

Prediction of vapour-liquid equilibrium of some binary liquid systems by Generalized London Potential method

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A novel *ab initio* method (named the generalized London Potential method) has been developed by Homer *et al.*^{6,9} to predict vapour- liquid equilibrium data for binary mixtures. By this approach, the activity coefficients, vapour- phase composition and total vapour pressures of series of different kinds of binary liquid mixtures such as (i) C₆H₆-CCl₄, (ii) cC₆H₁₂-CCl₄, (iii) cC₅H₁₀-CCl₄, (iv) cC₆H₁₂-C₆H₆, (v) cC₅H₁₀-C₆H₆, (vi) C₆H₆-CH₃OH, (vii) C₆H₆-C₂H₅OH (viii) cC₆H₁₂-C₂H₅OH, (ix) CH₃OH-C₂H₅OH, (x) water-C₂H₅OH are calculated and the result obtained are compared with experimental data. Reasonable agreement is found between predicted and experimental data for only non-polar simple systems.

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Multiphase equilibria are at the heart of numerous industrial and environmental processes. Much attention has been paid on the vapour-liquid equilibria (VLE) in chemical engineering for the performance of chemical plants. Several experimental techniques¹ are often time consuming and expensive and too difficult to be practicable. Thus, the accurate prediction of VLE data for mixtures is of importance.

The classical method of determination of activity coefficients from excess thermodynamic functions of binary liquid mixture is traditionally a very general treatment based on rational functions, for e.g. G^E , the excess free energy.

Modern theoretical developments in the molecular thermodynamics of liquid-solution behaviour are now-a-days based on the concept of local composition, presumed to account for the short-range order and non-random molecular orientations that result from difference in molecular size and intermolecular forces. The local composition models have limited flexibility in the fitting of data, but they are adequate for most engineering purposes. Moreover, they can be used for multi component systems, without the introduction of any parameter, beyond those required to describe the constituent binary systems. Some well known existing models are the NTRL equation², UNIQUAC method³, UNIFAC method⁴ etc.

Any theory for the prediction of the bulk physical properties of liquid mixtures must address two essential problems. The first, an entropy-based problem, is to describe quantitatively the structures of liquids in terms of the arrangement of the molecules of a liquid mixture in space. The second, an energy-interaction problem, is to quantify the net attractive energy between like and unlike molecules. In 1937, London in his paper⁵ suggested that for two spherically symmetrical non-polar molecules, the total intermolecular potential energy (U) becomes,

$$U = be^{-R/p} - \frac{c}{R^6} - \frac{d}{R^8} + \frac{e_1 e_2}{R} \quad \dots (1)$$

where b , p , d are adjustable parameters; c , e_1 , e_2 are regarded as theoretically given for dispersion forces. Obviously U is a function of intermolecular separation (R). However, when considering only the average equilibrium intermolecular separation at a given temperature, London speculated that the first and third terms of the above equation 'having different signs, may to a large extent cancel each other' and modified the above equation in such a way, that, no adjustable parameters would be involved. Thus, the expression becomes,

$$U = \begin{cases} -c/R^6 & \text{for } R \geq R_0 \\ +\infty & \text{for } R < R_0 \end{cases} \quad \dots(2)$$

R_0 is the shortest possible atomic distance or atomic diameter.

On this hypothesis, Homar and Mohammadi⁶ have derived a generalized form of London's dispersion potential (GLP) for polyatomic molecules to calculate the unlike molecular interaction energies needed, considering only rotational motion of corresponding bonded atoms in two rotating molecules. The application of the GLP method to the calculation of intermolecular potential (ϕ) is equivalent to the assumption, that, the net attractive potential affecting the excess free energy value, is totally described by the attractive potential of a distributed London potential between the bonded atoms averaged over all orientations. In the present paper, the above approach is used to calculate activity coefficient for several binary liquid mixtures, and using these values, attempts have been made to estimate the vapour-liquid equilibria of different binary systems.

Method of calculation

Thermodynamic principle

For each component i , in the fluid phase equilibria at temperature T , it is well known that⁷ the vapour phase mole fraction y_i and liquid phase mole fraction x_i are related at low and moderate⁷ total pressure P , through the activity coefficient γ_i by,

$$y_i \cdot P = \gamma_i \cdot x_i \cdot P_{i,\text{sat}}^0 \quad \dots(3)$$

where $P_{i,\text{sat}}^0$ is the saturated vapour pressure of pure component i . As the gas solubility is very low, the vapour phase is assumed to exhibit ideal behaviour⁷. The fugacity at standard state is the estimation set equal to the vapour pressure of the pure component⁸. The activity coefficient accounts for deviations from Raoult's law, and in a mixture is related to the excess molar Gibbs energy,

$$n_T G^E = RT \sum_i n_i \ln \gamma_i$$

$$\therefore RT \ln \gamma_i = \left(\frac{\partial (n_i G^E)}{\partial n_i} \right)_{T,P,n_j(j \neq i)} \quad \dots(4)$$

where n_i is the number of moles of i in the total number of moles n_T .

Generalised London Potential

When two molecules, 1 and 2 form a homogeneous, binary vapour-liquid phase system in the fluid phase, GLP enables the calculation of dispersion forces between polyatomic molecules from the additivity of bonded atom pair potentials. Homar and Mohammadi⁶ showed that the average of the inverse sixth power of the intermolecular distance (R) of one atom (i) in one molecule and another atom (j) in a second molecule is related to the net intermolecular attractive potential (ϕ) by a molecular structure dependent factor, F , by the equation,

$$\phi_{ij} = -\frac{1}{4} R^{-6} \sum_i \sum_j w_i w_j F_{ij} \left(\alpha_i \langle m^2 \rangle_j + \alpha_j \langle m^2 \rangle_i \right) \quad \dots(5)$$

where w defines the number of structurally equivalent atoms or other species i or j and α and $\langle m^2 \rangle$ are the polarizability and mean square electric dipole moment of the interacting bonded species. This equation represents a general expression for the net dispersion potential between polyatomic molecules for liquid phase. It accounts for the contribution from all electron centers whether they are bonded atoms, π -bond electrons or single electrons.

Equation for activity coefficients

Using the above expression, Homer *et al.*⁹ have derived the equation for excess free energy and corresponding activity coefficients of compounds 1 and 2 respectively,

$$(g^e / RT) = x_1 \ln \frac{v_1}{x_1} + x_2 \ln \frac{v_2}{x_2} + \frac{1}{2} Z (x_1 + x_2 q)$$

$$\times \ln \left[\frac{(x_1 + rx_2)}{(x_1 + qx_2)} \right] - \frac{1}{2} Z q x_2 \ln \frac{r}{q}$$

$$+ \frac{LZ}{2R} \left(\frac{x_1 \Delta U_{11}}{b_1} \ln \left\{ \frac{1 + a \exp(-b_1/T)}{1 + a} \right\} \right)$$

$$+ \frac{x_2 \Delta U_{22}}{b_2} \ln \left\{ \frac{1 + a^{-1} \exp(-b_2/T)}{1 + a^{-1}} \right\} \quad \dots(6)$$

$$\ln \gamma_1 = \ln \frac{v_1}{x_1} + \frac{x_2(r-1)}{x_1 + rx_2} + \frac{1}{2} Z \left\{ \frac{x_2(q-r)}{x_1 + rx_2} + \ln \frac{x_1 + rx_2}{x_1 + qx_2} \right\}$$

$$+ \frac{LZ}{2R} \left[\frac{\Delta U_{11}}{b_1} \left(\frac{a[1 - \exp(-b_1/T)]}{[1 + a \exp(-b_1/T)](1+a) + \ln \frac{1 + a \exp(-b_1/T)}{1+a}} \right) \right]$$

$$\left. + \frac{\Delta U_{22} V_1}{b_2 V_2} \frac{\exp(-b_2/T) - 1}{[1 + a^{-1} \exp(-b_2/T)][1 + a^{-1}]} \right] \quad \dots(7)$$

$$\ln \gamma_2 = \ln \frac{v_2}{x_2} + \frac{x_1(r-1)}{x_1 + rx_2}$$

$$+ \frac{1}{2} Z \left\{ \frac{x_1(r-q)}{x_1 + rx_2} + q \ln \frac{q(x_1 + rx_2)}{r(x_1 + qx_2)} \right\} + \frac{LZ}{2R}$$

$$\times \left[\frac{\Delta U_{22}}{b_2} \left(\frac{a^{-1}[1 - \exp(-b_2/T)]}{[1 + a^{-1} \exp(-b_2/T)]/(1 + a^{-1}) + \ln \frac{1 + a^{-1} \exp(-b_2/T)}{1 + a^{-1}}} \right) \right.$$

$$\left. + \frac{\Delta U_{11} V_2}{b_1 V_1} \frac{\exp(-b_1/T) - 1}{[1 + a \exp(-b_1/T)][1 + a]} \right] \quad \dots(8)$$

Here, v_1 and v_2 are the volume fractions of components 1 and 2, respectively given by, $v_1 = \frac{x_1 V_1}{x_1 V_1 + x_2 V_2}$ and $v_2 = \frac{x_2 V_2}{x_1 V_1 + x_2 V_2}$ where, V_1 and V_2 are the corresponding molar volumes and x_1 and x_2 are their mole fractions. L is the Avogadro's number and r reflects the ratio that governs the relative number of whole molecular contact between molecule 1 and 2 and q represents the relative contact areas. Their values are calculated from the ratios 2/1 of Van der Waals volumes and areas, respectively, i.e., $r = V_2/V_1$; $q = r/2$. Both r and q are pure-component parameters. Z is the coordination number of the mixtures. It was assumed that for a binary mixture there is a fixed value of the coordination number at any temperature. For organic liquid binary mixtures, Homar *et al.*¹⁰ took the coordination number of mixture either 11 or 7 considering all possible variation in the molecular geometry. So the choice of Z is somewhat arbitrary, however, according to Homer¹⁰ Z was originally chosen as 11 by analogy with liquids just above their melting points but lower values such as 7 may be more appropriate for the systems studied by him. ΔU_{11} and ΔU_{22} are the change in total molar energy of mixing of the corresponding components given by the following equations⁹

$$\Delta U_{11} = \phi_{11} - \phi_{21} V_1 / V_2 \quad \dots(9A)$$

$$\Delta U_{22} = \phi_{22} - \phi_{12} V_2 / V_1 \quad \dots(9B)$$

Here, ϕ is the corresponding net attractive intermolecular potential; ϕ_{ii} and ϕ_{ij} for like molecules,

ϕ_{ii} for unlike molecules. For a pure liquid, the molar energy of vaporization may be described as⁹

$$U_{11}^{\text{vap}} = \frac{1}{2} LZ \phi_{11} \quad \dots(10)$$

and

$$U^{\text{vap}} = \Delta_{\text{vap}} H - RT \quad \dots(11)$$

thus, the intermolecular potential energy can be calculated from latent heat of vapourization at a specified temperature. ϕ_{ij} is the average net intermolecular potential between two freely rotating molecules. From the theory of GLP, its value can be calculated from Eq. (3). For pure components, the average value of R (intermolecular separations) can be deduced from a probabilistic approach¹¹ as, $R_{0.17} = 2(0.17 V_m)^{1/3}$ where V_m is the molecular volume. For mixing of two components, R_{12} is calculated using the Lorentz approximation $R_{12} = (R_1 + R_2)/2$. However, if the molecular interactions behave comparably, then the Berthelot combining rules for unlike interactions might reasonably be expected to apply¹²:

$\phi_{12}^{\text{GM}} = (\phi_{11} \phi_{22})^{1/2}$. The vapour pressures of the pure materials are deduced using the data given in literature¹³; b_1 , b_2 and a are three variables, i.e.,

$$a = \frac{V_2 x_2}{V_1 x_1} \quad \dots(12)$$

$$b_1 = \frac{L(\phi_{21} - \phi_{11})}{R} \quad \dots(13)$$

$$b_2 = \frac{L(\phi_{12} - \phi_{22})}{R} \quad \dots(14)$$

Discussion

In the preliminary work, a series of 10 binary liquid mixtures of both polar and non-polar components are selected for verification of the predicted vapour-liquid equilibrium using GLP method. The systems taken are: (i) C_6H_6 - CCl_4 , (ii) cC_6H_{12} - CCl_4 , (iii) cC_5H_{10} - CCl_4 , (iv) cC_6H_{12} - C_6H_6 , (v) cC_5H_{10} - C_6H_6 , (vi) C_6H_6 - CH_3OH , (vii) C_6H_6 - C_2H_5OH , (viii) cC_6H_{12} - C_2H_5OH , (ix) CH_3OH - C_2H_5OH , (x) water- C_2H_5OH . The physical properties of the selected components at 298.2 K and 1 atmospheric pressure in pure form, required for calculation of activity coefficients by GLP method are shown in Table 1. The net intermolecular potential values of individual

Table 1 — Physical properties of pure components required for GLP calculations at 298K and 1 atmospheric pressure

S. No.	Name	Molar volume ⁽¹³⁾ (cc/mole)	$\Delta_{\text{vap}}H^{(6)}$ (KJ/mole)	Vapour pressure ⁽¹³⁾ (Pa)	ϕ_{11} eV $10^{-19}J$
1	Benzene	89.48	30.7	12638.9	-0.1339
2	Carbon tetrachloride	97.14	34.52	15213	-0.1520
3	Cyclohexane	108.86	32.73	13202.6	-0.1435
4	Cyclopentane	94.01	30.98	56990.0	-0.1352
5	Methanol	40.58	38.35	16791.45	-0.1702
6	Ethanol	58.62	40.5	7927.721	-0.1804
7	Water	18.015	40.82	3157.4	-0.1819

Table 2 — Values of net interaction parameters of binary mixtures determined by GLP method at 298 K¹⁰

S. No.	Name	ϕ_{12} eV ^(a) $10^{-19}J$	S. No.	Name	ϕ_{12} eV ^(a) $10^{-19}J$
1	Benzene- Carbon tetrachloride	-0.14465	6	Benzene-Methanol	-0.1438
2	Cyclohexane-Carbon tetrachloride	-0.1431	7	Benzene-Ethanol	-0.1517
3	Cyclopentane-Carbon tetrachloride	-0.1451	8	Cyclohexane – ethanol	-0.1524
4	Benzene- Cyclohexane	-0.137	9	Methanol-ethanol	-0.1787
5	Benzene- Cyclopentane	-0.1345	10	Water-ethanol	-0.1800

Table 3 — Comparison of vapour-liquid equilibrium data with experimental values

S. No	System	X_{liquid}	$(P_T)_{\text{cal}}$	$(P_T)_{\text{exptal}}$	$(Y)_{\text{cal}}$	$(Y)_{\text{exptal}}$
1	Benzene-CCl ₄	$X_{\text{CCl}_4}=0.4865$	16272	17863 ¹⁴	0.574	0.5298 ¹⁴
2	Cyclohexane-CCl ₄	$X_{\text{CCl}_4}=0.5$	18890		0.577	
3	Cyclohexane-C ₆ H ₆	$X_{\text{benzene}}=0.4952$	18100	18125 ¹⁵	0.488	0.4948 ¹⁵
4	Cyclopentane-CCl ₄	$X_{\text{c-pentane}}=0.46$	47407		0.72	0.71 ¹⁵
5	Cyclopentane-C ₆ H ₆	$X_{\text{c-pentane}}=0.46$	37344		0.81	
6	Benzene-methanol	$X_{\text{methanol}}=0.4742$	14031	24282 ¹⁶	4.452E-28	0.5343 ¹⁶
7	Benzene-ethanol	$X_{\text{ethanol}}=0.43$	12115		5.96E-24	
8	Cyclohexane-ethanol	$X_{\text{ethanol}}=0.43$	10981		2.993E-22	
9	Methanol-ethanol	$X_{\text{ethanol}}=0.43$	17114		0.331	
10	Ethanol-water	$X_{\text{ethanol}}=0.43$	3751.3		0.672	

components calculated from experimental latent heat of vapourisation of corresponding compounds are also summarized in Table 1. Table 2 represents values for net intermolecular potential energies of unlike molecules for the above systems. Only the attractive contributing term of London's original dispersion forces, which account for the interaction energy, is taken into account when calculating equilibrium data and ϕ is calculated by Homer *et al.* as the sum of the London dispersion based atom-atom net attractive interactions for two polyatomic molecules at an equilibrium separation. To avoid much complication in calculating vapour-liquid equilibria, these data were directly taken for these systems. However, in absence of data Berthelot combining rules have been used here for unlike interactions; this equation may reasonably be applied if the molecular interactions

behave comparable for any of the several reasons (hard-sphere approximation, molecules form conformal solutions, etc.)

For the initial appraisal of AGAPE (a general approach to phase equilibrium), the activity coefficient values are calculated for a range of binary mixtures with each components varying from liquid phase mole fraction range of 0.1 to 0.9. After that, the corresponding vapour-phase composition and total pressure of the above systems are calculated with different liquid mole fraction ranges. The calculated data are compared with the experimental data where available, and the comparisons are shown in Table 3. From this table it is obvious that, the agreement between the predicted data and the experimental data are found to be quite acceptable for the first five components. However, for last five components, the

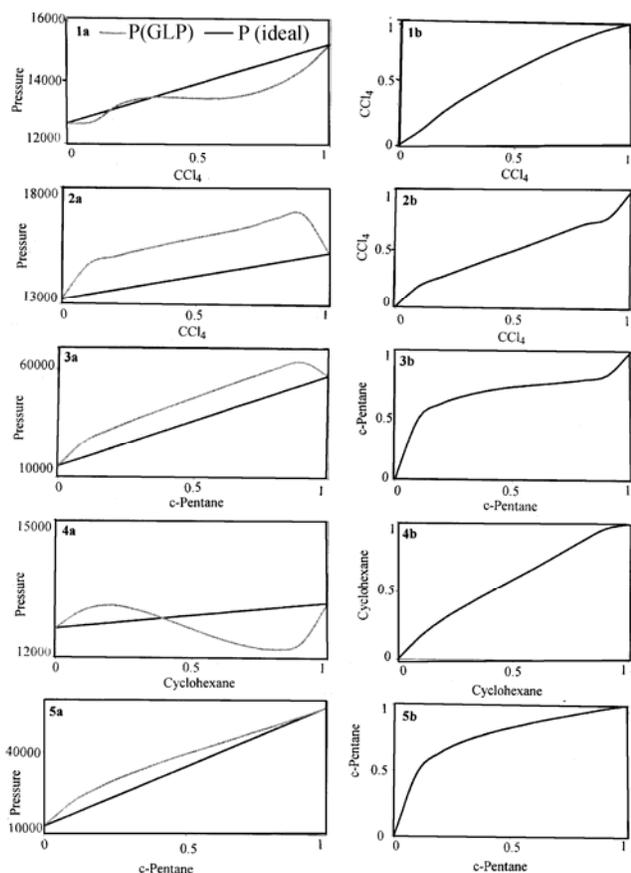


Fig. 1 — Variation of (a) total vapour pressure P_a and (b) vapour phase mole fraction with liquid phase mole fraction for the following systems: (i) benzene- CCl_4 , (ii) cyclohexane- CCl_4 , (iii) cycloheptane- CCl_4 , (iv) benzene-cyclohexane, (v) benzene-cyclopentane

calculated values are much lower than the experimental ones.

Thus, the prediction of thermodynamic properties of binary liquid mixtures by GLP method is quite satisfactory for the systems when both the components are non-polar in nature. But this theory fails for polar species, especially for hydrogen-bonded compounds (CH_3OH , $\text{C}_2\text{H}_5\text{OH}$, water). This discrepancy may be due to the cooperative and autogonistic effects between the dipoles of the neighbouring molecules, when these molecules are close together due to hydrogen bonding or parallel

alignment of dipoles. This effect may change the predicted R_{12} values and so ϕ_{12} for net interaction potential for unlike molecules. The solvent water is also expected to give bad result as the compound is both polar and contains hydrogen bonds. It is fair to say, however, that the generalized London potential is not theoretically able to handle polar or hydrogen-bonded molecules. Figure 1 shows the variation of vapour-phase composition and total pressure with liquid phase composition for the non-polar systems.

Thus, it can be said that, although in its infancy, AGAPE, which requires only a knowledge of available atomic and molecular parameters, has the potential to replace empirically based methods for the purpose of predicting VLE data.

References

- Alvarado J F J, *J Chem Eng Data*, 45 (2000) 1040; Makino T, Sugahava T & Ohgaki K, *J Chem Eng Data*, 50 (2005) 2058; Kapoor S & Rattan V K, *J Chem Eng Data*, 50 (2005) 1891.
- Renon H & Prausnitz J M, *AIChE J*, 14 (1968) 135.
- Abram D S & Prausnitz J M, *AIChE J*, 21 (1975) 116.
- Fredenslund A & Jones R L & Prausnitz J M, *AIChE J*, 21 (1975) 1086.
- London F, *Trans Faraday Soc*, 8 (1937) 33.
- Homer J & Mohammadi M S, *J Chem Soc Faraday Trans*, 2, 83 (1987) 1957.
- Reid R, Prausnitz J M & Sherwood T K, *The Properties of Gases and Liquids* (Mc-Graw-Hill, New York), 1977.
- Jenson A L B, Kakku A I, *Proceedings of the IChemE Research Event, Symposium*, London, Jan, 2 (1994) 731.
- Homer J, Jenkins J D, Porter K E & Kakku A I, *J Chem Soc Faraday Trans*, 87 (1991) 57.
- Homer J, McCoubrey J & Kakku A I, *J Chem Soc Faraday Trans*, 89 (1993) 3767.
- Hertz P, *Math Ann*, 67 (1909) 387.
- Rowlinson J S & Swinton F L, *Liquids & Liquid Mixtures*, 3rd edn (Butterworths, London), 1982.
- Perry R H & Green D W, *Chemical Engineer's Handbook*, 7th edn (McGraw Hill International Pub), 1998.
- Scatchard G, Wood S E & Mochel J M, *J Am Chem Soc*, 62 (1940) 712.
- Scatchard G, Wood S E & Mochel J M, *J Phy Chem*, 43 (1939) 119.
- Scatchard G, Wood S E & Mochel J M, *J Am Chem Soc*, 68 (1946) 1957.