N	number of components in a mixture
P	total pressure
P_i°	vapor pressure of pure component i
V_i^l	liquid molar volume of component i
T	absolute temperature
T_i°	boiling temperature of pure component i
t	temperature in °C
x_i, y_i	mole fraction of component i in the liquid and vapor phases
y	local deviation from observed values, $y = (y_{\text{obsd}} - y_{\text{calcd}})/y_{\text{obsd}}$
γ_i	activity coefficient of i
σ^2	error variance, eq 6
Δx, ΔP, Δt	errors in measurements of concentration, pressure, and temperature

Subscripts and Superscripts

calcd	calculated
obsd	observed
l	liquid phase
i	component i
max	maximum
min	minimum

Registry No. Methanol, 67-56-1; acetone, 67-64-1; methyl ethyl ketone, 78-93-3.

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Prediction of Multicomponent Azeotropic Latent Heats by Correlations for Pure Substances

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The idea that multicomponent mixtures may be considered in their behavior as a single component led to exploring the possibility of predicting the latent heat of vaporization of such mixtures by means of correlations, originally developed for a pure substance. The characteristic properties of the mixture were introduced into the single-component correlations through the physical properties: critical volume, critical temperature, and the acentric factor. Out of 20 correlations for predicting heat of vaporization of pure substances which were explored, the following three correlations were found most successful on the basis of being able to predict the latent heat of azeotropic mixtures within the accuracy needed for practical uses: (a) the Lee–Kesler correlation (eq 1) showing a relative mean deviation from observed data of $\bar{D}$ = 6.2% for 103 binary mixtures and $\bar{D}$ = 2.6% for 13 ternary mixtures; (b) the Nath correlation (eq 2) which has $\bar{D}$ = 6.2% for binary mixtures and $\bar{D}$ = 2.9% for ternary mixtures; (c) the Pitzer correlation (eq 3) which has $\bar{D}$ = 6.1% for binary mixtures and $\bar{D}$ = 3.9% for ternary mixtures.

Introduction

According to Tamir (*1*) about 90% of the data on the heat of vaporization correspond to a single component and about 10% to binary mixtures and systems with more than two components. Moreover, the experience accumulated in measuring heats of phase change for single components and mixtures indicated that it is not an easy task and that the amount of work required is quite enormous. Thus, developing means for predicting the heats of phase change for multicomponent mixtures from data of the pure components forming the mixtures is of utmost importance.

The objective of the present study is to explore the possibility of using available single-component correlations for the latent heat of vaporization with a view to predicting this quantity for multicomponent azeotropic mixtures which are important, for example, in distillation processes. The heat of phase change, by itself, is a most important property needed in the design of equipment for transfer of heat and it is also useful for testing thermodynamic theories related to the behavior of pure fluids and mixtures.

The approach of predicting azeotropic heats of vaporization by using pure component correlations stems from the so-called "single-component theory" of azeotropes in a multicomponent system developed by Licht and Denzler (*2*) which leads to the following conclusions: (1) The Clausius–Clapeyron equation for multiazeotropes becomes identical with that for a pure substance. (2) As a result of the above conclusion, every azeotrope will possess a vapor pressure–temperature curve which will have properties precisely like those of the ordinary vapor pressure curve of a pure substance. (3) The latent heat of vaporization of the azeotropic mixture may be estimated by methods similar to those for a single component.

Correlations for the Azeotropic Latent Heat

In exploring the above approach, we tested 20 single-component correlations from which we recommend for practical applications only 3. The following correlations were selected on the basis of being able to predict the multicomponent latent

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Table I. Relative Deviations from Observed Values for 103 Binary and 13 Ternary Azeotropic Mixtures[a]

binary system	$\bar{D}$, % eq 1	$\bar{D}$, % eq 2	$\bar{D}$, % eq 3
total mean for 103 systems	5.1	5.0	4.7

ternary systems	L, J/(kg-mol)	D, % eq 1	D, % eq 2	D, % eq 3
cyclohexane–benzene–ethanol[b]	33.9	1.6	−4.3	−0.3
cyclohexane–benzene–propanol[b]	32.8	0.1	−2.9	1.4
cyclohexane–benzene–2-methyl-1-propanol[b]	31.8	1.3	−1.9	2.6
cyclohexane–benzene–butanol[b]	31.4	1.2	−1.9	2.6
benzene–ethanol–water[c]	35.0	−2.5	−4.1	−0.4
ethyl acetate–ethanol–water[c]	35.7	2.4	1.1	5.5
trichloroethylene–ethanol–water[c]	36.2	−2.3	−3.8	−0.1
propanol–benzene–water[c]	35.6	3.0	1.4	4.8
pyridine–acetic acid–heptane[d]	32.3	−1.8	−6.1	0.7
pyridine–acetic acid–octane[d]	36.8	2.6	−0.4	5.8
pyridine–acetic acid–nonane[d]	40.4	5.8	3.6	9.1
pyridine–acetic acid–decane[d]	42.0	7.2	5.8	11.1
pyridine–acetic acid–undecane[d]	39.8	1.7	0.4	6.1
total mean for 13 systems		2.6	2.9	3.9

[a] $D\ (\%) = (100/m)\sum_{i=1}^{m}|(L - L_{\text{calcd}})/L|_i$; $\bar{D}\ (\%) = (1/s)\sum_{i=1}^{s}|D_i|$; $m = 1$ and $s = 13$ for the ternary systems. [b] Swietoslawski (7). [c] Licht (2). [d] Pawlak (8).

heats within deviations of 2.5–6% from observed values, which is in the range of the accuracy needed for practical uses:

Lee–Kesler correlation (Reid et al. (3))

$$L = RT_c[6.09648 - 1.2886T_r + 1.0167T_r^7 + \omega(15.6875 - 13.4721T_r + 2.615T_r^7)] \quad (1)$$

Nath correlation (4) for $0.5 \leq T_r \leq 0.7$

$$L = RT[31.4589 - 58.0378T_r + 33.86T_r^2 + \omega(68.0973 - 147.6182T_r + 91.3371T_r^2) + \omega^2(43.5305 - 127.3007T_r + 91.8686T_r^2)] \quad (2)$$

Pitzer correlation (Reid et al. (3)) for $0.6 < T_r \leq 1$

$$L = RT_c[7.08(1 - T_r)^{0.354} + 10.95\omega(1 - T_r)^{0.456}] \quad (3)$$

where T is in kelvin, $R = 1.987$ cal/(g-mol K), and hence L is in cal/(g-mol).

For the evaluation of the critical temperature of the mixture the Li equation (5) was used, namely

$$T_c = \sum_{i=1}^{c} \phi_i T_{ci} \quad (4)$$

where

$$\phi_i = \frac{x_i V_{ci}}{\sum_{i=1}^{c} x_i V_{ci}} \quad (5)$$

The mixture acentric factor is given by the approximation (Reid et al. (3))

$$\omega = \sum_{i=1}^{c} x_i \omega_i \quad (6)$$

Results and Discussion

The data of the pure components needed for the calculations—T_{ci}, V_{ci}, and ω_i—were taken from Reid et al. (3). The test of correlations 1–3 was performed by comparing the predicted values with observed values of 22 binary systems reported in ref 9 and with 81 binary mixtures for which the azeotropic vapor pressure vs. temperature was reported by Tamir (6) in the form of a P–T correlation. This resulted in the azeotropic heat of vaporization, L, being given by the following equation:

$$L = -R(B_1 - C_1T^2) \quad (7)$$

The parameters B_1 and C_1 for azeotropic mixtures were reported in ref 6. Ternary data for the azeotropic heat of vaporization, reported in Table I, at almost 1 atm, were taken from Licht (2), Swietoslawski (7), and Pawlak (8). The azeotropic heats of Licht are based on vapor pressure data, and those of Swietoslawski and Pawlak were measured directly in a calorimeter.

Table I demonstrates the goodness of prediction of the azeotropic latent heat for 103 binary systems and for 13 ternary systems by correlations developed originally for pure substances. The goodness of prediction is evaluated by the relative deviation D (%) from observed values or data derived from the P–T correlations, and by the overall deviation, $\bar{D}$ (%), which is the mean value for all systems corresponding to a certain correlation equation. For the binary mixtures the following procedure was adopted: for each system, L was calculated for about 10 temperatures within the range of temperatures for which eq 7 is valid. For each temperature, the composition of the binary mixture was calculated from

$$X_1 = A_2 + B_2T$$

where the parameters B_2 and A_2 were reported by Tamir (6). When the composition is known, it is possible to calculate the physical properties by means of eq 4–6. For ternary mixtures, Table I gives the D's (%) for each system and its variation with a correlating equation. The behavior demonstrated in the table, for the ternary mixtures, is also typical of the behavior of the binary mixtures not mentioned here. The following conclusions have been drawn from Table I: (a) For binary mixtures all correlations have the same prediction ability of the azeotropic heat of vaporization, where $\bar{D}$ is about 6%. (b) For ternary mixtures the Lee–Kesler correlation (eq 1) is the best with $\bar{D} = 2.6\%$. The correlations of Pitzer and Nath show $\bar{D} = 2.9\%$ and 3.9%, respectively.

Finally, it should also be noted that the good agreement between the predicted latent heats and the observed values gives confidence that the correlating equations 1–3 would also be appropriate for mixtures composed of four components and more which were not tested, because of a lack of observed values for comparison.

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Glossary

c	number of components
D	relative deviation from observed value defined by $(100/m)\sum_{i=1}^{m}\|(L - L_{\mathrm{calcd}})/L\|_i$, %
$\bar{D}$	overall deviation defined by $(1/s)\sum_{i=1}^{s}\|D_i\|$, %
L	azeotropic heat of vaporization based on a direct measurement of this quantity, or derived from vapor pressure data
L_{calcd}	azeotropic heat of vaporization calculated on the basis of eq 1–3
m	number of observations
R	universal gas constant = 1.987 cal/(g-mol K)
s	number of systems
T	absolute temperature
T_{c}	true critical temperature of the mixture
$T_{\mathrm{c}i}$	critical temperature of pure i
T_{r}	reduced temperature defined by T/T_{c}
$v_{\mathrm{c}i}$	critical volume of pure i
x_i	mole fraction in the liquid phase
ω	acentric factor of the mixture defined by eq 6
ω_i	acentric factor of pure i

Subscripts

c	critical
i	of pure component i

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Isobaric Vapor–Liquid Equilibria for the Partially Miscible System of Water–Methyl Isobutyl Ketone

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Isobaric vapor–liquid equilibria of the partially miscible system water–methyl isobutyl ketone have been measured at 760 mmHg in the miscible region by using a Smith and Bonner still. The data have been correlated with Wilson's three-parameter equation by using a nonlinear regression technique. The data satisfy Herington's area test.

Introduction

Vapor–liquid equilibrium (VLE) data for the water–methyl isobutyl ketone (MIBK) binary system have been measured at 760 mmHg. To our knowledge, VLE data for this partially miscible system are not available in the literature. Water-saturated MIBK is used (*1*) as a solvent in the petroleum industry for wax deoiling and dewaxing of high oil content waxes and lube distillates, respectively. The wet MIBK solvent is recovered by distillation for recycling. Knowledge of mutual solubilities and VLE data is, therefore, essential in designing a distillation column. The VLE data generated on the water–MIBK system as a part of our VLE studies have been correlated by the Wilson equation.

Experimental Section

MIBK supplied by M/s. NOCIL, India, was purified by fractional distillation at high reflux ratio in an Oldershaw column. The density (d^{20}_4 = 0.8025) and refractive index (n^{20}_{D} = 1.3960) values of distilled MIBK compare well with those reported in the literature (*2, 3*) (d^{20}_4 = 0.8024; n^{20}_{D} = 1.3958) for pure product. The water used was doubly distilled and was checked for its purity.

***Apparatus*.** The VLE data for the water–MIBK system were generated in a Smith and Bonner still (*4*) provided with a magnetic stirrer. The still was thoroughly lagged to avoid heat losses by conduction. The equilibrium vapor temperatures were measured by a mercury-in-glass thermometer with an accuracy of ±0.05 °C and a stem correction (*5*) was applied for the exposed stem.

The pressure of the system was maintained at 760 ± 0.5 mmHg with the help of a suitable pressure regulating device. The still was operated for about 3 h. At the end about 2 mL of the vapor sample was withdrawn for analysis.

***Analysis*.** In all experiments about 400 g of the liquid charge of known composition was taken in the still and assumed to be unaltered after deducting the known constant holdup (based on its composition and weight) of condensed vapors in the side recirculation tube of the still. The vapor sample was condensed and weighed and transferred into a washing apparatus shown in Figure 1. Care was taken to transfer the total contents into the mixer, b, through a micropipet, a. The sampling tube was then thoroughly rinsed with water and the contents were also transferred into the mixer as above. The mixer, b, contained about 50 mL of water filled up to the $^3/_4$th mark with the proper adjustment of the level of funnel d. The funnel stopper and the micropipet stopcock were then closed and the contents in the mixer were shaken well (vertically). After mixing, the contents were allowed to settle. The micropipet stopcock was then opened and the contents in the mixer, b, were slowly raised into the micropipet with constant tapping of the mixer and by taking up slowly the funnel, d. The micropipet was graduated up to 0.02 mL. The exact volume of MIBK was noted at room temperature. The density of MIBK was taken from the density–temperature graph prepared from the data available in the literature (*6*). Knowing the density of MIBK at room temperature (about 27 ± 2 °C) and mutual solubilities (*3*) of water and MIBK, we calculated the amount of dissolved water in MIBK

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