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FORMULATION AND PREDICTION OF QUATERNARY VAPOR-LIQUID EQUILIBRIA ACCOMPANIED BY ESTERIFICATION*

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Quaternary vapor-liquid equilibria with esterification have been formulated mathematically. First, activity coefficients have been related to liquid compositions with polynomial equations derived from the Margules model, and second, the parameters B_i defined in an equation of the vapor-liquid equilibrium ratio with esterification reported previously have been represented by polynomials. Both correlations are adequate to describe the behavior of the given systems.

Vapor-liquid equilibrium with reaction of the system acetic acid-ethanol-water-ethyl acetate was predicted from Wilson's parameters obtained from binary system data only. Association equilibrium constants of dimerization and trimerization in acetic acid vapor were used to calculate modified activity coefficients, and Wilson's parameters were determined from six binary data. The agreement of the calculated and experimental data may be considered satisfactory for the practical use to design multicomponent distillation column reactors.

Although industrial esterification processes utilize fractionating columns as continuous reactors, the approach to their design and operation has been largely empirical. But many investigations have shown that the extent of conversion at each stage could be predicted from reaction-rate data, and that successive plate-to-plate design calculations could be made by utilizing experimental vapor-liquid equilibrium data and kinetic and equilibrium relations.

Previously, the authors reported on vapor-liquid equilibria of quaternary systems with esterification, such as acetic acid-methanol-water-methyl acetate⁸⁾, acetic acid-ethanol-water-ethyl acetate⁷⁾ and acetic acid-butanol-water-butyl acetate⁶⁾, and derived the relations with graphical correlation for the above systems.

In the present paper, we have tried to formulate relations between the liquid and vapor compositions or graphical correlations for solving the complex equations of multicomponent distillation column reactor design by

use of computer, and to estimate the above quaternary vapor-liquid equilibrium data from parameters obtained from binary system data only.

1. Formulation of the Quaternary Vapor-Liquid Equilibrium Data with Esterification

This work was started with the Margules equation⁵⁾ modified by Marek which might be applicable to express the quaternary system vapor-liquid equilibrium data in esterification. The Margules constants were evaluated so as to minimize the sum of the squares of the difference between the observed and fitted values of the excess free energy suggested by Wohl, using experimental quaternary data, and the validity in vapor compositions was tested. But this system is far from ideality in liquid phase, so this trial failed to obtain good relations.

We then tried to rearrange the Margules equation as a polynomial series in mole fractions of the components in the mixture. The corresponding equation for its coefficient can be rearranged to the form

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$$\begin{aligned}\log \gamma_1 = & A_1 x_2^2 + A_2 x_3^2 + A_3 x_4^2 + A_4 x_2 x_3 + A_5 x_2 x_4 \\ & + A_6 x_3 x_4 + A_7 x_1 x_2^2 + A_8 x_1 x_3^2 + A_9 x_1 x_4^2 \\ & + A_{10} x_1 x_2 x_3 + A_{11} x_2 x_3 x_4 + A_{12} x_3 x_4 x_1 \\ & + A_{13} x_4 x_1 x_2 + A_{14} x_2 x_3^2 + A_{15} x_2 x_4^2 \\ & + A_{16} x_3 x_4^2\end{aligned}\quad (1)$$

where x_i represents the mole fraction of the i -th component in the liquid phase, γ_i is the activity coefficient and A_1 through A_{16} are constants which are determined by quaternary equilibrium data. The expressions for the activity coefficient of the remaining components can be obtained by a cyclic permutation of the indices; $1 \rightarrow 2 \rightarrow 3 \rightarrow 4 \rightarrow 1$.

Eq. (1) is the linear function for A_1 through A_{16} and an optimum set of these values was determined by the least-squares fit to Eq. (1), using a digital computer. The constants of the Antoine equation used to calculate the vapor pressure of pure liquid are listed in **Table 1**.

Computed regression coefficients of each component for Eq. (1) and estimated standard errors in Q function suggested by Redlich and Kister, activity coefficients, temperature and vapor compositions for the three systems are shown in **Tables 2, 3** and **4**. Calculated values are in good agreement with experimental data for each system in the practical use to design a multicomponent distillation column reactor.

Further, some similar polynomial equations with more than sixteen constants were tested to get a more accurate relation, but the results showed little difference. Then it may be concluded that Eq. (1) is most suitable for our purpose.

2. Formulation of the Graphical Correlations

The authors suggested⁶⁻⁸⁾ that the x - y relation of the reacting system varied continuously with the change

of liquid compositions by reaction, and the path of the variation of x - y relation might be determined definitely by the relation at hypothetical conversion 0 or 1.

The following equations summarize the above work. Vapor-liquid equilibrium ratio, K_i , is shown as follows

$$\log K_i = -2.30 \times 10^3 \left(\frac{1}{T} \right) + B_i \quad (2)$$

But, for acetic acid, K_1 is given by

$$\begin{aligned}K_1 &= 2.25 \times 10^{-2} t - 1.666 & t > 74.0 \\ K_1 &= 0.001 & t \leq 74.0\end{aligned}$$

where B_i is function of the liquid components at hypothetical conversion 0 or 1, and has been shown as six kinds of graphs.

For reduction of these graphs, B_{23} , B_{24} , B_{31} , B_{32} , B_{41} and B_{42} , to equations, a preliminary analysis indicated that polynomials in two variables might be suitable. We assumed the following functional relationship:

$$B_{ij} = f(F_1, F_2) \quad (3)$$

where F_1 and F_2 are the dependent variables of liquid composition.

Further analysis of several trial regressions led to some modifications in the terms in the regression equation to obtain a better fit with the arbitrary limitation

Table 1 Antoine constants used in this paper

Substance	a	b	c	Data reference
methanol	7.87863	1473.11	230.0	(11)
ethanol	7.83124	1440.52	212.71	(9)
<i>n</i> -butanol	8.27488	1873.90	230.0	(9)
acetic acid	7.55960	1644.05	233.524	(2)
methyl acetate	7.20211	1232.83	228.0	(11)
ethyl acetate	7.09808	1238.71	217.0	(11)
butyl acetate	7.12530	1426.90	210.156	(9)
water	7.96681	1668.21	228.0	*

* values determined from the data of reference (10) by authors

Table 2 Computed regression coefficients for Eq. (1) and standard errors of estimate in Q , γ_i , t , y_i for the system acetic acid-methanol-water-methyl acetate

Number of data points used; 170

Coefficients	Acetic acid	Methanol	Water	Methyl acetate
A_1	-0.565327 E0	0.220421 E1	0.507431 E2	-0.176293 E0
A_2	-0.272620 E1	0.121955 E2	-0.993873 E-1	0.257847 E0
A_3	-0.141799 E2	-0.167642 E0	0.585876 E0	-0.170627 E1
A_4	-0.296412 E1	-0.289375 E0	-0.824075 E2	0.178298 E0
A_5	0.174107 E1	-0.691180 E1	-0.862661 E2	-0.200939 E0
A_6	0.953302 E1	-0.255861 E2	0.111392 E1	0.336902 E1
A_7	0.820185 E0	-0.118730 E2	-0.770021 E2	-0.373925 E0
A_8	0.281103 E1	0.706607 E1	-0.882569 E0	-0.311324 E1
A_9	0.188169 E2	-0.103195 E1	0.958974 E0	0.610441 E1
A_{10}	0.102712 E2	0.227980 E1	0.106578 E3	0.162085 E1
A_{11}	-0.359400 E2	0.509270 E2	0.179496 E3	-0.467115 E1
A_{12}	-0.567641 E1	0.335891 E1	-0.762537 E1	-0.322066 E1
A_{13}	-0.930224 E1	0.232413 E2	0.117444 E3	-0.332442 E1
A_{14}	0.768782 E1	-0.267237 E2	0.862398 E2	0.944822 E0
A_{15}	0.381214 E2	0.457576 E1	0.842563 E2	0.649635 E1
A_{16}	0.828829 E0	0.271497 E2	-0.228941 E0	0.800948 E0
Standard errors in all data				
Q	0.015899			
γ_i	0.053854	0.068103	0.016527	0.078420
$t(^{\circ}\text{C})$	0.93162			
y_i (mol %)	1.0148	0.82866	1.3678	1.5458

* In this paper, "Ea" indicates 10^a .

Table 3 Computed regression coefficients for Eq. (1) and standard errors of estimate in Q , γ_i , t , y_i for the system acetic acid-ethanol-water-ethyl acetate

Coefficients	Number of data point used; 247			
	Acetic acid	Ethanol	Water	Ethyl acetate
A_1	-0.554296 E0	0.581778 E0	0.688636 E0	-0.601367 E-1
A_2	-0.324357 E0	0.209245 E0	0.243031 E-1	0.229575 E0
A_3	-0.103685 E0	-0.257329 E0	0.375534 E0	0.186575 E1
A_4	-0.705455 E0	-0.562636 E0	0.127548 E1	0.355191 E0
A_5	-0.201335 E1	-0.314853 E0	0.177863 E1	0.468416 E0
A_6	-0.225362 E1	0.451732 E0	0.696279 E0	0.151110 E1
A_7	0.837926 E0	-0.115411 E0	0.936722 E0	-0.599682 E-1
A_8	0.523760 E0	0.695310 E-1	0.449356 E0	0.673994 E-1
A_9	0.434061 E0	0.740529 E-1	0.717790 E0	-0.315997 E1
A_{10}	-0.534056 E0	0.187010 E0	0.144973 E1	0.941858 E0
A_{11}	-0.325231 E1	-0.369985 E0	-0.211099 E1	-0.192225 E1
A_{12}	0.590329 E1	-0.823390 E-1	0.746905 E0	-0.755731 E0
A_{13}	0.335400 E1	-0.409472 E0	0.112914 E1	0.103791 E1
A_{14}	0.197296 E0	0.109247 E1	0.120436 E0	0.365254 E0
A_{15}	-0.452660 E0	0.192416 E0	-0.164268 E1	-0.136587 E1
A_{16}	0.147152 E-1	-0.172565 E0	0.330018 E0	-0.213818 E1
Standard errors in all data				
Q	0.018585			
γ_i	0.064442	0.060124	0.16398	0.29487
t [°C]	1.2089			
y_i [mol %]	1.2061	0.7899	1.2903	1.3252

Table 4 Computed regression coefficients for Eq. (1) and standard errors of estimate in Q , γ_i , t , y_i for the system acetic acid-butanol-water-butyl acetate

Coefficients	Number of data points used; 97			
	Acetic acid	Butanol	Water	Butyl acetate
A_1	0.621909 E1	0.109686 E1	0.537395 E2	-0.809230 E0
A_2	-0.467747 E0	0.120872 E2	-0.674166 E0	0.638384 E2
A_3	-0.256615 E1	0.565434 E0	0.198171 E3	-0.501678 E0
A_4	-0.264249 E1	0.250634 E1	-0.192251 E3	0.126996 E2
A_5	-0.107039 E2	0.559804 E0	0.647689 E2	0.499868 E1
A_6	0.374885 E1	-0.172787 E2	0.154656 E2	-0.215444 E2
A_7	-0.233394 E1	-0.404033 E1	-0.106354 E3	-0.480678 E1
A_8	0.192890 E0	-0.300803 E2	-0.404050 E1	-0.140943 E3
A_9	0.962654 E1	-0.745638 E1	-0.287382 E3	-0.177893 E1
A_{10}	0.927400 E0	0.309111 E2	0.118859 E3	0.143813 E2
A_{11}	-0.132085 E2	0.180904 E0	0.429985 E3	-0.597740 E2
A_{12}	0.271947 E1	0.295925 E2	0.343773 E2	-0.161187 E2
A_{13}	-0.499595 E1	-0.140431 E0	0.860108 E2	0.574879 E2
A_{14}	-0.846960 E0	-0.268435 E2	0.173370 E3	-0.110391 E3
A_{15}	0.230523 E2	0.921191 E0	-0.650247 E3	-0.313072 E1
A_{16}	-0.323718 E1	0.305518 E2	-0.374382 E3	0.266626 E2
standard errors in all data				
Q	0.048361			
γ_i	0.045144	0.055327	0.098601	0.030941
t [°C]	2.8454			
y_i [mol %]	1.6560	3.3294	3.3955	1.6100

of F_1 and F_2 . The results of analysis are shown in Table 5 to 7.

The equation finally accepted follows.

$$B_{ij} = C_1 + C_2 F_1 + C_3 F_1 F_2 + C_4 F_1^2 + C_5 F_1^2 F_2 + C_6 F_1^3 + C_7 F_1^3 F_2 + C_8 F_1 F_2^2 + C_9 F_1^2 F_2^2 + C_{10} F_1^2 F_2^3 + C_{11} F_1^3 F_2^2 + C_{12} F_1 F_2^3 + C_{13} F_1^3 F_2^3 \quad (4)$$

where

$$F_1 = \frac{1 - x_i}{1 + x_i}, \quad F_2 = \frac{1 - x_j}{1 + x_j}$$

C_1 to C_{13} ; regression constants

The regression coefficients were evaluated, and the results, as shown in Tables 7 and 8, are reasonably accurate fits to the experimental for the acetic acid-ethanol-water-ethyl acetate system.

3. Prediction of Quaternary Vapor-Liquid Equilibrium Data with Esterification from Binary Phase Equilibria

For quaternary system vapor-liquid equilibria with esterification, it may be assumed that ordinary vapor-liquid relations are used, if the system is nearly in the equilibrium state.

Wilson's model⁽¹²⁾ is useful for calculating the activity coefficient of any component in a quaternary solution using only parameters obtained from binary vapor-liquid equilibrium data. The activity coefficient of any component is

$$\ln \gamma_k = -\ln \left[\sum_{j=1}^4 x_j A_{kj} \right] + 1 - \sum_{i=1}^4 \frac{x_i A_{ik}}{\sum_{j=1}^4 x_j A_{ij}} \quad (5)$$

Table 5 Definitions of quantities used in regression Eq. (3)

$$\begin{aligned}
A: B_{ij} &= C_1 + C_2 F_1 + C_3 F_1 F_2 + C_4 F_1^2 F_2^2 + C_5 F_1^3 + C_6 F_1^2 F_2 + C_7 F_1^2 F_2^2 \\
B: B_{ij} &= C_1 + C_2 F_1 + C_3 F_1 F_2 + C_4 F_1^2 + C_5 F_1^2 F_2 + C_6 F_1^3 + C_7 F_1^3 F_2 \\
C: B_{ij} &= C_1 + C_2 F_1 + C_3 F_1 F_2 + C_4 F_1^2 + C_5 F_1^2 F_2^2 + C_6 F_2 + C_7 F_2^2 \\
D: B_{ij} &= C_1 + C_2 F_1 + C_3 F_1 F_2 + C_4 F_1^2 + C_5 F_1 F_2^2 + C_6 F_1^2 F_2 + C_7 F_1^3 F_2^2 + C_8 F_1^3 + C_9 F_1^3 F_2 + C_{10} F_1^3 F_2^2 \\
E: B_{ij} &= C_1 + C_2 F_1 + C_3 F_1 F_2 + C_4 F_1^2 + C_5 F_1^2 F_2^2 + C_6 F_2 + C_7 F_2^2 + C_8 F_1 F_2^2 + C_9 F_1 F_2^3 + C_{10} F_1^2 F_2^3 + C_{11} F_1^3 F_2^3 \\
F: B_{ij} &= C_1 + C_2 F_1 + C_3 F_1 F_2 + C_4 F_1^2 + C_5 F_1^2 F_2 + C_6 F_1^3 + C_7 F_1^3 F_2 + C_8 F_1 F_2^2 + C_9 F_1^2 F_2^2 + C_{10} F_1^2 F_2^3 + C_{11} F_1^3 F_2^2 + C_{12} F_1 F_2^3 + C_{13} F_1^3 F_2^3
\end{aligned}$$

where F_1 and F_2 are defined as follows;

	F_1	F_2		F_1	F_2
1	x_i	x_j	6	$\frac{x_i}{1-x_j}$	x_j
2	$\frac{2x_i}{1+x_i}$	$\frac{2x_j}{1+x_j}$	7	$\frac{x_i}{x_i+x_j}$	$\frac{x_j}{x_i+x_j}$
3	$\frac{1-x_i}{1+x_i}$	$\frac{1-x_j}{1+x_j}$	8	$\frac{x_i}{x_i+x_j}$	x_j
4	$1-x_i^2$	$1-x_j^2$	9	$\frac{x_i}{1-x_j^2}$	$\frac{x_j}{1-x_i^2}$
5	$\frac{x_i}{1-x_i}$	$\frac{x_j}{1-x_j}$			

Table 6 Comparison of standard errors of estimate in B_{41} , B_{31} , B_{32} for the equations of Table 5

Figure used as source of data

	B_{41}	B_{31}	B_{32}		B_{41}	B_{31}	B_{32}
A-1	0.2022	0.1104	0.0775	D-1	9.8395	2.2143	1.7772
A-2	0.1895	0.1054	0.0767	D-2	4.3970	1.1994	1.4984
A-3	0.0503	0.0385	0.0153	D-3	1.3849	3.2936	2.7848
A-4	0.1788	0.0885	0.0565	D-4	59.0840	0.3863	2.2167
A-5	0.1261	0.0486	0.0969	D-5	4.4660	1.5311	7.9903
A-6	0.1155	0.0444	0.0173	D-6	7.5533	1.5494	7.4093
A-7	0.3009	0.2375	0.1902	D-7	14.6489	10.6241	40.9145
A-8	0.2363	0.1581	0.1696	D-8	23.9443	2.7290	3.9732
A-9	0.1876	0.0550	0.0716	D-9	2.0339	0.3812	4.5541
B-1	0.2034	0.1051	0.0748	E-1	2.4826	0.3766	0.9044
B-2	0.1707	0.1014	0.0722	E-2	1.4673	0.8989	1.1487
B-3	0.0607	0.0460	0.0199	E-3	1.0670	0.5189	0.8950
B-4	0.1847	0.0599	0.0558	E-4	27.1133	7.8596	6.5803
B-5	0.0872	0.0432	0.0968	E-5	8.4856	3.6029	19.3417
B-6	0.0913	0.0384	0.0187	E-6	1.6614	3.2811	10.6566
B-7	0.3009	0.2375	0.1903	E-7	14.5146	23.7552	18.6266
B-8	0.2477	0.1576	0.1694	E-8	2.4435	4.4261	4.0371
B-9	0.0992	0.0457	0.0766	E-9	1.9540	3.0439	6.3141
C-1	0.0720	0.0358	0.0162	F-1	0.1350	0.0958	0.0728
C-2	0.0578	0.0347	0.0170	F-2	0.1216	0.0929	0.0712
C-3	0.0579	0.0321	0.0099	F-3	0.0580	0.0284	0.0093
C-4	0.2929	0.0653	0.0547	F-4	0.1376	0.0569	0.0472
C-5	0.0846	0.0400	0.0969	F-5	0.0778	0.0382	0.0965
C-6	0.0760	0.0408	0.0198	F-6	0.0755	0.0337	0.0128
C-7	0.2416	0.2170	0.1778	F-7	0.2437	0.2339	0.1902
C-8	0.1652	0.1306	0.1579	F-8	0.1927	0.1531	0.1692
C-9	0.0831	0.0406	0.0713	F-9	0.1034	0.0415	0.0681

Table 7 Computed regression coefficients for the Eq. (4) and standard error of estimate in B_{ij} of the system acetic acid-ethanol-ethyl acetate

$$\text{Equation; } B_{ij} = C_1 + C_2 F_1 + C_3 F_1 F_2 + C_4 F_1^2 + C_5 F_1^2 F_2 + C_6 F_1^3 + C_7 F_1^3 F_2 + C_8 F_1 F_2^2 + C_9 F_1^2 F_2^2 + C_{10} F_1^2 F_2^3 + C_{11} F_1^3 F_2^2 + C_{12} F_1 F_2^3 + C_{13} F_1^3 F_2^3$$

$$\text{where } F_1 = \frac{1-x_i}{1+x_i} \quad F_2 = \frac{1-x_j}{1+x_j}$$

	B_{23}	B_{24}	B_{31}	B_{32}	B_{41}	B_{42}
x_i	x_2	x_2	x_3	x_3	x_4	x_4
x_j	x_3	x_4	x_1	x_2	x_1	x_2
C_1	0.6547 E1	0.6550 E1	0.6149 E1	0.6166 E1	0.6499 E1	0.6557 E1
C_2	-0.8590 E0	0.2145 E1	-0.2666 E1	-0.1731 E1	0.9418 E0	0.2721 E1
C_3	0.2593 E1	-0.8176 E1	0.4999 E1	0.4697 E1	-0.9598 E1	-0.3385 E1
C_4	0.4030 E1	-0.3615 E1	0.5322 E1	0.5475 E1	-0.3208 E1	-0.5165 E1
C_5	-0.5310 E1	0.1272 E2	0.3065 E1	-0.2381 E1	0.4407 E2	-0.4144 E1
C_6	-0.2526 E1	0.1798 E1	-0.2480 E1	-0.3283 E1	0.2379 E1	0.2805 E1
C_7	-0.2511 E1	-0.5253 E1	-0.8912 E1	-0.5258 E1	-0.4009 E2	0.9514 E1
C_8	-0.2538 E1	0.1172 E2	-0.1457 E1	-0.3692 E1	0.2571 E2	-0.1084 E1
C_9	-0.3799 E1	-0.1385 E2	-0.1321 E2	0.1978 E1	-0.1169 E3	0.1007 E2
C_{10}	0.1105 E2	0.1350 E1	0.1586 E2	0.1252 E1	0.1106 E3	0.3226 E0
C_{11}	0.9007 E0	-0.5594 E1	0.1660 E0	0.1498 E1	-0.1602 E2	0.2722 E1
C_{12}	0.7680 E0	0.3864 E1	0.4473 E1	-0.4705 E1	0.7521 E2	-0.1530 E1
C_{13}	-0.5543 E1	0.2558 E1	-0.4116 E1	0.7155 E1	-0.7146 E2	-0.1139 E2
Standard errors in all data						
	0.03414	0.00976	0.02842	0.00934	0.05798	0.06296

Table 8 Standard errors of estimate in t , y_i using Eq. (4) for the system acetic acid-ethanol-water-ethyl acetate

t [°C]	Number of data points used; 247 errors of vapor composition in all data [mol %]			
	y_1	y_2	y_3	y_4
1.7646	1.95	1.46	1.87	3.14

Table 9 Parameters of the Wilson equations obtained from binary data and standard errors of vapor compositions

System	Wilson's parameter		Standard error y [%]	Data reference
	A_{12}	A_{21}		
acetic acid-ethanol	0.27558	2.28180	1.93	(15)
acetic acid-water	0.26838	1.22642	0.93	(16)
acetic acid-ethyl acetate	0.61790	0.89277	1.93	*
ethanol-water	0.15347	0.92038	1.28	(1)
ethyl acetate-ethanol	0.55046	0.76670	1.61	(4)
ethyl acetate-water	0.12353	0.14907	1.80	(3)

* values determined from our experimental data

Table 10 Standard errors of estimate in t , y_i using Wilson's parameters obtained from binary data only for the system acetic acid-ethanol-water-ethyl acetate

t [°C]	Number of data points used; 247 errors of vapor composition in all data [mol %]			
	y_1	y_2	y_3	y_4
2.0492	2.05	1.17	2.97	4.15

where A_{ij} is Wilson's constant.

The binary systems, which contain acetic acid, were treated with the consideration that dimers and trimers were present in acetic acid vapor, and the modified activity coefficients¹⁷⁾ were calculated using equilibrium constants of dimerization, K_2 and of trimerization, K_3 which were given by Potter and Ritter¹³⁾. Wilson's parameters were calculated from these modified activity coefficients for the six binary systems.

Table 9 presents the standard errors of calculated vapor compositions for the six binary systems. In all cases we found that the Wilson equation was in good agreement with the experimental data.

The extension of the binary system model to mixtures containing more than two components follows in a straightforward way and does not require any additivity assumptions.

The following equations represent the calculating method for a quaternary system containing acetic acid. Between apparent vapor composition y_i obtained from the experiment and true composition η_k modified by considering the association in acetic acid vapor, the following relation may be derived¹⁷⁾

$$\left. \begin{aligned} y_A &= \frac{\eta_1 + 2\eta_2 + 3\eta_3}{\eta_1 + 2\eta_2 + 3\eta_3 + \sum_{k=b}^d \eta_k} \\ y_i &= \frac{\eta_k}{\eta_1 + 2\eta_2 + 3\eta_3 + \sum_{k=b}^d \eta_k} \end{aligned} \right\} \quad (6)$$

As with Eq. (6)

$$\left. \begin{aligned} \eta_2 &= K_2 \pi \eta_1^2 \\ \eta_3 &= K_3 \pi^2 \eta_1^3 \end{aligned} \right\} \quad (7)$$

From the above equations, η_1 can be obtained.

For the case of pure acetic acid, similar equations can also be derived.

$$\left. \begin{aligned} \eta_{2A} &= K_{2A} P_A^0 \eta_{1A}^2 \\ \eta_{3A} &= K_{3A} P_A^0 \eta_{1A}^3 \end{aligned} \right\} \quad (8)$$

and

$$\eta_{1A} + \eta_{2A} + \eta_{3A} = 1 \quad (9)$$

η_{1A} is calculated from Eqs. (8) and (9).

Then the activity coefficient is

$$\left. \begin{aligned} \gamma_A &= \frac{\pi \eta \phi_1}{P_A^0 \eta_{1A} \phi_A} \\ \gamma_i &= \frac{\pi \eta_k \phi_i}{P_i^0 x_i} \end{aligned} \right\} \quad (10)$$

where vapor-phase fugacity coefficient ϕ_i is calculated by the Redlich and Kwong equation.

A comparison of calculated and experimental results is given in **Table 10**. The agreement of the calculated and experimental data with esterification may be considered satisfactory, particularly if we remember that only binary equilibrium data with no reaction are used for the prediction, and that the Wilson's constants are considered independent of temperature in the range of temperature studied. Then it is sufficient to express this quaternary system with esterification by the Wilson equation if some further procedure may be considered to express it more accurately by other equations.

4. Conclusion

Quaternary vapor-liquid equilibria with esterification have been formulated, first using Margules model. Activity coefficient may be related to liquid compositions, and second vapor-liquid equilibrium ratio may be related to temperature and liquid compositions used in our graphical relationship reported previously.

Both correlation of vapor-liquid equilibrium with esterification on quaternary systems gives a reasonable representation of the given system.

Next we tested Wilson equation for the system acetic acid-ethanol-water-ethyl acetate using the activity coefficient, which is modified with association equilibrium constants of dimerization and trimerization in acetic acid vapor, and have come to the conclusion that it provides an excellent basis for a calculation of quaternary vapor-liquid equilibrium with esterification using only experimental data for binary mixtures.

Nomenclature

- A_k = regression coefficients defined by Eq. (1)
- B_i, B_{ij} = constant defined by Eq. (2), i and j indicate component and parameter, respectively.
- C_k = regression coefficients defined by Eq. (4)
- F_1, F_2 = independent variables
- K_i = vapor-liquid equilibrium ratio of i -th component
- K_2, K_3 = dimerization and trimerization equilibrium constants of acetic acid
- K_{2A}, K_{3A} = dimerization and trimerization equilibrium constants of acetic acid in pure acetic acid
- P_i^0 = vapor pressure in pure substance
- Q = Q function ($= \sum x_i \ln \gamma_i$)
- x_i = mole fraction in liquid phase
- y_i = mole fraction in vapor phase

T = absolute temperature ($^{\circ}\text{K}$)
 t = temperature ($^{\circ}\text{C}$)
 A_{ij} = Wilson's parameter
 η_i = true mole fraction in vapor phase
 π = total pressure
 γ_i = activity coefficient

Subscripts

1, 2, 3 = monomer, dimer and trimer of acetic acid vapor in Eqs. (6) to (10)
 A, B, C, D = acetic acid, alcohol, water and ester, respectively
 1A, 2A, 3A = monomer, dimer and trimer in pure acetic acid

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EVALUATION OF THE WILSON PARAMETERS BY NOMOGRAPHS*

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To evaluate the Wilson parameters from the activity coefficients in an infinitely dilute binary solution, nomographs have been prepared which show the following features of the Wilson equation.

- i. In a system of positive deviations from ideal behaviour only 1 set of parameters exists.
- ii. In a system of negative deviations, 1 through 3 sets of parameters satisfy the Wilson equation.

By these nomographs, the authors have evaluated the Wilson parameters for the acetone-chloroform system, which give a good representation of the data.

To calculate vapor-liquid equilibrium relationships, many equations have been proposed^{2,8,11)}, based on various models. Without losing effectiveness, it is desirable that these equations be used with as few parameters as possible so long as accuracy is not sacrificed.

The Margules, van Laar and Redlich-Kister equations are typical and have been employed for many systems. A new equation by Wilson, based on the theory of Flory-Huggins¹⁰⁾, was proposed in 1964.

Prausnitz et al.⁷⁾ have successfully applied this equation to almost seventy systems and have shown that it accurately represents vapor-liquid equilibrium relationships with only two parameters.

These typical equations used before the Wilson equation are either linear with respect to the parameters (Margules, Redlich-Kister) or suitable to obtain the parameters from activity coefficients by simple calculations (van Laar).

As a result, the parameters can be evaluated with ease (even if nonlinear estimation procedure is applied

to calculate the parameters, their initial value can be guessed with no difficulties). On the other hand, the Wilson equation is not a linear combination of parameters, therefore the determination of the initial value is not always an easy matter. For this problem, Prausnitz proposed several methods. These are, however, not clear to assure the uniqueness and convergence of the solutions.

The authors have tried to obtain the Wilson parameters by nomographs which relate the parameters to the activity coefficients in infinitely dilute solution and have found that the parameters determined are sufficiently accurate compared with the rigorous solutions obtained by an electronic computer.

Design of Nomograph

The Wilson equation for the coefficients in a binary vapor-liquid equilibrium is as follows:

$$\ln \gamma_1 = -\ln(x_1 + A_{12}x_2) + x_2 \left(\frac{A_{12}}{x_1 + A_{12}x_2} - \frac{A_{21}}{A_{21}x_1 + x_2} \right) \quad (1)$$

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