Butadiene Purification Using Polar Solvents. Analysis of Solution Nonideality Using Data and Estimation Methods

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Abstract

The classical problem of 1,3-butadiene recovery from steam cracker C_4 hydrocarbons is reconsidered using modern tools of quantum mechanics and molecular simulation. The effectiveness of n,n-dimethylformamide (DMF) and acetonitrile (ACN) to act as extractive-distillation solvents is explored with an emphasis on the predictive capability of various models. The quantum mechanical method of interest is the COSMO-RS method. The chosen molecular simulation method is the SPEADMD model. These methods are compared to conventional methods such as UNIFAC and "thermodynamic intuition." The COSMO-RS method is found to predict the trends of infinite-dilution activity coefficients quantitatively, but requires a systematic empirical correction to provide accuracy comparable to UNIFAC. It is noted that the COSMO-RS method has a special capability to predict subtle trends. The SPEADMD model is found to provide unique qualitative insights, but requires empirical refinement of the interaction-potential models that is similar to the regression of UNIFAC parameters. This work is intended to serve as an objective framework to evaluate tools – traditional and modern – to predict solution nonideality.

Keywords

Process simulation, thermodynamic properties, activity coefficient, group contribution, UNIFAC, COSMO-RS, quantum mechanics, molecular simulation, SPEADMD, 1,3-butadiene, extractive distillation

Introduction

The recovery of 1,3-butadiene and other valuable products from steam cracker C_4 hydrocarbons is an important industrial problem. The separation needs to be accomplished by extractive distillation using polar solvents because the boiling points of the hydrocarbons are very close and several azeotropes may form. Design of separation schemes requires an accurate model for the liquid-phase nonideality. In this paper we evaluate the data and estimation methods for the liquid-phase nonideality for processes employing two popular polar solvents: n,n-dimethylformamide (DMF) and acetonitrile (ACN). Although this problem has been discussed previously, we are reconsidering it

using modern tools to show what insights the new tools can contribute. A key goal of this paper is to analyze the status and challenges of modern predictive methods based upon quantum mechanics and molecular simulation.

Background

1,3-butadiene (13BD) is produced mainly as a by-product from the steam cracking of liquid feedstocks.[1,2,3,4] It is separated from the steam-cracker C_4 stream by using extractive distillation. Simple fractionation cannot separate 13BD from other components because of the closeness of their boiling points and consequent formation of many azeotropes. The boiling point range of the C_4 stream is about 17°C and the three major components (1,3-butadiene, isobutene and 1-butene) have a boiling range of less than 3°C.

In the extractive-distillation process, the steam cracker C_4 stream is distilled with a polar solvent to separate the paraffins and olefins from the diolefins and acetylenes, and to accomplish further separation of the diolefins and the acetylenes. Commonly used solvents are DMF and ACN. Other solvents used in industry are n-methylpyrrolidine (NMP), furfural, beta-methoxypropionitrile (BMOPN), dimethylacetamide (DMAC) and cuprous ammonium acetate solution.

The DMF extractive process,[5] which Nippon Zeon commercialized in 1965, is a typical 13BD recovery process. The process uses extractive distillations coupled with conventional distillation. In the first extractive distillation, components in the feed that are less soluble in the DMF solvent than 13BD are taken overhead. 13BD and the more soluble compounds pass to a stripping column where they are stripped from the higher-boiling solvent. The 13BD and more soluble compounds then pass to a second extractive distillation column where 13BD is recovered overhead and the more soluble compounds are removed together with the solvent as bottoms. The 13BD is finally recovered from minor amounts of the high- and low-boiling impurities in the conventional distillation section. Effective design of these integrated process schemes requires sophisticated modeling technologies.[3]

Process simulation is an important enabling technology for 13BD purification, and the physical-property model that describes the vapor-liquid equilibrium and other thermodynamic properties is the foundation of the modeling programs.[6,7] Standard thermodynamic frameworks, for example the NRTL[8] activity-coefficient model coupled with the Redlich-Kwong[9] equation for the vapor phase, are well capable of correlating the thermodynamic properties. The challenging modeling issues are data evaluation and filling gaps in the data, for which various analysis and estimation methods must be used.

The focus of this paper is the analysis and estimation methods. We study a range of approaches that use a combination of experimental data, thermodynamic knowledge and experience (i.e., "intuition"), group-contribution methods, and modern predictive methods based upon quantum mechanics and molecular simulation. We assess the strengths and weaknesses of each method, and conclude that the best practical approach is to use a judicious combination of all available methods. A key emphasis of this paper has been to analyze current and needed capability of modern methods based upon quantum mechanics and molecular simulation.

Experimental Data and Analysis Based Upon Thermodynamic Intuition

Table 1 presents the chemical species considered in this work, in order of increasing normal boiling point (T_b). The last four species are the solvent components. ACN and DMF are the solvents highlighted here. Water and ethanol are usually present in the solvent because they occur in the process or are added to improve the solvent characteristics. These two additional solvent species help establish the patterns of the experimental data and provide a test of the estimation methods.

The last column of Table 1 presents a typical C_4 feed that is based upon the authors' experience; these data are presented graphically in Figure 1. The hydrocarbon feed components that exceed a concentration of 1 wt% are clustered in the boiling-point range of 261-278 K (-12 to 5ºC), a span of only 17°C. The three major components (13BD, isobutene and 1-butene) have a boiling-point range of 2.4°C. Hence, it is necessary to introduce a polar solvent that selectively absorbs the unsaturated hydrocarbons – or, perhaps more accurately, selectively rejects the saturated hydrocarbons.[1,2]

Table 2 presents experimental data for the infinite-dilution activity coefficients of hydrocarbons in DMF at 40°C, which has been chosen as a representative value since it is typical of temperatures encountered in extraction-distillation columns. Only the infinite-dilution activity coefficients have been reported here since at plant conditions the solubility of the hydrocarbons in the liquid phase is relatively low. The infinite-dilution activity coefficients have been obtained by fitting the experimental data using the NRTL-Redlich-Kwong model[8,9] and extrapolating the activity coefficients to zero concentration of the hydrocarbon.

The results in Table 2 demonstrate that the data fall into the pattern expected from thermodynamic intuition. The infinite-dilution activity coefficients fall as the degree of unsaturation of the hydrocarbon increases, i.e., the activity coefficients progressively decrease as the hydrocarbon class goes from paraffin to olefin to diolefins to triple bond to olefin plus triple bond. This, of course, is the reason why DMF is chosen as an extractive solvent, but the fact that the activity coefficients fall into the expected pattern provides confidence in the experimental data and offers some capability to fill in data gaps.

Table 3 shows analogous results for ACN as the extractive solvent. Again, the data fall into the expected pattern, which increases confidence in the entire set of data and offers further capability to fill gaps in the data. Figure 2 explores the relationship between the activity coefficients of the hydrocarbons in the two solvents, DMF and ACN, and demonstrates that there is a simple linear relationship between the two sets of activity coefficients on the logarithm scale. This relationship provides additional ways to test the experimental data and to fill gaps in the data. Further, Figure 2 suggests that DMF may be a better extractive agent than ACN since it provides larger selectivity between the saturated and unsaturated hydrocarbons.

Table 4 indicates that the activity coefficients of the hydrocarbons in ethanol and water fall into the same pattern as those shown above for DMF and ACN. Figure 3 is an extension of Figure 2 and demonstrates that the activity coefficients of the hydrocarbons in ethanol and water are related to those in ACN analogously to the DMF-ACN relationship. The dashed lines in Figure 3 are best-fit linear relationships. The scatter in the water-ACN relationship suggests there is considerable uncertainty in the hydrocarbon-water infinite-dilution activity coefficients, but more likely is caused by the "limits of simple thermodynamic intuition."

The results presented in this section demonstrate that methods based upon thermodynamic intuition are powerful because the simple expected relationships are usually accurate and, importantly, a vast database of experimental measurements is available to support the analysis.

Estimation Methods: UNIFAC and COSMO-RS

Methods based upon thermodynamic intuition are limited to the range of the experimental database. Theoretically-based estimation methods have the potential to extend the range of the experimental data and even predict data for mixtures that have not been experimentally studied. This section explores the capabilities of two estimation methods (UNIFAC and COSMO-RS) to advance process technology for the separation of C_4 hydrocarbons using extractive distillation.

UNIFAC is a group-contribution method that was introduced by Fredenslund et al.,[10] and systematically refined and improved by Gmehling and co-workers over three decades.[11,12] It has been demonstrated to be a powerful estimation tool in its domain of validity. The present UNIFAC estimations use the implementation available in the Aspen Plus[54] process simulator.

The Conductor-like Screening Model for Real Solvents (COSMO-RS[13,14,15,16]) is a relatively new estimation method. The method starts from first-principles quantum-chemical calculations of the state of the individual molecules in a virtual conductor (DFT/COSMO calculations[16,17,18]), and the resulting surface polarization charge densities are used to quantify the surface-interaction energies of the molecules with respect to electrostatics and hydrogen bonding. These generic expressions for the surface interactions together with efficient, but exact, statistical thermodynamics of pair-wise interacting surfaces[19] lead to expressions for the chemical potentials of the molecule in the liquid mixtures, and hence to activity coefficients and all other derivative thermodynamic properties. The surface polarization charge densities are accurate to about 0.3 kcal/mol.

COSMO-RS has a relatively small number of adjusted parameters ($\approx$20-30, depending on the number of chemical elements involved) compared to force-field methods, and especially compared to group-contribution methods. A force-field covering roughly the same chemical space usually requires about an order of magnitude more parameters, and UNIFAC requires about two orders of magnitude more parameters.

COSMO-RS is comparable to UNIFAC in computational efficiency. The time-demanding steps of COSMO-RS are the DFT/COSMO calculations for individual compounds. For compounds of the size considered in this study, these calculations typically require about one hour on a single 3 GHz CPU. For the present study, the DFT/COSMO calculations were taken from the COSMObase database,[20] and hence the activity-coefficient calculations with COSMOtherm[21] only took a few seconds of computational time; the standard version of COSMOtherm was used without any adjustments for this work. The computational time of COSMO-RS certainly does not limit its use in industrial practice.

Table 5 and Table 6 present estimations by the UNIFAC and COSMO-RS methods for the infinite-dilution activity coefficients at 40°C of the hydrocarbons in the four solvent components (DMF, ACN, ethanol and water). Figure 4 and Figure 5 evaluate how well

the UNIFAC and COSMO-RS methods predict the activity coefficients of the hydrocarbons in DMF and ACN, respectively. These figures show that the predictions of UNIFAC are good; the average error is close to zero and the predictions are typically accurate to about ± 20-25%, except for the activity coefficients of the saturated hydrocarbons in DMF where the model under-predicts the experimental values. COSMO-RS shows a clear bias compared to the experimental data. This result may be anticipated since COSMO-RS has far fewer fitted parameters and none fit specifically to the data of this study. However, we may expect that COSMO-RS will capture the data trends. In order to test this notion, we have developed an empirical relationship for the hydrocarbon-DMF infinite-dilution activity coefficients in terms of the COSMO-RS predictions as follows:

$$\ln \gamma^{Correlated} = 0.8887 + 1.2972 \ln \gamma^{COSMO-RS} + 0.2824 \left(\ln \gamma^{COSMO-RS} \right)^2 \qquad (1)$$

Figure 4 demonstrates that the correlated method [labeled "COSMO-RS (corr.)"], which combines COSMO-RS with limited experimental data, may be used to develop a better correlation than UNIFAC for a particular family of chemical species. This suggests that COSMO-RS is able to capture the effect of subtle chemical interactions on macroscopic properties like activity coefficients. Note also that UNIFAC cannot distinguish between isomers (e.g., 13BD and 12BD), while COSMO-RS correctly predicts the relative values.

Figure 6 shows predictions of the UNIFAC and COSMO-RS methods for the infinite-dilution activity coefficients of hydrocarbons at 40°C in ethanol. Both methods work poorly. It is not clear why ethanol systems pose such a great estimation challenge because the data trends appear reasonable (see Figure 3); this issue presents an opportunity for future researchers.

Figure 7 presents predictions of the UNIFAC and COSMO-RS methods for the infinite-dilution activity coefficients of hydrocarbons at 40°C in water. The COSMO-RS method provides a good prediction of the data. The errors are typically within a factor of two, and this is a good prediction especially because there may be considerable uncertainty in the experimental data (see Figure 3). UNIFAC clearly underestimates the hydrocarbon-water infinity-dilution activity coefficients. While the UNIFAC method may be numerically improved by extending the method to take second-order effects into account,[22,23] or a separate database may be developed for liquid-liquid systems,[24] we consider such extensions to be excessively correlated for the purpose of our study.

Background on Molecular Simulation

Molecular simulation offers the prospect of detailed quantitative insights at the molecular level, but it must be properly understood to appreciate what it can and cannot achieve. In the C_4 systems of this study, molecular simulation can provide quantitative results for the entropy of mixing, the energy of mixing, and the accessibility of all the interaction sites to polar-solvent solvation. Molecular simulation, however, cannot independently determine the intermolecular forces. The intermolecular forces must be inferred from experimental data or predicted from quantum mechanical calculations. Molecular simulation simply applies Newton's laws using the force field as an input. Once the forces have been inferred from experimental data for one set of mixtures, they can be applied to other compounds and mixtures through the principle of transferability. For example, transferability implies that the forces surrounding a central $-CH_2-$ site in n-pentane would be the same as the forces surrounding a central $-CH_2-$ site in n-pentadecane. Transferability and Newton's laws are the primary assumptions of molecular simulation, but the characterization of the transferable forces for all types of molecules comprises a large identification problem. In the discussion below, we demonstrate what can be achieved with molecular simulation and elaborate on the range of capabilities of molecular simulation and its relationship to quantum mechanics.

What Molecular Simulation Can Tell Us?

Analyzing the polar solvents for 13BD extraction systems naturally leads to hypotheses about the solvation interactions between the polar solvents and the olefinic moieties in the hydrocarbon compounds. One might readily observe that the presence of two olefin moieties in butadiene doubles the solvation, but perhaps there is more to consider. For example, the moieties on the diene appear at the end of the molecule but are in the middle of the 2-butenes. Molecular simulation can quantify these differences in accessibility. Figure 8 shows the pair distribution functions between polar solvent and olefin sites derived from purely repulsive (sterically hindered) simulations. The specific polar solvent site considered is the carbonyl oxygen in DMF and the nitrile nitrogen in ACN. The terminal and central olefin sites are averaged in the case of butadiene. Noting that solvation interactions are relatively short range, the primary point of interest is the region where the radial distance is near contact with the diameter of the site. Although there are small differences between polar solvents, the major difference is between 13BD and the 2-butenes. The terminal positions of the olefins in butadiene lead to a 50% enhancement of these sites relative to the 2-butenes. One might also speculate that the cis olefins would be more accessible, owing to the methyl sites being pinned back from the olefin sites. Figure 8 shows a very slight impact of this effect for DMF solvation, but it appears to be minor.

In principle, similar insights could be obtained experimentally by small-angle neutron scattering (SANS) or small-angle x-ray scattering (SAXS). In practice, however, one must note that all the sites in the fluid contribute to scattering, not just the sites of interest. This leads to a very noisy signal with scattering from both intramolecular and intermolecular distributions convoluted together. Isolating the intermolecular

interactions of interest would be subject to large variability. In contrast, analyzing the distributions from molecular simulation is straightforward, and the sizes and shapes that affect intermolecular contacts are reliably characterized.

Molecular simulation can lead to confirmation and debunking of other molecular speculations as well. One manner in which this appears is when interpolating between state points. In general, molecular simulations operate like experiments in the sense that a single temperature, pressure, and composition specify the simulation conditions. One alternative is to leverage the simulated fluctuations around the ensemble average to connect regions between state points.[25] The SPEADMD[26,27] model, on the other hand, applies classical engineering methods for this interpolation, with the benefits that the results can be immediately adapted to existing engineering tools and greater insight into the classical equations may be gained. For many years, researchers have speculated about the entropy and energy of mixing and their impacts on phase equilibria. These speculations have lead to models based on local composition theory and lattice models as well as van der Waals mixing-like regular solutions and Flory-Huggins theory. Molecular simulations permit detailed examination of the fundamental bases of these theories. For example, properly defined "local compositions" must be related to the pair distribution functions, and these are readily available as discussed above. Lattice models involve many artificial assumptions about coordination number, lattice size, and packing fraction whereas molecular simulation obviates all of these. Furthermore, simulations can be performed to analyze specific contributions to the free energy. We examine below the contributions to the free energy from the athermal entropy of mixing and the disperse attractions independently from the solvation interactions. Traditional models lump all of these influences together into one or two parameters, making it difficult to distinguish the chemical effects that would help to design superior polar solvents.

To illustrate this effect, consider Figure 9, which analyzes the excess thermodynamic properties arising from repulsive and attractive dispersion forces. Figure 9a shows that the athermal excess entropy of mixing is extremely small for the C_4 mixtures. In fact, it is so small that the signal to noise ratio is quite low, making the data appear to be scattered. This is consistent with observations by Gray et al.[28] that the excess entropy approaches zero as the molecular volume ratio approaches unity. The trend is much clearer in the case of the excess energy of mixing, but the conclusion is the same. Figure 9b shows that the same volume-ratio skewness to the curves is apparent in the first order energetic contribution. Note that Gray et al.[28] studied a broad range of molecular volume ratios from 1-10. The results of that work show that trends like those in Figure 10 can be easily interpolated using conventional engineering mixing rules.

The solvation interactions are relatively strong and short-range. There is an open question regarding whether these are best characterized by point charges representing the multipole moments of the molecule or by potentials like those considered by Wertheim,[29] which is essentially a chemical theory of mixing. Solvation interactions like those between DMF and 13BD would usually require a polarizable potential in the point charge approach, increasing CPU requirements roughly 10-fold. Similar issues arise in the treatment of hydrogen bonding mixtures. Coleman and Painter[30] have studied a large

number of mixtures with a wide range of molecular weights using both infrared (IR) spectroscopy and a theory that is equivalent to that of Wertheim. On the whole, they find general agreement with the chemical model. Furthermore, the chemical model is very efficient to apply.[31,32]

For these reasons, we favor Wertheim's model[29] at the present time. Wertheim's model characterizes complexation with so-called blister potentials. The complex interactions take the form of square-well attractions with small radii centered near the edge of the repulsive core. These short-range, but strong, attractions are asymmetric because prospective bonding sites must approach at the correct angle for a compatible blister to overlap. Otherwise, the attractive wells overlap with the repulsive core and no bond is formed. This kind of potential mimics the key features of complexation. Furthermore, extensive testing of Wertheim's theory with molecular simulation shows that the theory provides practically quantitative accuracy when properly adapted.[33,34] With Wertheim's theory to quantitatively describe complex formation and second-order perturbation theory to describe disperse attractions, the only part of the potential that requires detailed molecular simulation is the repulsive reference system. This greatly expedites the practical applicability of molecular simulation.

The present work treats the solvation interactions between the polar solvents and the C_4 compounds with one solvation site per "–CH= or =CH$_x$" segment. Figure 10 presents a comparison of vapor-liquid equilibrium (VLE) behavior for butadiene – polar-solvent systems with transferable characterization of the solvation interaction energy between the olefinic protons and the polar-solvent base sites. The characterization begins with the bonding volume and energy of DMF. Association energies of amides were characterized by Baskaya et al.,[35] so we assume the bonding volume and energy of DMF to be the same as that of primary amides, despite the observation that DMF possesses no donor sites. For simplicity acetonitrile is treated as a pure base, despite evidence of additional weak acidic character.[36] The bonding volume of ACN is assumed to be the same as that of DMF. The bonding energy of $CH_2=CH–$ is assumed to be small (0.5 kcal/mol). Estimating the solvation energy between dissimilar sites requires a guideline similar to a combining rule. The primary guideline corresponds to estimating the solvation energy as the average between the site-site energies, such that the solvation energy with DMF is (4.5+0.5)/2=2.5. There are few guidelines for olefin solvation since it is so unusual. Solvation is clearly indicated by the VLE, however. Positive values of solvation energy are required to characterize the VLE of both DMF and ACN with butadiene. At this point, we have described general guidelines for establishing all the key parameters except the bonding volume of the olefin donors. These were treated as adjustable parameters in characterizing the VLE for the 13BD+DMF system. The same characterization of butadiene was applied for ACN, but the solvation energy for 13BD+ACN was treated as an adjustable parameter. In both cases, the binary interaction parameter (k_{ij}) was assumed to be zero while optimizing the solvation energy.

Figure 10 shows that the optimal solvation model is reasonably accurate over most of the composition range. Solvation leads to relatively favorable interactions in the dilute regions. This flattens the bubble pressure curve toward that of an ideal solution. In dilute

regions, the bonding sites of the dilute component are nearly completely saturated owing to the overwhelming presence of the diluent. At intermediate compositions, both components are similarly saturated, leading to an apparent upward bulge in the *P-x* diagram. The inferred solvation energy for 13BD+ACN (1.75 kcal/mol) is slightly lower than that of 13BD+DMF (2.5 kcal/mol); note that these relative solvation energies are consistent with the results in Figure 2.

The effort to characterize the phase behavior of mixtures requires systematic adjustment of the molecular interaction energies to characterize the solvation behavior. Readers will note that refining the model potential in this way blurs the lines between straightforward molecular simulation of a known potential and engineering analysis of the observed phase behavior. This transition from demonstrating feasibility of the methodology to refining it for quantitative application is an important reason for involving engineers in further development of molecular simulation as a useful tool. The adaptation of perturbation theory is instructive in that refining the attractive interactions can be performed without need for re-simulation. Since the attractive interactions are perturbations, their impacts can be recomputed instantly.

Given an estimate of the solvation energy for an olefin with polar solvent, we can proceed to predict the activities of all the species. Table 5 and Table 6 show the comparison of estimated infinite dilution activity coefficients from the SPEADMD model to experimental data. The comparisons are also shown graphically in Figure 4 to Figure 7. Since 13BD was fit to the data, the SPEADMD errors in Figure 4 and Figure 5 are approximately zero. But the SPEADMD model does not capture the wide variation of infinite-dilution activity coefficients from saturated butane to vinyl acetylene. For ethanol and water as solvents, Figure 6 and Figure 7 indicate that the COSMO-RS and SPEADMD results are similar for ethanol-hydrocarbon and water-hydrocarbon systems.

Limitations of Molecular Simulation

Molecular simulation is not a panacea. On the surface, one might believe that there are no assumptions in molecular simulation beyond Newton's laws of motion. Unfortunately, a highly multidimensional assumption is also implicit in the assumed forces between the interaction sites. These forces arise from quantum mechanical distributions of electrons around nuclei in the presence of covalent bonds to neighboring atoms. They also arise from polarizable responses of the electron distributions resulting from interactions with neighboring colliding molecules. In principle, these forces can be computed from quantum mechanical simulations. In practice, however, current quantum mechanical simulations are accurate only to within ~3,000 cal/mol[37] in an absolute sense or 340 cal/mol for the relative difference as applied in COSMO-RS. Our experience with estimating vapor pressure has shown that deviations in vapor pressure can change from 5% error to 15% with a change in the disperse interaction of only 2 cal/mol. For example, a change in the well-depth of the outer well of the CH_2 site from 43.6 to 45.6 cal/mol causes a change in the %error in vapor pressure for n-pentane from 3.4% to 14.4% when applying a linear model of the disperse interactions. Note that the absolute value of 3,000 cal/mol and relative value of 340 cal/mol refers to complete molecules, not

to repeated sites. Therefore, we must conclude that quantum mechanical simulations may serve as semi-quantitative guidelines for trends in the forces, but they cannot serve as a reliable basis of predicting intermolecular forces entirely on their own. In many instances, quantum simulations may suggest charge distributions for characterizing the multipole moments,[38] but experimental data must ultimately be applied to characterize the total energy of interaction. The COSMO-RS approach makes the transition from qualitative trends to quantitative estimates by characterizing the 20-30 generalized parameters in the COSMO-RS model relative to experimental data. The generalized parameters bring the estimates within the general range of experimental results and the variations in the surface charge distributions are sufficient to provide the system specific accuracy observed in the COSMO-RS method. Molecular simulation incorporates experimental data by characterizing the transferable potentials. Clearly, one desirable approach would be to merge these two perspectives, applying transferability as broadly as possible, but refining the potentials when indicated by the quantum mechanics. This is a subject of current research.

Case et al.[39] provide an introduction to the role of intermolecular potentials in molecular simulation that should be useful to non-experts. They describe an industrial "challenge" for simulation experts to predict properties based on transferable potentials. They also discuss nuances that distinguish molecular simulation from other forms of molecular modeling. The cited references present a range of methodologies targeted at quantitative property prediction. The tradeoffs and limitations of the various methodologies are especially clear in this context.

Conclusions

This paper has studied various ways in which the liquid-phase nonideality of hydrocarbon-solvent systems associated with the extractive distillation of C_4 hydrocarbons may be established. Experimental data is the most reliable and best source of thermodynamic properties, and this paper demonstrates that simple expected patterns based upon thermodynamic intuition help evaluate the data accuracy and consistency, and even fill gaps in the data. Estimation methods like UNIFAC and COSMO-RS provide useful additional information and estimation capability. UNIFAC is widely applicable and often provides good accuracy because of many years of careful data evaluation and correlation development. UNIFAC is limited in its predictive capability because of its inability to distinguish between isomers and to predict proximity effects. COSMO-RS often does not provide the same level of accuracy as UNIFAC - especially for systems where the group interaction parameters of UNIFAC have been optimized - but can capture subtle effects (as shown for the hydrocarbon-DMF systems) and sometimes offers better predictive capability (e.g., hydrocarbon-water systems). Molecular simulations provide insights on the molecular scale (and this aspect has been examined extensively in this paper), but cannot yet compete with methods like UNIFAC and COSMO-RS for quantitative prediction of liquid nonideality.

Dedication

This paper is in honor of Professor John O'Connell, a special chemical engineer, thermodynamicist, educator, mentor and friend.

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Table 1 – Component List and Basic Properties

Component ID	Name	Formula	T_b (K)	MW	HC Feed (Weight%)
Propene	Propene	C_3H_6	225.4	42.08	0.005
Propane	Propane	C_3H_8	231.1	44.10	0.005
Propadiene	Propadiene	C_3H_4	238.7	40.06	0.001
Meth-Ac	Methyl-acetylene	C_3H_4	249.9	40.06	0.2
Isobutane	Isobutane	C_4H_{10}	261.4	58.12	1.5
Isobutene	Isobutene	C_4H_8	266.3	56.11	25.1
1-Butene	1-Butene	C_4H_8	266.9	56.11	9.6
13BD	1,3-Butadiene	C_4H_6	268.7	54.09	49.9
n-Butane	n-Butane	C_4H_{10}	272.7	58.12	3.4
t-Butene	trans-2-Butene	C_4H_8	274.0	56.11	5.5
c-Butene	cis-2-Butene	C_4H_8	276.9	56.11	3.1
Vinyl-Ac	Vinyl-acetylene	C_4H_4	278.3	52.08	1.2
1-Butyne	1-Butyne	C_4H_6	281.2	54.09	0.2
12BD	1,2-Butadiene	C_4H_6	284.0	54.09	0.3
Meth-butene	2-Methyl-1-Butene	C_5H_{10}	304.3	70.13	0.010
Ethanol	Ethanol	C_2H_6O	351.4	46.07	--
ACN	Acetonitrile	C_2H_3N	354.8	41.05	--
Water	Water	H_2O	373.2	18.02	--
DMF	DMF	C_3H_7NO	426.2	73.09	--

Table 2 – Infinite-Dilution Activity Coefficients of Hydrocarbons in DMF at 40°C

Compound	γ^∞ in DMF at 40°C	Data Reference	Class of Hydrocarbon
Vinyl-Ac	0.84	Braude et al.[40]	Olefin and triple bond
Meth-Ac	1.09	Braude et al.[40]	Triple bond
13BD	2.38	Wilding et al.[41]	Diolefin
12BD	2.80	Doering and Stoeck[42]	
c-Butene	4.51	Hradetzky, et al.[43]	Olefin
1-Butene	4.97	Wilding et al.[41]	
Isobutene	5.21	Hradetzky, et al.[43]	
t-Butene	6.46	Utzig[44]	
n-Butane	10.40	Gerrard[45]	Paraffin
Isobutane	13.50	Knipp[46]	

Table 3 – Infinite-Dilution Activity Coefficients of Hydrocarbons in ACN at 40°C

Compound	γ^∞ in ACN at 40°C	Data Reference	Class of Hydrocarbon
Vinyl-Ac	1.78	Owens et al.[47]	Olefin and triple bond
Meth-Ac	1.95	Zelentsova et al.[48]	Triple bond
1-Butyne	2.98	Owens et al.[47]	
13BD	3.73	Laird and Howat[49]	Diolefin
Propylene	4.64	Zelentsova, et al.[48]	Olefin
1-Butene	7.22	Jingzhou[50]	
c-Butene	7.44	Gorshkov, et al.[51]	
Isobutane	12.18	Zhang and Hayduk[52]	Paraffin
n-Butane	10.36	Warowny[53]	

Table 4 – Infinite-Dilution Activity Coefficients of Hydrocarbons in Ethanol and Water at 40°C

Compound	γ^∞ at 40°C		Data Reference	
	Ethanol	**Water**	**Ethanol**	**Water**
Vinyl-Ac		585		Aspen Plus[54]
Meth-Ac		121		Aspen Plus[54]
1-Butyne		587		McAuliffe[56]
13BD	4.43	1,517	Bushmakin and Kuchinskaya[55]	McAuliffe[56]
Propylene	6.85	1,146	Verazzi et al.[58]	McAuliffe[56]
1-Butene		5,065	Rojas et al.[57]	McAuliffe[56]
c-Butene	6.87	6,060	Verazzi et al.[58]	Aspen Plus[54]
t-Butene	7.14		Verazzi et al.[58]	
Isobutane	9.45	20,521	Zabaloy et al.[59]	Aspen Plus[54]
n-Butane	7.59	20,192	Dahlhoff et al.[60]	Wehe and McKetta[61]

Table 5 – Estimation of Infinity-Dilution Activity Coefficients of Hydrocarbons in DMF and ACN at 40°C by UNIFAC, COSMO-RS and SPEADMD Estimation Methods

Component ID	γ^∞ in DMF at 40°C			γ^∞ in ACN at 40°C		
	UNIFAC	**COSMO-RS**	**SPEADMD**	**UNIFAC**	**COSMO-RS**	**SPEADMD**
Vinyl-Ac	1.02	0.32	1.1	1.59	0.87	2.0
Meth-Ac	0.84	0.48	2.0	1.75	0.96	2.6
1-Butyne	1.17	0.53	2.4	2.47	1.43	3.1
13BD	3.56	1.02	2.0*	3.28	2.41	3.3
12BD	--	1.13	2.0	--	2.99	
Propylene	3.01	1.30	2.9	3.78	3.33	4.2
1-Butene	4.48	1.60	3.9	5.61	5.62	5.3
c-Butene	4.71	1.62	2.8	6.39	5.56	3.6
t-Butene	4.71	1.70	3.1	6.39	6.21	3.9
Isobutane	6.69	2.69	5.0	11.38	14.89	11.4
n-Butane	6.71	2.79	9.2	11.4	16.23	6.1

∗ *Used to train SPEADMD solvation parameter*

Table 6 – Estimation of Infinity-Dilution Activity Coefficients of Hydrocarbons in Ethanol and Water at 40°C by UNIFAC, COSMO-RS and SPEADMD Estimation Methods

Component ID	γ^∞ in Ethanol at 40°C			γ^∞ in Water at 40°C		
	UNIFAC	COSMO-RS	SPEADMD	UNIFAC	COSMO-RS	SPEADMD
Vinyl-Ac	5.76	2.20	3.5	45.7	680	750
Meth-Ac	3.08	2.29	3.0	13.6	187	194
1-Butyne	3.99	2.44	3.4	44.1	680	393
13BD	6.53	3.29	4.4	582	1,452	1,900
1-Butene	4.96	3.71	5.0	616	2,596	3,900
c-Butene	4.62	3.71	4.7	578	2,391	2,600
t-Butene	4.62	3.87	4.7	578	3,062	2,700
Isobutane	4.48	4.98	5.5	776	6,401	3,036
n-Butane	4.48	5.21	5.2	775	7,909	5,400

Feed Concentration vs. Boiling point
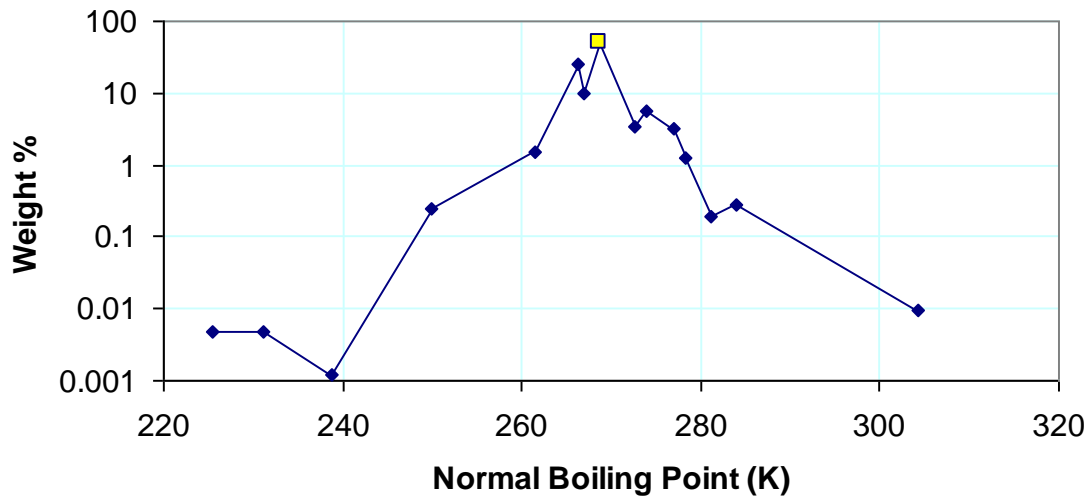
Figure 1 – Hydrocarbon Feed Concentration Versus Normal Boiling Point. The Data Point for 13BD is Highlighted.

**Relationship Between Hydrocarbon Activity
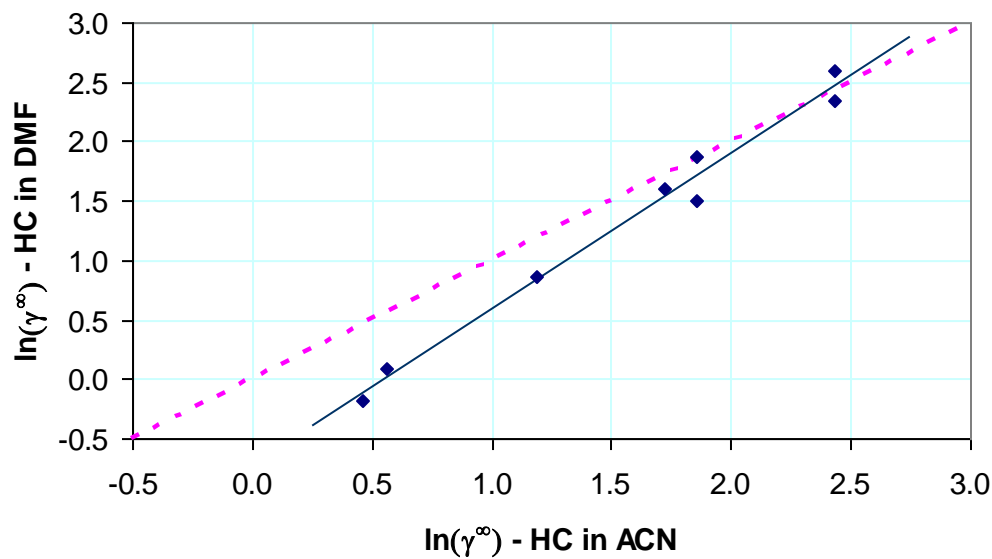Coefficients in ACN and DMF**

**Figure 2 – Relationship Between Hydrocarbon Activity Coefficients in DMF and
ACN at 40°C.   The Solid Line is the Best-fit Straight Line. The Dashed Line shows
"y=x."**

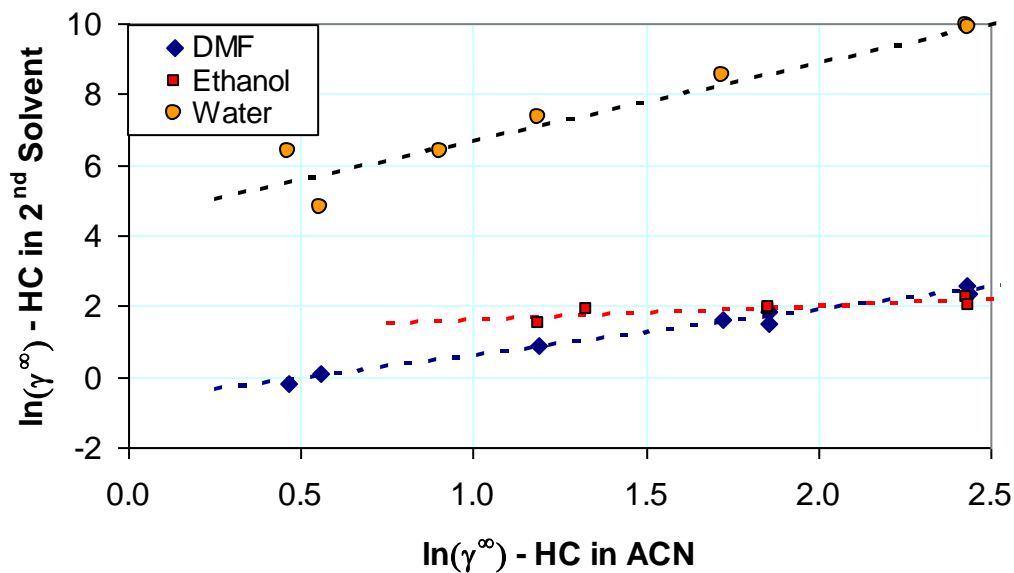## Relationship Between Hydrocarbon Activity Coefficients in (DMF, Ethanol, Water) and ACN

Figure 3 – Correlation Between Hydrocarbon Infinite-Dilution Activity Coefficients in DMF, Ethanol and Water and Those in ACN. All Activity Coefficients are at 40°C. The dashed Lines are Best-Fit Straight Lines.
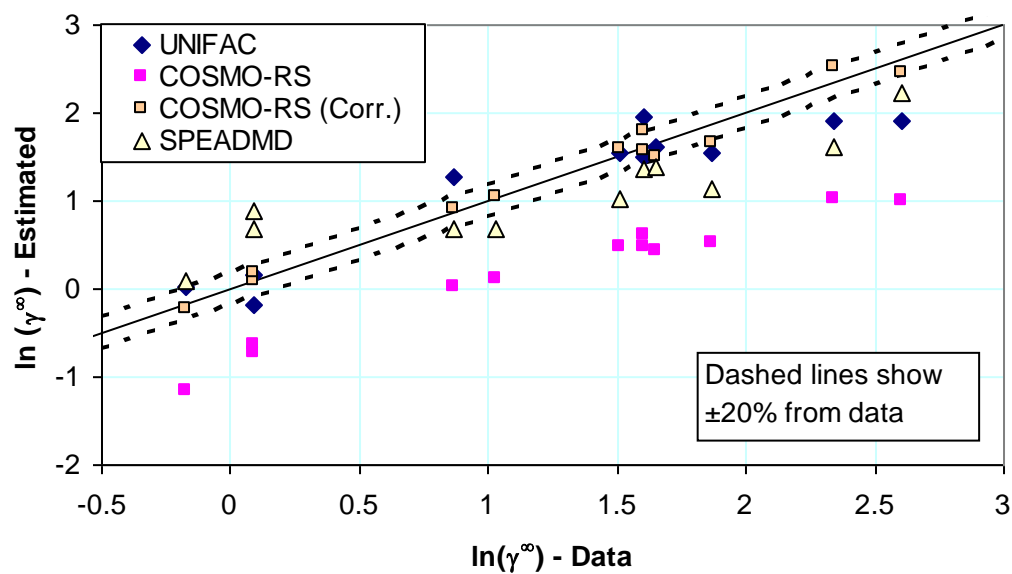
Figure 4 – Estimation of Infinite-Dilution Activity Coefficients of Hydrocarbons in DMF by UNIFAC, COSMO-RS Estimation and SPEADMD Methods.
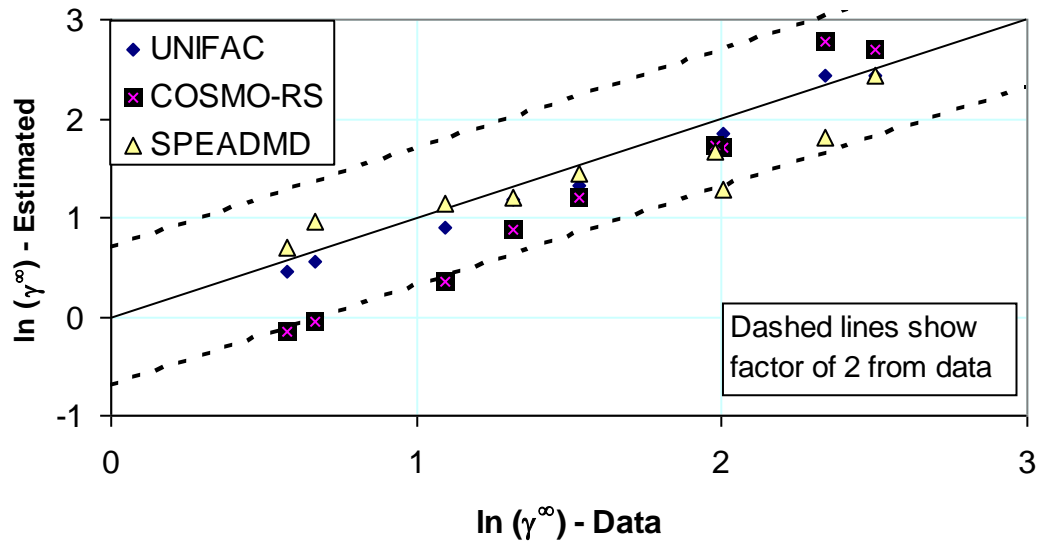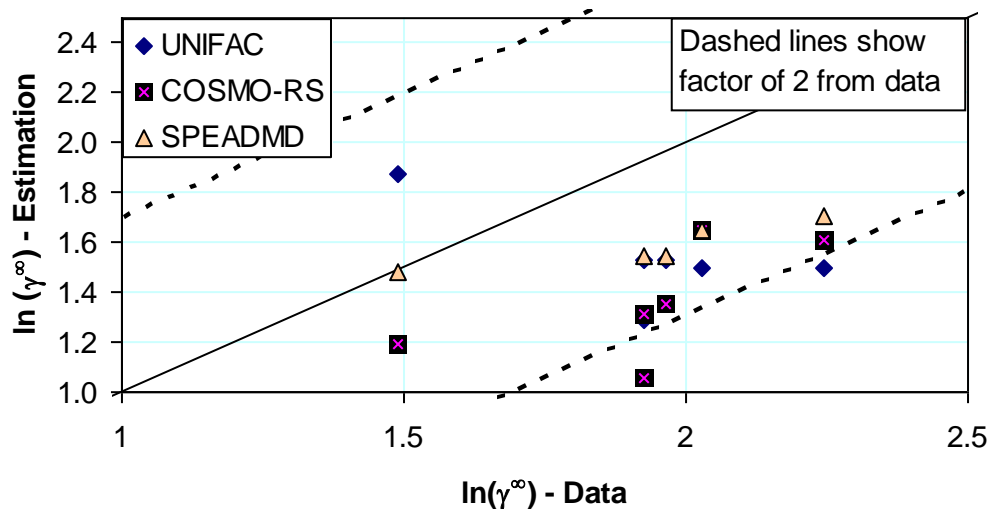
Figure 5 – Estimation of Infinite-Dilution Activity Coefficients of Hydrocarbons in ACN by UNIFAC, COSMO-RS and SPEADMD Estimation Methods.

Estimation of Infinite-Dilution Activity Coefficients of C_4 Hydrocarbons in Ethanol at 40°C

Figure 6 – Estimation of Infinite-Dilution Activity Coefficients of Hydrocarbons in Ethanol by UNIFAC, COSMO-RS and SPEADMD Estimation Methods.

Estimation of Infinite-Dilution Activity Coefficients of C$_4$ Hydrocarbons in Water at 40°C
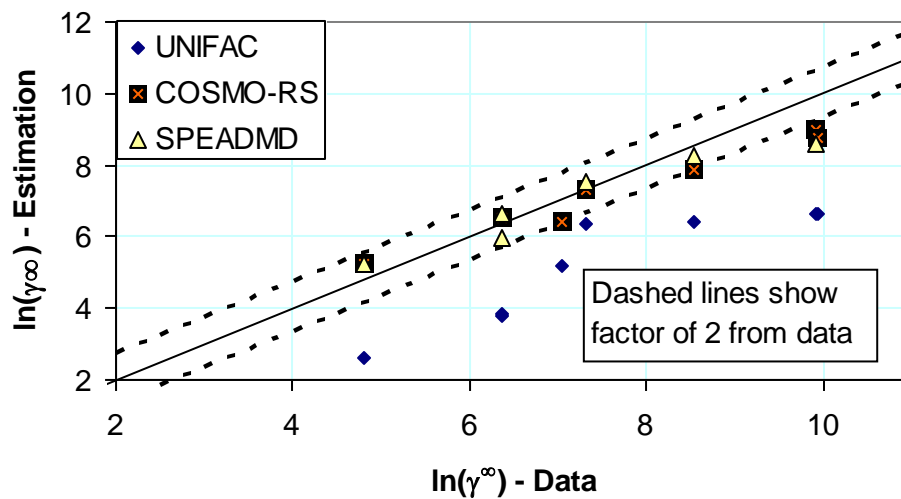

Figure 7 – Estimation of Infinite-Dilution Activity Coefficients of Hydrocarbons in Water by UNIFAC, COSMO-RS and SPEADMD Estimation Methods.
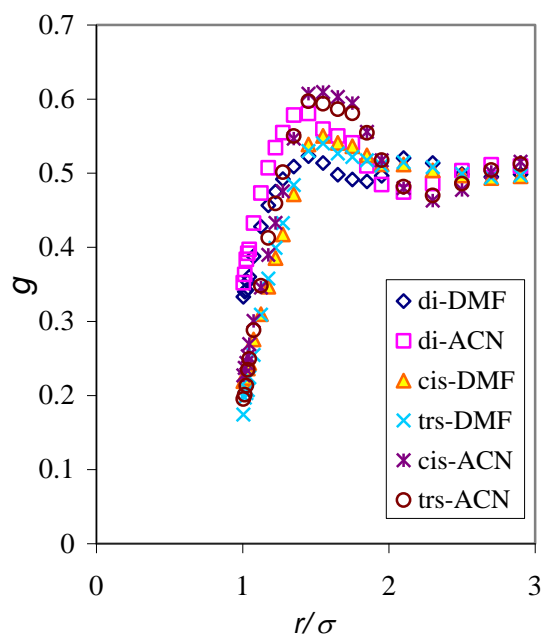
Figure 8 – Pair Distribution Functions Between Polar Solvent and Olefin sites. The Simulations were Performed at 0.41 Packing Fraction and Equivocal Composition for the Purely Repulsive Molecular Interaction Model.
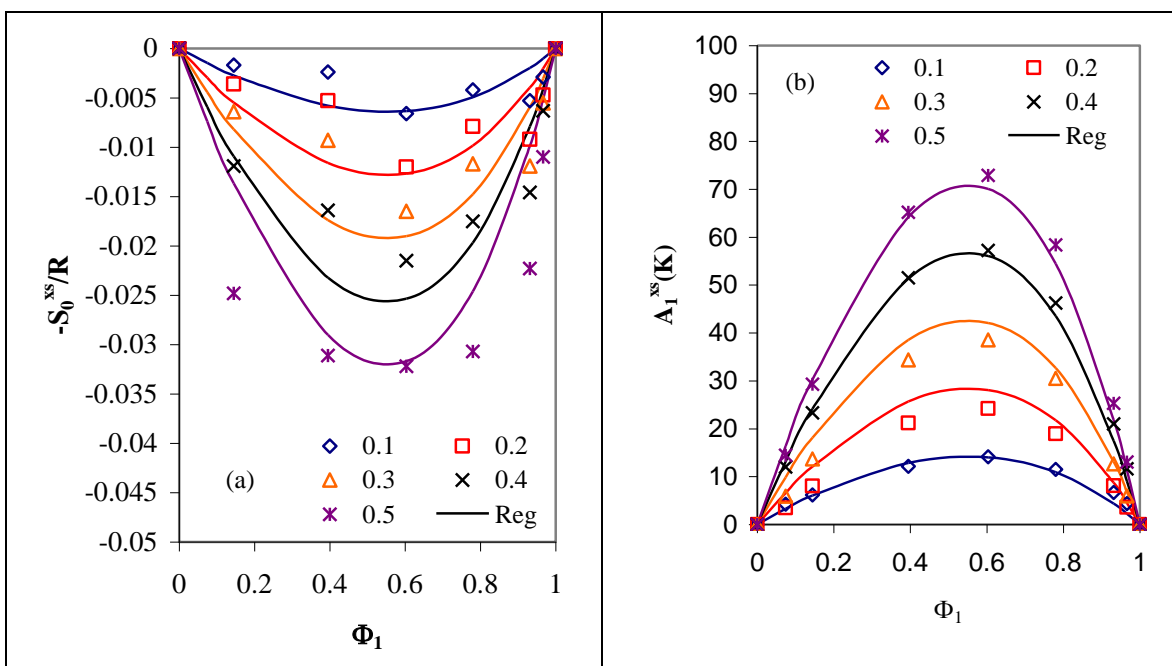
Figure 9 – Excess Entropy (a) and Energy of Mixing (b) of t-Butene+ACN from Molecular Simulations Neglecting the Solvation Interactions. The Packing Fractions are Indicated by the Numbers in the Legend.
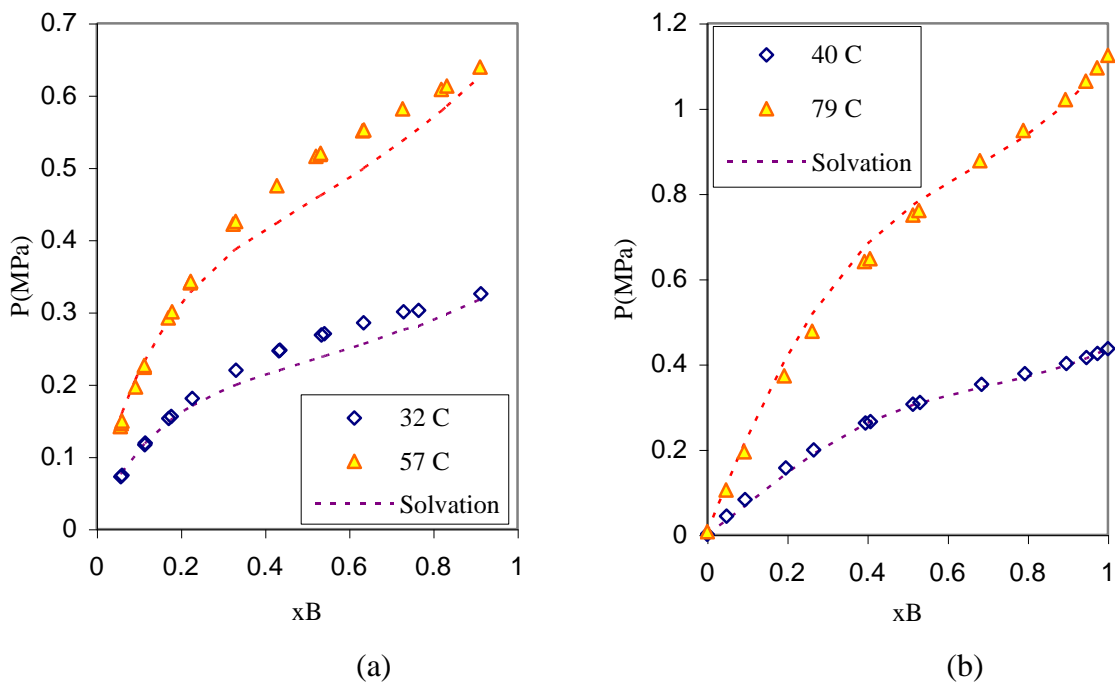
Figure 10. **The Role of Solvation Compared to Disperse Attractions (k_{ij}) in Characterizing Butadiene+Entrainer Interactions. (a) Butadiene+ACN, Symbols Experimental data.[49] (b) Butadiene+DMF, Symbols Sxperimental data.[41]**

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