Electronic Supplementary Material (ESI) for Molecular Systems Design & Engineering.

Supplementary Information

New computational method for molecular design of liquid-liquid extractant and related phase equilibrium based on group contribution

Yingying Guo, Hong Zeng, Hang Song*, Shun Yao*

School of Chemical Engineering, Sichuan University, Chengdu, 610065, P. R. China

Corresponding author: Hang Song, e-mail: pharmposter2012@163.com, Shun Yao, e-mail: Cusack@scu.edu.cn

Tel.: +86-028-85405221; fax:+86-028-85405221

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Combinational selectivity (S^C)

From Eq. (8) on the page 7 of the paper, there is:

$$\ln S^C = \ln[(\frac{\gamma_1^C}{\gamma_2^C})^r \Big/ (\frac{\gamma_1^C}{\gamma_2^C})^e]$$

$$= \ln(\frac{\gamma_1^C}{\gamma_2^C})^r - \ln(\frac{\gamma_1^C}{\gamma_2^C})^e \tag{S1}$$

The combined activity coefficient of the combinatorial part (Eq. (3)) is substituted into the above equation to obtain Eq. (S2).

$$\ln S^c = \ln(\frac{\gamma_1^C}{\gamma_2^C})^r - \ln(\frac{\gamma_1^C}{\gamma_2^C})^e$$

$$= \ln(\gamma_1^C)^r - \ln(\gamma_2^C)^r - \left(\ln(\gamma_1^C)^e - \ln(\gamma_2^C)^e\right)$$

$$= 5(q_1 - q_2)\ln\frac{\sum_{j=1}^{3} q_j y_j}{\sum_{j=1}^{3} q_j x_j} + (r_1 - r_2)[\frac{\sum_{j=1}^{3} y_j l_j}{\sum_{j=1}^{3} r_j y_j} - \frac{\sum_{j=1}^{3} x_j l_j}{\sum_{j=1}^{3} r_j x_j}] - 5(q_1 - q_2)\ln\frac{\sum_{j=1}^{3} r_j y_j}{\sum_{j=1}^{3} r_j x_j}$$

$$= 5(q_1 - q_2)\ln(\frac{\sum_{j=1}^{3} q_j y_j}{\sum_{j=1}^{3} r_j y_j} \Big/ \frac{\sum_{j=1}^{3} q_j x_j}{\sum_{j=1}^{3} r_j x_j}) + (r_1 - r_2)[\frac{\sum_{j=1}^{3} y_j l_j}{\sum_{j=1}^{3} r_j y_j} - \frac{\sum_{j=1}^{3} x_j l_j}{\sum_{j=1}^{3} r_j x_j}] \tag{S2}$$

If parameter B is introduced here as:

$$B = \frac{\sum_{j=1}^{3} y_j l_j}{\sum_{j=1}^{3} r_j y_j} - \frac{\sum_{j=1}^{3} x_j l_j}{\sum_{j=1}^{3} r_j x_j} \tag{S3}$$

Due to $l_i = 5(r_i - q_i) - (r_i - 1) = 4r_i - 5q_i + 1$ (S4)

Now Eq. (S4) is substituted into Eq. (S3) and Eq. (S5) can be obtained as follows.

$$B = 4 - 5\frac{\sum_{j=1}^{3} y_j q_j}{\sum_{j=1}^{3} r_j y_j} + \frac{1}{\sum_{j=1}^{3} r_j y_j} - [4 - 5\frac{\sum_{j=1}^{3} x_j q_j}{\sum_{j=1}^{3} r_j x_j} + \frac{1}{\sum_{j=1}^{3} r_j x_j}]$$

$$= 5\left(\frac{\sum_{j=1}^{3} x_j q_j}{\sum_{j=1}^{3} r_j x_j} - \frac{\sum_{j=1}^{3} y_j q_j}{\sum_{j=1}^{3} r_j y_j}\right) + \frac{\sum_{j=1}^{3} r_j (x_j - y_j)}{\sum_{j=1}^{3} r_j y_j \cdot \sum_{j=1}^{3} r_j x_j} \tag{S5}$$

Then Eq. (S6) is obtained by substituting Eq. (S3) into Eq. (10).

$$\ln S^C = 5(q_1 - q_2)\left(\ln \frac{\sum_{j=1}^{3} q_j y_j}{\sum_{j=1}^{3} r_j y_j} - \ln \frac{\sum_{j=1}^{3} q_j x_j}{\sum_{j=1}^{3} r_j x_j}\right) + (r_1 - r_2)\left[5\left(\frac{\sum_{j=1}^{3} x_j q_j}{\sum_{j=1}^{3} r_j x_j} - \frac{\sum_{j=1}^{3} y_j q_j}{\sum_{j=1}^{3} r_j y_j}\right) + \frac{\sum_{j=1}^{3} r_j (x_j - y_j)}{\sum_{j=1}^{3} r_j y_j \cdot \sum_{j=1}^{3} r_j x_j}\right]$$

$$= 5(q_1 - q_2)\ln \frac{\sum_{j=1}^{3} q_j y_j}{\sum_{j=1}^{3} r_j y_j} - 5(r_1 - r_2)\frac{\sum_{j=1}^{3} q_j y_j}{\sum_{j=1}^{3} r_j y_j} - \left[5(q_1 - q_2)\ln \frac{\sum_{j=1}^{3} q_j x_j}{\sum_{j=1}^{3} r_j x_j} - 5(r_1 - r_2)\frac{\sum_{j=1}^{3} q_j x_j}{\sum_{j=1}^{3} r_j x_j}\right]$$

$$+(r_1 - r_2)\frac{\sum_{j=1}^{3} r_j (x_j - y_j)}{\sum_{j=1}^{3} r_j y_j \cdot \sum_{j=1}^{3} r_j x_j} \tag{S6}$$

If parameters A_1 and A_2 are introduced here as:

$$\frac{\sum_{j=1}^{3} q_j y_j}{\sum_{j=1}^{3} r_j y_j} = A_1 ; \quad \frac{\sum_{j=1}^{3} q_j x_j}{\sum_{j=1}^{3} r_j x_j} = A_2 \tag{S7}$$

Eq. (S7) is substituted into Eq. (S6), and then Eq. (9) on the page 7 in the paper is obtained.

Four situations for function *f*(*A*)

2.1 The first situation ($q_1 > q_2$ *,* $r_1 > r_2$ *)*

From Eq. (11), when $f^{'}(A) > 0$, there is $A < \frac{q_1 - q_2}{r_1 - r_2} = A_0$; When $f^{'}(A) < 0$, there is

$A > \frac{q_1 - q_2}{r_1 - r_2} > A_0$.

If A is equal to A_1 in Eq. (S7), then

$$A_1 - A_0 = \frac{q_1 y_1 + q_2 y_2 + q_3 y_3}{r_1 y_1 + r_2 y_2 + r_3 y_3} - \frac{q_1 - q_2}{r_1 - r_2}$$

$$= \frac{(y_1 + y_2)(r_1 q_2 - r_2 q_1) + y_3 (q_3 (r_1 - r_2) - r_3 (q_1 - q_2))}{(r_1 y_1 + r_2 y_2 + r_3 y_3)(r_1 - r_2)} \tag{S8}$$

(I) From Eq. (S8), if $\frac{r_1}{q_1} > \frac{r_2}{q_2}$, and $0 < \frac{r_3}{q_3} < \frac{r_1 - r_2}{q_1 - q_2}$, $A_1 > A_0$, The function is a decreasing function in this region. Then, the relationship between A_2 and A_1 is discussed.

From Eq. (S7),

$$A_2 - A_1 = \frac{q_1 x_1 + q_2 x_2 + q_3 x_3}{r_1 x_1 + r_2 x_2 + r_3 x_3} - \frac{q_1 y_1 + q_2 y_2 + q_3 y_3}{r_1 y_1 + r_2 y_2 + r_3 y_3}$$

$$= \frac{(x_2 y_1 - x_1 y_2)(r_1 q_2 - r_2 q_1) + (x_3 y_1 - x_1 y_3)(r_1 q_3 - r_3 q_1) + (x_3 y_2 - x_2 y_3)(r_2 q_3 - r_3 q_2)}{(r_1 x_1 + r_2 x_2 + r_3 x_3)(r_1 y_1 + r_2 y_2 + r_3 y_3)} \tag{S9}$$

When phase equilibrium is reached, $y_1 > x_1$, $y_2 < x_2$, $y_3 > x_3$.

From above equation, when $\frac{r_3}{q_3} > \frac{r_1}{q_1} > \frac{r_2}{q_2}$, $A_2 > A_1$, hence $f(A_1) - f(A_2) > 0$.

Next, the value A_1 with the same function value $A_1^{'}$ will be solved.

From Eq. (10),

$$f(A_1) = (q_1 - q_2)\ln A_1 - A_1(r_1 - r_2) \tag{S10}$$

$$f(A_1^{'}) = (q_1 - q_2)\ln A_1^{'} - A_1^{'}(r_1 - r_2) \tag{S11}$$

Set $f(A_1) = f(A_1^{'})$, then Eq. (S12) was obtained.

$$\frac{A_1 - A_1^{'}}{\ln A_1 - \ln A_1^{'}} = \frac{q_1 - q_2}{r_1 - r_2} \tag{S12}$$

When $\frac{1}{2} \le \frac{A_1}{A_1^{'}} \le 2$, Eq. (S12) can be approximated as Eq. (S13).

$$A_1^{'} = 2\frac{q_1 - q_2}{r_1 - r_2} - A_1 \tag{S13}$$

At this point, since $A_1^{'}$ is on the side of the increasing function, when $A_2 < A_1^{'}$, then $f(A_1^{'}) - f(A_2) > 0$, that is $f(A_1) - f(A_2) > 0$.

So, $A_2 - A_1^{'} < 0$.

That is, $\frac{q_1x_1 + q_2x_2 + q_3x_3}{r_1x_1 + r_2x_2 + r_3x_3} - [2\frac{q_1 - q_2}{r_1 - r_2} - \frac{q_1y_1 + q_2y_2 + q_3y_3}{r_1y_1 + r_2y_2 + r_3y_3}] < 0$

$$\frac{(x_1 + x_2)(r_1q_2 - r_2q_1) + x_3[q_3(r_1 - r_2) - r_3(q_1 - q_2)]}{(r_1 - r_2)(r_1x_1 + r_2x_2 + r_3x_3)} +$$

$$\frac{(y_1 + y_2)(r_1q_2 - r_2q_1) + y_3[q_3(r_1 - r_2) - r_3(q_1 - q_2)]}{(r_1 - r_2)(r_1y_1 + r_2y_2 + r_3y_3)} < 0 \tag{S14}$$

Therefore $r_1q_2 - r_2q_1 > 0$, if Eq. (S14) is satisfied, then

$q_3(r_1 - r_2) - r_3(q_1 - q_2) < 0$

That is, $\frac{r_3}{q_3} > \frac{r_1 - r_2}{q_1 - q_2}$ (S15)

Since this result is contradicted with the previous conclusion ($0 < \frac{r_3}{q_3} < \frac{r_1 - r_2}{q_1 - q_2}$), the case of A_1 and A_2 on the same side of A_0 was considered in the following discussion.

Besides, when $\sum_{j=1}^{3} r_j(x_j - y_j) > 0$, that is $(r_1 - r_3)(x_1 - y_1) + (r_2 - r_3)(x_2 - y_2) > 0$, Due to $r_1 > r_2$, when $r_3 > r_1$, $\frac{\sum_{j=1}^{3} r_j(x_j - y_j)}{\sum_{j=1}^{3} r_jy_j \cdot \sum_{j=1}^{3} r_jx_j} > 0$.

Hence,

$$\ln S^C = 5(q_1 - q_2)\ln A_1 - 5(r_1 - r_2)A_1 - [5(q_1 - q_2)\ln A_2 - 5(r_1 - r_2)A_2]$$

$$+(r_1 - r_2)\frac{\sum_{j=1}^{3} r_j(x_j - y_j)}{\sum_{j=1}^{3} r_j y_j \cdot \sum_{j=1}^{3} r_j x_j}$$

$$= 5[f(A_1) - f(A_2)] + (r_1 - r_2)\frac{\sum_{j=1}^{3} r_j(x_j - y_j)}{\sum_{j=1}^{3} r_j y_j \cdot \sum_{j=1}^{3} r_j x_j} > 0 \quad \text{(S16)}$$

That is $S^C > 1$.

(II) From Eq. (S8), if $\frac{r_1}{q_1} < \frac{r_2}{q_2}$, and $\frac{r_3}{q_3} > \frac{r_1 - r_2}{q_1 - q_2} > 0$. Then $A_1 < A_0$, *f*(*A*) is an increasing function.

When $\frac{r_3}{q_3} < \frac{r_1}{q_1} < \frac{r_2}{q_2}$, then $A_2 - A_1 < 0$, $f(A_1) - f(A_2) > 0$, meanwhile, $r_3 > r_1$ is satisfied, the combinational selectivity is $S^C > 1$.

From what has been discussed above, when $q_1 > q_2$, $r_1 > r_2$,

a. If $\frac{r_3}{q_3} > \frac{r_1}{q_1} > \frac{r_2}{q_2}$ and $r_3 > r_1$ are satisfied at the same time, the combinational selectivity is $S^C > 1$.

b. If $\frac{r_3}{q_3} < \frac{r_1}{q_1} < \frac{r_2}{q_2}$ and $r_3 > r_1$ are simultaneously satisfied, the combinational selectivity is $S^C > 1$.

2.2 The second situation ($q_1 < q_2$, $r_1 < r_2$ *)*

(I) From Eq. (S8), if $\frac{r_1}{q_1} < \frac{r_2}{q_2}$, $\frac{r_3}{q_3} > \frac{r_1 - r_2}{q_1 - q_2} > 0$, and $A_1 > A_0$. The function *f*(*A*) is a decreasing function in the region, then the relationship between A_2 and A_1 will be discussed.

From Eq. (S9), when $\frac{r_3}{q_3} < \frac{r_2}{q_2}$, $A_2 > A_1$, then $f(A_1) - f(A_2) > 0$.

Moreover, when $\sum_{j=1}^{3} r_j (x_j - y_j) > 0$, that is $(r_1 - r_3)(x_1 - y_1) + (r_2 - r_3)(x_2 - y_2) > 0$,

Because of $r_1 < r_2$, when $r_3 < r_1$, $\frac{\sum_{j=1}^{3} r_j (x_j - y_j)}{\sum_{j=1}^{3} r_j y_j \cdot \sum_{j=1}^{3} r_j x_j} > 0$. It equates to $\ln S^C > 0$, $S^C > 1$.

(Ⅱ) From Eq. (S8), when $\frac{r_1}{q_1} > \frac{r_2}{q_2}$, and $0 < \frac{r_3}{q_3} < \frac{r_1 - r_2}{q_1 - q_2}$, $A_1 < A_0$. The function $f(A)$ is an increasing function in the region, then the relationship between A_2 and A_1 will be discussed.

From Eq. (S9), when $\frac{r_3}{q_3} > \frac{r_2}{q_2}$, $A_2 < A_1$, then $f(A_1) - f(A_2) > 0$.

Besides, when $\sum_{j=1}^{3} r_j (x_j - y_j) > 0$, that is $(r_1 - r_3)(x_1 - y_1) + (r_2 - r_3)(x_2 - y_2) > 0$,

Because of $r_1 < r_2$, when $r_3 < r_1$, $\frac{\sum_{j=1}^{3} r_j (x_j - y_j)}{\sum_{j=1}^{3} r_j y_j \cdot \sum_{j=1}^{3} r_j x_j} > 0$. That is $\ln S^C > 0$, and $S^C > 1$.

From what has been discussed above, when $q_1 < q_2$, and $r_1 < r_2$

a. If $\frac{r_3}{q_3} > \frac{r_2}{q_2} > \frac{r_1}{q_1}$, and $r_3 < r_1$. Then, the combinational selectivity is $S^C > 1$.

b. If $\frac{r_3}{q_3} < \frac{r_2}{q_2} < \frac{r_1}{q_1}$, and $r_3 < r_1$. The combinational selectivity is $S^C > 1$.

2.3 The third situation ($q_1 > q_2$, $r_1 < r_2$)

From Eq. (11), $f^{'}(A) = \frac{q_1 - q_2}{A} - (r_1 - r_2) > 0$, thus the function $f(A)$ is an increasing function. If $A_1 - A_0 < 0$, then $\frac{r_1}{q_1} > \frac{r_2}{q_2}$, and $0 < \frac{r_3}{q_3} < \frac{r_1 - r_2}{q_1 - q_2}$.

When $A_2 - A_1 < 0$, then $f(A_2) < f(A_1)$.

So, $\frac{r_1}{q_1} < \frac{r_3}{q_3}$ and $\frac{r_2}{q_2} < \frac{r_3}{q_3}$ are taken from Eq. (S9).

In addition, when $r_3 < r_1$, the last term in Eq. (9) is greater than 0.

Therefore, when $q_1 > q_2$, $r_1 < r_2$, $r_3 < r_1$, $\frac{r_3}{q_3} < \frac{r_2}{q_2} < \frac{r_1}{q_1}$, the combinational selectivity is $S^C > 1$.

2.4 The fourth situation ($q_1 < q_2$, $r_1 > r_2$ *)*

From Eq. (11), $f'(A) = \frac{q_1 - q_2}{A} - (r_1 - r_2) < 0$, so the function *f*(*A*) is a decreasing function. If $A_1 - A_0 > 0$, then $\frac{r_1}{q_1} > \frac{r_2}{q_2}$, and $0 < \frac{r_3}{q_3} < \frac{r_1 - r_2}{q_1 - q_2}$.

When $A_2 - A_1 > 0$, $f(A_2) < f(A_1)$,

Hence, it could be obtained from Eq. (S9) that $r_1 q_3 - r_3 q_1 < 0$ and $r_2 q_3 - r_3 q_2 < 0$.

That is $\frac{r_1}{q_1} < \frac{r_3}{q_3}$ and $\frac{r_2}{q_2} < \frac{r_3}{q_3}$, or expressed as $\frac{r_3}{q_3} > \frac{r_1}{q_1} > \frac{r_2}{q_2}$.

Besides, when $r_3 > r_2$, the last term in Eq. (9) is greater than 0.

Therefore, when $q_1 < q_2$, $r_1 > r_2$, $r_3 > r_2$, $\frac{r_3}{q_3} > \frac{r_1}{q_1} > \frac{r_2}{q_2}$, the combinational selectivity is $S^C > 1$.

Residual selectivity S^R

The residual term Eq. (4) of activity coefficient is substituted into the Eq. (12) to obtain:

$$\ln S^R = \ln(r_1^R)^r - \ln(r_1^R)^e - [\ln(r_2^R)^r - \ln(r_2^R)^e]$$
$$= \sum_k v_k^{(1)}[\ln \Gamma_k - \ln \Gamma_k^{(1)}]^r - \sum_k v_k^{(1)}[\ln \Gamma_k - \ln \Gamma_k^{(1)}]^e$$
$$-\{\sum_k v_k^{(2)}[\ln \Gamma_k - \ln \Gamma_k^{(2)}]^r - \sum_k v_k^{(2)}[\ln \Gamma_k - \ln \Gamma_k^{(2)}]^e\} \quad \text{(S17)}$$

$[\ln \Gamma_k^{(i)}]^r$ and $[\ln \Gamma_k^{(i)}]^e$ are only related to the group in component *i*. For the separated component *i*, there is: $[\ln \Gamma_k^{(i)}]^r = [\ln \Gamma_k^{(i)}]^e$.

Hence, the Eq. (S18) can be obtained.

$$\ln S^R = \sum_{k=1}^{k_1} v_k^{(1)}[\ln \Gamma_k^r - \ln \Gamma_k^e] - \sum_{k=1}^{k_1} v_k^{(2)}[\ln \Gamma_k^r - \ln \Gamma_k^e]$$
$$= \sum_{k=1}^{k_1} (v_k^1 - v_k^2)(\ln \Gamma_k^r - \ln \Gamma_k^e) \quad \text{(S18)}$$

In Eq. (S18),

$$\ln \Gamma_k^r - \ln \Gamma_k^e = Q_k[\ln \frac{\sum_m^{k_1} \theta_m^e \psi_{mk}}{\sum_m^{k_1} \theta_m^r \psi_{mk}} + \sum_m^{k_1} \frac{\theta_m^e \psi_{km}}{\sum_n^{k_1} \theta_n^e \psi_{nm}} - \sum_m^{k_1} \frac{\theta_m^r \psi_{km}}{\sum_n^{k_1} \theta_n^r \psi_{nm}}] \quad \text{(S19)}$$

Here $\theta_m^r = \frac{Q_m X_m}{\sum_n^{k_1} Q_n X_n}$; $\theta_m^e = \frac{Q_m Y_m}{\sum_n^{k_1} Q_n Y_n}$ (S20)

$$X_m = \frac{\sum_{i=1}^{3} v_m^{(i)} x_i}{\sum_{i=1}^{3} \sum_{k=1}^{k_1} v_k^{(i)} x_i} ; \quad Y_m = \frac{\sum_{i=1}^{3} v_m^{(i)} y_i}{\sum_{i=1}^{3} \sum_{k=1}^{k_1} v_k^{(i)} y_i} \quad \text{(S21)}$$

In the above equations, k_1 is the total number of groups contained in components 1, 2 and 3. It is assumed that the groups in component 3 (solvent, also called extractant in this case) are different from those in components 1 and 2, and even if they are the same, they are treated as different groups and the calculated results are the same.

Set $v_k^{(1)} - v_k^{(2)} = v_k^{'}$ (S22)

$$Z_{k,m}^{e} = \frac{\theta_m^e \psi_{km}}{\sum_{n}^{k_1} \theta_n^e \psi_{nm}}; \quad Z_{k,m}^{r} = \frac{\theta_m^r \psi_{km}}{\sum_{n}^{k_1} \theta_n^r \psi_{nm}} \tag{S23}$$

Thus, the Eq. (S18) can be reduced to the following Eq. (S24).

$$\begin{aligned}
\ln S^R &= v_1^{'} Q_1 (\ln \sum_m^{k_1} \theta_m^e \psi_{m,1} - \ln \sum_m^{k_1} \theta_m^r \psi_{m,1} + \sum_m^{k_1} Z_{1,m}^e - \sum_m^{k_1} Z_{1,m}^r) \\
&\quad + v_2^{'} Q_2 (\ln \sum_m^{k_1} \theta_m^e \psi_{m,2} - \ln \sum_m^{k_1} \theta_m^r \psi_{m,2} + \sum_m^{k_1} Z_{2,m}^e - \sum_m^{k_1} Z_{2,m}^r) \\
&\quad + \cdots \\
&\quad + v_k^{'} Q_k (\ln \sum_m^{k_1} \theta_m^e \psi_{m,k} - \ln \sum_m^{k_1} \theta_m^r \psi_{m,k} + \sum_m^{k_1} Z_{k,m}^e - \sum_m^{k_1} Z_{k,m}^r) \\
&\quad + \cdots \\
&\quad + v_{k_1}^{'} Q_{k_1} (\ln \sum_m^{k_1} \theta_m^e \psi_{m,k_1} - \ln \sum_m^{k_1} \theta_m^r \psi_{m,k_1} + \sum_m^{k_1} Z_{k_1,m}^e - \sum_m^{k_1} Z_{k_1,m}^r) \\
&= v_1^{'} Q_1 (\ln \sum_m^{k_1} \theta_m^e \psi_{m,1} + \sum_m^{k_1} Z_{1,m}^e) + v_1^{'} Q_1 (-\ln \sum_m^{k_1} \theta_m^r \psi_{m,1} - \sum_m^{k_1} Z_{1,m}^r) \\
&\quad + v_2^{'} Q_2 (\ln \sum_m^{k_1} \theta_m^e \psi_{m,2} + \sum_m^{k_1} Z_{2,m}^e) + v_2^{'} Q_2 (-\ln \sum_m^{k_1} \theta_m^r \psi_{m,2} - \sum_m^{k_1} Z_{2,m}^r) \\
&\quad + \cdots \\
&\quad + v_k^{'} Q_k (\ln \sum_m^{k_1} \theta_m^e \psi_{m,k} + \sum_m^{k_1} Z_{k,m}^e) + v_k^{'} Q_k (-\ln \sum_m^{k_1} \theta_m^r \psi_{m,k} - \sum_m^{k_1} Z_{k,m}^r) \\
&\quad + \cdots \\
&\quad + v_{k_1}^{'} Q_{k_1} (\ln \sum_m^{k_1} \theta_m^e \psi_{m,k_1} + \sum_m^{k_1} Z_{k_1,m}^e) + v_k^{'} Q_k (-\ln \sum_m^{k_1} \theta_m^r \psi_{m,k_1} - \sum_m^{k_1} Z_{k_1,m}^r)
\end{aligned} \tag{S24}$$

The final expression Eq. (13) of ln S^R can be obtained from Eq. (S24).

Table S1. θ $\boldsymbol{\Psi}$ matrix

$$\begin{bmatrix}
\theta_1\psi_{1,1} & \theta_1\psi_{1,2} & \cdots & \theta_1\psi_{1,k} & \theta_1\psi_{1,k+1} & \theta_1\psi_{1,k+2} & \cdots & \theta_1\psi_{1,k1} \\
\theta_2\psi_{2,1} & \theta_2\psi_{2,2} & \cdots & \theta_2\psi_{2,k} & \theta_2\psi_{2,k+1} & \theta_2\psi_{2,k+2} & \cdots & \theta_2\psi_{2,k1} \\
\cdots & \cdots & \cdots & \cdots & \cdots & \cdots & \cdots & \cdots \\
\theta_k\psi_{k,1} & \theta_k\psi_{k,2} & \cdots & \theta_k\psi_{k,k} & \theta_k\psi_{k,k+1} & \theta_k\psi_{k,k+2} & \cdots & \theta_k\psi_{k,k1} \\
\theta_{k+1}\psi_{k+1,1} & \theta_{k+1}\psi_{k+1,2} & \cdots & \theta_{k+1}\psi_{k+1,k} & \theta_{k+1}\psi_{k+1,k+1} & \theta_{k+1}\psi_{k+1,k+2} & \cdots & \theta_{k+1}\psi_{k+1,k1} \\
\theta_{k+2}\psi_{k+2,1} & \theta_{k+2}\psi_{k+2,2} & \cdots & \theta_{k+2}\psi_{k+2,k} & \theta_{k+2}\psi_{k+2,k+1} & \theta_{k+2}\psi_{k+2,k+2} & \cdots & \theta_{k+2}\psi_{k+2,k1} \\
\cdots & \cdots & \cdots & \cdots & \cdots & \cdots & \cdots & \cdots \\
\theta_{k1}\psi_{k1,1} & \theta_{k1}\psi_{k1,2} & \cdots & \theta_{k1}\psi_{k1,k} & \theta_{k1}\psi_{k1,k+1} & \theta_{k1}\psi_{k1,k+2} & \cdots & \theta_{k1}\psi_{k1,k1}
\end{bmatrix}$$