

LIMITS ON THE PREDICTION OF ISOBARIC QUINARY PHASE EQUILIBRIA BY WILSON AND UNIQUAC EQUATIONS

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SUMMARY

The isobaric separation of multicomponent mixtures by distillation require reliable vapour-liquid equilibrium data. Since the experimental determination of multicomponent vapour-liquid equilibrium data is laborious and time consuming, there is a need to use a predictive method for the liquid-phase activity coefficients. The abilities of Wilson and UNIQUAC equations to predict isobaric quinary vapour-liquid equilibria using only binary constants of both equations were compared in this paper. The quinary system under study, is n. Hexane / Methylcyclopentane / Cyclohexane / Benzene / Toluene. UNIQUAC equation was found to be superior in the prediction of quinary vapour-liquid equilibria with the R.M.S. Deviations ranging from 0,0033-0,0103 where as the Wilson equation could predict the quinary vapour phase with the accuracy of 0,0048-0,0104 R.M.S.D.

ÖZET

Çok bileşenli karışımların distilasyon ile isobarik ayrılmasında güvenilir buhar-sıvı denge verisi gerekmektedir. Çok bileşenli buhar-sıvı denge verisinin deneysel ölçümü yorucu, zahmetli ve uzun zaman alan bir işlem olduğundan, sıvı faz aktivite katsayılarının belirlenmesinde tahmin metodlarından birisine gereksinim duyulmaktadır. Bu makalede, isobarik beşli buhar-sıvı dengesinin tahmininde yalnız ikili sabitleri kullanarak düzenlenen Wilson ve UNIQUAC bağıntılarının, her ikisinin başarı dereceleri karşılaştırılmaktadır. Bu çalışmada beşli sistem, n. Hegzan / Metilsiklopentan / Siklohegzan / Benzen / Toluen, araştırılmıştır. Beşli sistemin buhar-sıvı dengesinin tahmininde UNIQUAC bağıntısı 0.0033-0.0103 aralığında değişen standart sapma ile 0.0048-0.0104'lük standart sapma gösteren Wilson bağıntısına karşı üstün bulundu.

INTRODUCTION

The simulation of the separation of multicomponent mixtures by distillation requires information on VLE data. A great number of articles containing experimental VLE data for binary systems have appeared in the literature. However, the vast majority of industrial separations involves several components and experimental data for systems containing four or more components are almost nonexistent. There is then the choice of performing experimental determination of VLE data or estimating the data with one of the theoretical prediction relationships. Obtaining good experimental binary and especially multicomponent VLE data requires appreciable experimental skill, experience and patience. It is therefore an economic necessity to consider techniques for calculating phase equilibria for multicomponent system from few experimental data.

Product compositions obtained from multicomponent simulation will be dependent on the particular VLE model used in simulation. The variation in product predicted compositions is very important in designing multicomponent distillation columns. With the speedy development of computers there is more concern for thermodynamic relations to predict multicomponent VLE data from corresponding binary properties and pure component data because generally binary properties are more readily available.

Two major group methods have developed to calculate the liquid activity coefficient of component in a multicomponent mixture. Generally these methods can be divided into those which require binary pair interactions and those which split the component molecules into fundamental groups.

The aim of the present study is to see which of the two well known binary interaction methods, Wilson Eq. (1964) or UNIQUAC Eq. (Abrams, 1975) of predicting quinary VLE data is more practical in estimating vapour phase mole fraction values.

THERMODYNAMICS OF PHASE EQUILIBRIA

The fundamental thermodynamic condition for multicomponent phase equilibria is expressed by the equality of fugacities f_i , in all phases for each component. (Souders, 1932).

$$f_i^v = f_i^L \quad (1)$$

The fugacities in Eq. (1) are related to the experimentally determined quantities x , y , T and P , through two auxillary functions which contain the fugacity coefficient ϕ and the activity coefficient γ . The first of these, the fugacity coefficient ϕ , relates the vapour-phase fugacity f_i^v to the mole fraction y_i and to the total pressure P .

$$f_i^v = \phi_i y_i P \quad (2)$$

The activity coefficient γ relates the liquid-phase fugacity f_i^L to the mole fraction x_i and to the standard-state fugacity f_i^{OL}

$$f_i^L = \gamma_i x_i f_i^{OL} \quad (3)$$

From Eqs. (1), (2), (3) the equation of equilibrium vapour-phase composition for any component i becomes.

$$y_i = \gamma_i x_i f_i^{OL} / \phi_i P \quad (4)$$

The standard-state fugacity of any component must be evaluated at the same temperature as that of the solution, regardless of whether the symmetric or unsymmetric convention is used for activity coefficient normalization. At low pressures, the effect of pressure on the thermodynamic properties of condensed phases is negligible and under such conditions the standard-state fugacities are essentially independent of pressure but at higher pressures it is no longer the case.

The liquid-phase fugacity of component i , for condensable component i is given by Prausnitz (1969) as

$$f_i^L = x_i f_i^{OL} \exp(V_i^L P / RT) \quad (5)$$

Where f_i^{OL} is the fugacity of pure component i , at the temperature of solution and at the reference pressure p^r . V_i^L is the partial molar liquid volume. The exponential term is the Poynting correlation which corrects the liquid fugacity to a zero-pressure reference. The liquid molar volume V_i^L is assumed constant over the range of the integral and is calculated using Rackett's equation as modified by Spencer and Danner (1972). This equation has been further modified by O'Connell (1975) for reduced temperatures greater than 0.75. The saturated-liquid molar volume is given by the equation.

$$V_i^L = R T_{ci} Z_{ai} / P_{ci} \quad (6)$$

$$\text{Where } \tau = 1 + (1 - T_r)^{0.286} \text{ for } T_r \leq 0.75 \quad (7)$$

Z_{ai} is the modified Rackett parameter.

The liquid reference fugacity at zero pressure f_i^{OL} is fit to a function of the form given by Lykman (1965) correlation by Prausnitz (1980) as a function of temperature.

$$\ln f_i^{OL} = C_1 + C_2/T + C_3T + C_4 \ln T + C_5 T^2 \quad (8)$$

Where T is in Kelvin and F_i^{OL} is in bars.

From Eqs. (4), (5), (8), for multicomponent vapour-liquid equilibria, the equation of equilibrium for every condensable component i is,

$$y_i = \frac{\gamma_i}{\phi_i P} x_i f_i^{OL} \exp(V_i^L P / RT) \quad (9)$$

The vapour-phase fugacity coefficient is calculated from the below given relation (O'Connell, 1967).

$$\ln \phi_i = [2 \sum_{j=1}^m y_j B_{ij} - B_m] (P / RT) \quad (10)$$

Where values of second virial coefficients, B_{ij} , are experimental values. When experimental values of second virial coefficients are not available, the equation of Pitzer and Curl (1957) is used for pure non-polar gases.

$$\frac{B_{ji} P_{ci}}{R T_{ci}} = (0.1445 + 0.0073w) - (0.33 - 0.46w) T_r^{-1} - (0.1385 + 0.5w) T_r - (0.0121 + 0.097w) T_r^{-3} - (0.0073w) T_r^{-8} \quad (11)$$

Where w is the acentric factor calculated from

$$w = -1 - \log \frac{P'_{0.7}}{P_{ci}} \quad (12)$$

and $P'_{0.7}$ is the vapour pressure at $T/T_{ci} = T_r = 0.7$.

The $B_{mixture}$ is obtained from the relation given in the following.

$$B_{mixture}(T, y_1, \dots, y_m) = \sum_{j=1}^m \sum_{i=1}^m y_i y_j B_{ij}(T) \quad (13)$$

The composition of a vapour in equilibrium with a liquid can then be calculated by the Eq. (9) with the knowledge of the liquid phase activity coefficient, γ_i .

Although assuming liquid phase activity coefficient equals to unity, VLE data for ideal system can be easily calculated by Raoult's Law, Dalton's Law, VLE data for real solutions which are subject to distillation can not be evaluated so easily. In order to overcome the difficulties met in design and operation of the equipment, the estimation methods for non-ideal systems have become subject to many investigators. In the past 25 years two major group methods have developed to calculate the activity coefficient of component in a multicomponent mixture. Generally, these methods can be divided into those which require binary pair interactions, and those which split the component molecules into fundamental groups.

DETERMINATION OF ACTIVITY COEFFICIENTS

In order to express the non-ideality of a liquid mixture, Scatchard (1937) proposed the most useful thermodynamics concept, called Gibbs excess energy, G^E . The G^E is defined as a function of liquid-phase activity coefficient at constant temperature and pressure. So one may compute activity coefficients γ_i , from G^E model, by applying the relation.

$$\ln \gamma_i = \left[\frac{\partial (n_T G^E)}{\partial x_i} \right]_{T,P,X_{k \neq i}} \quad (14)$$

Many solution models which relate activity coefficients to liquid composition and satisfy the Gibbs-Duhem equation have been proposed. Two solution models, Wilson Eq. (1964) and the UNIQUAC model of Abrams (1975) as slightly modified by Anderson (1978), for liquid phase activity coefficients have been compared in this study.

WILSON EQUATION

Wilson (1964) proposed the following logarithmic function as an expression for the molar-excess free-energy for multicomponent systems.

$$\frac{G^E}{RT} = - \sum_{i=1}^m x_i \ln \left[\sum_{j=1}^m \Lambda_{ij} x_j \right] \quad (15)$$

When Eq. (14) is applied to the expression above, the Wilson equation for a multicomponent system becomes (Orje, 1965).

$$\ln \gamma_i = 1 - \ln \left[\sum_{j=1}^m x_j \Lambda_{ij} \right] - \sum_{j=1}^m \frac{x_j \Lambda_{kj}}{\sum_{j=1}^m x_j \Lambda_{kj}} \quad (16)$$

Where

$$\Lambda_{ij} = \frac{V_i}{V_i} \exp \left(- \frac{\lambda_{ij} - \lambda_{ii}}{RT} \right), \Lambda_{ji} = \frac{V_i}{V_j} \exp \left(- \frac{\lambda_{ji} - \lambda_{jj}}{RT} \right) \quad (17)$$

and $(\lambda_{ij} - \lambda_{ii})$, $(\lambda_{ji} - \lambda_{jj})$ are adjustable binary energy parameters.

UNIQUAC EQUATION

The UNIQUAC equation for excess Gibbs energy G^E is given by Prausnitz (1980)

$$\begin{aligned} G^E / RT = & \sum_i x_i \ln (\varnothing_i / x_i) + (z/2) \sum_i q_i x_i \ln (\theta_i / \varnothing_i) \\ & - \sum_i q'_i x_i \ln \left(\sum_j \theta'_j \tau_{ji} \right) \end{aligned} \quad (18)$$

Where segment fraction \varnothing and area fractions θ and θ' are given by

$$\varnothing_i = \frac{r_i x_i}{\sum_j r_j x_j} \quad \tau_{ij} = \exp (-A_{ij}/T) \quad (19)$$

$$\theta_i = \frac{q_i x_i}{\sum_j q_j x_j} \quad \theta'_i = \frac{q'_i x_i}{\sum_j q'_j x_j} \quad (20)$$

For any component i , the activity coefficient is given by

$$\begin{aligned} \ln \gamma_i = & \ln (\varnothing_i / x_i) + (z/2) q_i \ln (\theta_i / \varnothing_i) + l_i - (\varnothing_i / x_i) \sum_j x_j l_j \\ & - q'_i \ln \left(\sum_j \theta'_j \tau_{ji} \right) + q'_i - q'_i \sum_i \frac{\theta'_j \tau_{ij}}{\sum_k \theta'_k \tau_{kj}} \end{aligned} \quad (21)$$

Where

$$l_j = (z/2) (r_j - q_j) - (r_j - 1) \quad (22)$$

Equation (21) requires only pure-component and binary parameters, and in Eq. (22) coordination number 2 equals to 10. The parameters r , q , and q' are pure-component molecular-structure constants depending on molecular size and external surface areas. For non-polar components $q=q'$ can be taken.

PREDICTION PROCEDURE OF QUINARY VLE DATA

Apart from their intrinsic value for the design of distilling plants, experimental multicomponent VLE data provide an important means of the testing the validity of thermodynamic models of liquid mixtures and the associated methods of data processing and prediction.

The Quinary System (Weatherford, 1970), n. Hexane (2) / Cyclohexane (3) / Benzene (4) / Toluene (5) has been chosen to study the prediction of isobaric multicomponent vapour-liquid equilibria with Wilson and UNIQUAC Equations.

Adjustable binary energy parameters of Wilson Eq. and UNIQUAC Eq. for 10 binary systems which comprise the quinary system studied in this work and their data sources are presented in Table I. To use the Wilson Eq. it is also necessary to have the liquid molar volume as a function of temperature for each component. The volumetric data used for the calculation of binary energy parameters were also used in this study. The volumetric data taken from Holmes (1970) are listed in Table II. Using the molar volumes at three different temperatures, the constants in the quadratic equation.

$$V_i(T) = a + bT + cT^2 \quad (23)$$

were calculated for each component and are also given in Table II.

The UNIQUAC eq. constants r , q for each pure component i are given in Table III.

The vapour phase fugacity coefficients were calculated by using the virial eq. (10). The self virial coefficients were computed where necessary by Pitzer and Curl (1957) method. Constants required for the calculation of the Poynting correction factor are taken from Prausnitz (1980) and are listed in Table III. together with the constants required for the calculation of f_i^{OL} data.

The calculated activity coefficients in turn were used in Eq. (9) to evaluate y_1, y_2, \dots, y_5 values at 1 atm. For practical purposes, a

Table 1. Parameters of Wilson Eq. and UNIQUAC Eq.

System (1)-(2)	Wilson Parameters			UNIQUAC Parameters		
	$\lambda_{12}-\lambda_{11}$	$\lambda_{21}-\lambda_{22}$	Ref. Data	A ¹²	A ²¹	Ref. Data
n. Hexane-M.C.P.	348.3	-219.53	Myers (1957)	-138.84	162.13	Beyer (1965)
n. Hexane-Cyclohexane	439.96	-230.57	Myers (1957)	-145.56	172.73	Ridgway (1967)
n. Hexane-Benzene	279.52	134.35	Myers (1955)	-4.34	43.93	Park (1986)
n. Hexane-Toluene	-121.00	383.89	Myers (1955)	29.59	4.38	Myers (1955)
M.C.P.-Cyclohexane	327.06	-247.40	Weatherford (1970)	-118.82	144.37	Susarev (1962)
M.C.P.-Benzene	94.10	162.93	Myers (1956)	147.22	-76.06	Beyer (1965)
M.C.P.-Toluene	-465.89	1004.73	Myers (1956)	89.77	-48.05	Myers (1956)
Cyclohexane-Benzene	151.22	107.28	Richards (1944)	66.85	-16.85	Ridgway (1956)
Cyclohexane-Toluene	446.10	981.96	Myers (1956)	83.67	-44.04	Myers (1956)
Benzene-Toluene	75.54	-88.83	Heertjies (1960)	17.12	-12.32	Park (1986)

Table 2. Molar Volume Data (Holmes, 1970)

Component Name	T ₂ K	L V ₁ cm ³ /gmol	T ₂ K	L V ₂ cm ³ /gmol	T ₃ K	L V ₂ cm ³ /gmol	Constants		
							a	b	c
n. Hexane	273.15	127.301	323.15	148.211	373.15	125.959	-0.1445	5.472 10 ⁻⁴	
M.C.P.	273.15	109.670	303.15	113.810	373.15	105.456	-0.0951	4.044 10 ⁻⁴	
Cyclohexane	288.15	107.470	306.30	109.841	352.35	93.648	-0.0298	2.699 10 ⁻⁴	
Benzene	273.15	86.783	323.15	92.263	373.15	70.862	0.0149	1.588 10 ⁻⁴	
Toluene	303.15	107.415	353.15	113.717	440.00	99.064	-0.0570	2.789 10 ⁻⁴	

Table 3. Pure Component Data (Prausnitz, 1980)

Component Name	T _c K	P _c Bars	Z _{RA}	UNIQUAC P		Constants for Standart-State Fugacity Equation				
				r	q	C ₁	C ₂	C ₃	C ₄	C ₅
n. Hexane	507.43	30.12	0.2635	4.50	3.86	-350.52	3318.3	-0.02025	68.4900	8.8924 10 ⁻⁵
M.C.P.	532.89	37.85	0.2700	3.97	3.01	53.797	-5690.0	0.000945	-6.4352	-4.565 10 ⁻⁷
Cyclohexane	553.54	40.75	0.2729	3.97	3.01	-121.38	-1884.5	-0.08534	25.948	3.6812 10 ⁻⁵
Benzene	552.16	48.98	0.2696	3.19	2.40	97.209	-6976.1	0.019082	-14.212	-6.718 10 ⁻⁶
Toluene	591.79	41.09	0.2646	3.92	2.97	20.899	-5790.2	-0.02074	71.440	1.151 10 ⁻⁵

detailed computer program was prepared for each of the two equations, to predict the isobaric quinary VLE data. In the liquid phase activity coefficient programme the liquid composition, the boiling point and the total pressure were fixed by the experimental data and the Wilson and the UNIQUAC eq. s were used to predict the equilibrium vapour compositions.

Liquid phase activity coefficients calculated from the Wilson Eq. and the UNIQUAC Eq. are tabulated together with the experimental activity coefficients in Table IV. Vapour compositions predicted by the Wilson and the UNIQUAC Eq. are also given in Table IV. together with the experimental vapour phase compositions (Weatherford, 1970).

RESULTS AND DISCUSSION

Table (IV) summarises the result of testing the Wilson and UNIQUAC eqs. using the published quinary VLE data. R.M.S.D.'s between the experimental and the calculated vapour mol fractions are tabulated in Table V together with the mean composition errors for comparison. An examination of VLE errors in the predicted vapour phase compositions show errors of the order of 0.0048—0.0104 mol fractions with Wilson Eq. and errors of the order of 0.0033—0.0103 mol fractions with UNIQUAC Eq. Comparison of mean composition errors show that UNIQUAC produce the lower mean composition errors. While the mean vapour composition error is 0.0058 mol fractions, the individual errors can be large with some UNIQUAC predicted points having an error of 0.0247 mol fractions for M.C.P. (in RUN 2) and with Wilson Eq. predicted points having an error of 0.0274 mol fractions for the same component. If the experimental values of RUN 2 is excluded from the calculations, R.M.S.D.'s drop below 0.0100 for component M.C.P. for both equations. One may see from Table VI that after the exclusion of RUN 2 from calculations, agreement between mean deviations is within the estimated limits of experimental error.

The quinary system, understudy, provides two binary azeotropes. If table IV is closely observed one may find out that RUN 7 contains approximately the relative amounts of M.C.P. and Benzene reported in the binary azeotrope (Belknap, 1961) (0.125 mol fraction Benzene). The resulting normalized (based on the sum of the azeotropic components) experimental liquid and vapour benzene compositions were $0.089 / (0.089 + 0.583) = 0.132$ and $0.095 / (0.95 + 0.676) = 0.123$ mol frac-

Table 4. Quinary Vapour-Liquid Equilibrium Data for n. Hexane /M.C.P./ Cyclohexane/
Benzene /Touene.

Run No	Temp. T, °C	Comp Comp.	Experimental Values			Wilson Eq. Predictions		UNIQUAC Eq. Predictions	
			x	y	λ	y	λ	y	λ
1	78.27	Mex.	0.186	0.274	1.1043	0.2817	1.1352	0.2750	1.1085
		M.C.P.	0.257	0.328	1.0514	0.3309	1.0608	0.3269	1.0479
		Ch.	0.118	0.118	1.0777	0.1165	1.0639	0.1202	1.0156
		Bz.	0.153	0.167	1.1554	0.1609	1.0656	0.1629	1.2370
		Tol.	0.286	0.113	1.0924	0.1100	1.0565	0.1150	1.1117
2	84.41	Hex.	0.129	0.243	1.1843	0.2464	1.2009	0.2441	1.1897
		M.C.P.	0.159	0.224	0.9729	0.2514	1.918	0.2487	1.0802
		Ch.	0.132	0.168	1.1420	0.1605	1.0910	0.1574	1.0652
		Bz.	0.100	0.128	1.1231	0.1151	1.0101	0.1226	1.0758
		Tol.	0.480	0.237	1.1066	0.2266	1.0262	0.2272	1.0608
3	80.45	Hex.	0.132	0.219	1.1676	0.2271	1.2104	0.2180	1.1623
		M.C.P.	0.095	0.132	1.0891	0.1322	1.0757	0.1307	1.0628
		Ch.	0.218	0.241	1.1150	0.2344	1.0847	0.2483	1.0692
		Bz.	0.253	0.284	1.1104	0.2869	1.0461	0.2769	1.0826
		Tol.	0.302	0.122	1.0356	0.1194	1.0137	0.1261	1.0704
4	80.50	Hex.	0.069	0.112	1.404	0.1212	1.2338	0.1147	1.1679
		M.C.P.	0.166	0.238	1.1071	0.2335	1.0859	0.2314	1.0764
		Ch.	0.215	0.241	1.1290	0.2316	1.0848	0.2480	1.0695
		Bz.	0.261	0.290	1.0975	0.2999	1.0400	0.2857	1.0812
		Tol.	0.288	0.119	1.0534	0.1138	1.0080	0.1202	1.0640
5	76.58	Hex.	0.132	0.192	1.1463	0.1976	1.1794	0.1879	1.1215
		M.C.P.	0.155	0.202	1.1287	0.1899	1.0612	0.2151	1.0533
		Ch.	0.228	0.213	1.0599	0.2153	1.0713	0.2101	1.0455
		Bz.	0.333	0.336	1.1257	0.3240	1.0855	0.3302	1.1063
		Tol.	0.152	0.057	1.0997	0.0518	1.0000	0.0567	1.0939
6	77.98	Hex.	0.067	0.105	1.1843	0.1084	1.2222	0.0993	1.1200
		M.C.P.	0.081	0.106	1.0877	0.1035	1.0622	0.1007	1.0333
		Ch.	0.360	0.362	1.0929	0.3657	1.0770	0.3790	1.1443
		Bz.	0.359	0.374	1.1122	0.3850	1.0793	0.3694	1.0356
		Tol.	0.133	0.053	1.1128	0.0465	0.9772	0.0516	1.0832
7	75.71	Tex.	0.066	0.087	1.0654	0.0887	1.0868	0.0856	1.0483
		M.C.P.	0.583	0.676	1.0306	0.6850	1.0442	0.6749	1.0289
		Ch.	0.077	0.070	1.0602	0.0682	1.0324	0.0646	0.9748
		Bz.	0.089	0.097	1.2238	0.0895	1.0814	0.939	1.2096
		Tol.	0.185	0.072	1.0767	0.0686	1.1218	0.0712	1.1636
8	78.83	Hex.	0.098	0.153	1.1517	0.1591	1.1975	0.1498	1.1276
		M.C.P.	0.149	0.206	1.1207	0.1960	1.0666	0.1929	1.0495
		Ch.	0.269	0.272	1.0712	0.2728	1.0740	0.2672	1.0523
		Bz.	0.265	0.282	1.1066	0.2901	1.1384	0.2811	1.1031
		Tol.	0.219	0.088	1.0895	0.0820	1.0246	0.0879	1.0883
9	78.54	Hex.	0.186	0.273	1.0916	0.2832	1.1324	0.2870	1.1076
		M.C.P.	0.255	0.339	1.0391	0.3834	1.0610	0.3409	1.0449
		Ch.	0.127	0.126	1.0604	0.1265	1.0646	0.1207	1.0158
		Bz.	0.128	0.137	1.1232	0.1293	1.0599	0.1377	1.1299
		Tol.	0.304	0.125	1.1257	0.1177	1.0605	0.1237	1.1140
10	76.02	Hex.	0.130	0.178	1.0971	0.1786	1.1004	0.1737	1.0706
		M.C.P.	0.471	0.563	1.0527	0.5629	1.0525	0.5746	1.0743
		Ch.	0.060	0.055	1.0583	0.0543	1.0448	0.0511	0.9838
		Bz.	0.109	0.115	1.0289	0.1203	1.0763	0.1129	1.0101
		Tol.	0.230	0.089	1.1571	0.0839	1.0908	0.0877	1.1314

Table 5. Mean Deviations of Experimental and Calculated Vapour Compositions in the Quinary System at 1 atm.

Component Name	Wilson Eq.	UNIQUAC Eq.
n. Hexane	0.0064	0.0033
M.C.P.	0.0104	0.0103
Cyclohexane	0.0048	0.0077
Benzene	0.0093	0.0042
Toluene	0.0058	0.0035
Mean Composition Error	0.0073	0.0058

Table 6. Mean Deviations of Experimental and Calculated Vapour Compositions after RUN 2 is excluded.

Component Name	Wilson Eq.	UNIQUAC Eq.
n. Hexane	0.0066	0.0034
M.C.P.	0.0060	0.0071
Cyclohexane	0.0044	0.0073
Benzene	0.0088	0.0040
Toluene	0.0050	0.0017
Mean Composition Error	0.0062	0.0047

tions respectively. These relative experimental concentrations are in good agreement with the binary azeotrope (0.125 mol fraction for benzene) when the estimated errors are considered. The corresponding estimated vapour phase concentrations for this run are $0.095 / (0.095 + 0.0676) = 0.123$ by Wilson and $0.0939 / (0.0939 + 0.6749) = 0.122$ by UNIQUAC.

The other azeotrope that quinary system provides is cyclohexane-benzene azeotrope (Ridgway, 1967). When RUN 6 is carefully examined the resulting normalized experimental liquid and vapour compositions where 0.494, 0.508, respectively as compared to the azeotropic binary benzene concentrations of 0.498 mol fraction. The corresponding estimated vapour phase concentrations for RUN 6 are 0.519 by Wilson and 0.494 mol fraction by UNIQUAC.

For RUN 8 the corresponding experimental azeotrope benzene liquid and vapour mol fractions where 0.496, 0.509, but the corresponding estimated vapour mol fractions are 0.515 by Wilson and 0.512 by UNIQUAC.

Run 9, the corresponding experimental azeotrope benzene liquid and vapour mol fractions were 0.502, 0.521 respectively, and the corresponding predicted vapour mol fractions are 0.505 by Wilson and 0.533

by UNIQUAC. From these comparison results the UNIQUAC Eq. appears to be more successful in evaluation of azeotrope vapour phase composition of the quinary system under study.

When Table IV is closely examined one may notice that for the composition region having the liquid phase composition of M.C.P. 0.159 (RUN 2), 0.155 (RUN 5) and 0.149 (RUN 8) the vapour compositions predicted, by means of both equations, show a great deviations from experimental values comparing to mean composition deviations. For that reason the liquid composition region having 0.150 mol fractions for the component M.C.P. should receive careful consideration in analyzing the output from simulation study of distillation plants.

CONCLUSIONS

The simulation of separation of multicomponent mixtures by distillation required reliable information on VLE data. Experimental data for binary systems are frequently available, but data for multicomponent mixtures are rare must be calculated. Prediction methods provides an important economic advantage since the experimental work required to characterize a multicomponent solution is thereby very much reduced. Since the separation is dependent on the predictive thermodynamic method used for the estimation of VLE data, the limitations used of these predictive methods must be considered in the design and operation of distillation columns. There would appear to be a major problem in selecting one thermodynamic model as "the best" as the choice may be system dependent.

In this study, Wilson and UNIQUAC equations are chosen for the prediction of liquid phase activity coefficients of the quinary system, n. Hexane / M.C.P. / Cyclohexane / Benzene / Toluene. Examination of calculations show that while both equations failed in predicting the vapour phase mole fractions for one run for the component M.C.P. (R.M. S.D.'s 0.0274, 0.0247 respectively for RUN 2), the UNIQUAC Ea. appears to be a much better off method for the estimation of the multicomponent vapour-liquid equilibria.

NOMENCLATURE

A_{ij}	UNIQUAC Binary Parameter
B_{ij}	Virial Coefficient
f_i	Fugacity

G^E	Gibb's Excess Free Energy
m	Number of Components in a multicomponent mixture
P	Total Pressure (mmHg) or (Bars)
P_{ci}	Critical pressure of component i
P_r	Reduced pressure (P_i/P_{ci})
q_i	Pure component molecular size constant
R	Ideal gas constant (cal/g. mol K°)
r_i	Pure component external surface area constants
T	Absolute temperature (K°)
T_{ci}	Critical temperature of component i
T_{ri}	Reduced temperature of component i
V_i^L	Saturated-Liquid molar volume of component i
x_i	Mole fraction of component i in liquid phase
y_i	Mole fraction of component i in vapour phase
Z_{ai}	Modified Rackett number

ABBREVIATIONS

M.C.P.	Methylcyclohexane
R.M.S.D.	Root Mean Square Deviation
VLE	Vapour-Liquid Equilibrium

GREEK LETTERS

γ_i	Liquid-phase activity coefficient of component i
θ_i, θ'_i	Area fractions of UNIQUAC Equation
$\lambda_{ij} - \lambda_{ii}$	Adjustable energy parameters of Wilson Equation
Λ_{ij}	Wilson Equation parameter
ϕ_i	Gas-phase fugacity coefficient

SUPERSCRIPTS AND SUBSCRIPTS

i, j, k	Component i, j, k in a multicomponent system
L	Liquid phase
O	Standart State
r	Reduced
v	Vapour phase

REFERENCES

- ABRAMS, D.S., PRAUSNITZ, J.M., 1975, *A.I.Ch.E.J.*, 21, 116.
- ANDERSON, J.F., and PRAUSNITZ, J.M., 1978, *Ind. Eng. Chem. Process Des. Dev.*, 17, 552.
- BELKNAP, R.C., and WEBER, J.H., 1961, *J. Chem. Eng. Data*, 6, 485.
- BEYER, W., SCHUBERTH, H., and LEIBNITZ, E., 1965, *J. Chem. Eng. Data*, 12, 509.
- HEERTJIES, P.M., 1960, *Chem. Prog. Eng.*, 41, 385.
- HOLMES, M.J., and WINKLE+ M.V., 1970, *Ind. Eng. Chem.*, 62, 21.
- LYKMAN, E.W., ECKERT, C.A., and PRAUSNITZ, J.M., 1965, *Chem. Eng. Sci.*, 20, 685.
- MYERS+ H.S., 1957, *Petrol. Refiner*, 36, 175.
- MYERS, H.S., 1955, *Ind. Eng. Chem.*, 47, 2215.
- MYERS, H.S., 1956, *Ind. Eng. Chem.*, 48, 1104.
- O'CONNELL, J.P., and PRAUSNITZ, J.L., 1967, *Ind. Eng. Chem. Process. Des. Dev.*, 6, 245.
- ORJE, R.V., and PRAUSNITZ, J.M., 1965, *Ind. Eng. Chem.*, 58, 18.
- PARK, J.O., and NAM, S.J., 1986, *Hwahak Kongkha*, 24, 311.
- PITZER, K.S., and CURL, R.F., 1957, *J. Am. Chem. Soc.*, 79, 2369.
- PRAUSNITZ, J.M., 1969, "Molecular Thermodynamics of Fluid Phase Equilibria", Prentice Hall, New Jersey.
- PRAUSNITZ, J.M., ANDERSON, T., GRENS, E., ECKERT, C., HSIEH, R., and O'CONNELL, J., 1980, "Computer Calculations for Multicomponent Vapour-Liquid and Liquid-Liquid Equilibria" Prentice Hall, New Jersey.
- RICHARDS, A.R., and HARGREAVES, E., 1944, *Ind. Eng. Chem.*, 36, 805.
- RIDGWAY, K., and BUTLER, P.A., 1967, *J. Chem. Eng. Data*, 12, 509.
- SCATHARD, G., 1937, *Trans. Faraday Soc.*, 33, 160.
- SOUDERS, M., SELHEIMER, C.W., and BROWN, C.G., 1932, *Ind. Eng. Chem.*, 24, 517.
- SPENCER, C.F., DANNER, R.P., 1972, *J. Chem. Eng. Data*, 17, 236.
- SUSAREV, M.P., and LYSLOVA, R.C., 1962, *Zh. Fiz. Ehim.*, 36, 437.
- WEATHERFORD, R.M., and WINKLE, M.V., 1970, *J. Chem. Eng. Data*, 15, 387.
- WILSON, G.M., 1964, *J. Am. Chem. Soc.*, 86, 127.