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Alternatives Research Center

Vapor-Liquid Equilibria for HFCs + Propane

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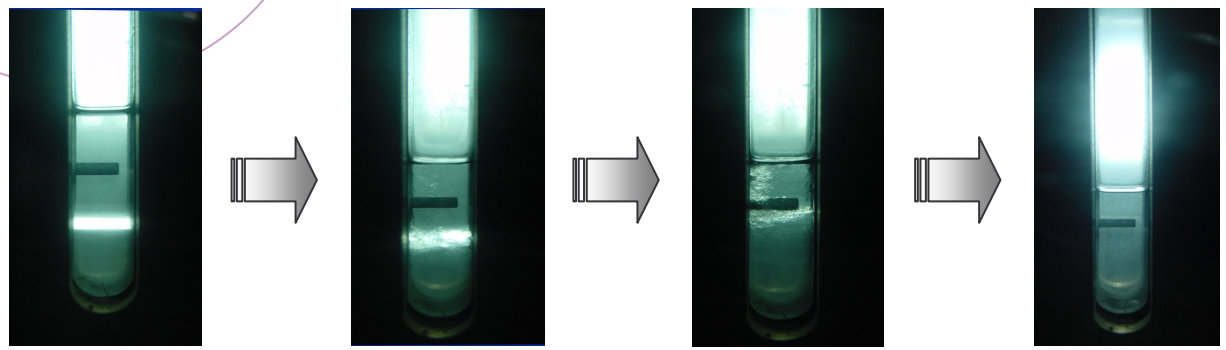

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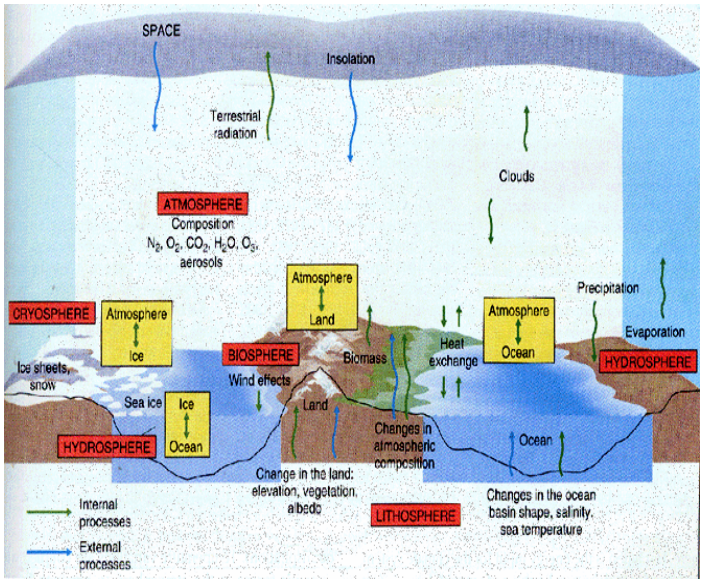
Introduction

Air conditioning has to use refrigerants and although there are many types of refrigerants, including air and water, it is necessary to use chemicals for reasonsof efficiency and ultimately to conserve energy.



Hydrofluorocarbons (HFCs) are a family of refrigerants that have been specifically developed to provide alternatives to CFCs and HCFCs. They have many of the favorable characteristics of CFCs especially those of zero flammability and zero toxicity. However, HFCs are powerful greenhouse gases that are identified in the Kyoto Protocol.

This can be done either by :

minimising leakage of HFC refrigerants to the lowest practical level

or by using low Global Warming Potential refrigerants such as ammonia or HCs (hydrocarbons)

Introduction

R11(CCl_3F) is a single chlorofluorocarbon or CFC compound. It has a high chlorine content and ozone depletion potential (ODP) and high global warming potential (GWP).

ODP = 1, GWP = 4000

R22($CHClF_2$) is a single hydrochloro-fluorocarbon or HCFC compound. It has low chlorine content and ozone depletion potential and only a modest global warming potential.

ODP = 0.05, GWP = 1700

R134a(CH_2FCF_3) is a single hydro-fluorocarbon or HFC com-pound. It has no chlorine content, no ozone depletion potential, and only a modest global warming potential.

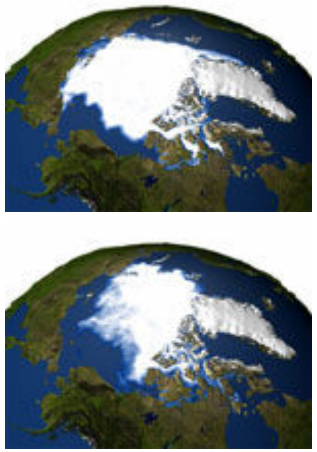
ODP = 0, GWP = 1300

R236ea (CHF_2CHFCF_3) is a single hydrofluorocarbon or HFC com-pound. Currently, one of the leading candidates to replace CFC-114 is R236ea.

ODP = 0, GWP = 1200

R290(CH_3CH_2CH) - Pure propane, a hydrocarbon (HC) an efficient naturally occurring refrigerant with similar properties to R22.

ODP = 0, GWP = 3



Side by side comparison of sea ice from 1979 and 2003
Courtesy NASA

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Purpose of research

- Vapor liquid equilibrium data are required as one of the most important types of information in evaluating the performance of refrigeration cycles and determining their optimal compositions.
- In the present study, a blend of propane and nonflammable HFCs refrigerant are reduced both in global warming impact and flammability.
- In this work, we measured VLE data for the binary mixture of Hydrofluorocarbons (HFCs) + propane at 273.15, 283.15, 293.15, 303.15, 313.15 and 323.15 K.
- Experimental data were correlated with the Peng-Robinson and Peng-Robinson-Stryjek–Vera equation of state using the Wong-Sandler and Huron-Vidal mixing rules.

CSD EoS

It was found that the CSD-EoS has been demonstrated to represent the P-V-T properties. This equation of state is expressed as follows

$$\frac{PV}{RT} = \frac{1 + y + y^2 - y^3}{(1-y)^3} - \frac{a}{RT(V+b)} \qquad y = \frac{b}{4V}$$

V : molar volume

In case of pure component, the temperature dependence of 'a' and 'b' are represented by the following forms:

$$a = \alpha_0 \, exp\left(\alpha_1 T + \alpha_2 T^2\right) \qquad b = \beta_0 + \beta_1 T + \beta_2 T^2$$

The coefficient of $\alpha_0, \alpha_1, \alpha_2$ in equation (3) and $\beta_0, \beta_1, \beta_2$ in equation (4) were cited from REFPROP 5.0

CSD EoS

In the application of CSD-EoS to mixture, there exists the effective molecular parameters am and bm defined by using the following mixing rules:

$$a_m = \sum_{i=1}^{n}\sum_{j=1}^{n} x_i x_j a_{ij} \qquad b_m = \sum_{i=1}^{n}\sum_{j=1}^{n} x_i x_j b_{ij}$$

When i = j, the value of a_{ii} and b_{ii} are those of 'a' and 'b' of the pure Components which are determined by equation (3) and (4). The values of a_{12} and b_{12} can be expressed as following forms

$$a_{12} = (1 - f_{12})(a_{11}a_{22})^{1/2} \qquad b_{12} = \frac{1}{8}\left(b_{11}^{1/3} + b_{22}^{1/3}\right)^3$$

The model involves the adjustable binary parameters, f_{12}, which must be determined from experimental data.

PR EoS

The VLE data were correlated with the Peng-Robinson equation of state, which is expressed as follows

$$P = \frac{RT}{V_M - b} - \frac{a(T)}{V_M(V_M + b) + b(V_M - b)}$$

$$a(T) = \left(0.457235 \frac{R^2 T_c^2}{P_c} \right) \alpha(T) \qquad b = 0.077796 \frac{RT_c}{P_c}$$

$$\alpha(T) = \left[1 + k\left(1 - \sqrt{T / T_c} \right) \right]^2$$

$$k = 0.37464 + 1.54226\ \omega - 0.26992\ \omega^2$$

W-S mixing rule

The Wong-Sander mixing rule was used in this work to obtain equation of state parameters for a mixture from those of the pure components. This mixing rule for a cubic equation of state can be written

$$b_m = \frac{\sum_i \sum_j x_i x_j (b - a/RT)_{ij}}{\left(1 - A_\infty^E / CRT - \sum_i x_i a_i / RTb_i\right)}$$

$$(b - a/RT)_{ij} = \frac{1}{2}\left[(b - a/RT)_i + (b - a/RT)_j\right](1 - k_{ij})$$

$$\frac{a_m}{b_m} = \sum_i x_i \frac{a_i}{b_i} + \frac{A_\infty^E}{C}$$

where C is a constant equal to in for the PR-EOS used in this work, k_{ij} is binary interaction parameter

NRTL model

is an excess Helmholtz free energy model at infinite pressure which can be equated to a low-pressure excess Gibbs free energy

$$\frac{A_{\infty}^{E}}{RT} = \sum_{i} x_i \frac{\sum_{j} x_j G_{ji} \tau_{ji}}{\sum_{r} x_r G_{ri}}$$

$$G_{ji} = \exp\left(-\alpha_{ji}\tau_{ji}\right) \quad and \quad \tau_{ji} = A_{ji}/(RT)$$

where Gji is the local composition factor for the NRTL model, τji is the NRTL model binary interaction parameter, Aji= (gji-gii), where gji is an interaction energy parameter of the i-j component, αji is a nonrandomness parameter and equal to 0.3 for the binary mixture Investigated here

Experimental procedure

A certain amount of HFCs was introduced into the cell.

After the desired temperature was achieved, the pressure of the pure component was measured.

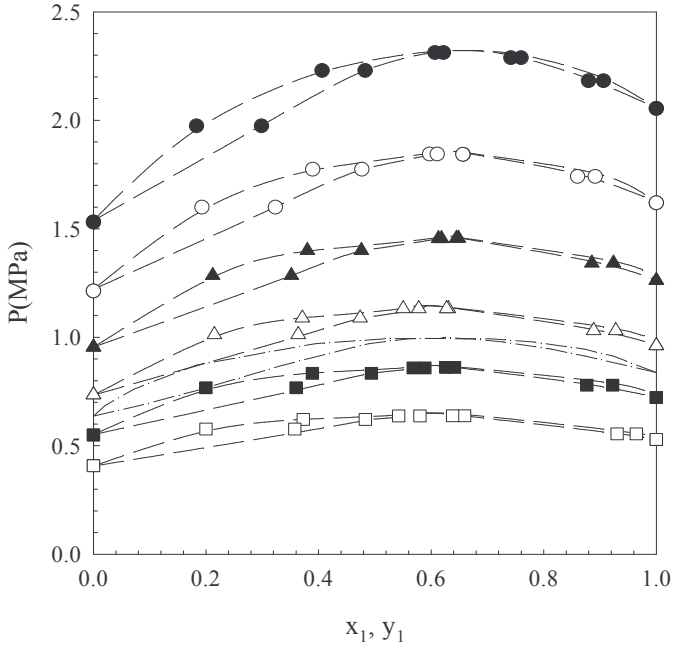
A proper amount of propane was supplied to the cell from a charging cylinder.

When the equilibrium was attained, pressure was measured.

The composition of the samples were measured by immediately injecting them into the gas chromatograph.

Result and Discussion

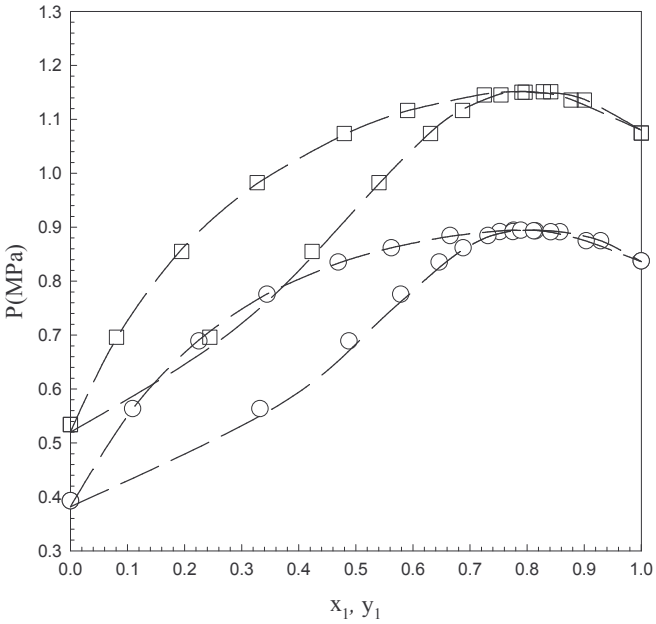
<VLE curve>



HFC-143a + Propane

Calc. with CSD-EoS (---)

P-x-y diagram for the HFC-143a + Propane system Experimental data at 273.15(□); 283.15(■); 293.15(△); 303.15(▲); 313.15 (○); 323.15K(●).



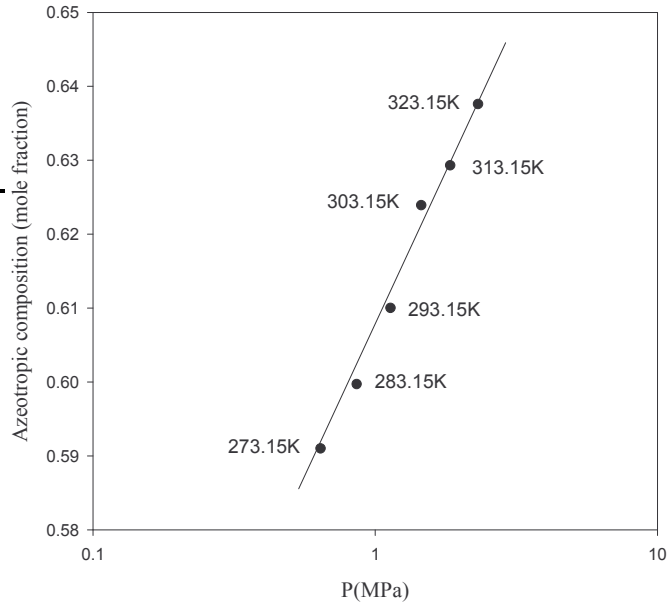
HFC-227ea + Propane

Calc. with RP-EoS using W-S mixing(---)

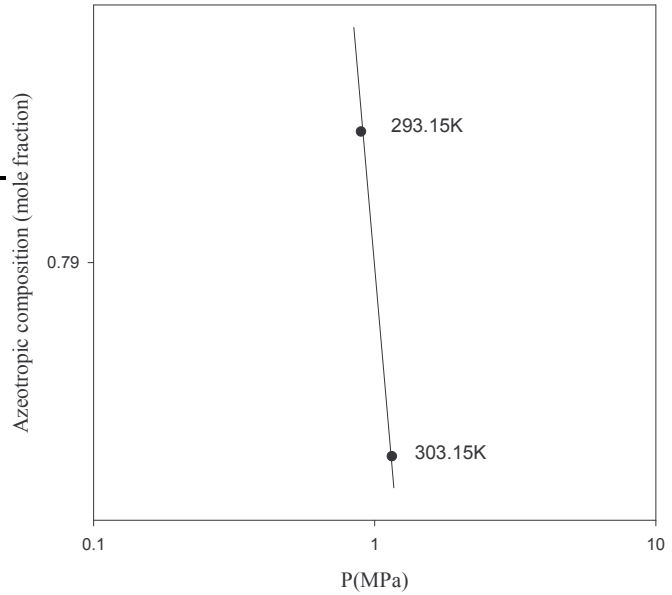
P-x-y diagram for the HFC-227ea + Propane system. Experimental data at 293.15(○); 303.15K(□).

Result and Discussion

<The azeotropic composition with pressure>



HFC-143a + Propane



HFC-227ea + Propane

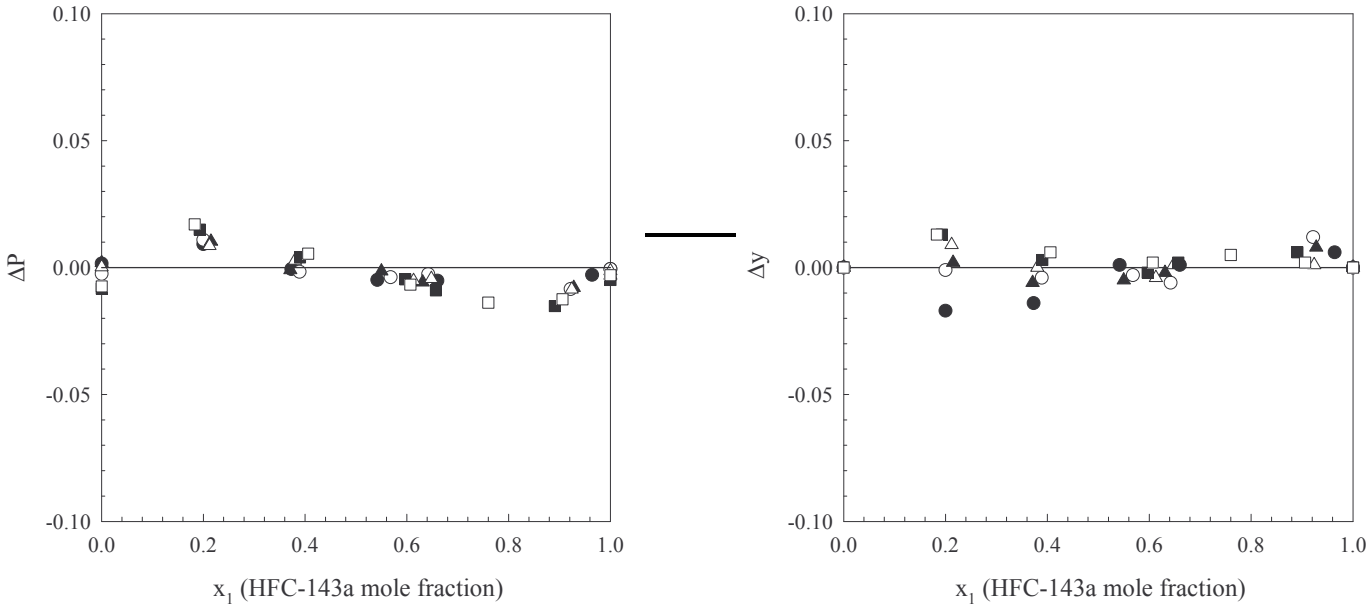
Result and Discussion

<The azeotropic data>

T	HFC-143a + propane		HFC-227ea + propane	
	x_1	P(MPa)	x_1	P(MPa)
273.15	0.5910	0.6397	·	·
283.15	0.5997	0.8594	·	·
293.15	0.6100	1.1320	0.7925	0.8938
303.15	0.6239	1.4551	0.7862	1.1511
313.15	0.6293	1.8426	·	·
323.15	0.6376	2.3139	·	·

Result and Discussion

<Deviation of ΔP and Δy>

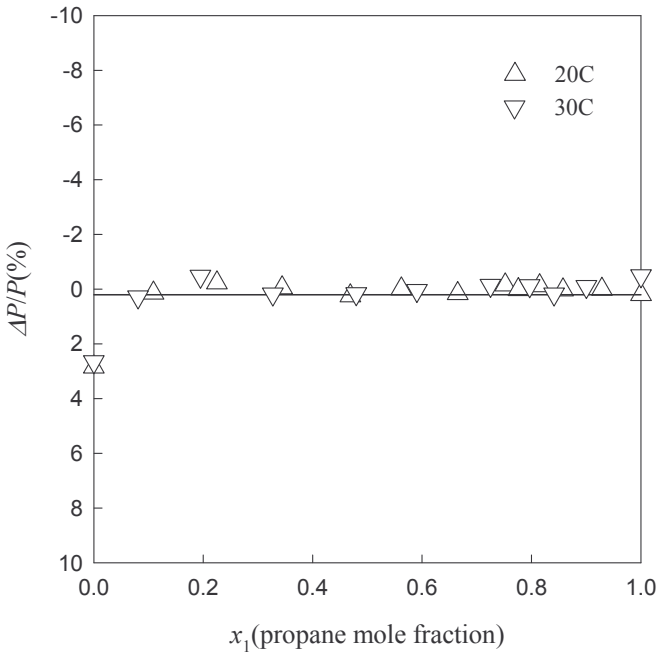


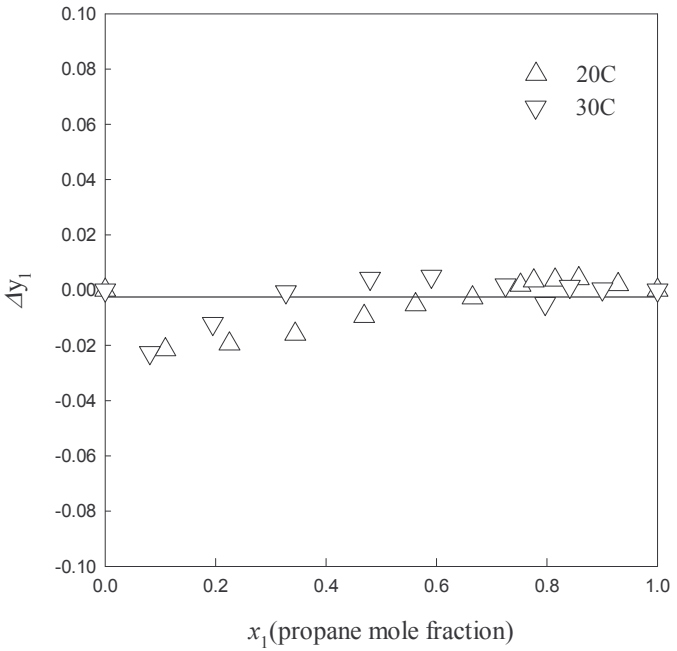
HFC-143a + Propane

273.15(□); 283.15(■); 293.15(△); 303.15(▲); 313.15 (○); 323.15K(●).

Result and Discussion

<Deviation of ΔP/P(%) and Δy>





HFC-227ea + Propane

HFCs + propane

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conclusion

- The VLE of HFC-143a and HFC-227ea with propane system were used the PR EoS combined Wong-Sandler mixing rule and NRTL excess Helmholtz free energy model and CSD EoS
- This mixing rule combined with PR equation of state and an activity coefficient model (NRTL) for the A^{ex} term show very good correlation
- The vapor-liquid equilibrium between measured and calculated values (AAD-P(%)) for HFCs + propane from 273.15K to 323.15K and the deviations were less than 0.61%
- In this temperature, azeotropic behavior has been found in HFCs + propane systems.

HFCs + propane