

Assessing the use of NMR chemical shifts for prediction of VLE in non-ideal binary liquid mixtures

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Abstract

A method of estimating vapour liquid equilibrium (VLE) using NMR chemical shift data has been proposed by Xu et al. (2012). This method is based on the concept that the average local composition around each species is determined by the thermodynamics of the system, and also determines the screening of the NMR active groups within that molecule, and so their NMR chemical shifts. Xu et al.'s method has been replicated and verified; results are confirmed to be accurate for alcohol + hydrocarbon mixtures, giving VLE predictions of comparable accuracy to the UNIFAC, generally considered the best predictive activity coefficient model available. However, for more strongly non-ideal mixtures, the method becomes less reliable, giving significantly less accurate predictions of total pressure than UNIFAC. Several causes for this are identified. The model proposed by Xu et al. (2012) is unable to fit minima or maxima in chemical shifts, which are observed experimentally in some binary mixtures. Different NMR resonances within the same molecule lead to different predictions of VLE, clearly an un-physical result. The thermodynamics of strongly non-ideal mixtures are determined by more complex interactions than a simple description of average local composition around each component in the mixtures, for example strong and directional hydrogen bonds. Different groups within the same molecule may have different local compositions in their immediate vicinity; for example in the case of alcohol + water mixtures, one would expect a clustering of water molecules around the hydroxyl group but not the aliphatic group. Hence, the concept of a simple local composition model is not valid for these more complex cases, and it is therefore not surprising that a model based on this simple concept is often not effective in predicting VLE.

Keywords: VLE, Wilson model, NMR spectroscopy, UNIFAC

Letter to the Editor

Knowledge of vapour-liquid equilibrium (VLE) data is essential in many technological applications, including modelling of distillation columns and other separation processes. In a recent paper, Xu *et al.* (2012) reported that by measuring ^1H NMR chemical shifts it is possible to accurately predict VLE data in alcohol + hydrocarbon binary mixtures. Starting from Wilson's local composition model (Wilson, 1964), they proposed an expression relating the measured chemical shift of component i , $\delta_{i,obs}$, to the compositions, x_i and x_j of the two components, according to:

$$\delta_{i,obs} = \delta_i^0 \frac{x_i}{x_i + \Lambda_{ji}x_j} + \delta_i^\infty \frac{\Lambda_{ji}x_j}{x_i + \Lambda_{ji}x_j} \quad (1)$$

where δ_i^0 and δ_i^∞ are the chemical shift of the pure component and that at infinite dilution, respectively, and Λ_{ji} is a Wilson parameter. Therefore, by measuring the NMR chemical shifts of component i and j as a function of composition, and using Equation (1), and its equivalent for component j , it is possible to obtain the Wilson parameters, Λ_{ji} and Λ_{ij} , which can be used to calculate the activity coefficients, γ_i and γ_j (Gothard *et al.*, 1976), which can then be used for VLE predictions. Xu *et al.* (2012) used this approach to calculate VLE data for several binary mixtures of alcohol + hydrocarbon mixtures and good agreement between the predicted VLE and experimental data reported in the literature was demonstrated.

However, the proposed method raises some important questions that were not addressed in the original paper. The method described was proposed as an alternative for the prediction of VLE data in cases for which the data is difficult to measure directly. However, no discussion of the range of validity and applicability was given; without knowledge of this, it is not possible to know *a priori* if the predicted VLE is accurate, and so the method is of little practical value. Another issue is which chemical shift should be used in Equation (1), and whether using the chemical shifts of different groups in the same molecule will give the same result. Consider, for example, a simple case discussed by Xu *et al.* (2012), a mixture of methanol and benzene; although there is no problem about what chemical shift needs to be used for benzene (since it has only a single ^1H NMR resonance), a question arises as to whether the chemical shift of the methyl group of methanol could be used in Equation (1), instead of the chemical shift of the $-\text{OH}$ group used by Xu *et al.* (2012), and whether the same result is obtained in either case.

We therefore carried out ^1H NMR chemical shifts measurements for a variety of binary mixtures, in order to assess and rationalise the range of validity of the proposed model. We started by reproducing the results obtained by Xu *et*

al. for 1-hexanol + n-hexane; predictions of pressure for this system were very good and consistent with the work of Xu *et al.* (2012). We then applied the same approach to other types of binary mixtures. We first focused on alcohol + water mixtures and found that the model predicts well the VLE data for aqueous methanol mixtures; predictions become less accurate for aqueous ethanol mixtures. In the case of aqueous 1-propanol and 2-propanol, the predictions become rather poor. This trend of decreasing accuracy with increasing size of aliphatic group of the alcohol reflects the extent of non-ideality of the mixtures. Indeed, beyond the propanols, full miscibility of alcohol and water does not occur; 1-butanol + water shows partial miscibility at room temperature.

In addition, a difference between the predictions based on the –OH and the aliphatic chemical shift of the alcohol was also observed, particularly for aqueous propanol mixtures. This calls into question the validity of the model, since it is based on the average local composition surrounding each component of the mixture, which should be independent of the NMR resonance being considered. It seems that use of the –OH chemical shift of methanol and ethanol describes slightly better the thermodynamics of the system. Because in such cases the dominant interaction in alcohol + water mixture is that of hydrogen bonding, it is reasonable that use of the –OH resonance of the alcohol gives a better prediction. For the aqueous propanols both analyses show a poor fit to experimental VLE data. An example of VLE predictions is shown in Figure 1, where we compare experimental VLE data with those predicted by using the model proposed by Xu *et al.* as well as UNIFAC, which is a standard predictive tool for VLE data. The original version of the UNIFAC method was used (Fredenslund *et al.*, 1975), with interaction parameters taken from Hansen *et al.* (1991) and Wittig *et al.* (2003).

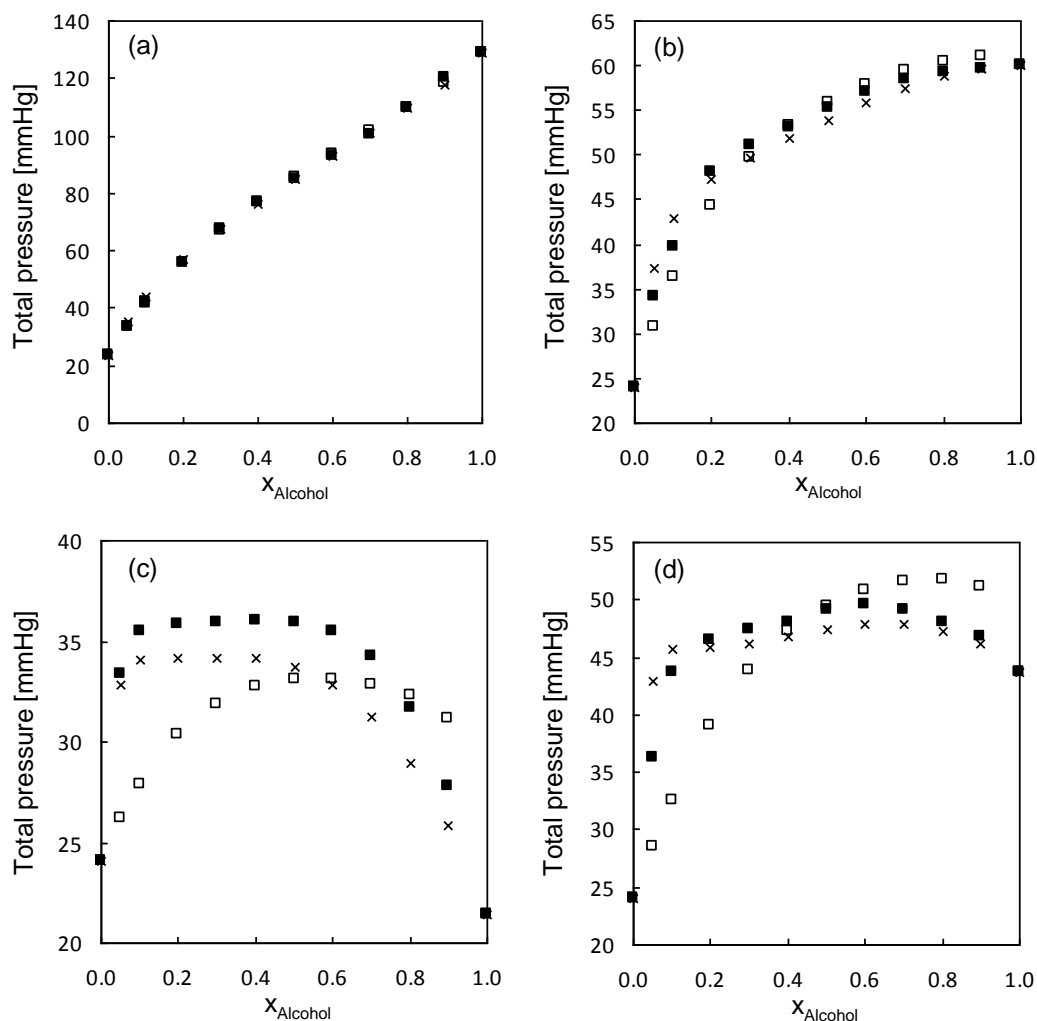


Figure 1. VLE data as total pressure for various alcohol + water mixtures using the $-OH$ alcohol chemical shift: (a) methanol + water; (b) ethanol + water; (c) 1-propanol + water; (d) 2-propanol + water. The symbols are: (■) experimental values; (□) predictions using the chemical shift data reported in this work; (x) predictions from UNIFAC. The experimental data for methanol + water are taken from Koner *et al.* (1980); the experimental data for the other alcohol + water mixtures are taken from Hu *et al.* (2003).

We have also carried out experiments on the acetone + chloroform system, which shows a negative deviation from Raoult's law (see supporting information S1). Again, VLE predictions using Xu *et al.*'s chemical shift method are not very accurate and more accurate prediction can be obtained using UNIFAC method.

Another issue that we have found is that some mixtures, such as acetone + water, show a maximum in chemical shift versus composition, which cannot be fitted by using the model proposed by Xu *et al.* (see supporting information S2).

In summary, we have confirmed that the model proposed by Xu *et al.* (2012), summarised as Equation (1), gives reliable predictions of VLE for alcohol +

hydrocarbon mixtures. However, our results demonstrate that this model is not of general validity, with predictions of total pressure becoming less accurate for increasingly non-ideal mixtures. The first limit is in the form of Equation (1), which cannot predict chemical shift profiles showing maxima or minima. Secondly, even when excellent fits to the chemical shift data can be achieved (for example in the case of chloroform + acetone mixtures), VLE predictions are often poor, particularly for highly non-ideal mixtures. Thirdly, significantly different predictions are obtained using the chemical shifts of different resonances from the same molecule. Our results clearly suggest that if a relationship exists between NMR chemical shift and local composition, it is the case that different groups within the same molecule (e.g., aliphatic and –OH moieties in alcohols) have different local compositions. This results in the variation of chemical shift as a function of composition being different for the different moieties within the same molecule. This is unsurprising given the different energy of interactions between water and the different moieties of alcohols, aliphatic or –OH. Different local compositions surrounding different groups within a molecule are implicit in group contribution methods for predicting VLE, such as UNIFAC. It is possible that Xu *et al.*'s model could be refined by application of such a group contribution method, but this would only be practical in cases where the NMR chemical shift of all groups could be observed.

We have confirmed that Xu *et al.* (2012) model is effective for predicting VLE of alcohol-hydrocarbon mixtures (although it is no more accurate than UNIFAC). However we have shown that the method does not have general validity for other binary liquid mixtures. From a practical point of view, undermines its value, since one cannot know *a priori* whether Xu *et al.*'s model will be accurate for VLE or not. Established methods such as UNIFAC remain more reliable for the prediction of VLE in the absence of experimental data. Nonetheless Xu *et al.*'s findings have considerable interest since they raise (and partially answer) the question of the relationship between local composition in activity coefficient models and its effect on chemical shift in NMR measurements. Based on our findings, it could be of interest to extend the approach **proposed** by Xu *et al.* to predict UNIFAC group contribution parameters. These are related to individual groups within a molecule, and so it is reasonable to assume that these should be related more directly to the chemical shifts of those same groups.

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