Electronic Supplementary Information

Aqueous biphasic systems comprised of random ethylene/propylene oxide copolymers, choline acetate, and water for triazine-based herbicide partitioning study

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1. Characterization of the Synthesized Choline Acetate

The [Cho][OAc] was obtained as crystalline solid and characterized using \textsuperscript{1}H-NMR, \textsuperscript{13}C-NMR, and FTIR spectrometer to confirm its structure. \textsuperscript{1}H-NMR (500 MHz, d\textsubscript{6}DMSO, TMS): \(\delta= 1.62\) (s, 3H, –OOCCH\textsubscript{3}), 3.13 (s, 9H, –NCH\textsubscript{3}), 3.43 (t, 2H, –NCH\textsubscript{2}), 3.84 (m, 2H, –OCH\textsubscript{2}) ppm. \textsuperscript{13}C-NMR (100 MHz, d\textsubscript{6}DMSO), \(\delta= 25.5, 53.5, 55.4, 67.7, 173.8\) ppm. The FTIR spectrum of [Cho][OAc] (Figure S1) matched the reported spectrum; specific peaks: 3145, 3025, 2850, 1573, 1386, and 1080 cm\textsuperscript{-1}.\textsuperscript{[1]}
Figure S1. FTIR spectra of the synthesized [Cho][OAc].

2. $^1$H-NMR spectra of the Two Phases in the ABS

Figure S2. $^1$H-NMR spectra of (from top to bottom) the top and bottom phases (30 wt% EOPO-2500 and 35 wt% [Cho][OAc] ABS), respectively, pure [Cho][OAc], and pure EOPO-2500.
3. Phase Behavior of the EOPO/[Cho][OAc] ABS

The binodal data of the EOPO/[Cho][OAc] ABS at different temperatures are provided in Table S1. The experimental binodal curves were fit to the empirical relationship described by Eq. 1, and the regression parameters obtained for the ABS with the lowest SD values at different temperatures are provided in Table S2. The SD values of the binodal data at different temperatures are lower than 0.006, indicating that Eq. 1 well correlated the binodal data of the ABS at the investigated temperatures.

Table S1. Experimental weight fraction data for the EOPO/[Cho][OAc] ABS at different temperatures

|       | 20 °C | 25 °C | 30 °C | 40 °C |
|-------|-------|-------|-------|-------|
|       | 100w₁ | 100w₂ | 100w₁ | 100w₂ | 100w₁ | 100w₂ | 100w₁ | 100w₂ |
| 2.098 | 77.702 | 4.021 | 70.131 | 3.245 | 76.544 | 2.519 | 77.277 |
| 3.810 | 69.630 | 5.803 | 68.204 | 4.902 | 60.785 | 3.883 | 67.017 |
| 6.807 | 59.502 | 6.602 | 63.503 | 6.760 | 55.411 | 5.377 | 60.599 |
| 8.996 | 54.570 | 8.712 | 57.910 | 7.906 | 51.321 | 6.576 | 55.024 |
| 11.744 | 48.189 | 10.314 | 53.005 | 10.659 | 47.290 | 7.836 | 51.823 |
| 12.801 | 44.704 | 14.306 | 43.808 | 11.730 | 44.666 | 9.072 | 48.405 |
| 14.071 | 42.681 | 16.701 | 39.304 | 13.820 | 41.001 | 10.101 | 45.911 |
| 14.290 | 40.713 | 21.200 | 31.109 | 14.215 | 37.669 | 12.271 | 42.890 |
| 15.714 | 38.197 | 25.204 | 23.702 | 15.027 | 35.799 | 12.852 | 39.874 |
| 17.245 | 36.009 | 31.006 | 14.608 | 15.776 | 34.367 | 13.807 | 38.316 |
| 17.930 | 34.427 | 34.801 | 9.121 | 16.501 | 33.319 | 14.270 | 36.401 |
| 19.001 | 32.103 | 39.112 | 5.004 | 17.119 | 32.402 | 15.080 | 34.846 |
| 23.841 | 24.053 | 40.106 | 4.510 | 17.723 | 31.224 | 15.613 | 33.228 |
| 25.112 | 22.201 | 41.602 | 4.404 | 16.137 | 32.057 |
| 25.727 | 21.694 | 42.501 | 3.803 |

Balance readability: 0.1 mg.
Table S2. Correlation parameters used in Equation (1) to describe the binodal data EOPO/[Cho][OAc] ABS at different temperatures

| Temperature (°C) | Parameters | R²  | sd⁻ | a  | b  | c  | d  |
|-----------------|------------|-----|------|----|----|----|----|
| 20              | -16.17     | 11.63 | -4.426 | 0.857 | 0.998 | 0.0060 |
| 25              | 0.443      | 2.584 | -3.048 | 0.827 | 0.998 | 0.0009 |
| 30              | -237.2     | 87.42 | -12.35 | 1.063 | 0.985 | 0.0015 |
| 40              | -231.5     | 78.7  | -10.89 | 0.996 | 0.998 | 0.0006 |

\[sd = \left( \frac{1}{n} \sum_{i=1}^{n} (w_{i}^{\text{cal}} - w_{i}^{\text{exp}})^2 \right)^{0.5},\] where \(n\) is the number of binodal data, \(w_{i}^{\text{cal}}\) and \(w_{i}^{\text{exp}}\) are the calculated and experimental mass fraction of EOPO, respectively.

Table S3. Experimental LLE data for the EOPO/[Cho][OAc] ABS with the same mass fractions of EOPO-2500

| TL | Overall (wt%) | Top phase (wt%) | Bottom phase (wt%) | 100 TLL | STL |
|----|---------------|-----------------|--------------------|---------|-----|
|    | IL  | EOPO | IL  | EOPO | IL  | EOPO |       |       |
| 1  | 27.94 | 25.00 | 39.70 | 5.33 | 8.73 | 57.34 | 60.5 | -0.60 |
| 2  | 30.27 | 24.93 | 43.70 | 2.98 | 5.68 | 65.56 | 73.2 | -0.61 |
| 3  | 31.87 | 25.00 | 46.13 | 1.72 | 4.02 | 70.13 | 80.3 | -0.62 |
| 4  | 33.91 | 25.08 | 48.36 | 1.43 | 2.86 | 75.98 | 87.3 | -0.61 |
| 5  | 36.14 | 24.94 | 51.29 | 0.57 | 2.22 | 79.83 | 93.2 | -0.62 |

Balance readability: 0.1 mg.

Table S4. Experimental LLE data for the EOPO/[Cho][OAc] ABS with the same mass fractions of [Cho][OAc]

| TL | Overall (wt%) | Top phase (wt%) | Bottom phase (wt%) | 100 TLL | STL |
|----|---------------|-----------------|--------------------|---------|-----|
|    | IL  | EOPO | IL  | EOPO | IL  | EOPO |       |       |
| 1  | 27.94 | 25.00 | 39.70 | 5.33 | 8.73 | 57.34 | 60.5 | -0.60 |
| 2  | 27.91 | 27.94 | 43.57 | 2.45 | 6.50 | 62.80 | 70.8 | -0.61 |
| 3  | 27.91 | 30.57 | 45.64 | 1.68 | 5.70 | 67.18 | 76.7 | -0.61 |
| 4  | 27.98 | 33.99 | 47.72 | 1.42 | 3.22 | 75.59 | 86.5 | -0.60 |
| 5  | 28.01 | 36.94 | 49.82 | 1.25 | 2.58 | 78.34 | 90.4 | -0.61 |

Balance readability: 0.1 mg.

4. Tie Line Measured Compositions Fitted to Othmer-Tobias Correlations

The tie-line data at 25 °C was used to correlate the Othmer-Tobias equation’s parameters as Eq. 4. showed. The linear dependence between the plots \(\ln [(1-W_T)/W_T] = F + G \ln [(1+W_B)/W_B]\) is shown in Figure S3. The \(R^2\) value is greater than 0.98, and the high correlation expresses the
reliability of the methodology used to obtain the tie-lines.

Figure S3. Linear dependency of the Othmer-Tobias equation at 25 °C.

5. HPLC Determination

Figure S4. Chromatogram of the herbicide standard solution (5 µg/mL) separated by HPLC: 1-Simazine; 2-Cyanazine; 3-Atrazine.
**Figure S5.** (A) Chromatograms of the top phase, and (B) bottom phase in the ABS blank sample (25.6 wt% EOPO, 26.8 wt% [Cho][OAc]).

**Figure S6.** (A) Chromatograms of the top phase, and (B) bottom phase in the ABS spiked sample (25.6 wt% EOPO, 26.8 wt% [Cho][OAc], spiked concentration 0.1 µg/g): 1-Simazine; 2-Cyanazine; 3-Atrazine.

**Reference**

1. Kalla, R. M. N.; Lim, J.; Bae, J.; Kim, I. Sulfated choline ionic liquid-catalyzed acetamide synthesis by grindstone method. *Tetrahedron Lett.* 2017, 58, 1595-1599.