

1992

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Gage, C. L. and Kazachid, O. S., "Predictions of Azeotropes Formed from Fluorinated Ethers, Ethanes, and Propanes" (1992).
International Refrigeration and Air Conditioning Conference. Paper 201.
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PREDICTIONS OF AZEOTROPES FORMED FROM FLUORINATED ETHERS, ETHANES, AND PROPANES

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ABSTRACT

The synthesis of new non-chlorinated refrigerants expands the base of alternatives for replacing ozone-depleting chlorofluorocarbons (CFCs) and their first-generation replacements, hydrochlorofluorocarbons (HCFCs). Besides the direct use of these refrigerants, there is also the potential to combine them with other compounds to form blends. In this work, the potential for azeotrope formation and performance was evaluated for fluorinated ethers, ethanes, and propanes.

Azeotrope formation was predicted using an interaction parameter for the mixture which was based on the dipole moments and volumes of the components. Dipole moments for the new compounds were predicted from the molecular structure. Of 20 fluorinated ether and hydrocarbon pairs tested, seven were found to form azeotropes. Results from this work predicted azeotropes with boiling points between -46°C (-52°F) and -19°C (-2°F), indicating potential replacements for CFC-12 and R-502, an azeotrope of HCFC-22 and CFC-115. Azeotrope performance in vapor-compression cycles was then evaluated.

INTRODUCTION

Ozone depletion has inspired intensive research to identify chemicals to replace the CFCs which break down in the stratosphere and deplete ozone. This research begins with the identification of replacement chemicals through property analysis and ends with the optimization of systems to use these chemicals. Early on, the Environmental Protection Agency (EPA) and the Electric Power Research Institute (EPRI) recognized that at the time there were not many chemical options to choose from, and thus, they jointly funded work at two universities to synthesize new fluorinated ethers and propanes (1). This work identified 39 compounds for which some property data were collected. The work presented in this paper extends the use of the new chemicals through identification and evaluation of potential azeotropes formed from these chemicals and other known alternatives. Since it is expected that all chlorine containing refrigerants will be banned from production, only azeotropes without chlorine are discussed.

BACKGROUND AND OBJECTIVES

Synthesis of the new chemicals has expanded the choices to replace the ozone-depleting CFCs and HCFCs. Table 1 lists the existing chlorine-free hydrofluorocarbons (HFCs) and some hydrocarbons (HCs) with their normal boiling points. Also shown are the newly synthesized refrigerants, HFCs and hydrofluoroethers (HFEs) which are being evaluated by EPA. This table only contains compounds which have boiling points in the range from -52°C (-62°F) to 25°C (77°F). This range covers the boiling points of the following chlorine-containing compounds: HCFC-22, CFC-12, HCFC-124, HCFC-142b, CFC-114, CFC-11, HCFC-123, and the azeotrope refrigerants, R-500 and R-502. Compounds which are known to be flammable are indicated by italics. Flammability tests on the new chemicals are being performed by EPA. Based on the ratio of hydrogen to fluorine in these chemicals, most are expected to be nonflammable.

Many of the theoretical evaluations which have been performed on the alternative refrigerants use the Carnahan-Starling-DeSantis (CSD) equation-of-state (2). This work has resulted in several cycle codes which use this equation-of-state and many of the associated subroutines for the calculation of refrigerant properties. These codes involve various levels of simulation complexity from the simple cycle at saturated conditions to systems which incorporate some equipment details (3-6).

For mixtures, the use of the CSD equation requires the specification of an interaction parameter which is specific to the refrigerant pair. This parameter accounts for the interaction of the pure component's molecules in the mixture. In the studies mentioned above which evaluated mixtures, the unknown interaction parameters of the mixtures were set at the same value.

Table 1: Non-Chlorinated Refrigerant Options and Their Normal Boiling Points. T_{nbp}
(Italics indicate compounds known to be flammable.)

<u>Existing Chemical</u>	<u>T_{nbp}, °C (°F)</u>	<u>New Chemical</u>
<i>HFC-32</i>	-52 (-62)	
<i>HFC-125</i>	-49 (-56)	
<i>HFC-143a</i>	-48 (-54)	
<i>HC-290 (Propane)</i>	-42 (-44)	
	-35 (-31)	HFE-125
<i>HC-270 (Cyclopropane)</i>	-33 (-27)	
<i>HFC-134a</i>	-26 (-15)	
<i>HFC-152a</i>	-24 (-11)	HFE-143a
<i>HFC-134</i>	-20 (-4)	
	-18 (0)	HFC-245cb
	-16 (3)	HFC-227ca
	-15 (5)	HFC-227ea
<i>HC-600a (Isobutane)</i>	- 6 (21)	
<i>HC-600 (Butane)</i>	- 1 (30)	HFC-236cb, HFC-236fa, HFC-254cb
<i>HFC-143</i>	5 (41)	
	7 (45)	HFC-236ea
	15 (59)	HFC-245fa
	25 (77)	HFC-245ca

Interaction parameters have been measured for several of the CFC refrigerant pairs (2). However, the parameters for most combinations, especially for the alternative refrigerants, have been neither measured nor estimated. The lack of reliable data for the interaction parameter has been a hindrance to the research. In the search for alternative compounds, the initial steps involve preliminary thermodynamic evaluations in order to prescreen the options. Without interaction parameters it is impossible to evaluate mixtures to perform this prescreening. This implies that it would be necessary to test all possible combinations in order to gather the interaction parameters for use in screening. This would be a sizeable task and would in the end yield data for combinations which may not be pursued because of poor performance predicted during the prescreening. Therefore, it became clear that a method of estimating the interaction parameter was needed.

This work addresses the search for better alternative refrigerants in terms of capacity, efficiency, and flammability. The objectives include the development of a method for predicting interaction parameters, the prediction of azeotropes from the non-chlorinated refrigerants included in Table 1, and the evaluation of these azeotropes in vapor-compression cycles.

METHOD OF PREDICTION

Using the data from measured interaction parameters, an empirical correlation was developed based on the nature of molecular interactions in mixtures. This correlation expresses the interaction parameter as a function of dipole moments and volumes for the refrigerant pair. These variables were chosen based on several considerations. In the mixing of real fluids, the properties of the mixtures are affected by the ability of the molecules to form weak links. In this case, the bonds of interest are those that occur from dipole-dipole attractions. For dipole-dipole interactions, the force varies with the difference in the dipole moments and $1/r^3$, where r is the distance between the molecules. Since this force operates in three dimensions (i.e., within a volume), it indicates that a correlation which is inversely proportional to molecular volume can be expected. The CSD equation-of-state uses a parameter, b , which represents the average closest approach of the molecules and has units of volume(2). Although the prediction method is not tied to the CSD equation-of-state, this equation is widely used and, therefore, the parameter "b" can be chosen as the representative volume. The following equation shows the general correlation which was assumed to express the interaction parameter:

$$f_{12} = A + B(\Delta DP) + C(\Delta DP)^2 + D/(V_1 V_2)$$

where

- ΔDP = (dipole moment of the low boiler) - (dipole moment of the high boiler),
- V_1 = molecular volume for the low boiler, and
- V_2 = molecular volume for the high boiler.

It should be noted that this expression neglects any dependence on the temperature, while earlier work indicates that for a few compounds there may be a temperature dependence of the interaction parameter (2).

Interaction parameters for 22 refrigerant pairs were used to regress the coefficients of the interaction parameter expression. Four of these refrigerant pairs are azeotropes. The values of all measured interaction parameters ranged from -0.014 to 0.12. For the molecular volumes, the individual "b" parameters calculated from the CSD equation-of-state were used as the representative volumes. These parameters lead to the following values for the coefficients:

$$\begin{array}{ll} A = -0.0105822 & B = 0.1988274 \\ C = 0.033164561 & D = 0.000102909 \end{array}$$

The expression for f_{12} has been used to calculate the interaction parameter for more than 100 refrigerant pairs. It has been noted that for a few pairs, which include a compound with a zero dipole moment, the correlation predicts an interaction parameter which falls significantly out of the range of observed values. Therefore, when the correlation predicted values much greater than 0.12, a value for f_{12} of 0.12 has been used.

AZEOTROPE PREDICTION

The correlation shown above between the dipole moments, volumes, and the interaction parameter was successfully used in 1990 to predict the formation of an azeotrope between HFC-32 and HFC-125 (7). The existence of this azeotrope was later confirmed by Allied-Signal (8). In this work, the correlation was used to predict azeotropes of recently synthesized fluorinated compounds.

Since dipole moments have not been measured for the new chemicals, it was necessary to estimate their values. Dipole moments were calculated using the Modified Neglected Differential Overlaps method (9). Using known dipole moments for nine carbon-fluorine molecules, the C-F bondlengths were optimized to give a fit to the known compounds with an average deviation of about 4 percent (10). The "optimized" bondlengths were then used to calculate the dipole moments of the new chemicals. The predicted dipole moments as well as the dipole moments of the other components of the azeotropes are shown in Table 2. Also shown are the volumes calculated at 298 K (537°R) using the temperature dependence expression for the CSD parameter, b. For some compounds, dipole moments are a function of temperature (11). When this occurs, the value reported for 298 K (537°R) has been used in the prediction of the interaction parameter.

Once the interaction parameters were estimated, potential azeotropes containing the new chemicals were evaluated. Using up to 10 degrees difference in normal boiling points as pairing criteria, 20 refrigerant pairs were initially selected for screening. Applying the CSD refrigerant property routines, dew points and bubble points were calculated for each refrigerant pair between -40°C (-40°F) and +20°C (68°F) and across the composition range. An azeotrope was identified when both the vapor composition at the bubble point and the liquid composition at the dew point matched the specified composition. Of the more than 20 pairs which were screened, seven indicated azeotropic formations. Table 3 lists these compounds along with their estimated interaction parameters, compositions, normal boiling points, T_{nbp} , and critical temperatures, T_c . Critical temperatures were estimated using the correlation of Li which was shown to predict the critical temperatures of 10 other refrigerant azeotropes within 3°C (5.4°F) (13). The pressure dependence of the azeotrope compositions is shown in Figure 1. Here the pressure is represented by the saturation temperature. In the future, the existence of these azeotropes will be tested in the EPA laboratory.

Two of the azeotropes, HFE-143a/HFC-152a and HFE-125/HC-270, contain known flammable components. It would be hoped that the formation of the azeotrope would suppress the flammable characteristics. This is true for the R-500 azeotrope which is formed from 26 percent HFC-152a and 74 percent CFC-12 (13). The potential flammability of these mixtures will also be evaluated in the EPA laboratory.

Table 2: Pure Component Parameters for Compounds Which Formed Azeotropes

Compound	Dipole Moment (debye)	Reference	Volume	
			(m ³ /kmol)	(ft ³ /lbmol)
HFC-134a	2.058	(11)	0.0873	(1.400)
HFC-134	0.991	(11)	0.0873	(1.400)
HFC-152a	2.262	(11)	0.0795	(1.275)
HC-270	0	(11)	0.0721	(1.156)
HFE-143a	2.45	(12)	0.0810	(1.299)
HFE-125	2.55	(10)	0.0987	(1.582)
HFC-245cb	2.44	(10)	0.1192	(1.911)
HFC-227ea	2.05	(10)	0.1244	(1.994)

EVALUATION OF THE PREDICTED AZEOTROPES AS REFRIGERANTS

The boiling points of the seven predicted azeotropes indicate potential replacements for CFC-12, HCFC-22, and R-502. The cycle efficiency, volumetric capacity, and the temperature at the end of isentropic compression were compared to evaluate the potential performance of the azeotropes in vapor-compression cycles against their pure component constituents and against the existing chemicals which they could replace. Here, the cycle efficiency is COP/COP_c , where COP is defined as the cooling capacity divided by the work of compression, and COP_c is $(T_c - T_e)/T_e$. The simple cycle is defined by saturated liquid exiting the condenser, isenthalpic expansion, saturated vapor exiting the evaporator, and isentropic compression. However, real systems do not operate at these conditions. Domestic refrigerator/freezers (R/Fs) and supermarket systems are two applications which have additional subcooling and superheating: R/Fs through suction-line heat exchange, and supermarkets through mechanical subcooling and the unavoidable heat gains occurring in the long lines between the evaporator and the compressor. Recent work has shown that the losses associated with expansion and compression superheating are strongly dependant on the refrigerant's properties (14,15). This has significant implications when making comparisons for real systems where additional subcooling and superheating may occur because of internal heat exchange, ambient heat gains or losses, or direct addition of subcooling. A more detailed thermodynamic analysis of the azeotropes across a wider range of operating conditions has also been performed (16).

For this analysis, the applications of supermarkets and domestic R/Fs are of interest. The two low-boiling ether azeotropes were evaluated at operating conditions chosen to simulate supermarket systems. These conditions include 43°C (110°F) condensing temperature, 5°C (9°F) condenser subcooling, mechanical subcooling of the liquid to 12.8°C (55°F), 5°C (9°F) evaporator superheating, and ambient heat gains to bring the suction vapor temperature to 18.3°C (65°F). A range of evaporating temperatures was chosen to include conditions for ice cream cases and frozen foods. For these conditions, supermarkets presently use either R-502 or HCFC-22.

Figures 2 to 4 show the predicted results for the HFE-125 azeotropes, their pure components, R-502, and HCFC-22. In Figure 2, which shows the efficiency of the cycle relative to Carnot, the performances of both azeotropes are between the performances of their pure components. This figure indicates that the efficiencies of both ether azeotropes are very close to that of R-502. Figure 3 indicates that the volumetric capacity of the HFE-125/HC-270 azeotrope is also very similar to those of R-502 and HCFC-22, while the HFE-125/HFC-134a azeotrope and the pure components have much lower capacities. Figure 4 shows that both azeotropes have lower compressor discharge temperatures than R-502 and HCFC-22. Another important parameter to consider in low temperature systems is the suction pressure. The only compounds which operated above atmospheric pressure at all evaporating temperatures were R-502, HCFC-22, and HFE-125/HC-270.

The remaining five azeotropes were evaluated as replacements for CFC-12. The operating conditions were 43°C (110°F) condensing temperature with internal heat exchange applied to increase the suction vapor temperature to 18.3°C (65°F). A range of evaporating temperatures were chosen to include conditions for domestic R/Fs and supermarket cases for dairy products, produce, and frozen meats. The performance results are shown in Figure 5, and the volumetric capacities are shown in Figure 6.

Table 3: Predicted Azeotropes and Their Critical Temperatures

Azeotrope Pair	Mass Ratio	f_{12}	T_{bnp}		T_c
			°C	(°F)	°C (°F)
HFE-125/HC-270	0.77/0.22	0.1200	-46.5	(-51.7)	66 (151)
HFE-125/HFC-134a	0.81/0.19	0.0681	-39.1	(-38.3)	75 (167)
HFE-143a/HFC-134	0.55/0.45	0.1025	-30.3	(-22.6)	91 (196)
HFC-134a/HFE-143a	0.66/0.34	0.0174	-26.7	(-16.1)	101 (214)
HFE-143a/HFC-152a	0.56/0.44	0.0067	-24.9	(-12.8)	107 (225)
HFC-134/HFC-245cb	0.53/0.47	0.0390	-23.2	(-9.7)	99 (210)
HFC-245cb/HFC-227ea	0.30/0.70	0.0092	-19.4	(-2.9)	100 (212)

Figure 5 shows that only one azeotrope, HFE-143a/HFC-152a, outperforms CFC-12. This is an azeotrope whose pure components also outperform CFC-12. Two other azeotropes have performances close to CFC-12. Figure 5 indicates that for two of the azeotropes, HFC-134a/HFE-143a and HFE-143a/HFC-134, the pure components outperformed their respective mixtures. The evaporator inlet qualities for these azeotropes were higher than those for their pure components, where the quality is defined as the mass of vapor ratioed to the total mass. For the other three azeotropes, whose performances were between the pure components, the qualities were also between those of their pure components. Higher evaporator inlet qualities are indicators of higher throttling losses. It has been shown previously that refrigerants which have high throttling losses will be those which can gain the most from additional internal heat exchange (15). It was also demonstrated in the same work that it is important to compare refrigerants not in the same cycle but rather between cycles which have been tailored to the refrigerant properties. Thus this comparison should be performed before any refrigerant is rejected from further consideration.

Figure 6 shows the volumetric capacities for the azeotropes and their pure components. Here the HFE-143a/HFC-152a azeotrope is seen to have lower capacity than CFC-12, while the capacity of the HFC-134a/HFE-143a azeotrope is close to those of both CFC-12 and HFC-134a. The suction pressures of three of the azeotropes were high enough that they could be expected to operate above atmospheric pressure at R/F conditions. Two azeotropes, HFC-134/HFC-245cb and HFC-245cb/HFE-227ea, would probably operate under vacuum at these conditions. Discharge temperatures for all of the azeotropes were found to be lower than that for CFC-12.

CONCLUSIONS

1. A method was developed for evaluating interaction parameters of mixtures as a function of dipole moments and molecular volume.
2. Seven new, non-chlorinated azeotropes were identified in the boiling point range of -46°C (-52°F) to -19°C (-2°F).
3. At operating conditions appropriate to supermarkets, two low-temperature ether azeotropes (HFE-125/HFC-134a and HFE-125/HC-270) have performance efficiencies near that of R-502, and one azeotrope, HFE-125/HC-270, has a volumetric capacity which also matches that of R-502. Therefore, this azeotrope can be considered as an alternative and eventual replacement for R-502.
4. Three azeotropes (HFE-143a/HFC-152a, HFE-143a/HFC-134, and HFC-134a/HFE-143a) have boiling points which would make them acceptable replacements for CFC-12. However, at operating conditions close to those of refrigerator/freezers, none matched both performance and volumetric capacity.

ACKNOWLEDGEMENTS

The property determinations for the new chemicals were jointly funded with the Electric Power Research Institute. The authors thank N. Dean Smith of EPA for providing supporting information for this work, and they thank James A. Register III of EPA for his participation in the computer simulations.

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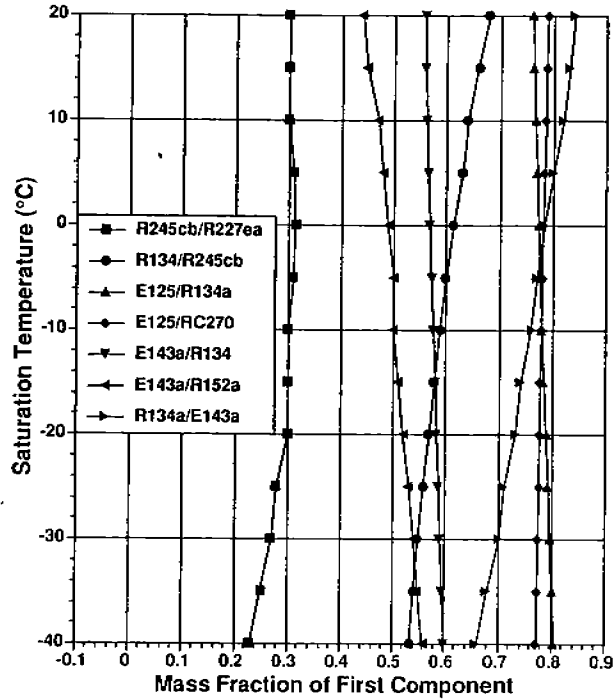


Figure 1: Temperature Dependence of Azeotrope Composition.

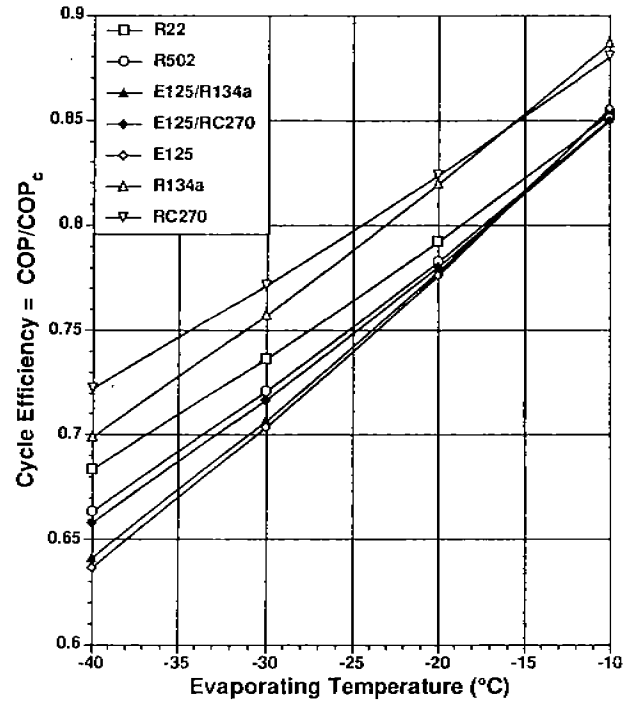


Figure 2: Performance of Low Temperature Refrigerants at 43°C Condensing.

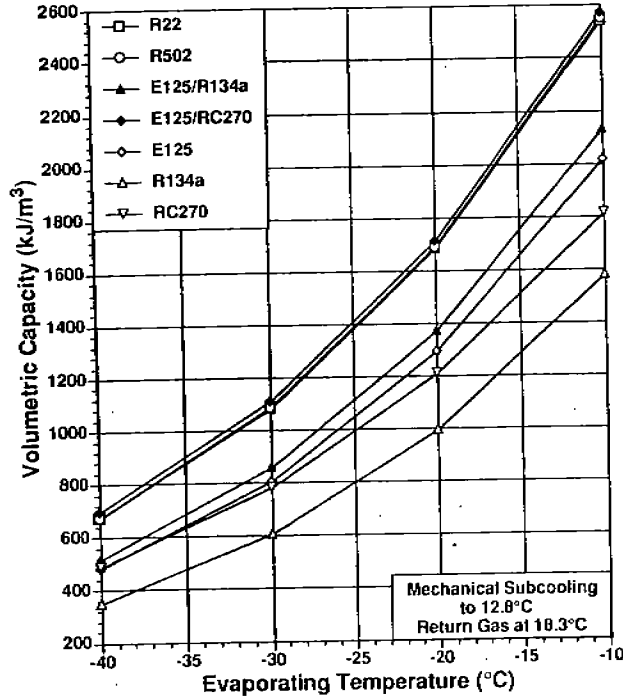


Figure 3: Volumetric Capacity of Low Temperature Refrigerants at 43°C Condensing.

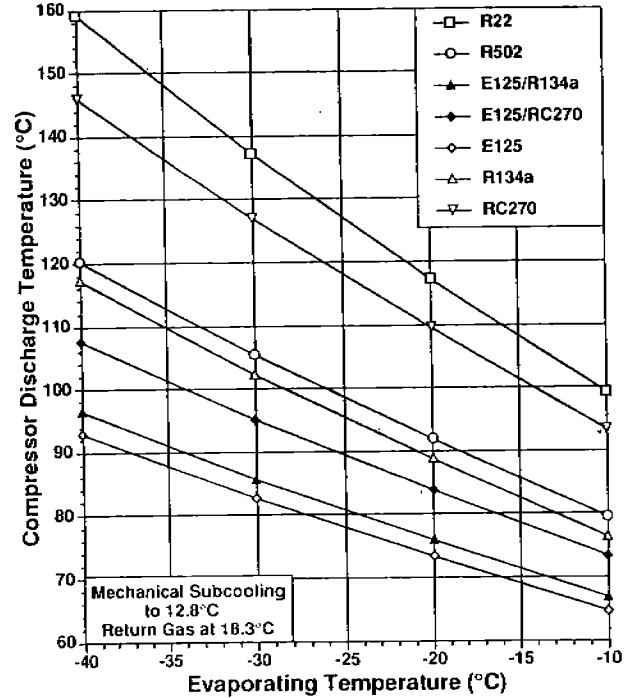


Figure 4: Compressor Discharge Temperature at 43°C Condensing.

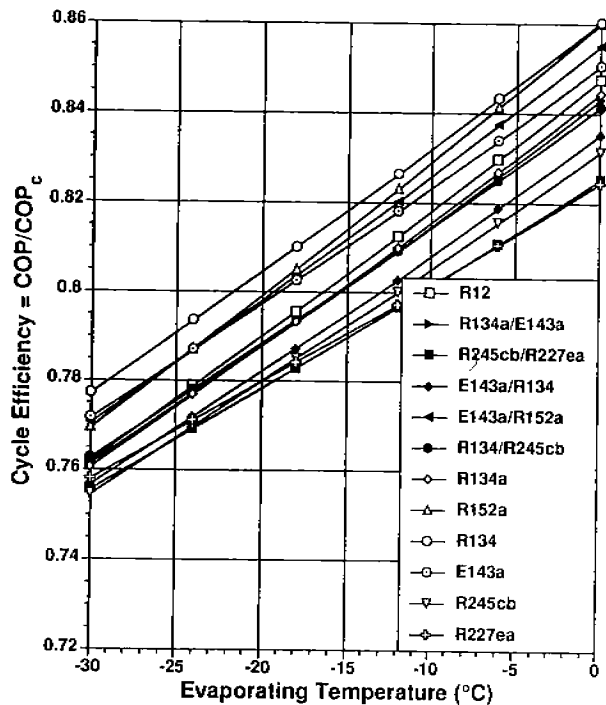


Figure 5: Efficiency of Cycle with Internal Heat Exchange at 43°C Condensing. Vapor heated to 18.3°C

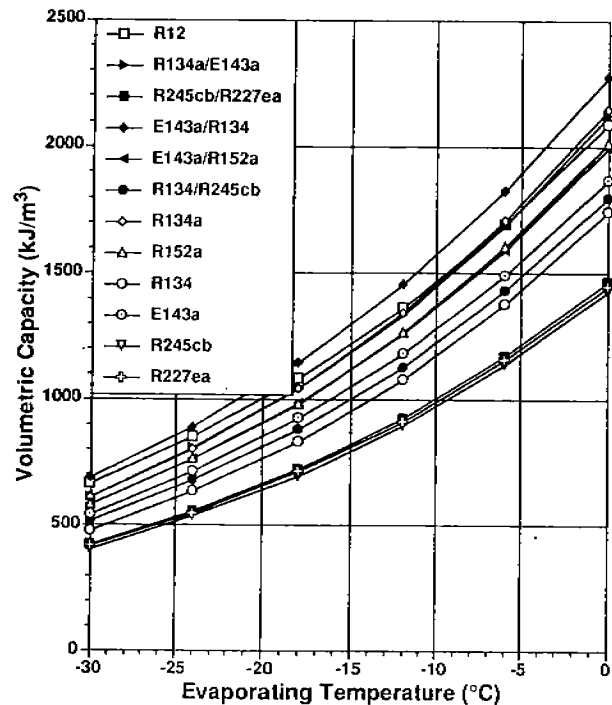


Figure 6: Volumetric Capacity with Internal Heat Exchange at 43°C Condensing. Vapor heated to 18.3°C