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LIMITS ON THE PREDICTIVE THERMODYNAMIC MODELS, WILSON AND UNIQUAC IN MULTICOMPONENT PHASE EQUILIBRIA OF ETHANOL-BENZENE-HEPTANE AND HEXANE-ETHANOL-BENZENE

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ABSTRACT

The accurate isobaric separation of multicomponent mixtures by distillation require reliable vapour-liquid equilibrium data. For non-ideal liquid-phase behaviour, there is a need to use a predictive model for the liquid-phase activity coefficients since the experimental determination of multicomponent vapour-liquid equilibrium data is laborious and time consuming. The estimated vapour-phase compositions are dependent on the predictive thermodynamic method used. The abilities of Wilson and UNIQUAC equations in the prediction of isobaric binary and ternary vapour-liquid equilibria were compared in this paper. The ternary systems, Ethanol-Benzene-Heptane and Hexane-Ethanol-Benzene which have highly non-ideal liquid-phase behaviour and provide binary azeotropes have been chosen to study in this work. UNIQUAC Eq. was found to be little superior in the prediction of ternary vapour-liquid equilibria with mean deviations ranging from 0.0146-0.0334 whereas the Wilson Eq. could predict the ternary vapour compositions within the accuracy of 0.0158-0.0333.

INTRODUCTION

The separation of multicomponent mixtures by distillation requires knowledge of the vapour-liquid equilibrium behaviour of the system under consideration. For binary mixtures experimental VLE data are generally available and reliable, but the same is not true for most multicomponent systems. For highly non-ideal multicomponent liquid phase behaviour, particularly with the formation of azeotropes and multiple azeotropes, it may be economic necessity to use a predictive model for the liquid phase activity coefficients in order to reduce the amount of experimental data required. With the speedy development of computers, there is more concern for thermodynamic relation 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 been developed to calculate the activity coefficient of component i 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 well known binary interaction methods are the Wilson (Wilson, 1964), NRTL (Renon, 1968) and UNIQUAC models (Abrams, 1975). The major group contribution methods are ASOG (Derr, 1969) and UNIFAC (Fredenslund, 1975). The aim of the present study is to see which of the two well known binary interaction methods, Wilson Eq. or UNIQUAC-For-Non-Ideal-Conditions is more practical in estimating ternary vapour phase mole fraction values. For this purpose, the ternary systems, Ethanol(1)-Benzene(2)-Heptane(3) (Wagner, 1958) and Hexane(1)-Ethanol(2)-Benzene(3) (Park, 1986) which have highly non-ideal liquid phase behaviour and provide binary azeotropes have been chosen to study.

THERMODYNAMICS OF PHASE EQUILIBRIA

The fundamental thermodynamic condition for multicomponent phase equilibria is expressed by the equality of fugacities in all phases for each component. Fugacities can be expressed in terms of fugacity or activity coefficients which approach unity for nearly ideal systems (Sounders, 1932):

$$\phi_i y_i P = \gamma_i x_i f_i^{o(p_o)} \exp(V_i^L P/RT) \qquad (1)$$

where $f_i^{o(p_o)}$ is the fugacity of pure component i, ϕ_i is the vapour-phase fugacity coefficient, γ_i is the liquid-phase fugacity coefficient and V_i^L is the partial molar liquid volume. The liquid molar volume V_i^L is assumed constant and calculated using Rackett's Eq. as modified by Spencer and Danner (1972).

$$V_i^L = R\,T_{ci}\,Z_{ai}^{\tau} / P_{ci} \qquad (2)$$

where Z_{ai} is the modified Rackett parameter, (O'Connell, 1967) and

$$\tau = 1 + (1 - T_r)^{0.286}$$

In Eq. 1. the exponential term is the Poynting correlation which corrects the liquid fugacity to a zero-pressure reference.

The vapour-phase fugacity coefficient is given by Prausnitz (1980).

$$\ln \phi_i = \frac{2.0}{V_{mix}} \left(\sum_{j=1}^{m} y_i \, B_{ij} \right) - \ln Z_{mix} \qquad (3)$$

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. The virial equation of state truncated after the second term is used to evaluate the compressibility factor Z.

The composition of vapour in equilibrium with a liquid phase can then be calculated by using Eq. 1 with the knowledge of the liquid phase activity coefficient γ_i.

PREDICTION OF ACTIVITY COEFFICIENTS

Although assuming liquid phase activity coefficient equals to unity VLE data for ideal systems can be easily evaluated by Raoult's and Dalton Law. VLE data for non-ideal systems can not be evaluated so easily. For real systems, non-ideality of a liquid mixture is expressed as Gibbs excess energy, G^E, which is defined as a function of liquid phase activity coefficients at constant temperature and pressure (Scatchard, 1937).

$$R\,T \ln \gamma_i = \left[\frac{\partial (n_T G^E)}{\partial x_i} \right]_{T,P,x_{k \neq i}} \qquad (4)$$

Many solution models which relate activity coefficients to liquid composition and satisfy the Gibbs equation have been proposed. Two solution models, Wilson Eq (1964) and 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 liquid-phase activity coefficients of multicomponent system.

$$\ln \gamma_i = 1 - \ln \left[\sum_{j=1}^{m} x_j \, \Lambda_{ij} \right] - \sum_{j=1}^{m} \frac{x_k \, \Lambda_{ki}}{\sum_{j=1}^{m} x_j \, \Lambda_{kj}} \qquad (5)$$

$$\text{where } \Lambda_{ij} = \frac{V_j^L}{V_i^L} \exp\left[- \lambda_{ij} - \lambda_{ii} / RT\right] \text{ and } \Lambda_{ij} \neq \Lambda_{ji} \tag{6}$$

and $(\lambda_{ij} - \lambda_{ii})$, $(\lambda_{ij} - \lambda_{jj})$ are adjustable binary energy parameters. The Wilson equation for a multicomponent system requires only parameters that can be obtained from related binary VLE data and pure component data.

UNIQUAC EQUATION

The UNIQUAC Eq. (UNIversal-QUAsi-Chemical eq.) for multicomponent liquid-phase activity coefficient for any component i is given by Prausnitz (1980) by

$$\ln \gamma_i = \ln (\phi_i/x_i) + (z/2)\, q_i \ln (\theta_i/\phi_i) + l_i - (\phi_i/x_i) \sum_j x_j\, l_j$$

$$- q'_i \ln \left(\sum_j \theta'_j\, \tau_{ji}\right) + q'_i - q'_i \sum_i \frac{\theta'_j\, \tau_{ij}}{\sum_i \theta'_k\, \tau_{kj}} \tag{7}$$

where

$$l_j = (z/2)(r_j - q_j) - (r_j - 1) \tag{8}$$

$$\phi_i = r_i x_i \Big/ \sum_j r_j\, x_j \quad \theta_i = q_i x_i \Big/ \sum_j q_j\, x_j \quad \theta'_i = q'_i x_i \Big/ \sum_j q'_j\, x_j \tag{9}$$

$\tau_{ij} = \exp(-A_{ij}/T)$, $\tau_{jj} = \tau_{ii} = 1$ and coordination number $z = 10$. Eq. 7. requires only pure component and binary parameters. The parameters r, q, q' are pure-component moleculer structure constants depending on molecular size and external surface areas. For non-polar compounds q=q' can be taken.

DETERMINATION OF CORRELATION PARAMETERS

In order to determine the correlation parameters necessary for predicting the vapour-liquid equilibrium behavior of the ternary system, Wilson and UNIQUAC Equations were fitted to published experimental VLE data for the binary systems, Ethanol-Benzene (Landwehr, 1958), Ethanol-Heptane (Kurt, 1956), Benzene-Heptane (Seig, 1950), Hexane-Ethanol (Sinor, 1960), Hexane-Benzene (Prabhu, 1963) that had passed the

Fredenslund's (1977) consistency test. Then the correlation parameters were optimized by using the Quasi-Newton fit programme which minimizes the objective functions.

$$O.F = \sum_{i=1}^{N} (\gamma_{1exp} - \gamma_{1calc})^2/N + \sum_{i=1}^{N} (\gamma_{2exp} - \gamma_{2calc})_i^2/N \qquad (10)$$

Table I. lists the optimized correlation parameters evaluated in this work, as well as the parameters obtained from the published data (Prausnitz, 1980), (Holmes, 1970). The liquid molar volumes needed for the correlation with the Wilson Eq. were calculated by using the molar volumes measured at three different temperatures and arranging a quadratic equation with them. The values of the parameters r, q, q' required by the UNIQUAC Eq. were taken from the published data (Prausnitz, 1980).

PREDICTION OF THE VLE DATA FOR BINARIES AND TERNARY SYSTEMS

The activity coefficients of the components of the ternary systems and the five binaries comprising the ternary systems were calculated by the Wilson and the UNIQUAC equations by using the binary correlation parameters given in Table I.

Table I. Optimized Parameters of Wilson and UNIQUAC Equations and Mean Deviations Between the Experimental Vapour Compositions and the Predicted by Those Estimated Binary Parameters at 1 atm.

System(1)-(2)	Wilson Parameters				UNIQUAC Parameters			
	λ_{12}-λ_{11}	λ_{21}-λ_{22}	Δy	Ref,Data	A_{12}	A_{21}	Δy	Ref. Data
Ethanol-Benzene	1325.45	218.98	0.0113	This work	-129.09	864	0.0114	This work
	1489.3	125.3	0.0161	HOLMES, 1970	-128.88	997.41	0.0266	BROWN, 1954
Ethanol-Heptane	2096.5	617.57	0.0256	HOLMES, 1970	-113.4	1435.59	0.0184	This work
					-110.15	1356.9	0.0237	PENA, 1970
Benzene-Heptane	99.35	292.94	0.0037	HOLMES, 1970	-32.03	68.52	0.0041	This work
					19.07	31.35	0.0075	PALMER, 1972
Hexane-Ethanol	283.63	2281.99	0.0085	HOLMES, 1970	1441.57	-108.93	0.0138	This work
					485.55	-57.96	0.0246	PARK,NAM,1986
Hexane-Benzene	225.97	139.54	0.0041	This work	132.43	-77.13	0.0033	This work
	169.92	173.93	0.0034	HOLMES, 1970	-4.34	43.91	0.0052	PARK,NAM,1986
	279.52	134.35	0.0057	MYERS, 1955				

Table II. Ternary Vapour-Liquid Equilibrium Predictions from UNIQUAC Equation for Ethanol-Benzene-Heptane at 1 atm.

Run	Temp.	Liquid Composition			Expt. Vapour Compn.			Calcd. Vapour Compn.			Expt. Activity Coeff.			Calcd. Activity Coeff.		
No	°K	X_1	X_2	X_3	Y_1	Y_2	Y_3	Y_1	Y_2	Y_3	γ_1	γ_2	γ_3	γ_1	γ_2	γ_3
1	348.25	0.044	0.213	0.743	0.424	0.212	0.364	0.3679	0.2136	0.4185	10.9278	1.1491	0.9871	9.4702	1.1578	1.0316
2	345.85	0.084	0.323	0.593	0.420	0.265	0.315	0.4194	0.2929	0.2877	6.2203	1.0194	1.1899	6.2203	1.1267	1.0868
3	345.85	0.069	0.415	0.516	0.370	0.371	0.259	0.3621	0.3680	0.2699	6.6807	1.1106	1.0514	6.5381	1.1016	1.0957
4	344.55	0.086	0.584	0.330	0.340	0.478	0.182	0.3429	0.4800	0.1771	5.1893	1.0586	1.2265	5.2336	1.0630	1.1935
5	343.65	0.103	0.651	0.246	0.359	0.506	0.135	0.3453	0.5160	0.1387	4.7438	1.0340	1.2386	4.5628	1.0544	1.2725
6	342.65	0.138	0.750	0.112	0.371	0.560	0.069	0.3553	0.5775	0.0672	3.8117	1.0290	1.5098	3.6504	1.0570	1.4704
7	345.15	0.155	0.115	0.739	0.575	0.091	0.334	0.5457	0.1091	0.3452	4.7529	1.0044	1.0897	4.5107	1.2042	1.1262
8	343.65	0.252	0.212	0.536	0.518	0.201	0.281	0.5323	0.1988	0.2689	2.7981	1.2611	1.3473	2.8753	1.2473	1.2893
9	342.95	0.242	0.310	0.448	0.502	0.260	0.238	0.4945	0.2765	0.2290	2.9051	1.1405	1.3641	2.8617	1.2129	1.3125
10	342.15	0.257	0.407	0.336	0.452	0.364	0.184	0.4646	0.3507	0.1847	2.5450	1.2473	1.3981	2.6159	1.2017	1.4034
11	342.75	0.238	0.495	0.267	0.468	0.387	0.145	0.4363	0.4088	0.1549	2.8923	1.1041	1.3408	2.6964	1.1663	1.4323
12	341.65	0.244	0.651	0.105	0.415	0.520	0.065	0.4134	0.5280	0.0586	2.5121	1.1317	1.8398	2.5024	1.1491	1.6587
13	344.35	0.350	0.065	0.585	0.598	0.065	0.337	0.6002	0.0694	0.3304	2.2607	1.3006	1.4524	2.2691	1.3886	1.4240
14	344.05	0.168	0.084	0.748	0.587	0.082	0.331	0.5372	0.0781	0.3847	4.6791	1.2817	0.9789	4.2821	1.2208	1.1377
15	342.95	0.356	0.193	0.451	0.534	0.199	0.267	0.5413	0.1929	0.2658	2.1008	1.4025	1.5029	2.1295	1.3595	1.4962
16	342.15	0.378	0.261	0.361	0.527	0.255	0.218	0.5136	0.2562	0.2302	2.0174	1.3623	1.5181	1.9661	1.3687	1.6031
17	341.55	0.406	0.391	0.203	0.485	0.370	0.145	0.4820	0.3794	0.1386	1.7716	1.3451	1.9429	1.7607	1.3793	1.8572
18	341.05	0.602	0.320	0.078	0.510	0.401	0.089	0.5048	0.4021	0.0931	1.2827	1.8099	2.8715	1.2696	1.8149	3.0038
19	341.05	0.419	0.544	0.037	0.440	0.520	0.040	0.4534	0.5252	0.0214	1.5898	1.3806	4.3058	1.6382	1.3944	2.3036
20	343.85	0.467	0.044	0.489	0.614	0.051	0.335	0.6073	0.0519	0.3408	1.7752	1.6331	1.6802	1.7558	1.5602	1.7093
21	343.55	0.399	0.069	0.532	0.599	0.092	0.309	0.5867	0.0750	0.3383	2.0515	1.7799	1.4039	2.0094	1.4510	1.5370
22	342.75	0.522	0.139	0.339	0.572	0.179	0.249	0.5660	0.1658	0.2682	1.5470	1.7626	1.8526	1.5308	1.6326	1.9954
23	341.75	0.527	0.272	0.201	0.511	0.318	0.171	0.5187	0.3114	0.1699	1.4264	1.6514	2.2579	1.4479	1.6171	2.2434
24	341.35	0.541	0.361	0.098	0.498	0.407	0.095	0.4978	0.4156	0.0866	1.3765	1.6127	1.8065	1.3760	1.6468	2.5943
25	341.05	0.524	0.428	0.048	0.477	0.471	0.052	0.4810	0.4777	0.0413	1.3781	1.5893	3.4140	1.3897	1.6119	2.7115
26	343.95	0.622	0.036	0.342	0.632	0.053	0.315	0.6279	0.0515	0.3206	1.3662	1.9421	2.3117	1.3573	1.8871	2.3528
27	343.25	0.635	0.071	0.294	0.617	0.099	0.284	0.6038	0.1010	0.2952	1.3441	1.8784	2.4015	1.3154	1.9163	2.4962
28	343.15	0.640	0.172	0.188	0.563	0.240	0.197	0.5811	0.2443	0.1746	1.2219	1.8851	3.1489	1.2612	1.9192	2.7906
29	341.35	0.467	0.397	0.136	0.524	0.362	0.114	0.4842	0.4116	0.1042	1.6777	1.3042	2.3841	1.5503	1.4829	2.1792
30	371.15	0.642	0.314	0.044	0.510	0.421	0.069	0.5136	0.4259	0.0605	1.1978	1.9300	3.9503	1.2063	1.9525	3.4637
31	343.55	0.725	0.050	0.225	0.631	0.083	0.286	0.6277	0.0832	0.2891	1.1894	2.2156	3.1519	1.1832	2.2209	3.1861
32	343.15	0.727	0.091	0.182	0.622	0.141	0.237	0.6093	0.1503	0.2404	1.1884	2.0939	3.3216	1.1641	2.2320	3.3693
33	342.45	0.751	0.166	0.083	0.592	0.273	0.135	0.5832	0.2847	0.1321	1.1266	2.2718	4.2469	1.1099	0.3692	4.1557
34	342.35	0.766	0.196	0.038	0.583	0.344	0.073	0.5802	0.3502	0.0678	1.0922	2.4323	4.7327	1.0800	0.4761	4.7327
35	344.25	0.825	0.045	0.130	0.669	0.094	0.237	0.6673	0.0939	0.2388	1.0772	2.7260	4.5815	1.0745	0.7231	4.6163
36	343.95	0.842	0.078	0.080	0.658	0.170	0.172	0.6583	0.1697	0.1720	1.0508	2.8731	5.3255	1.0513	0.8680	5.3255
37	344.25	0.862	0.105	0.033	0.678	0.237	0.085	0.6697	0.2467	0.0836	1.0325	2.9471	6.4205	1.0321	3.0677	6.3148
38	346.65	0.932	0.035	0.033	0.791	0.098	0.111	0.7801	0.1054	0.1145	1.0240	3.3934	7.7180	1.0099	3.6496	7.9614
39	342.55	0.154	0.792	0.054	0.365	0.597	0.038	0.3622	0.6126	0.0252	3.3741	1.0381	2.4053	3.3482	1.0652	1.5951
40	341.45	0.277	0.673	0.050	0.423	0.538	0.039	0.4178	0.5589	0.0233	2.2740	1.1400	3.0900	2.2461	1.1843	1.8461
41	345.65	0.054	0.892	0.054	0.251	0.712	0.037	0.2324	0.7208	0.0468	5.8380	0.9979	1.1502	5.4054	1.0102	1.4548
42	349.35	0.020	0.927	0.053	0.129	0.831	0.040	0.1223	0.8322	0.0455	6.9959	1.0012	1.2460	6.6326	1.0026	1.4173
43	346.25	0.049	0.841	0.110	0.234	0.693	0.073	0.2290	0.6940	0.0770	5.8551	1.0112	1.2920	5.7300	1.0127	1.3628
44	351.65	0.024	0.402	0.574	0.240	0.430	0.330	0.2336	0.4288	0.3376	9.9266	1.1154	1.0251	9.6619	1.1123	1.0487
45	350.15	0.027	0.508	0.465	0.230	0.504	0.266	0.2200	0.5041	0.2083	8.9571	1.0817	1.3816	8.5677	1.0819	1.0819
46	348.55	0.034	0.622	0.344	0.232	0.570	0.198	0.2240	0.5717	0.2043	7.6387	1.0484	1.1054	7.3753	1.0515	1.1406
47	347.55	0.038	0.735	0.227	0.229	0.633	0.138	0.2154	0.6402	0.1444	7.0170	1.0156	1.1706	6.6003	1.0272	1.2249

$\Delta Y_1 = 0.0164$ $\Delta Y_2 = 0.0123$ $\Delta Y_3 = 0.0150$ $\Delta Y_T = 0.0146$

Table III. Ternary Vapour-Liquid Equilibrium Predictions from UNIQUAC Equation for Hexane-Ethanol-Benzene at 1 atm.

Run	Temp.	Liquid Composition			Expt. Vapour Compn.			Calcd. Vapour Compn.			Expt. Activity Coeff.			Calcd. Activity Coeff.		
No	°K	X_1	X_2	X_3	Y_1	Y_2	Y_3	Y_1	Y_2	Y_3	γ_1	γ_2	γ_3	γ_1	γ_2	γ_3
1	343.15	0.038	0.118	0.844	0.070	0.296	0.634	0.0651	0.3276	0.6073	1.7705	3.4848	1.0866	1.6466	3.8568	1.0408
2	340.25	0.032	0.298	0.670	0.076	0.414	0.509	0.0603	0.4016	0.5381	2.5003	2.1741	1.1475	1.9838	2.1090	1.2131
3	393.85	0.022	0.449	0.529	0.025	0.456	0.518	0.0506	0.4358	0.5136	1.2115	1.6162	1.4693	2.4520	1.5446	1.4568
4	340.05	0.020	0.548	0.432	0.070	0.467	0.463	0.0544	0.4631	0.4825	3.7120	1.3449	1.6158	2.8848	1.3337	1.6839
5	340.65	0.019	0.625	0.356	0.074	0.498	0.428	0.0609	0.4948	0.4443	4.0503	1.2265	1.8420	3.3333	1.2186	1.9122
6	342.95	0.031	0.704	0.265	0.081	0.568	0.351	0.1239	0.5701	0.3060	2.5273	1.1299	2.5283	3.8659	1.1341	1.2042
7	344.25	0.022	0.832	0.146	0.082	0.666	0.252	0.1278	0.6532	0.2190	3.4639	1.0633	3.3266	5.3986	1.0429	2.8910
8	347.05	0.018	0.916	0.066	0.075	0.775	0.150	0.1481	0.7801	0.0718	3.5521	1.0049	7.4250	7.0144	1.0115	3.5541
9	341.45	0.082	0.115	0.803	0.126	0.328	0.546	0.1270	0.3060	0.5670	1.5577	4.2474	1.0025	1.5701	3.9625	1.0411
10	345.65	0.077	0.280	0.643	0.150	0.385	0.465	0.1595	0.4962	0.3443	1.7341	1.7266	1.6057	1.8438	2.2253	1.1889
11	338.15	0.052	0.456	0.492	0.124	0.431	0.445	0.1103	0.4085	0.4812	2.6865	1.6150	1.3613	2.3897	1.5307	1.4720
12	338.15	0.053	0.591	0.356	0.153	0.469	0.378	0.1403	0.4390	0.4207	3.2512	1.3563	1.6209	2.9813	1.2695	1.8031
13	339.65	0.061	0.675	0.264	0.210	0.481	0.308	0.1973	0.4908	0.3119	3.6951	1.1436	2.0568	3.4716	1.1669	2.0828
14	340.45	0.046	0.799	0.155	0.248	0.521	0.231	0.2075	0.5476	0.2449	5.6427	1.0425	2.5167	4.7212	1.0637	2.6682
15	342.65	0.032	0.896	0.072	0.242	0.631	0.127	0.2082	0.6436	0.1482	7.3830	0.9984	2.8712	6.3518	1.0183	3.3505
16	339.65	0.161	0.138	0.702	0.261	0.311	0.428	0.2230	0.3148	0.4622	1.7405	3.6161	1.0386	1.4871	3.6603	1.0653
17	337.35	0.126	0.337	0.536	0.262	0.370	0.367	0.2053	0.3711	0.4236	2.4029	1.9409	1.1053	1.8829	1.9467	1.2757
18	336.65	0.136	0.474	0.390	0.289	0.390	0.321	0.2573	0.3921	0.3506	2.5131	1.4912	1.3905	2.2374	1.5063	1.5187
19	336.65	0.149	0.572	0.279	0.314	0.420	0.265	0.3243	0.4147	0.2610	2.4917	1.3372	1.7844	2.5734	1.3203	1.7575
20	339.65	0.075	0.777	0.148	0.279	0.536	0.185	0.2979	0.5242	0.1779	3.9934	1.1070	2.6350	4.2638	1.0826	2.5339
21	340.35	0.290	0.137	0.573	0.348	0.310	0.342	0.3715	0.3381	0.2904	1.3842	3.5263	1.2854	1.3448	3.8459	1.0915
22	337.95	0.293	0.121	0.587	0.366	0.303	0.331	0.3428	0.2921	0.3651	1.4161	4.3158	0.9809	1.3264	4.1606	1.0819
23	335.65	0.223	0.367	0.410	0.350	0.355	0.295	0.3271	0.3593	0.3136	1.9176	1.8386	1.2647	1.7921	1.8609	1.3444
24	335.35	0.215	0.481	0.303	0.366	0.351	0.283	0.3657	0.3787	0.2556	2.0999	1.4050	1.7221	2.0986	1.5159	1.5554
25	335.65	0.209	0.613	0.178	0.466	0.364	0.170	0.4439	0.4126	0.1435	2.9307	1.1285	2.2442	2.5949	1.2792	1.8944
26	336.65	0.155	0.761	0.084	0.468	0.439	0.093	0.4804	0.4648	0.0548	3.5703	1.0506	4.1503	3.6649	1.1123	2.4456
27	336.15	0.400	0.107	0.492	0.422	0.300	0.279	0.4099	0.2709	0.3192	1.2678	5.2167	0.9674	1.2315	4.7107	1.1068
28	334.65	0.312	0.369	0.319	0.433	0.349	0.218	0.4159	0.3529	0.2312	1.7521	1.8768	1.3020	1.6829	1.8978	1.3808
29	334.15	0.262	0.550	0.188	0.497	0.348	0.155	0.4562	0.3784	0.1654	2.4351	1.2832	1.6304	2.2352	1.3953	1.7398
30	333.95	0.291	0.625	0.084	0.557	0.363	0.080	0.5545	0.3956	0.0499	2.4732	1.1881	3.1628	2.4621	1.2948	1.9728
31	335.15	0.538	0.153	0.309	0.488	0.275	0.237	0.5206	0.3145	0.1649	1.1265	3.4904	1.7284	1.2018	3.9918	1.2026
32	333.35	0.456	0.344	0.199	0.534	0.325	0.141	0.5218	0.3439	0.1343	1.5388	1.9835	1.4846	1.5083	2.0989	1.4141
33	333.65	0.647	0.141	0.212	0.576	0.281	0.143	0.5699	0.3043	0.1258	1.1617	4.1295	1.4218	1.1494	4.4720	1.2508
34	333.65	0.633	0.182	0.185	0.579	0.286	0.135	0.5805	0.3229	0.0966	1.1937	3.2564	1.7987	1.1968	3.6766	1.2871
35	332.35	0.599	0.323	0.078	0.635	0.308	0.057	0.6139	0.3428	0.0433	1.4448	2.0919	1.4942	1.3968	2.3283	1.4755
36	333.15	0.762	0.159	0.079	0.658	0.275	0.067	0.6544	0.3262	0.0194	1.1459	3.6637	1.7660	1.1396	4.3458	1.3443
37	335.85	0.932	0.034	0.033	0.792	0.176	0.032	0.7785	0.1943	0.0272	1.0313	10.0437	1.6088	1.0137	11.0880	1.3675
38	349.15	0.013	0.959	0.028	0.056	0.865	0.079	0.1336	0.7667	0.0997	3.4474	1.1316	3.2691	8.2244	1.0030	4.0016
39	348.15	0.016	0.056	0.928	0.031	0.209	0.761	0.0312	0.2562	0.7126	1.5965	4.2439	1.0786	1.6068	4.0016	1.0100

$\Delta Y_1 = 0.0288$ $\Delta Y_2 = 0.0326$ $\Delta Y_3 = 0.0386$ $\Delta Y_T = 0.0333$

Table IV. Mean Deviations of Experimental and Calculated Vapour Compositions in Ternary Systems at 1 atm.

System(1)-(2)-(3)	Wilson Equation With The Published Parameters Δy	UNIQUAC Equation With The Published Parameters Δy	Wilson Equation With The Parameters Of this work Δy	UNIQUAC Equation With The Parameters Of this work Δy
Ethanol-Benzene-Heptane	0.0174	0.0273	0.0158	0.0146
Hexane-Ethanol-Benzene	0.0348	0.0350	0.0333	0.0334

Table V. Boiling Point and Composition of Azeotropes of The Binary Mixtures at 1 atm.

System(1)-(2)	Method	t [°C]	Mole fraction	
			X_1	Y_1
Ethanol-Benzene	Experimental	67.80	0.460	0.460
	Wilson (this work)	67.90	0.460	0.4604
	UNIQUAC (this work)	67.70	0.460	0.4602
Ethanol-Benzene	Experimental	71.00	0.648	0.648
	Wilson (this work)	71.05	0.663	0.6639
	UNIQUAC (this work)	71.00	0.648	0.6478
Ethanol-Benzene	Experimental	80.05	0.993	0.993
	Wilson (this work)	79.95	0.992	0.9929
	UNIQUAC (this work)	79.95	0.993	0.9939
Ethanol-Benzene	Experimental	58.00	0.334	0.334
	Wilson (this work)	58.15	0.334	0.334
	UNIQUAC (this work)	57.82	0.334	0.334

Once the activity coefficients have been obtained, the equilibrium vapour compositions of the ternary mixtures; Ethanol(1)-Benzene(2)-n, Heptane(3) and Hexane(1)-Ethanol(2)-Benzene(3) were calculated taking into account the non-ideal nature of both phases. For practical purposes a detailed computer programme was prepared for each of the two equations, to predict the isobaric binary and ternary 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 then the Wilson and UNIQUAC Equations were used to predict the equilibrium vapour compositions.

RESULTS AND DISCUSSION

Table I summarizes the results of Quasi-Newton fit programme for five binary systems comprising the ternary systems studied in this work.

Tables II, III, IV summarize the results of testing the Wilson and UNIQUAC equations using the published VLE data for the systems; Ethanol(1)-Benzene(2)-Heptane(3) (Wagner, 1958) and Hexane(1)-Ethanol (2)-Benzene(3) (Park, 1986).

Mean deviations given in Table I show that both the Wilson and UNIQUAC equations accurately predict the binary VLE data at atmospheric pressure for the five possible binaries of Ethanol, Benzene, Heptane and Hexane, in the concentration range studied. But for the ternary systems studied in this work mean deviations given in Table IV show that UNIQUAC Eq. with non-ideality correction (for ethanol q'=0.92) proved to yield best predictions of equilibrium compositions.

Mean deviation between the experimental ternary vapour compositions and the ternary vapour compositions predicted by Wilson and UNIQUAC Eq.s using the binary parameters determined in this work, as well as the binary parameters obtained from the published data (PRausnitz, 1980) are listed in Table IV, for comparison. The Wilson and UNIQUAC predicted vapour compositions are shown in Fig.s 1-4 for the components Ethanol, Benzene, Heptane and Hexane. Theoretical predictions with Wilson Eq. for the Hexane-Ethanol-Benzene system agree quite well with each other. However individual deviations may exceed 0.10 mole fractions in the central composition ranges for ethanol as shown in Fig. 4. This region should receive a careful consideration in analysing the output from a simulation study of distillation column.

Table IV shows that the mean deviations in the prediction of vapour phase compositions of the ternary system, Ethanol-Benzene-Heptane are in teh order of 0.0146 mol fractions with UNIQUAC Eq. and 0.0158 mol fractions with Wilson Eq.s. Comparison of the mean deviations obtained in this work with the mean deviations taken from the pablushid data is given in Table IV. For the system Ethanol-Benzene-Heptane with UNIQUAC Eq. gave mean composition errors approximately twice that of this work (0.0273 to 0.0146). This great difference can be explained by the accomplishment in the estimation of binary parameters assuming the non-ideality coefficient q'=0.92 for ethanol in this work. Mean deviations in the prediction of vapour phase compositions of the ternary system, Hexane-Ethanol-Benzene with Wilson Eq. is in the order of 0.0333 mole fractions and with UNIQUAC Eq. is in the order of 0.0334 mole fractions. The mean composition deviations for Wilson and UNIQUAC

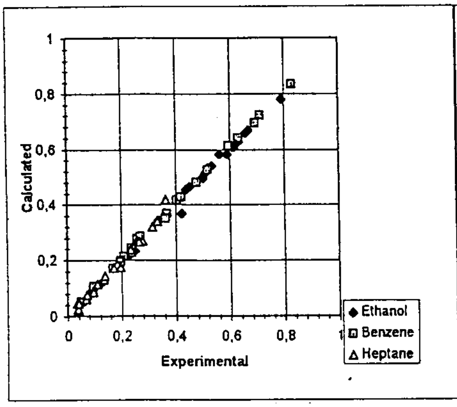

Fig. 1. Comparison of experimental and calculated vapour compositions for Ethanol(1)\ Benzene(2)\Heptane(3) at 1 atm. by UNIQUAC Eq.

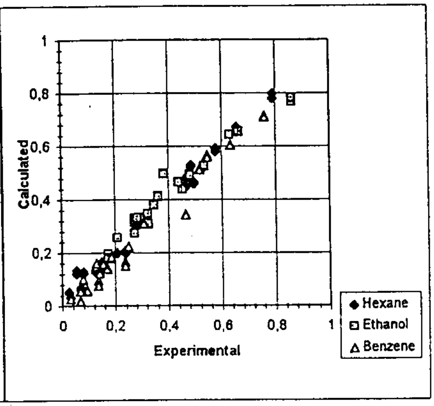

Fig. 2. Comparison of experimental and calculated vapour compositions for Hexane(1)\ Ethanol(2)\Benzene(3) at 1 atm. by UNIQUAC Eq.

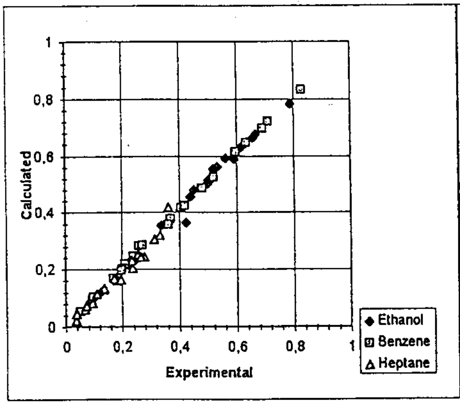

Fig. 3. Comparison of experimental and calculated vapour compositions for Ethanol(1)\ Benzene(2)\Heptane(3) at 1 atm. by Wilson Eq.

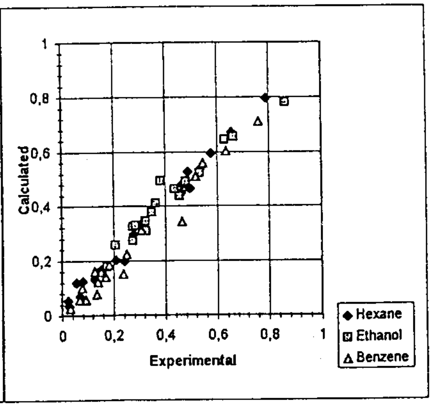

Fig. 4. Comparison of experimental and calculated vapour compositions for Hexane(1)\ Ethanol(2)\Benzene(3) at 1 atm. by Wilson Eq.

model of 0.0333-0.0334 mole fractions in the vapour compositions is normally an acceptable figure for simulation studies of distillation columns. From Table III one may see that mean deviations in the prediction of vapour-phase composition of the ternary system Hexane(1)-Ethanol (2)-Benzene(3) by UNIQUAC Eq. are in the order of 0.0288-0.03847 mole fractions whereas the same UNIQUAC Eq. could predict the ternary vapour-phase compositions of the system, Ethanol(1)-Benzene(2)-Heptane(3) within the accuracy of 0.0123-0.0164 mole fractions (from Table II). These differences become more severe when the liquid phase behavior becomes highly non-ideal.

Table V. lists the binary azeotrope boiling points and compositions determined a) experimentally, b) determined by Wilson eq. With parameters estimated in this work, c) determined by UNIQUAC Eq. with parameters estimated in this work. The theoretical predictions by both equations agree quite well with each other, only the Wilson result for Ethanol-Heptane, being slightly discrepant.

The ternary system, Ethanol-Benzene-Heptane provides two binary azeotropes. If Table II is closely observed one may find out that Run 19 contains approximately the relative amounts of Ethanol and Benzene reported in the binary azeotrope (Landwehr, 1958) (0.460 mol fraction for Ethanol at 67.8°C). The resulting normalized (based on the sum of the azeotropic components) experimental liquid and vapour ethanol compositions are 0.419/(0.419+0.544)=0.435 and 0.440/(0.440+0.520)=0.458 respectively at 67.9°C. These relative experimental concentrations are in good agreement with the binary azeotrope when the estimation errors are considered. The corresponding estimated vapour-phase concentrations for this run are 0.464 by Wilson and 0.458 by UNIQUAC Eq.

The other azeotrope that the Ethanol-Benzene-Heptane system provides is Ethanol-Heptane azeotrope (Kurt, 1956). When Run 26 is carefully examined the resulting normalized experimental liquid and vapour compositions were 0.645 and 0.667 respectively at 70.8°C. These relative experimental concentrations, are in good agreement with binary azeotrope (0.648 mole fraction for ethanol at 71°C). The corresponding estimated vapour-phase concentrations for this run are 0.680 by Wilson and 0.662 by UNIQUAC Eq.

The ternary system Hexane-Ethanol-Benzene provides also two binary azeotropes. In Table III, Run No: 3 contains approximately the relative amount of Ethanol and Benzene as reported in the binary azeotrope given in Table V. The resulting normalized experimental liquid and vapour composition for ethanol are, 0.459 and 0.468 respectively at 66.7°C. The other azeotrope that this ternary provides is Ethanol-Hexane azeotrope

(Sinor, 1960). The azeotrope formed at Run No: 35 where relative normalized liquid and vapour compositions of ethanol are 0.350 and 0.327 mole fractions respectively. The corresponding estimated vapour mole fractions are 0.349 by Wilson and 0.358 by UNIQUAC. From the comparison of these results, the UNIQUAC Eq. appears to be more succesfull in the evaluation of azeotropic vapour-phase composition of the binary systems under study.

None of two prediction methods discovered any ternary azeotrope for both systems understudied in this work.

CONCLUSIONS

The ternary VLE data have been predicted for Ethanol-Benzene-Heptane and Hexane-Ethanol-Benzene systems at 1 atm. using the thermodynamic methods Wilson and UNIQUAC. Theoretical predictions with both thermodynamic methods for the systems investigated in this work agree quite well with each other. But UNIQUAC Eq. with non-ideality correction factor was found to be little superior in the prediction of ternary VLE data with mean deviations ranging from 0.0146-0.0334 mole fractions whereas the Wilson Eq. could predict the ternary vapour phase within the accuracy of 0.0158-0.0333 mole fractions. However, individual mean deviations in a particular component may exceed 0.1000 mole fractions for Wilson model in the central composition ranges. This region should receive careful consideration in analysing the output from a simulation study of distillation column.

Mean deviations in the prediction of vapour phase composition of the Hexane-Ethanol-Benzene system with UNIQUAC are in the order of 0.0288-0.0384 mole fractions whereas the same UNIQUAC Eq. could predict the vapour phase compositions of the Ethanol-Benzene-Heptane system within the accuracy of 0.0123-0.0164 mole fractions. These differences in the predicted vapour phase compositions must be considered in the design and operation of distillation columns. There would appear to be a major difficulty in selecting one thermodynamic model as the "best" as the choice may be system dependent.

NOMENCLATURE

A_{ij} UNIQUAC Binary Parameter

m	Number of Components in a multicomponent mixture
N	Number of experimental Runs
P	Total pressure (mmHg) or (Bars)
Pci	Critical pressure of component i
R	Ideal gas constant (cal/g.mol.°K)
T	Absolute temperature (°K)
T_{ci}	Critical temperature of component i
T_{ri}	Reduced temperature of component i
X_i	Mole fraction of component i in Liquid phase
Y_i	Mole fraction of component i in vapour phase

ABBREVIATIONS

VLE	Vapour-Liquid Equilibrium

SUPERSCRIPTS AND SUBSCRIPTS

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

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