

Heat Capacity Measurement and Cycle Simulation of the Trifluoroethanol (TFE)+Quinoline Mixture as a New Organic Working Fluid Used in Absorption Heat Pump

Ki-Sub Kim, Jong-Won Lee, Jin-Soo Kim and Huen Lee[†]

Department of Chemical and Biomolecular Engineering, Korea Advanced Institute of Science and Technology,
373-1 Guseong-dong, Yuseong-gu, Daejeon 305-701, Republic of Korea
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Abstract—The 2,2,2-trifluoroethanol (TFE)+quinoline mixture was chosen as a potential working fluid used in an absorption chiller. Heat capacity was measured and correlated by a polynomial equation as a function of temperature and concentration, and the parameters of the regression equation were determined by a least-squares method. The cycle simulation for a double effect absorption cycle was carried out at various operation conditions. The appropriate operation condition and COP values were calculated for the absorption cycle by using the proposed working fluid. TFE+quinoline solution could be a promising working fluid as an alternative to the LiBr+H₂O and H₂O+NH₃ systems based on the operation range and simulation results.

Key words: Absorption Heat Pump, Organic Working Pair, TFE, Quinoline, Cycle Simulation

INTRODUCTION

The vapor-compression cycle as a conventional cooling system has been known to possess disadvantages such as the use of CFC refrigerants and expensive electric energy. The ozone depletion and the concomitant regulation of CFC refrigerants have created an urgent interest in non-ozone-depleting refrigerants for use in commercial chillers. For those reasons, the absorption heat pump could be one of the best alternatives to the vapor compression chiller with respect to energy saving and environment protection. The absorption cycle is similar to the vapor compression cycle, but the major advantage of the absorption cycle is to use heat as the energy source and non-ozone-depleting substances as the working fluids [Kim and Lee, 2001; Stoeker and Jones, 1982]. The performance and efficiency of the absorption heat pump are mainly determined by the physical and thermal properties of working fluids.

Conventional working pairs such as H₂O+LiBr and NH₃+H₂O have been widely used in an absorption heat pump. However, they were found to be unsatisfactory particularly because of the corrosion and crystallization problems for the H₂O+LiBr and high working pressure and toxicity for the NH₃+H₂O [Coronas et al., 1996; Kim and Lee, 2002; Zhuo and Machielsen, 1993]. We have investigated various additives to LiBr+water solution in order to overcome the crystallization limit of the absorbent [Kim and Lee, 2001, 2002b, c; Kim et al., 1996a, b, 1997, 2000; Lee et al., 2000; Park et al., 1997; Park and Lee, 2002]. The addition of a certain amount of proper surfactants to working fluids can, of course, enhance heat and mass transfer by a vigorous instability named Marangoni convection [Park and Lee, 2002; Ziegler, 1996], but this additive-induced enhancement might not be a complete key to overcome the inherent difficulties of the LiBr-based working fluids. In the previous work we proposed the TFE+quinoline pair [Kim and Lee, 2002a], for which the basic properties were given in Table 1. TFE has good

solubility in quinoline because of its permanent dipole interaction and hydrogen bonding [Zhuo and Machielsen, 1993; Nowaczyk and Steimle, 1992; Stephan and Hengerer, 1993]. TFE has the activated hydrogen atom available for interaction with a proton acceptor, while quinoline acts as an electron donor that can achieve effective hydrogen bonding with TFE. It is also worthwhile to note that these two organic chemicals can be easily separated by a heat source because of their large boiling point difference (164 K). Accordingly, the present research purpose is first to measure the heat capacities of the TFE+quinoline mixtures and carry out the performance simulation together with other basic properties to check the possibility of its potential use in an absorption heat transformer [Lee et al., 2003].

EXPERIMENTAL SECTION

1. Materials

Quinoline (98%) and 2,2,2-trifluoroethanol (99+%) were supplied by Aldrich Chemical Co. and used without any further purification.

2. Apparatus and Procedure

Isoperibol solution calorimeter (CSC 4300) was used to measure the heat capacity of the sample solution [Kim and Lee, 2002a, b, c; Kim et al., 1997, 2000]. The calorimeter primarily consisted of a constant temperature bath, a Dewar vessel with a volume of 25 cm³, a calibration heater including a 100 Ω resistor, a thermistor, and a glass stirring rod. The temperature resolution of the calorimeter was 2 μ K, the temperature noise level ± 30 μ K, and the bath temperature stability ± 0.0005 K. Accurately weighted sample solution (approximate volume of 25 cm³) of a desired concentration was placed into the Dewar vessel. The thermistor, calibration heater, and stirring rod were immersed when the vessel was clamped on the isoperibol solution calorimeter. The stirrer and heater were then turned on to heat the sample solution to a slightly lower (about 0.15 K) temperature than desired. After 300 seconds passed from that point, an actual measuring process including 200 seconds without heat-

[†]To whom correspondence should be addressed.
E-mail: hlee@mail.kaist.ac.kr

Table 1. Physical properties of TFE and quinoline

Chemicals	M.W.	M.P.	B.P.	T _c	P _c	D	η	σ
2,2,2-TFE	100.04 ¹⁶	-44 ⁵	74 ⁵	226.14 ¹⁶	4.8606 ¹⁶	1382 ⁴	1.73 ⁴	21.11 ⁴
Quinoline	129.16 ²⁴	-15 ²⁴	237.7 ²⁴	509 ²⁴	4.66 ⁶	1089 ⁴	3.36 ⁴	43.27 ⁴

M.W.: molecular weight (g·mol⁻¹), M.P.: melting point (°C), B.P.: boiling point (°C), T_c: critical temperature (°C), P_c: critical pressure (MPa), D: density (kg·m⁻³), η: viscosity (mPa·s), σ: surface tension (mN·m⁻¹)

ing, 400 seconds of heating, and 200 seconds of holding time was begun. The accurate value of the added heat in the heating process was calculated through measuring the current and voltage values with a built - in digital voltmeter. All the measuring procedures were completely controlled by a computer and the temperature difference calculated by the computer was used to calculate the heat capacity of the sample solution with the following equation.

$$Q = (mC_p + \varepsilon) \Delta T \quad (1)$$

Where Q is the total amount of heat added, m the mass of the sample solution, C_p the heat capacity of the sample, ε the heat capacity of the apparatus including Dewar vessel, stirring rod, heater and thermistor. The value of ε was calculated by the experimental result using water as a reference solution and its known heat capacity value at each temperature. The experimental apparatus and procedure were checked with organic solutions of ethanol, methanol, and water at various temperatures and the resulting data were reliable within 1.0% relative error [Lide, 1995-1996].

CYCLE SIMULATION

1. Main Assumptions

The following main assumptions are made for the cycle simulation of absorption heat pump:

- It is not necessary to rectify the vapors leaving the generator due to the large difference between the boiling points of TFE and quinoline.
- The vapor pressure of quinoline is too low to affect the operation conditions of generator.
- The analysis is carried out under steady-state conditions, and the solution is saturated upon leaving the generator, and the absorber.
- The solution and refrigerant are in equilibrium at the given condition.

2. Heat Capacity

Heat capacities of the TFE+quinoline mixture were measured at

Table 2. Measured heat capacity values of TFE-quinoline mixture

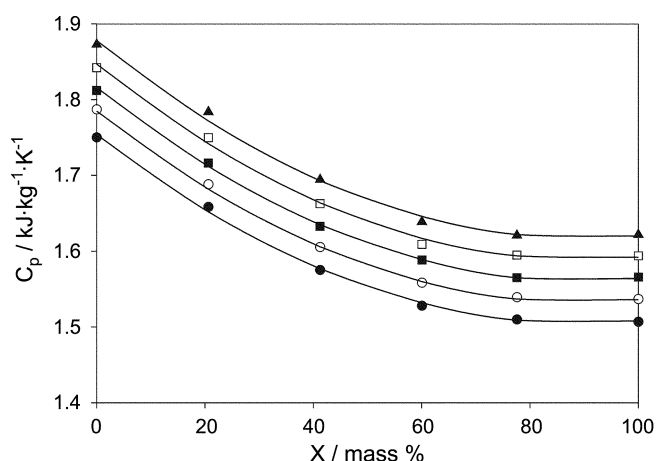
X	T / K				
	298.15	303.15	308.15	313.15	318.15
100	1.5070	1.5369	1.5660	1.5939	1.6220
77.58	1.5100	1.5394	1.5650	1.5950	1.6210
60.05	1.5281	1.5584	1.5884	1.6092	1.6390
41.25	1.5752	1.6055	1.6329	1.6628	1.6945
20.63	1.6585	1.6884	1.7164	1.7500	1.7840
0	1.7502	1.7872	1.8122	1.8422	1.8730

five temperatures (298.15, 303.15, 308.15, 313.15, and 318.15 K) and quinoline mass concentration ranges of (0 to 100%), respectively. The experimental results are presented in Table 2 and Fig. 1, and regressed by the following equation:

$$C_p = \sum_{i=0}^3 (A_i + B_i T) \cdot (100 - X)^i \quad (2)$$

The regression parameters were determined by a least-squares method and listed in Table 3. The average absolute deviation (AAD) was 2.05% between the experimental and calculated values. The heat capacities of the binary mixture decreased with increasing quinoline concentration and increased slightly with increasing temperature.

3. Enthalpy Calculation

**Fig. 1. Heat capacities of the TFE+quinoline system: ●, 298.15 K; ○, 303.15 K; ■, 308.15 K; □, 313.15 K; ▲, 318.15 K.****Table 3. Parameters for the correlation of Eqs. (2) and (3)**

C _p , Eq. (2)		
	A _i	B _i
i=0	9.272×10 ⁻¹	2.033×10 ⁻³
i=1	5.600×10 ⁻³	-2.176×10 ⁻⁵
i=2	-8.301×10 ⁻⁵	4.107×10 ⁻⁷
i=3	6.273×10 ⁻⁷	-2.292×10 ⁻⁹
AAD %	2.05	

H, Eq. (3)			
	A _i	B _i	C _i
i=0	1.950×10 ²	2.909×10 ⁻¹	3.560×10 ⁻³
i=1	-9.441	5.387×10 ⁻³	-6.020×10 ⁻¹⁰
i=2	1.340×10 ⁻¹	-8.182×10 ⁻⁴	1.112×10 ⁻⁶
i=3	-5.116×10 ⁻⁴	3.744×10 ⁻⁶	-5.056×10 ⁻⁹

The enthalpy calculation of a working fluid is important for the detailed design of an absorption heat pump especially for the calculation of energy balance. The enthalpy-concentration diagram (H-T-X) was constructed for the TFE+quinoline system. In the previous studies a similar simulation procedure was performed for the LiBr-based working fluids [Kim et al., 2000; Lee et al., 2000]. The enthalpy of solution was calculated by Haltenberger's procedure [Haltenberger, 1939] using vapor pressures [Lee et al., 2003] and heat capacities and the adopted equation is given as follows;

$$H = \sum_{i=0}^3 [A_i + B_i(T - 273.15) + C_i(T - 273.15)^2] X^i \quad (3)$$

where H is the relative enthalpy of the solution, X the concentration of quinoline in wt%, and A_i , B_i , and C_i regression parameters. The parameters A_i , B_i , and C_i were determined by a least-squares method and listed in Table 3. The reference state of solution for zero enthalpy is set to 273.15 K and 60 mass% of quinoline. Fig. 2 shows

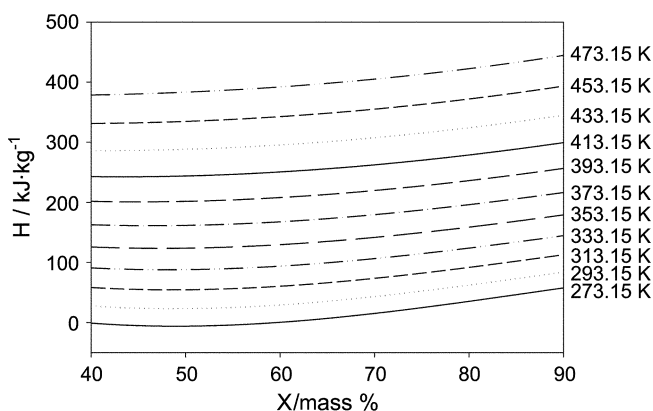


Fig. 2. Enthalpy-concentration diagram of the TFE+quinoline system.

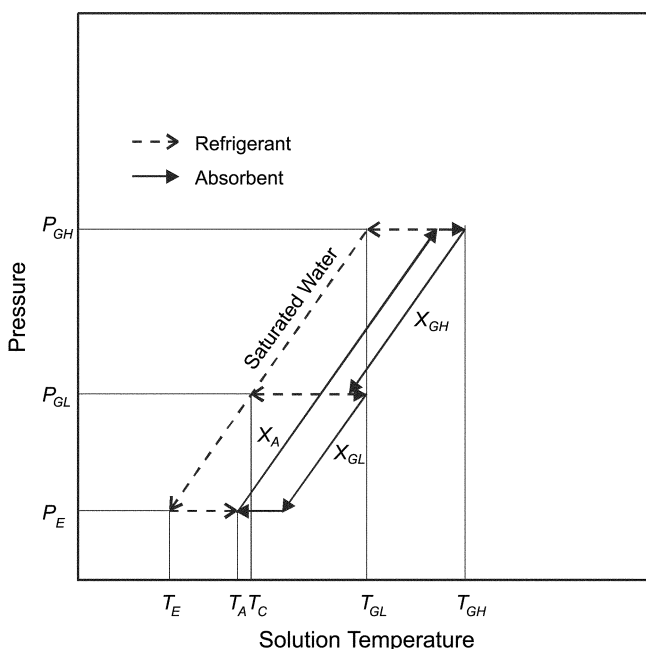


Fig. 3. Duhring diagram of a double-effect series flow absorption heat pump.

the complete enthalpy-concentration (H-T-X) diagram of the TFE+quinoline solution.

4. Performance Evaluation

The performance evaluations were carried out for the double effect series flow absorption chiller similar to our previous works [Lee et al., 2000; Kim et al., 1999; Won et al., 1991]. It needs to be stated again that the cycle simulation requires actual vapor pressure and heat capacity data [Lee et al., 2003]. The double effect flow cycles used for the simulation are represented in Fig. 3.

The theoretical COP of an absorption cycle can be calculated by material and energy balances assuming that each outlet flow from each unit is in the equilibrium state at the given unit condition. Accordingly, the thermodynamic properties of the absorbent and refrigerant should be known in each unit of the cycle. Material and energy balances applied to each unit are given as follows:

$$\sum_i F_i X_i = 0 \quad (4)$$

$$\sum_i F_i H_i = 0 \quad (5)$$

where F_i is the mass flow rate and H_i the specific enthalpy of solution or refrigerant which is a function of temperature and concentration. The evaporator temperature (T_E) was fixed at 276.15, 278.15, and 280.15 K and the absorber temperatures (T_A) at 303.15, 313.15, and 323.15 K. The condenser temperature (T_C) was identical with the absorber one. Based on these operation conditions for the cycle units, the cycle performance must be only dependent upon the temperature of the high-temperature generator (T_{GH}) and can be calculated through the procedure shown in Fig. 4.

RESULTS AND DISCUSSION

The coefficient of performance (COP) values of the double effect

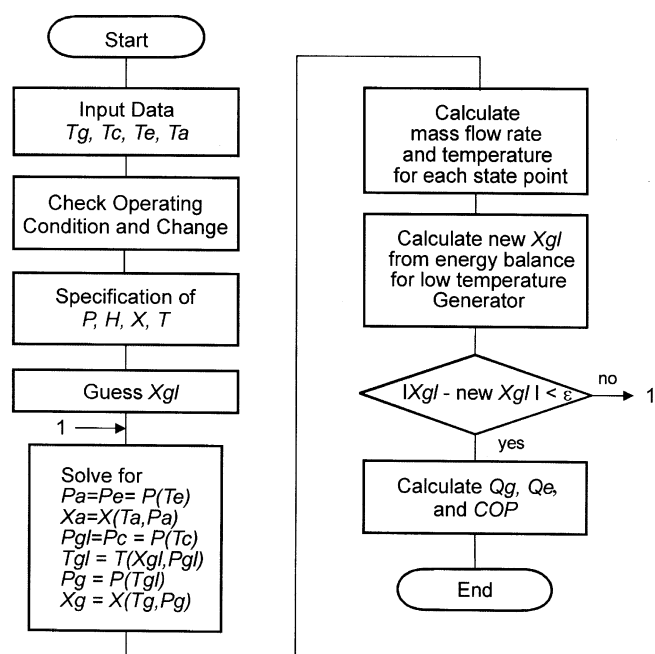


Fig. 4. Calculation of theoretical COP for the double effect absorption cycle.

absorption heat pumps using the TFE+quinoline system were calculated at various T_E , T_A , and T_C conditions in order to check its applicability of the solution to the operation of absorption heat pump. A double-effect absorption heat pump adopt two generators in order

Table 4. Coefficient of performance (COP) with the temperature of high temperature generator for the double-effect absorption heat at $T_E=276.15$ K

$T_A=T_C=303.15$ K		$T_A=T_C=313.15$ K		$T_A=T_C=323.15$ K	
T_{GH}	COP	T_{GH}	COP	T_{GH}	COP
366.65	0.00	398.75	0.00	435.35	0.00
368.35	0.47	400.75	0.31	436.95	0.11
369.95	0.73	402.85	0.51	438.65	0.20
371.55	0.91	404.95	0.66	440.05	0.28
373.15	1.03	407.15	0.77	441.75	0.35
374.95	1.11	409.35	0.86	443.25	0.42
376.65	1.17	411.75	0.92	445.05	0.47
378.35	1.22	414.15	0.98	446.75	0.52
380.15	1.26	416.55	1.02	448.45	0.56
381.95	1.29	421.75	1.09	450.35	0.60
383.65	1.32	424.65	1.12	452.15	0.64
387.45	1.37	427.55	1.14	455.95	0.70
389.45	1.38	430.55	1.16	458.05	0.72
391.45	1.40	433.75	1.18	460.05	0.75
395.55	1.42	437.05	1.19	462.15	0.77
397.65	1.43	444.35	1.22	464.25	0.79
399.85	1.44	448.05	1.22	468.95	0.82
402.25	1.44	452.25	1.22	473.75	0.82

Table 5. Coefficient of performance (COP) with the temperature of high temperature generator for the double-effect absorption heat at $T_E=278.15$ K

$T_A=T_C=303.15$ K		$T_A=T_C=313.15$ K		$T_A=T_C=323.15$ K	
T_{GH}	COP	T_{GH}	COP	T_{GH}	COP
362.35	0.00	393.95	0.00	428.95	0.00
363.85	0.52	395.85	0.34	430.35	0.12
365.45	0.79	397.85	0.55	431.85	0.22
367.05	0.98	399.75	0.70	433.15	0.31
368.65	1.09	401.75	0.82	434.65	0.38
370.25	1.16	403.75	0.91	436.05	0.45
371.85	1.24	405.95	0.97	437.55	0.51
373.55	1.27	408.15	1.02	439.15	0.56
375.25	1.31	410.35	1.07	440.75	0.60
378.65	1.37	412.75	1.11	443.95	0.68
380.35	1.40	417.65	1.16	445.65	0.71
382.15	1.42	420.35	1.18	447.55	0.74
383.95	1.43	422.95	1.21	449.15	0.77
385.85	1.44	425.85	1.22	451.05	0.79
387.75	1.45	428.75	1.24	454.85	0.83
391.65	1.47	435.05	1.26	456.75	0.85
393.75	1.47	438.45	1.27	458.75	0.87
397.95	1.47	442.05	1.27	460.85	0.87

to use the heat of vapor from the high-temperature generator as energy source in the low temperature generator. The lithium bromide+water solution cannot be used as a proper working fluid at high absorber temperature due to the crystallization limit. Its operation below 273 K is also limited due to the freezing of the water. On the other hand, the TFE+quinoline system has no crystallization and freezing problems of the refrigerant at the same condition. The COP increased with increasing generator and evaporator temperatures and with decreasing absorber and condenser temperatures as shown Tables 4-6 and Fig. 5. Table 7 shows the quinoline concentration in the absorber at each temperature condition. The coefficient of per-

Table 6. Coefficient of performance (COP) with the temperature of high temperature generator for the double-effect absorption heat at $T_E=280.15$ K

$T_A=T_C=303.15$ K		$T_A=T_C=313.15$ K		$T_A=T_C=323.15$ K	
T_{GH}	COP	T_{GH}	COP	T_{GH}	COP
358.05	0.00	389.35	0.00	423.05	0.00
359.55	0.57	391.15	0.36	424.35	0.13
361.05	0.87	392.95	0.60	425.65	0.24
362.55	1.04	394.75	0.75	426.85	0.34
364.15	1.15	396.65	0.86	428.25	0.41
365.65	1.23	398.55	0.95	429.65	0.48
367.25	1.30	400.55	1.02	430.85	0.55
368.85	1.35	402.55	1.07	432.25	0.60
370.45	1.38	404.65	1.12	433.75	0.64
373.65	1.43	409.05	1.18	436.55	0.73
375.35	1.45	411.25	1.21	438.15	0.76
377.05	1.47	413.65	1.23	439.75	0.78
378.75	1.48	416.05	1.26	441.25	0.82
380.45	1.50	418.65	1.27	442.95	0.84
384.15	1.51	424.05	1.29	446.25	0.88
385.95	1.52	426.95	1.30	447.95	0.90
387.85	1.53	429.95	1.32	449.65	0.92
389.85	1.53	433.05	1.32	451.65	0.92

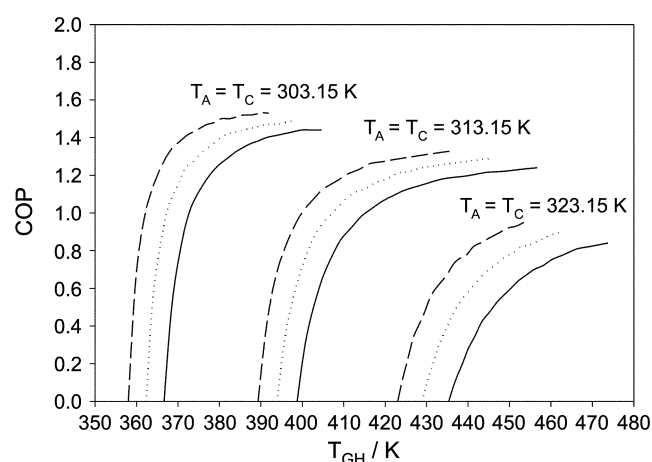
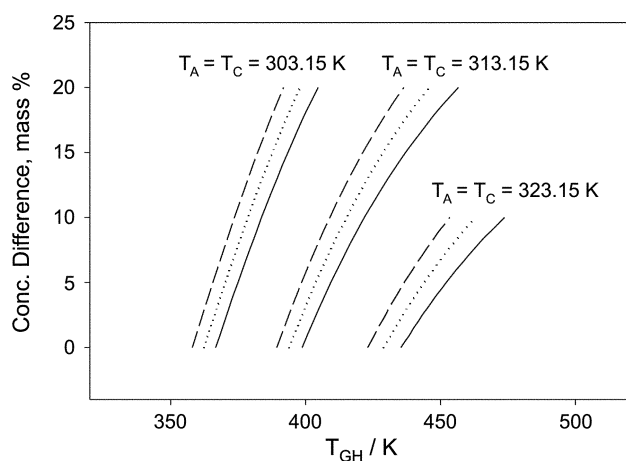


Fig. 5. Coefficient of performance (COP) with the temperature of high temperature generator for the double effect absorption heat pump: (—), $T_E=276.15$ K; (.....), $T_E=278.15$ K; (---), $T_E=280.15$ K.

Table 7. Quinoline concentration in the absorber at each unit temperature

T_E	$T_A = T_C$	$X_{A\text{-double}}$
276.15	303.15	60.04
	313.15	69.07
	323.15	77.07
278.15	303.15	57.87
	313.15	67.12
	323.15	75.33
280.15	303.15	55.65
	313.15	65.13
	323.15	73.57

**Fig. 6. Concentration difference with the temperature of high temperature generator for the double-effect absorption heat pump: (—), $T_E=276.15$ K; (.....), $T_E=278.15$ K; (---), $T_E=280.15$ K.**

formance value is the highest at $T_E=280.15$ K and $T_A=303.15$ K among various simulation conditions. This trend can be commonly shown in an absorption heat pump cycle. The operation at $T_A=323.15$ K is not desirable because the COP appears to be quite low.

The concentration difference between the inlet and outlet solutions in the absorber was calculated according to the generator temperature. The concentration difference represents the cooling capacity of the absorption chiller. Fig. 6 shows the relation between the concentration difference and generator temperature. The concentration difference increases as the generator temperature increases. During the process of the simulation we assumed the rectifier is not required due to the large difference of the boiling points between TFE and quinoline. However, as the temperature of a generator increased, the vaporization of the absorbent should be considered. At low temperature the vaporization of the absorbent does not matter, but as the temperature increases, it would be a more serious problem. To check and clarify this problem, low and atmospheric VLE experiments were also carried out [Lee et al., 2003]. The overall performance characteristic of the system is that the solution can be a new working fluid for absorption chiller which can be operated with the appropriate COP.

CONCLUSION

The new working fluid of the organic TFE+quinoline pair was proposed. The simulation was carried out to check the possibility of overcoming the limits of conventional working pairs typically referred to the LiBr+water and NH_3 +water solutions. Double effect absorption cooling cycles were investigated. The COP and concentration difference between the inlet and outlet solutions in an absorber were considered at various temperature conditions of each unit. The heat capacities were accurately measured and correlated with a proper regression equation to construct the enthalpy-concentration diagram needed for cycle simulation. The overall performance characteristics examined in the present study confirmed that the TFE+quinoline solution can be applicable to a highly potential working fluid. However, several additional considerations about the necessity of the rectifier and heat and mass transfer characteristics should be closely examined.

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NOMENCLATURE

- C_p : heat capacity [$\text{kJ} \cdot \text{kg}^{-1} \cdot \text{K}^{-1}$]
- ε : heat capacity of the apparatus [$\text{kJ} \cdot \text{K}^{-1}$]
- Q : heat [kJ]
- T : temperature [K]
- H : solution enthalpy [$\text{kJ} \cdot \text{kg}^{-1}$]
- X : quinoline concentration [weight %]
- F_i : mass flow rate [$\text{kg} \cdot \text{s}^{-1}$]
- T_E : evaporator temperature [K]
- T_A : absorber temperature [K]
- T_C : condenser temperature [K]
- T_G : generator temperature [K]
- T_{GH} : the temperature of high-temperature generator [K]
- T_{GL} : the temperature of low-temperature generator [K]
- P : pressure [kPa]
- COP : coefficient of performance
- TFE : 2,2,2-trifluoroethanol

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