Thoughts
on liquid mixtures of nonelectrolytes

Lech Dabrowski, Warsaw, Poland, www.mixtures.pl , e-mail: admin@mixtures.pl

1. Introduction

I am presenting the results of work I conducted several years ago, being a continuation of my proposal of activity coefficient description in liquid nonelectrolite mixtures, placed in my doctoral dissertation: *"Lech Dabrowski, Rownowagi ciecz-ciecz w ukladach wieloskladnikowych zawierajacych kwas akrylowy i jego estry, alkohole, weglowodory aromatyczne i wode, Praca doktorska, Instytut Chemii Fizycznej PAN, Warszawa 1984"* (Lech Dabrowski, *Liquid-liquid equilibrium in multicomponent systems, composed from acrylic acid and its esters, alcohols, aromatic hydrocarbons and water, Doctoral dissertation, Institute of Physical Chemistry, Polish Academy of Sciences, Warsaw 1984)*. It should not be treated as a paper because of (among other things) my ignorance of papers after 2002. I hope only that it may be of use for somebody.

2. From my dissertation

I have placed a proposition of activity coefficient description (in liquid nonelectrolite mixtures) in my dissertation, in order to try to correlate three-component liquid-liquid equilibrium data obtained with component two-component systems. As a starting point it was established two-component solution of solute (B) in solvent (A). For very diluted solutions Henry Law is in force, stating that solute activity (when pure substance, in mixture conditions of temperature and pressure, is assumed as standard state) is proportional to solute mole fraction in the solution, so its activity coefficient is constant. After exchange of solute concentration to its "local" concentration (concept introduced during derivation of Wilson equation *(G. M. Wilson, J. Am. Chem. Soc 86 (2), 127, 1964)*), I have obtained the

following expression describing solute activity:

$$a_{BA} = \frac{Q_{BA} x_B}{x_B + R_{BA} x_A}$$

where:

a_{BA} = activity of solute B in solvent A,

x_B = mole fraction of the solute,

x_A = mole fraction of the solvent,

Q_{BA}, R_{BA} = constants in given conditions of temperature and pressure (activity parameters),

giving the straight line on reciprocal of activity coefficient-concentration (mole fraction) diagram. After using of Gibbs-Duhem equation, following equation on solvent activity has been obtained:

$$a_{AA} = K_A \left(\frac{R_{BA} x_A}{x_B + R_{BA} x_A} \right)^{R_{BA}}$$

where:

a_{AA} = activity of solvent A,

K_A = constant in given conditions of temperature and pressure, equals 1 in good approximation,

which is one-parameter equation in good approximation. Foregoing equations have been named EHL (Extended Henry Law) equations.

3. Physical meaning

Excess thermodynamic potential (excess Gibbs free energy) of 1 mole of solution equals:

$$\frac{G_m^E}{RT} = x_B \ln \gamma_{BA} + x_A \ln \gamma_{AA}$$

where:

G_m^E = excess thermodynamic potential of 1 mole of solution of B in A,

R = gas constant,

T = temperature (K),

$\gamma_{BA} = a_{BA}/x_B$ = activity coefficient of the solute,

$\gamma_{AA} = a_{AA}/x_A$ = activity coefficient of the solvent,

and after substitution of EHL activity coefficient expressions and transformation we obtain the following expression for thermodynamic potential of mixing of 1 mole of solution of B in A::

$$\frac{G_m}{RT} = \frac{G_m^E}{RT} + x_A \ln x_A + x_B \ln x_B =$$

$$x_B \ln\left(\frac{x_B}{x_B + R_{BA} x_A}\right) + R_{BA} x_A \ln\left(\frac{R_{BA} x_A}{x_B + R_{BA} x_A}\right) + (1 - R_{BA}) x_A \ln 1 + \ln Q_{BA} x_B + \frac{\ln K_A}{R_{BA}} R_{BA} x_A$$

where:

G_m = thermodynamic potential of mixing of 1 mole of solution of B in A.

The above expression may be obtained after assumption of a system composed of:
- mixture of solute and certain part of solvent, and
- remaining amount of pure (unaffected) solvent.
The two last components of this expression results from the difference between values of molar thermodynamic potential of both components in the solution and in a pure state (it is a consequence of establishing pure substance as standard state). I assume that structural changes (so also thermodynamic potential changes) apply

to solvent connected with solute only. These changes are closely connected with behavior in high dilution range, when Henry Law is valid. The amount of solute is too small in this range, so it cannot influence solvent structure, and as a consequence solvent activity coefficient equals 1 (solute activity coefficient is constant). Some examples include methanol-water and ethanol- water systems (760 mm Hg), which meet Henry Law to alcohol mole fraction approximately equals 0,005 (Per Dalager, J. Chem. Eng. Data 14 (3), 298, 1969).

Below I give a schematic reciprocal of activity coefficient-mole fraction diagram in two-component system, congruent with EHL equations (Henry Law ranges are obviously too large).
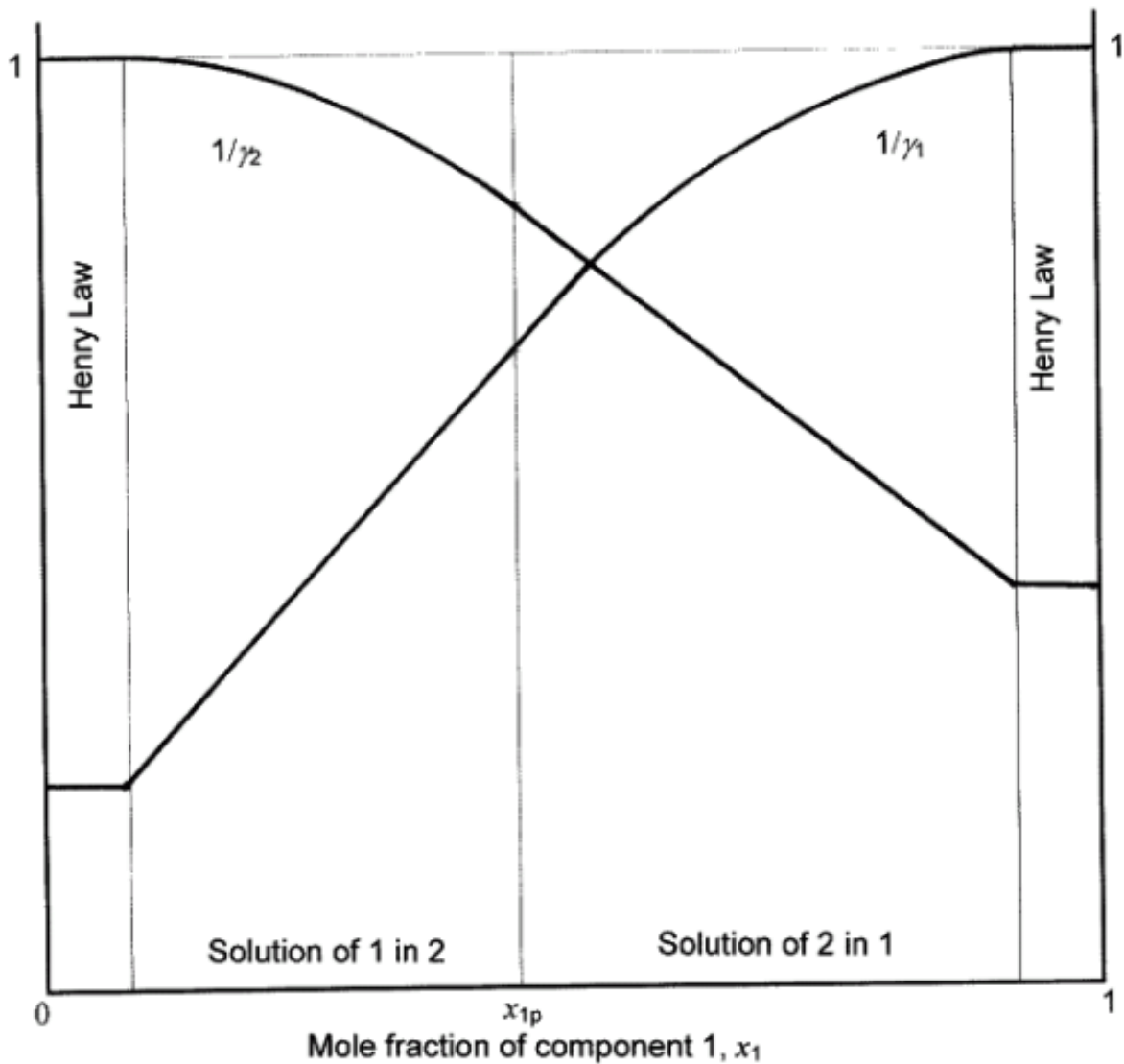
From the above considerations we may draw a conclusion, that, independent of the used equation, an exact description of activity coefficients in two-component system needs no less than four parameters: no less than two for a description of asymmetrical curve (in range out of Henry Law) and strictly two to take structural changes of mixture components into consideration.

4. Attempt to describe

I have attempted to describe activity coefficients in two-component system, in a whole concentration range, using EHL equations, so supposing the occurrence of two types of solution (substance "2" in substance "1" and substance "1" in substance "2"). In transition of one solution in the other point:

$$Q_{21} = \frac{x_{2p} + R_{21} \cdot x_{1p}}{x_{2p}} \left(\frac{R_{12} x_{2p}}{x_{1p} + R_{12} x_{2p}} \right)^{R_{12}}$$

$$Q_{12} = \frac{x_{1p} + R_{12} x_{2p}}{x_{1p}} \left(\frac{R_{21} x_{1p}}{x_{2p} + R_{21} x_{1p}} \right)^{R_{21}}$$

where:

x_{1p} = mole fraction of component "1" in the transition point,

x_{2p} = mole fraction of component "2" in the transition point.

I assume that $K_1 = 1$ and $K_2 = 1$.

Assuming a continuity of activity coefficient derivatives we obtain, after transformations:

$$x_{1p} = \frac{R_{12}(1-R_{21})}{R_{12}+R_{21}-2R_{12}R_{21}}$$

$$x_{2p} = 1 - x_{1p}$$

which leads to a two-parameter description. On the basis of 18 literature collections of activity coefficient data (calculated from full liquid-vapor equilibrium data in two-component systems in which chemical reactions, and/or associations or dissociations do not occur), including at least 20 data in full concentration range (and seeming sufficiently accurate), I have carried out comparison of foregoing equations with two-parameter Wilson equation (considered to be very good in describing nonelectrolite mixtures with complete mixing of components). I have carried out the calculations using least squares method, minimizing sum of activity coefficient square deviations for both components.

The results give marked superiority of Wilson equation, namely standard deviations count on average to:

- for three hydrocarbon mixtures: 0,0010 for Wilson equation and 0,0018 for EHL equations,
- for six halogenated hydrocarbon mixtures: 0,0022 for Wilson equation and 0,0034 for EHL equations,
- for nine remaining systems: 0,0018 for Wilson equation and 0,0029 for EHL equations.

The results for EHL equations do not seem to be bad so much so we do not take advantage from their properties (straight line for solute and practically one parameter for solvent), especially in limited concentration range.

5. Alcohol + aliphatic hydrocarbon

Aliphatic alcohols in pure state are associated, after the addition of aliphatic hydrocarbon follow their gradual dissociation, so accurate activity coefficient description in such mixture, e.g. using Wilson equation, is impossible. Using 9 collections of activity coefficient

literature data (selected as in ATTEMPT TO DESCRIBE) I have checked (using Wilson equation) how activity standard deviation is changed along with increasing of measurement point number, starting from pure alcohol. It turned out that the standard deviation has decreased to alcohol mole fraction approximately 0,4-0,6. Perhaps it may show that mixture characteristics in this concentration range differ from mixture characteristics in the remaining range, because the examined range fulfills the condition of solution of hydrocarbon in alcohol. Could the description with the aid of two solutions be better than continuous description of mixture?