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Theory Article

Partial Molar Volumes Based on Activity Coefficient Correlations

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Abstract

Partial molar volumes of components in solution are important design parameters. Based on the general definition of activity coefficient, it is shown that partial molar volumes can be very well correlated with the corresponding mole fractions of the solution components, by functions that are known to correlate activity coefficients.

Keywords: Partial molar volume; Activity coefficient; Ideal solution

Introduction

Process simulations based on thermodynamic principles and equations are at the heart of chemical engineering design. In general, a reliable simulation solves questions that are prevalent in the practice of chemical engineers, such as the final volumes of solutions, phase equilibria, and chemical equilibria. In many cases, small deviations in the predicted concentrations may lead to very significant financial implications. Thus, good correlations for thermodynamic properties are always in need. Obviously, good correlations may also lessen the need in expensive experiments.

A central property in physical and chemical equilibria phenomena is the Chemical Potential (CP) [1]. A gradient in CPs is the driving force for molecular mass transfer, and uniformity of CPs is a condition for equilibrium. As will be briefly summarized in the next section, there are, in principle, two ways to calculate CPs. One way is a theoretical calculation based on an Equation of State (EOS). The other way uses empirical correlations of activity coefficients based on experimental equilibrium data. These two options are schematically shown in Figure 1.

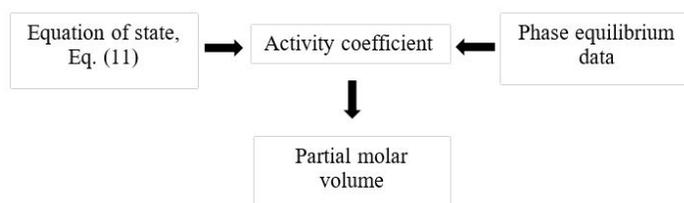


Figure 1: Top line: the two ways to get the activity coefficient. The present paper shows that the partial molar volume of a component in solution can be predicted by the same functional dependence on the mole fraction as the activity coefficient.

The present communication suggests using the knowledge accumulated about CP correlations for a different purpose altogether - calculating Partial Molar Volumes (PMVs) in solution. It shows that functional mole-fraction dependencies that are useful for predicting CPs are also useful for predicting PMVs. This is also schematically shown in Figure 1 and explained in more detail below.

Theory

Thermodynamic background

To enable full understanding of the theoretical objective

of this paper, we first briefly introduce and explain the necessary fundamental, thermodynamic concepts. As is well known, the combined first and second law of thermodynamics is given by

$$d\bar{U} = Td\bar{S} - Pd\bar{V} + \sum_1^m \mu_i dn_i \quad (1)$$

where \bar{U} is the internal energy of our system, T is the absolute temperature, \bar{S} is the entropy, P is the pressure, \bar{V} is the volume, m is the number of chemical species, μ_i is the chemical potential of species i , and n_i is the number of moles of this species.

Since \bar{U} is a homogeneous function of first degree (namely its value is multiplied by any factor k when the numbers of moles are each multiplied by the same factor k), the Euler equation holds. This implies that integration of Eq. (1) immediately gives

$$\bar{U} = T\bar{S} - P\bar{V} + \sum_1^m \mu_i n_i \quad (2)$$

Now, if we differentiate Eq. (2) and subtract the result from Eq. (1), we get

$$-\bar{S}dT + \bar{V}dP - \sum_1^m n_i d\mu_i = 0 \quad (3)$$

By definition, the volume of a solution consists of the molar average of the PMVs, \bar{V}_i

$$\bar{V} = \sum_1^m n_i \tilde{V}_i \quad (4)$$

So, when we substitute Eq. (4) into Eq. (3) for isothermal processes, we get

$$\left(\sum_1^m n_i \tilde{V}_i \right) dP = \sum_1^m n_i d\mu_i \quad (5)$$

The individual contribution of each species is

$$d\mu_i = \tilde{V}_i dP \quad (6)$$

Equation (6) can be used in its integral form for calculating the CP

$$\mu_i(T, P, x_i) - \mu_i(T, 0, x_i) = \int_0^P \tilde{V}_i dP \quad (7)$$

where the reference state is the state of an ideal gas ($P \rightarrow 0$) and the integration is done at constant temperature. Thus, it is clear, in principle, that exact EOS's enable calculations of CPs. As a side, technical remark, it should be noticed that the integral on the right-hand side must be done in parts when we need the CP of a liquid.

However, the liquid state is usually the weak part of EOS's. Therefore, the CP is usually extracted from phase equilibria data, using the concept of activity coefficient, as follows. Eq. (7) by itself does not yield CPs, because we do not know the CP at the reference, ideal-gas state. Yet we know the difference at the ideal gas state between the CP of component i in solution and of the pure component i , μ_{ip}

$$\mu_i(T, 0, x_i) - \mu_{ip}(T, 0) = RT \ln x_i \quad (8)$$

This equation, derived for the ideal gas state, reflects the fact that at this state there are no interactions between the molecules. It is just a matter of volume and randomness of positions.

Now we may combine Equations (7) and (8) to get the general equation

$$\begin{aligned} \mu_i(P, T, x_i) - \mu_{ip}(P, T) & \quad (9) \\ & = [\mu_i(0, T, x_i) - \mu_{ip}(0, T)] + \int_0^P [\tilde{V}_i(x_i, P) - V_{ip}(P)] dP \end{aligned}$$

This equation can be rewritten in a compact way

$$\mu_i(P, T, x_i) - \mu_{ip}(P, T) = RT \ln x_i + RT \ln \gamma_i = RT \ln \gamma_i x_i \quad (10)$$

where the activity coefficient is defined by

$$RT \ln \gamma_i \equiv \int_0^P [\tilde{V}_i(P, T, x_i, P) - V_{ip}(P, T)] dP |_{T=\text{const.}} \quad (11)$$

Theoretical objective of this paper

Quite a few successful correlations for calculating activity coefficients have been developed [1,2]. These correlations have been tested and tabulated over the years. The objective of the current paper is to use these successful correlations for a different purpose: calculating PMVs. This is important for improving EOS's of mixtures, especially in the liquid zone, and all properties derived from it. In a more mathematical language, we need to get a functional dependence of the integrand in Equation (11) on the mole fractions of the solution components and check its validity. The starting point is Equation (11) that can be rewritten in a short form, as follows

$$\int_0^P [\tilde{V}_i - V_{ip}] dP = \overline{[\tilde{V}_i - V_{ip}]} \int_0^P dP = \overline{[\tilde{V}_i - V_{ip}]} P = RT \ln \gamma_i \quad (12)$$

In this equation, $[\tilde{V}_i - V_{ip}]$ is the average value of $\overline{[\tilde{V}_i - V_{ip}]}$ over the range of the integral. This average may serve as a good approximation for a simple calculation of the integral in Equation (12) if this volume difference does not change much with pressure. This may be the case, since in the gas state, the molar volumes are large, but the difference may be small; for the liquid state the volumes are much smaller, but the relative difference may be bigger. Thus, our basic assumption is

$$\tilde{V}_i = V_{ip}[1 + f(x_i)] \quad (13)$$

$$f(x_i) = A^* \ln \gamma_i(x_i) \cong \frac{RT}{PV_{ip}} \ln \gamma_i(x_i) \quad (14)$$

In this equation, A^* is a constant to be determined by fitting the theory to the experimental data. Eq. (14) is the crux of the matter. The question to be answered is: can the functional dependence of PMVs on mole fractions of components in solution be well described by the same functions that fit the activity coefficient data? Two of the popular correlations [1,2] of activity coefficients were tested in this study. For simplicity, we demonstrate the idea using binary solutions. One correlation was developed by van Laar

$$RT \ln \gamma_1 = A \left(1 + \frac{Ax_1}{Bx_2}\right)^{-2} \quad (15)$$

$$RT \ln \gamma_2 = B \left(1 + \frac{Bx_2}{Ax_1}\right)^{-2} \quad (16)$$

and the other by Margules

$$RT \ln \gamma_1 = (A_M + 3B_M)x_2^2 - 4B_Mx_2^3 \quad (17)$$

$$RT \ln \gamma_2 = (A_M - 3B_M)x_1^2 + 4B_Mx_1^3 \quad (18)$$

Results and Discussion

Figures 2-7 show the results for six different combinations of various polarities. The systems studied were; methanol-water [3], ethanol-water [4], 1-propanol-water [5], 1-butanol-water [6], 1-octane-ethanol [7] 1-decane-ethanol [7], all at 298.15 K. Each figure shows three curves of the calculated molar volume of a solution, normalized by the experimentally measured molar volume. One curve demonstrates the extreme case of an ideal solution ($\tilde{V}_i = \bar{V}$). The maximum deviation of the ideal solution model from the experimental data is between ~1% to ~20%. This model is unrealistic in many cases, since it represents the simplest possible simulation model. The other curves represent the correlations of van Laar and Margules. These two correlations appear to be very similar, almost identical for the aqueous alcohol solutions. However, there is some preference for the van Laar correlation in ethanol-alkane solutions. The maximum deviation recorded in the present work for the van Laar correlation is ~1% and for the Margules it is ~2%. The deviation is much lower for most of the concentration range.

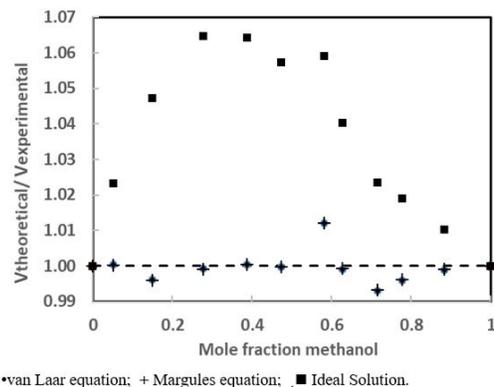


Figure 2: Ratio of theoretical to experimental molar volumes of methanol-water solutions.

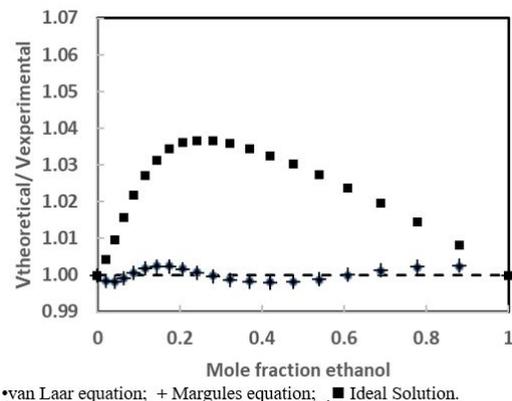


Figure 3: Ratio of theoretical to experimental molar volumes of ethanol-water solutions.

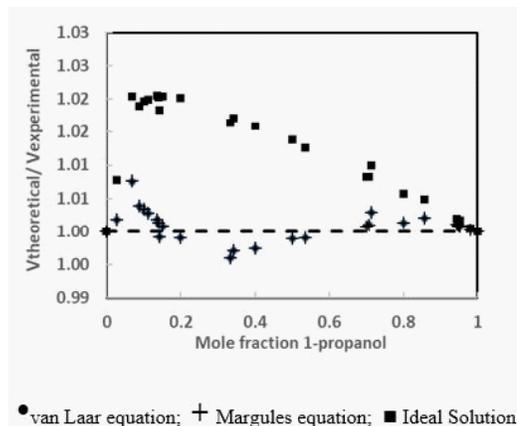


Figure 4: Ratio of theoretical to experimental molar volumes of 1-propanol-water solutions.

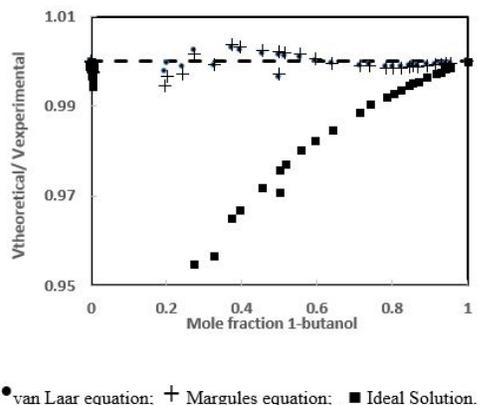


Figure 5: Ratio of theoretical to experimental molar volumes of 1-butanol-water solutions. The gap is a result of phase separation due to limited solubility.

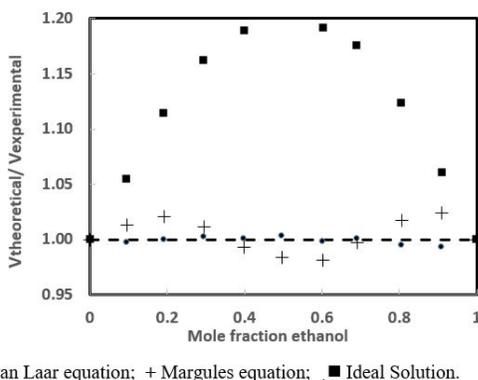


Figure 6: Ratio of theoretical to experimental molar volumes of ethanol-octane solutions.

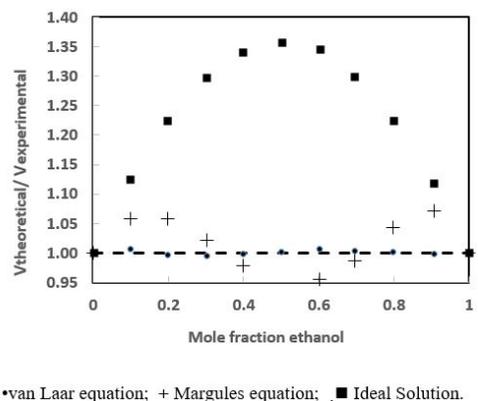


Figure 7: Ratio of theoretical to experimental molar volumes of ethanol-decane solutions.

It is interesting to note that the curves based on the ideal solution model give us interesting information about the interactions between the molecules. The assumption underlying the ideal solution model is that the molecular interaction between the different components is very similar to that between the molecules of the pure components. Thus, the maximum value of the normalized volume calculated using the ideal solution model may serve as a quantitative indication of the difference in properties between the components. With the alcohol-water solutions these maximum values decrease from ~ 1.07 for methanol to ~ 1.005 for 1-butanol. For the ethanol-alkane solutions, the numbers are much higher than for the alcohols-water values, indicating bigger differences.

Conclusions

Based on these results, it can be clearly concluded that the same functional correlations used to calculate activity coefficients can be successfully adapted for calculating PMVs, as suggested here. As the difference between the nature of the molecules of the components becomes bigger, there is some advantage to the van Laar correlation.

As a side issue, the ratio between the ideal solution volume and the real one may serve as a quantitative indication of the difference in molecular interactions associated with the pure components on the one hand and that related to the interaction between the different species.

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