Compressions: Isothermal: Liquid Mixtures  Binary: Compressibilities

The isothermal compressibility of a given binary liquid mixture having ideal thermodynamic properties is related to the isothermal compressions of the liquid components using equation (a) \[1\].

\[
\kappa_T^{\text{(mix;id)}} = \frac{K_T^{\ast}(\ell) + x_2 \cdot [K_{T2}^{\ast}(\ell) - K_T^{\ast}(\ell)]}{V_1^{\ast}(\ell) + x_2 \cdot [V_2^{\ast}(\ell) - V_1^{\ast}(\ell)]}
\] (a)

The excess compression for a given binary liquid mixture is defined by equation (b).

\[
K_{Tm}^{E} = K_{Tm}^{\ast}(\text{mix}) - K_{Tn}^{\ast}(\text{mix;id})
\] (b)

Or, \[K_{Tm}^{E} = K_{Tm}^{\ast}(\text{mix}) - [x_1 \cdot K_{T1}^{\ast}(\ell) + x_2 \cdot K_{T2}^{\ast}(\ell)]\] (c)

The isothermal compressibilities of ideal and real binary liquid mixtures are defined by equations (d) and (e) respectively.

\[
\kappa_T^{\text{(mix;id)}} = \frac{1}{V^{\text{(mix;id)}}} \left( \frac{\partial V^{\text{(mix;id)}}}{\partial p} \right)_T
\] (d)

\[
\kappa_T^{\text{(mix)}} = \frac{1}{V^{\text{(mix)}}} \left( \frac{\partial V^{\text{(mix)}}}{\partial p} \right)_T
\] (e)

For a given binary liquid mixture we can define an excess compressibility using equation (f).

\[
\kappa_T^{E} = \kappa_T^{\text{(mix)}} - \kappa_T^{\text{(mix;id)}}
\] (f)

\[
\kappa_T^{E}(\text{mix}) = \frac{1}{V^{\text{(mix)}}} \left( \frac{\partial V^{\text{(mix)}}}{\partial p} \right)_T + \frac{1}{[x_1 \cdot V_1^{\ast}(\ell) + x_2 \cdot V_2^{\ast}(\ell)]} \left( \frac{\partial [x_1 \cdot V_1^{\ast}(\ell) + x_2 \cdot V_2^{\ast}(\ell)]}{\partial p} \right)_T
\] (g)

A similar equation was used by Moelwyn-Hughes and Thorpe \[3\]. They introduced the concept of a compressibility of the excess volume.

\[
\Delta \kappa_T^{\text{(mix)}} = -\frac{1}{\Delta V^{\text{(mix)}}} \left( \frac{\partial \Delta V^{\text{(mix)}}}{\partial p} \right)_T
\] (h)

In publications by Prigogine and by Moelwyn-Hughes and Thorpe the analysis was taken a step further to facilitate analysis of experimental results. However approximations were made in both treatments. An exact formulation was given by Missen \[4\] in terms of volume fractions of both components in the corresponding having ideal thermodynamic properties, $\phi_1^{\text{(mix;id)}}$ and $\phi_2^{\text{(mix;id)}}$. 
Hence,  \( \kappa^E_T \text{(mix)} = -\frac{1}{V_m \text{(mix)}} \left[ \left( \frac{\partial V^E_m}{\partial p} \right)_T + V^E_m \cdot \kappa \text{(mix;id)} \right] \) \( (i) \)

A partial compressibility was defined by Moelwyn-Hughes [5]. For liquid 1 in a binary liquid mixture at defined \( T \) and \( p \), the partial compressibility is defined by equation (j).

\[
\kappa_{T_1} \text{(mix)} = -\frac{1}{V_1 \text{(mix)}} \left( \frac{\partial V_1 \text{(mix)}}{\partial p} \right)_T \quad (j)
\]

Similarly for component 2, \( \kappa_{T_2} \text{(mix)} = -\frac{1}{V_2 \text{(mix)}} \left( \frac{\partial V_2 \text{(mix)}}{\partial p} \right)_T \) \( (k) \)

The excess compressibility of a given binary liquid mixture \( \kappa^E_T \text{(mix)} \) was defined in equation (f). Hence,

\[
\kappa^E_T \text{(mix)} = \phi_1 \text{(mix)} \cdot \kappa^E_{T_1} \text{(mix)} + \phi_2 \text{(mix)} \cdot \kappa^E_{T_2} \text{(mix)} \\
+ [\phi_1 \text{(mix)} - \phi_1 \text{(mix;id)}] \cdot \kappa^\ell \text{'}_{T_1} (\ell) + [\phi_2 \text{(mix)} - \phi_2 \text{(mix;id)}] \cdot \kappa^\ell \text{'}_{T_2} (\ell) \quad (f)
\]

It may be noted that ‘true’ partial properties can also be defined for the isothermal compressibility [6]. Then the properties introduced in equations (j) and (k) would be termed specific partial isothermal compressions [6].

It is also possible to formulate a set of equations incorporating rational activity coefficients for the two components of the binary liquid mixture. We start with the equation for the partial molar volume of component 1.

\[
V_1 \text{(mix)} = V_1^* (\ell) + R \cdot T \cdot \left( \frac{\partial \ln(f_1)}{\partial p} \right)_T \quad (m)
\]

\[
K_{T_1} \text{(mix)} = K_{T_1}^\ell (\ell) - R \cdot T \cdot \left( \frac{\partial^2 \ln(f_1)}{\partial p^2} \right)_T \quad (n)
\]

Similary \( K_{T_2} \text{(mix)} = K_{T_2}^\ell (\ell) - R \cdot T \cdot \left( \frac{\partial^2 \ln(f_2)}{\partial p^2} \right)_T \) \( (o) \)

Therefore \( K_{Tm} \text{(mix;id)} = K_{Tm} \text{(mix;id)} - R \cdot T \cdot \left[ x_1 \cdot \left( \frac{\partial^2 \ln(f_1)}{\partial p^2} \right)_T \right] + x_2 \cdot \left( \frac{\partial^2 \ln(f_2)}{\partial p^2} \right)_T \) \( (p) \)

The two liquid components are characterised by their molar excess properties.

\[
K^E_{T_1} \text{(mix)} = -R \cdot T \cdot \left( \frac{\partial^2 \ln(f_1)}{\partial p^2} \right)_T \quad (q)
\]
and \( K_{T2}^{E}(\text{mix}) = -R \cdot T \left( \frac{\partial^2 \ln(f_2)}{\partial p^2} \right)_T \) (r)

Therefore \( K_{Tm}^{E}(\text{mix}) = -R \cdot T \left[ x_1 \left( \frac{\partial^2 \ln(f_1)}{\partial p^2} \right)_T + x_2 \left( \frac{\partial^2 \ln(f_2)}{\partial p^2} \right)_T \right] \) (s)

Also \( K_{T1}^{E} = -\left( \frac{\partial V_{1}^{E}}{\partial p} \right)_T \) and \( K_{T2}^{E} = -\left( \frac{\partial V_{2}^{E}}{\partial p} \right)_T \) (t)

In other words \( K_{Tm}^{E} = -\left( \frac{\partial V_{m}^{E}}{\partial p} \right)_T \) (u)

Isothermal compressions of liquid mixtures can be directly measured [7]. Hamann and Smith [8] report measurements using binary liquid mixtures at 303 K and two pressures. Hamann and Smith define excess isothermal molar compressions \( K_{T}^{E}(\phi) \) in terms of volume fraction weighted isothermal compressions of the pure liquids.

The volume fractions are defined as follows.

\[
\phi_1 = \frac{x_1 \cdot V_1^*(\ell)}{[x_1 \cdot V_1^*(\ell) + x_2 \cdot V_2^*(\ell)]} \quad (v)
\]

\[
\phi_2 = \frac{x_2 \cdot V_2^*(\ell)}{[x_1 \cdot V_1^*(\ell) + x_2 \cdot V_2^*(\ell)]} \quad (w)
\]

Then \( K_{T}^{E}(\phi) = K_{Tm}(\text{mix}) - [\phi_1 \cdot K_{T1}^{E}(\ell) + \phi_2 \cdot K_{T2}^{E}(\ell)] \) (x)

For most binary aqueous mixtures \( K_{T}^{E}(\phi) \) is negative, plots of \( K_{T}^{E}(\phi) \) against \( \phi_2 \) being smooth curves. The minima in aqueous mixtures containing THF and propanone the minima are near 0.4 and 0.6 respectively [0].

**Footnotes**

[1] For a binary liquid mixture having ideal thermodynamic properties,

\[
V_m(\text{mix}; \text{id}) = x_1 \cdot V_1^*(\ell) + x_2 \cdot V_2^*(\ell)
\]

Then \( K_{Tm}(\text{mix}; \text{id}) = x_1 \cdot K_{T1}^*(\ell) + x_2 \cdot K_{T2}^*(\ell) \)

But \( \kappa_T(\text{mix}; \text{id}) = \frac{K_{Tm}(\text{mix}; \text{id})}{V_m(\text{mix}; \text{id})} \)

Then, \( \kappa_1(\text{mix}; \text{id}) = \frac{K_{T1}^{*}(\ell) + x_2 \cdot [K_{T2}^{*}(\ell) - K_{T1}^{*}(\ell)]}{V_1^*(\ell) + x_2 \cdot [V_2^*(\ell) - V_1^*(\ell)]} \)

