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## PHYSICOCHEMICAL STUDIES OF SYSTEMS AND PROCESSES

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# Liquid–Liquid Phase Equilibrium in the System Heptane–Toluene–Mixed Extractant Triethylene Glycol–Sulfolane–Water

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**Abstract**—The experimental data on the liquid–liquid equilibrium in the system heptane–toluene–mixed extractant, a 38.4 : 57.5 : 4.1 wt% triethylene glycol–sulfolane–water mixture, at 50°C were obtained and compared with the data for the same model hydrocarbon system with sulfolane–triethylene glycol–8 wt% water mixture as extractant.

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For recovery of  $C_6$ – $C_8$  arenes from reforming catalysts of the 62–105°C fraction, KINEF Limited Liability Company employs extraction with mixed extractant, triethylene glycol (TEG)–sulfolane–water mixture, containing 20–30 wt% sulfolane. Replacement of TEG by the mixed extractant enabled a decrease in the extractant: feed ratio (by weight) from 8 : 1 to 4.9 : 1, as well as additional treatment in the extraction block of the benzene, and a part of the forxylene, fraction obtained at mixed xylenes setup [1].

Examination of the liquid–liquid equilibrium in the pseudoternary systems comprised of saturated hydrocarbons,  $C_6$ – $C_8$  arenes, and mixed extractant represented by triethylene glycol–sulfolane–water mixtures of various compositions showed that, when the sulfolane : TEG ratio is increased to 60 : 40 wt%, the equilibrium diagram is represented by a closed binodal curve even at 50°C. A decrease in the extraction temperature should enhance the selectivity of recovery of arenes, decrease the amount of spent recycling streams, and additionally improve the performance characteristics of the setup with respect to the feed.

To elucidate the advantages offered by a 38.4 : 57.5 : 4.1 wt% TEG–sulfolane–water mixture as mixed extractant, we examined the liquid–liquid phase equilibrium at 50°C

in the model system heptane–toluene–mixed extractant with indicated composition (Table 1).

Table 1 presents the toluene concentrations in the raffinate and extract, the toluene recovery in one-step extraction, distribution coefficients of toluene and heptane  $(K_p)_T$  and  $(K_p)_{hp}$ , and separation coefficients  $\beta = (K_p)_T/(K_p)_{hp}$  characterizing the extractant selectivity. All these parameters were calculated with the use of the experimental data.

To compare the performance characteristics of the mixed extractant, individual sulfolane, and TEG with 8 wt% water we used published data on the liquid–liquid equilibrium for the same model system heptane–toluene in the presence of sulfolane [2] and of TEG with 8 wt% water [3] and calculated the same extraction parameters (Table 1).

The correctness of our experimental data and those available in the literature was checked by the Othmer–Tobias and Hand methods (Table 2) [4].

Table 2 lists the correlation coefficients  $r$  and constants  $a$  and  $b$  from the linear equations. The  $r$  values suggest a higher degree of thermodynamic consistency of our experimental data, especially in comparison with the data available from the All-Russia Research Institute for Petrochemical Processes [3].

**Table 1.** Liquid-liquid phase equilibrium in heptane (1) toluene (2) extractant (3) ternary system

| Initial composition, wt%                                               |       |       |  | Raffinate phase composition, wt% |       |      |  | Extract phase composition, wt% |       |       |  | Toluene concentration, wt% |         | Toluene recovery, wt% | (K <sub>p</sub> ) <sub>T</sub> | (K <sub>p</sub> ) <sub>hp</sub> | β     |
|------------------------------------------------------------------------|-------|-------|--|----------------------------------|-------|------|--|--------------------------------|-------|-------|--|----------------------------|---------|-----------------------|--------------------------------|---------------------------------|-------|
| 1                                                                      | 2     | 3     |  | 1                                | 2     | 3    |  | 1                              | 2     | 3     |  | raffinate                  | extract |                       |                                |                                 |       |
| Mixed extractant: 38.4:57.5:4.1 wt% TEG-sulfolane-water mixture (50°C) |       |       |  |                                  |       |      |  |                                |       |       |  |                            |         |                       |                                |                                 |       |
| 46.5                                                                   | 6.8   | 46.7  |  | 87.50                            | 11.50 | 1.0  |  | 0.80                           | 2.92  | 96.38 |  | 11.62                      | 78.49   | 23.52                 | 0.254                          | 0.009                           | 28.21 |
| 42.45                                                                  | 14.29 | 43.06 |  | 76.52                            | 21.88 | 1.6  |  | 1.24                           | 6.57  | 93.17 |  | 22.23                      | 84.12   | 22.79                 | 0.300                          | 0.016                           | 18.76 |
| 38.5                                                                   | 24.0  | 38.5  |  | 64.70                            | 33.30 | 2.0  |  | 1.50                           | 12.20 | 86.30 |  | 33.98                      | 89.05   | 22.41                 | 0.366                          | 0.023                           | 15.79 |
| 35.4                                                                   | 31.2  | 34.4  |  | 56.20                            | 41.30 | 2.5  |  | 1.80                           | 16.80 | 81.40 |  | 42.36                      | 90.32   | 22.20                 | 0.407                          | 0.032                           | 12.71 |
| 29.74                                                                  | 40.32 | 29.94 |  | 44.86                            | 49.94 | 5.2  |  | 2.0                            | 23.42 | 74.54 |  | 52.68                      | 92.07   | 21.07                 | 0.463                          | 0.044                           | 10.52 |
| 23.92                                                                  | 51.72 | 24.36 |  | 33.0                             | 59.50 | 7.5  |  | 2.58                           | 31.20 | 66.22 |  | 64.32                      | 92.32   | 16.58                 | 0.524                          | 0.078                           | 6.72  |
| 19.48                                                                  | 61.76 | 18.76 |  | 21.27                            | 63.23 | 15.5 |  | 3.80                           | 41.50 | 54.70 |  | 74.83                      | 91.60   | 4.54                  | 0.656                          | 0.179                           | 3.67  |
| 18.0                                                                   | 64.10 | 17.90 |  |                                  |       |      |  |                                |       |       |  |                            |         |                       |                                |                                 |       |
| Homogeneous mixture                                                    |       |       |  |                                  |       |      |  |                                |       |       |  |                            |         |                       |                                |                                 |       |
| Extractant sulfolane <sup>a</sup> (50°C)                               |       |       |  |                                  |       |      |  |                                |       |       |  |                            |         |                       |                                |                                 |       |
| 50.0                                                                   | —     | 50.0  |  | 99.66                            | 0.00  | 0.34 |  | 1.46                           | 0.00  | 98.54 |  | —                          | —       | —                     | —                              | —                               | —     |
| 46.4                                                                   | 7.2   | 46.4  |  | 87.79                            | 11.76 | 0.45 |  | 2.31                           | 4.40  | 93.29 |  | 11.81                      | 65.54   | 37.80                 | 0.374                          | 0.0263                          | 14.20 |
| 42.25                                                                  | 15.5  | 42.25 |  | 76.47                            | 22.87 | 0.66 |  | 2.47                           | 9.67  | 87.86 |  | 23.02                      | 79.65   | 34.81                 | 0.423                          | 0.0323                          | 13.09 |
| 37.0                                                                   | 26.0  | 37.0  |  | 64.80                            | 34.02 | 1.17 |  | 2.66                           | 17.72 | 79.62 |  | 34.43                      | 86.94   | 33.52                 | 0.521                          | 0.0411                          | 12.68 |

Table 1 (Contd.)

| Initial composition, wt% |      |       | Raffinate phase composition, wt% |       |       | Extract phase composition, wt% |       |       | Toluene concentration, wt% |         | Toluene recovery, wt% | (K <sub>p</sub> ) <sub>r</sub> | (K <sub>p</sub> ) <sub>hp</sub> | β     |
|--------------------------|------|-------|----------------------------------|-------|-------|--------------------------------|-------|-------|----------------------------|---------|-----------------------|--------------------------------|---------------------------------|-------|
| 1                        | 2    | 3     | 1                                | 2     | 3     | 1                              | 2     | 3     | raffinate                  | extract |                       |                                |                                 |       |
| 33.0                     | 34.0 | 33.0  | 55.43                            | 42.53 | 2.03  | 3.00                           | 23.60 | 73.40 | 43.42                      | 88.73   | 31.29                 | 0.555                          | 0.0541                          | 10.26 |
| 28.5                     | 43.0 | 28.5  | 44.50                            | 52.11 | 3.39  | 4.35                           | 30.51 | 65.14 | 53.94                      | 87.53   | 29.94                 | 0.586                          | 0.0977                          | 5.99  |
| 24.0                     | 52.0 | 24.0  | 35.69                            | 58.44 | 5.88  | 4.89                           | 40.61 | 54.50 | 62.09                      | 89.25   | 28.21                 | 0.695                          | 0.1371                          | 5.07  |
| 21.5                     | 57.0 | 21.5  | 29.20                            | 62.11 | 8.69  | 7.40                           | 46.19 | 46.41 | 68.02                      | 86.19   | 26.00                 | 0.744                          | 0.2533                          | 2.94  |
| 19.25                    | 61.5 | 19.25 | 23.10                            | 63.39 | 13.51 | 11.92                          | 55.61 | 32.47 | 73.29                      | 82.35   | 21.95                 | 0.877                          | 0.5160                          | 1.70  |

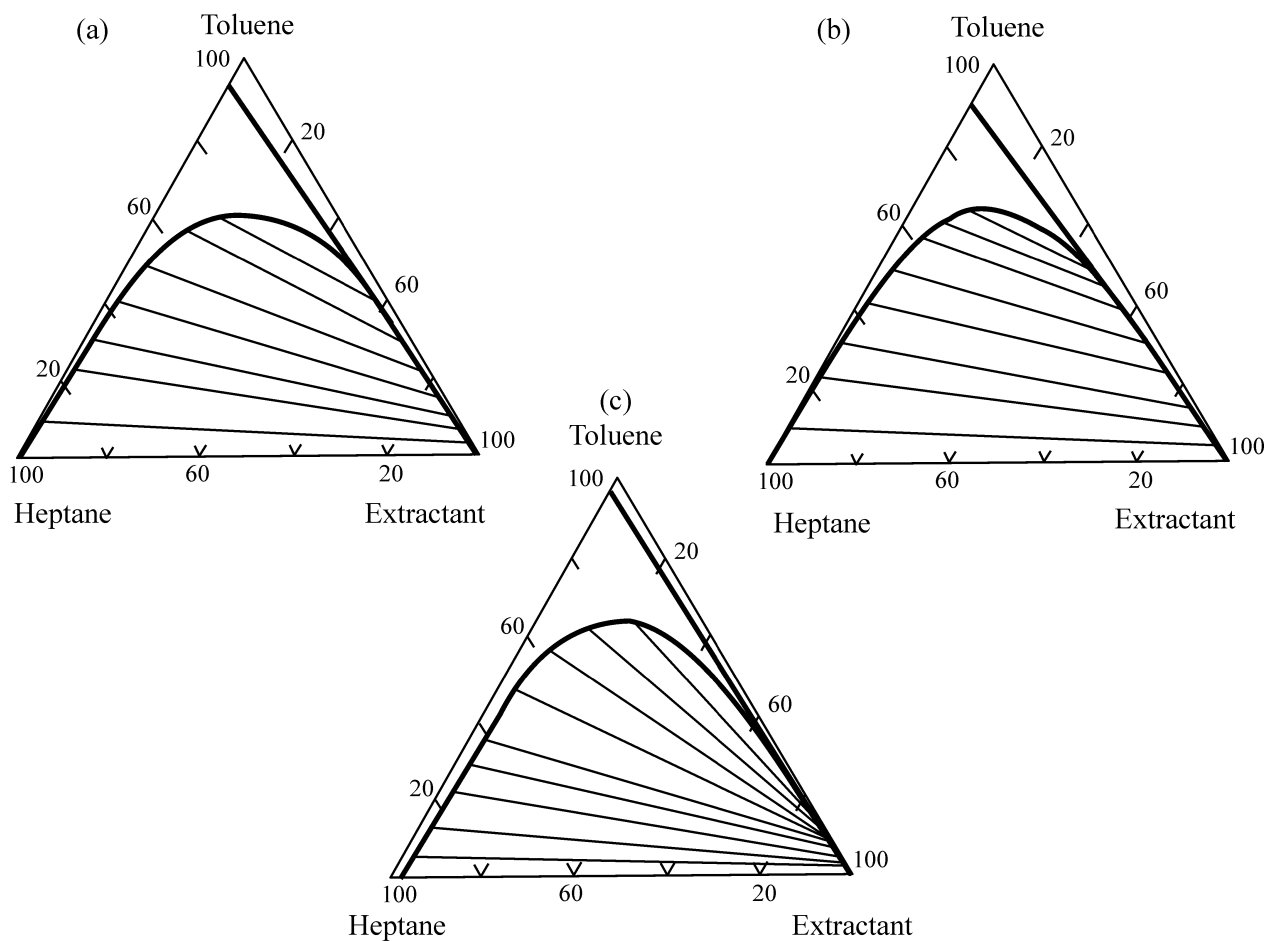
| Extractant 92:8 wt% TEG water mixture <sup>a</sup> (150°C) |      |       |      |      |      |     |      |      |       |       |       |       |       |     |
|------------------------------------------------------------|------|-------|------|------|------|-----|------|------|-------|-------|-------|-------|-------|-----|
| 50.0                                                       | —    | 50.0  | 95.9 | —    | 4.1  | 1.1 | —    | 98.9 | —     | —     | —     | —     | —     | —   |
| 48.25                                                      | 3.5  | 48.55 | 89.8 | 5.9  | 4.3  | 1.1 | 0.7  | 98.2 | 6.16  | 38.89 | 9.23  | 0.119 | 0.012 | 9.9 |
| 45.5                                                       | 9.0  | 45.5  | 82.1 | 13.6 | 4.3  | 1.1 | 1.7  | 97.2 | 14.21 | 60.71 | 7.30  | 0.125 | 0.013 | 9.6 |
| 43.0                                                       | 14.0 | 43.0  | 73.6 | 22.1 | 4.3  | 1.1 | 3.0  | 95.9 | 23.09 | 73.17 | 9.09  | 0.135 | 0.015 | 9.0 |
| 40.0                                                       | 20.0 | 40.0  | 65.1 | 29.6 | 5.3  | 1.1 | 4.3  | 94.6 | 31.25 | 79.63 | 8.16  | 0.145 | 0.017 | 8.5 |
| 37.0                                                       | 26.0 | 37.0  | 56.6 | 37.4 | 6.0  | 1.1 | 5.5  | 93.4 | 39.79 | 83.33 | 7.56  | 0.147 | 0.019 | 7.7 |
| 31.5                                                       | 37.0 | 31.5  | 43.8 | 49.2 | 7.0  | 1.1 | 8.3  | 90.6 | 52.90 | 88.30 | 6.69  | 0.169 | 0.025 | 6.8 |
| 25.75                                                      | 48.5 | 25.75 | 31.8 | 58.4 | 9.8  | 1.1 | 11.4 | 87.5 | 64.74 | 91.20 | 4.95  | 0.195 | 0.035 | 5.6 |
| 24.25                                                      | 51.5 | 24.25 | 20.8 | 66.4 | 12.8 | 0.9 | 14.2 | 84.9 | 76.15 | 94.04 | 7.87  | 0.214 | 0.043 | 5.8 |
| 8.5                                                        | 51.5 | 40.0  | 9.1  | 66.6 | 24.3 | 0.7 | 19.8 | 79.5 | 87.98 | 96.59 | 12.29 | 0.297 | 0.077 | 3.8 |

<sup>a</sup> For systems comprising sulfolane and aqueous TEG the initial compositions are given at the heptane:extractant = 1:1 ratio (by weight) (except for the last line in the table), and the compositions of the raffinate and extract phases, according to published data.

**Table 2.** Checking the correctness of the data on the liquid-liquid equilibrium in heptane-toluene-extractant systems by Othmer-Tobias and Hand methods<sup>a</sup> ( $y = ax + b$ )

| System                                                      | Correlation according to Othmer-Tobias |                                |          | Correlation according to Hand |                            |          |
|-------------------------------------------------------------|----------------------------------------|--------------------------------|----------|-------------------------------|----------------------------|----------|
|                                                             | $y = \log \frac{1 - Y_3}{Y_3}$         | $y = \log \frac{1 - X_1}{X_1}$ |          | $y = \log \frac{Y_2}{Y_3}$    | $y = \log \frac{X_2}{X_1}$ |          |
|                                                             | <i>a</i>                               | <i>b</i>                       | <i>r</i> | <i>a</i>                      | <i>b</i>                   | <i>r</i> |
| Heptane-toluene-mixed extractant TEG-sulfolane-water (50°C) | 0.2186                                 | -0.00306                       | 0.9948   | 1.0364                        | 0.5506                     | 0.9984   |
| Heptane-toluene-sulfolane (50°C)                            | 0.5857                                 | -0.00156                       | 0.9815   | 1.1443                        | -0.3323                    | 0.9992   |
| Heptane-toluene-TEG with 8 wt% water (150°C)                | 0.02228                                | -0.00441                       | 0.9321   | 0.7395                        | -0.6809                    | 0.8933   |

<sup>a</sup>  $X_1$ ,  $X_2$  are the heptane and toluene concentrations in the raffinate phase, wt%, respectively, and  $Y_1$ ,  $Y_2$ , toluene and solvent concentrations in the extract phase, wt%, respectively.



Liquid-liquid phase equilibrium diagram in heptane-toluene-extractant (wt%) systems. Extractant: (a) 38.4 : 57.5 : 4.1 wt% TEG-sulfolane-water (50°C); (b) sulfolane (50°C); and (c) 92 : 8 wt% TEG-water mixture (150°C).

**Table 3.** Phase equilibrium in the liquid–liquid ternary systems heptane (1)–toluene (2)–extractant (3) at different extractant:feed ratios (feed composition heptane: toluene = 60 : 40 wt%)

| Extractant:feed<br>ratio (by<br>weight) | Raffinate phase composition,<br>wt%                           |       |      | Extract phase composition,<br>wt% |      |       | Toluene<br>concentration, wt% |         | Raffinate<br>yield,<br>wt% | Toluene<br>recovery,<br>wt% | (K <sub>p</sub> ) <sub>T</sub> | (K <sub>p</sub> ) <sub>hp</sub> | β     |
|-----------------------------------------|---------------------------------------------------------------|-------|------|-----------------------------------|------|-------|-------------------------------|---------|----------------------------|-----------------------------|--------------------------------|---------------------------------|-------|
|                                         | 1                                                             | 2     | 3    | 1                                 | 2    | 3     | raffinate                     | extract |                            |                             |                                |                                 |       |
|                                         | Mixed extractant 38.4:57.5:4.1 wt% TEG–sulfolane–water (50°C) |       |      |                                   |      |       |                               |         |                            |                             |                                |                                 |       |
| 1:1                                     | 65.70                                                         | 32.30 | 2.0  | 1.50                              | 11.7 | 86.80 | 32.96                         | 88.64   | 40.29                      | 34.93                       | 0.362                          | 0.0228                          | 15.89 |
| 2:1                                     | 71.7                                                          | 26.5  | 1.8  | 1.3                               | 8.0  | 90.7  | 26.99                         | 86.02   | 28.65                      | 42.92                       | 0.302                          | 0.0181                          | 16.41 |
| 3:1                                     | 75.2                                                          | 23.2  | 1.6  | 1.27                              | 7.0  | 91.73 | 23.58                         | 84.64   | 18.52                      | 57.04                       | 0.301                          | 0.0168                          | 17.60 |
| 4:1                                     | 77.8                                                          | 20.8  | 1.4  | 1.2                               | 6.0  | 92.8  | 22.23                         | 83.33   | 13.51                      | 64.86                       | 0.288                          | 0.0154                          | 18.73 |
| 5:1                                     | 82.3                                                          | 16.5  | 1.2  | 1.0                               | 5.2  | 94.0  | 16.70                         | 81.82   | 13.27                      | 67.31                       | 0.273                          | 0.0121                          | 22.47 |
|                                         | Extractant sulfolane (50°C)                                   |       |      |                                   |      |       |                               |         |                            |                             |                                |                                 |       |
| 1:1                                     | 68.38                                                         | 30.2  | 1.45 | 2.2                               | 12.0 | 85.8  | 30.61                         | 84.51   | 44.03                      | 33.58                       | 0.398                          | 0.0321                          | 12.39 |
| 2:1                                     | 74.3                                                          | 25.5  | 1.1  | 2.1                               | 9.2  | 88.7  | 25.78                         | 81.42   | 25.15                      | 51.77                       | 0.360                          | 0.0283                          | 12.75 |
| 3:1                                     | 77.78                                                         | 21.4  | 0.82 | 2.08                              | 7.49 | 90.43 | 21.58                         | 78.27   | 18.04                      | 61.38                       | 0.350                          | 0.0267                          | 13.11 |
| 4:1                                     | 80.3                                                          | 19.0  | 0.7  | 2.0                               | 6.4  | 91.6  | 18.63                         | 76.19   | 12.70                      | 69.84                       | 0.337                          | 0.0249                          | 13.53 |
| 5:1                                     | 83.94                                                         | 16.7  | 0.65 | 1.98                              | 5.5  | 92.52 | 16.81                         | 73.53   | 10.71                      | 73.29                       | 0.329                          | 0.0236                          | 13.95 |
|                                         | Extractant 92:8 wt% TEG–water (150°C)                         |       |      |                                   |      |       |                               |         |                            |                             |                                |                                 |       |
| 1:1                                     | 60.3                                                          | 34.0  | 5.7  | 1.1                               | 5.0  | 93.6  | 36.05                         | 81.97   | 51.72                      | 12.07                       | 0.147                          | 0.0182                          | 8.08  |
| 2:1                                     | 61.6                                                          | 32.9  | 5.5  | 1.1                               | 4.8  | 93.9  | 34.81                         | 81.35   | 48.75                      | 17.95                       | 0.146                          | 0.0178                          | 8.20  |
| 3:1                                     | 65.1                                                          | 29.6  | 5.3  | 1.1                               | 4.3  | 94.6  | 31.25                         | 79.63   | 22.53                      | 33.32                       | 0.145                          | 0.0170                          | 8.50  |
| 4:1                                     | 67.0                                                          | 28.0  | 5.0  | 1.1                               | 4.0  | 94.9  | 29.47                         | 78.43   | 16.67                      | 41.67                       | 0.143                          | 0.0164                          | 8.72  |
| 5:1                                     | 69.6                                                          | 25.7  | 4.7  | 1.1                               | 3.6  | 95.3  | 26.97                         | 76.60   | 14.03                      | 46.19                       | 0.140                          | 0.0158                          | 8.86  |

To more clearly illustrate our findings, we used the equilibrium data for calculating the data for of one-step extraction of toluene from a mixture with heptane (40 wt% toluene in the feed) at the extractant : feed ratio (by weight) ranging from 1:1 up to 5:1 (Table 3). Table 4 characterizes the phase diagrams presented in the figure.

Table 3 suggests the following.

(1) In all the extraction parameters, including the toluene concentration in the extract, recovery, and distribution coefficients, the mixed extractant TEG-sulfolane considerably surpasses TEG when used at 150°C, which is the real temperature at which the commercial extraction is run.

(2) At identical extractant : feed ratios, the mixed extractant, a 38.4 : 57.5 : 4.1 wt% TEG-sulfolane-water mixture, is slightly superseded by sulfolane in the distribution coefficients and recovery, but exhibits a higher selectivity, as suggested by enhanced values of the  $\beta$  parameter and toluene concentrations in the extract.

(3) Mixed extractant TEG-sulfolane is characterized by a higher proportion of the heterogeneity area in the phase diagram and an enhanced maximal concentration of toluene in the extract. This should entail a decrease in the amount of spent recycle stock compared to the case of sulfolane.

An important advantage over sulfolane, offered by TEG-sulfolane mixed extractant, consists in that its application does not require major redesigning on an LG-35-8/300B setup. As known, with sulfolane, the recycle stock and extract from the extract phase are stripped in separate columns; the stripper for the extract is a vacuum column, and the steam pressure should be 1.6 MPa.

## CONCLUSIONS

(1) Mixed extractant, a 38.4 : 57.5 : 4.1 wt% triethylene glycol-sulfolane-water mixture, in all the extraction parameters surpasses triethylene glycol with 8 wt% water under commercial extraction conditions.

**Table 4.** Characterization of the phase diagrams presented in Figs. 1a–1c.

| System                                                       | Heterogeneity area proportion, % | Maximal toluene concentration in extract, wt% |
|--------------------------------------------------------------|----------------------------------|-----------------------------------------------|
| Heptane–toluene–mixed extractant: TEG–sulfolane–water (50°C) | 76.0                             | 92.5                                          |
| Heptane–toluene–sulfolane (50°C)                             | 75.2                             | 90.0                                          |
| Heptane–toluene–TEG with 8 wt% water (150°C)                 | 76.7                             | 98.5                                          |

(2) Mixed extractant of the recommended composition is slightly superseded by sulfolane in distribution coefficient and toluene recovery but exhibits a higher selectivity. Specifically, it is characterized by higher separation coefficient and toluene concentration in the extract, which should entail a decrease in the amount of spent recycling streams.

(3) Another important benefit from application of the mixed extractant is that it does not require redesigning of the existing setups.

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