A GENERALIZED CORRESPONDING STATES METHOD FOR PREDICTING THE LIMITS OF SUPERHEAT OF MIXTURES

APPLICATION TO THE NORMAL ALCOHOLS†

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Abstract—The limits of superheat of the normal alcohols from methanol to octanol and of ethanol/n-propanol, n-propanol/n-butanol, and n-butanol/n-pentanol mixtures were measured at atmospheric pressure. The results were predicted using a new method based on the generalized corresponding states principle (GCSP) in which properties of two reference substances were used to predict the superheat limits of the liquids studied. Ethanol and n-butanol, and the two components of each mixture studied, were used as reference fluids for predicting the superheat limits of the pure alcohols and mixtures respectively.

Results showed that it is possible to predict superheat limits to well within the accuracy of measured values (< 1%). The method requires only accurate vapor pressure correlations and acentric factors of the reference fluids, and an accurate method for predicting the variation of the true critical mixture temperature with composition. It is shown that the GCSP reduces to an expression for the superheat limit of a mixture which is a mole fraction weighted average of the limits of superheat of the individual components in solution when the mixture and its components satisfies certain conditions. In the general case, both linear and nonlinear variations of mixture superheat limit with mole fraction can be predicted with the proposed method.

Considerable simplification using the GCSP over the approach based on classical homogeneous nucleation theory is derived from the fact that no mixture surface tension or bubble point pressure data are required.

1. INTRODUCTION

The limits of superheat of liquid mixtures are required in a number of applications involving problems associated with the vapor explosion phenomenon. Among these include the fragmentation or "microexplosion" phenomenon which occurs during combustion of fuel droplets which are miscible mixtures of liquids[1], and vapor explosion of LNG spills on water[2]. These effects are believed to be triggered by homogeneous bubble nucleation within the superheated region of the mixture which is relatively dilute in the nonvolatile components. A reliable method for predicting mixture superheat limits is therefore of great practical interest.

In this work, we describe a new method for accurately predicting the limit of superheat of liquids. The method is based on the so-called generalized corresponding states principle (GCSP)[3]. In this method, the superheat limits of two arbitrairly chosen reference fluids are used for predicting the superheat limits of the liquid in question. For mixtures, the reference fluids used are the mixture components. Because of their current environmental relevance, the normal alcohols and their mixtures were used as model test fluids to demonstrate the power of the present

method. For this purpose, we have measured the limits of superheat at atmospheric pressure of the pure normal alcohols from methanol to n-octanol, and of ethanol/n-propanol, n-propanol/n-butanol, and n-butanol/n-pentanol mixtures.

2. EXPERIMENTAL

The bubble column method[4–6] was used to measure the homogeneous nucleation temperature of the test alcohols. Modifications of the technique consisted of using a rope heater (Hottwatt Co. No. GR16-120 500 watt heater) to heat the field liquid, and a smaller diameter glass tube for the bubble column. The rope heater was found to be a significant improvement for controlling the field liquid temperature gradient over previous methods which used nichrome wire wrapped around the bubble column. Spacing between windings could easily be adjusted with the rope heater to provide a wide range of stable temperature gradients. The bubble column itself consisted of a glass tube 1.9 cm o.d., 1.3 cm i.d. and 56 cm long. A single thermocouple (Chromel/ Alumel) calibrated to ± 0.05K was used to measure the field liquid temperature at the level in the column at which the test droplets were observed to explode. The thermocouple was connected to a linear rack and pinion traversing mechanism to permit precise positioning of the thermocouple at any desired location in the bubble column.

The success of the method for achieving high liquid superheats is primarily dependent on choosing a field

liquid which is immiscible with the test liquid and has a boiling point higher than the superheat limit of the test liquid. For these reasons, the bubble column method has not often been used for measuring the superheat limits of polar liquids. Recent work[7, 8] has suggested that Krytox 143 AD, a perfluoroalkylpolyether oil manufactured by E. I. Dupont Co., has physical properties favorable for its use in bubble column experiments employing the normal alcohols as test liquid. Accordingly, we used this fluid as the field liquid in the present experiments.

The superheat limits at atmospheric pressure of the following pure liquids were measured: methanol, ethanol, n-propanol, n-butanol, n-pentanol, n-hexanol, n-heptanol and n-octanol. Ethanol/n-propanol, n-propanol/n-butanol and n-butanol/n-pentanol mixtures were also studied. All alcohols were obtained from the Aldrich Chemical Company with a stated purity of 99%, and were used directly as received (in particular, the alcohols were not degassed).

Intrinsic errors associated with this method are due to underheating of the test droplets due to their finite size, and heat losses through the thermocouple. The cummulative correction of these effects to measured nucleation temperatures has been estimated to be less than 2K[9] for droplet diameters (1 mm), rise velocities (3 cm/s), and field liquid temperature gradients (1K/cm) characteristic of the present experiments. Further details of the apparatus, procedures for obtaining the data, and experimental observations have been reported elsewhere[9, 10].

3. PREDICTING LIMITS OF SUPERHEATS

3.1 Introduction

Homogeneous nucleation theory leads to an expression for the nucleation temperature, T, of the following form[4]

$$T = \frac{\epsilon \sigma^3}{K(P - P_0)^2} \qquad (1)$$

where the proportionality constant ϵ is given by

$$\epsilon \simeq -\frac{16\pi}{3\beta} \qquad (2)$$

and

$$\beta \equiv \ln J - C < 0 \qquad (3)$$

where β is relatively insensitive to temperature and pressure. Equation (1) displays the essential dependence of T on physical properties, namely the surface tension cubed and vapor pressure squared. Inaccurate estimation of nucleation temperatures are principally due to inabilities to accurately predict the temperature dependence of these two properties at the high reduced temperatures (> 0.9 at $0.01 < P_0/P_c < 0.04$) characteristic of homogeneous nucleation. As such, superheat limit predictions for

mixtures in particular often turn into excercises for estimating the composition and temperature dependence of surface tension and, to some extent, bubble point pressure[5, 6]. It is therefore desirable to seek a means for predicting nucleation temperature which avoids these problems. Such a means is presented in the next two sections.

3.2 Corresponding states and the superheat limit

There is a theoretical upper value to the superheat limit at a given ambient pressure P_0 (the nucleation pressure). This limit falls on the so-called "spinodal" curve. For pure substances this curve is the locus of states for which[4]

$$\left.\frac{\partial P}{\partial V}\right|_{T,n} = 0. \qquad (4)$$

Similar though different expressions may be derived for multicomponent systems[11].

Because the spinodal curve is naturally part of a $P-V-T$ surface for a given substance, it should be subject to the law of corresponding states. Recent work by Lienhard and Karimi[12] has shown this to be the case. The limiting convergence of the thermodynamic (eqn 4) and kinetic superheat limits (eqn 1) on the liquid side leads to the conclusion that the kinetic superheat limit should also follow corresponding states[12, 13].

The great advantage of seeking to express the kinetic superheat limit in a corresponding states form is that, if successful, only the critical constants of the fluid in question and, possibly, one additional easily obtained parameter are required. We now present a generalized corresponding states method for the kinetic limit of superheat applicable to both pure liquids and mixtures which has these features.

3.3 A generalized corresponding states principle for the limit of superheat

The corresponding states theory as originally advanced by van der Waals assumed the existence of a universal relation between a generalized thermodynamic property of a given substance, α (in the present case the reduced nucleation pressure or temperature), and properties of a reference substance, α_0, of the form

$$\alpha = \alpha_0(T_r, P_r). \qquad (5)$$

This correspondence would, in principle, apply to any reduced thermodynamic property. In reality, the simple form of eqn (5) accurately represents the properties of only a relatively few substances which have come to be called "simple fluids"—Ar, Kr, Xe, CH_4. This fact led Pitzer et al.[14] to introduce a third parameter into eqn (5), in addition to P_r and T_r which would in principle improve volumetric property prediction. This parameter would be an expression of the deviation of real fluid behavior from that of a simple substance. The acentric factor,

defined as

$$\omega \equiv - \log_{10} P_r|_{T_r = 0.7} - 1 \qquad (6)$$

was empirically found to be nearly zero for simple fluids, and therefore used for this purpose. The acentric factor was incorporated in eqn (5) by means of a power series expansion around the properties of a simple fluid

$$\alpha = \alpha_0 + \omega \alpha_1 + \cdots \qquad (7)$$

where α_0, α_1, ... are each universal functions of T_r and P_r for the particular property α. Higher terms α_2, α_3, ..., failed to exhibit any definite variations with T_r and P_r[14]. Fortunately, the linear relation between α and ω expressed by eqn (7) has been found to be adequate for many substances.

The practical difficulty with eqn (7) is two-fold: (1) while α_0 is generally known with high precision, α_1 exhibits greater uncertainty; and (2) if the substance in question deviates significantly from the simple fluid predictive accuracy diminishes.

By expressing α_0 and α_1, in terms of reference fluid properties which are similar to the fluid in question, accuracy can be improved. Thus, if α_{r1} and α_{r2} denote thermodynamic properties of two reference fluids each of which follows the correspondence expressed by eqn (7), then we can write that

$$\alpha_{r1} = \alpha_0 + \omega_{r1} \alpha_1 \qquad (8)$$

and

$$\alpha_{r2} = \alpha_0 + \omega_{r2} \alpha_1. \qquad (9)$$

Eliminating α_0 and α_1 from eqns (7)–(9) yields

$$\alpha = \alpha_{r1} + \frac{\omega - \omega_{r1}}{\omega_{r2} - \omega_{r1}} (\alpha_{r2} - \alpha_{r1}) \qquad (10)$$

which was first presented by Teja[15]. Equation (10) is an expression of the generalized corresponding states principle (GCSP). Although it still preserves a linear relation between α and ω, improved predictions are achieved because of the absence of simple fluid properties, α_0, and potential inaccuracies in knowledge of the deviation function α_1.

Equation (10) has been successfully used to predict a variety of thermodynamic properties, including viscosity, thermal conductivity, vapor pressure, saturated liquid density, and surface tension[15–19]. Given that the limit of superheat is a well defined property (at a given pressure and nucleation rate), we use the GCSP to predict the superheat limits of liquids. For single component substances, we express our result in terms of reduced nucleation pressure—$\alpha \rightarrow P_{ro} \equiv P_o/P_c$. Equation (10) therefore becomes

$$P_{ro} = P_{ro1} + \frac{\omega - \omega_{r1}}{\omega_{r2} - \omega_{r1}} [P_{ro2} - P_{ro1}] \qquad (11)$$

where the P_{roi} are the reduced nucleation presures of the reference substances $i(P_{oi}/P_{ci})$ at the same reduced temperature (T/T_c) and nucleation rate as the substance in question. The choice of reference fluids is, in principle, arbitrary. In the present work, we chose ethanol and n-butanol as reference substances for pure liquids. Similar calculations using the normal alkanes as reference fluids—n-pentane and n-hexane—yielded results which were within a degree of those reported below in Table 1. Our results were suggestive of the possibility that superheat limits of pure substances predicted from eqn (11) might not generally be very sensitive to the choice of the reference fluids. The emphasis of this work was on mixture calculations, and for this purpose we used the mixture components as the reference fluids in the extension of eqn (10) to mixtures as described below.

The reference fluid nucleation pressures, P_{roi} in eqn (11), were calculated from a recently presented correlation of superheat limit data as[13]

$$P_{roi} = P_{rsi} - \frac{f_i}{\sqrt{-\beta}} (1 - T_{ri})^{1.83} \qquad (12)$$

where $T_{ri} = T/T_{ci}$. Although Lienhard[13] was able to achieve a correlation for f_i in terms of ω_{ri}, we preferred to determine f_i from our measurements. In this way, the full power of eqn (11) could be demonstrated by removing any question of accuracy of estimating reference fluid superheat limits. An average value of the kinetic prefactor C in eqn (3) was estimated from calculations reported previously[10] as $C \simeq 84.588$. This value differed by no more than 0.5% for all the pure fluids tested. Pure substance critical temperatures and pressures were obtained from the compilation of Reid *et al.*[21] and acentric factors were estimated from available data[22, 23]. For conditions of our experiment, a nucleation rate of $J \simeq 10^4$ nuclei/cm^3-s was found to be appropriate[9, 10] for all pure liquids and mixtures tested, and $P_0 = 0.101$ MPa.

Expressions for reduced saturation pressure of the reference substances, P_{rsi} in eqn (12), were obtained from the results of Gomez and Thodos[20]:

$$P_{rsi} = \exp [\beta_i(T_r^{-m_i} - 1) + \gamma_i(T_{ri}^7 - 1)] \qquad (13)$$

where the constants β_i, γ_i and m_i were obtained from the listing in Ref. [20]. Equations (11)–(13) were then combined ($i = 1, 2$) and the resulting equation solved numerically for temperature, given an ambient pressure, P_0, and a nucleation rate, J. In this solution, the reduced temperature of the reference substance becomes the reduced temperature of the liquid in question so that $T_{ri} \rightarrow T/T_c$ in eqns (12) and (13).

Table 1 lists measured and predicted (eqns 11–13) superheat limits of six pure alcohols. The overall absolute deviations between predicted and measured values is under 1%. The largest deviations exist for heptanol and octanol which, coincidently, are the two

Table 1. Comparison of predicted and experimental superheat limits of several n-alcohols at 0.101 MPa and $J \simeq 10^4$ based on known superheat limits of ethanol and n-butanol

n − alcohol	T_s(°K)	T_{exp}(°K)	T_{calc}(°K)	%error†
Methanol	337.8	462.2	462.6	.09
Ethanol	351.5	466.0	--	--
n-Propanol	370.4	487.4	491.3	.80
n-Butanol	390.9	511.9	--	--
n-Pentanol	411.0	531.5	529	.47
n-Hexanol	430.2	551.7	551.7	0.
n-Heptanol	449.5	566.3	572.9	1.17
n-Octanol	468.4	586.	594.2	1.40
Overall				.66%

$$†\%error = 100 \cdot \frac{|T_{exp} - T_{cal}|}{T_{exp}}$$

substances which exhibited the greatest difficulty in measurement[9]. Thus, the relatively high predictions for these two alcohols are more indicative of experimental difficulties than a defect in the predictive scheme.

The effect of ambient pressure and nucleation rate on the superheat limit of a pure liquid may also be predicted by eqn (11) (the dependence of superheat limit on J is carried entirely in β in eqn 12). This is illustrated in Table 3, where superheat limit data for methanol[4] are listed, along with values calculated from eqn (11). As shown in Table 3, $T/T_c \rightarrow 1$ as $P_0 \rightarrow P_c$, and eqns (11)–(13) accurately predict this trend. Also, as J increases at constant P_0 (see listing for $P_0 = 0.101$ MPa), eqn (11) accurately predicts the attendant increase in the superheat limit.

The GCSP may be extended to mixtures using the van der Waals one fluid model[3]. For this purpose we took the reduced superheat limit of the mixture as the generalized property in eqn (10): $\alpha \rightarrow T_{rm} \equiv T/T_{cm}$. Mixture superheat limits calculated using reduced temperature as the generalized property were the same as those calculated using reduced nucleation pressure of the mixture as the generalized property (as in eqn 11 for pure liquids). The result given below, however, is more illustrative when α is taken as reduced temperature for calculating the limit of superheat of a mixture.

Using the reference fluids as the mixture components, it can be shown that eqn (10) as applied to an n component mixture reduces to (see Appendix A)

$$T_{rm} = T/T_{cm} = \sum_{i=1}^{n} x_i T_{roi} \qquad (14)$$

where $T_{roi} \equiv T_{ni}/T_{ci}$. The T_{ni} are the superheat limits of the mixture components at the *same reduced pressure*

and nucleation rate as the mixture, and T_{cm} is the critical temperature of the mixture which may be a complicated function of mole fraction. The T_{ni} will be dependent on mixture composition through the variation of P_{cm} with x_i because $P_{roi} \rightarrow P_0/P_{cm}$ (and $T_{ri} \rightarrow T_{roi}$ in eqn 12). Thus, the precise variation of the mixture superheat limit itself with mole fraction in eqn (14) is not generally known (and is certainly not linear in the general case). The T_{roi} may be calculated from eqns (11)–(13) if the superheat limits of the mixture components are not known, but the limits of superheat of two similar reference fluids are available. In the present work it was found that values of T_{ni} calculated from eqns (1) or (11)–(13) were essentially constant (to the fourth significant digit) over the range of mixture critical pressures (calculated from formulations presented in Ref. [24]) corresponding to $0 \leq x_i \leq 1$. Thus, values of T_{ni} were taken directly from Table 1 with no loss of accuracy. Finally, the true critical temperatures of the mixtures were calculated from the method of Chueh and Prausnitz[24], with the appropriate binary interaction constants obtained from available data[25].

Table 2 illustrates the results. The agreement between measured and predicted superheat limits is excellent. The overall agreement between calculated and measured values is 0.28%, which is far better than could be obtained by solving eqn (1) directly using best estimates for the temperature and composition dependence of surface tension and vapor pressure.

Figures 1–3 graphically illustrate the variation of mixture superheat limit (Table 2) with composition. As shown in these figures, the limits of superheat of the binary normal alcohol mixtures we studied vary nearly linearly with mole fraction. This observation is not unique, as others have also noted similar results for other mixtures (e.g. [4–6]).

Table 2. Comparison of experimental and predicted superheat limits of several binary n-alcohol mixtures at 0.01 MPa and $J \simeq 10^4$

Mixtures	Mole Fraction Second Component	T_{exp}(°K)	T_{calc}(°K)	%error†
C_2H_5OH/C_3H_7OH	.08	468.1	467.2	.19
	.251	471.6	470.2	.30
	.439	475.7	474.0	.36
	.646	480.2	478.7	.31
	.875	484.3	484.2	.02
C_3H_7OH/C_4H_9OH	.083	488.2	488.7	.10
	.259	493.8	491.9	.38
	.450	498.7	496.2	.50
	.656	504.4	501.5	.57
	.880	509.2	508.1	.22
$C_4H_9OH/C_5H_{11}OH$	.086	511.6	513.0	.27
	.266	513.2	515.7	.49
	.458	518.7	519.1	.08
	.664	525.2	523.4	.34
	.884	529.2	528.6	.11
Overall				.28%

†%error $= 100 \cdot \left| \dfrac{T_{exp} - T_{calc}}{T_{exp}} \right|$

Table 3. Comparison of predicted superheat limits (T_{cal}) of methanol (using eqn 11 with the known superheat limits of ethanol and n-butanol at 0.101 MPa and $J \simeq 10^4$ as reference fluids) with measured values[4] (T_{exp}) at various ambient pressures (P_0) and nucleation rates (J)

P_0 (MPa)	J (nuclei/cm³−s)	T_{exp} (°K)	T_{cal}†† (°K)	% error†††	T_{exp}/T_c (°K/°K)
.101	10^4	462.2†	462.6	.09	.902
.101	3.2×10^{19}	469.2	470.5	.28	.915
1.04	10^{20}	471.2	472.5	.28	.919
2.0	3.2×10^{20}	478.2	476.6	.33	.933
2.96	3.2×10^{21}	482.2	481.1	.23	.941
3.95	10^{22}	488.7	485.8	.59	.953
4.91	3.2×10^{22}	494.7	490.7	.81	.965
5.89	10^{23}	501.2	496.2	1.00	.978
6.87	3.2×10^{23}	507.7	502.5	1.02	.99
overall				.51%	

†   This Study (Table 1)

††   Equation (11)

††† *%error $= 100 \cdot \left| \dfrac{T_{exp} - T_{calc}}{T_{exp}} \right|$
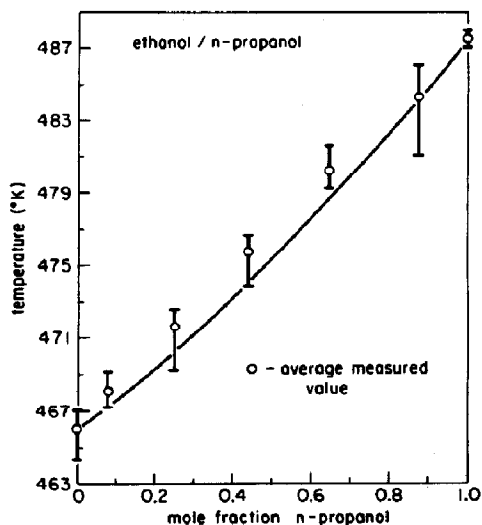
Fig. 1. Variation of limit of superheat with mole fraction for an ethanol/n-propanol mixture at $J \simeq 10^4$ nuclei/cm^3-s and $P_0 = 0.101$ MPa. Solid line is prediction of eqn (14) with the T_{ni} taken from Table 1.
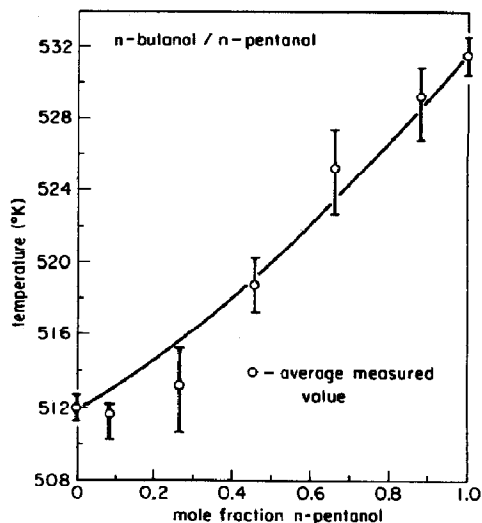

Fig. 3. Variation of limit of superheat with mole fraction for an n-butanol/n-pentanol mixture at $J \simeq 10^4$ nuclei/cm^3-s and $P_0 = 0.101$ MPa. Solid line is prediction of eqn (14) with the T_{ni} taken from Table 1.
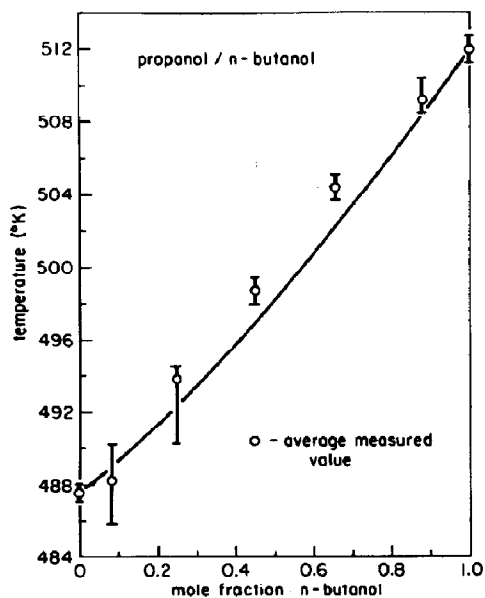

Fig. 2. Variation of limit of superheat with mole fraction for an n-propanol/n-butanol mixture of $J \simeq 10^4$ nuclei/cm^3-s and $P_0 = 0.101$ MPa. Solid line is prediction of eqn (14) with the T_{ni} taken from Table 1.

It is interesting to examine the conditions under which eqn (14) reduces to an expression for mixture superheat limit which varies linearly with mole fraction. Equation (14) shows only that the *reduced* superheat limit of a mixture is a mole fraction weighted average of the *reduced* limits of superheat of the mixture components. This fact is generally *not* equivalent to assuming that the superheat limit of a mixture itself varies linearly with mole fraction.

Assuming for a particular mixture that its critical temperature is a simple mole fraction weighted sum of the critical temperature of the mixture components,

$$T_{cm} = \sum_{i=1}^{n} x_i T_{ci},\qquad (15)$$

and that for solution components i the T_{roi} are the same (e.g. see Table 1), then in view of the fact that $\sum_{i=1}^{n} x_i = 1$ eqn (14) reduces to

$$T = \sum_{i=1}^{n} x_i T_{ni}\qquad (16)$$

which is the desired result. Though eqn (16) has been experimentally verified for a number of mixtures as noted above, it has not apparently been derived before.

It is clear that eqn (16) is not a universal result, though the contrary has often been implied in the literature. The critical temperature of a mixture is not generally given by eqn (15), nor are the reduced superheat limits of the mixture components generally equal at the same reduced pressure and nucleation rate. The more general eqn (14) should be used to predict the limit of superheat of a mixture. The only restrictions on eqn (14) are that the mixture be treated as a pseudo pure component and that the mixture components follow the correspondence expressed by eqn (7).

That eqn (14) is capable of representing nonlinear variations of superheat limit will mole fraction is illustrated in Fig. 4 for the cyclohexane/benzene system. This particular mixture was chosen for com-
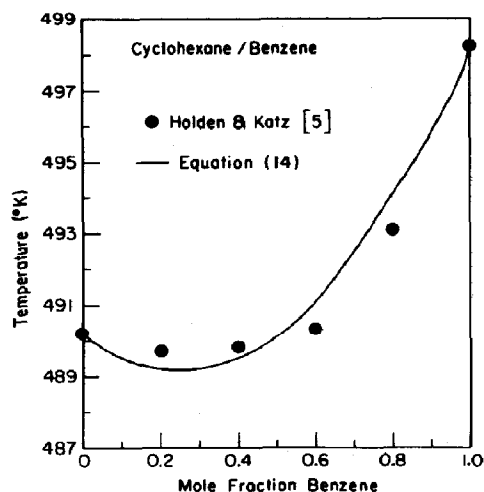
Fig. 4. Variation of limit of superheat with mole fraction for a cyclohexane/benzene mixture at $J \simeq 10^4$ nuclei/cm^3-s and $P_0 = 0.101$ MPa. Measured values were obtained from Ref. [5] and calculations were made using eqn (14).

parison because its critical temperature has been accurately measured for a variety of compositions[26], thus minimizing any ambiguities in predicting this quantity (required in eqn 14). Super-heat limit data were obtained from Holden and Katz[5] ($P_0 = 0.101$ MPa and $J \simeq 10^4$ nuclei/cm^3-s). The T_{roi} for benzene and cyclohexane were again found to be constant over the range of critical pressures corresponding to $0 < x_i < 1$, thus obviating the need to calculate these quantities from eqns (1) or (11)–(13): the measured values corresponding to $x_i = 1$ at 0.101 MPa were used. The agreement be-tween measured superheat limits and values calcu-lated from eqn (14) is excellent as shown in Fig. 4, and is certainly far better than could be obtained by assuming eqn (16) was valid. Equation (14) is also much easier to use than eqn (1), with only an accurate method for predicting the true critical temperatures of the mixture (and to a lesser extent the true critical pressure) being required.

CONCLUSION

The GCSP has been used to accurately predict superheat limits of pure liquids and mixtures. With suitable choices for the reference fluids, good agree-ment can be achieved for pure component superheat limits. For mixtures, it is best to use the mixture components as reference fluids, and the true critical temperature and pressure of the mixture.

NOTATION

C kinetic prefactor, eqn (3)
f_i arbitrary function of ω_i for species i, eqn (12)
J nucleation rate
K Boltzmann constant
n number of moles
P pressure
P_0 ambient (or nucleation) pressure
P_{oi} nucleation pressure of fluid i
T temperature
T_{ni} limit of superheat of reference fluid i
x mole fraction

Greek symbols
α generalized reduced thermodynamic property
α_0 generalized property for a simple fluid
α_{ri} generalized property for a reference fluid i
β defined by eqn (3)
ϵ defined by eqn (2)
ω acentric factor
ω_{ri} acentric factor for reference fluid i

Subscripts
c critical property
cm mixture critical property
i species i
ri reduced property of species i
ro reduced ambient quantity
roi reduced ambient quantity for reference species i
rse reduced saturation quantity for reference spe-cies i

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APPENDIX A

The two fluid expansion for a property α of a pure substance—eqn (10)—may be extended to yield an expression for predicting the same property of an n component mixture in terms of the mixture component properties. The purpose of this Appendix is to show how this can be done.

Taking α_{r1} to be the property of the mth *component* in the n component mixture ($m \leq n$), and α_{r2} to be the property of a *mixture* containing m-1 components consisting of n_1 moles of 1, n_2 moles of 2, ... up to n_{m-1} moles of the $m-1$st component, eqn (10) becomes

$$\alpha_{12\ldots m} = \alpha_m + \frac{\omega_{12\ldots m} - \omega_m}{\omega_{12\ldots m-1} - \omega_m}(\alpha_{12\ldots m-1} - \alpha_m) \quad (A1)$$

where $\alpha_{12\ldots m}$ is the property of a mixture containing m components (similarly for $\alpha_{12\ldots m-1}$), α_m is the property of the mth component, $\omega_{12\ldots m}$ is the acentric factor of an m component mixture (similarly for $\omega_{12\ldots m-1}$), and ω_m is the acentric factor of the mth component in the mixture in question which contains $n(>m)$ total components. The mixture referred to by the subscript notation $12\ldots m$ is one containing the *same* number of moles of each component as the original mixture (which contains $n > m$ components). A mixture of m components is thus a subset of one containing n components.

The term containing the acentric factors on the right hand side of eqn (A1) can be expressed in terms of mole fraction as follows. The acentric factor of an m component mixture is given by

$$\omega_{12\ldots m} = \frac{\sum_{j=2}^{m+1} n_{j-1}\omega_{j-1}}{\sum_{j=2}^{m+1} n_j - 1} \quad (A2)$$

where ω_{j-1} is the acentric factor of the $j-1$st component in the mixture and n_{j-1} is the corresponding number of moles of that component. Now $\sum_{j=2}^{m+1} n_{j-1} \neq n$ unless $m = n$ in which case

$$n = \sum_{j=2}^{n+1} n_{j-1} = \sum_{j=2}^{m+1} n_{j-1} + \sum_{j=m+2}^{n+1} n_{j-1}. \quad (A3)$$

Since

$$x_{j-1} = \frac{n_{j-1}}{n} \quad (A4)$$

and

$$\sum_{j=2}^{n+1} x_{j-1} = 1 = \sum_{j=2}^{m+1} x_{j-1} + \sum_{j=m+2}^{n+1} x_{j-1} \quad (A5)$$

eqns (A2)–(A5) can be combined to yield

$$\omega_{12\ldots m} = \frac{\sum_{j=2}^{m+1} x_{j-1}\omega_{j-1}}{\sum_{j=2}^{m+1} x_{j-1}}. \quad (A6)$$

Finally, since

$$\sum_{j=2}^{m+1} x_{j-1}\omega_{j-1} = x_m\omega_m + \sum_{j=2}^{m} x_{j-1}\omega_{j-1} \quad (A7)$$

we have that

$$\frac{\omega_{12\ldots m} - \omega_m}{\omega_{12\ldots m-1} - \omega_m} = \frac{\sum_{j=2}^{m} x_{j-1}}{\sum_{j=2}^{m+1} x_{j-1}}. \quad (A8)$$

Substituting eqn (A8) into eqn (A1) yields

$$\alpha_{12\ldots m} = \alpha_m + A_m(\alpha_{12\ldots m-1} - \alpha_m) \quad (A9)$$

where in general

$$A_i \equiv \frac{\sum_{j=2}^{i} x_{j-1}}{\sum_{j=2}^{i+1} x_{j-1}} \quad (A10)$$

and $2 \leq m \leq n$. (In eqn A10 we define $A_i = 0$ for $i = 1$.)

In the set of eqns (A9), the α_m are known, but the mixture properties—$\alpha_{12\ldots m}$—are not (indeed the intent is to express any mixture property in terms of its corresponding component properties). Thus, eqn (A9) will only be useful if we can eliminate the mixture properties appearing therein. The easiest way to accomplish this is by first writing out the set of eqns (A9) as follows. (Note that $\alpha_{12\ldots n} \equiv \alpha$ is the property of the n component mixture we are seeking to express in terms of its component properties, $\alpha_1, \alpha_2, \ldots, \alpha_n$.)

$$m = n: \quad \alpha = \alpha_n A_n(\alpha_{12\ldots n-1} - \alpha_n)$$

$$m = n-1: \quad \alpha_{12\ldots n-1} = \alpha_{n-1} + A_{n-1}(\alpha_{12\ldots n-2} - \alpha_{n-1})$$

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$$m = 3: \quad \alpha_{123} = \alpha_3 + A_3(\alpha_{12} - \alpha_3)$$

$$m = 2: \quad \alpha_{12} = \alpha_2 + A_2(\alpha_1 - \alpha_2).$$

By successively back substituting in the above set of equations to eliminate $\alpha_{12}, \alpha_{123}, \ldots, \alpha_{12\ldots n-1}$ we find that

$$\alpha = \alpha_n(1 - A_n) + \alpha_{n-1}A_n(1 - A_{n-1})$$
$$+ \alpha_{n-2}A_nA_{n-1}(1 - A_{n-2}) + \cdots. \quad (A11)$$

In more compact notation, eqn (A11) can be written as

$$\alpha = \alpha_n(1 - A_n) + \sum_{i=1}^{n-1} \alpha_i(1 - A_i) \prod_{k=i+1}^{n} A_k. \quad (A12)$$

In view of eqn (A10), it is easy to show that

$$(1 - A_i) \prod_{k=i+1}^{n} A_k = x_i \quad (A13)$$

and

$$(1 - A_n) = x_n. \quad (A14)$$

Equation (A12) can therefore be written as

$$\alpha = \sum_{i=1}^{n} x_i \alpha_i. \qquad \text{(A15)}$$

For

$$\alpha_i = T_{roi} = T_{ri}/T_{ci}$$

and

$$\alpha = T_{rm} = T/T_{cm},$$

eqn (A15) yields

$$T_{rm} = T/T_{cm} = \sum_{i=1}^{n} x_i T_{roi} \qquad \text{(A16)}$$

which is eqn (14).