene (5) + TTEG (6) + water (7) 60 °C (this work). 2. Heptane (1) + *p*-xylene (5) + TTEG (6) + water (7) 140 °C (this work). 3. Heptane (1) + benzene (3) + TTEG water (7) 120 °C (Rawat et al., 1980). 4. Heptane (1) + toluene (4) + TTEG (6) + water (7) 100 °C (Wang et al., 1993). 5. Heptane (1) + benzene (3) + toluene (4) + *p*-xylene (5) + TTEG (6) + water (7) 60 °C (this work). 6. Cyclohexane (2) + benzene (3) + toluene (4) + *p*-xylene (5) + TTEG (6) + water (7) 60 °C (this work).

Parameter Estimation

In the analysis process, TTEG and water were treated as a pseudo-component so that the concentration of each of them could not be determined separately. In the UNIFAC model, however, the concentration of each component in both phases is required. As water and TTEG are all polar solvents, water is soluble in TTEG and very

difficult to dissolve in hydrocarbons. Moreover, the content of water is not high. We assume that the molar ratio between TTEG and water is a constant in both phases and it equals that in the original solvent. The assumption was verified by eight sets of experimental data (Wang, 1996).

According to the rules of the determination of the UNIFAC group (Fredenslund, et al., 1977), a new UNIFAC group, TETRA, is defined, which treats the whole molecule of TTEG as a UNIFAC group. The UNIFAC model requires two group interaction parameters (a_{mn} and a_{nm}) per pair of groups and group volumes (R_k) and surface area (Q_k) of an individual group (Reid et al., 1977). The parameters concerning the new group should be obtained by regression of experimental data. Phase equilibrium criterion and material balance suggest that the objective function for evaluation of the parameters is as follows

$$f = \min \left[\frac{1}{n_y n} \sum_{j=1}^{n_y} \sum_{i=1}^n \left(\chi_{ij}^{\alpha} \gamma_{ij}^{\alpha} - 1 \right)^2 \right] \quad (1)$$

where n is the number of components and n_y is the number of data points. The group volume and surface area of TETRA are estimated as 5.920 and 4.200, respectively. The estimated values of group interaction parameters for TETRA are presented in Table 1.

Prediction of LLE

To illustrate the applicability of the UNIFAC model, particularly that of the estimated parameters for the

prediction of LLE data of the aromatics extraction system with TTEG, the calculated phase equilibrium compositions have been compared with the experimental data in Tables 2–5.

Table 6 lists the average absolute deviations of the mole fraction of the compounds in the experimental systems.

It can be seen that the calculated data are in good agreement with the experimental values. The fact that the temperature of these measurements, ranging from 60 to 140 °C, covers the operating temperature and the components presented in the experiments include the main components in the feed stock demonstrates that the UNIFAC model can be used to predict the LLE data in the aromatics extraction system with TTEG with sufficient accuracy for the engineering design.

Conclusion

Five ternary and two multicomponent LLE data of the aromatics extraction systems with TTEG at different temperatures were determined in this study. A new UNIFAC group, TETRA, was defined, and its parameters required were estimated by the experimental data. From the good agreement between the calculated and both the

experimental and literature data, it can be concluded that the UNIFAC group contribution model with the estimated parameters can be used for the prediction of the LLE data with good accuracy for the design and analysis of the actual extraction units in petrochemical engineering.

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