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| Table S1                                |            |           |     |                              |      |           |                    |
|---|------------|-----------|-----|------------------------------|------|-----------|--------------------|
| Experimental binodal da                 | ta in mass | fractions | for | $PEG400(w_1)$ -salt( $w_2$ ) | ATPS | at 298.15 | $\mathbf{K}^a$ and |
| <u>101.325 KPa<sup><i>a</i></sup></u> . |            |           |     |                              |      |           |                    |

| 101.525 KF | 100w <sub>2</sub> | 100w <sub>1</sub> | 100w <sub>2</sub>       | 100w <sub>1</sub>                                 | 100w <sub>2</sub> | 100w <sub>1</sub> | 100w <sub>2</sub> |
|------------|-------------------|-------------------|-------------------------|---|-------------------|-------------------|-------------------|
|            |                   |                   | PEG400-(NH              | (4)2SO4 ATPS                                      |                   |                   |                   |
| 52.038     | 0.761             | 31.296            | 7.874                   | 14.956  | 18.28             | 6.212             | 25.484            |
| 47.117     | 2.178             | 29.206            | 9.025                   | 13.729  | 19.057            | 4.902             | 26.731            |
| 44.231     | 2.793             | 25.896            | 11.121                  | 12.253  | 20.107            | 3.451             | 27.767            |
| 41.813     | 3.401             | 23.224            | 12.993                  | 10.863  | 21.136            | 1.867             | 30.564            |
| 38.972     | 4.344             | 20.518            | 14.723                  | 10.097  | 22.249            | 1.335             | 32.435            |
| 35.652     | 5.702             | 18.307            | 16.147                  | 8.966   | 23.169            | 0.980             | 33.949            |
| 33.313     | 6.861             | 16.507            | 17.303                  | 7.192   | 24.587            | 0.688             | 35.838            |
|            |                   |                   | PEG400-K <sub>3</sub> C | C <sub>6</sub> H <sub>5</sub> O <sub>7</sub> ATPS |                   |                   |                   |
| 45.651     | 12.859            | 30.066            | 19.591                  | 17.190  | 29.341            | 9.590             | 36.138            |
| 41.500     | 14.463            | 27.183            | 21.707                  | 15.942  | 30.211            | 8.495             | 37.223            |
| 40.208     | 14.914            | 24.508            | 24.106                  | 14.495  | 31.349            | 7.283             | 38.402            |
| 38.119     | 15.462            | 22.213            | 25.658                  | 13.263  | 32.369            |                   |                   |
| 35.473     | 16.502            | 20.219            | 27.101                  | 12.148  | 33.387            |                   |                   |
| 33.029     | 17.749            | 18.538            | 28.346                  | 10.772  | 34.813            |                   |                   |
|            |                   |                   | PEG400-K <sub>2</sub>   | HPO4 ATPS   |                   |                   |                   |
| 34.252     | 5.048             | 20.856            | 11.497                  | 7.746   | 20.804            | 1.936             | 26.904            |
| 32.048     | 6.044             | 18.982            | 12.573                  | 6.354   | 21.678            | 1.692             | 27.512            |
| 30.135     | 6.963             | 18.055            | 13.335                  | 5.297   | 22.507            | 1.316             | 28.012            |
| 28.139     | 7.975             | 16.626            | 14.251                  | 4.424   | 23.108            | 1.027             | 29.373            |
| 26.448     | 8.670             | 15.071            | 15.110                  | 3.679   | 23.815            | 0.806             | 30.165            |
| 24.915     | 9.243             | 13.574            | 16.224                  | 3.084   | 24.608            | 0.641             | 31.007            |
| 23.658     | 9.781             | 11.463            | 17.849                  | 2.613   | 25.377            | 0.479             | 31.873            |
| 22.364     | 10.398            | 9.468             | 19.463                  | 2.240   | 26.163            | 0.359             | 32.854            |

Experimental binodal data in mass fractions for  $PEG1000(w_1)$ -salt( $w_2$ ) ATPS at 298.15 K<sup>*a*</sup> and 101.325 kPa<sup>*a*</sup>.

| 101.323 KI        | u .               |                   |                          |  |                   |                   |                   |
|-------------------|-------------------|-------------------|--------------------------|--|-------------------|-------------------|-------------------|
| 100w <sub>1</sub> | 100w <sub>2</sub> | 100w <sub>1</sub> | 100w <sub>2</sub>        | 100w <sub>1</sub>                                  | 100w <sub>2</sub> | 100w <sub>1</sub> | 100w <sub>2</sub> |
|                   |                   |                   | PEG1000-(NH              | H <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> ATPS |                   |                   |                   |
| 43.362            | 2.348             | 26.305            | 7.794                    | 11.975   | 14.977            | 5.160             | 19.150            |
| 39.241            | 3.650             | 23.130            | 8.804                    | 10.025   | 16.079            | 3.309             | 20.361            |
| 33.680            | 4.812             | 20.777            | 10.406                   | 8.292  | 17.165            | 2.231             | 21.388            |
| 31.336            | 5.686             | 18.214            | 11.585                   | 7.130  | 17.955            | 1.390             | 23.250            |
| 28.651            | 6.809             | 14.163            | 12.924                   | 6.043  | 18.617            | 0.693             | 25.994            |
|                   |                   |                   | PEG1000-K <sub>3</sub> ( | С <sub>6</sub> Н <sub>5</sub> О7 АТР <b>S</b>      |                   |                   |                   |
| 32.618            | 8.368             | 15.784            | 15.866                   | 9.790  | 18.734            | 5.481             | 21.450            |
| 29.698            | 9.650             | 14.837            | 16.334                   | 9.255  | 19.086            | 5.141             | 21.692            |
| 26.738            | 10.841            | 14.020            | 16.698                   | 8.759  | 19.228            | 4.633             | 22.200            |
| 24.627            | 11.977            | 13.321            | 17.007                   | 8.333  | 19.340            | 4.183             | 22.650            |
| 23.160            | 12.647            | 12.662            | 17.284                   | 7.894  | 19.603            | 3.698             | 23.148            |
| 21.797            | 13.186            | 12.101            | 17.575                   | 7.381  | 19.930            | 3.259             | 23.641            |
| 20.634            | 13.635            | 11.564            | 17.857                   | 6.998  | 20.220            | 2.866             | 24.124            |
| 19.096            | 14.382            | 11.106            | 18.111                   | 6.642  | 20.456            |                   |                   |
| 17.953            | 14.647            | 10.660            | 18.295                   | 6.261  | 20.784            |                   |                   |
| 16.856            | 15.215            | 10.256            | 18.446                   | 5.843  | 21.165            |                   |                   |
|                   |                   |                   | PEG1000-K2               | HPO4 ATPS  |                   |                   |                   |
| 35.702            | 4.135             | 20.396            | 8.674                    | 7.835  | 14.317            | 0.799             | 19.485            |
| 32.420            | 4.798             | 19.401            | 9.085                    | 6.713  | 14.700            | 0.586             | 21.283            |
| 29.971            | 5.617             | 17.399            | 9.747                    | 5.805  | 15.314            | 0.459             | 22.606            |
| 28.068            | 6.001             | 15.683            | 10.534                   | 5.031  | 15.837            | 0.358             | 23.335            |
| 26.272            | 6.546             | 14.239            | 11.391                   | 3.707  | 16.494            | 0.225             | 24.510            |
| 24.790            | 7.100             | 11.859            | 12.457                   | 2.249  | 17.116            |                   |                   |
| 23.335            | 7.549             | 10.106            | 13.299                   | 1.043  | 18.768            |                   |                   |

| Table S3                   |         |           |     |                       |                       |           |    |     |
|----------------------------|---------|-----------|-----|-----------------------|-----------------------|-----------|----|-----|
| Experimental binodal data  | in mass | fractions | for | $PEG2000(w_1)$ -salt( | w <sub>2</sub> ) ATPS | at 298.15 | Ka | and |
| 101.325 kPa <sup>a</sup> . |         |           |     |                       |                       |           |    |     |

| 101.325 KP | 'a".              |                   |                        |  |                   |       |                   |
|------------|-------------------|-------------------|------------------------|--|-------------------|-------|-------------------|
| 100w1      | 100w <sub>2</sub> | 100w <sub>1</sub> | 100w <sub>2</sub>      | 100w1  | 100w <sub>2</sub> | 100w1 | 100w <sub>2</sub> |
|            |                   |                   | PEG2000-(NI            | H <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> ATPS | 5                 |       |                   |
| 40.558     | 2.492             | 19.171            | 7.994                  | 8.819  | 13.311            | 3.019 | 17.065            |
| 37.256     | 3.148             | 17.331            | 8.914                  | 7.931  | 13.590            | 2.625 | 17.549            |
| 34.792     | 3.988             | 15.125            | 10.109                 | 6.706  | 14.313            | 1.944 | 17.989            |
| 31.148     | 4.820             | 14.250            | 10.555                 | 5.755  | 14.939            | 1.419 | 18.375            |
| 28.375     | 5.318             | 12.102            | 11.425                 | 4.874  | 15.513            | 1.060 | 18.971            |
| 25.999     | 5.887             | 10.997            | 11.939                 | 4.355  | 15.913            | 0.638 | 19.856            |
| 21.897     | 7.136             | 10.440            | 12.363                 | 3.453  | 16.494            |       |                   |
|            |                   |                   | PEG2000-K <sub>3</sub> | C <sub>6</sub> H <sub>5</sub> O <sub>7</sub> ATPS  | 6                 |       |                   |
| 31.501     | 5.713             | 17.440            | 11.072                 | 8.800  | 15.657            | 1.817 | 21.660            |
| 28.209     | 6.841             | 16.600            | 11.589                 | 8.088  | 16.251            | 1.610 | 21.758            |
| 26.991     | 7.238             | 15.639            | 12.023                 | 7.292  | 16.840            | 1.357 | 22.316            |
| 25.615     | 7.755             | 14.876            | 12.499                 | 6.464  | 17.636            | 1.144 | 22.914            |
| 24.590     | 8.134             | 14.077            | 12.580                 | 5.660  | 18.426            | 0.913 | 23.724            |
| 23.354     | 8.742             | 13.381            | 12.621                 | 4.977  | 18.892            | 0.674 | 24.875            |
| 22.372     | 9.095             | 12.805            | 13.100                 | 4.308  | 19.306            | 0.653 | 24.098            |
| 21.486     | 9.379             | 12.143            | 13.658                 | 3.704  | 19.633            | 0.616 | 22.744            |
| 20.772     | 9.660             | 11.516            | 13.914                 | 3.230  | 20.032            | 0.653 | 22.744            |
| 20.120     | 9.910             | 10.783            | 14.433                 | 2.780  | 20.583            |       |                   |
| 19.452     | 10.129            | 10.085            | 14.908                 | 2.414  | 20.920            |       |                   |
| 18.513     | 10.670            | 9.467             | 15.228                 | 2.082  | 21.403            |       |                   |
|            |                   |                   | PEG2000-K <sub>2</sub> | HPO4 ATPS  |                   |       |                   |
| 39.626     | 2.178             | 19.018            | 5.625                  | 6.144  | 10.449            | 0.402 | 16.717            |
| 34.949     | 2.680             | 15.628            | 6.659                  | 4.900  | 11.444            | 0.337 | 17.523            |
| 31.733     | 3.256             | 13.094            | 7.114                  | 3.730  | 12.284            | 0.261 | 18.628            |
| 29.269     | 3.715             | 11.482            | 7.698                  | 2.993  | 13.071            | 0.203 | 19.420            |
| 26.968     | 4.123             | 9.365             | 8.498                  | 2.076  | 13.607            | 0.161 | 20.860            |
| 24.754     | 4.513             | 8.632             | 9.256                  | 1.575  | 14.059            |       |                   |
| 23.094     | 4.642             | 7.412             | 9.671                  | 0.941  | 15.032            |       |                   |
| 21.023     | 5.156             | 6.92              | 9.982                  | 0.787  | 15.962            |       |                   |
|            |                   |                   |                        |  |                   |       |                   |

Experimental binodal data in mass fractions for PEG4000( $w_1$ )-salt ( $w_2$ ) ATPS at 298.15 K<sup>*a*</sup> and 101.325 kPa<sup>*a*</sup>.

| 100w <sub>1</sub> | 100w <sub>2</sub> | 100w <sub>1</sub> | 100w <sub>2</sub>        | 100w <sub>1</sub>                                  | 100w <sub>2</sub> | 100w <sub>1</sub> | 100w <sub>2</sub> |
|-------------------|-------------------|-------------------|--------------------------|--|-------------------|-------------------|-------------------|
|                   |                   |                   | PEG4000-(NH              | I <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> ATPS | 5                 |                   |                   |
| 45.014            | 1.266             | 22.451            | 5.747                    | 9.662  | 10.111            | 1.825             | 13.706            |
| 41.346            | 1.902             | 20.719            | 6.142                    | 9.366  | 10.127            | 1.404             | 14.087            |
| 36.846            | 2.750             | 19.252            | 6.696                    | 7.747  | 10.819            | 0.840             | 14.795            |
| 33.587            | 3.296             | 18.161            | 6.983                    | 6.448  | 11.422            | 0.459             | 15.538            |
| 30.399            | 4.049             | 16.206            | 7.489                    | 5.620  | 11.857            | 0.328             | 16.539            |
| 27.957            | 4.514             | 14.355            | 8.199                    | 4.269  | 12.351            | 0.164             | 17.037            |
| 26.702            | 4.825             | 12.999            | 8.810                    | 3.167  | 12.672            |                   |                   |
| 24.403            | 5.308             | 11.400            | 9.378                    | 2.372  | 13.220            |                   |                   |
|                   |                   |                   | PEG4000-K <sub>3</sub> 0 | C <sub>6</sub> H <sub>5</sub> O <sub>7</sub> ATPS  |                   |                   |                   |
| 29.949            | 4.938             | 12.990            | 10.760                   | 7.290  | 13.637            | 1.700             | 17.624            |
| 26.459            | 6.079             | 12.069            | 10.989                   | 6.870  | 13.991            | 1.560             | 18.561            |
| 26.459            | 6.079             | 11.928            | 11.361                   | 6.270  | 14.317            | 1.182             | 18.967            |
| 23.610            | 6.708             | 11.788            | 11.645                   | 5.453  | 14.590            | 0.689             | 19.607            |
| 21.966            | 7.312             | 11.349            | 11.701                   | 5.236  | 15.113            | 0.513             | 20.046            |
| 20.229            | 7.849             | 10.840            | 11.855                   | 5.015  | 15.208            | 0.501             | 20.512            |
| 18.570            | 8.488             | 10.462            | 11.990                   | 4.895  | 15.700            | 0.471             | 21.038            |
| 17.325            | 8.878             | 10.028            | 12.364                   | 4.345  | 15.764            | 0.419             | 21.807            |
| 16.296            | 9.393             | 9.799             | 12.703                   | 3.901  | 16.094            | 0.270             | 22.311            |
| 15.381            | 9.786             | 9.235             | 12.896                   | 3.458  | 16.320            | 0.180             | 23.394            |
| 14.472            | 10.141            | 8.920             | 13.184                   | 2.891  | 16.602            | 0.105             | 24.178            |
| 13.575            | 10.567            | 7.909             | 13.316                   | 2.057  | 16.955            |                   |                   |
|                   |                   |                   | PEG4000-K <sub>2</sub>   | HPO <sub>4</sub> ATPS                              |                   |                   |                   |
| 29.774            | 1.807             | 11.762            | 4.987                    | 4.354  | 9.531             | 1.166             | 12.886            |
| 25.230            | 1.912             | 10.207            | 5.661                    | 3.695  | 9.961             | 0.896             | 13.510            |
| 21.920            | 2.090             | 9.750             | 6.087                    | 3.256  | 10.287            | 0.693             | 13.892            |
| 19.870            | 2.356             | 9.056             | 6.385                    | 3.154  | 10.632            | 0.521             | 14.709            |
| 17.620            | 2.873             | 8.093             | 7.081                    | 2.697  | 10.924            | 0.387             | 15.212            |
| 16.042            | 3.311             | 6.787             | 7.747                    | 2.566  | 11.278            | 0.376             | 15.708            |
| 14.750            | 3.687             | 5.938             | 8.328                    | 1.824  | 12.063            |                   |                   |
| 13.303            | 4.084             | 5.020             | 9.059                    | 1.501  | 12.577            |                   |                   |

Value of fitting parameters of Equation 7 for binodal data of PEG-salt ATPS at 298.15 K<sup>*a*</sup> and 101.325 kPa<sup>*a*</sup>.

|         | a        | b         | c   | d          | R <sup>2</sup> | 100sd <sup>a</sup> |
|---------|----------|-----------|---|------------|----------------|--------------------|
|         |          | PE        | G-(NH4)2SO4 A   | ГРЅ        |                |                    |
| PEG400  | -0.35303 | -3.68286  | 5.57285   | -30.44505  | 0.99784        | 0.12600            |
| PEG1000 | 0.14889  | -9.03954  | 19.45296  | -78.10975  | 0.99724        | 0.07852            |
| PEG2000 | 0.20489  | -9.67614  | 20.05261  | -105.35207 | 0.99713        | 0.10900            |
| PEG4000 | -0.14182 | -7.53197  | 18.22119  | -170.96386 | 0.99787        | 0.11000            |
|         |          | PE        | G-K <sub>3</sub> C <sub>6</sub> H <sub>5</sub> O <sub>7</sub> A | ГРЅ        |                |                    |
| PEG400  | 6.09643  | -37.03296 | 56.26374  | -49.99948  | 0.99924        | 0.02188            |
| PEG1000 | 1.97133  | -23.09237 | 52.91806  | -120.18344 | 0.99945        | 0.01245            |
| PEG2000 | 1.66244  | -21.31430 | 47.12112  | -124.36448 | 0.99825        | 0.05823            |
| PEG4000 | 3.03322  | -35.58803 | 85.88786  | -226.26962 | 0.99791        | 0.05683            |
|         |          | Pl        | EG-K2HPO4 AT  | PS         |                |                    |
| PEG400  | 1.06831  | -16.23062 | 34.15983  | -79.01709  | 0.99875        | 0.04234            |
| PEG1000 | 2.84156  | -35.03202 | 88.70531  | -238.48584 | 0.99865        | 0.03889            |
| PEG2000 | -0.22212 | -3.90536  | -4.18574  | -83.90421  | 0.99887        | 0.04124            |
| PEG4000 | 3.41658  | -56.11184 | 167.5267  | -569.22517 | 0.99367        | 0.10800            |

 $sd^{a} = \left(\sum_{i=1}^{n} \left(w_{1}^{cal} - w_{1}^{exp}\right)^{2} / N\right)^{0.5}$ , where  $w_{1}$  and N are the mass fractions of PEG and the number of binodal points,

respectively.  $w_1^{exp}$  is the experimental mass fraction of PEG, and  $w_1^{cal}$  is the corresponding data calculated using eq 7.

|         | a       | b         | c             | d         | <b>R</b> <sup>2</sup> | 100sd <sup>a</sup> |
|---------|---------|-----------|---------------|-----------|-----------------------|--------------------|
|         |         | PEG-(N    | NH4)2SO4 ATPS |           |                       |                    |
| PEG400  | 0.51178 | -0.270015 | 3.93045       | -0.84456  | 0.99869               | 0.31780            |
| PEG1000 | 0.49965 | -3.47771  | 5.70140       | 1.60889   | 0.99943               | 0.40340            |
| PEG2000 | 0.51679 | -5.06880  | 15.08817      | -11.83723 | 0.99971               | 0.19650            |
| PEG4000 | 0.51836 | -6.07505  | 17.96931      | 0.84940   | 0.99979               | 0.27640            |
|         |         | PEG-K     | 3C6H5O7 ATPS  |           |                       |                    |
| PEG400  | 4.88752 | -5.14570  | -1.92838      | -0.17219  | 0.99898               | 0.23650            |
| PEG1000 | 0.42709 | -15.02506 | -0.07426      | 40.77208  | 0.99998               | 0.30380            |
| PEG2000 | 0.54638 | -2.05019  | -1.24224      | 11.48332  | 0.99992               | 0.49370            |
| PEG4000 | 0.67186 | -1.75115  | -1.48594      | 12.57309  | 0.99964               | 0.27860            |
|         |         | PEG-I     | K₂HPO₄ ATPS   |           |                       |                    |
| PEG400  | 0.46105 | -1.83591  | -1.09532      | 6.09833   | 0.99966               | 0.30180            |
| PEG1000 | 0.51358 | -2.65631  | -1.13540      | 19.39792  | 0.99930               | 0.27810            |
| PEG2000 | 2.06401 | -2.70530  | -1.87288      | 22.27260  | 0.99967               | 0.37670            |
| PEG4000 | 5.17240 | -5.43030  | -1.97619      | 5.63522   | 0.98987               | 0.19820            |

**Table S6** Value of fitting parameters of Equation 8 for binodal data of PEG-salt ATPS at 298.15 K<sup>*a*</sup> and 101.325 kPa<sup>*a*</sup>.

 $sd^{a} = \left(\sum_{i=1}^{n} \left(w_{1}^{cal} - w_{1}^{exp}\right)^{2} / N\right)^{0.5}$ , where  $w_{1}$  and N are the mass fractions of PEG and the number of binodal points,

respectively.  $w_1^{exp}$  is the experimental mass fraction of PEG, and  $w_1^{cal}$  is the corresponding data calculated using eq 8.

Value of fitting parameters of Equation 9 for binodal data of PEG-salt ATPS at 298.15 K<sup>*a*</sup> and 101.325 kPa<sup>*a*</sup>.

|         | a        | b                                   | c         | <b>R</b> <sup>2</sup> | 100sd <sup>a</sup> |
|---------|----------|-------------------------------------|-----------|-----------------------|--------------------|
|         |          | PEG-(NH <sub>4</sub> ) <sub>2</sub> | SO4 ATPS  |                       |                    |
| PEG400  | -0.30287 | -0.27401                            | 0.06548   | 0.99713               | 0.28930            |
| PEG1000 | -0.29207 | -0.36924                            | 0.03926   | 0.99566               | 0.24700            |
| PEG2000 | -0.25393 | -0.39472                            | 0.01657   | 0.99802               | 0.18270            |
| PEG4000 | -0.27858 | -0.48833                            | 0.02016   | 0.99428               | 0.30280            |
|         |          | PEG-K <sub>3</sub> C <sub>6</sub> H | I5O7 ATPS |                       |                    |
| PEG400  | -0.35637 | -0.25749                            | 0.00918   | 0.99792               | 0.19250            |
| PEG1000 | -0.37073 | -0.45853                            | 0.03310   | 0.99362               | 0.28740            |
| PEG2000 | -0.21963 | -0.32039                            | -0.00441  | 0.99632               | 0.21760            |
| PEG4000 | -0.16139 | -0.27191                            | -0.02337  | 0.98555               | 0.23650            |
|         |          | PEG-K₂HP                            | PO4 ATPS  |                       |                    |
| PEG400  | -0.23577 | -0.26616                            | 0.02150   | 0.99285               | 0.30870            |
| PEG1000 | -0.21898 | -0.34456                            | -0.00215  | 0.98878               | 0.31220            |
| PEG2000 | -0.17220 | -0.33273                            | -0.00821  | 0.99192               | 0.28730            |
| PEG4000 | -0.07908 | -0.15409                            | -0.01383  | 0.99119               | 0.32560            |

 $sd^{a} = \left(\sum_{i=1}^{n} \left(w_{1}^{cal} - w_{1}^{exp}\right)^{2} / N\right)^{0.5}$ , where  $w_{1}$  and N are the mass fractions of PEG and the number of binodal points,

respectively.  $w_1^{exp}$  is the experimental mass fraction of PEG, and  $w_1^{cal}$  is the corresponding data calculated using eq 9.

| The data | of tie line | s in mass | fractions | for PEG- | $(NH_4)_2SO_4$ | 4 ATPS at | t 298.15 Ka | and 10 | )1.325 k | cPa <sup>a</sup> . |
|----------|-------------|-----------|-----------|----------|----------------|-----------|-------------|--------|----------|--------------------|
|          |             |           |           |          |                |           |             |        |          |                    |

| Total s | ystem             | Polymer            | rich phase                     | Salt ric   | h phase            |                               | average of |
|---------|-------------------|--------------------|--------------------------------|--|--------------------|-------------------------------|------------|
| 100w1   | 100w <sub>2</sub> | 100w1 <sup>t</sup> | 100w <sub>2</sub> <sup>t</sup> | 100w1 <sup>b</sup>                               | 100w2 <sup>b</sup> | <ul> <li>Slope (k)</li> </ul> | slope      |
|         |                   |                    | PEG400-(NH <sub>4</sub> )      | <sub>2</sub> SO <sub>4</sub> -H <sub>2</sub> O   |                    |                               |            |
| 20.977  | 20.440            | 45.697             | 2.100                          | 1.340  | 35.010             | -1.3478                       |            |
| 21.165  | 21.05             | 47.267             | 1.320                          | 1.056  | 36.250             | -1.3233                       | 1 2107     |
| 22.392  | 21.725            | 49.435             | 1.090                          | 0.577  | 38.210             | -1.3162                       | -1.5197    |
| 22.135  | 23.57             | 51.618             | 0.420                          | 0.436  | 40.050             | -1.2915                       |            |
|         |                   | ]                  | PEG1000-(NH4                   | ) <sub>2</sub> SO <sub>4</sub> -H <sub>2</sub> O |                    |                               |            |
| 15.601  | 14.695            | 28.721             | 6.810                          | 2.196  | 22.900             | -1.6483                       |            |
| 15.314  | 15.587            | 29.609             | 6.450                          | 1.359  | 24.680             | -1.5496                       | 1 4082     |
| 15.820  | 16.500            | 30.722             | 6.010                          | 0.596  | 27.420             | -1.4070                       | -1.4982    |
| 16.039  | 17.460            | 33.510             | 4.980                          | 0.370  | 28.860             | -1.3879                       |            |
|         |                   | ]                  | PEG2000-(NH4                   | ) <sub>2</sub> SO <sub>4</sub> -H <sub>2</sub> O |                    |                               |            |
| 14.221  | 11.450            | 25.495             | 6.260                          | 3.981  | 16.260             | -2.1517                       |            |
| 14.980  | 12.320            | 29.875             | 4.930                          | 1.801  | 18.980             | -1.9985                       | 1.0752     |
| 15.100  | 12.861            | 31.187             | 4.570                          | 1.231  | 20.140             | -1.9244                       | -1.9755    |
| 15.760  | 13.210            | 32.141             | 4.320                          | 0.762  | 21.500             | -1.8267                       |            |
|         |                   | ]                  | PEG4000-(NH4                   | ) <sub>2</sub> SO <sub>4</sub> -H <sub>2</sub> O |                    |                               |            |
| 13.214  | 9.869             | 25.826             | 5.070                          | 2.258  | 14.110             | -2.6075                       |            |
| 16.590  | 10.060            | 34.605             | 3.060                          | 0.898  | 16.260             | -2.5539                       | 2 5145     |
| 18.200  | 10.574            | 39.875             | 2.060                          | 0.452  | 17.680             | -2.5246                       | -2.3143    |
| 21.700  | 10.702            | 43.780             | 1.480                          | 0.138  | 19.880             | -2.3719                       |            |

| The data of the lines in mass machons for PEO-N <sub>3</sub> U <sub>6</sub> $\Pi_5$ U <sub>7</sub> ATPS at 290.15 N <sup>*</sup> and 101.525 Kr | The data of | of tie line | s in mass | fractions | for PEG-K | C3C6H5O | 7 ATPS a | at 298.15 K | <sup><i>a</i></sup> and 101.325 kF |
|---|-------------|-------------|-----------|-----------|-----------|---------|----------|-------------|------------------------------------|
|---|-------------|-------------|-----------|-----------|-----------|---------|----------|-------------|------------------------------------|

| Total s | ystem             | Polymer            | rich phase                           | Salt ric  | h phase            |             | average of |
|---------|-------------------|--------------------|--------------------------------------|---|--------------------|-------------|------------|
| 100w1   | 100w <sub>2</sub> | 100w1 <sup>t</sup> | 100w <sub>2</sub> <sup>t</sup>       | 100w1 <sup>b</sup>                              | 100w2 <sup>b</sup> | - Slope (k) | slope      |
|         |                   |                    | PEG400-K <sub>3</sub> C <sub>6</sub> | H <sub>5</sub> O <sub>7</sub> -H <sub>2</sub> O |                    |             |            |
| 25.010  | 24.981            | 39.179             | 15.080                               | 10.065  | 35.50              | -1.4257     |            |
| 25.320  | 25.580            | 41.065             | 14.380                               | 9.727   | 36.050             | -1.4461     | 1 4606     |
| 25.160  | 26.310            | 44.186             | 13.380                               | 8.678   | 37.110             | -1.4963     | -1.4090    |
| 25.410  | 26.710            | 46.360             | 12.780                               | 7.115   | 38.760             | -1.5106     |            |
|         |                   |                    | PEG1000-K3C6                         | H <sub>5</sub> O <sub>7</sub> -H <sub>2</sub> O |                    |             |            |
| 16.010  | 16.410            | 29.744             | 9.620                                | 4.656   | 22.130             | -2.0924     |            |
| 16.203  | 16.730            | 31.234             | 8.950                                | 3.168   | 23.600             | -1.9961     | 1 0777     |
| 16.105  | 17.100            | 31.980             | 8.620                                | 2.410   | 24.560             | -1.9229     | -1.9///    |
| 16.100  | 17.420            | 34.050             | 7.740                                | 2.013   | 25.160             | -1.8997     |            |
|         |                   |                    | PEG2000-K3C6                         | H <sub>5</sub> O <sub>7</sub> -H <sub>2</sub> O |                    |             |            |
| 15.000  | 13.200            | 24.128             | 8.280                                | 3.948   | 19.270             | -1.8356     |            |
| 15.060  | 13.860            | 25.988             | 7.570                                | 2.236   | 21.370             | -1.7207     | 1 (070     |
| 15.100  | 14.370            | 27.040             | 7.190                                | 1.497   | 22.690             | -1.6476     | -1.68/9    |
| 15.300  | 14.930            | 27.824             | 6.920                                | 0.867   | 24.330             | -1.5480     |            |
|         |                   |                    | PEG4000-K3C6                         | H <sub>5</sub> O <sub>7</sub> -H <sub>2</sub> O |                    |             |            |
| 13.120  | 11.510            | 20.475             | 7.820                                | 3.235   | 16.560             | -1.9715     |            |
| 13.090  | 12.030            | 22.994             | 6.930                                | 2.109   | 17.790             | -1.9228     | 1.0771     |
| 13.540  | 12.510            | 24.760             | 6.370                                | 1.097   | 19.440             | -1.8102     | -1.8001    |
| 13.780  | 13.040            | 26.486             | 5.880                                | 0.670   | 20.550             | -1.7597     |            |

| The data of tie lines in mass fractions for PEG-K <sub>2</sub> HPG | PO <sub>4</sub> ATPS at 298.15 K <sup><i>a</i></sup> and 101.325 kPa <sup>4</sup> |
|--|---|
|--|---|

| The data of       | tie lines in n    | nass fractions     | for PEG-K <sub>2</sub> H | PO <sub>4</sub> ATPS at           | 298.15 K <sup>a</sup> | and 101.325 | kPa <sup>a</sup> . |
|-------------------|-------------------|--------------------|--------------------------|-----------------------------------|-----------------------|-------------|--------------------|
| Total s           | ystem             | Polymer            | rich phase               | Salt ric                          | h phase               |             | average            |
| 100w <sub>1</sub> | 100w <sub>2</sub> | 100w1 <sup>t</sup> | 100w2 <sup>t</sup>       | 100w1 <sup>b</sup>                | 100w2 <sup>b</sup>    | – Slope (к) | of slope           |
|                   |                   |                    | PEG400-K <sub>2</sub> H  | PO <sub>4</sub> -H <sub>2</sub> O |                       |             |                    |
| 16.172            | 16.691            | 28.642             | 7.380                    | 1.700                             | 27.700                | -1.3256     |                    |
| 15.318            | 18.056            | 30.680             | 6.480                    | 1.260                             | 28.850                | -1.3482     | 1 2040             |
| 17.038            | 18.385            | 32.720             | 5.710                    | 0.514                             | 31.990                | -1.2253     | -1.2848            |
| 16.400            | 19.530            | 33.312             | 5.510                    | 0.366                             | 33.070                | -1.2399     |                    |
|                   |                   |                    | PEG1000-K <sub>2</sub> H | PO <sub>4</sub> -H <sub>2</sub> O |                       |             |                    |
| 10.813            | 15.022            | 25.636             | 6.770                    | 0.682                             | 20.770                | -1.7834     |                    |
| 11.540            | 15.721            | 28.409             | 5.850                    | 0.289                             | 22.420                | -1.6979     | 1 ( 40(            |
| 12.440            | 16.230            | 29.985             | 5.400                    | 0.170                             | 23.970                | -1.6064     | -1.0490            |
| 12.740            | 17.290            | 31.364             | 5.050                    | 0.0355                            | 25.80                 | -1.5107     |                    |
|                   |                   |                    | PEG2000-K <sub>2</sub> H | PO <sub>4</sub> -H <sub>2</sub> O |                       |             |                    |
| 10.000            | 12.346            | 24.755             | 4.440                    | 0.610                             | 17.470                | -1.9079     |                    |
| 12.720            | 18.890            | 30.077             | 3.500                    | 0.250                             | 19.770                | -1.9588     | 1.0250             |
| 14.380            | 13.170            | 33.249             | 3.010                    | 0.152                             | 20.980                | -1.9215     | -1.9359            |
| 16.342            | 13.592            | 38.230             | 2.330                    | 0.094                             | 22.100                | -1.9557     |                    |
|                   |                   |                    | PEG4000-K <sub>2</sub> H | PO <sub>4</sub> -H <sub>2</sub> O |                       |             |                    |
| 5.694             | 9.600             | 13.111             | 4.090                    | 0.795                             | 13.300                | -1.3379     |                    |
| 5.815             | 10.000            | 14.639             | 3.530                    | 0.529                             | 13.940                | -1.3562     | 1 2622             |
| 6.132             | 10.980            | 17.591             | 2.830                    | 0.201                             | 15.280                | -1.3980     | -1.3032            |
| 6.024             | 11.870            | 18.609             | 2.660                    | 0.088                             | 16.280                | -1.3608     |                    |

Values of parameters of Equations (14) and (15) for the PEG-K<sub>2</sub>HPO<sub>4</sub>/K<sub>3</sub>C<sub>6</sub>H<sub>5</sub>O<sub>7</sub>/(NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> ATPSs at 298.15 K<sup>*a*</sup> and 101.325 kPa<sup>*a*</sup>.

| T/K     | $k_{I}$ | п      | <i>k</i> <sub>2</sub> | r   | $R_1^2$ | $R_2^2$ | $\mathrm{sd}_1^{\alpha}$ | $\mathrm{sd}_2^{\alpha}$ |
|---------|---------|--------|-----------------------|---|---------|---------|--------------------------|--------------------------|
|         |         |        | PEG-                  | (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> A | TPS     |         |                          |                          |
| PEG400  | 0.8030  | 1.0934 | 1.2255                | 0.9686  | 0.954   | 0.996   | 0.6391                   | 0.2494                   |
| PEG1000 | 1.0623  | 0.6462 | 1.0108                | 1.3912  | 0.8712  | 0.8774  | 0.8199                   | 0.2908                   |
| PEG2000 | 0.7932  | 0.9714 | 1.3336                | 0.9513  | 0.9773  | 0.9713  | 0.4951                   | 0.2554                   |
| PEG4000 | 0.3274  | 1.9816 | 1.7743                | 0.4840  | 0.9679  | 0.9614  | 0.2266                   | 0.8656                   |
|         |         |        | PEG-                  | $K_3C_6H_5O_7A^{\prime\prime}$                    | TPS     |         |                          |                          |
| PEG400  | 0.6990  | 2.0799 | 1.1802                | 0.3194  | 0.9529  | 0.9650  | 0.6442                   | 0.2705                   |
| PEG1000 | 1.2299  | 1.0699 | 1.3213                | 0.7608  | 0.9052  | 0.9133  | 0.6190                   | 0.2806                   |
| PEG2000 | 1.0898  | 0.6566 | 0.9739                | 1.4094  | 0.9853  | 0.9799  | 0.7853                   | 0.2906                   |
| PEG4000 | 0.7611  | 1.2179 | 1.3201                | 0.7569  | 0.9829  | 0.9799  | 0.6909                   | 0.3191                   |
|         |         |        | PEG                   | -K <sub>2</sub> HPO <sub>4</sub> AT               | 'PS     |         |                          |                          |
| PEG400  | 1.0521  | 0.8055 | 0.9882                | 1.2229  | 0.9504  | 0.9488  | 0.9905                   | 0.3139                   |
| PEG1000 | 0.8867  | 0.9870 | 1.1678                | 1.0196  | 0.9658  | 0.9658  | 0.7303                   | 0.2833                   |
| PEG2000 | 0.4006  | 2.0864 | 1.5653                | 0.4764  | 0.9794  | 0.9805  | 0.4698                   | 0.6622                   |
| PEG4000 | 0.5265  | 1.7859 | 1.4566                | 0.5468  | 0.9755  | 0.9743  | 0.9102                   | 0.5419                   |

<sup>a</sup>  $sd = \left[\sum_{i=1}^{N} \left( \left( w_{i,j,cal}^{top} - w_{i,j,exp}^{top} \right)^2 + \left( w_{i,j,cal}^{bot} - w_{i,j,exp}^{bot} \right)^2 \right) / 2N \right]^{0.5}$ , where N is the number of tie lines and j = 1 and j = 2, sd<sub>1</sub> and sd<sub>2</sub> represent the mass percent standard deviations for PEG and salt, respectively.

Extraction efficiencies of nine model compounds by PEG (0.18, w/w)-(NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> ATPE.

|                   |                | E(%) <sup>a</sup> | E(%) <sup>b</sup> | E(%) <sup>b</sup> | E(%) <sup>b</sup> |
|-------------------|----------------|-------------------|-------------------|-------------------|-------------------|-------------------|-------------------|-------------------|-------------------|-------------------|
| W <sub>salt</sub> | WPEG=0.18      | HRP               | BSA               | CYT               | ANT               | CAR               | CHL               | ASP               | FRU               | PUP               |
|                   | DEC4000        | 81.68             | 75.05             | 72.60             | 85.74             | 73.32             | 94.06             | 82.61             | 85.17             | 84.04             |
|                   | PEG4000        | $\pm 0.03$        | $\pm 0.06$        | $\pm 0.09$        | $\pm 0.09$        | $\pm 0.06$        | $\pm 0.10$        | $\pm 0.01$        | $\pm 0.11$        | $\pm 0.08$        |
|                   | DEC2000        | 71.25             | 70.06             | 58.40             | 74.29             | 70.37             | 76.12             | 73.32             | 77.17             | 74.71             |
| 0.10              | PEG2000        | $\pm 0.08$        | $\pm 0.09$        | $\pm 0.13$        | $\pm 0.14$        | $\pm 0.09$        | $\pm 0.06$        | $\pm 0.08$        | $\pm 0.06$        | $\pm 0.02$        |
| 0.18              | <b>DEC1000</b> | 70.78             | 68.28             | 57.33             | 72.37             | 69.53             | 68.90             | 62.87             | 73.42             | 70.38             |
|                   | PEG1000        | ±0.06             | $\pm 0.09$        | $\pm 0.07$        | $\pm 0.13$        | $\pm 0.03$        | $\pm 0.09$        | $\pm 0.08$        | $\pm 0.05$        | $\pm 0.01$        |
|                   | <b>DEC 400</b> | 64.33             | 65.24             | 57.07             | 70.16             | 61.49             | 67.13             | 61.11             | 72.80             | 68.52             |
| PEG400            | PEG400         | $\pm 0.07$        | $\pm 0.02$        | $\pm 0.11$        | $\pm 0.01$        | $\pm 0.09$        | $\pm 0.07$        | $\pm 0.02$        | $\pm 0.14$        | $\pm 0.14$        |
|                   | DEC 4000       | 79.05             | 74.93             | 74.14             | 82.49             | 67.85             | 93.70             | 83.72             | 84.83             | 85.95             |
| PEG40<br>PEG20    | PEG4000        | $\pm 0.11$        | $\pm 0.01$        | $\pm 0.07$        | $\pm 0.05$        | $\pm 0.08$        | $\pm 0.12$        | $\pm 0.05$        | $\pm 0.10$        | $\pm 0.05$        |
|                   | DEC2000        | 63.50             | 69.70             | 60.27             | 73.44             | 61.35             | 60.95             | 71.18             | 78.86             | 69.04             |
|                   | PEG2000        | $\pm 0.04$        | $\pm 0.06$        | $\pm 0.02$        | $\pm 0.14$        | $\pm 0.13$        | $\pm 0.07$        | $\pm 0.07$        | $\pm 0.08$        | $\pm 0.14$        |
| 0.19              | <b>DEC1000</b> | 57.80             | 66.29             | 63.18             | 71.36             | 60.81             | 61.84             | 65.53             | 75.34             | 67.29             |
|                   | PEGI000        | $\pm 0.06$        | $\pm 0.14$        | $\pm 0.07$        | $\pm 0.05$        | $\pm 0.03$        | $\pm 0.06$        | $\pm 0.03$        | $\pm 0.14$        | $\pm 0.03$        |
|                   | DEC 400        | 56.88             | 64.08             | 57.00             | 69.07             | 55.42             | 66.99             | 60.91             | 71.22             | 65.37             |
|                   | PEG400         | $\pm 0.09$        | $\pm 0.11$        | $\pm 0.02$        | $\pm 0.01$        | $\pm 0.14$        | $\pm 0.11$        | $\pm 0.16$        | $\pm 0.03$        | $\pm 0.06$        |
|                   | DEC 4000       | 77.27             | 82.77             | 71.57             | 85.06             | 78.65             | 92.74             | 81.19             | 87.05             | 84.83             |
|                   | PEG4000        | $\pm 0.09$        | $\pm 0.06$        | $\pm 0.07$        | $\pm 0.05$        | $\pm 0.10$        | $\pm 0.08$        | $\pm 0.07$        | $\pm 0.13$        | $\pm 0.01$        |
|                   | DEC2000        | 61.60             | 71.54             | 67.20             | 81.29             | 70.92             | 86.13             | 70.10             | 80.47             | 70.56             |
| 0.20              | PEG2000        | $\pm 0.06$        | $\pm 0.04$        | $\pm 0.01$        | $\pm 0.11$        | $\pm 0.14$        | $\pm 0.15$        | $\pm 0.02$        | $\pm 0.02$        | $\pm 0.14$        |
| 0.20              | <b>DEC1000</b> | 68.28             | 68.87             | 67.80             | 75.14             | 68.36             | 77.74             | 59.45             | 77.61             | 66.37             |
|                   | PEGI000        | $\pm 0.08$        | $\pm 0.06$        | $\pm 0.02$        | $\pm 0.03$        | $\pm 0.01$        | $\pm 0.14$        | $\pm 0.03$        | $\pm 0.11$        | $\pm 0.04$        |
|                   | <b>PEC400</b>  | 53.52             | 61.56             | 64.46             | 70.25             | 65.40             | 61.84             | 61.11             | 73.65             | 63.98             |
|                   | 1 E0400        | $\pm 0.06$        | $\pm 0.13$        | $\pm 0.04$        | $\pm 0.09$        | $\pm 0.05$        | $\pm 0.14$        | $\pm 0.13$        | $\pm 0.03$        | $\pm 0.11$        |

Table S13

| Extraction efficiencies of nine model compounds by PEG $(0.20, w/w)$ - $(NH_4)_2SO_4$ A I | PE. |
|---|-----|
|---|-----|

|                                       |                 | E(%) <sup>a</sup> | E(%) <sup>b</sup> | E(%) <sup>b</sup> | E(%) <sup>b</sup> |
|---------------------------------------|-----------------|-------------------|-------------------|-------------------|-------------------|-------------------|-------------------|-------------------|-------------------|-------------------|
| Wsalt                                 | WPEG=0.20       | HRP               | BSA               | CYT               | ANT               | CAR               | CHL               | ASP               | FRU               | PUP               |
|                                       | DEC 4000        | 85.41             | 86.35             | 82.94             | 85.92             | 82.22             | 96.60             | 84.03             | 87.74             | 86.65             |
|                                       | PEG4000         | $\pm 0.11$        | $\pm 0.08$        | $\pm 0.05$        | ±0.11             | ±0.04             | ±0.06             | ±0.06             | $\pm 0.10$        | $\pm 0.04$        |
|                                       | <b>DEC2</b> 000 | 68.28             | 75.36             | 66.90             | 75.21             | 77.18             | 81.27             | 67.6              | 83.52             | 84.28             |
| 0.10                                  | PEG2000         | $\pm 0.06$        | $\pm 0.07$        | $\pm 0.01$        | ±0.09             | ±0.02             | ±0.13             | ±0.13             | ±0.06             | ±0.15             |
| 0.18                                  | DEC1000         | 70.3              | 72.39             | 62.05             | 73.35             | 73.16             | 74.65             | 67.09             | 79.21             | 73.46             |
|                                       | PEGI000         | $\pm 0.04$        | ±0.15             | ±0.11             | ±0.18             | ±0.04             | ±0.17             | ±0.13             | ±0.18             | ±0.15             |
|                                       | DEC 400         | 57                | 62.39             | 61.53             | 69.24             | 70.09             | 53.59             | 58.25             | 77.45             | 69.56             |
|                                       | PEG400          | ±0.06             | $\pm 0.11$        | ±0.06             | ±0.03             | ±0.05             | ±0.03             | ±0.09             | ±0.04             | ±0.07             |
|                                       | DEC 4000        | 82.45             | 84.25             | 82.65             | 86.67             | 86.37             | 93.69             | 86.02             | 87.82             | 86.77             |
| PEG20<br>0.19                         | PEG4000         | $\pm 0.06$        | $\pm 0.03$        | $\pm 0.08$        | $\pm 0.08$        | ±0.01             | ±0.06             | ±0.04             | $\pm 0.05$        | $\pm 0.07$        |
|                                       | DEC 2000        | 77.39             | 74.06             | 79.02             | 79.89             | 72.85             | 88.63             | 69.67             | 81.74             | 80.46             |
|                                       | PEG2000         | $\pm 0.02$        | ±0.06             | $\pm 0.05$        | ±0.06             | ±0.14             | ±0.03             | ±0.09             | ±0.07             | $\pm 0.02$        |
|                                       | DEC1000         | 60.6              | 70.29             | 76.45             | 77.12             | 71.54             | 54.48             | 61.01             | 78.69             | 77.45             |
|                                       | PEGI000         | $\pm 0.08$        | $\pm 0.04$        | ±0.03             | $\pm 0.02$        | $\pm 0.02$        | ±0.06             | $\pm 0.08$        | ±0.09             | ±0.06             |
|                                       | <b>DEC400</b>   | 53.33             | 67.34             | 75.73             | 76.25             | 60.49             | 76.27             | 57.94             | 76.10             | 73.56             |
| I<br>P<br>0.19<br>P<br>I<br>P<br>0.20 | FEO400          | $\pm 0.07$        | $\pm 0.09$        | $\pm 0.08$        | ±0.01             | $\pm 0.09$        | ±0.06             | $\pm 0.08$        | ±0.06             | ±0.02             |
|                                       | <b>DEC4000</b>  | 81.08             | 82.96             | 82.20             | 86.74             | 82.5              | 91.23             | 85.65             | 89.42             | 87.74             |
|                                       | FE04000         | $\pm 0.05$        | $\pm 0.05$        | $\pm 0.11$        | ±0.07             | ±0.10             | ±0.09             | ±0.13             | $\pm 0.12$        | $\pm 0.09$        |
|                                       | DEC 2000        | 62.05             | 71.67             | 65.7              | 80.01             | 70.83             | 90.69             | 64.64             | 81.52             | 79.46             |
| 0.20                                  | 1 E02000        | ±0.06             | ±0.03             | $\pm 0.05$        | ±0.06             | ±0.13             | ±0.15             | ±0.06             | ±0.18             | ±0.18             |
| 0.20                                  | PEG1000         | 58.08             | 65.45             | 61.48             | 78.25             | 65.23             | 82.45             | 67.79             | 76.89             | 72.67             |
|                                       | 1 EQ1000        | $\pm 0.04$        | ±0.06             | $\pm 0.11$        | ±0.12             | ±0.11             | ±0.18             | ±0.06             | ±0.17             | ±0.06             |
|                                       | <b>DEC400</b>   | 60                | 60.35             | 60.29             | 73.56             | 60.14             | 70.82             | 60.67             | 74.32             | 70.35             |
|                                       | 1 EU400         | $\pm 0.11$        | $\pm 0.07$        | $\pm 0.08$        | ±0.09             | $\pm 0.06$        | ±0.02             | $\pm 0.06$        | ±0.01             | ±0.09             |

Extraction efficiencies of nine model compounds by PEG (0.22, w/w)-(NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> ATPE.

| 14              | E(%) <sup>a</sup>  | E(%) <sup>a</sup>   | E(%) <sup>a</sup>  | E(%) <sup>a</sup>  | E(%) <sup>a</sup>   | E(%) <sup>a</sup>  | E(%) <sup>b</sup>   | E(%) <sup>b</sup>                                      | E(%) <sup>b</sup>  |
|-----------------|--|---|--|--|---|--|---|--|--|
| WPEG=0.22       | HRP  | BSA   | CYT  | ANT  | CAR   | CHL  | ASP   | FRU  | PUP  |
| DEC 4000        | 84.79  | 88.87   | 83.25  | 84.67  | 82.22   | 93.37  | 80.80   | 87.21  | 83.39  |
| PE04000         | $\pm 0.12$   | $\pm 0.06$  | $\pm 0.05$   | $\pm 0.11$   | $\pm 0.14$  | $\pm 0.10$   | $\pm 0.04$  | $\pm 0.05$   | $\pm 0.08$   |
| <b>DEC2</b> 000 | 70.46  | 65.54   | 71.10  | 74.35  | 76.57   | 90.11  | 63.1  | 80.47  | 78.29  |
| PEG2000         | $\pm 0.07$   | $\pm 0.06$  | $\pm 0.07$   | $\pm 0.07$   | $\pm 0.02$  | $\pm 0.07$   | ±0.07   | $\pm 0.07$   | ±0.07  |
| DEC1000         | 71.57  | 64.35   | 70.05  | 72.30  | 70.98   | 70.67  | 68.37   | 77.13  | 73.97  |
| PEGI000         | ±0.07  | $\pm 0.01$  | ±0.07  | $\pm 0.03$   | ±0.07   | ±0.07  | ±0.07   | ±0.07  | ±0.07  |
| DEC 400         | 60.55  | 60.35   | 67.43  | 70.29  | 67.43   | 69.64  | 55.08   | 75.80  | 67.45  |
| PEG400          | ±0.07  | ±0.07   | $\pm 0.13$   | $\pm 0.09$   | ±0.07   | $\pm 0.14$   | ±0.07   | ±0.07  | ±0.07  |
| DEC 4000        | 82.50  | 89.24   | 83.60  | 83.11  | 84.10   | 91.23  | 83.39   | 87.02  | 84.03  |
| PEG4000         | $\pm 0.05$   | $\pm 0.12$  | $\pm 0.12$   | $\pm 0.06$   | $\pm 0.04$  | $\pm 0.06$   | ±0.12   | $\pm 0.12$   | ±0.09  |
| DEC2000         | 69.30  | 67.79   | 72.33  | 79.73  | 80.57   | 64.93  | 68.64   | 81.94  | 78.45  |
| PEG2000         | ±0.07  | $\pm 0.05$  | ±0.07  | $\pm 0.11$   | ±0.07   | ±0.07  | ±0.07   | ±0.07  | ±0.02  |
| DEC1000         | 52.50  | 65.30   | 67.77  | 74.27  | 73.05   | 70.81  | 62.28   | 76.20  | 72.77  |
| PEGI000         | ±0.07  | $\pm 0.01$  | ±0.07  | $\pm 0.03$   | ±0.07   | ±0.07  | ±0.07   | ±0.07  | ±0.07  |
| DEC 400         | 57.74  | 63.49   | 66.43  | 71.19  | 71.49   | 66.4   | 56.7  | 73.08  | 69.35  |
| PEG400          | ±0.07  | ±0.07   | ±0.07  | ±0.07  | ±0.07   | ±0.07  | ±0.07   | ±0.07  | ±0.07  |
| DEC 4000        | 81.60  | 82.53   | 77.58  | 83.65  | 77.77   | 94.06  | 81.76   | 86.02  | 83.03  |
| PE04000         | $\pm 0.12$   | $\pm 0.12$  | $\pm 0.08$   | $\pm 0.12$   | $\pm 0.08$  | $\pm 0.09$   | ±0.01   | $\pm 0.05$   | ±0.12  |
| DEC 2000        | 64.60  | 65.47   | 66.18  | 80.41  | 75.92   | 74.5   | 67.6  | 80.63  | 76.12  |
| PEG2000         | ±0.07  | $\pm 0.05$  | $\pm 0.04$   | ±0.07  | ±0.07   | ±0.07  | ±0.07   | ±0.07  | ±0.07  |
| DEC1000         | 61.80  | 62.38   | 64.75  | 78.23  | 73.62   | 74.2   | 66.74   | 75.75  | 75.38  |
| FEGIUUU         | ±0.05  | ±0.06   | $\pm 0.11$   | $\pm 0.07$   | ±0.02   | $\pm 0.06$   | ±0.04   | $\pm 0.09$   | ±0.07  |
| DEC400          | 55.00  | 60.22   | 62.30  | 75.90  | 70.93   | 70.67  | 55.82   | 72.44  | 70.45  |
| r£0400          | $\pm 0.02$   | ±0.07   | $\pm 0.04$   | $\pm 0.03$   | $\pm 0.02$  | $\pm 0.13$   | ±0.07   | ±0.06  | ±0.08  |
|                 | WPEG=0.22           PEG4000           PEG2000           PEG400           PEG400           PEG400           PEG2000           PEG400           PEG2000           PEG2000           PEG2000           PEG1000           PEG1000           PEG400           PEG400           PEG400           PEG400           PEG400           PEG400           PEG400           PEG400           PEG400 | WPEG=0.22E(%)*<br>HRP $WPEG=0.22$ 84.79<br>± 0.12 $PEG4000$ $20.44$<br>± 0.07 $PEG1000$ $71.57$<br>± 0.07 $PEG1000$ $60.55$<br>± 0.07 $PEG4000$ $82.50$<br>± 0.07 $PEG4000$ $69.30$<br>± 0.07 $PEG2000$ $69.30$<br>± 0.07 $PEG1000$ $52.50$<br>± 0.07 $PEG4000$ $57.74$<br>± 0.07 $PEG4000$ $57.74$<br>± 0.07 $PEG4000$ $61.60$<br>± 0.12 $PEG4000$ $61.60$<br>± 0.07 $PEG10000$ $61.80$<br>± 0.05 $PEG10000$ $55.00$<br>± 0.05 $PEG4000$ $55.00$ | $W_{PEG=0.22}$ E(%)aE(%)a $W_{PEG=0.22}$ HRPBSA $PEG4000$ $\& 4.79$ $\& 88.87$ $\mu EG2000$ $2 0.01$ $\pm 0.02$ $PEG2000$ $70.46$ $65.54$ $\mu EG2000$ $71.57$ $64.35$ $PEG1000$ $\pm 0.07$ $\pm 0.01$ $PEG4000$ $a0.77$ $\pm 0.07$ $PEG4000$ $a0.77$ $\pm 0.07$ $PEG4000$ $69.30$ $67.79$ $PEG2000$ $69.30$ $67.79$ $PEG1000$ $52.50$ $65.30$ $PEG1000$ $57.74$ $63.49$ $PEG4000$ $57.74$ $63.49$ $PEG4000$ $\$0.07$ $\pm 0.01$ $PEG4000$ $\$1.60$ $\$2.53$ $\mu EG4000$ $\& 1.60$ $\& 2.53$ $\mu EG4000$ $\& 1.60$ $\& 2.53$ $\mu EG1000$ $\& 1.60$ $\pounds 0.05$ $\mu EG1000$ $\& 1.80$ $\& 2.38$ $\mu EG4000$ $\& 55.00$ $\boxdot 0.02$ $\mu EG4000$ $\& 55.00$ $a0.22$ $\mu EG4000$ $a0.74$ $a0.74$ $\mu EG1000$ $a0.75$ $a0.76$ $\mu EG4000$ $a0.75$ $a0.76$ < | $W_{PEG=0.22}$ $E(\%)^a$ $E(\%)^a$ $E(\%)^a$ $PEG4000$ $84.79$ $88.87$ $83.25$ $\pm 0.12$ $\pm 0.06$ $\pm 0.05$ $\pm 0.12$ $\pm 0.06$ $\pm 0.07$ $PEG2000$ $\pm 0.07$ $\pm 0.06$ $\pm 0.07$ $PEG1000$ $\pm 0.07$ $\pm 0.06$ $\pm 0.07$ $PEG1000$ $\pm 0.07$ $\pm 0.01$ $\pm 0.07$ $PEG4000$ $\pm 0.07$ $\pm 0.01$ $\pm 0.07$ $PEG4000$ $82.50$ $89.24$ $83.60$ $\pm 0.05$ $\pm 0.12$ $\pm 0.12$ $PEG4000$ $\pm 0.05$ $\pm 0.12$ $\pm 0.12$ $PEG1000$ $52.50$ $65.30$ $67.77$ $PEG1000$ $52.50$ $65.30$ $67.77$ $PEG400$ $57.74$ $63.49$ $66.43$ $\pm 0.07$ $\pm 0.07$ $\pm 0.07$ $\pm 0.07$ $PEG4000$ $81.60$ $82.53$ $77.58$ $\pm 0.12$ $\pm 0.12$ $\pm 0.08$ $\pm 0.04$ $PEG2000$ $64.60$ $65.47$ $66.18$ $\pm 0.07$ $\pm 0.05$ $\pm 0.04$ $\pm 0.05$ $\pm 0.12$ $\pm 0.05$ $\pm 0.04$ $\pm 0.04$ $PEG1000$ $61.80$ $62.38$ $64.75$ $\pm 0.02$ $\pm 0.06$ $\pm 0.01$ $\pm 0.01$ $\pm 0.02$ | $W_{PEG=0.22}$ $E(\%)^a$ $E(\%)^a$ $E(\%)^a$ $E(\%)^a$ $HRP$ BSA $CYT$ ANT $PEG4000$ $\pm 0.12$ $\pm 0.06$ $\pm 0.05$ $\pm 0.11$ $\mu CG2000$ $\pm 0.12$ $\pm 0.06$ $\pm 0.07$ $\pm 0.07$ $\mu CG2000$ $\pm 0.07$ $\pm 0.06$ $\pm 0.07$ $\pm 0.07$ $\mu CG2000$ $\pm 0.07$ $\pm 0.06$ $\pm 0.07$ $\pm 0.07$ $\mu CG2000$ $\pi 1.57$ $64.35$ $70.05$ $72.30$ $\mu CG1000$ $\pm 0.07$ $\pm 0.01$ $\pm 0.07$ $\pm 0.07$ $\mu CG4001$ $\pm 0.07$ $\pm 0.01$ $\pm 0.07$ $\pm 0.13$ $\mu CG4000$ $82.50$ $89.24$ $83.60$ $83.11$ $\mu CG2000$ $69.30$ $67.79$ $72.33$ $79.73$ $\mu CG1000$ $\pm 0.07$ $\pm 0.05$ $\pm 0.07$ $\pm 0.07$ $\mu CG1000$ $52.50$ $65.30$ $67.77$ $74.27$ $\mu CG4001$ $\pm 0.07$ $\pm 0.07$ $\pm 0.07$ $\pm 0.07$ $\mu CG4001$ $\pm 0.07$ $\pm 0.07$ $\pm 0.07$ $\pm 0.07$ $\mu CG4000$ $61.80$ $82.53$ $77.58$ $83.65$ $\mu CO17$ $\pm 0.12$ $\pm 0.04$ $\pm 0.07$ $\mu CG20001$ $61.80$ $62.38$ $64.75$ $78.23$ $\mu CG1000$ $61.80$ $62.38$ $64.75$ $78.23$ $\mu CG4001$ $\pm 0.07$ $\pm 0.06$ $\pm 0.11$ $\pm 0.07$ $\mu CG4001$ $\pm 0.02$ $\pm 0.07$ $\pm 0.04$ $\pm 0.07$ $\mu CG4001$ $\pm 0.02$ $\pm 0.07$ $\pm 0.04$ $\pm 0.07$ <td><math>W_{PEG=0.22}</math>         E(%)<sup>a</sup>         E(%)<sup>a</sup>         E(%)<sup>a</sup>         E(%)<sup>a</sup>         E(%)<sup>a</sup>           HRP         BSA         CYT         ANT         CAR           PEG4000         ± 0.12         ± 0.06         ± 0.05         ± 0.11         ± 0.14           PEG2000         ± 0.12         ± 0.06         ± 0.07         ± 0.11         ± 0.14           PEG2000         ± 0.07         ± 0.06         ± 0.07         ± 0.07         ± 0.02           PEG1000         ± 0.07         ± 0.01         ± 0.07         ± 0.03         ± 0.07           PEG4000         ± 0.07         ± 0.01         ± 0.07         ± 0.03         ± 0.07           PEG4000         ± 0.07         ± 0.01         ± 0.07         ± 0.03         ± 0.07           PEG4000         ± 0.07         ± 0.07         ± 0.13         ± 0.09         ± 0.07           PEG4000         ± 0.05         ± 0.12         ± 0.12         ± 0.06         ± 0.04           PEG2000         £ 0.05         ± 0.12         ± 0.06         ± 0.04         ± 0.07           PEG1000         £ 0.07         ± 0.05         ± 0.07         ± 0.07         ± 0.07         ± 0.07           PEG4001         £ 0.12         ± 0.07<td><math>W_{PEG=0.22}</math>         E(%)<sup>a</sup>         E(%)<sup>a</sup>         E(%)<sup>a</sup>         E(%)<sup>a</sup>         E(%)<sup>a</sup>         E(%)<sup>a</sup>           PEG4000         <math>84.79</math>         88.87         83.25         84.67         82.22         93.37           <math>\pm 0.12</math> <math>\pm 0.06</math> <math>\pm 0.05</math> <math>\pm 0.11</math> <math>\pm 0.14</math> <math>\pm 0.10</math>           PEG2000         <math>70.46</math> <math>65.54</math> <math>71.10</math> <math>74.35</math> <math>76.57</math> <math>90.11</math> <math>\pm 0.07</math> <math>\pm 0.06</math> <math>\pm 0.07</math> <math>\pm 0.02</math> <math>\pm 0.07</math> <math>PEG2000</math> <math>71.57</math> <math>64.35</math> <math>70.57</math> <math>70.46</math> <math>65.54</math> <math>0.07</math> <math>\pm 0.01</math> <math>\pm 0.07</math> <math>\pm 0.02</math> <math>\pm 0.07</math> <math>\pm 0.07</math> <math>PEG1000</math> <math>71.57</math> <math>64.35</math> <math>70.57</math> <math>72.30</math> <math>70.98</math> <math>70.67</math> <math>PEG4000</math> <math>60.55</math> <math>60.35</math> <math>67.43</math> <math>70.29</math> <math>67.43</math> <math>69.64</math> <math>PEG4000</math> <math>82.50</math> <math>89.24</math> <math>83.60</math> <math>83.11</math> <math>84.10</math> <math>91.23</math> <math>pEG2000</math> <math>69.30</math> <math>67.79</math> <math>72.33</math> <math>79.73</math> <math>80.57</math> <math>64.93</math></td><td><math display="block">\begin{array}{ c c c c c c c c c c c c c c c c c c c</math></td><td><math>w_{PEG-0.22}</math> <math>E(\%)^a</math> <math>E(\%)^a</math></td></td> | $W_{PEG=0.22}$ E(%) <sup>a</sup> E(%) <sup>a</sup> E(%) <sup>a</sup> E(%) <sup>a</sup> E(%) <sup>a</sup> HRP         BSA         CYT         ANT         CAR           PEG4000         ± 0.12         ± 0.06         ± 0.05         ± 0.11         ± 0.14           PEG2000         ± 0.12         ± 0.06         ± 0.07         ± 0.11         ± 0.14           PEG2000         ± 0.07         ± 0.06         ± 0.07         ± 0.07         ± 0.02           PEG1000         ± 0.07         ± 0.01         ± 0.07         ± 0.03         ± 0.07           PEG4000         ± 0.07         ± 0.01         ± 0.07         ± 0.03         ± 0.07           PEG4000         ± 0.07         ± 0.01         ± 0.07         ± 0.03         ± 0.07           PEG4000         ± 0.07         ± 0.07         ± 0.13         ± 0.09         ± 0.07           PEG4000         ± 0.05         ± 0.12         ± 0.12         ± 0.06         ± 0.04           PEG2000         £ 0.05         ± 0.12         ± 0.06         ± 0.04         ± 0.07           PEG1000         £ 0.07         ± 0.05         ± 0.07         ± 0.07         ± 0.07         ± 0.07           PEG4001         £ 0.12         ± 0.07 <td><math>W_{PEG=0.22}</math>         E(%)<sup>a</sup>         E(%)<sup>a</sup>         E(%)<sup>a</sup>         E(%)<sup>a</sup>         E(%)<sup>a</sup>         E(%)<sup>a</sup>           PEG4000         <math>84.79</math>         88.87         83.25         84.67         82.22         93.37           <math>\pm 0.12</math> <math>\pm 0.06</math> <math>\pm 0.05</math> <math>\pm 0.11</math> <math>\pm 0.14</math> <math>\pm 0.10</math>           PEG2000         <math>70.46</math> <math>65.54</math> <math>71.10</math> <math>74.35</math> <math>76.57</math> <math>90.11</math> <math>\pm 0.07</math> <math>\pm 0.06</math> <math>\pm 0.07</math> <math>\pm 0.02</math> <math>\pm 0.07</math> <math>PEG2000</math> <math>71.57</math> <math>64.35</math> <math>70.57</math> <math>70.46</math> <math>65.54</math> <math>0.07</math> <math>\pm 0.01</math> <math>\pm 0.07</math> <math>\pm 0.02</math> <math>\pm 0.07</math> <math>\pm 0.07</math> <math>PEG1000</math> <math>71.57</math> <math>64.35</math> <math>70.57</math> <math>72.30</math> <math>70.98</math> <math>70.67</math> <math>PEG4000</math> <math>60.55</math> <math>60.35</math> <math>67.43</math> <math>70.29</math> <math>67.43</math> <math>69.64</math> <math>PEG4000</math> <math>82.50</math> <math>89.24</math> <math>83.60</math> <math>83.11</math> <math>84.10</math> <math>91.23</math> <math>pEG2000</math> <math>69.30</math> <math>67.79</math> <math>72.33</math> <math>79.73</math> <math>80.57</math> <math>64.93</math></td> <td><math display="block">\begin{array}{ c c c c c c c c c c c c c c c c c c c</math></td> <td><math>w_{PEG-0.22}</math> <math>E(\%)^a</math> <math>E(\%)^a</math></td> | $W_{PEG=0.22}$ E(%) <sup>a</sup> E(%) <sup>a</sup> E(%) <sup>a</sup> E(%) <sup>a</sup> E(%) <sup>a</sup> E(%) <sup>a</sup> PEG4000 $84.79$ 88.87         83.25         84.67         82.22         93.37 $\pm 0.12$ $\pm 0.06$ $\pm 0.05$ $\pm 0.11$ $\pm 0.14$ $\pm 0.10$ PEG2000 $70.46$ $65.54$ $71.10$ $74.35$ $76.57$ $90.11$ $\pm 0.07$ $\pm 0.06$ $\pm 0.07$ $\pm 0.02$ $\pm 0.07$ $PEG2000$ $71.57$ $64.35$ $70.57$ $70.46$ $65.54$ $0.07$ $\pm 0.01$ $\pm 0.07$ $\pm 0.02$ $\pm 0.07$ $\pm 0.07$ $PEG1000$ $71.57$ $64.35$ $70.57$ $72.30$ $70.98$ $70.67$ $PEG4000$ $60.55$ $60.35$ $67.43$ $70.29$ $67.43$ $69.64$ $PEG4000$ $82.50$ $89.24$ $83.60$ $83.11$ $84.10$ $91.23$ $pEG2000$ $69.30$ $67.79$ $72.33$ $79.73$ $80.57$ $64.93$ | $\begin{array}{ c c c c c c c c c c c c c c c c c c c$ | $w_{PEG-0.22}$ $E(\%)^a$ |

Extraction efficiencies of nine model compounds by PEG(0.18, w/w)-K<sub>2</sub>HPO<sub>4</sub> ATPE.

|                |                       | $E(\%)^a$  | E(%) <sup>a</sup> | E(%) <sup>a</sup> | $E(\%)^a$  | $E(\%)^a$  | E(%) <sup>a</sup> | E(%) <sup>b</sup> | E(%) <sup>b</sup> | E(%) <sup>b</sup> |
|----------------|-----------------------|------------|-------------------|-------------------|------------|------------|-------------------|-------------------|-------------------|-------------------|
| $w_{\rm salt}$ | $W_{\text{PEG}=0.18}$ | HRP        | BSA               | CYT               | ANT        | CAR        | CHL               | ASP               | FRU               | PUP               |
|                | DEC 4000              | 75.00      | 73.54             | 72.19             | 78.29      | 67.10      | 65.96             | 62.84             | 78.35             | 75.26             |
|                | PEG4000               | ±0.11      | ±0.16             | ±0.12             | $\pm 0.17$ | ±0.12      | ±0.03             | ±0.09             | ±0.05             | ±0.06             |
|                | DEC 2000              | 60.50      | 71.34             | 60.91             | 73.78      | 66.91      | 80.09             | 67.09             | 75.23             | 72.98             |
| 0.10           | PEG2000               | ±0.09      | ±0.09             | ±0.04             | ±0.09      | ±0.09      | ±0.09             | ±0.07             | ±0.09             | ±0.09             |
| 0.18           | <b>DEC1000</b>        | 64.2       | 67.59             | 58.85             | 71.24      | 68.34      | 77.74             | 64.49             | 73.87             | 67.45             |
| PE             | PEG1000               | ±0.02      | ±0.09             | ±0.05             | ±0.19      | ±0.01      | ±0.17             | ±0.03             | ±0.01             | ±0.14             |
|                | DEC 400               | 53.7       | 63.65             | 53.22             | 68.89      | 61.36      | 72.44             | 50.16             | 70.80             | 65.68             |
| PEG40          | PEG400                | ±0.06      | $\pm 0.08$        | ±0.02             | $\pm 0.13$ | ±0.06      | ±0.11             | ±0.04             | ±0.13             | ±0.09             |
|                | DEC 4000              | 74.48      | 73.67             | 71.75             | 79.35      | 65.18      | 63.16             | 71.67             | 77.18             | 70.17             |
|                | FE04000               | ±0.02      | ±0.06             | ±0.05             | $\pm 0.01$ | ±0.02      | ±0.01             | ±0.03             | ±0.05             | $\pm 0.08$        |
|                | DEC2000               | 52.67      | 70.27             | 61.60             | 73.92      | 59.72      | 72.88             | 65.10             | 75.09             | 71.27             |
| 0.10           | FEG2000               | ±0.03      | ±0.15             | ±0.11             | ±0.09      | ±0.02      | ±0.07             | ±0.02             | ±0.05             | ±0.07             |
| 0.19           | <b>DEC1000</b>        | 54.18      | 63.48             | 59.47             | 70.08      | 58.46      | 74.50             | 65.35             | 73.24             | 66.24             |
|                | PEGI000               | ±0.02      | ±0.03             | ±0.01             | ±0.09      | ±0.12      | $\pm 0.04$        | ±0.07             | $\pm 0.06$        | $\pm 0.02$        |
|                | DEC 400               | 45.62      | 63.19             | 52.43             | 65.72      | 57.87      | 68.90             | 57.04             | 69.87             | 62.63             |
|                | PEG400                | ±0.06      | ±0.02             | ±0.01             | ±0.12      | ±0.02      | ±0.03             | ±0.04             | ±0.07             | $\pm 0.08$        |
|                | DEC 4000              | 75.68      | 71.23             | 68.20             | 80.35      | 69.06      | 84.81             | 64.63             | 75.21             | 69.27             |
|                | FE04000               | $\pm 0.02$ | ±0.01             | ±0.14             | $\pm 0.09$ | $\pm 0.05$ | $\pm 0.05$        | ±0.07             | ±0.03             | ±0.07             |
|                | DEC2000               | 66.18      | 71.01             | 65.91             | 77.80      | 68.99      | 63.16             | 60.40             | 71.36             | 70.83             |
| 0.20           | FEG2000               | $\pm 0.02$ | ±0.11             | ±0.09             | ±0.09      | ±0.13      | $\pm 0.09$        | ±0.09             | $\pm 0.09$        | ±0.09             |
| 0.20           | DEC1000               | 63.18      | 66.49             | 62.90             | 74.23      | 67.98      | 72.73             | 58.24             | 68.90             | 64.35             |
|                | FEGIUUU               | ±0.06      | ±0.09             | ±0.04             | ±0.11      | ±0.12      | ±0.07             | ±0.02             | ±0.02             | ±0.06             |
|                | DEC400                | 39.38      | 62.38             | 60.43             | 70.67      | 64.70      | 67.14             | 59.72             | 64.11             | 61.62             |
|                | re0400                | ±0.01      | ±0.09             | ±0.09             | $\pm 0.04$ | $\pm 0.08$ | ±0.05             | ±0.03             | ±0.11             | ±0.05             |

Extraction efficiencies of nine model compounds by PEG(0.20, w/w)-K<sub>2</sub>HPO<sub>4</sub> ATPE.

|   |                | E(%) <sup>a</sup> | E(%) <sup>b</sup> | E(%) <sup>b</sup> | E(%) <sup>b</sup> |
|---|----------------|-------------------|-------------------|-------------------|-------------------|-------------------|-------------------|-------------------|-------------------|-------------------|
| wsait         wPEG=0.20           PEG4000         PEG2000           0.18         PEG1000           PEG400         PEG400           0.19         PEG2000           PEG400         PEG2000           0.19         PEG2000           PEG1000         PEG4000           PEG4000         PEG4000 | HRP            | BSA               | CYT               | ANT               | CAR               | CHL               | ASP               | FRU               | PUP               |                   |
|   | DEC4000        | 82.13             | 75.23             | 69.35             | 81.67             | 70.92             | 84.8              | 68.16             | 80.25             | 83.29             |
|   | re04000        | $\pm 0.01$        | $\pm 0.05$        | $\pm 0.11$        | $\pm 0.02$        | ±0.04             | ±0.02             | ±0.07             | ±0.05             | ±0.03             |
|   | DEC2000        | 60.57             | 73.24             | 66.30             | 74.89             | 70.14             | 79.51             | 64.82             | 78.00             | 80.67             |
| 0.10  | PEG2000        | $\pm 0.08$        | $\pm 0.11$        | $\pm 0.13$        | $\pm 0.08$        | $\pm 0.02$        | ±0.09             | ±0.07             | ±0.14             | ±0.11             |
| 0.18  | <b>DEC1000</b> | 69.55             | 70.89             | 64.46             | 71.23             | 70.03             | 66.25             | 62.59             | 76.21             | 71.45             |
|   | PEG1000        | $\pm 0.01$        | ±0.15             | $\pm 0.04$        | $\pm 0.08$        | ±0.07             | ±0.13             | ±0.07             | ±0.03             | ±0.07             |
|   | DEC 400        | 39.78             | 62.12             | 61.18             | 67.49             | 65.65             | 72.44             | 57.94             | 74.76             | 67.34             |
|   | PEG400         | ±0.11             | $\pm 0.11$        | $\pm 0.13$        | $\pm 0.14$        | ±0.05             | ±0.05             | ±0.13             | ±0.02             | $\pm 0.08$        |
|   | DEC 4000       | 78.33             | 72.39             | 78.50             | 79.53             | 74.78             | 87.60             | 69.89             | 78.62             | 78.23             |
|   | PEG4000        | $\pm 0.06$        | $\pm 0.04$        | $\pm 0.11$        | ±0.08             | $\pm 0.08$        | ±0.05             | ±0.07             | ±0.03             | ±0.12             |
| 0.10  | DEC2000        | 57.75             | 72.18             | 73.04             | 77.57             | 70.25             | 74.20             | 63.21             | 77.94             | 76.35             |
|   | PEG2000        | ±0.13             | $\pm 0.18$        | $\pm 0.11$        | $\pm 0.01$        | ±0.11             | $\pm 0.08$        | $\pm 0.02$        | $\pm 0.08$        | ±0.05             |
| 0.19  | DEC1000        | 60.9              | 69.18             | 70.23             | 75.03             | 69.49             | 81.27             | 61.29             | 73.29             | 74.39             |
|   | FEGI000        | ±0.09             | $\pm 0.02$        | $\pm 0.04$        | $\pm 0.07$        | ±0.05             | ±0.03             | $\pm 0.11$        | ±0.12             | ±0.09             |
|   | DEC 400        | 47.10             | 67.76             | 69.05             | 73.10             | 60.35             | 61.54             | 60.40             | 70.67             | 71.20             |
|   | FEO400         | $\pm 0.06$        | $\pm 0.11$        | $\pm 0.05$        | ±0.02             | ±0.03             | ±0.01             | $\pm 0.02$        | ±0.06             | ±0.09             |
|   | DEC4000        | 79.10             | 72.25             | 66.79             | 79.35             | 72.81             | 72.88             | 71.67             | 78.21             | 79.23             |
|   | FE04000        | ±0.09             | $\pm 0.02$        | $\pm 0.13$        | $\pm 0.01$        | ±0.07             | ±0.11             | ±0.03             | ±0.10             | ±0.03             |
|   | DEC2000        | 57.05             | 70.28             | 63.29             | 77.61             | 70.49             | 68.90             | 64.32             | 76.33             | 79.94             |
| 0.20  | PEG2000        | ±0.07             | $\pm 0.04$        | $\pm 0.07$        | ±0.02             | ±0.11             | ±0.03             | ±0.03             | ±0.02             | ±0.12             |
| 0.20  | DEC1000        | 58.04             | 63.29             | 63.18             | 75.88             | 64.87             | 64.78             | 63.46             | 74.26             | 71.50             |
|   | PEG1000        | $\pm 0.06$        | $\pm 0.07$        | $\pm 0.02$        | $\pm 0.13$        | $\pm 0.04$        | ±0.14             | $\pm 0.05$        | ±0.01             | ±0.12             |
|   | DEC400         | 39.67             | 60.19             | 61.40             | 74.82             | 58.92             | 68.90             | 55.82             | 71.39             | 68.46             |
|   | r EU400        | ±0.06             | $\pm 0.07$        | $\pm 0.08$        | ±0.02             | $\pm 0.11$        | ±0.02             | ±0.03             | ±0.01             | ±0.05             |

Extraction efficiencies of nine model compounds by PEG (0.22, w/w)-K<sub>2</sub>HPO<sub>4</sub> ATPE.

| 142 .   | 14/      | E(%) <sup>a</sup> | E(%) <sup>b</sup> | E(%) <sup>b</sup> | E(%) <sup>b</sup> |
|---|----------|-------------------|-------------------|-------------------|-------------------|-------------------|-------------------|-------------------|-------------------|-------------------|
| wsalt         wPEG=0.22           PEG4000           0.18           PEG1000           PEG400           PEG400           PEG400           PEG400           PEG400           PEG400           PEG400           PEG400           0.19           PEG400           PEG400           PEG400           PEG400           PEG400           PEG400           PEG400           PEG400           PEG400           PEG400 | HRP      | BSA               | CYT               | ANT               | CAR               | CHL               | ASP               | FRU               | PUP               |                   |
|   | DEC4000  | 68.25             | 67.29             | 72.80             | 78.23             | 72.88             | 90.11             | 70.73             | 79.62             | 78.19             |
|   | PEG4000  | $\pm 0.02$        | ±0.03             | ±0.05             | $\pm 0.02$        | $\pm 0.01$        | ±0.03             | ±0.05             | ±0.03             | $\pm 0.08$        |
|   | DEC2000  | 68.00             | 64.93             | 64.90             | 73.90             | 71.65             | 79.51             | 67.6              | 77.54             | 78.01             |
| 0.10  | PEG2000  | $\pm 0.07$        | ±0.05             | $\pm 0.13$        | $\pm 0.01$        | ±0.04             | ±0.09             | ±0.07             | ±0.02             | $\pm 0.08$        |
| 0.18  | DEC1000  | 61.05             | 60.04             | 63.12             | 71.11             | 68.43             | 67.73             | 66.35             | 76.94             | 72.57             |
|   | PEG1000  | $\pm 0.08$        | $\pm 0.03$        | ±0.05             | ±0.12             | ±0.05             | ±0.02             | ±0.06             | ±0.06             | ±0.07             |
|   | DEC 400  | 48.43             | 60.12             | 62.83             | 66.24             | 66.92             | 66.25             | 56.33             | 74.24             | 66.24             |
|   | PEG400   | ±0.11             | $\pm 0.03$        | ±0.05             | $\pm 0.08$        | $\pm 0.11$        | ±0.04             | ±0.05             | ±0.02             | $\pm 0.08$        |
|   | DEC 4000 | 73.45             | 68.27             | 73.78             | 77.47             | 76.58             | 81.71             | 72.60             | 78.50             | 72.38             |
|   | PEG4000  | $\pm 0.08$        | $\pm 0.01$        | $\pm 0.13$        | ±0.06             | ±0.05             | ±0.13             | ±0.02             | ±0.01             | $\pm 0.07$        |
|   | DEC2000  | 64.67             | 66.59             | 73.46             | 77.03             | 74.69             | 70.82             | 62.59             | 77.43             | 70.34             |
| 0.10  | PEG2000  | $\pm 0.06$        | ±0.05             | ±0.05             | ±0.13             | $\pm 0.03$        | ±0.04             | $\pm 0.14$        | ±0.03             | $\pm 0.08$        |
| 0.19  | DEC1000  | 54.78             | 65.40             | 69.88             | 73.55             | 72.54             | 77.73             | 63.55             | 74.69             | 71.02             |
|   | FEGI000  | $\pm 0.08$        | $\pm 0.02$        | ±0.15             | $\pm 0.11$        | $\pm 0.01$        | $\pm 0.05$        | ±0.04             | ±0.07             | $\pm 0.05$        |
|   | DEC400   | 47.78             | 63.13             | 67.09             | 70.23             | 70.93             | 79.51             | 55.47             | 70.71             | 67.35             |
|   | FE0400   | $\pm 0.06$        | ±0.05             | $\pm 0.13$        | $\pm 0.05$        | $\pm 0.07$        | $\pm 0.05$        | $\pm 0.03$        | ±0.09             | $\pm 0.07$        |
|   | DEC4000  | 75.54             | 68.48             | 78.85             | 75.92             | 70.84             | 84.81             | 70.26             | 68.63             | 71.23             |
|   | FE04000  | $\pm 0.08$        | ±0.06             | $\pm 0.01$        | $\pm 0.02$        | ±0.02             | $\pm 0.05$        | $\pm 0.08$        | ±0.05             | $\pm 0.07$        |
|   | DEC2000  | 60.90             | 61.21             | 67.25             | 73.64             | 68.88             | 74.20             | 66.57             | 66.85             | 70.27             |
| 0.20  | FEG2000  | $\pm 0.06$        | ±0.05             | $\pm 0.04$        | $\pm 0.08$        | $\pm 0.03$        | $\pm 0.04$        | ±0.07             | ±0.05             | $\pm 0.04$        |
| 0.20  | DEC1000  | 59.21             | 60.28             | 65.55             | 70.31             | 70.24             | 66.40             | 66.56             | 64.42             | 70.09             |
|   | I EG1000 | ±0.06             | $\pm 0.13$        | ±0.05             | ±0.05             | $\pm 0.11$        | $\pm 0.03$        | ±0.01             | ±0.07             | $\pm 0.02$        |
|   | PEG400   | 54.60             | 55.39             | 62.04             | 67.19             | 67.36             | 74.65             | 54.94             | 61.03             | 65.23             |
|   | 1 EG400  | ±0.09             | ±0.15             | ±0.01             | ±0.02             | $\pm 0.01$        | ±0.05             | $\pm 0.04$        | ±0.05             | $\pm 0.03$        |

Extraction efficiencies of nine model compounds by PEG (0.18, w/w)-K<sub>3</sub>C<sub>6</sub>H<sub>5</sub>O<sub>7</sub> ATPE.

|            |                | E(%) <sup>a</sup> | E(%) <sup>b</sup> | E(%) <sup>b</sup> | E(%) <sup>b</sup> |
|------------|----------------|-------------------|-------------------|-------------------|-------------------|-------------------|-------------------|-------------------|-------------------|-------------------|
| $w_{salt}$ | WPEG=0.18      | HRP               | BSA               | CYT               | ANT               | CAR               | CHL               | ASP               | FRU               | PUP               |
|            | DEC4000        | 73.15             | 70.93             | 70.67             | 73.28             | 65.49             | 77.50             | 67.09             | 75.32             | 70.49             |
|            | FE04000        | $\pm 0.05$        | ±0.05             | $\pm 0.08$        | $\pm 0.04$        | ±0.02             | ±0.03             | $\pm 0.08$        | ±0.11             | ±0.15             |
|            | DEC2000        | 70.11             | 66.45             | 66.05             | 70.26             | 63.18             | 64.58             | 67.36             | 71.66             | 61.28             |
| 0.10       | PEG2000        | ±0.06             | ±0.05             | $\pm 0.01$        | ±0.07             | $\pm 0.08$        | $\pm 0.05$        | $\pm 0.04$        | $\pm 0.07$        | ±0.13             |
| 0.18       | DEC1000        | 59.33             | 61.65             | 58.23             | 66.98             | 62.39             | 76.27             | 64.32             | 67.39             | 55.87             |
|            | PEG1000        | ±0.05             | ±0.03             | $\pm 0.08$        | ±0.04             | ±0.09             | $\pm 0.06$        | $\pm 0.08$        | ±0.02             | $\pm 0.11$        |
|            | DEC 400        | 47.60             | 63.25             | 57.34             | 61.02             | 58.23             | 63.60             | 50.86             | 64.24             | 53.41             |
|            | PEG400         | $\pm 0.02$        | ±0.07             | $\pm 0.13$        | $\pm 0.08$        | ±0.03             | $\pm 0.02$        | $\pm 0.11$        | $\pm 0.08$        | ±0.05             |
|            | DEC 4000       | 65.80             | 70.56             | 71.33             | 74.35             | 64.27             | 64.05             | 66.43             | 76.80             | 65.29             |
|            | PEG4000        | $\pm 0.02$        | ±0.05             | $\pm 0.01$        | $\pm 0.09$        | ±0.03             | $\pm 0.08$        | ±0.02             | $\pm 0.04$        | $\pm 0.07$        |
|            | DEC2000        | 56.35             | 66.56             | 69.73             | 72.54             | 58.64             | 63.90             | 64.10             | 73.53             | 61.20             |
| 0.10       | PEG2000        | $\pm 0.04$        | ±0.03             | $\pm 0.05$        | $\pm 0.09$        | ±0.02             | $\pm 0.08$        | $\pm 0.04$        | ±0.07             | $\pm 0.02$        |
| 0.19       | DEC1000        | 56.00             | 60.79             | 58.28             | 68.90             | 57.05             | 50.06             | 65.33             | 70.75             | 60.38             |
|            | FEGI000        | $\pm 0.02$        | ±0.09             | $\pm 0.02$        | $\pm 0.04$        | $\pm 0.06$        | $\pm 0.11$        | ±0.12             | $\pm 0.08$        | $\pm 0.06$        |
|            | DEC400         | 41.71             | 58.45             | 56.38             | 63.22             | 55.82             | 70.82             | 54.24             | 67.61             | 57.24             |
|            | PEG400         | $\pm 0.03$        | ±0.01             | $\pm 0.01$        | $\pm 0.06$        | ±0.14             | ±0.07             | ±0.02             | ±0.13             | $\pm 0.08$        |
|            | DEC4000        | 69.30             | 67.56             | 71.37             | 76.56             | 68.38             | 70.67             | 63.10             | 76.98             | 67.02             |
|            | FE04000        | $\pm 0.06$        | ±0.11             | ±0.15             | $\pm 0.08$        | ±0.12             | $\pm 0.07$        | ±0.02             | ±0.09             | $\pm 0.04$        |
|            | DEC2000        | 50.70             | 66.35             | 66.50             | 71.87             | 67.29             | 63.16             | 64.82             | 70.80             | 65.37             |
| 0.20       | FEG2000        | ±0.09             | ±0.04             | ±0.07             | $\pm 0.08$        | ±0.03             | $\pm 0.08$        | ±0.04             | $\pm 0.03$        | ±0.09             |
| 0.20       | <b>DEC1000</b> | 46.67             | 64.35             | 61.33             | 70.35             | 65.58             | 63.90             | 64.31             | 66.42             | 62.36             |
|            | PEG1000        | $\pm 0.01$        | ±0.07             | $\pm 0.13$        | $\pm 0.08$        | ±0.06             | $\pm 0.08$        | ±0.05             | ±0.05             | $\pm 0.04$        |
|            | <b>DEC400</b>  | 50.10             | 64.46             | 60.88             | 61.30             | 62.16             | 70.82             | 51.70             | 63.79             | 60.91             |
|            | 1 E0400        | $\pm 0.08$        | ±0.04             | $\pm 0.05$        | $\pm 0.07$        | ±0.11             | ±0.02             | $\pm 0.04$        | $\pm 0.08$        | ±0.09             |

Extraction efficiencies of nine model compounds by PEG (0.20, w/w)-K<sub>3</sub>C<sub>6</sub>H<sub>5</sub>O<sub>7</sub> ATPE.

| W <sub>salt</sub> | 147       | E(%) <sup>a</sup> | E(%) <sup>b</sup> | E(%) <sup>b</sup> | E(%) <sup>b</sup> |
|-------------------|-----------|-------------------|-------------------|-------------------|-------------------|-------------------|-------------------|-------------------|-------------------|-------------------|
|                   | WPEG=0.20 | HRP               | BSA               | CYT               | ANT               | CAR               | CHL               | ASP               | FRU               | PUP               |
| 0.19              | DEC4000   | 76.28             | 71.24             | 70.25             | 79.45             | 70.26             | 87.60             | 72.18             | 77.85             | 80.38             |
|                   | FE04000   | $\pm 0.02$        | $\pm 0.01$        | ±0.03             | $\pm 0.05$        | ±0.04             | $\pm 0.02$        | ±0.03             | ±0.06             | ±0.13             |
|                   | PEG2000   | 52.25             | 67.23             | 64.45             | 77.81             | 68.27             | 84.81             | 61.93             | 75.37             | 77.49             |
|                   |           | $\pm 0.05$        | $\pm 0.01$        | $\pm 0.12$        | ±0.03             | $\pm 0.14$        | ±0.03             | $\pm 0.08$        | ±0.06             | ±0.11             |
| 0.18              | DEC1000   | 56.73             | 63.45             | 61.77             | 70.32             | 67.36             | 70.82             | 62.28             | 74.24             | 70.37             |
|                   | PEGI000   | $\pm 0.08$        | ±0.16             | $\pm 0.02$        | $\pm 0.08$        | $\pm 0.02$        | ±0.06             | $\pm 0.05$        | $\pm 0.05$        | ±0.03             |
|                   | DEC 400   | 44.67             | 63.32             | 61.09             | 69.03             | 65.78             | 59.92             | 50.97             | 71.90             | 66.26             |
|                   | PE0400    | ±0.03             | $\pm 0.04$        | $\pm 0.02$        | $\pm 0.04$        | $\pm 0.05$        | $\pm 0.05$        | ±0.03             | $\pm 0.08$        | ±0.02             |
|                   | PEG4000   | 80.88             | 71.45             | 69.85             | 77.58             | 73.21             | 72.88             | 69.30             | 72.44             | 74.58             |
| 0.10              |           | ±0.07             | $\pm 0.02$        | ±0.06             | $\pm 0.06$        | ±0.03             | ±0.15             | $\pm 0.07$        | ±0.02             | ±0.09             |
|                   | PEG2000   | 57.90             | 67.39             | 68.07             | 75.94             | 70.03             | 70.08             | 62.85             | 71.25             | 70.41             |
|                   |           | ±0.14             | $\pm 0.08$        | $\pm 0.01$        | $\pm 0.03$        | ±0.01             | ±0.09             | $\pm 0.08$        | ±0.02             | ±0.07             |
| 0.19              | PEG1000   | 52.00             | 61.29             | 67.78             | 73.07             | 67.31             | 72.73             | 66.09             | 71.04             | 65.25             |
|                   |           | $\pm 0.04$        | $\pm 0.13$        | $\pm 0.07$        | $\pm 0.08$        | $\pm 0.02$        | $\pm 0.11$        | $\pm 0.04$        | ±0.02             | $\pm 0.06$        |
|                   | PEG400    | 60.67             | 59.38             | 65.98             | 70.83             | 58.32             | 67.14             | 52.55             | 68.97             | 64.14             |
|                   |           | $\pm 0.03$        | ±0.09             | $\pm 0.05$        | $\pm 0.01$        | ±0.03             | $\pm 0.08$        | ±0.03             | ±0.13             | $\pm 0.07$        |
|                   | PEG4000   | 65.17             | 68.39             | 68.33             | 77.36             | 70.44             | 87.46             | 71.22             | 71.35             | 72.12             |
|                   |           | ±0.09             | ±0.03             | $\pm 0.04$        | $\pm 0.11$        | ±0.04             | ±0.06             | $\pm 0.02$        | ±0.05             | $\pm 0.06$        |
|                   | DEC2000   | 59.70             | 67.46             | 60.92             | 76.94             | 68.25             | 56.68             | 57.33             | 70.43             | 70.39             |
| 0.20              | PEG2000   | $\pm 0.14$        | $\pm 0.02$        | ±0.13             | ±0.11             | $\pm 0.06$        | ±0.07             | $\pm 0.03$        | ±0.04             | ±0.09             |
|                   | PEG1000   | 53.53             | 63.48             | 59.68             | 74.25             | 63.27             | 63.60             | 51.26             | 67.66             | 67.46             |
|                   |           | $\pm 0.01$        | $\pm 0.13$        | $\pm 0.08$        | $\pm 0.07$        | ±0.03             | ±0.07             | $\pm 0.02$        | ±0.03             | $\pm 0.08$        |
|                   | PEG400    | 50.35             | 65.03             | 58.67             | 72.10             | 60.94             | 68.90             | 49.36             | 65.28             | 65.45             |
|                   | PEG400    | ±0.03             | $\pm 0.01$        | $\pm 0.05$        | $\pm 0.11$        | ±0.03             | $\pm 0.02$        | ±0.03             | ±0.07             | $\pm 0.02$        |
|                   |           |                   |                   |                   |                   |                   |                   |                   |                   |                   |

Extraction efficiencies of nine model compounds by PEG (0.22, w/w)-K<sub>3</sub>C<sub>6</sub>H<sub>5</sub>O<sub>7</sub> ATPE.

| Wsalt | WPEG=0.22 | E(%) <sup>a</sup> | E(%) <sup>b</sup> | E(%) <sup>b</sup> | E(%) <sup>b</sup> |
|-------|-----------|-------------------|-------------------|-------------------|-------------------|-------------------|-------------------|-------------------|-------------------|-------------------|
|       |           | HRP               | BSA               | CYT               | ANT               | CAR               | CHL               | ASP               | FRU               | PUP               |
| 0.10  | DEC 4000  | 73.13             | 70.27             | 72.00             | 73.26             | 70.23             | 76.27             | 61.83             | 78.82             | 70.27             |
|       | FE04000   | $\pm 0.06$        | $\pm 0.08$        | $\pm 0.07$        | ±0.02             | $\pm 0.01$        | ±0.05             | ±0.11             | ±0.03             | ±0.07             |
|       | PEG2000   | 60.90             | 65.31             | 68.83             | 70.39             | 69.34             | 79.51             | 56.70             | 76.64             | 69.58             |
|       |           | $\pm 0.13$        | ±0.04             | $\pm 0.13$        | ±0.07             | ±0.05             | ±0.02             | ±0.03             | ±0.06             | ±0.06             |
| 0.18  | DEC1000   | 56.73             | 62.38             | 62.40             | 63.04             | 67.88             | 64.78             | 60.23             | 74.37             | 67.09             |
|       | PEG1000   | $\pm 0.08$        | ±0.02             | $\pm 0.04$        | ±0.01             | $\pm 0.13$        | ±0.07             | ±0.03             | ±0.11             | ±0.05             |
|       | DEC 400   | 56.26             | 60.46             | 60.25             | 60.25             | 65.24             | 65.37             | 46.11             | 70.02             | 63.26             |
|       | PEG400    | ±0.12             | ±0.11             | $\pm 0.08$        | ±0.01             | $\pm 0.11$        | ±0.05             | ±0.01             | ±0.09             | $\pm 0.06$        |
| 0.10  | PEG4000   | 80.40             | 70.57             | 69.63             | 71.78             | 73.97             | 82.45             | 65.82             | 69.25             | 70.32             |
|       |           | ±0.05             | ±0.12             | ±0.03             | $\pm 0.08$        | $\pm 0.06$        | ±0.11             | ±0.03             | $\pm 0.02$        | ±0.12             |
|       | PEG2000   | 60.87             | 64.17             | 69.28             | 70.07             | 72.15             | 63.60             | 59.34             | 67.93             | 68.21             |
|       |           | $\pm 0.10$        | ±0.13             | ±0.05             | ±0.01             | $\pm 0.14$        | ±0.05             | ±0.12             | ±0.13             | $\pm 0.06$        |
| 0.19  | PEG1000   | 57.56             | 60.22             | 67.45             | 68.45             | 71.46             | 83.92             | 41.01             | 67.34             | 66.45             |
|       |           | ±0.13             | ±0.05             | ±0.05             | ±0.09             | $\pm 0.03$        | ±0.11             | ±0.14             | ±0.12             | ±0.09             |
|       | PEG400    | 51.59             | 57.59             | 64.73             | 64.80             | 69.20             | 58.30             | 55.92             | 65.25             | 62.78             |
|       |           | ±0.11             | ±0.11             | $\pm 0.08$        | ±0.04             | $\pm 0.03$        | ±0.04             | ±0.01             | ±0.05             | ±0.09             |
|       | PEG4000   | 78.58             | 66.34             | 69.25             | 72.15             | 68.25             | 77.74             | 68.37             | 70.37             | 70.67             |
|       |           | $\pm 0.05$        | ±0.03             | $\pm 0.03$        | ±0.01             | $\pm 0.07$        | ±0.11             | ±0.02             | $\pm 0.04$        | $\pm 0.08$        |
|       | PEG2000   | 61.60             | 65.31             | 65.06             | 71.23             | 66.46             | 79.50             | 60.64             | 66.26             | 68.42             |
| 0.20  |           | $\pm 0.13$        | ±0.03             | ±0.12             | $\pm 0.04$        | $\pm 0.13$        | $\pm 0.08$        | ±0.12             | $\pm 0.08$        | ±0.03             |
|       | DEC1000   | 59.50             | 62.30             | 61.80             | 67.31             | 65.98             | 72.73             | 59.17             | 64.31             | 67.23             |
|       | PEGI000   | $\pm 0.11$        | ±0.05             | $\pm 0.01$        | $\pm 0.04$        | $\pm 0.07$        | ±0.14             | $\pm 0.11$        | ±0.03             | ±0.09             |
|       | DEC400    | 52.67             | 61.23             | 60.94             | 65.85             | 63.12             | 61.83             | 52.57             | 60.29             | 64.56             |
|       | PEG400    | $\pm 0.03$        | ±0.01             | $\pm 0.08$        | ±0.02             | ±0.09             | $\pm 0.13$        | ±0.11             | ±0.11             | $\pm 0.02$        |
|       |           |                   |                   |                   |                   |                   |                   |                   |                   |                   |

| traction efficiencies of nine model compounds by PEG4000-(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> ATPE. |                   |                  |                  |                  |                  |                  |                  |                  |                  |                  |
|--|-------------------|------------------|------------------|------------------|------------------|------------------|------------------|------------------|------------------|------------------|
|  |                   | Ε                | Е                | E                | Ε                | Ε                | Ε                | Ε                | Ε                | Е                |
| WPE  | w <sub>salt</sub> | (%) <sup>a</sup> | (%) <sup>b</sup> | (%) <sup>b</sup> | (%) <sup>b</sup> |
| G  |                   | HRP              | BSA              | CYT              | ANT              | CAR              | CHL              | ASP              | FRU              | PUP              |
|  | 0.19              | 81.68            | 75.05            | 72.60            | 85.74            | 73.32            | 94.06            | 82.61            | 85.17            | 84.04            |
|  | 0.18              | $\pm 0.03$       | $\pm 0.06$       | $\pm 0.09$       | $\pm 0.09$       | $\pm 0.06$       | $\pm 0.10$       | $\pm 0.01$       | $\pm 0.11$       | $\pm 0.08$       |
| 0.10   | 0.10              | 79.05            | 74.93            | 74.14            | 82.49            | 67.85            | 93.70            | 83.72            | 84.83            | 85.95            |
| 0.18   | 0.19              | $\pm 0.11$       | $\pm 0.01$       | $\pm 0.07$       | $\pm 0.05$       | $\pm 0.08$       | $\pm 0.12$       | $\pm 0.05$       | $\pm 0.10$       | $\pm 0.05$       |
|  | 0.20              | 77.27            | 82.77            | 71.57            | 85.06            | 78.65            | 92.74            | 81.19            | 87.05            | 84.83            |
|  | 0.20              | $\pm 0.09$       | $\pm 0.06$       | $\pm 0.07$       | $\pm 0.05$       | $\pm 0.10$       | $\pm 0.08$       | $\pm 0.07$       | $\pm 0.13$       | $\pm 0.01$       |
|  | 0.19              | 85.41            | 86.35            | 82.94            | 85.92            | 82.22            | 96.60            | 84.03            | 87.74            | 86.65            |
|  | 0.18              | $\pm 0.11$       | $\pm 0.08$       | $\pm 0.05$       | $\pm 0.11$       | $\pm 0.04$       | $\pm 0.06$       | $\pm 0.06$       | $\pm 0.10$       | $\pm 0.04$       |
| 0.20   | 0.10              | 82.45            | 84.25            | 82.65            | 86.67            | 86.37            | 93.69            | 86.02            | 87.82            | 86.77            |
| 0.20   | 0.19              | $\pm 0.06$       | $\pm 0.03$       | $\pm 0.08$       | $\pm 0.08$       | $\pm 0.01$       | $\pm 0.06$       | $\pm 0.04$       | $\pm 0.05$       | $\pm 0.07$       |
|  | 0.20              | 81.08            | 82.96            | 82.20            | 86.74            | 82.5             | 91.23            | 85.65            | 89.42            | 87.74            |
|  | 0.20              | $\pm 0.05$       | $\pm 0.05$       | $\pm 0.11$       | $\pm 0.07$       | $\pm 0.10$       | $\pm 0.09$       | $\pm 0.13$       | $\pm 0.12$       | $\pm 0.09$       |
|  | 0.19              | 84.79            | 88.87            | 83.25            | 84.67            | 82.22            | 93.37            | 80.80            | 87.21            | 83.39            |
|  | 0.18              | $\pm 0.12$       | $\pm 0.06$       | $\pm 0.05$       | $\pm 0.11$       | $\pm 0.14$       | $\pm 0.10$       | $\pm 0.04$       | $\pm 0.05$       | $\pm 0.08$       |
| 0.22   | 0.10              | 82.50            | 89.24            | 83.60            | 83.11            | 84.10            | 91.23            | 83.39            | 87.02            | 84.03            |
| 0.22   | 0.19              | $\pm 0.05$       | $\pm 0.12$       | $\pm 0.12$       | $\pm 0.06$       | $\pm 0.04$       | $\pm 0.06$       | $\pm 0.12$       | $\pm 0.12$       | $\pm 0.09$       |
|  | 0.20              | 81.60            | 82.53            | 77.58            | 83.65            | 77.77            | 94.06            | 81.76            | 86.02            | 83.03            |
|  | 0.20              | $\pm 0.12$       | $\pm 0.12$       | $\pm 0.08$       | $\pm 0.12$       | $\pm 0.08$       | $\pm 0.09$       | $\pm 0.01$       | $\pm 0.05$       | $\pm 0.12$       |

Extraction efficiencies of nine model compounds by PEG4000-(NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> ATPE

<sup>a</sup> extraction efficiency of target in PEG-rich phase; <sup>b</sup> extraction efficiency of target in salt-rich phase.

Table S21

|                |            | HRP                | BSA                | CYT                | ANT                | CAR                | CHL                | ASP                | FRU                | PUP                |
|----------------|------------|--------------------|--------------------|--------------------|--------------------|--------------------|--------------------|--------------------|--------------------|--------------------|
| DEC 4000       | К          | 2.840 <sup>a</sup> | 2.851ª             | 2.823ª             | 2.836 <sup>a</sup> | 2.810 <sup>a</sup> | 3.127 <sup>a</sup> | 0.367 <sup>b</sup> | 0.368 <sup>b</sup> | 0.361 <sup>b</sup> |
|                |            | $\pm 0.03$         | $\pm 0.04$         | $\pm 0.02$         | $\pm 0.02$         | $\pm 0.04$         | $\pm 0.01$         | $\pm 0.01$         | $\pm 0.02$         | $\pm 0.04$         |
| $(NH_4)_2SO_4$ | E (%)      | 85.41ª             | 86.35 <sup>a</sup> | 82.94ª             | 85.92ª             | 82.22ª             | 96.60 <sup>a</sup> | 84.03 <sup>b</sup> | 87.74 <sup>b</sup> | 86.65 <sup>b</sup> |
| AIPS           |            | $\pm 0.11$         | $\pm 0.08$         | $\pm 0.05$         | $\pm 0.11$         | $\pm 0.04$         | $\pm 0.06$         | $\pm 0.06$         | $\pm 0.10$         | $\pm 0.04$         |
|                | К          | 0.352°             | 0.353°             | 0.351°             | 3.125 <sup>d</sup> | 2.807 <sup>d</sup> | 2.825 <sup>d</sup> | /                  | /                  | /                  |
| Electrolyte    |            | $\pm 0.02$         | $\pm 0.01$         | $\pm 0.01$         | $\pm 0.03$         | $\pm 0.04$         | $\pm 0.02$         |                    |                    |                    |
| regulation     | E (%)      | 84.39°             | 80.31°             | 82.37°             | 93.28 <sup>d</sup> | 80.34 <sup>d</sup> | 84.30 <sup>d</sup> | /                  | /                  | /                  |
|                |            | $\pm 0.04$         | $\pm 0.02$         | $\pm 0.04$         | $\pm 0.01$         | $\pm 0.02$         | $\pm 0.04$         |                    |                    |                    |
| Copolymer      | K<br>E (%) | 0.350 <sup>e</sup> | 2.806 <sup>f</sup> | 2.812 <sup>f</sup> | /                  | / /                | 1                  | /                  | /                  | /                  |
| purification   |            | $\pm 0.02$         | $\pm 0.02$         | $\pm 0.03$         |                    |                    | /                  |                    |                    |                    |
|                |            | 84.26 <sup>e</sup> | 80.19 <sup>f</sup> | 81.35 <sup>f</sup> | /                  | /                  | /                  | /                  | /                  | /                  |
|                |            | $\pm 0.02$         | $\pm 0.01$         | $\pm 0.02$         |                    |                    |                    |                    |                    |                    |

The partition coefficients (K) and extraction efficiencies (E) of nine model compounds by the integrated method.

<sup>a</sup> Extraction efficiency and distribution coefficient of target in PEG-rich phase of PEG4000-(NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> ATPS;

<sup>b</sup> Extraction efficiency and distribution coefficient of target in salt-rich phase of PEG4000-(NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> ATPS;

<sup>c</sup> Extraction efficiency and distribution coefficient of target in salt-rich phase of PEG4000-Na<sub>3</sub>C<sub>6</sub>H<sub>5</sub>O<sub>7</sub> ATPS;

<sup>d</sup> Extraction efficiency and distribution coefficient of target in PEG-rich phase of PEG4000-Na<sub>3</sub>C<sub>6</sub>H<sub>5</sub>O<sub>7</sub> ATPS;

<sup>e</sup> Extraction efficiency and distribution coefficient of target in the coacervate phase of temperature-controlled affinity precipitation;

<sup>f</sup>Extraction efficiency and distribution coefficient of target in the dilute phase of the temperature-controlled affinity precipitation;



Scheme S1. Schematic illustration for the synthesis of PEG<sub>113</sub>-b-PVBA<sub>49</sub>-b-PNIPAM<sub>105</sub>

### Synthesis of Benzyl trithiocarbonate (BTPA)

First, CS<sub>2</sub> (3.65 mL) was slowly dropped into the mixture solution contained 3mercaptopropionic acid (MPA, 5.00 mL, 28.65 mmol) and KOH (1.84 mol/L, 65.00 mL), and then the mixture reacted in a round bottom for 5 h at room temperature. Subsequently, the reactants were heated to 85 °C and turned on the condenser pipe reflux for 12 h after adding benadryl bromide (10 g, 28.65 mmol) drop by drop within 1 h. After the reaction, chloroform (80 mL) was added to dilute the solution, and then a large amount of concentrated hydrochloric acid was added into the reaction solution to wash until the upper phase was clear and transparent. Finally, the lower phase was condensed into an orange oily liquid by rotary evaporator and washed with deionized water to obtain the yellow powder sample. <sup>1</sup>HNMR (CDCl<sub>3</sub>,  $\delta$ , ppm: 7.33 (5H, ArH), 4.64 (2H, ArCH<sub>2</sub>–), 3.65 (2H, –CH<sub>2</sub>COOH), 2.87(2H, –C(=S)SCH<sub>2</sub>).

#### Synthesis of PEG-based MacroRAFT agent

First, PEG (10.00 g, 2.00 mmol) and BTPA (1.60 g, 4.00 mmol) were dissolved in dichloromethane (50.00 mL). Then, 20 mL dichloromethane contained a catalyst (DMAP, 100 mg, 0.8 mmol) and a dehydrating agent (DCC, 2.00 g, 9.70 mmol) was slowly dropped into the mixture solution and reacted at room temperature for 48 h. When the reaction was over, excess ether was added to the filtrated liquid to precipitate the product. Finally, the product was dried in a vacuum dryer to obtain a yellowish powdery macromolecular chain transfer agent. <sup>1</sup>H NMR

(CDCl<sub>3</sub>, *δ*, ppm: 7.29 (5H, ArH), 4.62 (2H, ArCH<sub>2</sub>-), 4.27 (2H, -CH<sub>2</sub>OCOCH<sub>2</sub>-), 3.65 (452H, -CH<sub>2</sub>CH<sub>2</sub>O-), 3.39 (3H, CH<sub>3</sub>O-), 2.82 (2H, -CH<sub>2</sub>OCOCH<sub>2</sub>CH<sub>2</sub>SC-(=S)-).

### Synthesis of PEG-b-PNIPAM

NIPAM (0.91 g, 8.00 mmol), PEG macromolecular chain transfer agent (0.28 g, 0.05 mmol), AIBN (2.00 mg, 12.00 mol) and 1, 4-dioxane (2.00 g) were injected into a round bottom flask with a magnetic agitation stick. Then, the mixture was reacted at nitrogen for 1.5 h at 75°C. After the reaction, the impurities were removed three times with excessive ethyl ether, and the light yellow powder was obtained after vacuum drying.

### Synthesis of thermo-responsive triblock copolymer PEG<sub>113</sub>-b-PVBA<sub>49</sub>-b-PNIPAM<sub>105</sub>

PEG-b-PNIPAM (1.20 g), AIBN (2.00 mg, 12.00 mol), 1, 4-dioxane (2 mL) and 4-vinyl benzene boric acid (0.14 g, 1.16 mmol) were placed in a dry round bottom flask with a magnetic stirring rod under nitrogen protection. Then, the mixed solution was reacted at 70°C for 20 h. After the reaction, the final polymer  $PEG_{113}$ -b-PVBA<sub>49</sub>-b-PNIPAM<sub>105</sub> was obtained in the form of white powder.



**Fig. S1.** <sup>1</sup>H NMR spectra. (a) BTPA, (b) PEG<sub>113</sub>-based macroRAFT agent, (c) PEG<sub>113</sub>-b-PNIPAM<sub>105</sub>, (d) PEG<sub>113</sub>-b-PVBA<sub>49</sub>-b- PNIPAM<sub>105</sub>.



Figure S2. Liquid-liquid equilibrium of PEG-K<sub>2</sub>HPO<sub>4</sub> ATPSs at 298.15 K and 101.325 kPa.



Figure S3. Liquid-liquid equilibrium of PEG-(NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> ATPSs at 298.15 K and 101.325 kPa.



Figure S4. Liquid-liquid equilibrium of PEG-K $_3C_6H_5O_7$  ATPSs at 298.15 K and 101.325 kPa.