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Ternary Vapor–Liquid Equilibria at 760 mmHg in the System Methanol–Acetone–Methyl Ethyl Ketone

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The vapor–liquid equilibria for the ternary system methanol–acetone–methyl ethyl ketone was determined at 760 mmHg by using a Dvorak and Boublik recirculation still. The data were correlated by means of the Wilson and Redlich–Kister equations. Direct correlation of the ternary data without considering binary data was found very efficient. Boiling points of the ternary mixture were predicted by an empirical correlation within a mean error of ±0.7%.

Introduction

The aim of the present study was to establish new vapor–liquid equilibria at 760 mmHg for the ternary system methanol–acetone–methyl ethyl ketone (MEK) and to check the possibility for its prediction from available binary data.

The possibility and the advantage of direct correlation of the ternary data without considering the binary data was also checked.

The following binary data were employed: for methanol–acetone the data of Gmehling (*1*), for methanol–MEK the data of Eduljee and Tiwari (*2*), and for acetone–MEK the data of Othmer (*3*).

It should be noted that we did not reproduce any binary data because they seemed reliable on the basis of the reported accuracy and their being thermodynamically consistent.

Analytical-grade reagents purchased from Merck and Frutarom (Haifa, Israel) were used. The physical properties of the pure component (refractive index and boiling point which were measured in our equilibrium still) agreed with literature data. The equilibrium determinations were made in a modified all-glass Dvorak and Boublik recirculation still (*4*) and the experimental features have been described previously (*5*). All analyses were carried out by gas chromatography on a Packard-Becker Model 417 apparatus provided with a thermal conductivity detector and an Autolab Minigrator type of electronic integrator. The chromatographic column was packed with OV17-20% and operated isothermally at 50 °C. The injector temperature was 130 °C and the detector was operated at 170 °C.

Treatment of the Data

The correlation of ternary data by a series expansion of the Redlich–Kister type is usually based on the binary data; the ternary data are used to compute the so-called ternary constant. The magnitude of this constant also gives an indication of whether it is possible to predict the ternary data from the binaries alone. When handling multicomponent data, one can avoid complex equations and a large number of adjustable variables by direct correlation of the available information, without consideration of lower order data (namely, the binary data in the case of ternary mixtures or binary and ternary data in the case of quaternary mixtures, etc.). It has been shown elsewhere (*6*) that direct correlation can be more efficient for the following arguments: (1) fewer parameters are needed in the correlated equations for the same degree of the fit of data; and (2) for an identical number of parameters, the goodness of the fit is better by means of direct correlation of the multicomponent data. The above conclusions will be demonstrated here since the binary data are available.

The following equations were used for correlating the multicomponent vapor–liquid equilibria data:

(a) An equation which relates the boiling temperature of the mixture with the liquid composition solely has been derived (*6*) on the basis of the concept of "excess property", and it reads

$$T = \sum_{i=1}^{N} x_i T_i^\circ + \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} x_i x_j [A_{ij} + B_{ij}(x_i - x_j) + C_{ij}(x_i - x_j)^2 + ...] \quad (1)$$

Equation 1 is useful because of the following reasons:

(1) It may be used for correlating directly multicomponent boiling-temperature data solely vs. liquid composition, namely, to correlate for example ternary data without considering binary data. In other words, the parameters A_{ij}, B_{ij}, C_{ij}, etc., are obtained by fitting directly the ternary data by eq 15, which is an expansion of eq 1 for $N = 3$.

(2) When the parameters are established, eq 1 may be used for exploring azeotropic behavior (*6*) by solving simultaneously the set of equations $\partial T/\partial x_i = 0$, $i = 1, 2, ..., N - 1$ for the azeotropic composition $x_1, x_2, ..., x_{N-1}$ as well as the azeotropic-point boiling temperature.

(3) It may be used for obtaining isothermals as shown in Figure 1 and (4) to obtain the boiling temperature of a mixture for a given liquid composition.

(5) In condenser calculations, the most important magnitude is the vapor–liquid interfacial temperature which determines the condensation heat flux. Under total condensation, it may be calculated as follows: under such conditions, the condensate composition is equal to the vapor composition. Thus, the substitution of this composition in eq 1 yields the interfacial temperature.

For binary mixtures the second summation of the right-hand side of eq 1 is exactly that suggested by Redlich and Kister (*7*). For multicomponent mixtures, we kept the binary form of the Redlich and Kister equation, but the significance of the equation is different from that suggested by them in the sense that coefficients A_{ij}, B_{ij}, etc., are not binary constants; namely, they are not determined from the binary data. These coefficients are multicomponent parameters which are determined directly from the multicomponent data.

An equation for correlating boiling temperatures of multicomponent mixtures based on the complete data (binary, ternary, etc.) has been explained in ref *8*. For a ternary mixture, $N = 3$, it would read

$$T = \sum_{i=1}^{N} x_i T_i^\circ + \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} x_i x_j [A_{ij} + B_{ij}(x_i - x_j) + C_{ij}(x_i - x_j)^2 + ...] + x_1 x_2 x_3 [A + B(x_1 - x_2) + C(x_1 - x_3) + D(x_2 - x_3) + B'(x_1 - x_2)^2 + C'(x_1 - x_3)^2 + D'(x_2 - x_3)^2 + ...] \quad (2)$$

Here the indexed parameters are binary constants while A, B, B', etc., are ternary constants.

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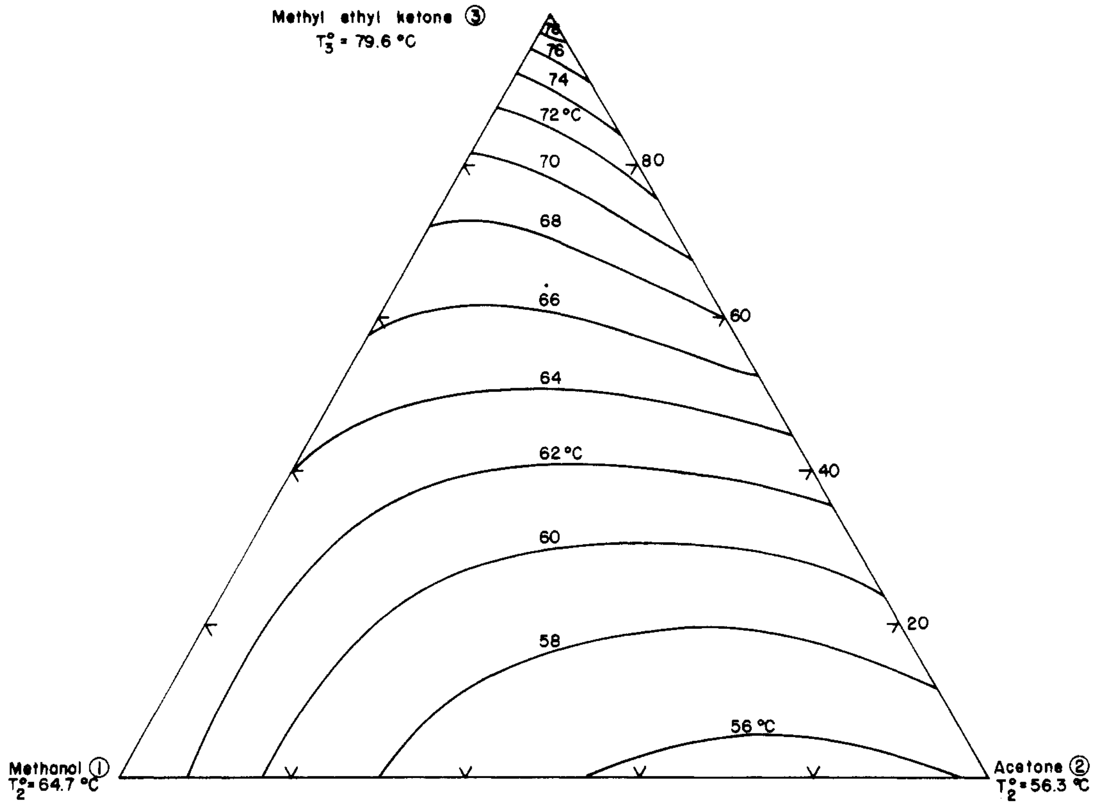

Figure 1. Isotherms for methanol–acetone–methyl ethyl ketone at 760 mmHg.

(b) An additional equation used here for correlating the activity coefficient, γ_i, is the Wilson equation for multicomponent mixtures (eq 3). It should be noted that according to the original concepts of Wilson, A_{ij} values are binary parameters. However, according to what has been previously said, they should also be considered as multicomponent parameters determined directly from the multicomponent data.

$$\ln \gamma_i = 1 - \ln \left[\sum_{j=1}^{N} A_{ij}x_j\right] - \sum_{k=1}^{N} \left[\frac{A_{ki}x_k}{\sum_{j=1}^{N} A_{kj}x_j} \right] \tag{3}$$

(c) In order to evaluate the correlation and predictive ability of the Wilson equation, we employed the following Redlich–Kister expansion for γ_i for correlating the ternary data:

$$\begin{aligned} \ln \gamma_1 = {} & x_2x_3[(B_{12} + B_{13} - B_{23}) + C_{12}(2x_1 - x_2) + \\ & C_{13}(2x_1 - x_3) + 2C_{23}(x_3 - x_2) + \\ & D_{12}(x_1 - x_2)(3x_1 - x_2) + \\ & D_{13}(x_1 - x_3)(3x_1 - x_2) - 3D_{23}(x_3 - x_2)^2 + C_1(1 - 2x_1)] + \\ & x_2^2[B_{12} + C_{12}(3x_1 - x_2) + D_{12}(x_1 - x_2)(5x_1 - x_2)] + \\ & x_3^2[B_{13} + C_{13}(3x_1 - x_3) + D_{13}(x_1 - x_3)(5x_1 - x_3)] \end{aligned} \tag{4}$$

where B_{ij}, C_{ij}, D_{ij} are binary constants and C_1 is a ternary constant. The equations for the other activity coefficients were obtained by cyclic rotation of the indexes. The binary constants were calculated from the following equations (*7*):

$$\ln \gamma_i = (B_{ij} + 3C_{ij} + 5D_{ij})x_j^2 - 4(C_{ij} + 4D_{ij})x_j^3 + 12D_{ij}x_j^4 \tag{5-1}$$

$$\ln \gamma_j = (B_{ij} - 3C_{ij} + 5D_{ij})x_i^2 + 4(C_{ij} - 4D_{ij})x_i^3 + 12D_{ij}x_i^4 \tag{5-2}$$

In order to evaluate the goodness of the fit by the various correlations, we used the following quantities:

The error variance σ^2 (*9*) of an intensive property M is defined by eq 6 and is a measure of the spread of the error distribution; m and c are respectively the number of the data points and parameters which correspond to the mixture of the highest order. σ^2 reaches a minimum vs. the degrees of freedom $m - c - 1$, and hence it is possible to choose the optimal number of parameters on the basis of its magnitude. By means of σ^2 it is also reasonable to compare two expansions of a specific property because it is normalized with respect to $m - c - 1$ and thus takes into account differences between the number of parameters c and the number of data points m.

$$\sigma^2 = \frac{\sum_{i=1}^{m} (M_{\text{obsd}} - M_{\text{calcd}})_i^2}{m - c - 1} \tag{6}$$

The mean overall deviation $\bar{D}$ is a more tangible element indicating the overall goodness of the fit of the data by the series expansion, and it reads

$$\bar{D} = \frac{1}{m} \sum_{i=1}^{m} \left| \frac{M_{\text{obsd}} - M_{\text{calcd}}}{M_{\text{obsd}}} \right|_i \tag{7}$$

The following procedure was adopted for determining the parameters by direct correlation of multicomponent data (eq 1): First parameters A_{12}, A_{13}, ..., A_{1N}, A_{23}, A_{24}, ..., A_{2N} were determined, and then A_{12} and B_{12}, A_{13} and B_{13}, A_{1N} and B_{1N}, A_{23} and B_{23}, ..., A_{2_N} and B_{2N}, etc. The optimal set of parameters was the one for which σ^2 was minimal. The correlation of multicomponent data based on the complete information (eq 2) was carried out as follows: At first parameters of all binary systems which compose the ternary system were determined. On the basis of the optimal sets of binary parameters (judged on the basis of minimal σ^2), the ternary constants were determined by considering the ternary data.

Table I. Equilibrium Data for Methanol (1)–Acetone (2)–MEK at 760 mmHg

T, °C	x_1	x_2	y_1	y_2
55.95	0.248	0.748	0.234	0.756
56.08	0.275	0.711	0.261	0.719
56.73	0.045	0.881	0.045	0.927
56.75	0.237	0.697	0.222	0.742
56.81	0.246	0.683	0.203	0.766
56.85	0.056	0.905	0.108	0.870
57.54	0.040	0.903	0.072	0.889
57.55	0.408	0.495	0.345	0.607
57.62	0.359	0.120	0.455	0.192
57.90	0.471	0.476	0.512	0.454
58.14	0.284	0.572	0.297	0.598
58.30	0.629	0.317	0.469	0.512
58.30	0.140	0.731	0.138	0.810
58.45	0.629	0.302	0.483	0.464
58.85	0.475	0.397	0.451	0.466
59.10	0.798	0.192	0.582	0.409
59.10	0.561	0.327	0.502	0.430
59.13	0.040	0.780	0.029	0.879
59.27	0.182	0.610	0.224	0.658
59.65	0.576	0.296	0.522	0.395
59.67	0.283	0.485	0.310	0.586
59.73	0.517	0.345	0.478	0.415
59.75	0.677	0.245	0.580	0.356
59.92	0.770	0.191	0.616	0.337
60.18	0.564	0.272	0.527	0.366
60.25	0.154	0.555	0.221	0.626
60.35	0.734	0.197	0.646	0.296
60.46	0.530	0.262	0.505	0.358
60.47	0.420	0.340	0.439	0.434
60.48	0.754	0.202	0.678	0.288
60.50	0.823	0.162	0.727	0.244
60.53	0.286	0.429	0.334	0.502
60.55	0.749	0.167	0.659	0.278
60.64	0.343	0.374	0.377	0.490
60.64	0.096	0.644	0.141	0.719
61.15	0.543	0.224	0.537	0.305
61.37	0.797	0.134	0.722	0.221
61.45	0.487	0.231	0.500	0.312
61.47	0.276	0.380	0.328	0.467
61.49	0.580	0.190	0.567	0.271
61.55	0.652	0.154	0.616	0.236
61.65	0.289	0.381	0.342	0.485
61.82	0.214	0.433	0.202	0.584
61.98	0.638	0.136	0.649	0.198
61.99	0.229	0.420	0.224	0.443
62.00	0.396	0.254	0.428	0.338
62.08	0.388	0.245	0.440	0.330
62.14	0.333	0.308	0.383	0.412
62.20	0.220	0.387	0.284	0.487
62.33	0.545	0.146	0.557	0.224
62.34	0.715	0.105	0.668	0.183
62.84	0.372	0.372	0.318	0.266
62.87	0.371	0.222	0.433	0.308
62.88	0.125	0.466	0.171	0.610
62.90	0.513	0.137	0.550	0.203
63.03	0.317	0.257	0.357	0.367
63.10	0.891	0.084	0.842	0.118
63.25	0.042	0.546	0.096	0.669
63.27	0.667	0.066	0.683	0.111
63.30	0.167	0.406	0.240	0.495
63.40	0.231	0.328	0.313	0.419
63.72	0.459	0.113	0.515	0.182
63.72	0.621	0.051	0.680	0.076
64.40	0.349	0.172	0.429	0.242
64.41	0.038	0.535	0.202	0.505
64.71	0.351	0.110	0.452	0.183
64.72	0.232	0.249	0.318	0.338
64.73	0.360	0.135	0.437	0.208
64.80	0.060	0.449	0.086	0.603
64.88	0.180	0.260	0.303	0.385
65.00	0.277	0.213	0.362	0.296
65.30	0.348	0.109	0.444	0.158
65.72	0.127	0.318	0.234	0.415
66.28	0.169	0.249	0.265	0.354
66.29	0.391	0.016	0.577	0.026
67.00	0.279	0.079	0.384	0.126
67.84	0.202	0.053	0.368	0.109
68.29	0.110	0.209	0.228	0.310
68.48	0.037	0.252	0.149	0.378
69.33	0.071	0.179	0.200	0.272
69.33	0.181	0.042	0.335	0.089

Table II. Wilson, Redlich–Kister Parameters for Methanol (1)–Acetone (2)–MEK (3) and the Binaries

		Wilson[a]		Redlich–Kister[b]		
system	ij	A_{ij}	A_{ji}	B_{ij}	C_{ij}	D_{ij}
		Binary				
methanol–acetone	12	0.6366	0.8874	0.6358	0.0728	0.0232
methanol–MEK	13	0.6865	0.5632	0.8132	0.0666	0.1321
acetone–MEK	23	1.8413	0.3471	0.0607	0.1478	0.0379
		Ternary (C_1 = 0.3833)				
methanol–acetone–MEK	12	0.2522[c]	1.3793[c]			
	13	0.1333[c]	1.4666[c]			
	23	2.5989[c]	0.0362[c]			

[a] Equation 3. [b] Equations 4, 5-1, and 5-2. [c] A_{ij} or A_{ji} parameters obtained by direct correlation of ternary data by Wilson's equation.

Results and Discussion

The temperature–concentration measurements at 760 mmHg for the ternary system methanol–acetone–DEK are reported in Table I. The liquid activity coefficients were calculated from

$$\ln \gamma_i = \ln \frac{y_i P}{x_i P_i°} + \frac{(B_{ii} - V_i^{l})(P - P_i°)}{RT} + \frac{P}{2RT} \sum_{j=1}^{m} \sum_{k=1}^{m} y_j y_k (2\delta_{ji} - \delta_{jk}) \tag{8}$$

where

$$\delta_{ij} = 2B_{ji} - B_{jj} - B_{ii} \tag{9}$$

Table III. Capability of Predicting the Vapor Composition for Methanol–Acetone–MEK at 760 mmHg by Wilson and Redlich–Kister Methods[a]

	y, %					
	Wilson[b]			Redlich–Kister[c]		
system	max	min	mean	max	min	mean
	Binary					
methanol–acetone	40.1	0.3	6.2	0.7	0.0	0.3
methanol–MEK	7.2	0.0	3.6	2.7	0.0	1.0
acetone–MEK	10.5	0.0	2.4	4.2	0.0	1.7
	Ternary					
methanol–acetone–MEK	68.2	0.0	9.1	100.1	0.2	13.3
	38.5	0.0	6.8	95.7	0.2	8.8

[a] The results for ternary mixtures are based either on direct correlation of ternary data (by Wilson equation) or on the binary plus ternary data (by Redlich–Kister equation). $y = (y_{\mathrm{obsd}} - y_{\mathrm{calcd}})/y_{\mathrm{obsd}}$; mean $= (1/m)\sum_{i=1}^{m}|y_i|$. [b] Equation 3. [c] Equation 4.

Vapor pressures $P_i°$ were calculated according to Antoine's equation:

$$\log P_i° = A_i - B_i/(t + C_i) \tag{10}$$

The constants A_i, B_i, and C_i were taken from ref 1. For the convenience of the reader the constants are reported here for $P_i°$ in mmHg:

	A_i	B_i	C_i
methanol	7.8970	1474.0	229.1
acetone	7.2316	1277.0	237.2
MEK	7.2086	1368.2	236.5

Table IV. Parameters[a] in Correlation of Binary T–x Data[b]

system	A_{ij}	B_{ij}	C_{ij}	D_{ij}	E_{ij}	D,[c] % max	D,[c] % min	D,[c] % mean[d]
methanol–acetone	−17.060	−4.489	−7.011	−0.682		0.16	0.00	0.04
methanol–MEK	−30.710	10.965	14.554	5.246	−65.95	0.74	0.07	0.31
acetone–MEK	−10.287	−5.195	−4.256	16.475		0.67	0.05	0.29

[a] Corresponding to minimal σ^2 (eq 9). [b] Equation 14. [c] $D = |(T_{\text{obsd}} - T_{\text{calcd}})/T_{\text{obsd}}|$. [d] mean $= (1/m)\sum D_i$.

Table V. Parameters[a] in Direct Correlation of T–x Data for Methanol (1)–Acetone (2)–MEK (3) at 760 mmHg and the Efficiency of Direct Correlation[b]

	direct correlation of ternary data							correlation based on binary and ternary data[c]					
				D, %									
ij	A_{ij}	B_{ij}	C_{ij}	max	min	mean	σ^2 min	c'	c	max	min	mean	σ^2 min
12	−14.435	−8.497	−4.457					4					
13	−27.379	19.511	−4.605					4					
23	−7.325	6.793	−19.136	11.4	0.00	0.60	0.81	4	4	11.3	0.06	0.73	0.84

[a] Corresponding to minimal σ^2 (eq 9). [b] $T_1° = 64.7$ °C; $T_2° = 56.29$; $T_3° = 79.64$ °C (measured in our equilibrium still). [c] Equation 2.

The virial coefficients B_{ii} and the mixed virial coefficients B_{ij} were estimated by the correlation of Tsonopoulos (*10*). It was found that the vapor nonideality has a negligible effect on γ_i, which changes at extreme cases by about 3%, and the governing effect is the nonideality of the liquid side.

The ternary data appearing in Table I are thermodynamically consistent and were tested by the McDermott–Ellis method (*11*). According to this test, two experimental points, a and b, are thermodynamically consistent if

$$D < D_{\max} \qquad (11)$$

The local deviation D is given by

$$D = \sum_{i=1}^{N} (x_{ib} + x_{ia})(\ln \gamma_{ib} - \ln \gamma_{ia}) \qquad (12)$$

According to ref *11* a fixed value for $D_{\max}$ is recommended; however, an equation can be derived (*12*) which reads

$$D_{\max} = \sum_{i=1}^{N} (x_{ia} + x_{ib})\left(\frac{1}{x_{ia}} + \frac{1}{y_{ia}} + \frac{1}{x_{ib}} + \frac{1}{y_{ib}}\right)\Delta x + 2\sum_{i=1}^{N} |\ln \gamma_{ib} - \ln \gamma_{ia}|\Delta x + 2\sum_{i=1}^{N} (x_{ia} + x_{ib})\frac{\Delta P}{P} + \log e \sum_{i=1}^{N} (x_{ia} + x_{ib})B_i\left(\frac{1}{[t_a + C_i]^2} + \frac{1}{[t_b + C_i]^2}\right)\Delta t \qquad (13)$$

In this study the errors in the measurements were estimated to be $\Delta P = \pm 2$ mmHg, $\Delta t = \pm 0.02$ °C, and $\Delta x = 0.01$ mole fraction unit. Usually the first term on the right-hand side of eq 13 was the dominant one.

The binary data reported elsewhere (*1–3*) were correlated by Wilson and Redlich–Kister equations (eq 3 and 4, respectively), and the binary parameters are reported in Table II. For the ternary mixture, the data were correlated directly by means of Wilson's equation. In the case of Redlich–Kister's equation (eq 4), the binary parameters were used, and the ternary constants C_1 were determined from ternary data. This information appears in Table II. Table III summarizes the predictive capability for the binary and ternary data of the various methods. The following general conclusions could be drawn on the basis of considering $y = (y_{\text{obsd}} - y_{\text{calcd}})/y_{\text{obsd}}$ and its mean values.

Binary Data. Redlich–Kister's equation best correlates the data, and the maximum mean deviation of predicting the vapor composition is ~1.7%.

Another correlation used here relates the boiling temperatures of the mixture with the liquid composition only according to eq 1. The binary form of this equation reads

$$T = x_1T_1° + x_2T_2° + x_1x_2[A_{12} + B_{12}(x_1 - x_2) + C_{12}(x_1 - x_2)^2 \ldots] \qquad (14)$$

The parameters are reported in Table IV and their number corresponds to minimal σ^2 (eq 6).

Ternary Data. Direct correlation of ternary data by Wilson's equation is superior (maximum mean deviation of 9.1%) to predictions of the ternary data from the binary parameters (maximum mean deviation from experimental data is 13.3%). In Table V we report the parameters obtained for direct correlation of the ternary data according to the ternary form of eq 1 which reads

$$T = \sum_{i=1}^{3} x_iT_i° + x_1x_2[A_{12} + B_{12}(x_1 - x_2) + C_{12}(x_1 - x_2)^2 \ldots] + x_1x_3(A_{13} + B_{13}(x_1 - x_3) + C_{13}(x_1 - x_3)^2 + \ldots] + x_2x_3(A_{23} + B_{23}(x_2 - x_3) + C_{23}(x_2 - x_3)^2 \ldots] \qquad (15)$$

The following conclusions may be drawn on the basis of Tables IV and V.

(1) From the values of the mean overall deviation, eq 1 may be considered as very useful in correlating directly T vs. x. Note that, with nine adjustable parameters, T may be correlated directly vs. x with a mean deviation of 0.66% (Table V).

(2) Direct correlation of T vs. x for the ternary mixture is very efficient, where for almost identical values of σ^2 (0.81 and 0.84 in Table V) nine parameters are required in direct correlation and 16 parameters are required when all binary parameters are taken into account.

Isotherms (Figure 1) were calculated on the basis of eq 15 and the parameters reported in Table V. The shape of the curves indicates that the system does not exhibit azeotropic behavior.

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Glossary

A_{ij}, B_{ij}, etc.	multicomponent adjustable parameters in Redlich–Kister or Wilson expansions
A_i, B_i, C_i	parameters in Antoine's equation, eq 10
C_1	ternary constant
c'	total number of parameters per binary system
c	total number of parameters which correspond to the mixture of the highest order (ternary) system
$\bar{D}$	mean overall deviation from observed values, eq 7
M	intensive property, $M = T$ or y
MEK	methyl ethyl ketone
m	total number of data points which correspond to the system of the highest order

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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