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A STUDY ON TERNARY VAPOR-LIQUID EQUILIBRIA FOR THE SYSTEM HEPTANE/METHYLCYCLOHEXANE/TOLUENE AT 101.325kPa

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ABSTRACT

The isobaric separation of multicomponent mixtures by distillation require reliable vapor-liquid equilibrium data. Since the experimental determination of multicomponent vapor-liquid equilibrium data is laborious and time consuming there is a need to use a predictive method for the liquid phase activity coefficients. The estimated vapor-phase compositions are dependent on the predictive thermodynamic method used. The ternary vapor-liquid equilibrium data for the system, heptane/ methylcyclohexane/ toluene at 101.325 kPa have been chosen to compare the abilities of the three-suffix Margules and the UNIQUAC Equations in the prediction of isobaric ternary vapor-liquid equilibria with parameters estimated from the corresponding binary vapor-liquid equilibria compositions taken from the literature. The predictions with the three-suffix Margules equations was found to be little superior with overall root mean square deviations of ±0.0047 whereas the UNIQUAC equations could predict the ternary vapor compositions with overall root mean square deviations of ± 0.0061.

INTRODUCTION

The separation of multicomponent mixtures by distillation requires knowledge of vapor-liquid equilibrium data (VLE data) of the system under consideration. For binary systems experimental VLE data are generally available and reliable, but the same is not true for most multicomponent systems. 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, specially multicomponent VLE data require appreciable experimental skill, experience and patience. It is therefore an economic necessity to consider techniques for calculating phase equilibria for multicomponent systems from few experimental

data. 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.

The aim of the present study is to see which of the two well known methods; the three suffix Margules equation (with binary parameters estimated from VLE data) (Wohl, 1953) or UNIQUAC equation (with pure-component molecular-structure constants and binary parameters) (Abrams, Prausnitz, 1975) is more practical in estimating multicomponent vapor phase mole fraction values. For this purpose the ternary system heptane/methylcyclohexane/toluene has been chosen to represent the multicomponent system. Although extensive information is available on the VLE data of the three binaries comprising the ternary system, there are only three data reported for the ternary system; the first one by Bromiley and Quiggle (1933) without giving the boiling points of the ternary mixtures, the second one by Wisniak and Tamir (1977) and the third one by Özalp and Ediz (1992). The vapor-liquid equilibrium data of Özalp and Ediz for the ternary system heptane(1)/methylcyclohexane(2)/toluene(3) at 101.325 kPa have been used here. In Özalp and Ediz's experimental work, 60 determinations spanning the whole space of ternary compositions specially covering the extreme ends of the corners of the ternary composition chart were carried out. Although the apparatus and the procedure had been described by Özalp and Ediz (1992), the summary of their technique has also been given here.

Experimental Method

Purity of Materials. All chemical products were Merck chromatographic grade, and were used as supplied without further purification. The densities at 20 °C, refractive indices at 20 °C and boiling points at 101.325 kPa of the pure components of the ternary system were measured and agreed with the published values in Beilstein's Handbook. The properties of the pure components appear in Table 1.

Table 1. Physical Properties of Pure Materials
(Lit values from Beilstein's Handbook)

Compound	Densities, gr/ml at 20 °C		Refractive Index at 20 °C		Boiling Point at 101.325 kPa	
	Lit. Value	Expt.	Lit. Value	Expt.	Lit. Value	Expt.
heptane	0.68376	0.6834	1.38777	1.38781	98.42	98.39
methylcyclohexane	0.76940	0.7692	1.42310	1.42350	101.00	100.96
toluene	0.86690	0.8671	1.49610	1.49510	110.62	110.64

Apparatus and Procedure. The ternary vapor-liquid equilibrium determinations were carried out in an all glass Ellis Still as described by Ellis (1952). The experimental technique outlined by Ellis was also followed. The pressure in the distillation unit was maintained at 101.325±0.067 kPa by bleeding nitrogen into the system: the temperature control was achieved by a 5 mm diameter Pt-100 temperature sensor with an accuracy of ±0.1 °C. Equilibrium was achieved usually within 40 minutes. When equilibrium was achieved, still liquid and distillate samples were taken by syringing simultaneously. Ternary samples of both the liquid and vapor phases were analyzed by means of gas liquid chromatography on a Pye Unicam series 104 apparatus provided with flame ionization detector. The column was 5.5 m long and 4 mm in diameter glass packed with 10% Squalane on 100-120 mesh Diatomite C operated at 70 °C. Injector and detector temperatures were 150 °C. Calibration analyses were carried out to convert the peak area ratio to the weight composition of the samples. Reproducibility of results were in the order of ±0.1 mole percent.

Vapor-Liquid Equilibrium Results

The temperature T and liquid phase x_i, and vapor phase y_i mole fraction measurements at 101.325 kPa pressure are reported in Table 2 together with activity coefficients γ_i that were calculated from the equality of fugacities in all phases for each component of a multicomponent system by considering the vapor phase nonideality.

$$\Phi_i P y_i = \gamma_i P_i^o x_i \Phi_i^s \exp\left[V_i^L (P - P_i^o)/RT\right]$$

For a ternary system (i=1,2,3), fugacities for components in a gaseous mixture, Φ_i is given by the virial equation of state truncated after the second term (O`Connell, Prausnitz, 1967)

$$\ln\Phi_i = \left(2\sum y_j B_{ij} - B_M\right)P/RT$$

where subscript M stands for mixture and for a mixture of m components, the second virial coefficient is given as (Mason, Spurling, 1969)

$$B_M = \sum_{i=1}^{m}\sum_{j=1}^{m} y_i y_j B_{ij}$$

Table 2. Ternary Vapor-Liquid Equilibrium Data For heptane(1)/methycyclohexane(2)/toluene(3) At 101.325 kPa by Experimental and Three-Suffix Margules Equations

Run No	T Exp. K	T Calc. K	Liquid Comp.		Obsd. Vapor Comp.			Calcd. Vapor Comp.			Obsd. Activity Coefficient			Calcd. Activity Coefficient		
			x_1	x_2	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	378.55	378.96	0.011	0.261	0.014	0.325	0.661	0.0159	0.3291	0.6414	1.0578	1.1089	1.0499	1.19747	1.12273	1.01881
2	377.60	377.89	0.017	0.345	0.022	0.415	0.563	0.0231	0.4122	0.5546	1.1028	1.0976	1.0485	1.15609	1.09020	1.03291
3	376.55	376.97	0.024	0.428	0.030	0.490	0.480	0.0307	0.4855	0.4702	1.0954	1.0735	1.0727	1.12101	1.06367	1.05074
4	375.99	376.16	0.030	0.514	0.037	0.565	0.398	0.0368	0.5631	0.3929	1.0972	1.0457	1.0866	1.09109	1.04207	1.07269
5	375.85	376.20	0.033	0.504	0.040	0.552	0.408	0.0404	0.5507	0.3967	1.0824	1.0458	1.1015	1.09290	1.04342	1.07103
6	375.01	375.29	0.044	0.612	0.050	0.645	0.305	0.0511	0.6410	0.2966	1.0380	1.0287	1.1361	1.06120	1.02230	1.10480
7	375.40	375.63	0.043	0.562	0.051	0.602	0.347	0.0511	0.5993	0.3398	1.0720	1.0349	1.1127	1.07354	1.03029	1.08974
8	374.57	374.75	0.060	0.676	0.067	0.694	0.239	0.0678	0.6929	0.2301	1.0323	1.0138	1.1754	1.04391	1.01214	1.13156
9	374.50	374.72	0.069	0.664	0.078	0.680	0.242	0.0778	0.6794	0.2321	1.0469	1.0132	1.1791	1.04411	1.01228	1.13112
10	374.15	374.41	0.076	0.715	0.084	0.724	0.192	0.0840	0.7210	0.1831	1.0335	1.0111	1.2078	1.03387	1.00693	1.15205
11	374.15	374.31	0.093	0.705	0.104	0.715	0.181	0.1027	0.7104	0.1776	1.0455	1.0127	1.1781	1.03229	1.00616	1.15584
12	373.95	373.97	0.096	0.787	0.105	0.787	0.108	0.1042	0.7852	0.1051	1.0283	1.0038	1.2215	1.02680	1.00150	1.18906
13	374.00	373.98	0.115	0.746	0.126	0.747	0.127	0.1253	0.7458	0.1243	1.0285	1.0038	1.2070	1.02309	1.00221	1.18175
14	374.00	373.99	0.122	0.730	0.134	0.734	0.132	0.1331	0.7300	0.1321	1.0309	1.0080	1.1781	1.02408	1.00256	1.17871
15	373.85	373.70	0.134	0.800	0.144	0.800	0.056	0.1443	0.7948	0.0603	1.0129	1.0065	1.1264	1.01498	0.99994	1.21371
16	373.86	373.65	0.153	0.781	0.166	0.778	0.056	0.1648	0.7760	0.0604	1.0222	1.0024	1.2137	1.01489	0.99985	1.21536
17	373.84	373.76	0.151	0.744	0.164	0.740	0.096	0.1632	0.7394	0.0948	1.0237	1.0014	1.2137	1.01867	1.00067	1.19852
18	373.45	373.54	0.206	0.717	0.220	0.707	0.073	0.2196	0.7045	0.0697	1.0171	1.0034	1.2730	1.01533	0.99979	1.21486

19	373.55	373.60	0.200	0.708	0.215	0.697	0.088	0.2141	0.6977	0.0830	1.0210	0.9991	1.2805	1.01671	1.00008	1.20786
20	373.40	373.39	0.254	0.686	0.274	0.676	0.050	0.2700	0.6729	0.0547	1.0284	1.0042	1.1207	1.01341	0.99951	1.22607
21	373.39	373.31	0.294	0.645	0.314	0.632	0.054	0.3124	0.6324	0.0557	1.0182	0.9989	1.1908	1.01288	0.99955	1.22849
22	373.15	373.16	0.341	0.615	0.359	0.601	0.040	0.3594	0.5991	0.0403	1.0101	1.0029	1.2316	1.01115	0.99966	1.23958
23	373.00	373.09	0.371	0.588	0.390	0.571	0.039	0.3892	0.5705	0.0375	1.0125	1.0007	1.2943	1.01050	0.99985	1.24297
24	374.93	374.29	0.420	0.217	0.480	0.228	0.292	0.4797	0.2268	0.3158	1.0436	1.0294	1.0330	1.04300	1.02407	1.11722
25	372.75	373.13	0.665	0.083	0.705	0.084	0.211	0.6984	0.0814	0.2152	1.0268	1.0527	1.1469	1.01714	1.02024	1.16970
26	373.01	372.97	0.683	0.105	0.721	0.107	0.172	0.7193	0.1034	0.1849	1.0150	1.0525	1.1032	1.01271	1.01703	1.18612
27	372.05	372.31	0.798	0.104	0.815	0.102	0.083	0.8110	0.0996	0.0869	1.0082	1.0401	1.1857	1.00327	1.01594	1.24101
28	371.35	371.91	0.896	0.054	0.895	0.054	0.051	0.8911	0.0510	0.0444	1.0053	1.0817	1.4587	1.00083	1.02110	1.26902
29	381.75	381.53	0.045	0.041	0.074	0.056	0.870	0.0764	0.0604	0.8665	1.2571	1.1217	1.0062	1.29848	1.21029	1.00221
30	381.15	380.87	0.065	0.048	0.104	0.065	0.831	0.1070	0.0688	0.8284	1.2420	1.1292	1.0070	1.27733	1.19452	1.00387
31	380.17	379.98	0.085	0.072	0.130	0.094	0.776	0.1332	0.0986	0.7687	1.2176	1.1161	1.0168	1.24731	1.17101	1.00733
32	379.07	379.06	0.091	0.125	0.131	0.163	0.706	0.1348	0.1625	0.6972	1.1794	1.1464	1.0259	1.21395	1.14314	1.01323
33	378.25	378.22	0.125	0.140	0.176	0.176	0.648	0.1770	0.1749	0.6430	1.1784	1.1289	1.0280	1.18493	1.12174	1.02008
34	377.32	377.49	0.154	0.161	0.207	0.195	0.598	0.2081	0.1929	0.5883	1.1529	1.1142	1.0453	1.15898	1.10232	1.02832
35	375.80	375.79	0.223	0.250	0.274	0.277	0.449	0.2736	0.2754	0.4475	1.0971	1.0604	1.0660	1.09538	1.05428	1.06237
36	374.67	374.50	0.315	0.325	0.360	0.339	0.301	0.3589	0.3368	0.3098	1.0516	1.0285	1.0816	1.04843	1.02182	1.11312
37	374.25	374.19	0.339	0.354	0.379	0.361	0.260	0.3781	0.3603	0.2653	1.0404	1.0168	1.1093	1.03790	1.01490	1.13200
38	373.75	373.68	0.380	0.412	0.413	0.411	0.176	0.4120	0.4101	0.1832	1.0252	1.0079	1.1252	1.02283	1.00578	1.17090
39	373.55	373.44	0.338	0.533	0.363	0.531	0.106	0.3622	0.5255	0.1158	1.0190	1.0116	1.0997	1.01677	1.00114	1.20116
40	372.97	373.05	0.485	0.419	0.510	0.411	0.079	0.5088	0.4068	0.0863	1.0130	1.0124	1.1204	1.01049	1.00203	1.22423
41	372.97	373.02	0.495	0.410	0.520	0.403	0.077	0.5191	0.3981	0.0855	1.0119	1.0145	1.1036	1.01017	1.00221	1.22523
42	372.03	372.32	0.795	0.107	0.812	0.105	0.083	0.8076	0.1024	0.0868	1.0088	1.0412	1.1864	1.00331	1.01573	1.24083

43	374.20	374.15	0.024	0.905	0.026	0.910	0.064	0.0261	0.9085	0.0649	1.0124	1.0024	1.1849	1.01536	1.00074	1.20106
44	374.10	374.18	0.044	0.842	0.048	0.842	0.110	0.0479	0.8439	0.1026	1.0220	0.9997	1.2714	1.02072	1.00190	1.18566
45	374.15	374.02	0.054	0.868	0.062	0.873	0.065	0.0587	0.8701	0.0712	1.0741	1.0041	1.0969	1.01632	1.00069	1.20121
46	374.11	373.99	0.100	0.733	0.111	0.773	0.116	0.1092	0.7748	0.1143	1.0390	0.9995	1.2029	1.02184	1.00185	1.18535
47	374.83	374.91	0.132	0.520	0.152	0.544	0.304	0.1521	0.5412	0.2995	1.0562	1.0263	1.1250	1.05701	1.02102	1.10820
48	374.15	374.03	0.140	0.685	0.155	0.690	0.155	0.1539	0.6886	0.1556	1.0347	1.0059	1.1646	1.02715	1.00381	1.16943
49	374.45	374.18	0.215	0.530	0.243	0.543	0.214	0.2404	0.5397	0.2240	1.0469	1.0153	1.0932	1.03585	1.00921	1.14406
50	376.63	376.63	0.170	0.225	0.202	0.254	0.544	0.2191	0.2585	0.5168	1.0381	1.0572	1.0982	1.12600	1.07587	1.04335
51	374.87	375.00	0.310	0.244	0.363	0.256	0.381	0.3614	0.2578	0.3771	1.0716	1.0294	1.0983	1.06697	1.03666	1.08700
52	372.95	373.12	0.670	0.075	0.713	0.076	0.211	0.7077	0.0740	0.2189	1.0250	1.0484	1.1269	1.01732	1.02093	1.16890
53	375.85	375.94	0.070	0.470	0.087	0.515	0.398	0.0854	0.5127	0.3950	1.1094	1.0464	1.0814	1.08902	1.04171	1.07332
54	372.75	372.89	0.602	0.280	0.628	0.273	0.099	0.6267	0.2711	0.1051	1.0105	1.0131	1.1498	1.00840	1.00620	1.22075
55	373.87	373.80	0.265	0.545	0.290	0.545	0.165	0.2887	0.5436	0.1680	1.0296	1.0065	1.1509	1.02512	1.00396	1.17159
56	375.02	374.86	0.402	0.135	0.472	0.142	0.386	0.4698	0.1439	0.3929	1.0697	1.0285	1.0674	1.06472	1.04203	1.08649
57	373.97	374.17	0.495	0.125	0.554	0.128	0.318	0.5505	0.1279	0.3211	1.0488	1.0301	1.1050	1.04212	1.02945	1.11570
58	374.15	374.29	0.155	0.601	0.173	0.615	0.212	0.1720	0.6070	0.2125	1.0429	1.0221	1.1419	1.03668	1.00874	1.14455
59	374.82	374.66	0.140	0.551	0.161	0.578	0.261	0.1600	0.5704	0.2689	1.0551	1.0292	1.0884	1.04872	1.01577	1.12119
60	376.30	376.39	0.080	0.395	0.100	0.443	0.457	0.1005	0.4419	0.4502	1.1023	1.0586	1.0737	1.10783	1.05604	1.05777

$\Delta T=0.207$ $\Delta_{y1}= 0.0030$ $\Delta_{y2}= 0.0031$ $\Delta_{y3}= 0.0081$ $\Delta_{yo}=0.0047$

All the self virial coefficients B_{ii} are determined from the correlation of the Pitzer-Tsonopoulos (Tsonopoulos, 1974). To calculate the cross-virial coefficients B_{ij} ($i \neq j$), the Pitzer-Tsonopoulos correlation is again used with parameters $T_{c_{ij}}$, $P_{c_{ij}}$, $T_{r_{ij}}$, $V_{c_{ij}}$ and W_{ij} which were defined by the semi-emprical combining rules given by Prausnitz (1969).

In Eq.1, V_i^L, the molar volume of pure component i at a system temperature T is calculated using Rackett's equation as modified by Spencer and Danner (1972). This equation has been further modified by O`Connell for reduced pressures greater than 0.75 and is given by the equation (Prausnitz, 1980)

$$V_i^L = RT_{c_i} Z_{r_i}^{\tau} / P_{c_i}$$

where

$$\tau = 1 + (1 - T_r)^{0.2857} \quad \text{for } T_r \leq 0.75$$

and Z_{r_i} is the modified Rackett parameter. The fugacity coefficient of saturated pure vapor i, Φ_i^s, in Eq(1) is computed by standard procedure given by Prausnitz et al (1967). The pure component vapor pressures P_i^o are calculated as a function of temperature by the Antoine equation

$$\log_{10} P_i^o = a_i - b_i/(c_i + t)$$

where the constants a_i, b_i and c_i are reported in Table 3.

Table 3. Antoine Constants for the Three Components (From Am. Pet. Inst. Research Project 44 (1953))

Component	a	b	C
heptane	6.90240	1268.115	216.900
methylcyclohexane	6.82689	1272.864	221.630
toluene	6.95334	1343.943	219.377

The vapor-liquid equilibrium data given in Table 2 were found to be thermodynamically consistent by the Li-Lu consistency test method rederived by McDermott (1965). Among the 60 experimental points only Run 25 and 58 were found to be somewhat inconsistent.

Correlation and Prediction of the Isobaric Vapor-Liquid Equilibria of Heptane(1)/Methylcyclohexane(2)/Toluene(3) at 101.325 kPa. Many solution models, which relate activity coefficients to liquid composition and satisfy the Gibbs excess energy equation have been proposed. Two solution models, Three Suffix Margules Eq. (Wohl, 1953) and UNIQUAC model of Abrams (1975) for liquid phase activity coefficients have been compared in this study.

Three-Suffix Margules Equation. The three-suffix Margules Equation for liquid-phase activity coefficients of a multicomponent system is given below (Wohl, 1953)

$$\log_{10}\gamma_i = x_j^2\left[A_{ij} + 2x_i\left(A_{ji} - A_{ij}\right)\right] + x_k^2\left[A_{ik} + 2x_i\left(A_{ki} - A_{ik}\right)\right]$$
$$+ x_j x_k\left[\left(A_{ji} + A_{ij} + A_{ki} + A_{ik} - A_{jk} - A_{kj}\right)/2\right.$$
$$\left. + x_i\left(A_{ji} - A_{ij} + A_{ki} - A_{ik}\right) + \left(x_j - x_k\right)\left(A_{jk} - A_{kj}\right) - C^*\left(1 - 2x_i\right)\right]$$

where A_{ij}, A_{ji}, A_{ik}, A_{ki}, A_{jk}, A_{kj} are adjustable binary parameters that can be obtained from related binary VLE data. C^* is a ternary constant and must be obtained from the ternary VLE data. The activity coefficients of a ternary system γ_1, γ_2, γ_3 are obtained from Eq.7 by rotating suffices one at a time in the order ijki (1231) etc.

UNIQUAC Equation. The UNIQUAC model of Abrams and Prausnitz (1975) for a multicomponent liquid-phase activity coefficient for any component i is given by

$$\ln\gamma_i = \ln\left(\Phi_i/x_i\right) + \left(Z/2\right)\ln\left(\theta_i/\Phi_i\right) + l_i - \left(\Phi_i/x_i\right)\sum_j x_j l_j$$

$$- q_i \ln\left(\sum_j \theta_j \tau_{ji}\right) + q_i - q_i \sum_j \frac{\theta_j \tau_{ij}}{\sum_k \theta_k \tau_{kj}} \qquad (8)$$

where

$$\tau_{ij} = \exp\left(-A_{ij}/T\right), \quad \tau_{ii} = \tau_{jj} = \tau_{kk} = 1.0,$$

$$l_i = \frac{Z}{2}(r_i - q_i) - (r_i - 1)$$

$$\theta_i = \frac{q_i x_i}{\sum_j q_j x_j}, \quad \Phi_i = \frac{r_i x_i}{\sum_j r_j x_j}$$

and the coordination number Z=10. Eq.8 requires pure component and binary parameters. The parameters r and q are pure component molecular-structure constants depending on molecular size and external surface areas. A_{ij} and A_{ji} are two adjustable binary parameters that can be obtained from related binary VLE data.

Determination of Correlation Parameters. In order to determine the correlation parameters necessary for predicting the ternary vapor-liquid equilibria, three-suffix Margules and UNIQUAC Equations were fitted to published experimental VLE data of the three binary systems; heptane/methylcyclohexane (Bromiley, Quiggle, 1933), heptane/toluene (Rose, Williams, 1955) and methylcyclohexane/toluene (Contractor, 1959), that had passed the Herington's consistency test (Ellis, Bourn, 1960). Then the correlation parameters were optimized by using the Quasi-Newton fit program, which minimizes the objective function.

$$O.F. = \sum_{i=1}^{N} \left(y_{1iexp} - y_{1icalc}\right)^2 /N + \sum_{i=1}^{N} \left(y_{2iexp} - y_{2icalc}\right)^2 /N$$

$$+ \sum_{i=1}^{N} \left(y_{1iexp} - y_{1icalc} + y_{2iexp} - y_{2icalc}\right)^2 /N$$

Table 4 lists the optimized correlation parameters evaluated in this work. The values of the parameters, r_i, q_i required by the UNIQUAC Eq. were taken from the published data (Prausnitz, 1980).

Table 4. Estimates for Parameters of Three-Suffix Margules and UNIQUAC Eq.

Binary System (i)/(j)	Three-Suffix Margules Eq. Parameters		UNIQUAC Eq. Parameters	
	A_{ij}	A_{ji}	A_{ij}	A_{ji}
heptane(1)/methylcyclohexane(2)	0.003073	0.012160	-115.00410	125.99703
heptane(1)/toluene(3)	0.136729	0.113741	107.77600	-75.13206
methylcyclohexane(2)/toluene(3)	0.102371	0.089263	25.67868	2.04943

Root Mean Square Deviations (R.M.S.D.) and Standard Deviation Percent of (S.D.%) the experimental and calculated vapor compositions by the three-suffix Margules and UNIQUAC Eq. using the binary correlation parameters evaluated in this work for the three binary systems are reported in Table 5.

Table 5. Root Mean Square Deviations and Standart Deviation % of Experimental and Calculated Vapor Compositions in Binary System at 101.325 kPa.

Binary System (i)/(j)	Three-Suffix Margules Eq.		UNIQUAC Eq.	
	R.M.S.D.* Δy	S.D.%**	R.M.S.D. Δy	S.D.%
heptane(1)/methylcyclohexane(2)	0.0033	0.65	0.0035	0.66
heptane(1)/toluene(3)	0.0008	0.12	0.0008	0.14
methylcyclohexane(2)/toluene(3)	0.0015	0.51	0.0015	0.48

* $$\text{R.M.S.D.}=\left(\sum_{1}^{N}\left(y_{exp}-y_{calc}\right)^{2}/N\right)^{1/2}$$

** $$\text{S.D.}\%=\frac{100}{N}\left(\sum_{1}^{N}\left(\left|y_{exp}-y_{calc}\right|/y_{exp}\right)\right)$$

The boiling points of the binary and the ternary system were also correlated with its composition by the equation proposed by Wisniak and Tamir (1976).

$$T = x_1T_1^o + x_2T_2^o + x_3T_3^o + \sum_{i,j=1}^{3} x_i x_j \sum_{k=0}^{3} c_k \left(x_i - x_j\right)^k + x_1x_2x_3\left[A + B\left(x_1 - x_2\right)\right.$$

$$\left. + C\left(x_1 - x_3\right) + D\left(x_2 - x_3\right)\right]$$

The values of the constants c_k, from binary boiling points and A, B, C, D from ternary boiling points were obtained by a Simplex optimization technique and are given in Table 6. Eq.12 predicts the ternary boiling points with an average percent deviation of 0.043 and R.M.S.D. of 0.207 °C.

Table 6. Correlation of Binary and Ternary Boiling Points (From Eq.12)

Binary System (i)/(j)	Constants of Eq.				R.M.S.D.	S.D.%
	c_0	c_1	c_2	c_3	ΔT, K	
heptane(1)/methylcyclohexane(2)	-0.723	-0.092	-0.872	1.745	0.026	0.005
heptane(1)/toluene(3)	-11.889	4.650	-3.074	1.825	0.015	0.003
methylcyclohexane(2)/toluene(3)	-8.795	2.461	-2.436	1.125	0.031	0.007
Ternary System (i)/(j)/(k)	A	B	C	D		
heptane(1)/methylcyclohexane(2)/ toluene(3)	6.092	10.842	14.222	-3.570	0.207	0.043

Results and Conclusion

The activity coefficients of the components of the ternary system were calculated by the three-suffix Margules and UNIQUAC Equations using the binary parameters. Since the last term (C^*) in the three-suffix Margules equations (Eq.7) contributed less than 0.7% to the activity coefficients and their influence was important only at very dilute concentrations of the particular component, the constant C^* was omitted in the predictions. The calculated activity coefficients by means of the three-suffix Margules equations at system boiling points are reported in Table 2. Once the activity coefficients have been obtained, vapor compositions of the ternary system at 101.325 kPa were calculated by Eq.1 and are also listed in Table 2. For practical purposes a detailed computer program was prepared for each of the two equations to predict the isobaric ternary VLE data.

The three-suffix Margules and UNIQUAC predicted vapor compositions are given in Fig.1-2 for the components, heptane, methylcyclohexane, toluene.

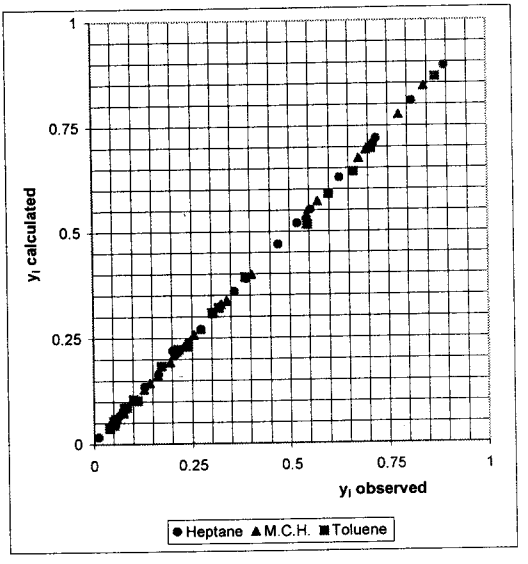

Fig 1. Comparison of Observed and Calculated Vapor Compositions for heptane(1)/methylcyclohexane(2)/ toluene(3) at 101.325 kPa by Three-Suffix Margules Equation.

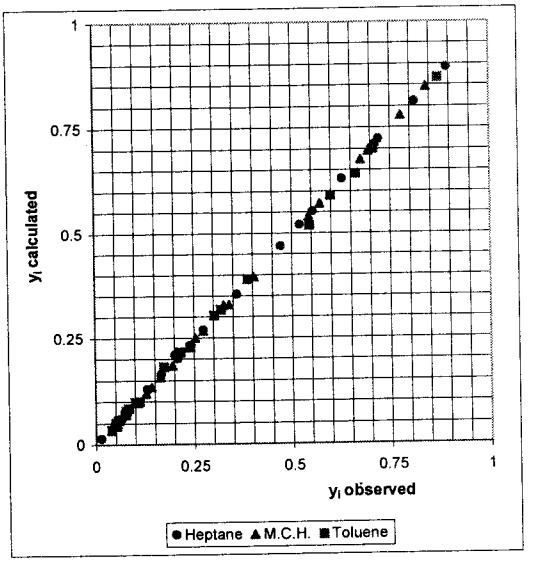

Fig 2. Comparison of Observed and Calculated Vapor Compositions for heptane(1)/methylcyclohexane(2)/ toluene(3) at 101.325 kPa by UNIQUAC Equation.

R.M.S.D.'s and S.D.% between the experimental ternary vapor compositions and the ternary vapor compositions predicted at two different boiling points (experimental, calculated) by the three-suffix Margules and UNIQUAC equations using the binary parameters determined in this work are listed in Table 7.

Table 7. Root Mean Square Deviations and Standard Deviation % of Experimental and Estimated VLE of the Ternary System.

Ternary System heptane(1)/methylcyclohexane(2)/toluene(3)	Three-Suffix Margules Eq.		UNIQUAC Eq.	
	R.M.S.D., Δy	S.D.%	R.M.S.D., Δy	S.D. %
Estimations Using Exp. Boiling Points				
heptane(1)	0.0030	1.24	0.0054	3.8
methylcyclohexane(2)	0.0031	1.08	0.0051	1.97
toluene(3)	0.0081	3.58	0.0077	3.4
overall	0.0047		0.0061	
Estimations Using Calc. Boiling Points				
heptane(1)	0.0033	1.38	0.0058	3.8
methylcyclohexane(2)	0.0035	1.04	0.0055	1.94
toluene(3)	0.0073	3.38	0.0068	3.23
overall	0.0047		0.0060	

Table 7 exhibits that the average R.M.S.D.'s of the predicted vapor phase compositions of the ternary system are in the order of ±0.0047 mole fractions with the three-suffix Margules Equations and ±0.0061 mole fractions with UNIQUAC Equations. S.D.% between the experimental and the predicted vapor compositions are in the range of 1.24-3.58% with the three-suffix Margules Equations and in the range of 1.97-3.80% with the UNIQUAC Equations. The comparison of the above results exhibit that both equations are capable of reproducing the values of vapor phase mole fractions for the ternary system. But the three-suffix Margules Equations produced better results for the ternary system, although there was not any difference in the theoretical predictions with the both thermodynamic methods for the binary systems comprising the ternary system (Table 5). This lack of agreement is believed due to the effect of temperature on the characteristic energy parameters A_{ij}, A_{ji}, in the UNIQUAC equation. Although UNIQUAC Eq. with two adjustable parameters was derived for solutions containing molecules of different sizes and requires only pure component data, it can not represent high-quality data with high accuracy for the ternary system with high boiling temperature differences of its components.

As a conclusion, experimental vapor-liquid equilibrium data were determined at 101.325 kPa for heptane/methylcyclohexane/toluene mixtures corresponding to almost all areas of the ternary composition chart. The behavior of the ternary system

was predicted by the three-suffix Margules and UNIQUAC Equations and the three-suffix Margules Equations achieved the smallest deviations from the experimental data. The experimental ternary VLE data, apart from its intrinsic value for the design of distilling plants, provided an important means of testing the validity of the three-suffix Margules and UNIQUAC Equations.

Glossary

A_{ij} Binary parameters of the three-suffix Margules and UNIQUAC equations defined by Eq.s 7 and 9.

B_{ii} Virial coefficient (cm^3/g.mol)

a,b,c Constants of Antoine Eq. (Eq. 6)

c^* Ternary constants of the three-suffix Margules equation

c_k Constants of Eq. 12 calculated from binary boiling points

A,B,C,D Ternary constants of Eq. 12

l Constant defined by Eq. 9

m Number of components in the multicomponent system

N Number of data points

P Total pressure

P_{c_i} Critical pressure

P_i^o Pure component vapor pressure at boiling point

q Pure component area parameter

r Pure component volume parameter

R Gas constant

t Temperature

T	Absolute temperature
T_{c_i}	Critical temperature of a component i
V_{c_i}	Critical volume (cm^3/g.mol)
w_{ij}	An acentric factor
x	Liquid phase mole fraction
y	Vapor phase mole fraction
Z_r	Rackett parameter

Greek Letters

γ	Activity coefficient
θ	Average area fraction defined by Eq. 10
τ	Coefficient defined by Eq. 9
ϕ_i	Fugacity coefficient defined by Eq. 1
θ_i	Average segment fraction defined by Eq. 10

Subscripts

c	critical constants
i,j,k	components i,j,k
L	Liquid phase

Abbreviations

R.M.S.D.	Root Mean Square Deviations
S.D.%	Standard Deviations Percent

VLE Vapor-Liquid Equilibrium

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