ChE AIChE special section

A SIMPLE EXPLANATION OF COMPLEXATION

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It seems that the freshmen are onto me. As part of our freshman "Chemical Engineering Computations" course, the students can choose speakers for four half-lectures. Last Spring, they chose me to give a presentation about hydrogen bonding. Rumor has it that they heard about a fanatical thermodynamics professor with a soft spot for the topic of hydrogen bonding. Their strategy was two-fold: first, to butter this guy up by asking him to ramble on about his favorite subject, and second, to scout this dangerous territory called thermodynamics. In my turn, I saw this as a teachable moment. If I made the presentation sufficiently accessible, they might actually learn something about thermodynamics.

But what computational model can be accessible to freshmen in 25 minutes and explain hydrogen bonding and its role in chemical and biomolecular engineering? The key thermodynamic impact of hydrogen bonding is on the activity coefficient, a dimensionless expression of the fugacity. Fugacity is one of the most dreaded words in chemical engineering, even among seniors. Therefore the presentation must very gently focus first on introducing the activity coefficient, then on the role of hydrogen bonding. A little scouting of my own revealed that they were already performing flash computations. So they knew about $K_i = y_i/x_i$,* but the only solution model they knew was Raoult's Law ($K_i = P_i^{sat}/P$). This, then, was my way in. Most students are aware of the ethanol+water azeotrope and that oil and water do not mix. Moreover, they are all aware of the term "hydrogen bonding" from high school courses in biology. From these familiar points of reference, I formulated the following introduction, emphasizing qualitative concepts and interactive computational exercises to appeal to a broad range of learners at an early stage in their studies. The approach emphasizes computations, since that is the course's subject, but introduces the vocabulary of solution thermodynamics.

A 5-MINUTE INTRODUCTION FOR FRESHMEN TO THE LIMITATIONS OF RAOULT'S LAW

According to Raoult's law, the vapor mole fraction of ethanol in water is greater than the liquid at all compositions. Then distillation to gasohol should be no problem because it is constantly enriching. But experiments show that $y_E < x_E$ when

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* *Commonly used symbols are defined in the Nomenclature section.*

$x_E > 0.9$. Furthermore, Raoult's Law cannot explain liquid phase separation, yet nobody would put a 10% water solution into their gas tank. Hydrogen bonding helps to explain these "non-idealities" and many more.

The reason for the azeotrope in the ethanol+water system is that the water does not entirely "like" the ethanol. We can characterize this disdain with "modified Raoult's Law" ($K_i = \gamma_i P_i^{sat}/P$), where γ_i is called the "activity coefficient." If a little ethanol mixes with the water, the vast majority of water molecules are surrounded by other water molecules so they barely know the difference. In that case, Raoult's law provides an adequate description for the water molecules. Mathematically, this is represented by $\gamma_W \approx 1$. But when water is surrounded by 90% ethanol, it can get very uncomfortable. We can relate to this kind of discomfort when we are in an unfamiliar crowd. Measurements show that $\gamma_W \approx 2$ at 90% ethanol. From the perspective of ethanol at 90% concentration, however, Raoult's Law is fine and $K_E = P_E^{sat}/P$. Furthermore, at 78 °C $P_E^{sat} = 1$ bar, so $K_E \approx 1$ at ambient pressure. But $P_W^{sat} \approx 0.55$ at 78 °C, so $K_W = \gamma_W P_W^{sat}/P \approx 1.1$. This means that the water becomes richer in the vapor than the ethanol, and distillation fails. This causes the separation to make gasohol to be less direct and more expensive both in terms of dollars and in terms of energy efficiency. The students nod when I say this, but five minutes have already elapsed.

DEVELOPING A COMPUTATION-BASED INTRODUCTION TO HYDROGEN BONDING

In the remaining 20 minutes, I introduce a simplified version of the "Modified Separation of Cohesive Energy Density" (MOSCED) model[1] and apply it in an example. The MOSCED model is a modification of Scatchard-Hildebrand theory that separates the cohesive energy density into a dispersion term, a polarity term, and two hydrogen bonding terms (one for acidity and one for basicity).[1] Characterizing acidity and basicity is the key to explaining hydrogen bonding. Although less known than models like van Laar or Margules, MOSCED is better suited to an intuitive explanation of hydrogen bonding, as detailed in the "rationale" section below. Keep in mind that this presentation is for a course in "Chemical Engineering Computations," so the students should not be surprised to see a few equations. Then I assign three homework problems. I refer to this model as the "simplified separation of cohesive energy density" (SSCED) model. The simplifications of SSCED are designed to convey key concepts in a manner that is consistent with presentations throughout thermodynamics and separations processes. Quantitative precision is not necessary for this qualitative introduction, but a computational model means that the students can "learn by doing." In other words, the concepts, symbols, and vocabulary become familiar as they practice their chemical engineering computations. Even qualitatively, the interpretation of a term like the binary interaction parameter of Scatchard-Hildebrand theory (k_{ij}) is fundamental and intellectually challenging to students. Learning its meaning and use at such an early stage would be worthwhile.

ORGANIZATION OF THE MANUSCRIPT

With this background, the remainder of the manuscript can be outlined. The section immediately after this one resumes the presentation to students, closely following the notes for the freshman lecture. The objective is that students should understand hydrogen bonding sufficiently to anticipate the sign of deviations from ideality and have some idea of its magnitude. Students are incidentally exposed to the relevance of hydrogen bonding in formulations, biofuels, distillation, liquid phase separation, environmental science, and "political intrigue." The interpretation that $k_{ij} < 0$ indicates favorable mixing can be illustrated graphically with the square-well potential, and reinforced with ConcepTesting[2] as demonstrated in the assessment section below. Assessments also show that students can quickly rank order solutions according to their non-ideality as an outcome of this presentation. As shown in the rationale section, the SSCED model reinforces the interpretation of k_{ij} and links it to the acidity and basicity

TABLE 1

Sample values of physical properties. δ, δ', α, and β all in (J/cm³)½

	T_c(K)	P_c(MPa)	ω	MW	ϱ_{298}	δ(J/cm³)$^{1/2}$	α	β	δ'
Acetone	508.2	4.70	0.306	58	0.79	19.64	0.00	11.14	19.64
Benzene	562.2	4.90	0.211	78	0.87	18.73	0.63	4†	18.60
Chloroform	536.4	5.40	0.216	119.2	1.48	18.92	5.80	0.12	18.88
Ethanol	516.4	6.38	0.637	46	0.79	26.13	12.58	13.29	18.67
Iso-octane	544.0	2.57	0.303	114	0.70	14.11	0	0	14.11
Methanol	512.6	8.10	0.566	32	0.79	29.59	17.43	14.49	19.25
MTBE	497.1	3.43	0.266	88	0.74	15.17	0	7.40	15.17
Water	647.3	22.12	0.344	18	1.00	47.86	50.13	15.06	27.94
p-xylene	616.3	3.51	0.326	106	0.86	17.90	0.27	1.87	17.87

† This value was modified slightly from the value of Lazzaroni, *et al.* (2.24)

that give rise to hydrogen bonding, while the Scatchard-Hildebrand model does not. Finer points about the advantages and limitations of the SSCED model are also addressed in the rationale section. Several of these finer points are intended for enthusiasts of thermodynamics and hydrogen bonding. I conclude with a brief review of the assessments of student learning and a perspective on how students may benefit from presentation of such a model at an early stage in the curriculum. Altogether, the presentation illustrates the current status of student preparedness, learning objectives, interactive learning, and assessment in thermodynamics at the 100th anniversary of AIChE.

RESUMING THE FRESHMEN PRESENTATION WITH A SIMPLE COMPUTATIONAL MODEL THAT ACCOUNTS FOR HYDROGEN BONDING

Resuming from the first five minutes of the lecture, the technical name for the factor, γ_i, is the "activity coefficient." When $\gamma_i = 1$ the situation of the i^{th} component is "ideal." When $\gamma_i < 1$, the i^{th} component is unusually comfortable. Such a formulation would make a great solvent if you had a nasty stain to remove. When $\gamma_i > 1$, the component is uncomfortable, like the water in 90% ethanol. Finally, when $\gamma_i > 10$, the component "hates" its environment so much that it may separate, like the water in gasoline. A very simple computational model can describe all of these situations and help to design formulations to achieve chemical engineering goals. It is,

$$RT\ln\gamma_1 = V_1\left(1-\Phi_1\right)^2\left[\left(\delta_2' - \delta_1'\right)^2 + 2k_{12}\delta_1'\delta_2'\right] \qquad (1)$$

Where R = 8.314 J/mole-K, T is the temperature in Kelvins, $V_i = MW_i/\rho_i^L$ is the liquid molar volume at 298K and $\Phi_i = x_iV_i/\Sigma x_jV_j$ is the volume fraction, analogous to weight fraction. The bracketed terms require some explanation. The term k_{12} is a correction factor that characterizes specific interactions, principally hydrogen bonding. We discuss k_{12} later. The other term addresses the modified solubility parameter, δ'. If we assume for the moment that $k_{12} = 0$, then $\Delta\delta'$ provides a concise and quantitative measure of γ_i. If $\Delta\delta' = 0$, then the solution is ideal and Raoult's Law is fine. Otherwise, the solution becomes non-ideal.

The solubility parameter is related to the energy density of a compound. This energy can be quantified by the heat of boiling. When you boil water, for example, molecules are extracted from their congenial environment to a lonely vapor, where they can share little energy with others. They prefer to share energy. That is why you must add heat. More heat must be added if they share more energy. If the same boiling pot is used to characterize various compounds, then more small molecules fit in it than large ones, and even more heat is required. Therefore, it is the energy density that characterizes how strongly a compound sticks to itself. This kind of energy density is something quite different from the explosive energy density of a compound like trinitrotoluene (TNT), so we need a distinctive name for it. That name is the "cohesive energy density," defined by,

$$\delta^2 = \left(U^{vap}/V\right) = J/cm^3 \qquad (2)$$

where U^{vap} is the energy of vaporization and the rationale for squaring δ is explained in the thermodynamics course. In the absence of hydrogen bonding, $\delta = \delta'$. Therefore, in terms of δ', discomfort of a component in solution is not caused by dislike for the other components, but by a strong preference for its own company. You may have heard that an extroverted engineer is one who looks at *your* feet when he is talking to you. Any introverted engineers in the room should relate to this perspective on the definition of discomfort.

In the presence of hydrogen bonding, the hydrogen bonding contribution must be separated from δ, hence the name for this model as the SSCED model (simplified separation of cohesive energy density model, pronounced "sked," like sled). This separation is given by

$$\delta^2 = \left(\delta'\right)^2 + 2\,\alpha\beta \qquad (3)$$

Where α characterizes the compound's acidity and β characterizes the basicity. The acidity and basicity can be measured spectroscopically by probing how strongly compounds interact with a standard reference base and a standard acid. Sample values of δ', α, and β are given in Table 1. The α and β contributions distinctly characterize the hydrogen bonding contributions. Counting them separately means that δ' is smaller than δ, making the estimated γ's closer to 1 when $k_{12}=0$. Acidity and basicity characterize favorable interactions when acids and bases combine ($k_{12}<0$) and unfavorable interactions when acids and bases cannot combine ($k_{12}>0$). This is the essential effect of hydrogen bonding. Note that water stands out in Table 1 as a compound with remarkably high energy density, both in terms of δ' and in terms of $\alpha\beta$. The water molecule is very small, essentially the size of a single oxygen atom, but it has a large dipole moment (reflected in δ') and strong hydrogen bonding (reflected in $\alpha\beta$).

We now return to the quantity k_{12}. If $k_{12} = 0$, then $\gamma_i \geq 1$, always, but there are situations when $\gamma_i < 1$. When mixing acids like HCl with water, for example, the compounds "like each other" so much that you need to be careful. A more moderate example is given by mixing acetone with chloroform, in which case mixture boiling experiments show that $\gamma_i < 1$. The proton of the chloroform is made mildly acidic by the electronegative chlorine atoms pulling on its electrons. The high density of electrons on the carbonyl oxygen of acetone makes it mildly basic. Organic chemistry courses should reinforce these concepts of electron distributions. These considerations are represented by the guideline that

$$k_{12} \approx \left(\alpha_2 - \alpha_1\right)\left(\beta_2 - \beta_1\right)/\left(4\delta_1'\delta_2'\right) \qquad (4)$$

For the chloroform+acetone example, this formula gives

$$k_{12} = (5.8 - 0)(0.12 - 11.14)/(4 * 19.64 * 18.88) = -0.035 \qquad (5)$$

Note how the order of subtraction results in a negative value for k_{12} when one of the components is acidic and the other is basic. If you switched the subscript assignments, then $\Delta\alpha$ would be negative and $\Delta\beta$ would be positive, but k_{12} would still be negative. This negative value makes the value of γ_i smaller, and that is basically what happens when hydrogen bonding is favorable.

Something else happens when one compound forms hydrogen bonds but the other is inert. Taking iso-octane(1) as representative of gasoline and mixing it with water(2),

$$k_{12} = (0 - 50.13)(0 - 15.06)/(4 * 27.94 * 14.11) = 0.479 \qquad (6)$$

This large positive value will add to the large $(\Delta\delta')^2$ such that $\gamma_1 >> 10$, indicating the liquid phase split that we anticipated. We can quantify the phase split by noting that

$$x_i \approx 1/\gamma_i \text{ when } \gamma_i > 100 \qquad (7)$$

Knowing the saturation limit of water contaminants can be useful in environmental applications.

As a final example, note that we recover an ideal solution when both components hydrogen bond, as in the case of methanol+ethanol.

$$k_{12} = (17.43 - 12.58)(14.49 - 13.29)/(4 * 19.25 * 18.67) = 0.003 \qquad (8)$$

In this case, we see that hydrogen bonding itself is not the cause of solution non-ideality. A mismatch of hydrogen bonding is required to cause non-ideality.

We can summarize our observations about hydrogen bonding as follows.

1) *Ignoring hydrogen bonding entirely* (i.e., *assuming* $\alpha=\beta=0$ *for all compounds) would lead to larger estimates of solution non-ideality in all cases* ($\delta' = \delta$ *then).*
2) *Ignoring hydrogen bonding would also undermine our ability to anticipate favorable interactions through Eq. (4), as in the acetone+chloroform system.*
3) *Hydrogen bonding solutions can also be ideal solutions if both components have similar acidity and basicity, as in the methanol+ethanol example.*
4) *Hydrogen bonding leads to very unfavorable interactions when one component associates strongly and the other is inert, as in the iso-octane+water example. This is known as the hydrophobic effect.*

Applications of these insights abound in chemical engineering. For example, what third compound could you add to ethanol+water to make the solution more ideal so that pure ethanol could be obtained? The extension of the SSCED model to multicomponent systems is simple, as discussed in the thermodynamics course. How soluble is vitamin C in the bloodstream relative to its solubility in body fat? What about vitamin E? Aspirin? Tylenol? You just need to know the activity coefficients of these compounds in water and n-octanol (a reasonable approximation of body fat). What solvent should you use to safely remove an undesirable embellishment from a classical painting? The embellishment probably used a different paint, so you need to find a solvent with $\gamma_i < 1$ in the embellished paint but $\gamma_i > 1$ in the classical paint. Quantitative understanding of fields from art restoration to zoology to agribusiness would be impossible without unifying concepts like hydrogen bonding. Students should retain these concepts and reinforce them as they take complementary courses throughout their curriculum.

The following example and homework assignments illustrate a range of behaviors that can be explained with the SSCED model. These behaviors include favorable interactions as in acetone+chloroform as well as unfavorable interactions as in isooctane+water. Illustrating the entire range of behaviors at the outset is intended to avoid misconceptions such as thinking that the activity coefficient is always greater than 1. To emphasize the qualitative nature of this model and the high value of experimental data, the final homework illustrates how the preliminary guideline can be refined using experimental data.

In terms of δ′, discomfort of a component in solution is not caused by dislike for the other components, but by a strong preference for its own company. You may have heard that an extroverted engineer is one who looks at* your *feet when he is talking to you. Any introverted engineers in the room should relate to this perspective on the definition of discomfort.

Example 1.

Estimate the K-value for 10mol%chloroform in 90% acetone at 350K and 0.1MPa. You may assume that $\log 10(P^{sat}/P_c)=7(1+\omega)(1-T_c/T)/3$.

Solution:

The value of $k_{12} = -0.035$ is given by Eq. (5). $V_C = 119.2/1.48 = 80.5$ and $V_A = 58/0.79 = 73.4$.

The volume fraction is: $\Phi_C = 0.1*80.5/(0.1*80.5+0.9*73.4) = 0.109$

$\gamma_C = \exp\{ 80.5*(1-0.109)^2*((19.64-18.88)^2 - 2*0.035*18.88*19.64)/(8.314*350) \} = 0.573$.

$P_C^{sat} = 5.40*10\text{^}(7*1.216*(1-536.4/350)/3) = 0.166$ MPa.

$K_C = \gamma_C *P_C^{sat}/P = 0.573*0.166/0.1 = 0.951$

Homework 1.

Gasohol is made by distilling a solution known as beer (~5mol% ethanol). Compute the K-values of ethanol and water at 5mol% ethanol and 358.5K and compare them to the K-values at 95mol%ethanol and 350.6K. Assume that P = 0.1MPa. Explain the impact of activity coefficient on your results. You may assume that $\log_{10}(P^{sat}/P_c)=7(1+\omega)(1-T_c/T)/3$.

Solution:

$k_{12} = (12.58-50.13)(13.29-15.06)/(4*18.67*27.94) = 0.032$

At 358.5K and 5% ethanol, $P_E^{sat} = 0.1327$ and $P_W^{sat} = 0.0658$ MPa according to the assumed vapor pressure equation. The water is nearly pure and computation confirms that

$\gamma_W = 1.016$.

Details for ethanol:

$\Phi_E = 0.05*58.5/(0.05*58.5+0.95*18) = 0.146$.

$\gamma_E = \exp\{ 58.5*(1-0.146)^2 ((18.67-27.94)^2 + 2*0.032*18.67*27.94)/(8.314*358.5) \} = 5.517$.

This gives $K_E = 7.319$ and $K_W = 0.669$.

At 350.6K and 95% ethanol, $P_E^{sat} = 0.0997$ and $P_W^{sat} = 0.0491$ MPa according to the assumed vapor pressure equation. The ethanol is nearly pure and computation confirms that $\gamma_E = 1.001$.

For water,

$\gamma_W = \exp\{18*((18.67-27.94)^2 + 2*0.032*18.67*27.94) /(8.314*350.6) \} = 2.046$

This gives $K_E = 0.998$ and $K_W = 1.002$.

Overall, the activity coefficient makes distillation easier at low concentrations of ethanol, but the large activity coefficient switches to the water at high ethanol concentrations and makes water slightly more volatile than ethanol. This is why distillation fails to completely purify this system.

Homework 2.

The American experience with methyl tert-butyl ether (MTBE) in the '90s approaches qualification as a fiasco. Rumor has it that congressmen from corn states thought that a mandate for 10% "oxygenated fuel" would boost demand for ethanol, but they did not specify ethanol as the oxygenated fuel of choice. Within four years MTBE was the number one synthetic chemical produced in the world. What nobody anticipated was how MTBE might affect groundwater. It imparts a bitter taste and nasty smell even at parts per billion. Gasoline is stored in underground tanks, and the tanks leak. Estimate the solubility of MTBE in water at 298K and compare it to that of iso-octane and benzene.

Solution: For iso-octane, Eq. (6) gives $k_{12} = 0.479$.

$x_O=1/\gamma_O = 1/\exp\{ 114/0.70*((14.11-27.94)^2 + 2*0.479*14.11*27.94)/(8.314*298) \} = 5.8E-17$

For benzene, $k_{12} = (0.63-50.13)(4 -15.06)/(4*27.94*18.6) = 0.263$

$x_B=1/\exp\{ 78/0.87*((18.6-27.94)^2 + 2*0.263*18.6*27.94) /(8.314*298) \} = 2.2E-6$

For MTBE, $k_{12} = (0-50.13)(7.4 -15.06)/(4*27.94*15.17) = 0.226$

$x_M =1/\exp\{88/0.74*((15.17-27.94)^2 + 2*0.226*15.17*27.94) /(8.314*298) \} = 4.0E-8$

So the solubility of MTBE is much higher than that of iso-octane. This estimate would need to be checked with experimental data, but the essential observation is that the basicity of the ether suggests checking it out. Benzene is interesting because its estimated solubility is similar to that of MTBE. Benzene does not taste or smell like MTBE, but it is carcinogenic. Nevertheless, nobody seems to be talking about the solubility of benzene in groundwater…at the moment.

Homework 3.

No theory should be mistaken as a substitute for experimental data, especially not such a simple theory as the SSCED model, and especially on a subject as sensitive as groundwater. Experimental measurements show that the mole fractions of iso-octane, benzene, and MTBE in water at 25 °C are actually closer to 4E-7, 5E-4, and 1E-2, respectively. Use these measurements to refine your estimates of k_{12} and predict the solubility of benzene in water at 38 °C. [Hint: typing Eq. (1) into a spreadsheet would make it easy to try various values of k_{12}.]

Solution: Iterating on k_{12} results in the following table.

Compound	**k_{12} (predicted)**	**k_{12} (fit)**
Iso-octane	0.479	0.04
Benzene	0.263	0.12
MTBE	0.226	-0.08

At 38 °C, $x_B=1/\exp\{ 78/0.87*((18.6-27.94)^2 + 2*0.12*18.6*27.94)/(8.314*311) \} = 0.00066$. These results illustrate limitations in the SSCED model for predicting water solubility, especially for hydrocarbons. The SSCED model predicts a liquid phase split and small solubility, but cannot estimate aqueous solubility precisely. It turns out that understanding the thermodynamics of water is very challenging, even for theories that are much more sophisticated than the SSCED model. In fact, the MOSCED model itself applies an empirical value of 36 (compared to 18) for the molar volume of water at 25 °C.[1] Empirical fitting in the SSCED model is constrained to adjusting k_{12}, however. The prediction at 38 °C suggests that the solubility of benzene increases by 70% when the temperature approaches body temperature. What does this suggest as a possible next step in worrying about benzene solubility? (Hint: reread the first sentence of this problem statement.)

RATIONALE

The SSCED model provides a simplified and generalized introduction to the MOSCED model, but the MOSCED model is designed for other purposes. Specifically, it is designed for infinite dilution activity coefficients instead of being a solution model at all concentrations. The MOSCED model is given by,

$$\ln \gamma_2^{\infty} = \frac{V_2}{RT}\left[(\lambda_2 - \lambda 1)^2 + \frac{q_1^2 q_2^2 (\tau_2 - \tau_1)^2}{\psi_1} + \frac{(\alpha_2 - \alpha_1)(\beta_2 - \beta_1)}{\xi_1}\right] + aa\ln\left(\frac{V_2}{V_1}\right) + 1 - \left(\frac{V_2}{V_1}\right)^{aa} \qquad (9)$$

Where λ_i is the dispersion factor, τ_i is the polarity factor, q_i is a factor ranging from 0.9 to 1. aa, ψ_i, and ξ_i are adjustable parameters characterizing solvent properties. At infinite dilution, they are specific values, but they must depend on composition to change from one solvent to the next. That composition dependence is not addressed by the MOSCED model, but it poses no problem for experts in thermodynamics. Parameters of an activity model like UNIQUAC could be determined from the infinite dilution activity coefficients and activity coefficients at all compositions computed from UNIQUAC. But activity models like UNIQUAC tend to be covered after models like MOSCED. The MOSCED model is based primarily on van der Waals mixing. The terms involving $(\Delta\lambda)^2$ and (V_2/V_1) comprise the Scatchard-Hildebrand and Flory-Huggins contributions derived from the van der Waals equation when constant packing fraction is assumed.[3] The other contributions are based on phenomenological arguments. The UNIQUAC model is based on the concept of local compositions. Developing the nuances of fitting parameters to one activity model then interpolating the free energy based on an entirely different activity model could overwhelm the attention span of sophomores as well as freshmen. Another alternative would be to articulate composition dependencies for all the parameters. This would detract from a simple explanation. On the other hand, eliminating the polarity factor (*i.e.*, $\psi = \infty$),

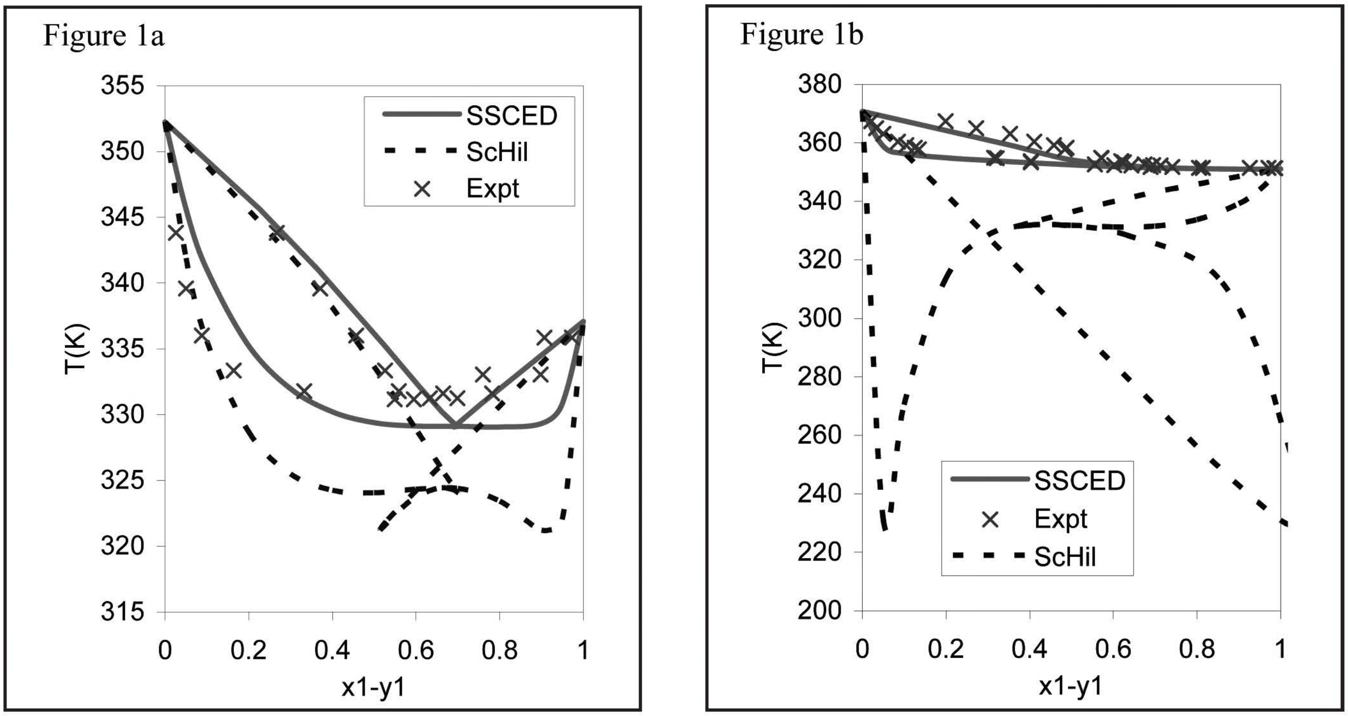

Figure 1. *Comparison of SSCED model to the conventional Scatchard-Hildebrand model. (a) methanol+benzene at 0.101MPa, data ref.8 SSCED: k12=0.123; ScHil: k12=0. (b) Ethanol+water at 0.101MPa, data ref.9; SSCED: k12=0.032; ScHil: k12=0.*

setting aa = 0, and $\xi = 2$ for all compositions makes the model much simpler and more broadly applicable while retaining the separation that enables consideration of hydrogen bonding influences.

The SSCED model was derived from the MOSCED model by minimizing deviations in a somewhat crude manner. The factor of 2 multiplying $\alpha\beta$ in Eq. (1) was determined by minimizing the differences between the physical contributions of the two models. Analyzing the physical contributions showed that $\delta^2 \approx (\lambda^2 + \tau^2/2)$ for non-associating compounds. Note that $\delta = \delta'$ in the absence of association. For associating compounds, Eq. (1) was rewritten as

$$\delta^2 = (\delta')^2 + m\alpha\beta \qquad (10)$$

where m was an adjustable parameter. Minimizing the objective function $\Sigma\{(\delta')^2 - (\lambda^2 + \tau^2/2)\}^2$ for 30 compounds in the database of Lazzaroni, *et al.*,[1] where δ' was computed from Eq. (10), yielded an optimal value of $m \approx 2.2$. The factor of 4 in the denominator of Eq. (4) was determined by minimizing deviations in vapor-liquid equilibrium (VLE) data for the 10 binary systems of the first five compounds in Table 1, and three VLE systems involving water with special emphasis on ethanol+water. These particular mixtures were chosen to illustrate the range of possibilities from strong solvation to hydrophobicity. The values of α and β in Table 1 were taken directly from the compilation of Lazzaroni, *et al.* Coincidentally, this manner of separation retains the consistent interpretation of cohesive energy density as a primary consideration (*e.g.*, $\delta_W' > \delta_B' > \delta_O'$, where W means water, B means benzene, and O means iso-octane). This consistency is not immediately apparent in MOSCED's λ parameters.

Other simple alternatives include the Hansen solubility parameters[4, 5] and the original Scatchard-Hildebrand model.[5, 6] The problem with the Scatchard-Hildebrand model is that it overestimates the non-ideality of the solution. For example, matching the experimental data for methanol+benzene requires a negative value of $k_{12} = -0.035$ when the Scatchard-Hildebrand model is applied. Students then conclude that methanol and benzene must "like" each other, because that is what $k_{12} < 0$ should mean. But in this case, the negative k_{12} is cancelling the overestimation of the non-ideality from the "unseparated" cohesive energy density. Figure 1a compares the Scatchard-Hildebrand model (with $k_{12} = 0$) to the SSCED model ($k_{12} = 0.123$). The positive value $k_{12} = 0.123$ from Eq. (4) conveys that the primary role of benzene is to disrupt methanol's hydrogen-bonding network, which is the correct interpretation. A similar problem occurs with water and nearly any other compound. Even ethanol+water is predicted to be immiscible with the Scatchard-Hildebrand model, as illustrated in Figure 1b, and a large negative value of k_{12} would be required to obtain reasonable agreement with experiment. This kind of "two steps forward and one step backward" makes the presentation unnecessarily confusing. The Hansen solubility parameters, on the other hand, have the advantage of being simpler than SSCED in some sense, because there is a single hydrogen bonding parameter instead of two. Nevertheless, Hansen's method cannot account for activity coefficients less than one. This undermines the scope of conceptual reasoning that should form the long-term basis for students' thermodynamic insight. In deference to Hansen's method, however, the separate contributions to the solubility parameter are constrained to sum to the original Scatchard-Hildebrand value. This adaptation from Hansen's method is helpful in clarifying that SSCED provides separation, but no elimination.

An advantage of the MOSCED model is its direct accounting of the specific molecular interactions involved in hydrogen bonding. This accounting is based on spectroscopic measurements that are independent of the desired activity coefficients.[7] Kamlet-Taft parameters are dimensionless measures of acidity and basicity, but the MOSCED model recasts their values to provide dimensional consistency with solubility parameters. This may open the door to more creative ways for students to mesh analytical techniques with engineering applications, as in catalysis for example. Interactions of zeolite acid sites with molecular base sites may seem less mysterious when the existence of molecular base sites has been acknowledged at the outset. This improved chemical insight can be pervasive throughout the curriculum.

Eq. (1) was deliberately expressed in terms of k_{12} instead of simply substituting Eq. (4) directly, as in MOSCED. Note that Eq. (4) is described as a "guideline." This means that it is a starting point, but it leaves open the possibility of refining the value as described in the third homework problem. The value of experimental data is hinted at in the presentation, and several assignments at the sophomore level lead students through the process of finding relevant data and inferring refined values of k_{12}. A model like UNIFAC can predict activity coefficients but sheds little light on the underlying chemical interactions that lead to the behavior. Furthermore, the UNIFAC model makes it difficult to refine predictions in light of experimental data for specific systems of interest.

Another alternative would be Wertheim's theory.[10] Wertheim's theory forms the basis of hydrogen-bonding equations of state like the SAFT,[11] PCSAFT,[12] and ESD[13] models. It is also based on rigorous statistical mechanics instead of phenomenological arguments. Therefore a simplified integration of Wertheim's theory with Scatchard-Hildebrand theory would have an advantage as a natural segue to the more sophisticated theories. In fact, this was the preferred alternative initially. Wertheim's theory and its implementations have been the driving forces in molecular thermodynamics for the past 15 years. These developments form the basis for appreciating the qualitative behavior evident in the SSCED model. For example, the ESD model of cyclohexane+methanol shows that the model indicates more stable solutions when hydrogen bonding is recognized explicitly, consistent with experiment.[14] Unfortunately, a direct implementation of Wertheim's theory would excessively complicate the model. Some indirect compromise may be feasible long-term, but the current form of the SSCED model is satisfactory for present purposes.

Finally, it may be possible to relate the dispersion, acidity, and basicity parameters to ab initio characterizations, as in the COSMO-RS model.[15] This would reinforce the value of quantum mechanical computations throughout the curriculum, but freshmen (and sophomores) would be unlikely to appreciate this level of sophistication. It would make more sense to recast the ab initio results as reinforcing the SSCED concepts after the fact, in the junior or senior year.

There is one substantial disadvantage of the SSCED model that motivates the coverage of more advanced models like UNIQUAC and SAFT. Since it has only one binary interaction parameter, the magnitude of deviations from non-ideality can be adjusted, but not the skewness. The skewness of the Gibbs energy is controlled by the volume ratio in the SSCED model. This limitation, however, pertains to quantitative modeling, not to the conceptual and educational device intended here.

ASSESSMENT

Assessments of student learning have not been performed for the freshmen yet, but a very similar presentation pertains to the sophomores and this has been assessed in class through the ConcepTest methodology and through traditional examination questions.

ConcepTests pose simple questions to the class and allow them to post their answers anonymously for quick compilation.[2] Electronic devices typically facilitate this approach, but it can be conducted with colored flash cards. In the strictest sense, ConcepTests should focus entirely on conceptual questions, but a small adaptation permits engagement in active learning for computational exercises as well. I refer to these as "CompuTests." A few examples are given below. The (%) quantities refer to the percentage of students who answered correctly.

ConcepTest 1.

Referring to Figure 2, cases A and B correspond to characterizations of the attractive energy between two molecules as described by the square well potential. This attractive energy is given by $\varepsilon_{12}= (\varepsilon_1{*}\varepsilon_2)\tfrac{1}{2}\,(1- k_{12})$ where ε_{12} gives the depth of the square well. Note that the bottom of the well is $-\varepsilon_{12}$. Provide the response (A or B) corresponding to each situation.

a. Which (A or B) corresponds to $k_{ij} > 0$*? (72%)*

b. Which corresponds to components "liking" each other? (100%)

c. Which corresponds to a higher "escaping tendency" for component 1? (94%)

d. Which will give the highest bubble point pressure? (50%)

ConcepTest 2. (94%)

Which of the images in Figure 3 properly depicts a maximum boiling azeotrope?

"CompuTest" 1. (43%)

Arrange the following mixtures from most compatible to least compatible according the SSCED solubility parameter criterion (k_{12}=0). 1) Pentane+hexane, 2) decane+decalin, 3) 1-hexene+ dodecanol, 4) pyridine+methanol, 5) diethyl ether+n-heptane

A. 12345 B. 12534 C. 54123 D. 21543

"CompuTest" 2. (76%)

An azeotrope exists for n-butane(1)+ethyleneOxide(2) at 1.013 bars at -6.5 °C and 78wt% butane. Estimate the activity coefficient of EtO (γ_2) at the azeotropic composition and temperature from the Scatchard-Hildebrand model assuming k_{ij} = 0. (See Table 2)

(a) 0.04 (b) 1.06 (c) 1.98 (d) 2.89

Examination Question 1. (89%)

Based on the Scatchard-Hildebrand solubility parameters (k_{12} = 0), arrange the following mixtures from most ideal to most non-ideal: a) 2-pentanone+1-pentene, b) 2-pentanone+ naphthalene, c) ethanol +naphthalene, d) n-hexane+ ethanol.

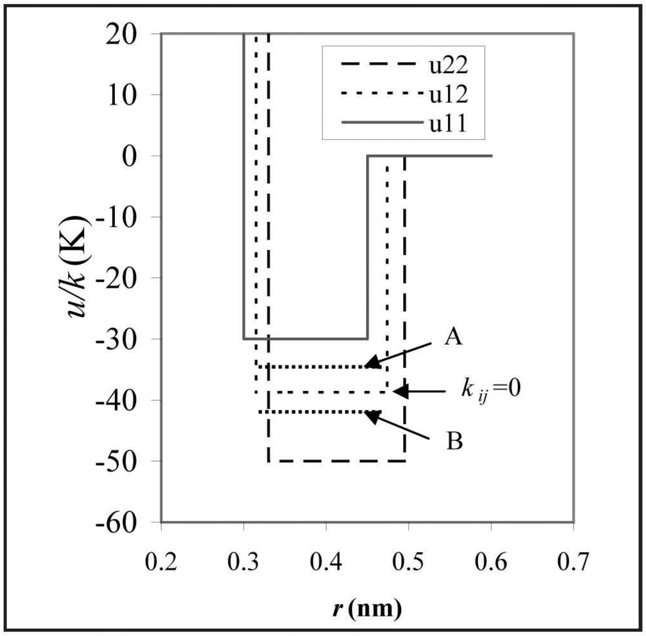

Figure 2.

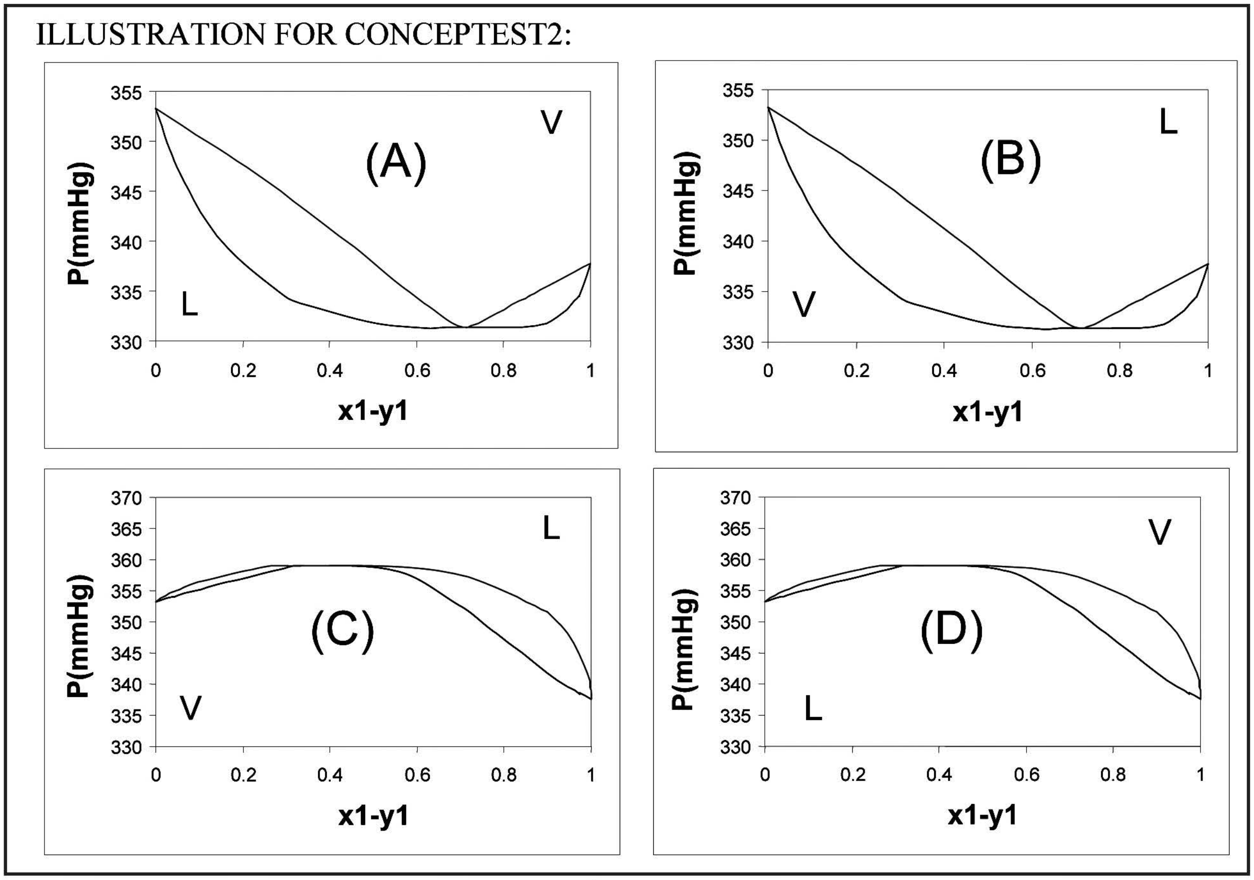

Figure 3.

TABLE 2							
Compound	Tc(K)	Pc(MPa)	w	CpIg/R	MW	$\delta(\text{cal/cc})^{1/2}$	ρ298
n-BUTANE	425.2	3.80	0.193	11.89	58	13.50	0.60
EtOxide	469.0	7.10	0.200	5.80	44	21.72	0.89

Examination Question 2. (61%)

A common problem with recycling polyester is the impurities from bottle caps and labels. The bottle caps typically weigh 0.05 g and the bottles are 2g. The caps are polypropylene (PP) with molecular weight of 60,000 g/mol. The bottles are polyethyleneterephthalate (PET), with molecular weight of 10,000g/mol. The solubility parameter and density of PP can be estimated as (δ_{pp}=14.11; ϱ=0.70), similar to those of isooctane. The solubility parameter and density of PET can be approximated as (δ_{pp}=17.90; ϱ=0.86), similar to those of p-xylene. Estimate the infinite dilution activity coefficient for PP in PET at 100 °C assuming k_{ij}=0.

CONCLUSIONS

Two issues pervade teaching in the chemical engineering curriculum: time constraints and knowledge retention. If you teach too much in too little time, little is retained. If you teach too little, students cannot "connect the dots" from one isolated fact to another. One approach is to articulate broadly applicable concepts, like the SSCED model presented here. This mindset leverages familiar chemical concepts like acidity and basicity while dovetailing with the physical interactions of the van der Waals model covered in physics coursework. Leveraging the concepts presented in other coursework has the two-fold advantage of saving time and rewarding students for retaining what they learn from course to course.

The assessments show that this perspective is accessible to sophomores at least. Assessments were not conducted for freshmen at this early stage of adapting the presentation for them, but we expect similar results to those for sophomores. Students are able to quickly recognize solution non-ideality and the impact this may have on solubility and volatility. Students whose careers take them away from process design may not remember how to compute an activity coefficient five years after graduating, but they can remember that acids and bases interact strongly and that organic chemicals as well as inorganic chemicals should be formulated to account for those interactions.

NOMENCLATURE

Latin

K_i – vapor-liquid partition coefficient
k_{12} is the binary interaction parameter
MW – molecular weight (g/mol)
P_i^{sat} – vapor pressure (MPa)
P – pressure (MPa)
R = 8.314 J/mole-K, the gas constant
T – absolute temperature (K)
U_{vap} = internal energy of vaporization at 298K (J/mol)
V_i = MW_i / ρ_i^L is the liquid molar volume at 298K (cm^3/mol)
x_i – mole fraction of i^{th} component in the liquid phase.
y_i – mole fraction of i^{th} component in the vapor phase.

Greek

α – characterizes the compound's hydrogen bonding acidity (Table 1, MPa$^{1/2}$)
β – characterizes the hydrogen bonding basicity (Table 1, MPa$^{1/2}$)
δ = $(U_{vap}/V)^{1/2}$ - total solubility parameter (MPa$^{1/2}$)
δ' = $(\delta^2 - 2\alpha\beta)^{1/2}$ is the dispersion contribution to the solubility parameter.(MPa$^{1/2}$)
Φ_i = $x_i V_i / \Sigma x_j V_j$ is the volume fraction
γ_i – activity coefficient

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