Method of Measuring the Vapor Pressure and Concentration of Fluids using VLE and Vibrating Tube Densitometer Apparatuses

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2. Refrigerants and Environmental Problems.
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1. Introduction: Refrigerant and Applications

- R152a
- R365mfc
- Expansion valve
- Condenser
- Evaporator
- Compressor

Phase β
\[ Z_1^\beta, Z_2^\beta, \ldots \]

Phase α
\[ Z_1^\alpha, Z_2^\alpha, \ldots \]
Most of the Radiation trapped by CFCs, HCFCs and carbon dioxide gases in the atmosphere.

*The GWP is the ratio of the warming caused by a substance "X" to the warming caused by a similar mass of carbon dioxide.*
2. Refrigerants and Environmental Problems

Ozone Depletion

- Ozone depletion refers to a lowered concentration of ozone in the upper atmosphere.
- More UV radiation is reaching the Earth’s surface.

- ODP is the ratio of the impact on ozone caused by a substance "X" to the impact on ozone caused by a similar mass of R11.
2. Refrigerants and Environmental Problems

- High ODP (Ozone Depletion Potential) → Ozone Depletion Problem.
- High GWP (Global Warming Potential) → Global Warming Problem.
2. Refrigerants and Environmental Problems

Choice of the Refrigerant

i. Zero ODP.

ii. Low GWP.

iii. Low toxicity.

iv. Low fire risk (flammability).

v. Low freezing point.

vi. High critical temperature.

vii. High vapor pressures for the operating temperature.

viii. Chemical stability.

ix. Low cost.

Environmental Requirements

Safety Requirements
2. Refrigerants and Environmental Problems

Choice of the Refrigerant

- Choice of the suitable fluid (Pure fluid and mixture)
  - Example: R134a (GWP=1300)
    - R134a has best solubility on the oil.
    - Previous works used R134a/R152a Mixture (see. z.B. Int. J.Thermophys. 13(6), 957)
    - R134a since 2011 and according to EU Laws is forbidden.

- In this work: R152a/R365mfc Mixture
  - R152a (GWP=120, ODP=0)
  - R365mfc (GWP=782, ODP=0)
  - Just a rare work stated in the literature for the vapor pressure and concentration of this mixture.
3. Phase Equilibrium Apparatus

Importance of the Phase Equilibrium Measurement

- Best understand of the phase change for the refrigerant mixture.
- The phase behavior is of great importance during the design of the refrigeration cycle.
- The known method for the measuring the phase equilibria:
  - Synthetic Method
    - Sample with known composition
    - Variation of the temperature and pressure till the separation of the phases.
  - Analytic Method
    - Given specified pressure and temperature.
    - Sample unit for the specified phases after reaching the equilibria.
3. Phase Equilibrium Apparatus

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<table>
<thead>
<tr>
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<tbody>
<tr>
<td>T</td>
<td>Temperature</td>
</tr>
<tr>
<td>p</td>
<td>Pressure</td>
</tr>
<tr>
<td>1</td>
<td>Equilibrium Cell</td>
</tr>
<tr>
<td>2</td>
<td>Mixer</td>
</tr>
<tr>
<td>3</td>
<td>Circulating Pump</td>
</tr>
<tr>
<td>4</td>
<td>Quick Sampling Valve</td>
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<tr>
<td>5</td>
<td>Sampling U-Tube</td>
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<tr>
<td>6</td>
<td>Heat Exchanger</td>
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<tr>
<td>7</td>
<td>Thermostat (isolation)</td>
</tr>
<tr>
<td>8</td>
<td>Vibrating Tube Densitometer</td>
</tr>
</tbody>
</table>

Concentration Analysis

July 11-14, 2016

Purdue Conferences
3. Phase Equilibrium Apparatus/Temperature Measurement

- The **temperature of the isothermal bath** was measured by **three thermocouple** (Rössel type K) suited at different positions of the thermal bath, and one inserted with a depth of 3mm at the circulation line.

- The **equilibrium cell internal temperature** was monitored by a Pt-100Ω (ICS Schneider Messtechnik, class A).

- This sensor was constructed of stainless steel type and has a **length of 150mm** and **core diameter of 2mm**. The sensor is certified to have a **precision of 0.03K** and **maximum allowable temperature** of 400 °C.

- This sensor is inserted with a **depth of 46mm inside the internal cell body**.
The pressure sensor used was (P3290S076020,tecsis), for the measurement of the absolute pressure. It has an **accuracy of 0.1%**, and a range of measurement between **0-16 bar**.
### 3. Phase Equilibrium Apparatus

<table>
<thead>
<tr>
<th></th>
<th>Description</th>
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<tbody>
<tr>
<td>1</td>
<td>Equilibrium Cell</td>
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<tr>
<td>3</td>
<td>Circulation Pump</td>
</tr>
<tr>
<td>4</td>
<td>Quick (Plug)Sampling Valve</td>
</tr>
<tr>
<td>5</td>
<td>Sampling U-Tube</td>
</tr>
<tr>
<td>6</td>
<td>Heat Exchanger</td>
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</tbody>
</table>

#### Diagram:

![Diagram of Phase Equilibrium Apparatus](image_url)
3. Phase Equilibrium Apparatus

1. Equilibrium Cell
2. Circulation Pump
3. Quick (Plug) Sampling Valve
4. Sampling U-Tube
5. Heat Exchanger
It was recommended to **construct two additional quick plug valves** (316 stainless steel, Swagelok) within the circulation loop, to sample a minimum amount of the fluid phase in a **U-tube located between these two valves**.

- The **length of the U-tube is about 170 mm** and is able to hold a fluid volume up to 10 ml.

- The **plug valve** was equipped with two connections (6mm) and designed to withstand a maximum **working pressure of 206 bar**.

- This quick connector body is connected with a **U-tube constructed of stainless steel** and designed to hold the required **sampled fluids**.
3. Phase Equilibrium Apparatus

- The **upper and lower parts of the U-tube** is connected with the **stem and body** quick connector.

- The stem and the body was designed to operate at temperature range of **-26-205 °C** and **maximum operating pressure of 205 bar**.

- By this method the **problem of changing the volume in the equilibrium cell and possibly changing the homogeneity of the phases was solved**.
4. Concentration Measurement/Vibrating Tube Densitometer

Density Experimental Set up:

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>P</td>
<td>Pressure Measurement</td>
</tr>
<tr>
<td>DMC</td>
<td>Density Measuring Cell</td>
</tr>
<tr>
<td>ISOCHAM</td>
<td>Isolation Chamber</td>
</tr>
<tr>
<td>VP</td>
<td>Vacuum Pump</td>
</tr>
<tr>
<td>CT</td>
<td>Cold Trap</td>
</tr>
<tr>
<td>WV</td>
<td>Waste Vessel</td>
</tr>
<tr>
<td>IN1, IN2</td>
<td>Inlet</td>
</tr>
<tr>
<td>EX</td>
<td>Exit</td>
</tr>
<tr>
<td>HP</td>
<td>Hand Pump</td>
</tr>
<tr>
<td>SP</td>
<td>Spindle Pump</td>
</tr>
<tr>
<td>V4, V5</td>
<td>Inlet Valve</td>
</tr>
<tr>
<td>V1, V2</td>
<td>Measuring Cell Valve</td>
</tr>
</tbody>
</table>
4. Concentration Measurement

Measurement of the concentration of the Mixture

- The U-tube is then connected with the entrance at the Vibrating Tube Densitometer Apparatus.

- The required concentrations for the mixture were detected as a function of the density and the period of oscillation. Also to verify the concentration of the pure fluids and mixtures a specific algorithm written in Matlab was executed, and the concentration was further obtained from the thermodynamic models.

\[
\begin{align*}
\gamma^V_1 &= \frac{p_{1,V}^2 - p_{1,1,V}^2}{p_{2,V}^2 - p_{1,V}^2} = \frac{\rho_V - \rho_{1,V}}{\rho_{2,V} - \rho_{1,V}} \\
\chi^L_1 &= \frac{p_{1,L}^2 - p_{1,L,1}^2}{p_{2,L}^2 - p_{1,L}^2} = \frac{\rho_L - \rho_{1,L}}{\rho_{2,L} - \rho_{1,L}}
\end{align*}
\]
5. Thermodynamic Modeling of Density and Phase Equilibria

**$G^E$-Models**

- Real fluid mixtures deviated from ideala mixture through the excess properties.
- Real Liquid Phase Behavior.
- All the excess properties are derived from Excess-Gibbs Energy as function of the Temperature $T$, Pressure $p$ and composition $x_i$

\[ G^E = f(T, p, x_i) \rightarrow S^E, H^E, V^E \]

- Models:
  - Wilson, (mod.) UNIFAC, UNIQUAC

**Thermal Equation of State (EOS)**

- Form of:
  \[ f(T, p, V, x_i) = 0 \]

- Real Vapor Phase Behavior.

- Example:
  - Virial, Cubic Equation of State (EOS)
**5. Thermodynamic Modeling of Density and Phase Equilibria**

G^E-Models: UNIFAC*, mod. UNIFAC**

- The solution is made of molecular fragments (subgroups).

- New variables (R_k and Q_k).

- Combinatorial part is the same as UNIQUAC.

Source: Gmehling

*AIChE J 21, 1086
** Ind. Eng. Chem. Res. 26, 1372
5. Thermodynamic Modeling of Density and Phase Equilibria

\( G^E - \text{Models: UNIFAC}\*, \text{mod. UNIFAC}\**

\[
g^E = h^E + Ts^E
\]

\[
\ln \gamma_i = \ln \gamma_i^R + \ln \gamma_i^C
\]

Residual Part: \( \ln \gamma_i^R = f(x_i, q_i, \psi) \)

Combinatorial Part: \( \ln \gamma_i^C = f(x_i, q_i, r_i) \)

\[
\Psi = \exp \left( - \frac{a_{nm} + b_{nm}T + c_{nm}T^2}{T} \right)
\]

\( a_{nm}, b_{nm}, c_{nm} \): interaction parameter between Group m and n.

\( q_i, r_i \): geometric molecular parameter

\*AIChE J 21, 1086

** Ind. Eng. Chem. Res. 26, 1372
Thermal Cubic Equation of State (TCEOS)

- General Form:
  \[ p = \frac{RT}{v-b} \left( a(T) \right) - \frac{a(T)}{v^2 + ubv + wb^2} \]
  - repulsive Part
  - attractive Part

- Parameter \( a \) and \( b \) from thermo-physical data
  - For mixture → Mixing rule
    \[ a_{Mix} = f(a_1, a_2, ...), b_{Mix} = f(b_1, b_2, ...) \]

- Different forms depend on \( u \) and \( w \):
  - \( u=1, w=0 \) (Soave-Redlich-Kwong):
    \[ p = \frac{RT}{v-b} - \frac{a(T)}{v(v+b)} \]
  - \( u=2, w=-1 \) (Peng-Robinson)
    \[ p = \frac{RT}{v-b} - \frac{a(T)}{v^2 + 2bv - b^2} \]
Volume Translated Peng Robinson Equation of State (Gmehling & Ahlers):

- Usually the liquid phase is not correctly described by the EOS method:
- Here is new criteria to modify this error.

- Introduced third parameter \( c \), known as **Volume Translation Parameter**.
- Volume translated PR (VT PR):

\[
c = -0.252 \frac{RT}{P_c} \left( 1.5448 Z_c - 0.4024 \right)
\]

\[
p = \frac{RT}{v + c - b} - \frac{a(T)}{(v + c)(v + c + b) + b(v + c - b)}
\]
5. Thermodynamic Modeling of Density and Phase Equilibria

Combination of G^E-Model and thermal Cubic EOS

- **Huron-Vidal-Method**
  - van-der-Waals u=w=0:
    \[
    g^E \frac{E}{RT} = \sum x_i \ln \left( \frac{v_i - b_i}{v - b} \right) + \frac{p}{RT} \left( v - \sum x_i v_i \right) + \left[ \frac{1}{RT} \left( \sum x_i \frac{a_i}{v_i} - \frac{a}{v} \right) \right]
    \]
  - Consider:
    \[
    v = b, \quad g^E = g^E_\infty \quad \text{for} \quad p \rightarrow \infty
    \]
  - Led to:
    \[
    \frac{a}{b} = \sum x_i \frac{a_i}{b_i} - g^E_\infty
    \]
  - Analogy for Peng-Robinson:
    \[
    \frac{a}{b} = \sum x_i \frac{a_i}{b_i} - 2\sqrt{2} g^E_\infty \left[ \ln \left( \frac{2 + \sqrt{2}}{2 - \sqrt{2}} \right) \right]^{-1}
    \]
  - and Soave-Redlich-Kwong:
    \[
    \frac{a}{b} = \sum x_i \frac{a_i}{b_i} - g^E_\infty \ln 2
    \]
5. Thermodynamic Modeling of Density and Phase Equilibria

Combination of $G^E$-Model and thermal Cubic EOS

- **Modified-Huron-Vidal First Order (MHV1)**
  - Cosider:
    \[ v^E = 0, \quad g^E = g_0^E \quad \text{for} \quad p \to 0 \]
  - Led to:
    \[ \frac{a}{b} = \sum_i x_i a_i \frac{f_i}{b_i f} + \frac{g_0^E}{f} + \frac{RT}{f} \sum_i x_i \ln \left( \frac{b}{b_i f_i} \right) \]
  - $f_i$ and $f$ set for every EOS.

- **Modified-Huron-Vidal Second Order (MHV2)**
  - MHV1 + EOS + mod. UNIFAC
  - SRK-EOS + MHV2 delivered

\[ f_1(\alpha - \sum x_i \alpha_i) + f_2(\alpha^2 - \sum x_i \alpha_i^2) = \frac{g_0^E}{RT} + \sum x_i \ln \left( \frac{b}{b_i} \right) \]

- With:
  \[ f_1 = -0.478, \quad f_2 = -0.0047, \quad \alpha = \frac{a}{bRT} \]

- MHV2 delivers non linear relations between parameter $a$ and $b.$
5. Thermodynamic Modeling of Density and Phase Equilibria

Combination of $G^E$-Model and thermal Cubic EOS

- The theoretical quadratic dependency of the Virial coefficient $B(T)$ was not considered by the MHV two mixing rules.

**Wong-Sandler-Mixing rule was introduced:**

$$B(T) = b - \frac{a}{RT} = \sum_i \sum_j x_i x_j \left( b - \frac{a}{RT} \right)_{ij} = B_{ij}(T)$$

- considering:

$$b = \sum_i \sum_j x_i x_j \left( b - \frac{a}{RT} \right)_{ij}, \quad f = a / b$$

$$1 - \frac{f}{RT}$$

- For Peng-Robinson considered:

$$f = \sum x_i \frac{a_i}{b_i} - \frac{g_0^E \sqrt{2}}{\ln(\sqrt{2} - 1)}, \quad p \to 0$$
5. Thermodynamic Modeling of Density and Phase Equilibria

Combination of GE-Model and thermal Cubic EOS

- **VTPR + MHV1 and MHV2**

\[ p = \frac{RT}{v + c - b} - \frac{a(T)}{(v + c)(v + c + b) + b(v + c - b)} \]

- Parameter \( a, b \) and \( c \) for pure fluids:

\[ a = f(T_c, p_c, \alpha(T)), \quad b = f(T_c, p_c), \quad c = f(T_c, p_c, v_c) \]

- Here Twu-Function:

\[ \alpha(T) = T_r^{N(M-1)} \exp[L(1-T_r^{MN})] \]

- Mixing rules for \( a, b \) and \( c \); from MHV1,MHV2 with UNIFAC:

\[ b = f(x_i, b_i), \quad c = f(x_i, c_i) \]

\[ \frac{a}{b} = \sum x_i \frac{a_i}{b_i} + \frac{g_{0.64663}^{E.R}}{-0.64663} \quad \text{Residual Part} \]
6. Results and Discussion

Mixture Attractive Energy Parameter (a) predicted for VTPR, PR EOS with VTPR; MHV1, WS and MHV2 mixing rules for the system R152a (1) and R365mfc (2):

![3D plot of mixture parameter a vs temperature and mole fraction](image1)

Co-Volume Parameter for Predictive Models with 30% and 70% R152a:

![Graphs of co-volume parameter b vs temperature for different models](image2)
6. Results and Discussion

Vapor Pressure for R365mfc with Saturation Temperature:

Relative Deviation in Vapor Pressure Measurement Data of R365mfc:
6. Results and Discussion

Measurement of mass fraction for the system R152a-R365mfc from vapor pressure and liquid density data:

Relative deviation in liquid mass fraction measurement data of R152a and R365mfc
6. Results and Discussion

Relative deviation to experimental data of NIST (Outcalt and McLinden, 1996), (McLinden and Lemmon, 2013) in saturated liquid density for the system R152a and R365mfc from VTPR:

![Graph 1]

Relative deviation to experimental data of NIST (Outcalt and McLinden, 1996), (McLinden and Lemmon, 2013) in saturated liquid density for the system R152a and R365mfc from VTPR-MHV2:

![Graph 2]
7. Conclusion and Recommendation

- The sample procedure used at the circulation loop of the VLE apparatus, has a great effect in solving the problems of changing the volume of the fluids inside the equilibrium cell, since the sampling unit needs a minimum amount of fluid to be sampled.

- The analysis procedure used at the Vibrating Tube Densitometer apparatus could be conducted at various conditions \((p, T)\).

- The work testify necessary applications of the new equation of state VTPR, combined with UNIFAC method as well as various mixing rules.

- McLinden et.al model (NIST) achieved vapor pressure deviations of less than 0.073% for R365mfc.

- The concentration deviations reached -3.1%,-9.8% for a composition of 33.6% R152a and 44.1% R365mfc respectively.

- The combination of the \(G^E\)-Model (Unifac-Modified Unifac) with the thermal CEOS VTPR was led to better results with minimum deviations from experimental data.
7. Conclusion and Recommendation

- The deviations of VTPR and VTPR-MHV2 have led to similar results data in the pure fluids and the mixture respectively.

- The Twu $\alpha$ function combined in the energy parameter (a) of the VTPR and VTPR-MHV2 models enables to widen the temperature range.

- The mixing rules for the energy (a) and co-volume parameters (b) integrated at VTPR and VTPR-MHV2 models allowed the prediction of the highly asymmetric fluids R152a.

- The vapor phase should also be sampled using the same method with special concerns to the vacuum problem.
Thank You