Evaluation of proper HFO refrigerant/ionic liquid mixture for absorption refrigeration system

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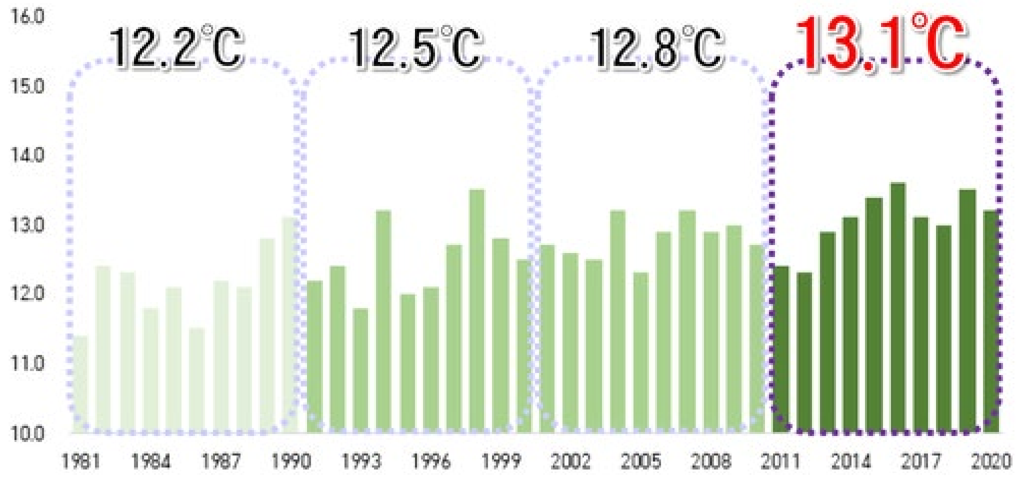
Introduction

- Absorption refrigeration system



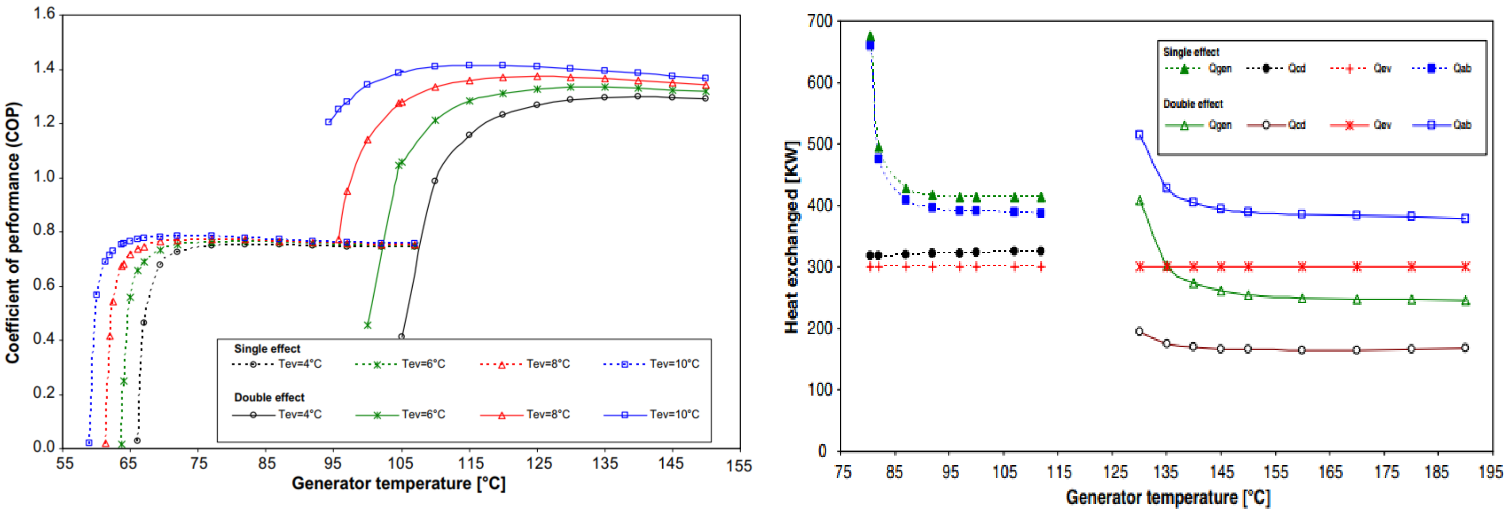
< changes in annual average temperature>

<Example of Absorption refrigeration system>

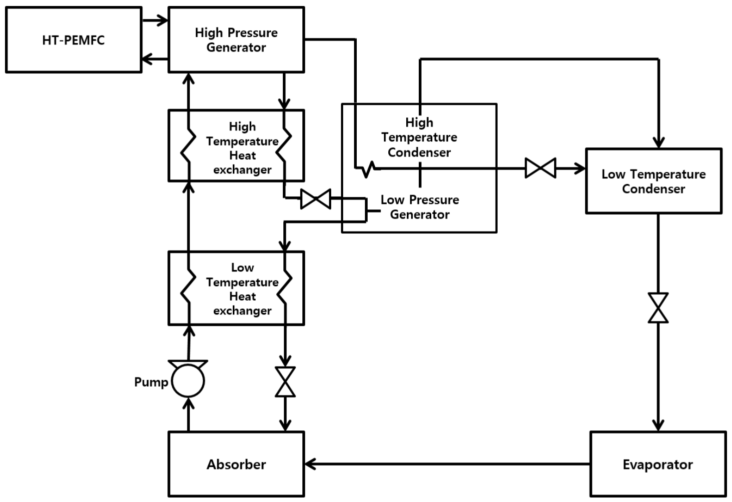
- Power consumption in summer days become larger due to global warming than winter days
- Absorption refrigeration system is beneficial than the compression system due to low power consumption
- The absorption refrigeration system can be operated by various waste heat, so that it can be installed with various power systems.

Introduction

- Hybrid system composed of HT-PEM/DEARS



<Comparison of COP/Heat between single/double absorption system>



<Schematics of the hybrid system>

- Single effect absorption refrigeration system uses heat source around 90 oC, and the COP is about 0.7.
- Double effect absorption refrigeration system (DEARS) uses heat sources around 200 ^{o}C, and the COP is about 1.3.
- DEARS has two generator and heat exchanges and the high pressure generator is connected to heat source. In case of HT-PEM/DEARS hybrid system, coolant of the fuel cell system pass through the high pressure generator.

Introduction

- Problem of absorption refrigeration system

<Crystallization of lithium bromide solution>

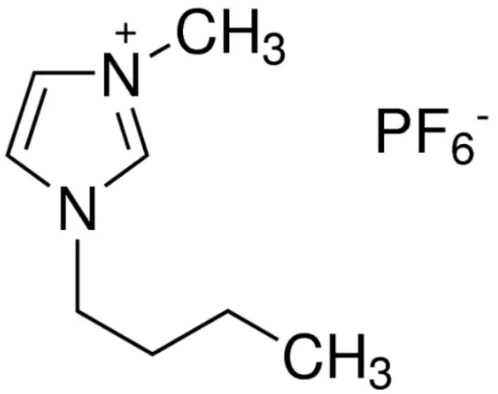
<Corrosion due to water >

Refrigerant/absorbent	Limit	Problem
Water/LiBr	Narrow operating range	Crystallization of absorbent
Water/LiBr	Narrow operating range	Freezing point of water
Water/LiBr	Limits of material selection	Corrosion of system
Ammonia/Water	Relatively low COP	Relatively low COP
Ammonia/Water	Toxicity, flammability	Safety

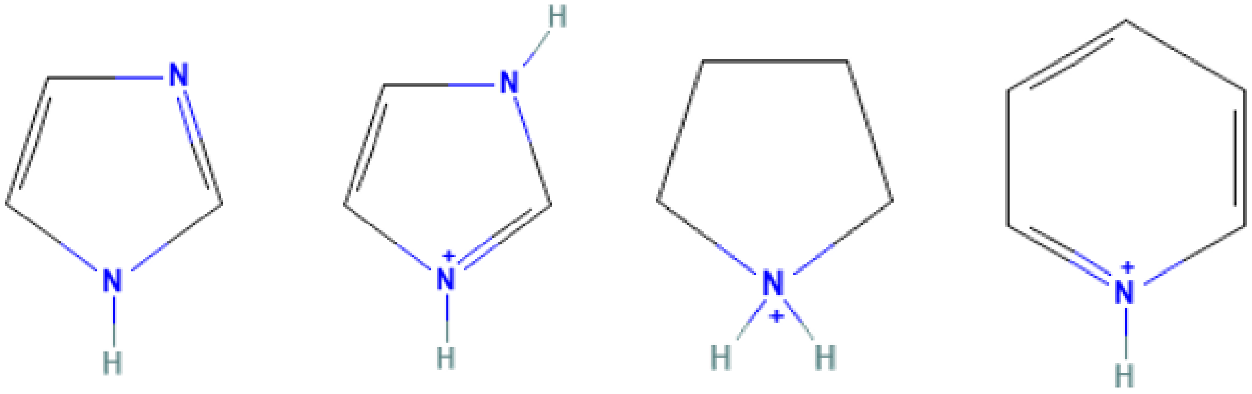
- Development of new refrigerant/absorbent pair is needed to solve above problems.

Water/Ionic liquid pair

- Examination of ionic liquids as absorbent



<[BMIM][PF_6]>

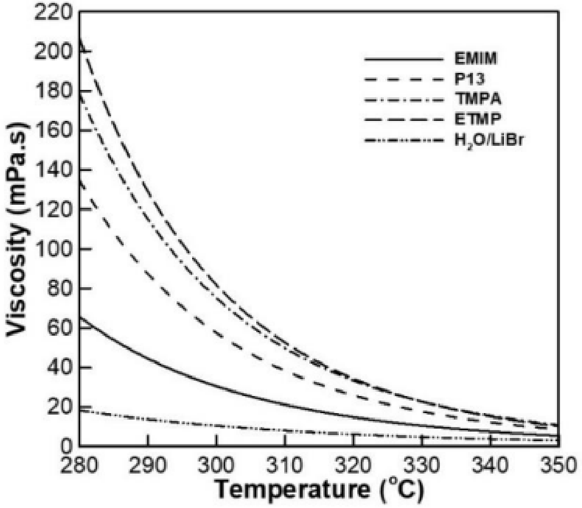


<Various positive ions: Imidazole, Imidazolium, pyrrolidinium, pyridinium>

- Ionic liquids (ILs) stays in liquid in large range due to asymmetry of positive and negative ions.
- The ionic liquids are named depending on positive ion and the characteristics are determined by negative ions.

Water/Ionic liquid pair

- Examination of ionic liquids as absorbent



<Comparison of viscosity of absorbents[1)]>

Refrigerant	Ionic Liquid	
Water	[DMIM][DMP]	[EMIM][Ac]
	[EMIM][DEP]	[EMIM][TfO]
	[EMIM][TFA]	[EMIM][DEP]
	[EMIM][EtSO4]	

<Candidates of absorbents for water>

- Viscosity of ionic liquids are determined by positive ions and various depending on temperature.
- When the viscosity is high, the COP become low. Therefore, imidazolium based ionic liquids are selected as absorbent because its viscosity is similar to that of LiBr.
- We listed imidazolium based ionic liquids based on previous studies.

1) Lee, Y., Lee, G., Cho, J., Choi, B., Han, N. G., & Kim, D. K. (2023). Evaluation of ionic liquids as absorbents for absorption refrigeration systems using hydrofluoro-olefin refrigerant. Case Studies in Thermal Engineering, 102920.

Water/Ionic liquid pair

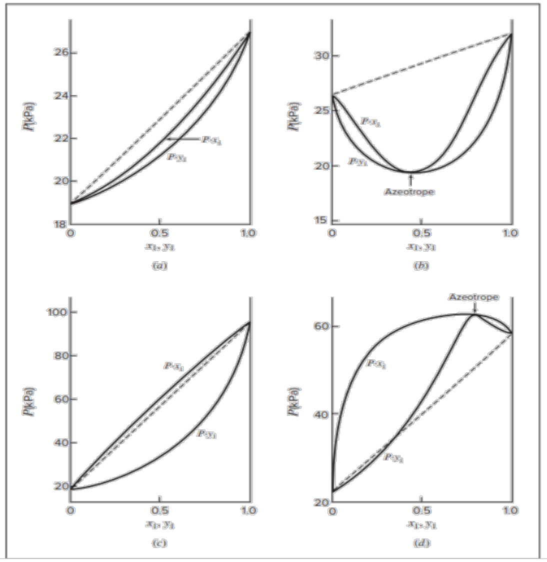
- Non-Random Two Liquid model

Raoult's law

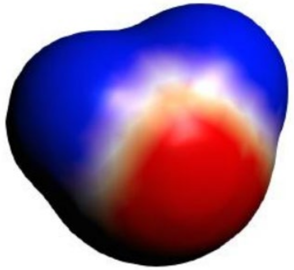
$$y_i P = x_i P_i^{sat}$$

Activity model

$$y_i P = x_i \gamma_i P_i^{sat}$$



<Raoult's law for real mixture>



<COSMO-RS>

$$h_{\text{mix}} = -RT^2 \left[x_r \left(\frac{\partial \ln \gamma_r}{\partial T} \right)_{p,x} + x_{\text{IL}} \left(\frac{\partial \ln \gamma_{\text{IL}}}{\partial T} \right)_{p,x} \right]$$

$$\ln \gamma_r = x_{\text{IL}}^2 \left[\tau_{21} \left(\frac{G_{21}}{x_r + x_{\text{IL}} G_{21}} \right)^2 + \frac{\tau_{12} G_{12}}{(x_{\text{IL}} + x_r G_{12})^2} \right]$$

$$\ln \gamma_{\text{IL}} = x_r^2 \left[\tau_{12} \left(\frac{G_{12}}{x_{\text{IL}} + x_r G_{12}} \right)^2 + \frac{\tau_{21} G_{21}}{(x_r + x_{\text{IL}} G_{21})^2} \right]$$

$$G_{12} = \exp(-\alpha \tau_{12}) \quad G_{21} = \exp(-\alpha \tau_{21})$$

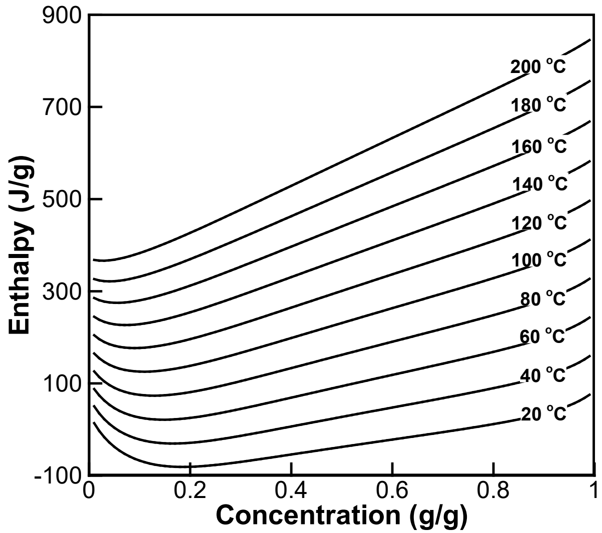
$$\tau_{12} = \tau_{12}^0 + \tau_{12}^1 / T \quad \tau_{21} = \tau_{21}^0 + \tau_{21}^1 / T$$

<NRTL model>

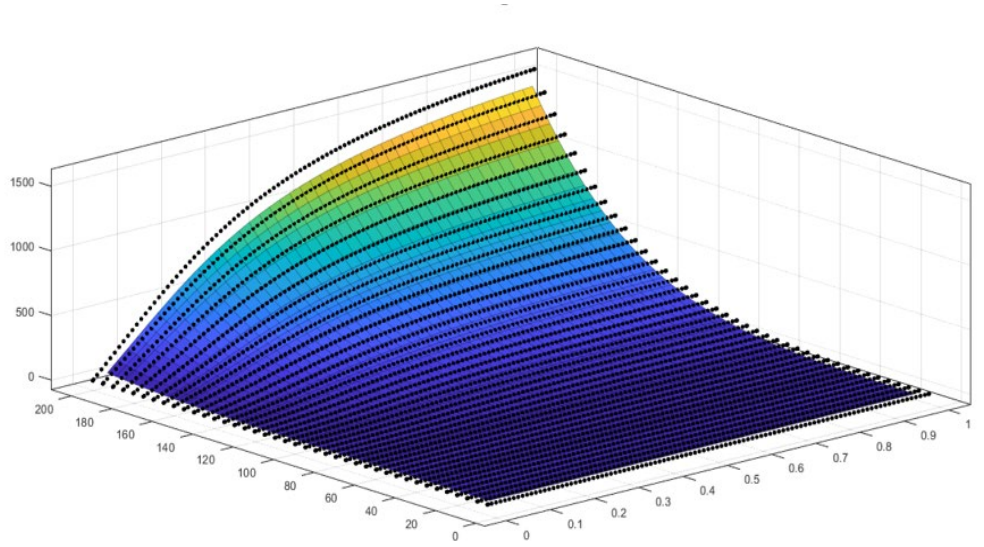
- The equations of state of real gas cannot be used for water/ionic liquid mixture.
- Difference of vapor liquid equilibrium (VLE) between ideal and real mixture is expressed by applying activity obtained by COSMO-RS that can consider surface charge density and chemical potential of the mixture.
- Enthalpy of refrigerant/ILs mixture is obtained by NRTL model with activity.

Water/Ionic liquid pair

- Enthalpy and P-T-x relations



<Enthalpy of water/[DMIM][DMP]>



<Vapor liquid equilibrium data>

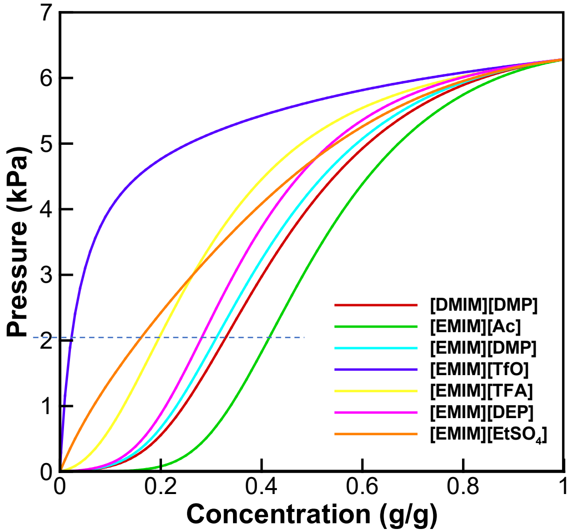
	Inlet/outlet temp. (°C)	Operating temp. (°C)	Operating pressure (kPa)
Evaporator	12/7	5	0.8726
Absorber	32/35	37	0.8726
Condenser	35/38	40	7.3849

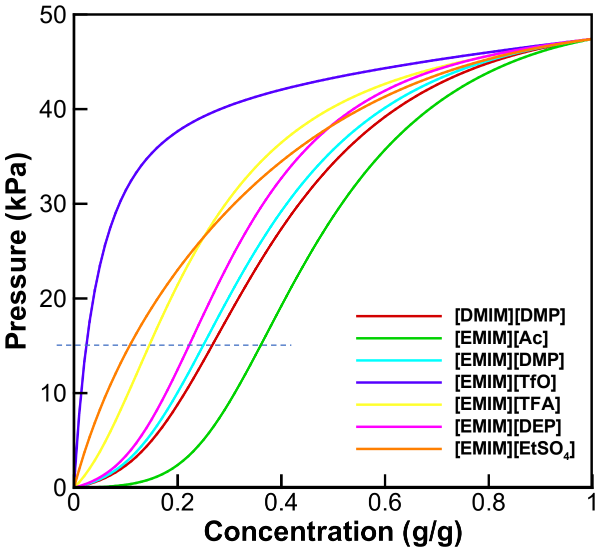
<Operating conditions for DEARS>

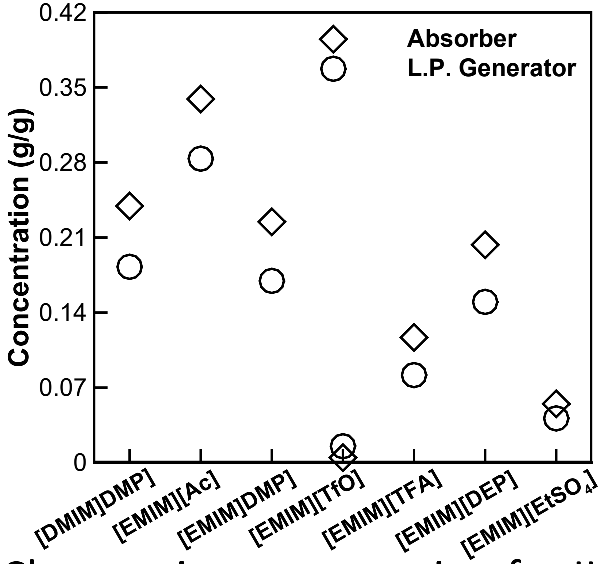
- The enthalpy and saturation pressure of the mixture are obtained using COSMO-RS and NRTL model.
- The enthalpy and P-T-x relation are used for DEARS system model.
- The operating conditions of DEARS are suggested based on KS B 6271.
- Pinch points are selected as 2 oC for all heat exchangers.

Water/Ionic liquid pair

- Changes in concentration depending on absorbents





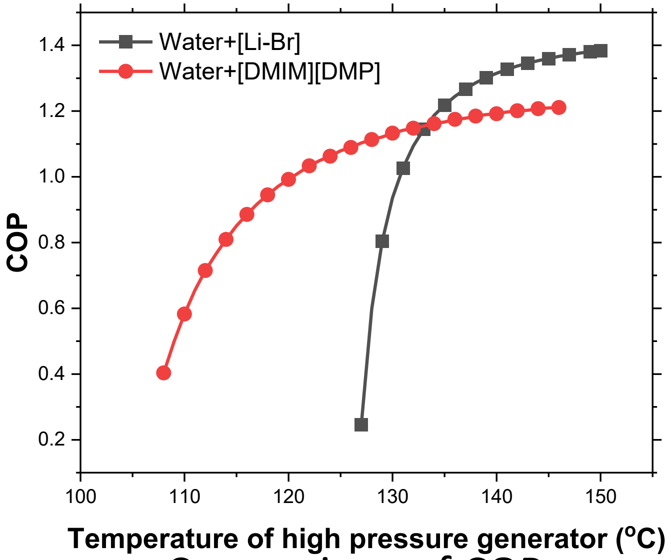


<Changes in pressure depending on concentration at absorber and low pressure generator> <Changes in concentration for ILs>

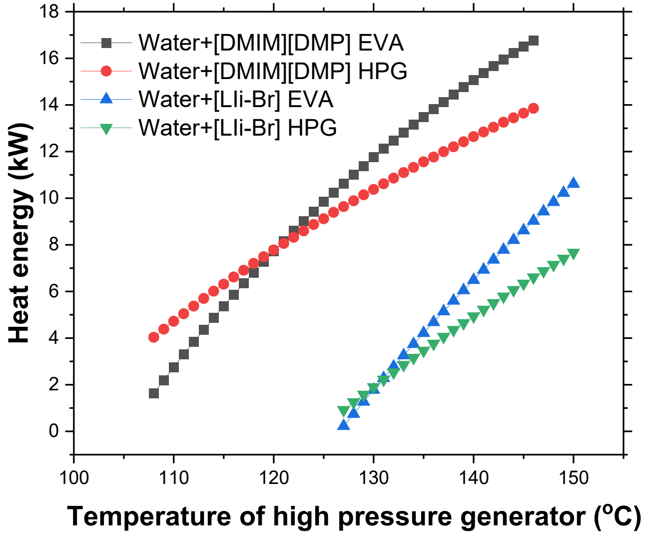
- The cooling capacity is larger when the difference between concentration at absorber and low pressure generator is large, because the amount of refrigerant is large.
- The concentration at absorber should higher that that of L.P. generator, but the case of [EMIM][TfO] shows opposite.
- Among ILs absorbents, [DMIM][DMP] has the largest concentration difference of 5.7%.

Water/Ionic liquid pair

- Performance of DEARS using [DMIM][DMP] as absorbent



<Comparison of COPs>

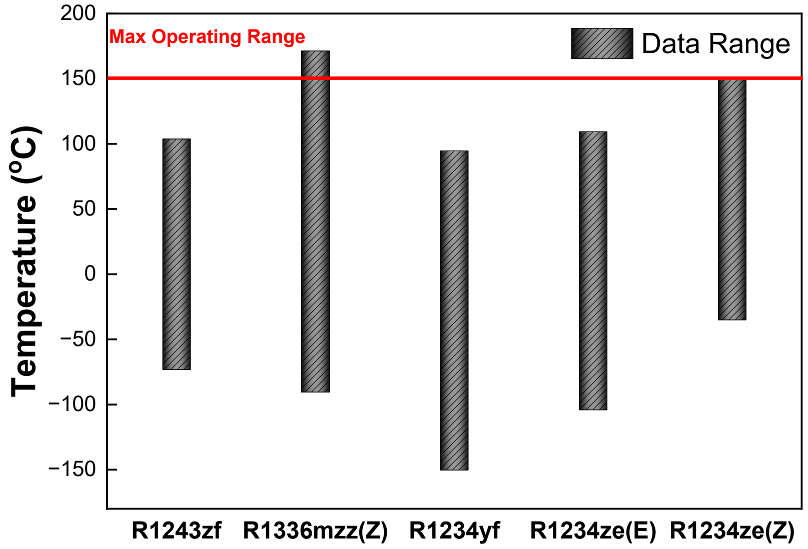


<Comparison of cooling capacity>

- Below 130 oC, COP of water/[DMIM][DMP] become higher than conventional system.
- Cooling capacity of water/[DMIM][DMP] pair shows higher value than conventional system because heat capacity of [DMIM][DMP] is large.
- Water/[DMIM][DMP] pair can solve crystallization problem, so that it can guarantee the safe operation of DEARS.

HFO refrigerant/Ionic liquid pair

- Examination of HFO refrigerant



<Operating range of HFO refrigerants>

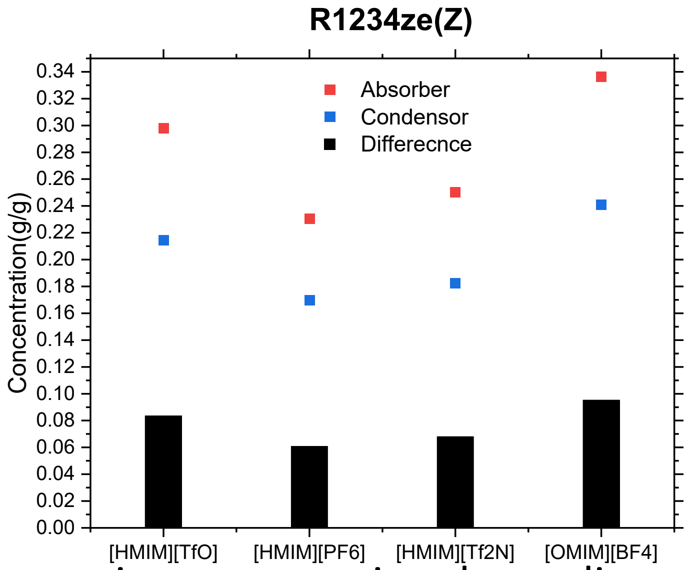
Safety	Lower Toxicity	Higher Toxicity
Higher Flammability	A3 / R-290(Propane), R-600a	B3
Lower Flammability	A2 / R-152a	B2
Lower Flammability	A2L / R1243zf ,R1234yf, R1234ze(E), R1234ze(Z), R32	B2L / R-717 (Ammonia)
No Flame Propagation	A1 / R1336mzz(Z), R407C, R507A	B1 / R-123

<Refrigerant safety classification>

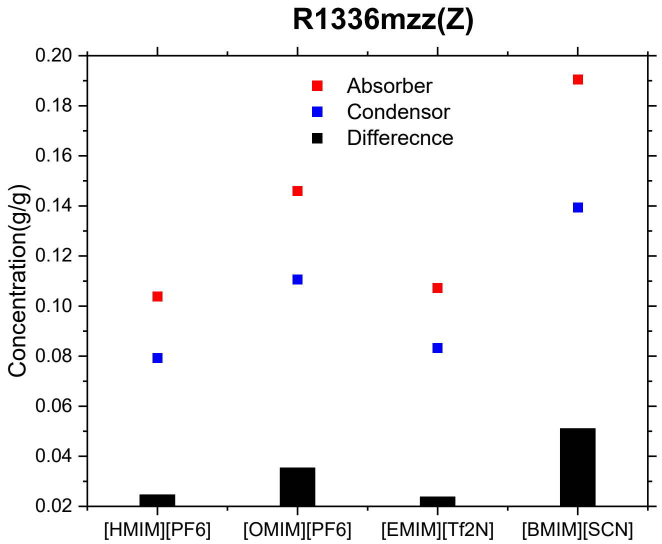
- Proper HFO refrigerants are selected considering operating range of HT-PEM/DEARS hybrid system and safety.
- R1234ze(Z) and R1336mzz(Z) are selected as promising refrigerant for DEARS using ILs as absorbent.
- The operating temperature of absorber and condenser assumed to be 30 ^{o}C because critical point of HFO refrigerants are lower than that of water.

HFO refrigerant/Ionic liquid pair

- Selection of absorbents



<Changes in concentration depending on ILs>

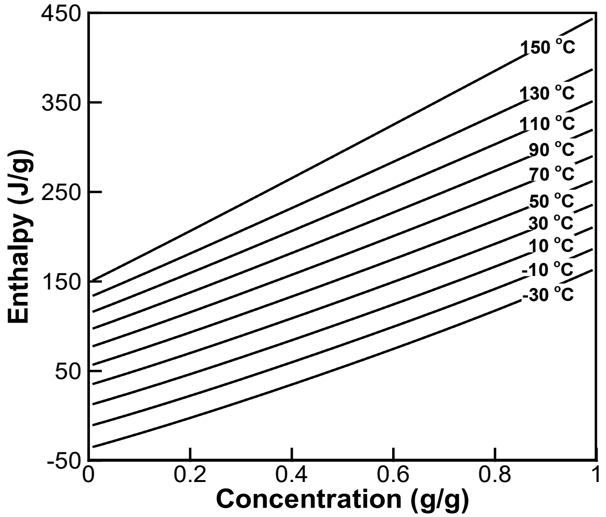


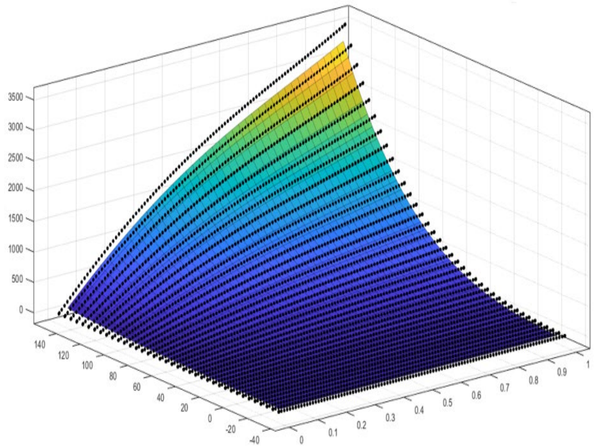
< Changes in concentration depending on ILs >

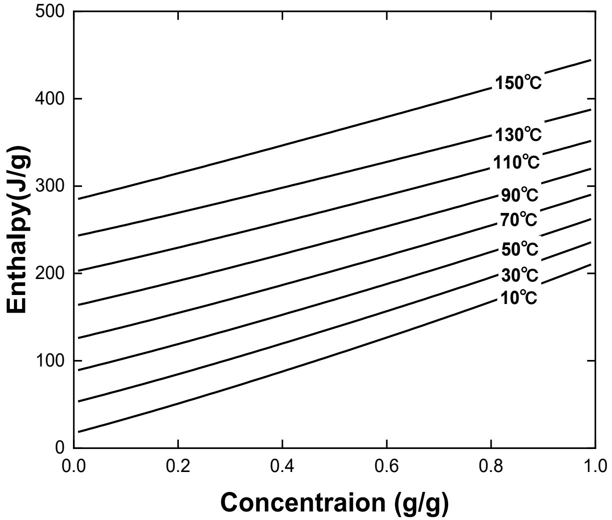
- In case of R1234ze(Z), when we use [OMIM][BF4] as absorbents, the difference of concentration between absorber and low pressure generator is the largest of 9.5%.
- In case of R1336mzz(Z), when we use [BMIM][SCN] as absorbents, the difference of concentration between absorber and low pressure generator is the largest of 5.1%.

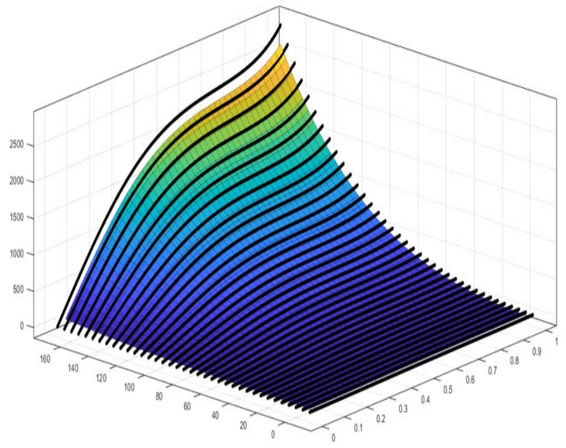
HFO refrigerant/Ionic liquid pair

- Enthalpy and P-T-x relations









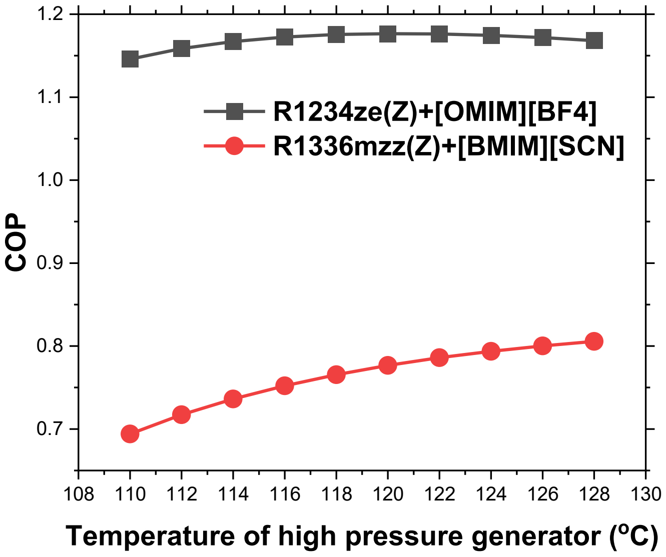
<Enthalpy and P-T-x diagram for R1234ze(Z)/[OMIM][BF4]>

<Enthalpy and P-T-x diagram for R1336mzz(Z)/[BMIM][SCN]>

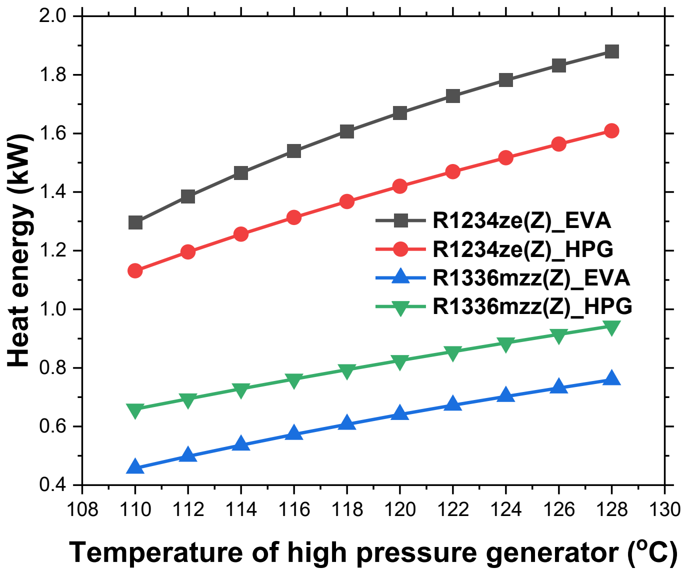
- In case of R1234ze(Z), the enthalpy of the real mixture is similar to that of ideal mixture because excessive enthalpy is low.
- In case of R1336mzz(Z), the change in enthalpy according to temperature is lower than that of R1234ze(Z) pair because specific heat of R1336mzz(Z) pair is low.

HFO refrigerant/Ionic liquid pair

- Performance of DEARS using HFO/ILs



<Comparison of COPs>



<Comparison of cooling capacity>

- COP of R1234/[OMIM][BF4] shows higher value than that of R1336mzz(Z)/[BMIM][SCN].
- Cooling capacity of R1234/[OMIM][BF4] is higher than that of R1336mzz(Z)/[BMIM][SCN] because heat capacity.
- R1336mzz(Z)/[BMIM][SCN], however, is safer pair than R1234/[OMIM][BF4].

Thank you

ElectroChemical Application for advanced Energy system Lab.

Everything's gonna be alright