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Vapor−Liquid Equilibrium of the Ternary System Ethyl Acetate + Hexane + Acetone at 101.32 kPa

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Experimental isobaric vapor−liquid equilibrium data at 101.32 kPa for the ternary system ethyl acetate + hexane + acetone and for its constituent binary systems are reported. These data were found to be thermodynamically consistent and were satisfactorily correlated with the Wilson, NRTL, and UNIQUAC equations. They were also compared with predictions of the ASOG and UNIFAC group contribution methods.

Introduction

In previously published work,[1] the possibility of using acetone as entrainer for separation of hexanes−ethyl acetate mixtures by azeotropic distillation was studied. Work included process simulation, but no isobaric vapor−liquid equilibrium data have been found for the ternary system and they had to be estimated. Good results obtained on the separation of hexane and ethyl acetate must be contrasted using rigorous equilibrium data. With this in mind, isobaric (101.32 kPa) vapor−liquid equilibrium (VLE) data for the ternary system ethyl acetate + hexane + acetone and their binary constituent systems were measured. In the literature there was only isobaric equilibrium experimental data for the binary systems: acetone + ethyl acetate,[2] acetone + hexane,[3,4] and hexane + ethyl acetate.[5]

Binary and ternary data measured in this work are fitted with the equations of Wilson,[6] NRTL,[7] and UNIQUAC,[8] and binary energetic parameters are presented. The prediction of equilibrium is also tested by the group contribution methods ASOG-KT,[9,10] UNIFAC,[11] UNIFAC-Dortmund,[12,13] and UNIFAC-Lyngby.[14]

Experimental Section

Materials. Ethyl acetate (99.9% mass, HPLC grade) and acetone (99.9% mass, HPLC grade) were purchased from Sigma, and hexane (>99.5% mass, HPLC grade) was supplied by Fluka. Gas chromatographic analysis of these solvents showed no impurities. Thus, they were used without further purification. The properties of pure solvents are shown in Table 1, together with published values for these parameters.[15]

Apparatus and Procedure. The VLE experiments in this study were performed using a commercial unit (Labodest model 602) built by Fischer. In this circulation-method apparatus, the mixture is heated to the boiling point with an immersion heater. The vapor−liquid mixture flows through a Cottrell pump that guarantees an intense phase exchange and then enters a separation chamber whose construction prevents an entrainment of liquid particles into the vapor phase. The vapor phase is condensed and with liquid is returned to a mixing chamber, where they are stirred with a magnetic stirrer, and returned again to the chamber of the immersion heater. The temperature was measured using a Heraeus QuaT100

Table 1. Densities ρ and Refractive Indices n_D at 298.15 K and Atmospheric Pressure and Normal Boiling Points T_b of the Pure Components

	ρ/g·cm^{-3}		n_D		T_b/K	
component	exp	lit.[15]	exp	lit.[15]	exp	lit.[15]
ethyl acetate	0.894 31	0.894 55	1.369 86	1.369 78	350.09	350.261
hexane	0.655 07	0.654 84	1.372 36	1.372 26	341.72	341.886
acetone	0.784 83	0.784 40	1.355 99	1.355 96	329.15	329.217

Table 2. Isobaric Vapor−Liquid Equilibrium Data for the Binary Systems at 101.32 kPa

T_b/K	x_1	y_1	γ_1	γ_2	T_b/K	x_1	y_1	γ_1	γ_2
Acetone (1) + Ethyl acetate (2)									
349.76	0.0060	0.0155	1.3874	1.0062	337.19	0.4825	0.6546	1.0550	1.0233
348.55	0.0426	0.0899	1.1729	1.0033	336.39	0.5260	0.6885	1.0433	1.0355
347.20	0.0820	0.1650	1.1623	1.0022	335.63	0.5674	0.7218	1.0381	1.0400
345.64	0.1306	0.2486	1.1502	1.0013	334.87	0.6134	0.7536	1.0265	1.0581
344.06	0.1842	0.3301	1.1339	1.0014	334.60	0.6261	0.7646	1.0290	1.0549
342.68	0.2365	0.3973	1.1070	1.0072	333.46	0.6970	0.8141	1.0200	1.0695
341.54	0.2810	0.4524	1.0975	1.0090	332.47	0.7617	0.8567	1.0134	1.0850
340.50	0.3241	0.5014	1.0879	1.0117	331.33	0.8405	0.9052	1.0063	1.1161
339.33	0.3811	0.5566	1.0640	1.0218	330.40	0.9066	0.9455	1.0039	1.1322
338.55	0.4145	0.5926	1.0665	1.0188	329.81	0.9479	0.9703	1.0042	1.1295
337.95	0.4445	0.6192	1.0583	1.0243	329.46	0.9752	0.9856	1.0028	1.1648
Acetone (1) + Hexane (2)									
340.07	0.0106	0.0575	3.9959	1.0060	322.67	0.5942	0.6294	1.3247	1.7213
338.78	0.0132	0.0994	5.7533	1.0025	322.67	0.6486	0.6438	1.2407	1.9122
336.35	0.0295	0.1811	5.0290	0.9996	322.69	0.6931	0.6570	1.1836	2.1086
333.36	0.0631	0.2749	3.8981	1.0088	322.82	0.7315	0.6706	1.1391	2.3061
330.00	0.1032	0.3764	3.6145	1.0126	322.93	0.7592	0.6829	1.1131	2.4678
326.82	0.1796	0.4666	2.8449	1.0552	323.16	0.7953	0.7012	1.0820	2.7169
325.08	0.2451	0.5173	2.4436	1.1029	323.83	0.8580	0.7428	1.0375	3.3032
324.16	0.3050	0.5446	2.1299	1.1678	324.60	0.8999	0.7840	1.0165	3.8433
323.43	0.3746	0.5773	1.8818	1.2373	325.73	0.9378	0.8386	1.0037	4.4641
322.88	0.4834	0.6042	1.5534	1.4315	327.02	0.9681	0.8999	0.9991	5.1912
322.78	0.5131	0.6102	1.4827	1.5015	327.84	0.9826	0.9383	0.9989	5.7235
322.69	0.5450	0.6172	1.4159	1.5835	328.67	0.9950	0.9763	0.9988	7.4637
Hexane (1) + Ethyl Acetate (2)									
349.42	0.0105	0.0311	2.4139	1.0055	338.47	0.5061	0.5748	1.2626	1.2742
348.17	0.0325	0.0907	2.3529	1.0042	338.26	0.5454	0.5948	1.2199	1.3293
346.33	0.0683	0.1732	2.2493	1.0062	338.16	0.5684	0.6080	1.2000	1.3595
345.09	0.0966	0.2304	2.1901	1.0059	338.04	0.6440	0.6498	1.1355	1.4798
344.16	0.1214	0.2695	2.0928	1.0124	337.99	0.6472	0.6513	1.1342	1.4895
343.04	0.1590	0.3208	1.9637	1.0208	338.08	0.7086	0.6888	1.0921	1.6057
341.74	0.2135	0.3806	1.8012	1.0402	338.30	0.7739	0.7337	1.0576	1.7593
340.93	0.2564	0.4191	1.6909	1.0608	338.61	0.8252	0.7754	1.0380	1.9009
340.13	0.3104	0.4599	1.5689	1.0933	339.19	0.8788	0.8266	1.0205	2.0776
339.43	0.3727	0.5004	1.4512	1.1392	340.07	0.9324	0.8908	1.0090	2.2804
338.90	0.4336	0.5356	1.3561	1.1949	341.09	0.9778	0.9602	1.0056	2.4499

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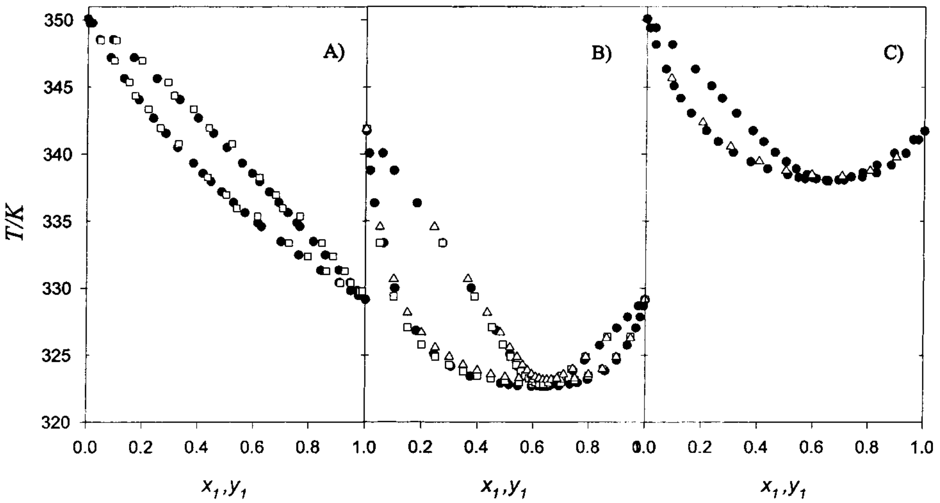

Figure 1. Vapor−liquid equilibria. (A) Acetone + ethyl acetate at 101.32 kPa: (●) this work; (□) ref 2. (B) Acetone + hexane at 101.32 kPa: (●) this work; (□) ref 3; (△) ref 4. (C) Ethyl acetate + hexane at 101.32 kPa: (●) this work; (△) ref 5.

quartz thermometer, with an accuracy of ±0.02 K, and the pressure was measured with a Fischer digital manometer with an accuracy of ±0.01 kPa.

Distillation was performed under an inert argon atmosphere at a constant pressure of 101.32 kPa. The system was held at the boiling point for 20 min to ensure a stationary state, and then threaded stoppers with silicone septa were used for extracting around 1.5 mL of liquid and vapor samples with syringes. Upon cooling of the samples, their compositions were determined by measuring their densities at 298.15 K with an Anton Paar DMA 60/602 vibrating tube densimeter and refractive indices with an Atago RX-1000 refractometer at 298.15 K. The composition dependence of densities and refractive indices has been previously reported.[16] The largest uncertainty found for these systems, with this method of composition analysis, was ±0.003 mole fraction.

Results

Liquid and vapor compositions, temperature and pressure determined experimentally, and activity coefficients calculated from these data are shown in Table 2 for the VLE of binary systems at 101.32 kPa. Thermodynamic consistency of the data has been demonstrated. All binary systems passed both Fredenslund's[11] test (median deviation between calculated and experimental $y_i < 0.01$) and Wisniak's[17] L−W test ($D < 3$). The acetone (1) + hexane (2) and ethyl acetate (1) + hexane (2) systems form an azeotrope at the minimum boiling point around $x_1 = 0.642$, $T = 322.7$ K and $x_1 = 0.657$, $T = 338.0$ K, respectively. Figure 1 shows a $T-xy$ diagram for our data and published data[2−5] for the three binary systems. Figure 2 shows the variation of $\ln \gamma_i$ and G^E/RT with liquid-phase composition also for binary systems.

The VLE data and the activity coefficients for the ternary system at 101.32 kPa are shown in Table 3. All ternary data passed both Wisniak's[17] L−W test of thermodynamic consistency ($0.92 < L_i/W_i < 1.08$ at all data points) and Wisniak and Tamir's[18] modification of the test of McDermott and Ellis[19] ($D < D_{max}$ at all data points). Figure 3 shows the isotherms of the liquid phase for the ethyl acetate + hexane + acetone system.

Data Treatment

Correlation. All data were processed by using the program ChemCAD IV. For the ternary system and each

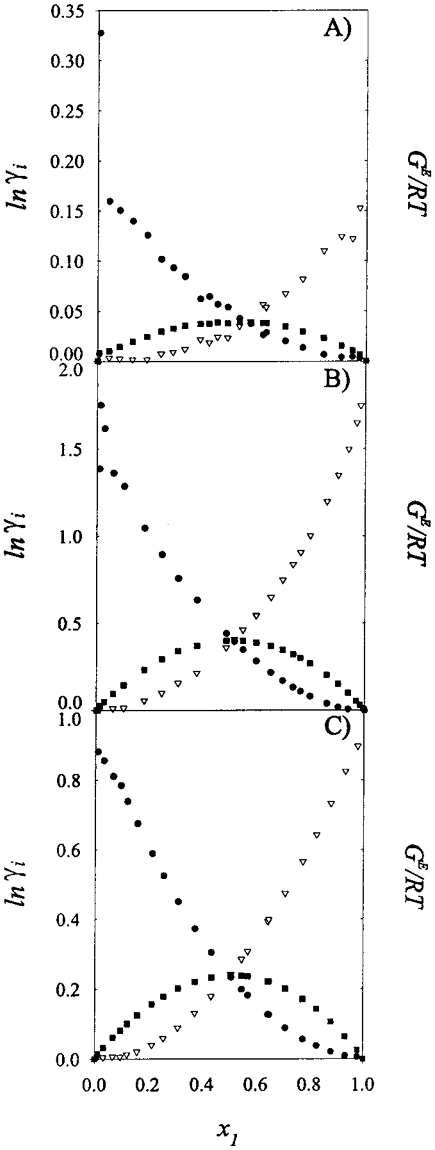

Figure 2. Variation of the logarithm of the activity coefficient of the first component (●), the logarithm of the activity coefficient of the second component (▽), and G^E/RT (■) with liquid-phase composition, for mixtures of (A) acetone + ethyl acetate, (B) acetone + hexane, and (C) ethyl acetate + hexane.

Table 3. Isobaric Vapor−Liquid Equilibrium Data for the System Ethyl Acetate (1) + Hexane (2) + Acetone (3) at 101.32 kPa

T_b/K	x_1	x_2	y_1	y_2	γ_1	γ_2	γ_3	T_b/K	x_1	x_2	y_1	y_2	γ_1	γ_2	γ_3
323.60	0.0707	0.3806	0.0309	0.3701	1.0923	1.7744	1.3230	333.11	0.2727	0.6350	0.2159	0.5532	1.4070	1.1483	2.2391
323.64	0.0529	0.4347	0.0285	0.3883	1.3449	1.6260	1.3783	333.34	0.3859	0.0289	0.2167	0.0832	0.9829	3.8585	1.0491
323.87	0.0589	0.2561	0.0320	0.3300	1.3430	2.3350	1.1170	333.38	0.4099	0.4461	0.2807	0.4764	1.2041	1.3983	1.4921
323.89	0.0384	0.5340	0.0250	0.4172	1.6107	1.4078	1.5681	333.50	0.4797	0.3004	0.2976	0.3966	1.0844	1.7273	1.2218
324.37	0.0284	0.6008	0.0256	0.4415	2.1913	1.3009	1.7014	333.67	0.1145	0.8260	0.1205	0.6605	1.8366	1.0330	3.2526
324.41	0.0501	0.1683	0.0228	0.2777	1.1010	2.9450	1.0524	333.71	0.0724	0.8849	0.0967	0.7103	2.3310	1.0346	3.9996
325.33	0.0551	0.1107	0.0273	0.2284	1.1574	3.5799	1.0162	334.02	0.3356	0.5797	0.2701	0.5531	1.3863	1.2211	1.8158
325.77	0.0620	0.6578	0.0411	0.4687	1.5304	1.2010	1.9786	334.25	0.5294	0.3242	0.3233	0.4099	1.0402	1.6138	1.5646
325.98	0.0584	0.0851	0.0279	0.1954	1.0889	3.9057	1.0101	334.60	0.5320	0.3214	0.3341	0.4133	1.0568	1.6228	1.4634
326.15	0.0956	0.5878	0.0606	0.4525	1.4429	1.2818	1.7164	334.70	0.5372	0.0745	0.3254	0.1746	1.0122	2.9844	1.0832
326.48	0.1878	0.1617	0.0770	0.2624	0.9189	2.7001	1.1142	334.72	0.5385	0.3362	0.3364	0.4211	1.0471	1.5741	1.6381
326.57	0.1956	0.1755	0.0850	0.2797	0.9711	2.6407	1.1056	334.76	0.3945	0.5298	0.3044	0.5373	1.2950	1.2681	1.7762
326.63	0.1796	0.1436	0.0777	0.2474	0.9641	2.8549	1.0883	334.93	0.5048	0.0497	0.2901	0.1248	0.9520	3.1860	1.0963
326.67	0.1512	0.1171	0.0666	0.2234	0.9796	3.1625	1.0571	335.05	0.5202	0.0601	0.2993	0.1416	0.9493	2.9744	1.1081
326.75	0.2145	0.2006	0.0962	0.2969	0.9960	2.4346	1.1294	335.22	0.5424	0.3619	0.3591	0.4432	1.0914	1.5133	1.7230
326.77	0.1285	0.0953	0.0575	0.2003	0.9911	3.4783	1.0377	335.38	0.5219	0.3904	0.3630	0.4745	1.1412	1.4925	1.5397
326.94	0.2277	0.2244	0.1027	0.3095	0.9949	2.2524	1.1608	335.38	0.5483	0.0850	0.3290	0.1906	0.9792	2.7918	1.0794
326.96	0.1136	0.0800	0.0511	0.1815	0.9891	3.7358	1.0260	335.51	0.4387	0.4863	0.3366	0.5231	1.2544	1.3138	1.5514
327.11	0.0939	0.0658	0.0428	0.1623	0.9964	4.0470	1.0146	335.68	0.5631	0.1030	0.3300	0.2134	0.9466	2.5519	1.1168
327.30	0.2519	0.2516	0.1173	0.3294	1.0142	2.1096	1.1923	335.77	0.5680	0.2743	0.3718	0.3997	1.0576	1.7725	1.1862
327.30	0.2291	0.3469	0.1195	0.3795	1.1372	1.7579	1.2663	335.86	0.5355	0.3967	0.3908	0.4896	1.1785	1.4917	1.4451
327.34	0.0903	0.0585	0.0389	0.1446	0.9337	4.0296	1.0208	335.94	0.5857	0.1234	0.3743	0.2564	1.0240	2.5307	1.0294
327.63	0.1613	0.5774	0.0928	0.4575	1.2406	1.2548	1.8297	336.06	0.5893	0.1543	0.3685	0.2896	0.9981	2.2738	1.0782
327.67	0.2634	0.2708	0.1264	0.3465	1.0315	2.0343	1.1968	336.17	0.5316	0.4133	0.4081	0.5143	1.2276	1.4880	1.1439
327.98	0.0625	0.0327	0.0306	0.0971	1.0363	4.7552	1.0041	336.33	0.0702	0.8980	0.1171	0.7970	2.6666	1.0520	2.2137
328.05	0.1107	0.0471	0.0679	0.1395	1.2959	4.7146	0.9784	336.54	0.5686	0.0422	0.3562	0.1078	0.9820	3.0804	1.0934
328.11	0.2845	0.2910	0.1405	0.3566	1.0450	1.9185	1.2354	336.66	0.6348	0.2066	0.3971	0.3387	0.9790	1.9439	1.3241
328.28	0.0435	0.0221	0.0229	0.0714	1.1020	5.1327	0.9995	336.82	0.6005	0.2340	0.4099	0.3811	1.0634	1.9177	1.0002
328.71	0.0225	0.0102	0.0129	0.0377	1.1815	5.8044	0.9979	337.89	0.6252	0.0364	0.3966	0.0887	0.9496	2.8186	1.1584
329.09	0.1564	0.0381	0.0841	0.1186	1.0940	4.7922	0.9946	337.89	0.6535	0.2395	0.4340	0.3730	0.9973	1.7741	1.3823
329.32	0.2453	0.5249	0.1491	0.4611	1.2334	1.3145	1.7070	338.69	0.6574	0.0394	0.4686	0.1141	1.0389	3.2585	1.0231
329.50	0.3347	0.3532	0.1818	0.3973	1.0941	1.6776	1.3461	338.71	0.6665	0.0512	0.4995	0.1547	1.0920	3.3879	0.9105
329.73	0.2950	0.4499	0.1740	0.4376	1.1791	1.4371	1.5107	338.88	0.6868	0.0703	0.5215	0.1965	1.1006	3.1096	0.8591
330.00	0.1128	0.7798	0.0951	0.5700	1.6723	1.0657	3.0839	338.94	0.6746	0.0566	0.5263	0.1794	1.1284	3.5225	0.8084
330.08	0.2108	0.0340	0.1069	0.1022	0.9957	4.4821	1.0190	339.08	0.6916	0.0812	0.4762	0.1935	0.9907	2.6374	1.0695
330.42	0.4037	0.2389	0.2014	0.3267	0.9708	1.9855	1.2764	339.12	0.6920	0.0982	0.4713	0.2197	0.9788	2.4699	1.0828
330.48	0.3970	0.2082	0.2067	0.3104	1.0108	2.1621	1.1796	339.86	0.6883	0.0251	0.5587	0.0986	1.1378	4.2609	0.8576
330.50	0.3994	0.2695	0.2073	0.3484	1.0076	1.8698	1.2948	339.90	0.0359	0.9510	0.0600	0.9019	2.3716	1.0068	2.1491
330.56	0.3628	0.3848	0.2089	0.4160	1.1170	1.5555	1.4345	339.98	0.7136	0.1182	0.5080	0.2565	0.9944	2.3281	1.0039
330.62	0.3717	0.1530	0.2125	0.2818	1.1040	2.6629	1.0207	340.05	0.0234	0.9636	0.0427	0.9192	2.5774	1.0081	2.1579
330.73	0.3706	0.1294	0.2164	0.2594	1.1229	2.8914	1.0017	340.07	0.0112	0.9736	0.0235	0.9250	2.9611	1.0034	2.4936
331.16	0.1724	0.7510	0.1340	0.5694	1.4795	1.0642	3.6895	340.39	0.7680	0.0548	0.6014	0.1303	1.0786	2.5312	1.0691
331.23	0.3700	0.0949	0.2008	0.2061	1.0242	3.0923	1.0410	340.80	0.0063	0.9856	0.0121	0.9558	2.6479	1.0018	2.8584
331.33	0.2677	0.0276	0.1384	0.0861	0.9709	4.4675	1.0286	341.09	0.7758	0.2020	0.5939	0.3640	1.0328	1.8584	1.3193
331.35	0.4186	0.2769	0.2340	0.3616	1.0532	1.8354	1.2476	341.27	0.7819	0.1763	0.5383	0.3035	0.9217	1.7717	2.6146
331.58	0.3739	0.0777	0.1965	0.1706	0.9792	3.0980	1.0712	342.03	0.8047	0.1331	0.5805	0.2548	0.9413	1.9285	1.7861
331.76	0.2987	0.4963	0.2419	0.4425	1.5064	1.2319	1.4315	343.02	0.8359	0.0767	0.6268	0.1671	0.9463	2.1379	1.5418
332.01	0.2054	0.7030	0.1654	0.5646	1.4874	1.0966	2.7330	343.69	0.8306	0.0274	0.6513	0.0663	0.9677	2.3390	1.2729
332.10	0.4322	0.2797	0.2552	0.3727	1.0836	1.8264	1.1851	343.94	0.8595	0.0768	0.6558	0.1645	0.9343	2.0446	1.7954
332.26	0.3816	0.0569	0.1978	0.1338	0.9425	3.2533	1.0807	344.02	0.8500	0.0380	0.6716	0.0956	0.9647	2.4035	1.3181
332.32	0.3189	0.0260	0.1695	0.0729	0.9640	3.8897	1.0473	344.08	0.8539	0.0508	0.6662	0.1196	0.9508	2.2427	1.4234
332.39	0.0698	0.8754	0.0725	0.6638	1.8953	1.0206	4.4280	345.26	0.8686	0.0133	0.7389	0.0398	0.9976	2.7611	1.1452
332.95	0.4694	0.2978	0.2787	0.3837	1.0576	1.7171	1.2958	346.82	0.9145	0.0149	0.8217	0.0460	1.0021	2.7166	1.0949

Table 4. Antoine Coefficients[15] *A*, *B*, and *C* for Eq 3

component	*A*	*B*	*C*
ethyl acetate	6.187 99	−1224.673	−57.4380
n-hexane	6.000 91	−1171.17	−48.7420
acetone	6.254 77	−1216.689	−42.8750

Table 5. Correlation of the VLE Data for the Binary Systems: Binary Interaction Parameters ($J\cdot mol^{-1}$) and rms Deviations in Equilibrium Temperature and Vapor-Phase Composition

model	parameters		rms T_b/K	rms y_1
	Acetone (1) + Ethyl Acetate (2)			
Wilson	$\Delta\lambda_{12} = 1330.19$	$\Delta\lambda_{21} = -778.04$	0.12	0.0018
NRTL ($\alpha = 0.2$)	$\Delta g_{12} = 473.81$	$\Delta g_{21} = 41.56$	0.13	0.0014
UNIQUAC	$\Delta u_{12} = -597.25$	$\Delta u_{21} = 940.34$	0.12	0.0015
	Acetone (1) + Hexane (2)			
Wilson	$\Delta\lambda_{12} = 4076.96$	$\Delta\lambda_{21} = 1615.60$	0.25	0.0061
NRTL ($\alpha = 0.3$)	$\Delta g_{12} = 3047.03$	$\Delta g_{21} = 1875.63$	0.39	0.0088
UNIQUAC	$\Delta u_{12} = -185.35$	$\Delta u_{21} = 2085.60$	0.37	0.0089
	Hexane (1) + Ethyl Acetate (2)			
Wilson	$\Delta\lambda_{12} = 567.59$	$\Delta\lambda_{21} = 2680.55$	0.17	0.0042
NRTL ($\alpha = 0.3$)	$\Delta g_{12} = 1529.17$	$\Delta g_{21} = 1416.28$	0.15	0.0023
UNIQUAC	$\Delta u_{12} = 1306.64$	$\Delta u_{21} = -359.24$	0.17	0.0035

Table 6. Correlation of the VLE Data for the Ethyl Acetate (1) + Hexane (2) + Acetone (3) System: Binary Interaction Parameters ($J\cdot mol^{-1}$) and rms Deviations in Equilibrium Temperature and Vapor-Phase Composition

model	parameters		rms *T*/K	rms y_1	rms y_2	rms y_3
Wilson	$\Delta\lambda_{12} = 2343.82$ $\Delta\lambda_{21} = 722.66$ $\Delta\lambda_{31} = 3948.04$	$\Delta\lambda_{13} = -2525.82$ $\Delta\lambda_{23} = 1546.49$ $\Delta\lambda_{32} = 4188.43$	0.45	0.0175	0.0143	0.0282
NRTL ($\alpha = 0.1$)	$\Delta g_{12} = 3566.14$ $\Delta g_{21} = -674.22$ $\Delta g_{31} = 1402.23$	$\Delta g_{13} = -1189.10$ $\Delta g_{23} = 242.72$ $\Delta g_{32} = 4319.34$	0.59	0.0183	0.0141	0.0294
UNIQUAC	$\Delta u_{12} = 7.32$ $\Delta u_{21} = 839.57$ $\Delta u_{31} = -1604.14$	$\Delta u_{13} = 2491.98$ $\Delta u_{23} = 2202.39$ $\Delta u_{32} = -265.16$	0.54	0.0175	0.0143	0.0283

binary system, the binary interaction parameters of the Wilson, NRTL, and UNIQUAC equations for activity coefficients were optimized by means of a simplex method for the minimum mean squared deviation between calculated and experimental liquid-phase mole fractions,

$$F = \sum_{i=1}^{N} (x_{i,\mathrm{calc}} - x_{i,\mathrm{exp}})^2 \qquad (1)$$

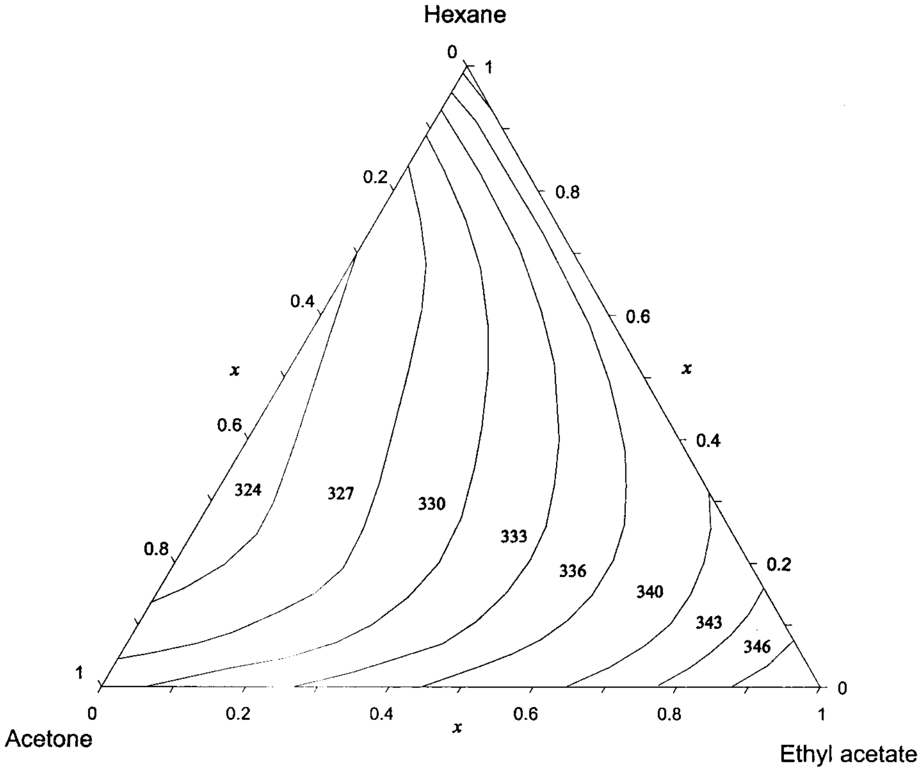

Figure 3. Isothermal liquid-phase compositions of ethyl acetate + hexane + acetone at equilibrium with its vapor at 101.32 kPa (temperatures in K).

Table 7. Root-Mean-Squared Deviations in Equilibrium Temperature and Vapor-Phase Composition of VLE Predictions by Group Contribution Methods for Binary Systems

model	rms T/K	rms y_1
Acetone (1) + Ethyl Acetate (2)		
ASOG-KT	0.12	0.0034
UNIFAC	0.21	0.0076
UNIFAC-Dortmund	0.40	0.0059
UNIFAC-Lyngby	0.11	0.0026
Acetone (1) + Hexane (2)		
ASOG-KT	0.35	0.0098
UNIFAC	0.26	0.0087
UNIFAC-Dortmund	0.43	0.0112
UNIFAC-Lyngby	0.70	0.0155
Hexane (1) + Ethyl Acetate (2)		
ASOG-KT	0.67	0.0108
UNIFAC	0.48	0.0084
UNIFAC-Dortmund	0.20	0.0039
UNIFAC-Lyngby	0.59	0.0085

Table 8. Root-Mean-Squared Deviations in Equilibrium Temperature and Vapor-Phase Composition of VLE Predictions by Group Contribution Methods for Ethyl Acetate (1) + Hexane (2) + Acetone (3)

model	rms T/K	rms y_1	rms y_2	rms y_3
ASOG-KT	0.64	0.0191	0.0182	0.0311
UNIFAC	0.79	0.0177	0.0144	0.0287
UNIFAC-Dortmund	0.63	0.0192	0.0166	0.0301
UNIFAC-Lyngby	0.59	0.0187	0.0160	0.0312

where the calculated values were obtained from the equilibrium equations,

$$y_i\phi_i P = x_i\gamma_i P^{S}_{i}\phi^{S}_{i} \exp[\nu^{L}_{i}(P - P^{S}_{i})/RT] \tag{2}$$

where $P = 101.32$ kPa, x_i and y_i are the mole fractions of component i in the liquid and vapor phases, respectively, γ_i is its activity coefficient, ν^{L}_{i} is its molar volume in the liquid phase, ϕ_i and ϕ^{S}_{i} are its fugacity coefficients under unsaturated and saturated conditions, respectively, and P^{S}_{i} is the vapor pressure at saturation; vapor pressures are obtained from the Antoine equation,

$$\log(P^{S}_{i}/\text{kPa}) = A + \frac{B}{T/\text{K} + C} \tag{3}$$

with the parameters shown in Table 4, liquid-phase molar volumes were calculated using data contained in the ChemCAD IV database, and the fugacity coefficients were calculated by using the Soave−Redlich−Kwong equation. The optimal value of the NRTL nonrandomness parameter α was determined in each case by trial and error.

The results for the binary systems are listed in Table 5, and those for the ternary system are in Table 6. In Figure 4 the calculated (using the Wilson equation) and experimental vapor-phase composition data are compared (for the sake of clarity, the number of data points shown has been reduced).

Prediction. The methods used to predict the VLE data for the binary and ternary systems were the ASOG-KT method; the original UNIFAC method, with the structural and group-interaction parameters recommended by Gmehling et al;[20] the UNIFAC-Dortmund method; and the UNIFAC-Lyngby method. Tables 7 and 8 list the rms deviations between the experimental VLE data and those obtained with these group contribution methods for binary and ternary systems, respectively. In Figure 5, the calculated (using the UNIFAC-Lyngby method) and experimental vapor-phase composition data are compared (for the

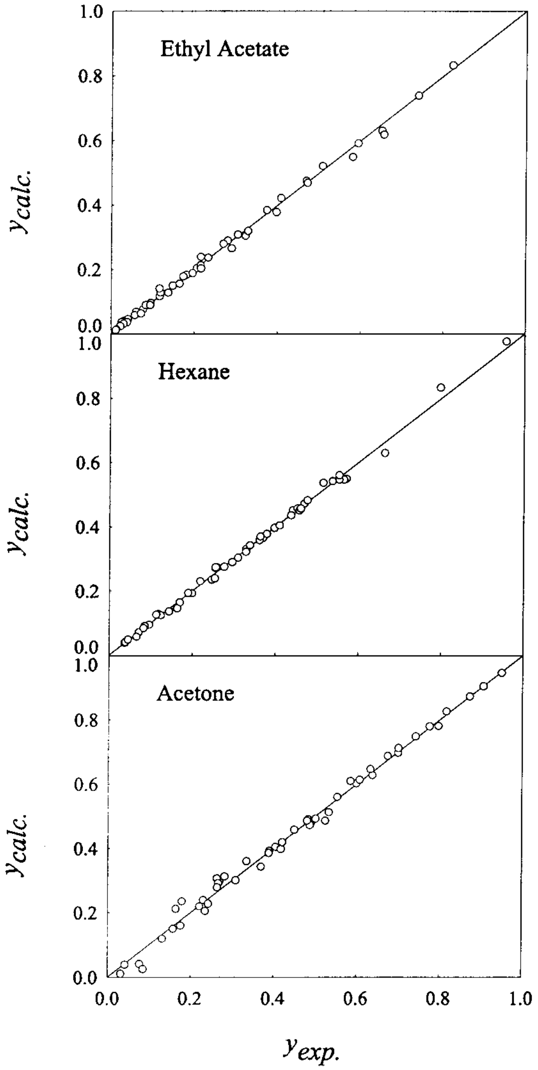

Figure 4. Comparison of experimental and correlated (with Wilson equation) vapor-phase compositions for the system ethyl acetate + hexane + acetone at 101.32 kPa.

sake of clarity, the number of data points shown has been reduced).

Conclusions

Thermodynamically consistent isobaric (101.32 kPa) VLE data were determined for the ternary system ethyl acetate + hexane + acetone and the constituent binary systems. No ternary azeotrope was found. As can be seen from the ternary diagram, the isotherms' liquid-phase compositions focus to a single point, which corresponds to the binary azeotrope formed by the system hexane + acetone and is the focus of the arrows in the composition diagrams. Thus, separation of hexane and ethyl acetate could be possible by distillation using acetone as entrainer.

The Wilson, NRTL, and UNIQUAC equations adequately correlate ternary VLE data. The deviations found in temperature and vapor composition were similar for all three equations. It was impossible to select one as the best for all the systems.

Prediction of equilibrium by the group contribution method gave good results. The deviations obtained were only slightly higher than those obtained in the correlation of the experimental data.

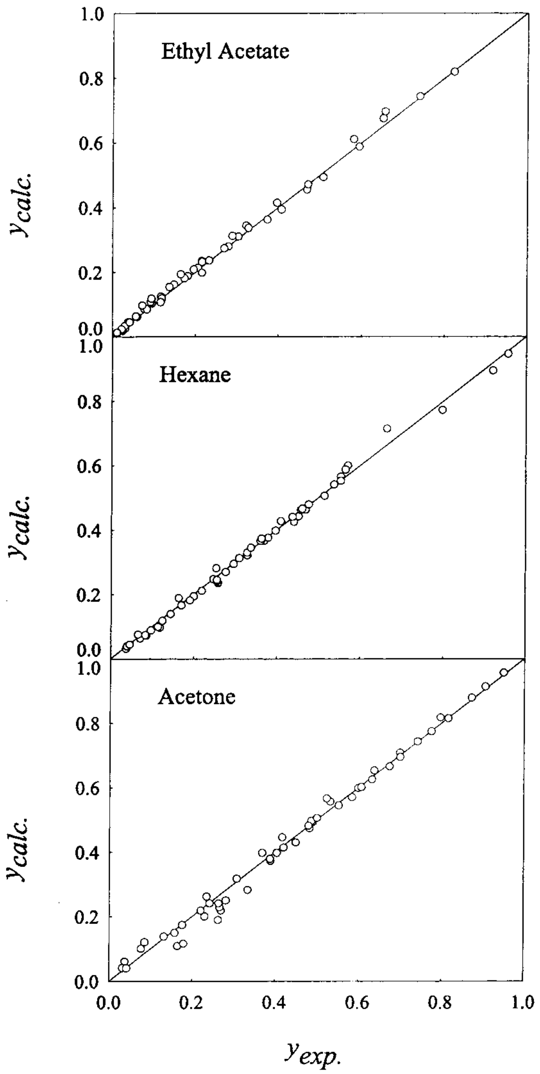

Figure 5. Comparison of experimental and predicted (with UNIFAC-Lyngby method) vapor-phase compositions for the system ethyl acetate + hexane + acetone at 101.32 kPa.

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