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Hydrofluoroolefin Refrigerants and an Organic Solvent as an Alternative to Ammonia-Water Mixtures in Diffusion Absorption Cooling Systems

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Abstract **-** This study explores the feasibility of Hydrofluoroolefin (HFO) refrigerants, specifically 2,3,3,3-Tetrafluoropropene (R1234yf) and 1-Chloro-3,3,3-trifluoropropene (R1233zd(E)), as working fluids in Diffusion Absorption Refrigeration (DAR) systems, in conjunction with Dimethylacetamide (DMAC). Recognizing the low Global Warming Potential (GWP) of HFOs, this research aims to evaluate their performance. Experimental investigations were conducted to determine the thermodynamic properties of the HFO-DMAC binary mixtures, including pressure-temperature-concentration relationships and enthalpy-temperature-concentration data at equilibrium. Utilizing these experimentally derived properties, the Coefficient of Performance (COP) of the DAR cycle for each HFO-DMAC working pair was calculated. The results demonstrate that HFO-based DAR systems have the potential to operate at lower generator temperatures compared to conventional ammonia-water systems. This characteristic suggests that these systems can be effectively driven by lower-temperature heat sources, such as waste heat or solar energy, thereby enhancing their energy efficiency and environmental sustainability.
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Keywords**:** Diffusion absorption systems, binary solutions, Vapor liquid equilibrium, Hydrofluoroolefin refrigerants.

1. Introduction

In recent years, HFO refrigerants, such as R1234yf, R1234ze, R1336mzz(Z), and R1336mzz(E), have been introduced, marking a significant advancement in the development of sustainable refrigerants due to their low global warming potential (GWP)[1].

Within commercial diffusion absorption cooling systems, binary solution options typically include ammonia-water or water-lithium bromide (LiBr) combinations. The ammonia-water solution is prevalent in diffusion absorption refrigeration systems due to its chemical stability under varying pressures and temperatures. Ammonia's high latent heat of vaporization and low freezing point (-77°C) further enhance its suitability for applications requiring low evaporation temperatures. However, the ammonia-water system's volatility necessitates a rectifier for separating evaporated water from ammonia, often resulting in energy losses and diminished efficiency. Although ammonia-water-hydrogen systems have been utilized in diffusion absorption refrigeration for an extended period, researchers are actively investigating alternative working mixtures to reduce activation energy requirements.

Fluorinated refrigerants demonstrate excellent solubility with organic solvents such as N,N'-dimethylformamide (DMF) and N,N'-dimethylacetamide (DMAC). These refrigerants are less toxic compared to ammonia and achieve temperatures below 0°C that are suitable for refrigeration. Their stability, non-corrosiveness, and complete miscibility across a broad temperature range enhance their appeal [2, 3]. DMF is often employed as an absorbent in absorption refrigeration systems and has been adapted for use in diffusion absorption systems. However, precautions are necessary to avert leaks when DMF interacts with certain metals in the presence of oxygen. Zohar et al. [3] analyzed refrigerants R32, R124, R125, and R134a with DMF as an absorbent, noting effective results under various operational conditions. They observed that these mixtures activated at lower temperatures (150°C) but presented lower coefficients of performance alongside higher condensation and evaporation temperatures compared to ammonia-water systems. Their model [3-5] incorporated several simplifying assumptions. These included assuming equal temperatures for solution and vapor bubbles leaving the generator, a 5°C temperature drop for the solution and vapor in the bubble pump, complete refrigerant condensation with no bypass flow, and no sub-cooling of the condensed refrigerant. The temperature of the gas mixture at the evaporator outlet was considered known. The bubble pump, solution, and gas heat exchangers were assumed to be perfectly insulated. The rich solution entering the generator was assumed to be in equilibrium, and hydrostatic pressure and pressure drops along the pipes were neglected. Gas mixtures were treated as ideal gases. The exit of the gas heat exchanger was considered the entrance to the reservoir, and the refrigerant leaving the rectifier was assumed to be pure. Adiabatic mixing was assumed at the evaporator inlet, and no absorption was considered to have occurred within the reservoir. Finally, equilibrium was assumed for both the rich solution entering the generator and the weak solution entering the absorber, allowing the use of pressure-temperature –concentration relationships. DMAC, a commercially available organic compound with favorable solubility, is also recognized as an absorbent in refrigeration applications [6]. Its combination with halogenated refrigerants in diffusion absorption scenarios necessitates a rectifier, as the close boiling temperatures can result in DMAC evaporation, affecting cooling capacity and elevating manufacturing costs. Research by [7] indicated that R124-DMAC formed an effective working pair, exhibiting lower vapor pressures than those with DMF and activation temperatures in the range of 80°C to 180°C, thus favoring activation through solar energy and other heat sources.

While the thermodynamic properties of pure absorbents and refrigerants are thoroughly documented, the thermodynamic characteristics of binary organic mixtures suitable for absorption refrigeration systems require further exploration. Moreover, the interaction of Hydrofluoroolefin (HFO) refrigerants with various absorbents remains significantly under-researched. This study aims to experimentally characterize the thermodynamic properties of binary mixtures, including pressure-temperature-concentration and enthalpy-temperature-concentration relations, at equilibrium. The acquired data will be subsequently integrated into the a diffusion absorption model. The refrigerants of interest include R1234yf and DMAC (N,N'-dimethylacetamide).

2. Experimental Procedure

Building upon the work of [8] and [9], an experimental setup was designed. It consisted of a 300 ml Parr 4383 pressure vessel equipped with pressure and temperature sensors to measure equilibrium data (Figure .1). A controlled electrical heating jacket provided uniform heating, while insulation minimized heat loss. Magnetic stirring with a Teflon-clad capsule ensured thorough mixing. Two thermocouples measured the liquid and gas phase temperatures, and a pressure gauge recorded the system's equilibrium pressure. In each experimental run, the reactor was weighed to accurately measure the initial mass of refrigerant and absorbent. The temperature was then gradually increased, and the system was allowed to reach equilibrium. At equilibrium, the pressure within the reactor was recorded. After each set of measurements, the reactor was cooled to ambient temperature, and a controlled amount of gas was inserted. This procedure was repeated multiple times to generate a comprehensive dataset. For the first set of experiments R1234yf and DMAC were the binary mixture components, whereas in the second experiment the refrigerant was replaced to R1233zd(E) and DMAC the absorbent remained the same.

Fig. 1: Experimental setup.

Equilibrium was reached when the temperatures of the two phases were the same. The weight fraction of the refrigerant in liquid phase can be defined by:

$$\xi_R = \frac{m_{RS}}{m_{RS} + m_{AS}} \tag{1}$$

m_{RS} is the mass of the refrigerant in the liquid phase, m_{RG} is the mass of the refrigerant in gas phase, m_{AS} is the mass of the absorbent in the liquid phase and m_{AG} is the mass of the absorbent in the gas phase.

When there is an equilibrium between two phases, the fugasities of each phase are equal $f_i^V = f_i^L$ and for each component obtained:

$$y_i p = \gamma_i x_i p_i^{sat} \Phi_i \tag{2}$$

y_i is the mole fraction of component i, p is the measured pressure of the system, γ_i is the activity coefficient (calculated based on Van Laar relation for the molar excess Gibbs free energy), x_i is the molar concentration of component i (refrigerant or absorber) in the liquid solution, p_i^{sat} is the saturation pressure of component i, Φ_i is the correction factor for pressure changes in the system.

After obtaining pressure-temperature-concentration data, it was expressed in as a polynomial function:

$$p = \sum_{j=0}^{j=5} \sum_{i=0}^{i=6} p_{ij} {\xi_R}^i T^j \tag{3}$$

The values of p_{ij} were obtained by regression of the equilibrium results. The temperature T is in Celsius. Figure 2 and Figure 3.illustrates the pressure-temperature-concentration data obtained in the study. Numerical values p_{ij} are provided in Table 1 and Table 2.

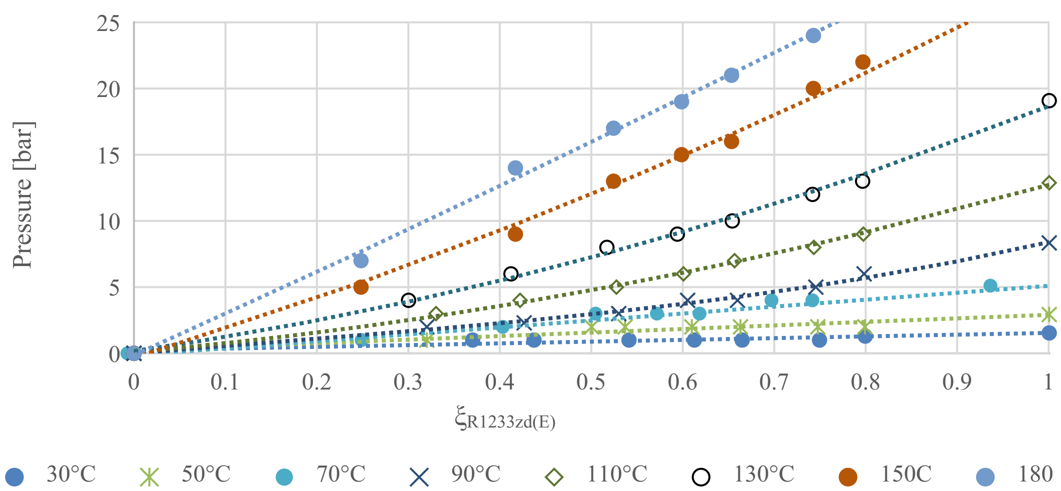

Fig. 2: Pressure-temperature-concentration diagram of R1233zd(E).

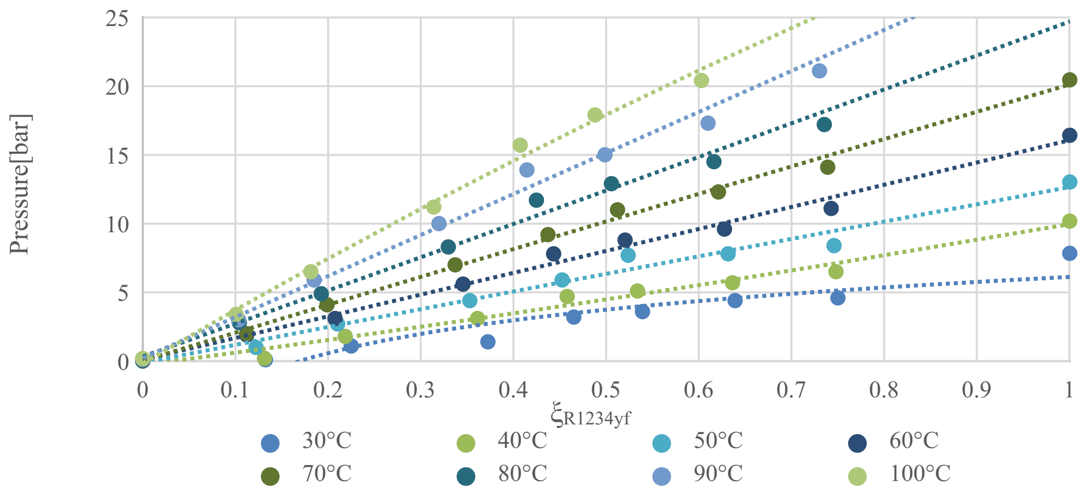

Fig. 3: Pressure-temperature-concentration diagram of R1234yf.

Table 1: p_{ij} coefficients of R1233zd(E).

	ξ^0	ξ^1	ξ^2	ξ^3	ξ^4	ξ^5
T^0	-3.57E+01	4.15E+02	-4.22E+03	1.28E+04	-1.47E+04	4.78E+03
T^1	3.08E+00	-3.37E+01	3.54E+02	-1.12E+03	1.39E+03	-5.87E+02
T^2	-1.01E-01	8.08E-01	-9.00E+00	2.92E+01	-3.65E+01	1.55E+01
T^3	1.65E-03	-8.66E-03	1.04E-01	-3.46E-01	4.39E-01	-1.88E-01

Table 1: p_{ij} coefficients of R1234yf.

	ξ^0	ξ^1	ξ^2	ξ^3	ξ^4	ξ^5	ξ^6
T^0	-2.79E+05	4.27E+04	-3.56E+05	9.33E+05	-9.97E+05	3.72E+05	5.67E+03
T^1	2.78E+04	-3.39E+03	2.84E+04	-7.51E+04	8.10E+04	-3.10E+04	0.00E+00
T^2	-1.10E+03	9.79E+01	-8.30E+02	2.20E+03	-2.38E+03	9.11E+02	0.00E+00
T^3	2.21E+01	-1.34E+00	1.15E+01	-3.04E+01	3.30E+01	-1.27E+01	0.00E+00
T^4	-2.41E-01	8.74E-03	-7.58E-02	2.02E-01	-2.19E-01	8.44E-02	0.00E+00
T^5	1.36E-03	-2.21E-05	1.94E-04	-5.17E-04	5.63E-04	-2.17E-04	0.00E+00

The enthalpy of the binary solution is given by:

$$h = h_R \xi_R + h_A \left(1 - \xi_R\right) + h^E \qquad (4)$$

The enthalpy of the solution in the liquid phase is h. h_R and h_A are the specific enthalpies of the refrigerants and the absorbent, h^E is the excess specific enthalpy of mixing since the solution is assumed to be not ideal. The data for the calculations of the specific enthalpies of the absorbent and the refrigerant can be found in the literature [10,8]. Molar excess enthalpy is derived from:

$$H^E = \left(\frac{\partial \left(G^E / T \right)}{\partial \left(1/T \right)} \right)_{p,x} \qquad (5)$$

G^E the excess molar Gibbs energy depends on the molar concentration x and activity coefficient γ of each component:

$$G^E = RT\left(x_R \ln\left(\gamma_R\right) + x_A \ln\left(\gamma_A\right)\right) \qquad (6)$$

The dependence of enthalpy on refrigerant mass concentration is graphically represented in Figure 4 and Figure 5.

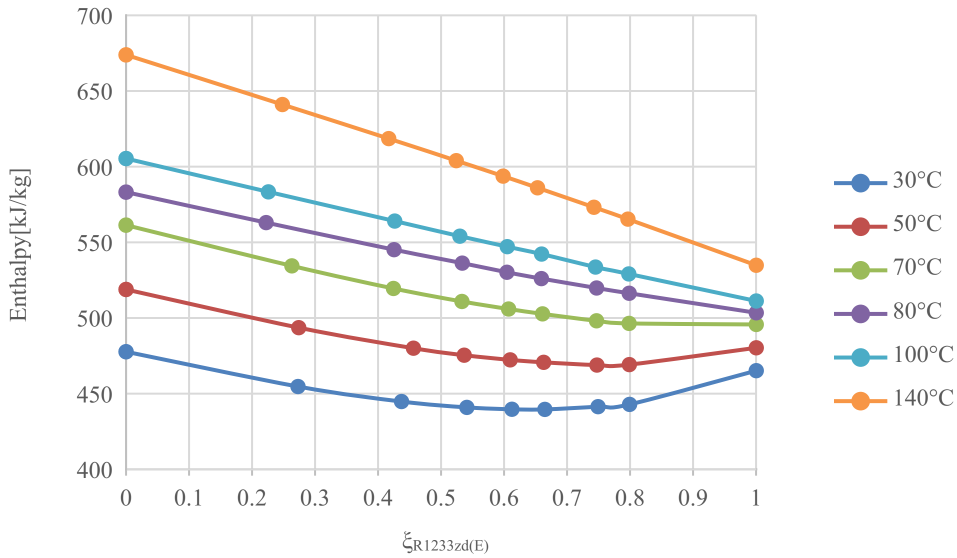

Fig. 4: Enthalpy-temperature-concentration diagram of R1233zd(E).

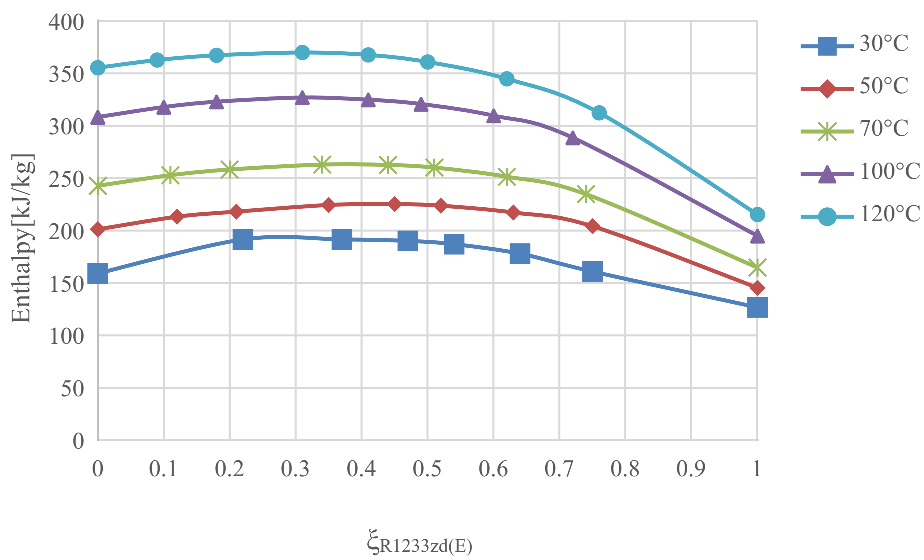

Fig. 5: Enthalpy-temperature-concentration diagram of R1234yf.

The enthalpy of the mixture can be represented by a polynomial equation. The coefficients h_{ij} are presented in Table3 and Table 4.

$$h = \sum\sum h_{ij} \xi_R{}^j T^i \qquad (7)$$

Table 3: h_{ij} coefficients of R1233zd(E).

	ξ^0	ξ^1	ξ^2	ξ^3	ξ^4	ξ^5	ξ^6
T^0	-2.79E+05	4.27E+04	-3.56E+05	9.33E+05	9.97E+05	3.72E+05	5.67E+03
T^1	2.78E+04	-3.39E+03	2.84E+04	-7.51E+04	.10E+04	-3.10E+04	0.00E+00
T^2	-1.10E+03	9.79E+01	-8.30E+02	2.20E+03	2.38E+03	9.11E+02	0.00E+00
T^3	2.21E+01	-1.34E+00	1.15E+01	-3.04E+01	.30E+01	-1.27E+01	0.00E+00
T^4	-2.41E-01	8.74E-03	-7.58E-02	2.02E-01	2.19E-01	8.44E-02	0.00E+00
T^5	1.36E-03	-2.21E-05	1.94E-04	-5.17E-04	.63E-04	-2.17E-04	0.00E+00
T^0	-3.08E-06	0.00E+00	0.00E+00	0.00E+00	.00E+00	0.00E+00	0.00E+00

Table 4: h_{ij} coefficients of R1234yf

	ξ^0	ξ^1	ξ^2	ξ^3	ξ^4	ξ^5	ξ^6
T^0	8.81E+03	1.78E+05	1.21E+06	-3.63E+06	4.88E+06	2.31E+06	-1.12E+05
T^1	-7.53E+02	1.58E+04	1.08E+05	3.26E+05	-4.45E+05	2.24E+05	0.00E+00
T^2	2.30E+01	5.03E+02	3.43E+03	-1.04E+04	1.42E+04	7.13E+03	0.00E+00
T^3	-3.20E-01	7.43E+00	-5.09E+01	1.54E+02	-2.11E+02	1.06E+02	0.00E+00
T^4	1.96E-03	5.13E-02	3.53E-01	-1.07E+00	1.47E+00	-7.36E-01	0.00E+00
T^5	-3.24E-06	1.34E-04	-9.24E-04	2.81E-03	-3.84E-03	1.93E-03	0.00E+00
T^0	-7.56E-09	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00

3. DAR Model Results

The obtained solutions properties were incorporated in a DAR model of [4], the scematic drawing of the DAR system is presented in Figure 6:

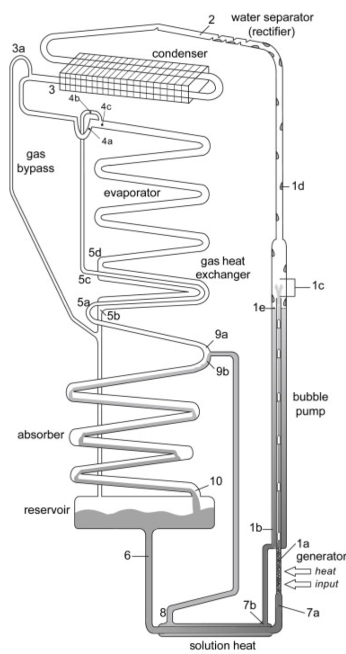

Fig. 6: DAR system layout [Zohar 2005].

The coefficient of performance (COP) was calculated as the ratio of the cooling capacity of the evaporator to the applied heat at the generator with EES[]:

$$COP=\frac{\dot{Q}_{evap}}{\dot{Q}_{gen}} \quad (8)$$

The coefficient of performance variations with the generator temperature for the two mixtures are presented in Figure 7. The input data for the results was $T_{cond}=45\ ^oC,\ T_{evap}=-5\ ^oC$. The analysis demonstrated that the maximum COP was achieved for rich solution concentration, $\xi_6 = 0.4$, and poor solution concentration , $\xi_6 = 0.2$ .For these input parameters the generator temperature was $110^o \le T_{1e} \le 127^o$. System pressure which is defined as the saturation pressure of the refrigerant at the condenser temperature was lower for R1233zd(E)-DAMC pair (*252kPa*) than for R1233zd(E)-DMAC pair (*1152kPa*).

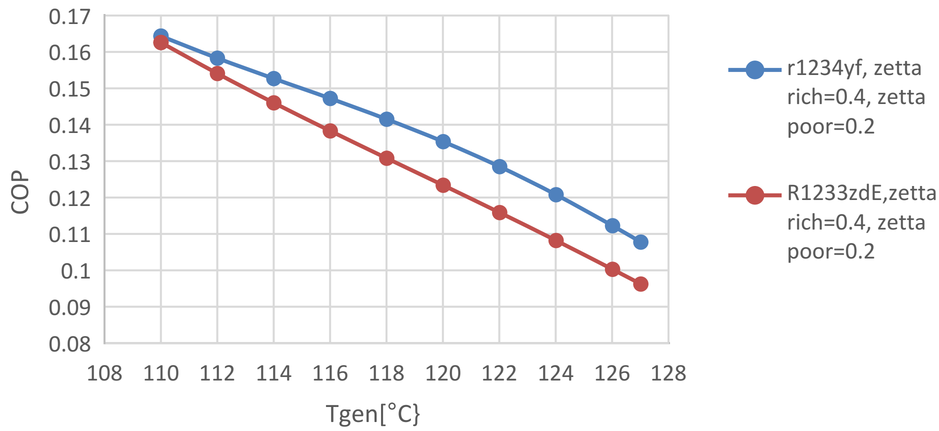

Fig.7: COP of the two mixtures for given rich and poor concentration as a function of the generator temperature..

4. Conclusion

This study combines experimental and theoretical approaches to investigate the feasibility of replacing ammonia-water with an HFO-DMAC binary solution in DAR systems. Experimental work was conducted to determine the pressure-temperature-concentration and enthalpy-temperature-concentration relationships of the binary mixtures at equilibrium. This experimental data was then integrated into a model that calculated the Coefficient of Performance (COP) of the diffusion absorption cycle for each of the two HFO-DMAC mixtures.

For a given set of operating conditions, the model computed the COP of the system across a range of generator temperatures. The results indicate that the achievable COP for the HFO-DMAC mixtures falls within the typical range observed for conventional DAR systems [3]. However, the generator temperatures required for effective operation with the HFO-DMAC mixtures were found to be lower than those typically needed for ammonia-water systems [6]. This suggests that DAR systems utilizing HFO-DMAC binary solutions could potentially be driven by lower-temperature heat sources, such as waste heat or solar energy.

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