International Journal of Thermophysics, Vol. 7, No. 4, 1986

Importance of Thermophysical Data in Process Simulation[1]

C. Black[2]

The need for thermophysical properties of components and their mixtures has grown as computer simulation of processes has developed and expanded. Although equations of state require fewer input data, they are not yet generally applicable to all types of systems. Accordingly, in many cases, the liquid activity models are still very much required. A long-time disadvantage of the liquid activity method, for systems containing supercritical components, is overcome if the Henry constant is utilized. A van Laar-type interpolative equation provides the Henry constant in liquid mixtures from the values in the pure liquid components. The addition of a ternary interaction in addition to the usual binary ones provides improved MVL prediction of phase equilibria, espcially VLLE involving three phases. Examination of the consistency of thermal properties is made feasible with the aid of a generalized reduced Frost–Kalkwarf vapor pressure equation. It is useful also for extending and supplementing sparse data and for predicting properties from the structure and boiling point. Possible trends in properties needed and their availability to simulators are discussed in view of available computer facilities.

KEY WORDS: activity coefficient; equation of state; heat of vaporization; Henry constant; phase equilibria; predictive methods; process simulation; ternary interactions; vapor pressure.

1. INTRODUCTION

Regardless of the nature of the process, the engineer's ability to simulate and design it depends on the availability of thermophysical data. The need has grown as computers have developed and expanded in capacity and

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[1] Invited paper presented at the Ninth Symposium on Thermophysical Properties, June 24–27, 1985, Boulder, Colorado, U.S.A.

[2] Process Simulation International (an affiliate of Simulation Sciences Inc.), 1051 West Bastanchury Road, Fullerton, California 92633, U.S.A.

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capabilities. Both pure-component properties and those properties needed to predict phase equilibria are required. This strong dependency on thermophysical properties places them in high priority for process simulation and design. They are important either as required data or as data for developing and testing predictive methods.

Since the time of van Laar and Dolezalek, who each recognized liquid phase nonideality but differed in his view as to its origin, liquid phase nonideality has become important in understanding phase equilibria. The effects of composition and temperature on liquid phase activity coefficients are of primary importance.

Indeed, van Laar [1], Margules [2], Hildebrand [3], Scatchard [4], Wohl [5], Black [6], Redlich and Kister [7], Wilson [8], Abrams and Prausnitz [9], Renon and Prausnitz [10], and others have developed useful models for representing activity coefficients versus composition of the liquid. The local composition models have been popular for a number of years. The concept of group interaction has led to several models, ASOG by Deal and Derr [11] and UNIFAC by Fredenslund et al. [12]. Fredenslund et al. [13] have expanded the interaction package for UNIFAC.

Attempts by some [8, 10, 14, 15, 16] to include the effect of temperature in their models have been of very limited value. The simple functions used are not sufficiently general to define behavior over a practical temperature range in most types of systems.

2. PHASE EQUILIBRIA FOR PROCESS SIMULATION

Phase equilibria for process simulation can be provided in several different important ways:

with the aid of a suitable equation of state,

by applying a liquid phase activity coefficient model,

by applying conformal solution models using reference systems, and

by applying electrolyte models which include dissociation into ions and their interactions.

We discuss only the first two methods. However, the conformal solution method was discussed by Chapelear et al. [17] in 1974. Further, Project 811 of the AIChE–DIPPR program will publish a book of recommended calculation procedures and data sources for the electrolyte methods.

2.1. Equations of State

Since the time of van der Waals, many modifications and variations of this cubic equation have been proposed. It has been reported [18] that some 4779 equations of state have been proposed in the last three decades. The BWR equation [19, 20], an enhanced extension of the Beattie-Bridgeman, was the early workhorse, but parameters were available for only a relatively few compounds. In 1949, Redlich and Kwong [21] proposed a simple modification of the van der Waals equation which gave a good representation of vapor properties, but the predicted liquid properties are not satisfactory unless further modifications are made. Soave [22] introduced the use of the acentric factor to improve the temperature effect and the predictive capabilities of the Redlich–Kwong equation (SRK). The Starling [23] and Lee–Kesler [24] modifications of the BWR equation and the Peng–Robinson [25] variation of the van der Waals equation all provide some small improved predictive capability for liquid properties with nonpolar and moderately polar compounds and their mixtures.

For mixtures of molecules of very different size and for those involving strongly polar compounds, much is still to be desired. It appears that the mixing rules for the pure-component parameters for these modified van der Waals equations, while being quadratic at low densities, must be more complex at high densities. Luedecke and Prausnitz [26] have used density-dependent mixing rules for binary mixtures but not yet for ternaries or multicomponent mixtures. The quadratic mixing rule is required at a low density to be consistent with that for the second virial coefficient, which must be predicted by the equation of state as the pressure approaches zero. Work is currently in progress to further improve and extend the use of equations of state for the representation of vapor–liquid and liquid–liquid equilibria [26–29].

Where a suitable equation of state and its associated parameters are available, only the ideal-gas heat capacity versus temperature is required to calculate the needed thermophysical data. Altering the mixing rule for the cohensive energy parameter by introducing a K_{ij} will often provide a more exact fit to experimental binary VLE data.

2.2. Liquid Phase Activity Coefficients

Predicting phase equilibria via a model for liquid phase activity coefficients is usually the most suitable method for mixtures of strongly polar compounds, especially aqueous mixtures. Where volatile gases are present in the mixture, the system temperature is sometimes higher than the critical temperature of the more volatile components. Since the vapor pressure is required in these calculations, they are normally limited to temperatures equal to or less than the critical temperature of the most volatile component. This has been a disadvantage of the liquid activity coefficient method compared to the equation-of-state approach.

The equilibrium vapor/liquid ratio K_i is calculated via the activity coefficient, vapor pressure, and vapor phase fugacity as

$$K_i = \frac{Y_i}{x_i} = \frac{\gamma_i P_i^\circ}{\theta_i P} \tag{1}$$

where γ_1 is the liquid phase activity coefficient, P_i° is the pure-component vapor pressure, x_i is the mole fraction of the component in the liquid, Y_i is the mole fraction of the component in the vapor, and P is the total pressure of the system, and

$$\ln \theta_i = \ln \frac{\phi_i}{\phi_i^\circ} - \int_{P_i^\circ}^{P} \left(\frac{\bar{V}_i^l}{\mathrm{RT}} \right) dP \tag{2}$$

where ϕ_i is the fugacity coefficient at system pressure, ϕ_i° is the fugacity coefficient at the vapor pressure of i, and $\bar{V}_i^l$ is the partial molar volume of i in the liquid mixture. A first approximation takes $\bar{V}_i^l = V_i^l$ for the pure liquid.

2.3. Henry Constants

If we define a Henry's law constant for component i in the mixture to be its partial pressure in the equilibrium vapor phase divided by its mole fraction in the liquid,

$$(H_i)_m = \left(\frac{Y_i P}{x_i} \right) = \left(\frac{\gamma_i P_i^\circ}{\theta_i} \right) \tag{3}$$

The value of $(H_i)_m$ can be obtained from experimental measurements for the solubility of the gas in the mixture or in each individual liquid component of the mixture and then computed for the mixture. Extensive data are available from which the Henry's constants can be evaluated for a gas i in a liquid component j. These can be represented versus temperature in a Rankine-type equation with an approximate pressure correction added, if necessary.

$$\ln(H_i)_j = C_1 + \frac{C_2}{T} + C_3 \ln T + C_4 P \tag{4}$$

where T is the absolute temperature and P is the total pressure. At very low concentrations of a gas in the liquid, the Henry constant is related to its activity coefficient at infinite dilution,

$$(H_i)_j^\infty = \frac{\gamma_i^\infty P_i^\circ}{\theta_i} \tag{5}$$

Consequently, the effect of the liquid composition on the Henry constant is given by the effect of the composition on γ_i^∞. A van Laar-type model provides the Henry constant for gas 1 in a mixture of liquids 2 and 3, at a constant temperature.

$$(\ln H_1)_m = \left[\frac{x_2(\ln H_1)_2 + x_3(\ln H_1)_3 R_{32}}{x_2 + x_3 R_{32}} + \frac{A_{23} R_{13} x_2 x_3 R_{32}^2}{(x_2 + x_3 R_{32})^2}\right] \tag{6}$$

where

$A_{23} = \ln \gamma_2^\infty$ for component 2 at infinite dilution in 3

$$R_{32} = \left(\frac{A_{32} - C_{32}}{A_{23} - C_{23}}\right) \quad \text{and} \quad C_{23} = C_{32}$$

$$R_{13} = \left(\frac{A_{13} - C_{13}}{A_{31} - C_{31}}\right) \quad \text{and} \quad C_{13} = C_{31}$$

$$= R_{12} \cdot R_{23}$$

Wherever van Laar or modified van Laar (MVL) models are used, the interaction constants A_{ij} are available also for the calculation of the Henry's constant in the liquid mixture.

It will be noted that as the liquid mixture of components 2 and 3 approaches ideality and the ratio A_{23}/A_{32} approaches unity, the equation reduces to a simple linear relation:

$$(\ln H_1)_m = x_2(\ln H_1)_2 + x_3(\ln H_1)_3 \tag{7}$$

With the aid of Henry constants for the supercritical components in each of the pure liquid components of the mixture, the liquid activity method is capable of calculating rigorously the phase equilibria also in these very special systems. A major disadvantage of the liquid activity coefficient method is overcome when Henry constants are available. A table of these for the most common gases in many liquids has been developed for such calculations. To be completely general and applicable also to high-pressure phase equilibria, vapor phase fugacities must be calculated for the liquid-type components. These are readily calculated by any of several methods, MVDW [30], HOCV [1], SRK [22], and PR [25]. For the strongly polar compounds, the first two methods are most suitable up to moderately high pressures. In addition, these represent the second virial coefficients best for the pure compounds.

Figure 1 shows the isothermal equilibrium results of Song and Kobayashi [32] for carbon dioxide and water at 304.19 K. The ordinate gives the pounds of water per million standard cubic feet of gas. The abscissa is the total pressure. A labeled curve gives calculated results using the Henry's law constant for CO_2 in water and the MVDW method for vapor fugacities for water. The Henry constant for CO_2-water is based on the data of Gillespie and Wilson [33].

A curve is also given in Fig. 1 to show the values predicted by the SRK equation of state. A better agreement with the experimental data up to more than 15 MPA is furnished with the aid of the Henry's law constant for CO_2 and MVDW for vapor fugacities for water.

Using Henry constants for CO_2 in triethylene glycol (TEG) and in water, the modified van Laar (MVL) method, and MVDW for the vapor fugacities of TEG and water, phase equilibria are calculated for the ternary CO_2–TEG–water. These are compared with the experimental data of Takahashi et al. [34] in Fig. 2. The isothermal results calculated at three pressures are seen to be in substantial agreement with the experimental data.

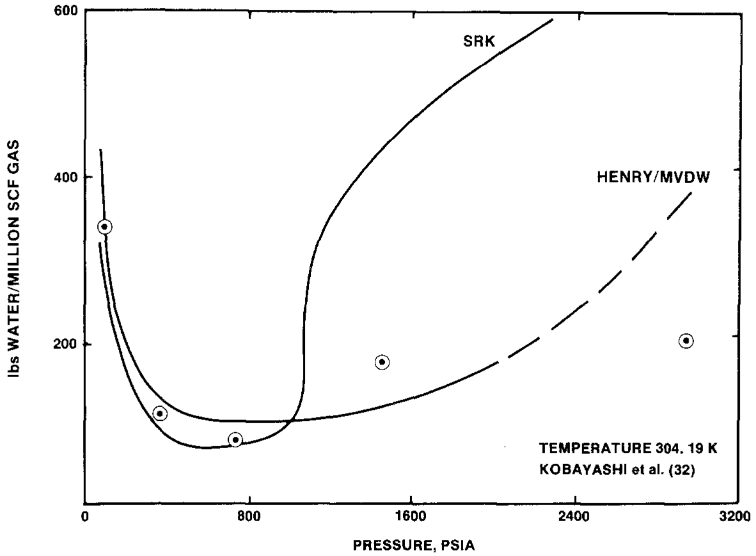

Fig. 1. Effect of pressure on the water content of a wet stream of carbon dioxide gas at 304.19 K. (1 $ft^3 = 0.028317\ m^3$ and 1 PSIA = 6.89474 kPa.)

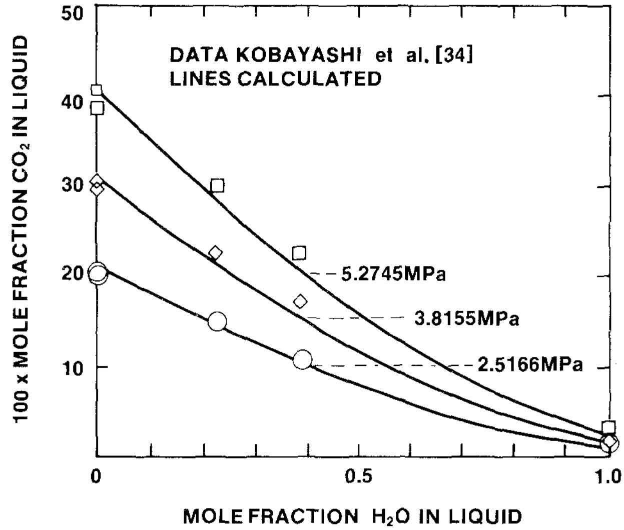

Fig. 2. Solubility of CO_2 gas in liquid mixtures of triethylene glycol and water at three pressures.

The Henry's constant for CO_2 in mixtures of TEG and water has been calculated for 297.04 K and 5.275 MPA. The calculated results fall significantly below a simple linear interpolation for the $\ln H$ values. The approximate interaction parameters for Eq. (6) are given:

$$A_{23} = -1.71247 + \frac{78.5895}{T} \tag{8}$$

$$R_{23} = 4.42025 - \frac{782.944}{T} \tag{9}$$

$$R_{32} = 1/R_{23} \tag{10}$$

$$R_{13} = 0.7573 + 0.1487 \left(\frac{V_i}{V_w}\right)^{5/6} \tag{11}$$

Where V_i is the liquid molar volume of gas i at 298.15 K and V_w is the liquid molar volume of water at 298.15 K.

The vapor–liquid equilibrium K_w values for water in the ternary CH_4–TEG–water at 299.82 K, with 5 %w water in the TEG liquid, have been calculated versus pressure. If plotted, a curve for the calculated K_w goes through a minimum in the pressure region of about 5.5 to 6.5 MPA. This is consistent with results reported by Porter [35] for a natural gas.

The effect of the water concentration in the TEG on the K_w for water is compared with the experimental data of Rosman [36] in Fig. 3. Over the range of the data the calculated results are in reasonable agreement with Rosman's data. The water concentration in the gas phase in equilibrium with TEG containing 3.5% (w) water and individual gas phases of CO_2, CH_4, and a 13-component natural gas is given in Fig. 4. The calculated results are compared with the reported experimental results of Katz et al. [37] for a natural gas and of Takahashi et al. [34] for CO_2. The results agree best with the experimental data at the highest of the three temperatures. While the absolute values at the lower temperature (below T_c for CO_2) are not in full agreement, the qualitative effects of temperature and pressure are consistent with the data of Kobayashi.

2.4. Ternary Interactions

The modified van Laar model for liquid phase activity coefficients was published by Black [6] in 1958. It provides activity coefficients in binary, ternary, and multicomponent systems using parameters derived only from binary data. Over the years it has been used to provide, successfully, the required phase equilibria for dozens of processes used in industry and in many licensed processes.

Our experience has shown that while most systems can be predicted from binary data alone, there are some which can be represented better if a

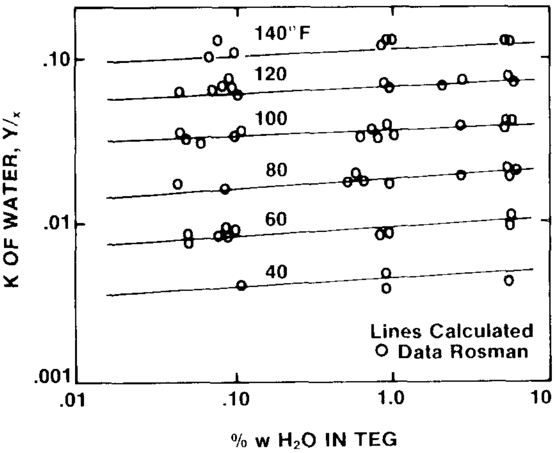

Fig. 3. Vapor–liquid K values for water in mixtures with triethylene glycol at 1-atm pressure and six temperatures (top to bottom: 140, 120, 100, 80, 60, and 40°F).

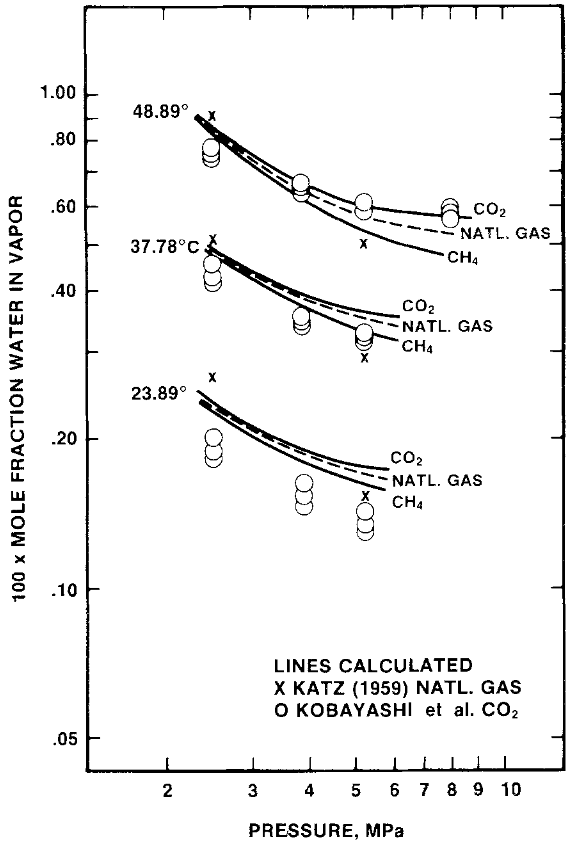

Fig. 4. Effect of pressure on water content of the vapor for three wet gas streams.

ternary interaction term is included. This makes it possible to orient better the predictions in the central portion of a ternary composition diagram. Often in liquid–liquid equilibria for extraction, the mutual solubilities for one or both components with the solvent are quite low. Sometimes one component and the solvent have low solubilities and the other component and the solvent are completely miscible. A ternary azeotrope, the plait point, a vapor–liquid equilibrium point, a tie line, or other liquid–liquid equilibria in the interior of the composition triangle can help define the calculations in the central region. Binary results are still valid but the predicted ternary results are improved. The modified van Laar (MVL) equation including a single ternary interaction parameter is

$$\ln \gamma_i = (\ln \gamma_i)_{\mathrm{V}} + (\ln \gamma_i)_{\mathrm{E}} + (\ln \gamma_i)_{\mathrm{T}} \tag{12}$$

$$(\ln \gamma_i)_{\mathrm{V}} = \sum_j Z_j(A_{ij} - C_{ij})(1 - Z_i) - \frac{1}{2}\sum_j \sum_k (A_{jk} - C_{jk})\, Z_j Z_k(R_{ij}) \tag{13}$$

$$\begin{aligned}(\ln \gamma_i)_{\mathrm{E}} = {} & \sum_{\mathrm{R}} \left[(\bar{x}_{\mathrm{S}} - \bar{x}_{\mathrm{R}})^2 \left(\sum_r CC_{ir} x_r \right) \right] + \sum_{\mathrm{R}} \left\{ (\bar{x}_{\mathrm{S}} - \bar{x}_{\mathrm{R}})[2 - 3(\bar{x}_{\mathrm{S}} - \bar{x}_{\mathrm{R}})] \right. \\ & \left. \cdot \left(\sum_s \sum_r C_{sr} X_s X_r \right) \right\} - \frac{3}{2} \sum_{\substack{\mathrm{RM} \\ \mathrm{R,M} \neq \mathrm{S}}}\!\!\sum \left[(\bar{x}_{\mathrm{R}} - \bar{x}_{\mathrm{M}})^2 \left(\sum_r \sum_m C_{rm} x_r x_m \right) \right]\end{aligned} \tag{14}$$

$$(\ln \gamma_i)_{\mathrm{T}} = \sum_j \sum_k A_{ijk} x_j x_k (1 - 2x_i) \tag{15}$$

where $Z_{\mathrm{I}} = x_{\mathrm{I}} R_{\mathrm{I}i}/(\sum_j x_j R_{ji})$ and $R_{13} = R_{12} \cdot R_{23}$; x_r is the fraction of component r in class R; $\bar{x}_{\mathrm{R}}$ is the sum of mole fractions of components in class R; A_{ij}, A_{ji}, and C_{ij} are binary parameters; $R_{ij} = [(A_{ij} - C_{ij})/(A_{ji} - C_{ji})]$ and $C_{ij} = C_{ji}$; and A_{ijk} is a ternary interaction and $A_{ijk} = A_{jki} = A_{kij} = A_{kji} = A_{jik} = A_{ikj}$. This is a thermodynamically consistent model which reflects the restrictions imposed by the Gibbs–Duhem relation.

Calculation of three phase equilibria VLLE with the aid of an activity coefficient model is important in process simulation. However, it has become the practice of some to regress vapor–liquid equilibria to obtain binary parameters for their model to be used in predicting vapor–liquid equilibria. Then, they regress liquid–liquid equilibria to get different binary parameters for representing liquid–liquid equilibria. Rarely do either of the two sets of parameters coincide or predict the three phase equilibria simultaneously as they should. If the equation model is adequate and the binary parameters are sufficient, both vapor–liquid and liquid–liquid equilibria can be calculated simultaneously. Only small changes in the liquid phase activity coefficients are necessary to alter significantly liquid–liquid equilibria. On the other hand, vapor–liquid equilibria depend on the vapor pressures and fugacity coefficients as well as the activity coefficients. As a result, vapor–liquid equilibria are not as sensitive to small changes in the activity coefficients. An approximate overall representation can be established from binary VLE data, and liquid–liquid equilibria in the ternary mixtures can help to fine-tune the results. Data sources [38–43] are useful for developing activity coefficients.

Figure 5 shows the liquid–liquid equilibria for benzene (1)–ethanol (2)–water (3) predicted at 348.15 K with the parameters given in Table I. The solid-line miscibility curves and the full tie lines are the result of these calculations. The circles are the experimental data from Morachevskii and

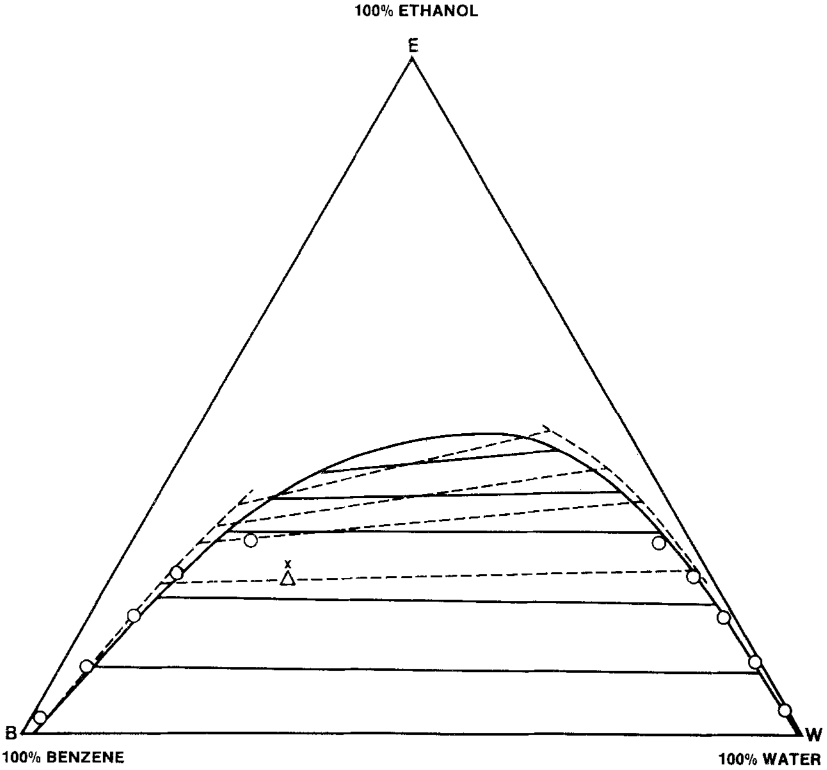

Fig. 5. Comparison of calculated liquid–liquid equilibria with and without a ternary interaction with experimental data. Parameters, Table I; data, Morachevskii and Belousov [44]. Solid lines, with ternary interaction; dashed lines, binary interactions only.

Table I. The System Benzene (1)–Ethanol (2)–Water (3) at 348.15 K

Binary MVL Parameters			
i,j	A_{ij}	A_{ji}	C_{ij}
1, 2	1.47900	1.553474	0.06400
1, 3	6.47826	4.00000	0.44590
2, 3	1.67628	0.937150	0.00000
Ternary MVL Parameter = −0.6000			

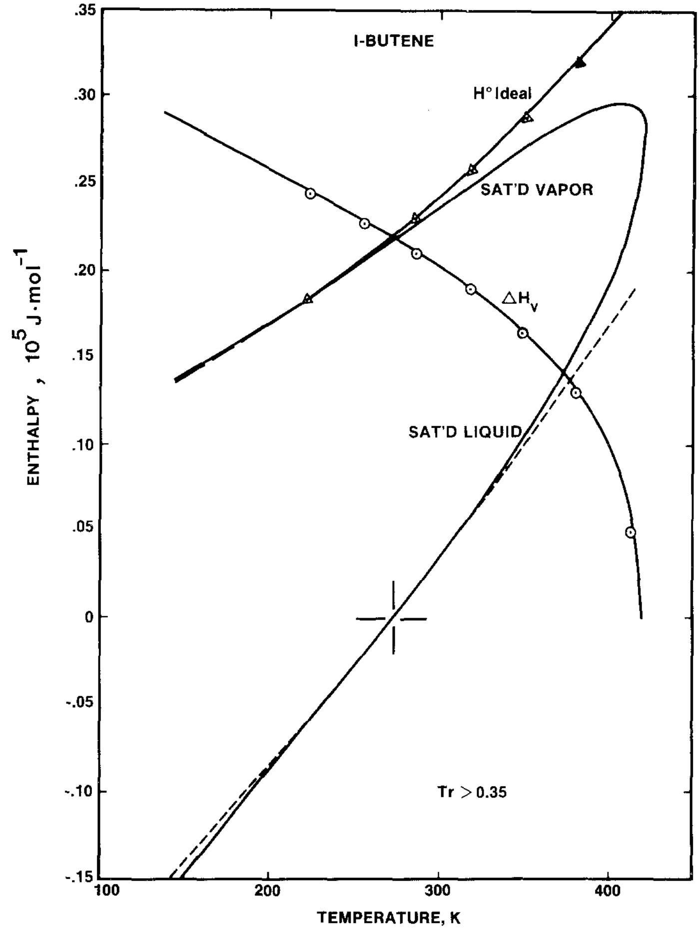

Fig. 6. Consistency of thermal properties for pure compounds.

Belousov [44] at 337.15 K, the data at a temperature nearest our calculated results. The triangular symbol shows the experimental [45] azeotropic composition. The predicted vapor composition, when the liquid composition is the azeotropic one, is shown by point X. The ternary coefficient was selected to give a reasonable representation for the tie lines at the ethanol concentration level of 20 to 35% mol.

Also shown in Fig. 5 via a few dashed tie lines is the representation when the ternary coefficient is set equal to zero. This prediction based on binary data alone gives tie lines which are too steep, sloping up from left to right, at high ethanol concentrations. As the ethanol concentration decreases, the two calculations approach each other. The binary mixtures are unchanged. When calculated from binary data alone, the system is too immiscible at high ethanol concentrations. The plait point is too high is ethanol concentrations and too low in water.

With the aid of one ternary parameter in addition to the usual binary parameters, both vapor–liquid and liquid–liquid equilibria can be calculated simultaneously. This is important when simulating an azeotropic distillation column for dehydrating aqueous ethanol using benzene as an entrainer.

3. PURE-COMPONENT THERMOPHYSICAL PROPERTIES

Since enthalpy data are interrelated, these data should be mutually consistent. As can be seen in Fig. 6, for 1-butene, ideal-gas enthalpies, departure corrections, saturated vapor enthalpies, heats of vaporization, and saturated liquid enthalpies must be mutually consistent. Liquid heat capacities should also be consistent with the saturated liquid enthalpies. When represented by analytical equations, it is important that the equations extrapolate properly above or below the range of the data for which they were developed.

At the AIChE meeting in Houston, April 1983, Black and Twu presented a paper describing the prediction of thermophysical properties for synthetic fuel compounds. Ideal-gas enthalpies were calculated from a modified Lee–Kesler equation. Fixed properties were calculated from the carbon number N and hydrogen deficiency, defined as Z in the equation C_NH_{2N+Z}. The Soave modification of the Redlich–Kwong equation (SRK) was used to calculate the departure corrections to provide saturated vapor enthalpies. Vapor pressures were predicted with the aid of a generalized reduced Frost–Kalkwarf equation.

3.1. Vapor Pressures via a Generalized Reduced Frost–Kalkwarf Equation

Vapor pressures can be predicted with the aid of a generalized reduced Frost–Kalkwarf equation.

$$\ln P_r^\circ = C_1 + C_2/T_r + C_3 \ln T_r + C_4 P_r^\circ/T_r^2 \tag{16}$$

where

$$C_1 = A_1 + \bar{\omega} A_4$$

$$C_2 = A_2 + \bar{\omega} A_5$$

$$C_3 = A_3 + \bar{\omega} A_6$$

$$C_4 = A_7$$

and

$$P_r^\circ = P^\circ/P_c, \qquad T_r = T/T_c$$

At the normal boiling point,

$$\bar{\omega} = \frac{\{[\ln(760/P_c) - A_7(760/P_c)/(T_r)_b^2] - f^\circ(T_r)_b\}}{f'(T_r)_b} \tag{17}$$

where

$$f^\circ(T_r) = A_1 + A_2/T_r + A_3 \ln T_r$$

$$f'(T_r) = A_4 + A_5/T_r + A_6 \ln T_r$$

$$(T_r)_b = T_b/T_c$$

Only the critical temperature and pressure and the normal boiling point must be known to make use of this vapor pressure equation.

3.2. Heat of Vaporization

With the aid of this vapor pressure equation and the Clapeyron relation, the heat of vaporization is readily calculated at the boiling point.

$$(\Delta H_v)_b = -RT_c(\Delta Z_v)_b \left[\frac{d(\ln P_r^\circ)}{d(1/T_r)}\right] \tag{18}$$

where

$$(\Delta Z_v)_b = (Z_b)_{\text{sat.vap.}} - (Z_b)_{\text{sat.liq.}}$$

Then the Watson relation is used to calculate the heat of vaporization at any temperature according to

$$(\Delta H_v)_T = (\Delta H_v)_{T_b} \left[\frac{T_c - T}{T_c - T_b}\right]^{0.378} \tag{19}$$

Subtracting the heat of vaporization from the saturated vapor enthalpies gives the enthalpies for the saturated liquid.

3.3. Checking, Extending, and Predicting Properties

The ability to start from the property which is best defined experimentally and calculate the other less well-defined properties provides a means of supplementing and testing the consistency and reliability of data. The generalized reduced Frost–Kalkwarf equation allows this to be done without experimental vapor pressure data. It is also the basis from which required thermophysical properties for compounds with no experimental data can be predicted from structure and boiling point. Indeed, the structural correlations of Lyderson [46] predict the criticals and those of Rihani and Doraiswamy [47] or Benson [48] furnish the ideal-gas heat capacity.

4. AVAILABILITY OF DATA FOR PROCESS SIMULATION

Simulating the design and operation of a process depends on the availability of the required thermophysical data for the pure components and their mixtures. The usual approach is to provide the pure-component data and calculate the values for the mixture. Handling and making these pure component properties available for process simulation depend somewhat on the computer hardware. Where main-frame computers are used, a private pure-components data library, e.g., 1000 compounds, can provide both fixed and temperature-dependent properties. If the storage capability of the smaller computers continues to grow and expand, private libraries will also be successful with these. Alternatively, process-oriented packages may become popular.

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