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Some Patterns of Fluid Phase Behavior

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ABSTRACT: Thermophysical properties often fall into simple, regular, and intuitive patterns within and among families, and these patterns can be used to fill in gaps in experimental measurements, to identify outliers that are likely in error, and to educate scientists and engineers to understand and anticipate expected behaviors. This notion is not new but has not been sufficiently exploited in the applied-thermodynamics literature, and it is particularly attractive today because large databases of thermophysical properties are widely available. This work presents some representative patterns of thermophysical properties related to fluid phase behavior and demonstrates their use to estimate missing properties, to identify those properties that may be in error, and to teach these patterns to scientists and engineers.

INTRODUCTION

Professor John Prausnitz has given practitioners of applied thermodynamics much valuable advice over several decades, and these instructions have ranged from exploiting fundamental theory in the development of new molecular-thermodynamic models to appreciating the importance of experimental data. Thirty four years ago, in his 1977 "State-of-the-Art Review of Phase Equilibria" presentation,[1] Prausnitz stated, "Finally, let us learn to use more the powerful methods of statistical mechanics; let us overcome our fear of partition functions and let us not hesitate to introduce some enlightened empiricism into their construction." In the Concluding Remarks at the end of the section "Fluid Phase Equilibria in Multicomponent Systems" of the book *The Properties of Gases and Liquids*,[2] Prausnitz and his coauthors give practical and common-sense guidelines about the importance of experimental data and gaining experience with specific phenomena. The first guideline states: "Face the facts. You cannot get something from nothing. Do not expect magic from thermodynamics. If you want reliable results, you will need some data. You may not need many, but you do need some." The tenth guideline discusses the importance of judgment and common sense: "Maintain perspective. Always ask yourself: Is this result reasonable? Do other similar systems behave in this way?"

In this work we attempt to follow the advice of Professor Prausnitz regarding the importance of experimental data and gaining a practical, intuitive understanding of chemical phenomena and the patterns of physical properties. We study the observation that physical properties fall into simple, regular patterns, and use these patterns to estimate missing data by interpolation and (limited) extrapolation, to identify outliers that may be in error, and to educate scientists and engineers who use physical properties in their professional work.

Attempts to understand the patterns of physical properties have traditionally been motivated by the goal of developing estimation methods. Mathias[3] highlighted the manner in which experimental data have played an important role in revealing theoretical concepts and determining the structure of thermodynamic models over the past 200 years. Kopp[4] is perhaps the father of "Patterns of Properties" and of group-contribution methods since he recognized that the molar volumes of organic molecules are, to a reasonable approximation, additive functions of effective volumes of their constitutive elements or groups. In a series of papers, Le Bas[5] built upon the ideas of Kopp and elucidated the effect of constitution on the molar volumes of families of compounds. Greenshields and Rossini[6] divide property-estimation methods into three categories: (1) total-property group-contribution methods, (2) homologous-series methods, and (3) isomeric-variation methods in which the isomeric increment in the value of a property is correlated rather than the total value of a property for each isomer. Today, group-contribution methods provide estimations for the physical properties of a wide range of substances. These estimations are often accurate,[2] and the resulting correlations are easily available to practicing engineers through commercial process simulators.[7] However, the second guideline from Prausnitz and coauthors[2] cautions us that "Correlations provide the easy route, but they should be used last, not first." One method of improving the accuracy and reliability of group-contribution methods is to evaluate each method for the family of compounds under consideration and thus choose the most appropriate method for the particular application, as has been demonstrated by Rowley et al.[8] Furthermore, it is good practice for engineers and scientists to apply the intended estimation method to compounds in the family of interest to determine their accuracy and also to analyze whether the method captures the pattern of variation within the family.

Serious efforts to systematically collect property data and improve the quality and extent of databases began in the 1960s with the leadership of Rossini.[9] Today, we have access (generally for a fee) to a large number of electronic databases,[10] and these include NIST,[11] NIST WebBook,[12] DIPPR,[13] PPDS,[14]

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Dortmund Data Bank,[15] DECHEMA Chemistry Data Series,[16] and the Korean Thermophysical Properties Data Bank.[17] Many kinds of errors can occur in large databases and these range from mistakes in the entry of data from publications to problems with the published data (typographical errors, high uncertainty, or even systematic bias). Frenkel et al.[18,19] presented standards for storage and exchange of experimental, predicted, and critically evaluated thermophysical and thermochemical property data that is expected to significantly reduce transcription errors and even identify potential errors in the published source through consistency checks. Rowley et al.[20] discuss several checks to improve the accuracy and reliability of the DIPPR801 Pure Chemical Database,[13] and key among these checks are "comparison of properties within chemical families, and consistent property trends with molecular structure."

With the widespread availability of powerful and easy-to-use commercial software,[7] education of industrial practitioners has become a serious concern.[21] Carlson[22] provided useful guidance to practicing engineers to improve the validity and accuracy of the physical properties used in process simulation, and an important part of these guidelines is the use of series and family plots. In our opinion, a necessary step in the education of engineers is developing an intuitive feel for the expected properties and this "thermodynamic intuition" comes from studying and internalizing the patterns of physical properties.

In the preceding brief discussion, we have presented the ways in which an understanding of the patterns of physical properties is useful for improving the performance of group-contribution methods, for improving the quality of databases of properties, and as an aid in educating practicing scientists and engineers. The procedure for detecting these patterns is actually quite simple, usually nothing more than the application of common sense; but the common sense is "thermodynamic intuition" that comes from experience. The availability of electronic databases facilitates the discovery of these property regularities. It is our hope that the patterns that we present in this paper will demonstrate the value of the technique and encourage others to report additional useful patterns. Kopp[4] identified the regularity of molar volumes of organic compounds over 160 years ago. Othmer[23] proposed a methodology to correlate and estimate the vapor pressure of liquids, solids, and solutions by plotting the logarithm of the desired vapor pressure against the logarithm of the vapor pressure of a reference substance at the same temperature. A linear relationship is usually obtained, and this enables the development of a useful correlation or estimation method. Greenshields and Rossini[6] noted that the regular variation of properties of homologous series and even isomers provides a good basis for developing estimation methods. Smith[24] demonstrated that extending the *series* plot to a *family* plot creates a more powerful way to identify outliers that may be in error while Peterson[25] further showed that the properties of the members of one family are related in a simple (often linear) fashion to properties of analogous materials in similar families. Finally, it should be noted that technical data books published by trade organizations such as API and GPA usually present the data graphically in the form of series or family plots.

The useful regularities of properties appear to be valid for a wide range of fluid-phase thermodynamic and transport properties.[20,24] Understanding the patterns of properties of solids requires that symmetry be taken into consideration.[26] In this paper we limit our scope to the thermodynamic properties of fluid systems mainly to keep the length of the paper within a reasonable limit. While we show some applications to pure fluids, we mainly focus on mixtures since these are usually the systems where the data are uncertain or missing.

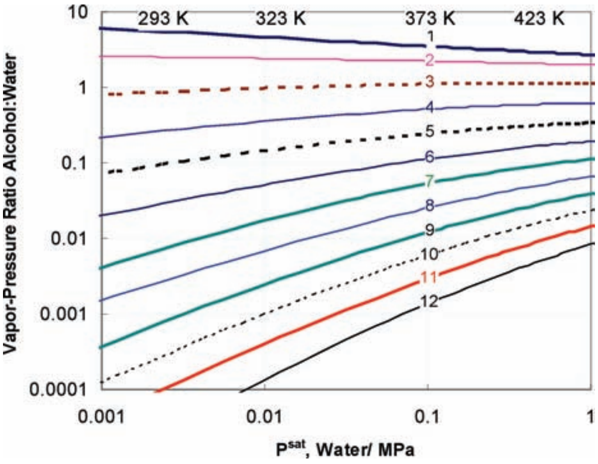

Figure 1. Ratio of the vapor pressure of the 1-alcohols to that of water plotted against the vapor pressure of water. The numbers on each curve show the carbon number of the 1-alcohol. The temperatures at the top of the chart correspond to the water vapor pressure.

■ PURE COMPONENTS

In this section, we present two representative examples that illustrate the power of series plots to understand and evaluate the properties of pure fluids.

Figure 1 is a variation of an Othmer plot.[23] It shows the ratio of the vapor pressures of the 1-alcohols to that of water plotted against the vapor pressure of water. For points on each curve, the same temperature is used to calculate the vapor pressure of the 1-alcohol and water. The vapor-pressure "data" have been taken from DIPPR[13] correlations. The first observation from Figure 1 is that the pattern of variation is regular and expected, which increases confidence in the accuracy and reliability of these DIPPR correlations. The chart also provides useful education about relative vapor pressures and enthalpies of vaporization. Methanol and ethanol have higher vapor pressures than water and the slopes of their curves are negative, which means that their enthalpies of vaporization are lower than that of water. The vapor pressure of 1-propanol is very close to that of water and so is its enthalpy of vaporization. As expected, the higher alcohols exhibit successively decreasing vapor pressures and also successively increasing enthalpies of vaporization.

Figure 2 presents the saturated-vapor temperatures at 50 mmHg (0.00667 MPa) of compounds representing several families of organic compounds plotted against their respective molecular weights. The compounds in Figure 2 consist of 53 alkanes, 62 1-alkenes, 62 alcohols, 47 aliphatic acids, 22 polyfunctional acids, 36 aldehydes, 35 amines, and 24 NO_2 compounds, adding up to a total of 341 compounds. The source of the data is again the DIPPR database.[13] The families show expected trends. The saturated hydrocarbons (alkanes) have the lowest boiling points. Branching tends to lower the saturated-vapor temperature. For the lower molecular weights, the boiling points follow the pattern: alkanes ≈ 1-alkenes < aldehydes ≈ amines < alcohols < aliphatic acids ≈ NO_2 compounds < polyfunctional acids. The effect of chemical composition diminishes for larger molecular weights, say MW > 300.

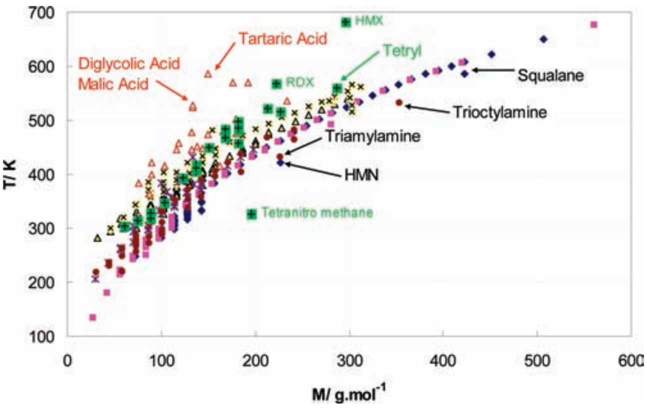

Figure 2. Saturated-vapor temperatures at 50 mmHg (0.00667 MPa) of compounds from several families of organic compounds. The saturated-vapor temperatures of the highly branched compounds (triamylamine, HMN, trioctylamine, and squalane) are relatively low, while the saturated-vapor temperatures of the polyfunctional acids (diglycolic acid, malic acid, and tartaric acid) are relatively high. The NO_2 compounds (RDX, tetryl, and HMX) have relatively high saturated-vapor temperatures, but their values are highly uncertain. The saturated-vapor temperature of tetranitromethane is relatively low because it is a nonpolar compound. Symbols: blue ◆, alkanes; pink ■, 1-alkenes; black △, alcohols; yellow ×, acids, aliphatic; orange △, acids, polyfunctional; purple ∗, aldehydes; red ●, amines; green +, NO2 compounds.

Figure 2 has also identified particular compounds that we comment upon. Branching causes a significant increase in vapor pressure, as demonstrated by HMN (2,2,4,4,6,8,8-heptamethylnonane), triamylamine (tri-*n*-pentylamine), trioctylamine, and squalane (2,6,10,15,19,23-hexamethyltetracosane). The saturated-vapor temperatures of diglycolic acid (527 K), malic acid (524 K), and tartaric acid (586 K) are relatively high, and this is likely because of their multifunctional groups. Diglycolic acid has two acid groups, malic acid has two acid groups and an alcohol group, and tartaric acid has two acid groups and two alcohol groups. However, note that the vapor pressures of all three of these multifunctional acids were estimated by Riedel's method[27] and are thus subject to uncertainty. The boiling point of HMX (1,3,5,7-tetranitro-1,3,5,7-tetraazaperhydroocine) appears high and this may be because it has nitramine groups. But it is not clear why the boiling point of HMX is significantly higher (on a relative basis) than that of tetryl (*N*-methyl-*N*,2,4,6-tetranitroaniline), which is a somewhat similar compound. Furthermore, DIPPR researchers choose not to use the estimated vapor-pressure data reported for HMX,[28] and these estimations give a saturated-vapor temperature of 649 K, which is more in line with the other NO_2 compounds. NO_2 compounds are unstable, and even explosive, at high temperatures (tetryl explodes above 460 K), and hence saturation-vapor temperatures even at the relatively low pressure of 0.00667 MPa are hypothetical. Therefore, estimation methods have large uncertainties. For example, NIST-TDE[29] estimates the saturation-vapor temperature of tetryl as 570 K with an uncertainty of ±85 K. It is likely that the saturated-vapor temperatures of the NO_2 compounds are relatively high and similar to those of the polyfunctional acids, but they inevitably have large uncertainties. The saturated-vapor temperature of tetranitromethane appears to be low. This compound has reliable experimental data, and it is likely that its low saturated-vapor temperature is due to its nonpolar nature.

The patterns of Figure 2 help advance the "education goal", since they graphically elucidate the effect of structure and molecular weight on the boiling point, but also teach about the limitations of simple patterns and the limited availability of experimental data. Branching clearly increases the vapor pressure. The high saturated-vapor temperatures of the three highlighted polyfunctional acids are probably reliable but need experimental confirmation. NO_2 compounds have relatively high saturation-vapor temperatures, but the estimated values are highly uncertain because they are unstable and even explosive. The vapor pressure of tetranitromethane is relatively high, and this cautions us about relying too much on simple patterns.

Table 1. Infinite-Dilution Activity Coefficients at 313 K of Hydrocarbons in DMF and ACN[a]

compound	γ^∞ in DMF	γ^∞ in ACN	class of hydrocarbon
vinyl acetylene	0.84	1.78	olefin and triple bond
1-propyne	1.09	1.95	triple bond
1-butyne		2.98	
1,3-butadiene	2.38	3.73	diolefin
1,2-butadiene	2.80		
cis-2-butene	4.51	7.44	olefin
1-butene	4.97	7.22	
isobutene	5.21		
trans-2-butene	6.46		
butane	10.4	10.36	paraffin
isobutane	13.5	12.18	

[a] Reproduced with permission from ref 30.

MIXTURES

In this section we present several examples that demonstrate the use of the patterns of mixture phase behavior to understand phase equilibria, to evaluate the consistency of experimental measurements, and to fill in gaps in the data.

Mathias, Elliott, and Klamt[30] studied the estimation of liquid-phase nonideality related to the extractive-distillation processes that recover 1,3-butadiene from steam-cracker hydrocarbons. The effectiveness of dimethylformamide (DMF) and acetonitrile (ACN, propenenitrile) as extractive solvents was explored to study the effectiveness of various predictive methods, including group contribution (UNIFAC[31]), quantum mechanical (COSMO-RS[32]), and molecular simulation (SPEADMD[33,34]). Here, the patterns of the data alone are studied and analyzed. Table 1 presents experimental data for the infinite-dilution activity coefficients of hydrocarbons in DMF and ACN at 313 K, which has been chosen as a representative value since it is typical of temperatures encountered in butadiene extractive-distillation columns. Only the infinite-dilution activity coefficients have been reported here since at plant conditions the solubilities of the hydrocarbons in the liquid phase are relatively low. The results in Table 1 demonstrate that the data fall into the pattern expected from "thermodynamic intuition". The infinite-dilution activity coefficients decrease 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 and ACN are effective as extractive solvents, but the fact that the activity coefficients fall into the expected pattern provides confidence in the experimental data and offers a method to fill in data gaps. Figure 3, which is an example of Peterson's[25] relationships between families of materials, graphically illustrates the

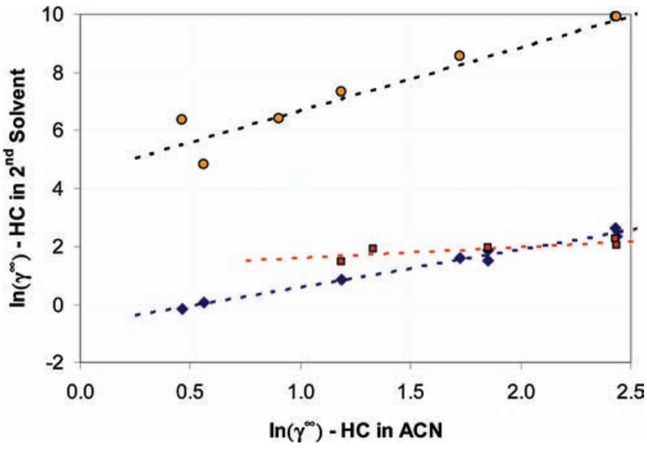

Figure 3. Correlation between hydrocarbon infinite-dilution activity coefficients in DMF, ethanol, and water and those in ACN. All activity coefficients are at 313 K. The dashed lines are best-fit straight lines. Symbols: blue ◆, DMF; red ■, ethanol; orange ○, water. Reproduced with permission from ref 30.

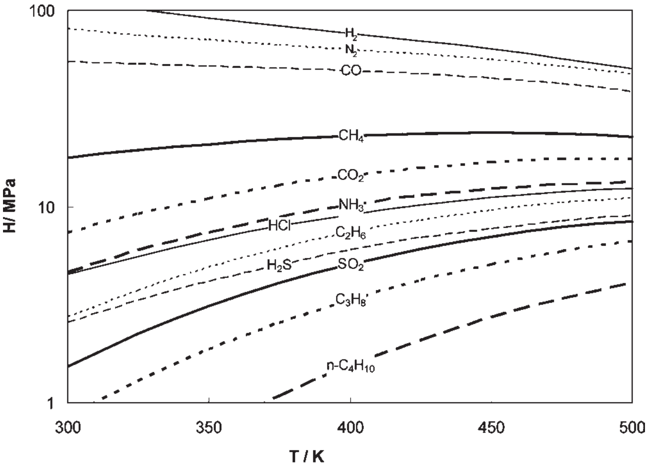

Figure 4. Henry's constants for 12 solutes in hexadecane. The curves were generated using Harvey's correlation.[42]

correlation among the infinite-dilution activity coefficients of hydrocarbons in DMF, ethanol, and water compared to that in ACN. Clearly, the regularity of the data itself, without any theoretical model, reveal a simple, clear pattern that helps to evaluate the consistency of the various data sources and also to fill in data gaps as needed. For example, it is easy to estimate the infinite-dilution activity coefficients of 1-butyne in DMF, and of 1,2-butadiene, isobutene, and *trans*-2-butene in ACN.

Henry's law,[35,36] now over 200 years old, is likely the very first model of applied thermodynamics.[37] It is used in numerous applications in chemical and environmental science and engineering and even today is an important tool of applied thermodynamics.[38−41] Carroll[38−40] and Smith and Harvey[41] have provided excellent background on Henry's Law and guidance on its application. Here we present some useful regularities of Henry's constants to provide insight into how they vary with temperature and the solute−solvent pair. Harvey[42] published a semiempirical correlation for the Henry's constants that is valid over a wide temperature range. Figure 4 graphically presents Harvey's correlation for the Henry's constants of 12 solutes in hexadecane; Figure 4 is essentially a reproduction of Figure 3 of Harvey's[42] 1996 paper. Most figures showing the temperature dependence of Henry's constants in a particular solvent have similar qualitative features. Solutes with large Henry's constants (low solubility) typically have a negative slope with temperature, which means that the heat of solution is positive (adiabatic absorption of solutes from the gas phase will cause a temperature reduction). As the Henry's constant of a solute decreases, the slope becomes increasingly positive, which means exothermic absorption and a temperature rise upon adiabatic absorption from the vapor phase. At a sufficiently high temperature, close to the critical temperature of the solvent, most curves have negative slopes, and hence the solutes with low Henry's constants go through a maximum. (It should be noted that the opposite trend usually occurs when the solute is less volatile than the solvent, e.g., propane dissolved in liquid methane, but the Henry's law approach is typically not used in this context.) This high-temperature behavior (outside the temperature range of Figure 4) is not a practical concern because the solvent becomes quite compressible and these high temperatures are usually outside the range of engineering applicability of the Henry's Law approach. In this circumstance, an equation-of-state model would likely be the better choice for the property method.[22]

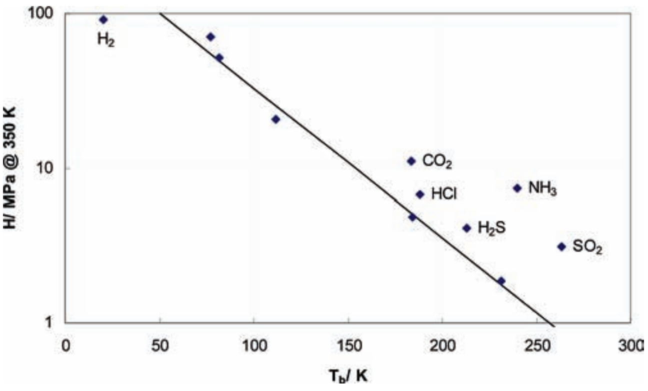

Figure 5. Henry's constants at 350 K of various solutes in hexadecane. The line is based upon the nonpolar solutes and assumes that the logarithm of the Henry's constant at 350 K varies linearly with the normal boiling temperature.

Figure 5 studies the pattern of the Henry's constants of various solutes in hexadecane by plotting the Henry's constant at a representative temperature of 350 K against the solute normal boiling point. (Note that CO_2 is a solid at its normal boiling point and hence an "effective" liquid normal boiling point of 183.7 K was estimated by extrapolating the liquid vapor pressure down to a vapor pressure of 1 atm.) Figure 5 indicates that for nonpolar compounds the logarithm of the Henry's constant at 350 K varies approximately linearly with the normal boiling point. The Henry's constants of the polar compounds (CO_2, HCl, H_2S, NH_3, and SO_2) are higher than the value based upon the nonpolar estimate, which indicates that they have relatively higher positive deviations from ideality in the nonpolar solvent, hexadecane. Hydrogen is another exception to the simple pattern, perhaps because it is a quantum gas.

For a polar solvent we would intuitively expect the opposite effect; i.e., nonpolar solutes will have higher nonideality than polar solutes, and we elucidate this premise with triethylene glycol (TEG) as the solvent. TEG is an important glycol for dehydration processes because it has good affinity for water and a desired low vapor pressure.[43] Figure 6 presents infinite-dilution activity coefficients of various solutes in TEG at a representative temperature of 298 K. The alkane data are from Jou et al.[44] and the compilation by

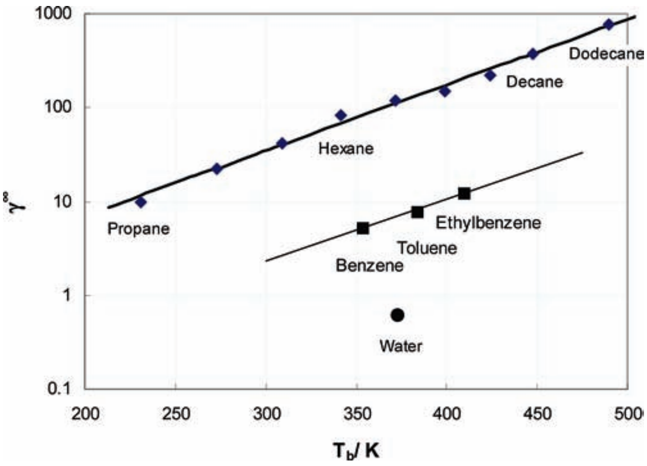

Figure 6. Infinite-dilution activity coefficients of various solutes (hydrocarbons from propane to dodecane, benzene, toluene, ethylbenzene, and water) in triethylene glycol (TEG) at 298 K. The lines are best fits based upon the assumption that the $\ln(\gamma^\infty)$ varies linearly with the solute normal boiling point.

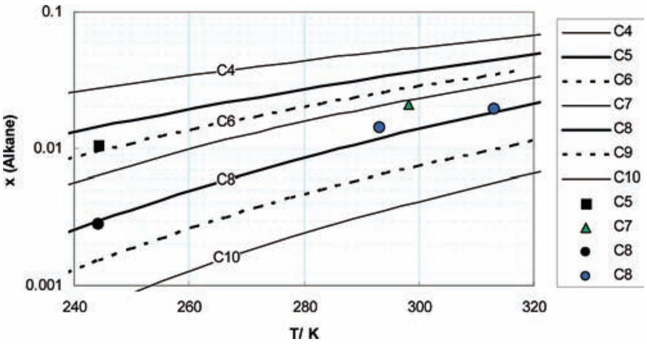

Figure 7. Solubility of *n*-alkanes, butane (C4) to decane (C10), in propylene carbonate (PC). The lines are from a Fluor proprietary model, the data at 244.3 K are from Fluor internal files,[48] the heptane data at 298 K are from Salem,[50] and the octane data at 293 and 313 K are from Fahim and Merchant.[49]

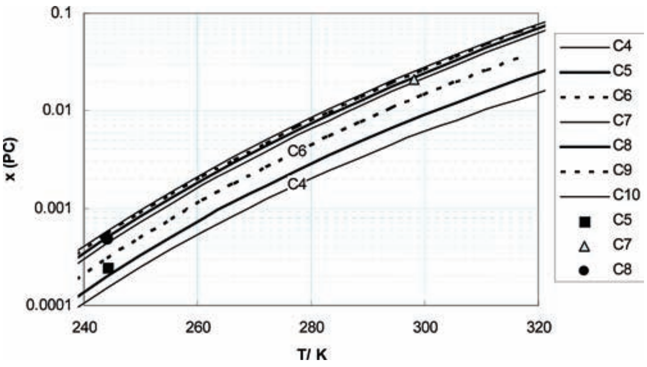

Figure 8. Solubility of propylene carbonate (PC) in *n*-alkanes, butane (C4) to decane (C10). The lines are from a Fluor proprietary model, the data at 244.3 K are from Fluor internal files,[48] and heptane data at 298 K are from Salem.[50]

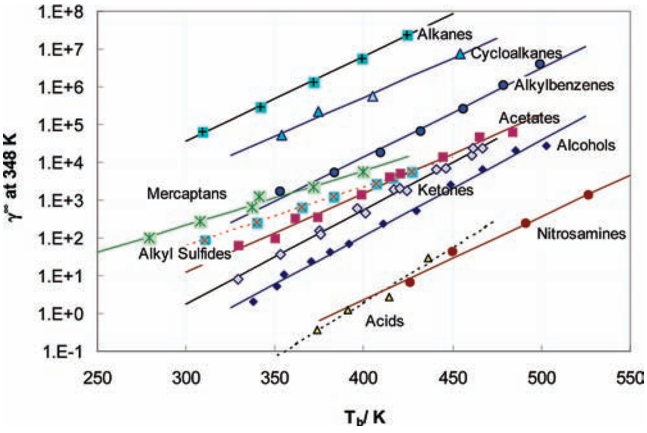

Figure 9. Infinite-dilution activity coefficients at 348 K of substances from various families of compounds in water. Background information for this figure is provided in Table 2. The points are calculated using methods described in Table 2, and the lines are best fits for each compound assuming that the logarithm of the infinite-dilution activity coefficient is linear in temperature.

Tiegs et al.,[45] the data for the aromatic compounds are from Sun, Gao, and Gao,[46] and the water infinite-dilution activity coefficient has been taken from the comprehensive analysis performed by Parrish, Won, and Baltatu.[47] Figure 6 shows that the activity coefficient of water is quite low (actually less than unity), which makes TEG an effective dehydrating solvent. The hydrocarbon activity coefficients are about 2 orders of magnitude higher than that of water, and this means that the hydrocarbon absorption will be small, as desired for process effectiveness. TEG is, unfortunately, a reasonably good solvent for aromatics, and this often causes a process problem since a significant fraction of these compounds reach the TEG regeneration system and appear as vapor in the stripping column of gas.[43] Figure 6 is useful because it enables design engineers to understand relative solubilities and thus anticipate broad design effects. The chart is also valuable because it provides insight into nonpolar−polar effects in chemical processes, and thus has educational benefits.

Liquid−liquid immiscibility occurs in many chemical processes, and here we provide one example to understand the regularity and patterns of this particular phase behavior. Gas purification processes based upon Fluor Solvent (propylene carbonate or PC) enjoy a significant advantage for applications where CO_2 removal requirements dictate the design (i.e., H_2S concentrations are small) and the process temperatures are low.[43] But heavier hydrocarbons are immiscible with PC, and design engineers need to understand the regions of composition and temperature where a hydrocarbon liquid may form in the gas-purification process. Figures 7 and 8 present solubilities in the two liquid phases formed for various PC−alkane binary mixtures at low temperatures. Only severely limited data are available for these systems, but the data are fortunately internally consistent and the patterns they reveal have enabled the development of a Fluor proprietary correlation. Figure 7 presents the solubility of *n*-alkanes in PC as a function of temperature. The lines are from the Fluor correlation, the low-temperature data (244.3 K) are from Fluor internal files,[48] and the ambient-temperature data are from Fahim and Merchant[49] and from Salem.[50] The solubility of PC in alkanes is shown in Figure 8, and here the lines are from the Fluor correlation, the low-temperature data are from Fluor internal files,[48] and the ambient-temperature data are from Salem.[50] The observed regularities of the alkane−PC liquid−liquid equilibrium are as follows: the solubility of hydrocarbons in PC decreases with increasing carbon number; the solubility of PC in hydrocarbons increases with carbon number; and carbon chain length has less affect for PC solubility in

Table 2. Infinite-Dilution Activity Coefficients at 348 K of Various Families of Compounds in Water. List of Compounds in the 10 Families in Figure 9. The Families Are Listed in Order of Increasing Activity Coefficients, and the Methods of Estimation of the Infinite-Dilution Activity Coefficients Are Provided in the Footnotes

family	compounds
acids[a,b]	formic acid, acetic acid, propionic acid, butyric acid
nitrosamines[c]	*N*,*N*-dimethylnitrous amide, *N*,*N*-diethylnitrous amide, *N*,*N*-dipropylnitrous amide, *N*,*N*-dibutylnitrous amide
alcohols[a,b]	methanol, ethanol, propan-2-ol, propan-1-ol, 2-methylpropan-1-ol, butan-1-ol, pentan-1-ol, hexan-1-ol, heptan-1-ol, octan-1-ol, 1-nonanol, decan-1-ol
ketones[a,b]	acetone, 2-butanone, pentan-3-one, pentan-2-one, hexan-3-one, hexan-2-one, heptan-4-one, heptan-3-one, heptan-2-one, octan-3-one, octan-2-one, nonan-3-one, nonan-5-one, nonan-2-one
acetates[a,b]	methyl acetate, ethyl acetate, isopropyl acetate, propyl acetate, butyl acetate, isopentyl acetate, pentyl acetate, hexyl acetate, heptyl acetate, octyl acetate
alkyl sulfides[a,b]	dimethyl sulfide, methyl ethyl sulfide, diethyl sulfide, dimethyl disulfide, ethyl methyl disulfide, dipropyl sulfide, diethyl disulfide
mercaptans[a,b]	methanethiol, ethanethiol, *n*-propylmercaptan, *tert*-butanethiol, butanethiol, 1-pentanethiol
alkylbenzenes[d]	benzene, toluene, ethylbenzene, propylbenzene, butylbenzene, pentylbenzene, hexylbenzene
cycloalkanes[d]	cyclohexane,methylcyclohexane, ethylcyclohexane, butylcyclohexane
alkanes[e]	pentane, hexane, heptane, octane, nonane

[a] Infinite-dilution activity coefficients obtained by fitting data using the NRTL model.[53] [b] Data obtained from NIST[11] and Dechema[16] electronic databases. [c] Infinite-dilution activity coefficients obtained from air−water partition coefficients listed by Abraham and Al-Hussaini.[54] [d] Infinite-dilution activity coefficients approximated as the inverse of the mole-fraction solubility in water, using the correlations developed by Tsonopoulos.[55] [e] Infinite-dilution activity coefficients approximated as the inverse of the mole-fraction solubility in water, using the correlations developed by Tsonopoulos.[51]

the alkanes than for alkane solubility in PC. These pattern regularities are qualitatively equivalent to the patterns observed for the liquid−liquid equilibrium in alkane−water systems reported by Tsonopoulos[51] and have enabled the development of a useful correlation, which is shown graphically in Figures 7 and 8. We hope that the example of PC−alkane liquid−liquid equilibrium shows our attempt to follow Prausnitz' first guideline: "If you want reliable results, you will need some data. You may not need many, but you do need some."

Aqueous systems usually exhibit the most complex behavior[52] and are the most difficult to understand and model. For example, Harvey[42] and Tsonopolous[51] have shown that the figure analogous to Figures 4 and 7 for aqueous systems (solubility of *n*-alkanes and other compounds in water) often show a minimum solubility at about 295−315 K. Nevertheless, even aqueous systems have useful regularities that aid in understanding their patterns and even enable property estimation by interpolation. Furthermore, an enormous number of data are available in the literature and electronic databases to reveal these regularities.

Figure 9 presents the aqueous infinite-dilution activity coefficients of substances from various representative families of organic compounds plotted against their respective normal boiling temperatures. A temperature of 348 K has been chosen to represent separations where the water concentration is fairly high and the pressure is close to atmospheric; however, the patterns of Figure 9 will not change significantly if a different representative temperature were chosen. Table 2 lists the compounds in the ten families shown in Figure 9. Note that the families in Table 2 are presented in order of increasing aqueous activity coefficients. The sources of the data and the methods of estimation of the infinite-dilution activity coefficients are presented as footnotes in Table 2.

Most of the infinite-dilution activity coefficients in Figure 9 were obtained by fitting the NRTL model[53] to data from the NIST[11] and Dechema[16] electronic databases. In the case of the nitrosamines the infinite-dilution activity coefficients were obtained from air−water partition coefficients listed by Abraham and Al-Hussaini.[54] The infinite-dilution activity coefficients of the alkylbenzenes and cycloalkanes were approximated as the inverse of the mole-fraction solubility in water, using the correlations developed by Tsonopoulos.[55] The infinite-dilution activity coefficients of the alkanes were obtained similarly to those of the alkylbenzenes and the cycloalkanes and by using the correlations developed by Tsonopoulos.[51]

The first observation about Figure 9 is that the results do indeed fall into a regular and expected pattern, even for aqueous systems. These patterns help scientists and engineers estimate the nonideality of the organic−water pair of particular interest and also identify data that may be in error. The variation of infinite-dilution activity coefficients is very large, ranging from the organic acids that form nearly ideal mixtures with water to alkane−water activity coefficients that are more than 7 orders of magnitude higher. The patterns accentuated by Figure 9 have helped us develop and test Fluor-proprietary correlations for aqueous separations in emerging biotechnology processes.[56]

These regularities invariably occur and are useful for data evaluation, for estimation and for education.

■ CONCLUSIONS

This work has used representative examples to demonstrate that useful regularities exist in the patterns of fluid phase behavior, and these patterns can be used to understand phenomena, to evaluate data, and to develop correlations. The usefulness of these regularities is particularly relevant today because large databases of thermophysical properties are widely available, which facilitates identifying and exploiting these regularities. We hope that our work is consistent with the recommendation of Professor Prausnitz to base applied thermodynamics and process technology on experimental data.

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■ DEDICATION

It is an honor to publish a paper in the JCED Festschrift that celebrates Professor John M. Prausnitz for his contributions to experiment, theory, and the application of thermodynamics to industrial practice and processes.

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