Supporting Online Material for

Vapor-Liquid-Liquid Equilibria of Hydrofluorocarbons and 1-Butyl-3-Methylimidazolium Hexafluorophosphate

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Thermodynamic Model

In this study, we have employed a generic RK (Redlich-Kwong) type of cubic equations of state (EOS), which is written in the following form:

$$P = \frac{RT}{V-b} - \frac{a(T)}{V(V+b)} \tag{S1}$$

$$a(T) = 0.427480 \frac{R^2 T_c^2}{P_c} a\,(T) \tag{S2}$$

$$b = 0.08664 \frac{RT_c}{P_c} \tag{S3}$$

The temperature-dependent part of the a parameter in the EOS for pure compounds is modeled by the following empirical form [S1]:

$$a\,(T) = \sum_{k=0}^{\leq 3} b_{\,k} \left(1/T_r - T_r\right)^k \text{ , for } T_{\mathrm{r}} \leq 1 \quad (T_r \equiv T/T_C), \tag{S4a}$$

$$a\,(T) = b_0 + b_1 \left[\exp\{2(1-T_r)\} - 1\right], \text{ for } T_{\mathrm{r}} > 1. \tag{S4b}$$

The coefficients, $b_{\,k}$, are determined so as to reproduce the vapor pressure of each pure compound. It should be mentioned that Eq. (S4b) is here implemented to properly deal with very high reduced temperatures such as a hydrogen case. The critical parameters (T_c and P_c) and b_k in Eqs. (S2-S4) were taken from our previous work[S1,S2], and the EOS constants for the present compounds are shown in Table S1.

Then, the a and b parameters for general N-component mixtures are modeled in terms of binary interaction parameters[S1,S3].

$$a = \sum_{i=1}^{N} \sum_{j=1}^{N} \sqrt{a_i a_j}\, f_{ij}(T)(1-k_{ij}) x_i x_j, \quad a_i = 0.427480 \frac{R^2 T_{ci}^2}{P_{ci}} a_i(T) \tag{S5}$$

$$f_{ij}(T) = 1 + t_{ij}/T, \quad \text{where } t_{ij} = t_{ji}, \text{ and } t_{ii} = 0. \tag{S6}$$

$$k_{ij} = \frac{l_{ij} l_{ji} (x_i + x_j)}{l_{ji} x_i + l_{ij} x_j}, \quad \text{where } k_{ii} = 0. \tag{S7}$$

$$b = \frac{1}{2} \sum_{i=1}^{N} \sum_{j=1}^{N} (b_i + b_j)(1-k_{ij})(1-m_{ij}) x_i x_j, \quad b_i = 0.08664 \frac{RT_{ci}}{P_{ci}}, \tag{S8}$$

where $m_{ij} = m_{ji}, m_{ii} = 0$.

T_{ci}: critical temperature of the *i*-th species.

P_{ci}: critical pressure of the *i*-th species.

R: universal gas constant

x_i: mole fraction of the *i*-th species.

In the above model, there are maximum four binary interaction parameters: l_{ij}, l_{ji}, m_{ij}, and t_{ij} for each binary pair. However, only two or three parameters are sufficient for most of the cases. Optimal binary interaction parameters determined from VLE data[S4,S5] alone for the present systems are shown in Table S2. The fugacity coefficient f_i of *i*-th species for the present EOS model, which is needed for the phase equilibrium calculation, is given by:

$$\ln f_i = \ln \frac{RT}{P(V-b)} + b'_i \left(\frac{1}{V-b} - \frac{a}{RTb(V+b)} \right) + \frac{a}{RTb} \left(\frac{a'_i}{a} - \frac{b'_i}{b} + 1 \right) \ln \frac{V}{V+b} \tag{S9}$$

where

$a'_i \equiv \left(\frac{\partial na}{\partial n_i}\right)_{n_{j\neq i}}$ and $b'_i \equiv \left(\frac{\partial nb}{\partial n_i}\right)_{n_{j\neq i}}$: n = total mole number and n_i = mole number of *i*-th species (or $x_i = n_i / n$). The explicit forms of $a_i^{'}$ and $b_i^{'}$ may be useful for readers.

$$a_i^{'} = 2\sum_{j=1}^{N}\sqrt{a_i a_j}\, f_{ij} x_j \left\{1 - k_{ij} - \frac{l_{ij} l_{ji}\left(l_{ij} - l_{ji}\right)x_i x_j}{\left(l_{ji} x_i + l_{ij} x_j\right)^2}\right\} - a \qquad \text{(S10)}$$

$$b_i^{'} = \sum_{j=1}^{N}\left(b_i + b_j\right)\left(1 - m_{ij}\right)x_j \left\{1 - k_{ij} - \frac{l_{ij} l_{ji}\left(l_{ij} - l_{ji}\right)x_i x_j}{\left(l_{ji} x_i + l_{ij} x_j\right)^2}\right\} - b \qquad \text{(S11)}$$

The equilibrium phase boundaries for binary systems can be obtained by solving the following equilibrium conditions:

$$x_i f_i^L = y_i f_i^V, \qquad (i = 1, 2) \text{ for VLE,} \qquad \text{(S12)}$$

$$x_i f_i^L = x_i^{'} f_i^{L'} = y_i f_i^V, \qquad (i = 1, 2) \text{ for VLLE.} \qquad \text{(S13)}$$

where

x_i, $x_i^{'}$: liquid mole fraction of the ***i-th*** species

y_i: vapor mole fraction of the ***i-th*** species

f_i^L, $f_i^{L'}$: liquid-phase (*L* or *L'*) fugacity coefficient of the ***i-th*** species

f_i^V: vapor-phase (*V*) fugacity coefficient of the ***i-th*** species.

References

S1. A. Yokozeki. Solubility of Refrigerants in Various Lubricants. *Int. J. Thermophys.*, **2001**, *22*, 1057-1071.

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Table S1. Pure Component EOS Constants Used in the Present Work.

Compound	Molar Mass / g·mol^{-1}	T_c / K	P_c / kPa	b_0 ---	b_1 ---	b_2 ---	b_3 ---
R-32	52.02	351.26	5782	1.0019	0.48333	-0.07538	0.00673
R-41	34.03	315.55	5600	1.0005	0.41708	-0.05450	-0.00079
R-125	120.22	339.19	3637	1.0001	0.47736	-0.01977	-0.01770
R-134	101.03	391.97	4641	1.0012	0.48291	-0.05071	0
R-134a	101.03	374.21	4059	1.0025	0.50532	-0.04983	0
R-143a	84.04	346.20	3759	1.0006	0.45874	-0.04846	-0.01430
R-152a	66.05	386.44	4520	1.0012	0.48495	-0.08508	0.01460
R-161	48.06	375.30	5020	1.0003	0.43448	-0.04065	-0.02039
[bmim][PF_6]	284.18	860.5	2645	1.0	0.62627	0	0

Table S2. Optimal Binary Interaction Parameters[*)] in Eqs. (S6) - (S8).

System (1) / (2)[**)]	l_{12}	l_{21}	$m_{12} = m_{21}$	$t_{12} = t_{21}$ / K
R-32 / RTIL	-0.15943	-0.003227	0.01268	5.901
R-41 / RTIL	0.05413	0.01218	---	3.229
R-125 / RTIL	0.15937	l_{12}	-0.21421	62.61
R-134 / RTIL	0.04937	0.05025	-0.05215	26.65
R-134a / RTIL	0.19480	l_{12}	-0.23700	65.96
R-143a / RTIL	0.21530	0.20817	-0.25485	51.69
R-152a / RTIL	0.20757	l_{12}	-0.24181	66.48
R-161 / RTIL	0.17876	0.16737	-0.18300	40.00

*) Estimated using non-linear least squares analyses with VLE data[S4,S5] alone.

**) RTIL = [bmim][PF_6]