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Physics and Chemistry of Liquids

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713646857>

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To cite this Article Iglesias, M. , Mattedi, S. , Santana, M. C. and Carvalho-Santos, N. A.(2006) 'Fluid phase topology of ethanol benzene cyclohexane at 101.3 kPa', *Physics and Chemistry of Liquids*, 44: 6, 607 – 621

To link to this Article: DOI: 10.1080/00319100500537711

URL: <http://dx.doi.org/10.1080/00319100500537711>

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Fluid phase topology of ethanol + benzene + cyclohexane at 101.3 kPa

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(Received 2 January 2005; in final form 9 October 2005)

In this article, isobaric vapor–liquid equilibria for the ternary mixture of ethanol + benzene + cyclohexane was experimentally investigated at atmospheric pressure. Vapor–liquid equilibria data for ethanol + benzene + cyclohexane at 101.3 kPa were obtained with a Othmer-type ebullimeter. Data were tested and considered thermodynamically consistent. The experimental results showed that this ternary mixture is completely miscible and exhibits three binary homogeneous azeotropes and a ternary minimum azeotrope at the studied conditions. Satisfactory results were obtained for correlation of equilibrium compositions with UNIQUAC activity coefficients model and also for prediction with UNIFAC method. In both cases, low root mean square deviations of vapor mole fraction and temperature were calculated. The capability of ethanol as modified distillation agent at atmospheric condition is discussed in terms of the thermodynamic topological analysis. However, owing to the complex topology of the ternary mixture it leads to a distillation scheme with three columns and difficult operation and thus, ethanol is not recommended as a separating agent for benzene + cyclohexane azeotrope.

Keywords: Phase; Equilibria; Data; Residual map; Ethanol; Benzene; Cyclohexane

1. Introduction

The separation of the components of a liquid mixture by distillation is of significant importance both industrially and in the laboratories, and the design of distilling devices for separation of a particular mixture is necessarily based on the vapor–liquid compositions existing at equilibrium condition. Separation of liquid mixtures by distillation is made possible by the fact that at equilibrium in most systems the liquid and vapor differ in composition. Certain liquid mixtures form azeotropes or constant boiling mixtures. This type of mixture will give a vapor of composition identical with

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that of the liquid at equilibrium, making it impossible to separate the components by distillation. The addition of a third component to a binary liquid mixture to effect an otherwise impossible separation is becoming more important industrially due to the increasing importance of low-cost and new clean procedures. However, an adequate selection of extractive compound and operation conditions in distillation sequence must be applied to avoid complex procedures and expensive costs. Due to these facts, knowledge of multicomponent vapor–liquid equilibrium (VLE) data is important in design of equipments for separation processes. In the last few years, a considerable effort has been developed in the field of phase equilibria and thermodynamic mixing properties, however, experimental data collections of phase equilibria for ternary or higher-order complexity mixtures are still scarce, mainly due to the highly time consuming experimental procedure to obtain a complete description of each mixture of industrial interest. Nowadays with the wide use of modified distillation processes a VLE multicomponent database are of increasing relevance.

The separation of benzene + cyclohexane mixture is one of the most important and difficult processes in the petrochemical industry, with conventional distillation operations not being practical due to the similar volatilities of the two components at any composition of the mixture. The principal use of benzene is as chemical raw material in the synthesis of compounds, being used in the production of drugs, dyes, insecticides, and plastics. Cyclohexane is used in the production of paints and varnishes, as a solvent in the plastic industry, and for the extraction of essential oils. The importance of cyclohexane lays mainly in its conversion to cyclohexanone, a feedstock for nylon precursors [1]. Cyclohexane is produced by catalytic hydrogenation of benzene, with the unreacted benzene being present in the products stream and needs to be recovered in order to obtain pure cyclohexane product. The breakage of this minimum binary azeotrope is not possible by means of conventional distillation processes and modified (azeotropic or extractive) distillation is necessary. These distillation procedures, although feasible and in use in many industries, are accompanied by high capital costs if non-optimized separation solvent and operating conditions are applied. Optimizing the operational conditions is not a trivial task and plenty of contradictory rules of thumb have been found in the literature in this field. With these facts in mind, and as an extension of earlier works concerning phase equilibria, [2–4], new phase equilibria data is presented concerning the ternary mixture of ethanol + benzene + cyclohexane at a pressure of 101.3 kPa. No other literature data have been made available for this system except any ancient works [5–7]. Because experimental data are often not available, group contribution methods may be used for the prediction of the required vapor–liquid in process synthesis. In the past several decades, the group contribution method UNIFAC [8] has become very popular and has thus been integrated in most commercial simulators. This kind of models require complete and fully updated experimental data in order to compute group interaction parameters and reproduce the behavior of systems at other mixing or operation conditions. The application of the UNIFAC group contribution method leads to satisfactory predictions in terms of activity coefficients and compositions for this ternary system, which is due to the molecular characteristics of the enclosed chemicals. Accordingly, fitting parameters corresponding to the boiling temperatures by the Tamir–Wisniak equation [9] and activity coefficients mole fraction dependence by UNIQUAC equation [10] are presented. The capability of ethanol as modified distillation agent at atmospheric condition is discussed in terms of the relative volatility

Table 1. Molar weight M_w , densities ρ , refractive indices on mixing n_D , and normal boiling temperature T_b of the pure components.

Component	M_w (g mol ⁻¹) ^a	ρ (298.15 K) (g cm ⁻³)		n_D (298.15 K)		T_b (K)	
		Exptl.	Lit.	Exptl.	Lit.	Exptl.	Lit. ^d
Ethanol	46.069	0.78589	0.78493 ^b	1.35941	1.35941 ^b	351.40	351.40
Benzene	78.114	0.8736	0.87370 ^c	1.49692	1.49792 ^c	353.16	353.250
Cyclohexane	84.162	0.7737	0.77389 ^c	1.42320	1.42354 ^c	353.79	353.888

^a[11], ^b[12], ^c[13], ^d[14].

and residual curve maps by means of the thermodynamic topological analysis. Final results show that owing to the complex topology of this mixture, ethanol is not adequate to be used as an entrainer for benzene + cyclohexane separation.

2. Experimental

2.1. Chemicals

All chemicals were of Merck's chromatographic grade. Purification was attempted by ultrasonic degassing and molecular sieves drying (4 Å, 1/16 inch). The purity of materials was checked by gas chromatography and found to be higher than 99.9 mass% for benzene and cyclohexane, and equal to 99.5 mass% for ethanol. The maximum water contents of the pure liquid were obtained by coulometry technique, being 3.0×10^{-2} , 4.9×10^{-3} , and 2.2×10^{-2} mass% for benzene, cyclohexane and ethanol, respectively. Their purity was also checked by determining different physical properties (density, refractive index, and normal boiling point), prior to the experimental work. Densities, refractive index at 298.15 K, and normal boiling temperatures are close to the values found in literature, as shown in table 1.

2.2. Apparatus and procedure

The VLE measurements were carried out under an atmosphere of dry nitrogen in a modified all-glass Othmer-type ebulliometer with secondary recirculations of both phases [3]. Thermal insulation was ensured with the whole apparatus being insulated except for the vapor condenser. Boiling temperatures of the mixtures were measured with an Anton Paar MKT-100 digital thermometer (accuracy $\pm 10^{-3}$, temperature scale ITS-90) over the entire range of working temperatures. Pressure was kept constant at $101.3 \pm 9.8 \times 10^{-2}$ kPa by a controller device, which introduced nitrogen to the apparatus in order to maintain the pressure difference with respect to the pressure at the laboratory. Each experiment was continued for at least 1 h after the stabilization of the boiling temperature. Samples of both liquid and vapor phases were taken at low temperature by a built-in refrigeration device and sealed in an ice-cooled graduated test tubes to prevent evaporation leakage. The composition of the samples was determined by gas-liquid chromatography (GLC) with a flame ionisation detector [15]. The peak areas were converted to the mole fractions using weight factors determined

by the GLC analysis of mixtures of known composition throughout the ternary composition diagram. Estimated uncertainty for mole fractions was determined as $\pm 7 \times 10^{-3}$ in both phases. A more detailed description of the experimental procedure may be found in earlier papers.

3. Results and discussion

3.1. Equilibrium equation and activity coefficients

The experimental VLE data are given in table 2 with values of the activity coefficients (γ_i) which were computed by means of equation (1):

$$\gamma_i = \phi_i \gamma_i^L P / \{ \phi_i^S x_i P_i^S \exp[v_i^L (P - P_i^S) / RT] \} \quad (1)$$

where the liquid molar volume, v_i^L , was calculated by the Yen and Woods equation [16] and the fugacity coefficients, ϕ_i and ϕ_i^S , were obtained using a value of the second virial coefficient computed by the Hayden and O'Connell method [17] to characterize the vapor phase deviation from the ideal behavior. P_i^S is the vapor pressure which was calculated from the Antoine equation:

$$\log P_i^S = A - \frac{B}{T + C} \quad (2)$$

where A , B , and C are fitting parameters. The properties of the pure components required to calculate γ_i are listed in table 3. Figure 1 shows the corresponding liquid and vapor experimental compositions for the ternary mixture.

3.2. Boiling temperature correlation

In order to obtain general parameters of the experimentally measured magnitudes, the Tamir–Wisniak equation [9] was applied to correlate the boiling temperature, which is expressed as follows:

$$T = \sum_{i=1}^N x_i T_i^0 + \sum_{i=1}^{N-1} \sum_{j=i+1}^N x_i x_j [A_{ij} + B_{ij}(x_i - x_j) + C_{ij}(x_i - x_j)^2 + D_{ij}(x_i - x_j)^3] \\ + x_1 x_2 x_3 [E_1 + E_2(x_1 - x_2) + E_3(x_1 - x_3) + E_4(x_2 - x_3)] \quad (3)$$

where N is the number of components ($N=3$), T_i^0 is the boiling temperature of every pure component and A_{ij} , B_{ij} , C_{ij} , D_{ij} , and E_i are correlation parameters, which are gathered in table 4. The root mean square deviation was computed for temperature (as defined by equation (4)) as $\sigma = 0.33$ K.

$$\sigma(M) = \left\{ \sum (M_{\text{exptl}} - M_{\text{calcd}})^2 / ND \right\}^{1/2} \quad (4)$$

In this equation, M is a general magnitude (as temperature, vapor phase composition, etc.) and ND is the number of experimental data. Figure 2 shows the equilibrium isotherms on the liquid-phase composition diagram calculated from equation (3).

Table 2. Experimental VLE data: temperature T , liquid x_i and vapor phase y_i mole fraction, activity coefficient γ_i for ethanol(1) + benzene(2) + cyclohexane(3) at 101.3 kPa.

T (K)	x_1	x_2	y_1	y_2	γ_1	γ_2	γ_3
351.40	1.000	0.000	1.000	0.000	1.000	4.358	6.649
353.16	0.000	1.000	0.000	1.000	7.268	1.000	1.510
353.79	0.000	0.000	0.000	0.000	18.223	1.398	1.000
340.19	0.678	0.234	0.487	0.336	1.152	2.207	3.121
338.17	0.556	0.047	0.441	0.054	1.388	1.915	2.110
341.53	0.169	0.770	0.367	0.568	3.297	1.079	1.598
343.98	0.030	0.099	0.259	0.095	11.903	1.296	1.013
339.52	0.164	0.459	0.362	0.333	3.661	1.135	1.281
338.95	0.586	0.224	0.444	0.267	1.281	1.903	2.473
339.59	0.413	0.455	0.419	0.416	1.672	1.431	1.980
347.91	0.963	0.012	0.837	0.039	1.002	4.004	5.949
338.09	0.432	0.028	0.434	0.028	1.765	1.652	1.659
343.52	0.033	0.085	0.275	0.081	11.766	1.302	1.013
339.95	0.078	0.106	0.366	0.087	7.685	1.269	1.046
341.06	0.060	0.155	0.327	0.130	8.547	1.246	1.038
343.30	0.036	0.190	0.260	0.171	10.153	1.237	1.028
338.97	0.128	0.192	0.382	0.148	5.086	1.227	1.114
340.10	0.083	0.212	0.347	0.167	6.772	1.211	1.070
339.43	0.121	0.298	0.361	0.223	4.981	1.176	1.137
338.55	0.206	0.253	0.394	0.194	3.294	1.242	1.248
338.92	0.146	0.249	0.380	0.188	4.437	1.207	1.154
338.33	0.237	0.192	0.405	0.153	2.982	1.295	1.278
338.30	0.192	0.117	0.413	0.093	3.748	1.298	1.182
338.17	0.292	0.128	0.417	0.108	2.502	1.385	1.359
338.35	0.282	0.230	0.404	0.186	2.497	1.322	1.382
341.84	0.061	0.393	0.282	0.307	6.929	1.129	1.102
339.16	0.221	0.443	0.380	0.330	2.898	1.181	1.381
339.11	0.178	0.385	0.373	0.284	3.538	1.168	1.262
338.65	0.257	0.328	0.393	0.255	2.633	1.254	1.382
338.56	0.325	0.307	0.401	0.254	2.134	1.341	1.530
338.92	0.337	0.393	0.401	0.326	2.020	1.327	1.636
338.77	0.328	0.362	0.400	0.299	2.084	1.325	1.583
338.89	0.346	0.384	0.402	0.322	1.976	1.342	1.655
338.12	0.378	0.097	0.423	0.090	1.965	1.518	1.544
338.10	0.400	0.081	0.426	0.077	1.872	1.562	1.593
338.09	0.396	0.049	0.430	0.047	1.909	1.576	1.569
338.09	0.412	0.063	0.428	0.061	1.827	1.594	1.619
338.09	0.430	0.056	0.430	0.056	1.757	1.631	1.667
338.09	0.455	0.042	0.433	0.043	1.672	1.687	1.735
343.01	0.049	0.464	0.245	0.368	7.207	1.103	1.118
343.76	0.042	0.495	0.222	0.399	7.432	1.093	1.124
338.24	0.174	0.038	0.426	0.031	4.279	1.331	1.140
338.11	0.317	0.072	0.426	0.063	2.357	1.446	1.391
340.57	0.113	0.529	0.328	0.381	4.601	1.089	1.239
342.34	0.067	0.561	0.270	0.422	5.980	1.070	1.190
342.54	0.067	0.599	0.267	0.449	5.855	1.059	1.214
344.95	0.035	0.604	0.189	0.490	7.244	1.058	1.174
339.89	0.176	0.552	0.363	0.399	3.362	1.117	1.372
339.61	0.276	0.534	0.393	0.415	2.344	1.213	1.603
340.05	0.287	0.591	0.400	0.467	2.251	1.216	1.707
339.99	0.206	0.591	0.374	0.434	2.943	1.132	1.478
340.36	0.215	0.647	0.380	0.480	2.817	1.131	1.563
341.21	0.137	0.699	0.341	0.502	3.847	1.063	1.427
343.36	0.063	0.699	0.254	0.526	5.690	1.035	1.284
350.06	0.017	0.967	0.104	0.875	6.704	1.001	1.500
350.65	0.011	0.953	0.074	0.878	6.955	1.001	1.467
347.80	0.031	0.923	0.165	0.779	6.277	1.004	1.468

(Continued)

Table 2. Continued.

T (K)	x_1	x_2	y_1	y_2	γ_1	γ_2	γ_3
348.94	0.020	0.915	0.120	0.801	6.706	1.003	1.436
345.16	0.061	0.890	0.250	0.695	5.344	1.012	1.492
346.89	0.035	0.872	0.177	0.718	6.266	1.007	1.411
343.81	0.083	0.855	0.288	0.644	4.813	1.021	1.493
342.85	0.104	0.822	0.315	0.607	4.353	1.033	1.501
342.30	0.122	0.803	0.333	0.588	4.013	1.044	1.519
342.74	0.088	0.760	0.293	0.558	4.811	1.032	1.390
340.94	0.215	0.715	0.386	0.538	2.793	1.123	1.654
340.87	0.294	0.674	0.414	0.547	2.194	1.217	1.856
339.24	0.319	0.461	0.399	0.374	2.093	1.284	1.651
340.08	0.385	0.530	0.421	0.472	1.764	1.368	1.981
338.10	0.466	0.069	0.430	0.070	1.622	1.692	1.785
338.32	0.362	0.224	0.409	0.196	1.969	1.428	1.573
338.20	0.385	0.163	0.416	0.149	1.890	1.493	1.599
338.47	0.428	0.255	0.414	0.239	1.671	1.523	1.801
338.60	0.384	0.305	0.407	0.269	1.829	1.427	1.698
338.91	0.434	0.344	0.415	0.323	1.624	1.499	1.915
339.33	0.446	0.398	0.421	0.380	1.573	1.507	2.037
340.20	0.484	0.455	0.442	0.467	1.465	1.574	2.315
340.36	0.461	0.491	0.441	0.489	1.524	1.517	2.262
339.92	0.513	0.403	0.443	0.430	1.402	1.651	2.371
339.22	0.498	0.343	0.429	0.353	1.442	1.633	2.193
347.33	0.951	0.024	0.808	0.075	1.003	3.899	5.797
345.87	0.930	0.031	0.746	0.090	1.007	3.718	5.450
344.64	0.914	0.026	0.700	0.069	1.011	3.594	5.162
344.55	0.897	0.060	0.687	0.154	1.014	3.458	5.053
344.34	0.901	0.043	0.683	0.113	1.014	3.492	5.041
343.96	0.872	0.092	0.656	0.220	1.022	3.268	4.811
343.24	0.865	0.078	0.633	0.179	1.025	3.225	4.652
343.57	0.853	0.117	0.635	0.265	1.029	3.128	4.631
342.83	0.826	0.138	0.602	0.289	1.041	2.953	4.354
342.13	0.799	0.156	0.573	0.302	1.055	2.793	4.087
342.80	0.874	0.036	0.627	0.085	1.024	3.304	4.622
341.90	0.822	0.101	0.578	0.204	1.044	2.946	4.177
342.37	0.779	0.201	0.571	0.375	1.066	2.674	4.011
341.57	0.738	0.230	0.536	0.385	1.095	2.462	3.658
341.07	0.625	0.359	0.491	0.477	1.211	1.985	3.016
340.22	0.595	0.341	0.466	0.420	1.254	1.890	2.749
338.82	0.505	0.280	0.426	0.291	1.436	1.671	2.138
338.25	0.480	0.156	0.423	0.160	1.540	1.672	1.900
338.72	0.564	0.210	0.437	0.241	1.324	1.847	2.332
339.78	0.627	0.267	0.466	0.346	1.212	2.013	2.812
338.66	0.600	0.162	0.444	0.198	1.269	1.972	2.458
339.14	0.692	0.110	0.475	0.160	1.152	2.313	2.960
339.78	0.702	0.165	0.488	0.247	1.132	2.329	3.158
340.03	0.760	0.090	0.513	0.153	1.088	2.619	3.483
338.35	0.588	0.099	0.442	0.119	1.307	1.969	2.310
338.17	0.534	0.081	0.435	0.091	1.426	1.837	2.046
338.27	0.604	0.033	0.449	0.041	1.298	2.058	2.319
338.57	0.647	0.076	0.457	0.101	1.217	2.169	2.607
339.09	0.718	0.051	0.485	0.078	1.134	2.456	3.054
339.61	0.756	0.049	0.505	0.082	1.098	2.625	3.357
340.94	0.817	0.049	0.555	0.096	1.052	2.941	3.957
338.10	0.307	0.029	0.433	0.026	2.482	1.458	1.356
346.81	0.940	0.035	0.784	0.105	1.005	3.804	5.656
343.05	0.042	0.309	0.251	0.261	8.650	1.172	1.057
338.09	0.416	0.054	0.430	0.053	1.817	1.606	1.625
338.09	0.428	0.045	0.431	0.045	1.771	1.634	1.656

(Continued)

Table 2. Continued.

T (K)	x_1	x_2	y_1	y_2	γ_1	γ_2	γ_3
338.10	0.445	0.074	0.428	0.074	1.693	1.646	1.720
338.09	0.445	0.043	0.432	0.044	1.710	1.665	1.703
338.09	0.448	0.029	0.434	0.030	1.704	1.681	1.706
343.42	0.092	0.846	0.301	0.632	4.609	1.026	1.502
344.61	0.069	0.874	0.264	0.673	5.164	1.015	1.487
346.15	0.049	0.910	0.221	0.731	5.692	1.008	1.491
341.00	0.205	0.722	0.382	0.539	2.899	1.113	1.632
340.55	0.452	0.514	0.442	0.507	1.548	1.496	2.261
340.67	0.443	0.532	0.443	0.520	1.573	1.475	2.251
340.49	0.421	0.538	0.435	0.507	1.638	1.432	2.154
340.66	0.409	0.563	0.436	0.524	1.679	1.406	2.142
340.86	0.418	0.570	0.442	0.540	1.649	1.422	2.200
346.99	0.017	0.527	0.119	0.471	8.751	1.089	1.113
347.04	0.017	0.543	0.118	0.483	8.637	1.083	1.121
345.28	0.029	0.545	0.175	0.456	7.854	1.078	1.135
345.40	0.027	0.518	0.171	0.439	8.126	1.088	1.120
338.10	0.454	0.011	0.437	0.012	1.695	1.704	1.713
338.09	0.425	0.013	0.436	0.013	1.805	1.648	1.630
338.09	0.409	0.035	0.432	0.034	1.861	1.606	1.596
338.10	0.428	0.074	0.427	0.073	1.754	1.616	1.671
338.18	0.425	0.144	0.420	0.138	1.732	1.570	1.702
338.36	0.396	0.232	0.411	0.210	1.806	1.478	1.677
338.58	0.362	0.307	0.405	0.264	1.928	1.393	1.635

The shape of the curves indicates that the system exhibits a lowest minimum azeotrope in ternary composition and three binary minimum azeotropes (benzene + cyclohexane, ethanol + benzene and ethanol + cyclohexane). This is in accordance with the previously published data [5–7,20,21].

3.3. VLE consistency data

The thermodynamic consistency of the measured VLE data have been checked with the McDermott and Ellis method [22] to reject possible inconsistent equilibrium points from the experimental data collection. According to this test, two experimental points (a) and (b) are thermodynamically consistent when:

$$D < D_{\max} \quad (5)$$

where D is the local deviation, which is expressed as:

$$D = \sum_{i=1}^{N_{\text{comp}}} [(x_{ia} + x_{ib})(\ln \gamma_{ib} - \ln \gamma_{ia})] \quad (6)$$

and D_{\max} is the maximum deviation. McDermott and Ellis proposed a value of 0.01 for D_{\max} if the uncertainty in the mole fraction of the liquid and vapor compositions are between ± 0.001 . However, since the maximum local deviation is not a constant, the expression proposed by Wisniak and Tamir [23], equation (7), has been used

Table 3. Physical properties of the pure components: critical pressure P_c , mean gyration radius of RD, dipole moment μ , association parameter ETA, critical temperature T_c , critical compressibility factor Z_c , and antoine parameters A , B , and C .

Compound	P_c (kPa) ^a	RD ^a $\times 10^{10}$ (m)	μ^a $\times 10^{30}$ (C m)	ETA ^b	T_c (K) ^a	Z_c^a	Antoine constants ^c			
							A	B	C	
Ethanol	6383.5	2.259	5.6372	1.40	516.25	0.248	8.11220	1592.864	226.184	159.05–516.25
Benzene	4898.051	3.0040	0.00	0.00	562.16	0.271	6.32580	1415.800	-25.122	278.68–562.12
Cyclohexane	4072.292	3.2420	0.00	0.00	553.54	0.273	6.24778	1418.380	-19.379	276.69–553.54

^a[18], ^b[19], ^c[20].

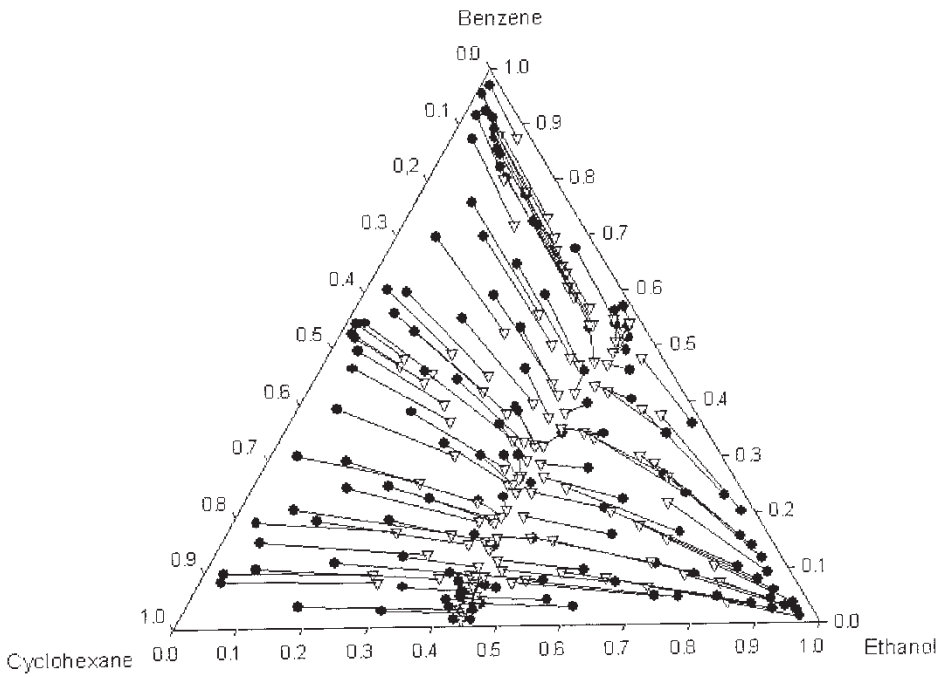


Figure 1. Composition (mole fractions) diagram for ethanol + benzene + cyclohexane at 101.3 kPa: (●) liquid phase, (▽) vapor phase.

Table 4. Parameters and deviations from correlation and prediction (Tamir–Wisniak, UNIQUAC equation and UNIFAC method) for ethanol + benzene + cyclohexane at 101.3 kPa.

Parameters of Tamir–Wisniak equation			
$A_{12} = -43.9019$	$B_{12} = -3.4655$	$C_{12} = -51.7761$	$D_{12} = 39.6769$
$A_{13} = -57.2881$	$B_{13} = -0.6076$	$C_{13} = -74.0481$	$D_{13} = 19.2652$
$A_{23} = -25.0099$	$B_{23} = 9.8743$	$C_{23} = -45.0387$	$D_{23} = 23.2563$
$E_1 = -0.4798$	$E_2 = 116.9021$	$E_3 = 96.5452$	$E_4 = -28.5612$
$\sigma = 0.33$			
Parameters of UNIQUAC equation Δu_{ij} (cal mol ⁻¹)			
$\Delta u_{12} = -124.72$	$\Delta u_{13} = -791.63$	$\Delta u_{23} = -1169.3$	
$\Delta u_{21} = -176.77$	$\Delta u_{31} = -247.87$	$\Delta u_{32} = -415.87$	
	σT (K)	σ (y_1)	σ (y_2)
UNIQUAC	0.24	0.0071	0.0032
UNIFAC	0.05	0.0009	0.0008

to compute this magnitude:

$$D_{\max} = \sum_{i=1}^{N_{\text{comp}}} (x_{ia} + x_{ib}) \left(\frac{1}{x_{ia}} + \frac{1}{x_{ib}} + \frac{1}{y_{ia}} + \frac{1}{y_{ib}} \right) \Delta x + 2 \sum_{i=1}^{N_{\text{comp}}} |\ln \gamma_{ib} - \ln \gamma_{ia}| \Delta x + \sum_{i=1}^{N_{\text{comp}}} (x_{ia} + x_{ib}) \frac{\Delta P}{P} + \sum_{i=1}^{N_{\text{comp}}} (x_{ia} + x_{ib}) B_i \left(\frac{1}{(t_a + C_i)^2} + \frac{1}{(t_b + C_i)^2} \right) \Delta t \quad (7)$$

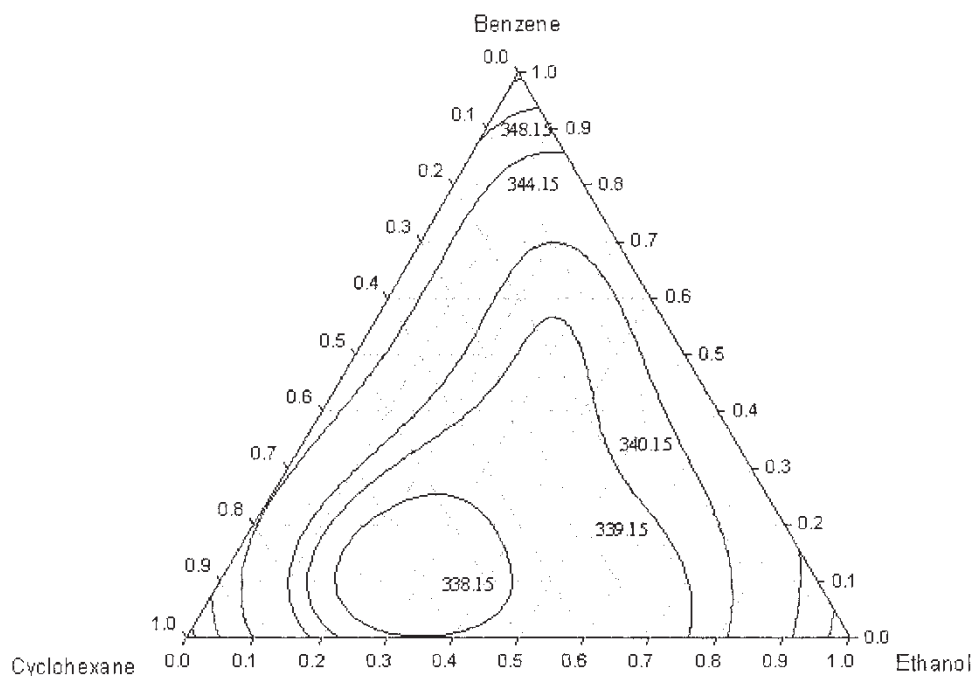


Figure 2. Isotherms (temperature in K) for ethanol + benzene + cyclohexane at 101.3 kPa using equation (3) with coefficients from table 4.

In the equation (7), B_i and C_i are the Antoine constant and Δx , ΔP , and Δt are the uncertainties of mole fraction, pressure, and temperature which have been found to be 7.0×10^{-3} , 0.098 kPa, and 10^{-2} K, respectively, in the experimental work. Therefore, according to the McDermott and Ellis test with the D_{\max} proposed by Wisniak and Tamir [23] the experimental data gathered in this work are considered thermodynamically consistent.

3.4. Activity coefficients correlation

Data were regressed to obtain UNIQUAC [9,10] parameters. The vapor phase was modeled by virial equation with coefficients calculated by Hayden and O'Connell method [17]. Fitted values and root mean square deviations on T and y_i are shown in table 4. It is observed that the UNIQUAC activity coefficient model is able to represent the VLE behavior of the ethanol + benzene + cyclohexane mixture.

3.5. Literature data

The present ternary mixture ethanol + benzene + cyclohexane forms four minimum temperature azeotrope under 101.3 kPa of pressure, as reported by different authors [5–7,20,21] and calculated from the temperature correlation in this study. A comparison of phase equilibrium data shows (figure 3) that the few data from Morachewsky

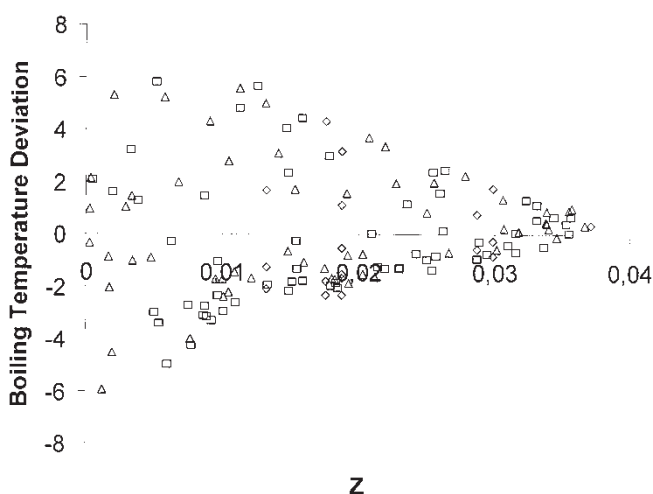


Figure 3. Comparison of the boiling point experimental data with those proposed in open literature (\diamond [5]; \triangle [6]; \square [7]) as a function of composition $z = (\sum_i x_i)$, where x_i is the molar fraction of the ternary mixture.

and Zharov [5] presents higher deviations in the intermediary compositions. On other hand, data from Deshpande and Liu [6] and Arce *et al.* [7] deviates more near binary compositions.

3.6. VLE prediction model

Prediction of VLE for the ternary system ethanol + benzene + cyclohexane at 101.3 kPa has been carried out by means of the UNIFAC group contribution method [8]. The results are compared with the experimental values, and the root mean square deviations for the temperature $\sigma(T)$ and the composition of the vapor phase $\sigma(y_i)$ are shown in table 4. A suitable description of the VLE behavior was obtained with the UNIFAC method owing to the molecular characteristics of the compounds enclosed in the mixture and to the common molecular groups enclosed in these solvents.

3.7. Thermodynamic topological analysis

The highly nonlinear VLE behavior of azeotropic or close-boiling mixtures complicates the further prediction of feasible separation columns sequences. In modified distillation, there are two possible modes of operation: (i) the original mixture to be separated is an azeotropic mixture and (ii) an azeotropic mixture is formed deliberately into a close-boiling mixture by adding one or more azeotrope-forming chemicals to the system. In the first procedure, one has to find a way to separate the azeotropic mixture and obtain the desired product specifications and recovery. In the second case, in addition, one has to select an azeotrope-forming component that is effective for the desired separation and can be recovered at low cost afterwards. In either case, a tool is needed to qualitatively predict the feasible separations for multicomponent

azeotropic mixtures. An available tool is the *thermodynamic topological analysis* which provides an efficient way for preliminarily analyzing nonideal distillation problems and qualitatively synthesizing separation columns sequences. This theoretical tool is based on the classical works of Schreinemakers and Ostwald (further explored in Widagdo and Seider) [24], where the relationship between the phase equilibrium of a mixture and the trend in open evaporation residue curves for mixtures was established. Although open evaporation with no reflux itself is not of much industrial interest, it nevertheless conceptually forms an important path for understanding distillation (a continuum of steps of partial vaporization with reflux). The reason for this renewed interest was the realization that, in spite of the advances in phase equilibrium calculations and simulations, there was a need for simpler tools to find the limitations and possibilities in modified distillation. Residue curve map and relative volatility analysis are included in the main recent publications in chemical engineering as important tools for distillation design of azeotropic/extractive trains of columns [25]. These allow one to determine the thermodynamic possibilities and boundaries of the separation attending to the nature and behavior of the mixture. After computing the feasible separation processes, one can synthesize alternative separation sequences that should be subjected to further analysis in order to choose the optimal one, in terms of economic and/or operational factors. Otherwise, as a result of the analysis it may turn out that the mixture cannot be separated by conventional distillation owing to the topology. Thermodynamic topological analysis (relative volatility and residual curve maps) provides then, a very useful tool for the screening of entrainers for modified distillation. The relative volatility diagram is a Gibbs triangular representation of the measure of differences in volatility between two components, and hence their boiling points. It indicates how easy or difficult a particular separation route will be and is a useful procedure to establish the flowsheet of the feasible separation columns sequence (the order of components recovery). Thus, if the relative volatility between two components is very close to one, it is an indication that they have very similar vapor pressure characteristics. The analysis of the different areas of the concentration range in the volatility map based on thermodynamic characteristics and pressure conditions of the mixture is important due to the different nature of each part of the concentration profile in each column. Typically a good entrainer is a component which “breaks” the azeotrope easily and yields high relative volatilities between the two azeotropic constituents. Because, these attributes can be easily identified in an entrainer from the equivolatility curve diagram of the ternary mixture azeotropic component #1 + azeotropic component #2 + entrainer, one can easily compare entrainers by examining the corresponding equivolatility curve diagrams. Useful information is obtained from this diagram in terms of minimum quantity of entrainer for a feasible separation [26]. Figure 4 presents the relative volatility map for the ethanol + benzene + cyclohexane mixture. Two regions of different volatility nature are observed in this map. In one of them, benzene is more volatile than cyclohexane and in the other one cyclohexane is more volatile than benzene. These regions are separated by an isoline of equivolatility that joints a point on a binary mixture with the azeotrope benzene + cyclohexane and a point in a binary mixture with 0.48 ethanol + cyclohexane. And so, if ethanol is used as an entrainer a reverse volatility scheme should be drawn, with cyclohexane being recovered in the top of the first column, and ethanol mole fraction should be higher than 0.48 in the azeotrope feed plate [26].

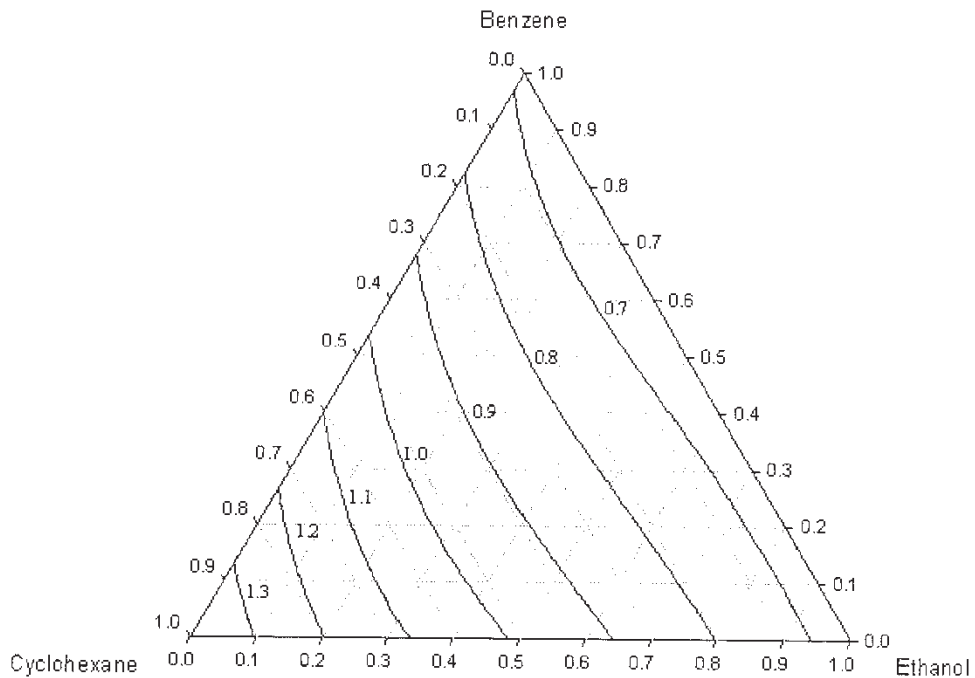


Figure 4. Isolines of relative volatility (adimensional) for ethanol + benzene + cyclohexane at 101.3 kPa derived from the experimental data.

A residual curve map is a diagram showing all of the azeotropic information of the constituent pairs and the residual curves of the mixture. A residual curve could be determined experimentally or mathematically, by simulating the experimental procedure using an adequate thermodynamic model [27]. For the azeotropic or extractive distillation, the azeotropic temperature and composition are the information needed for the process design. In a specific residual curve map, the azeotropic information is used to draw the distillation boundaries dividing the map into several distillation regions that any distillation operation cannot cross at usual conditions. For the system under study, the residual curve map was calculated using UNIFAC method for modeling liquid phase and Peng–Robinson equation of state for representing vapor phase (figure 5). The shape of the curves indicates that the system exhibits azeotropic behavior at each binary composition (saddle points, minimum azeotropes) and in ternary composition (unstable node, the lowest minimum azeotrope). This is in accordance with previously published data [5–7,20,21]. The distillation curves show a saddle behavior near each binary minimum azeotrope (benzene + cyclohexane, ethanol + benzene and ethanol + cyclohexane), a stable node trend in pure conditions and an unstable node trend around the ternary azeotrope in the Gibbs composition diagram (separation topology classified as 123-m [28]). The azeotropic data was confirmed from correlation in the present work and literature. Three distillation boundaries are shown, corresponding to three distillation regions. This type of equilibrium topology with distillation boundaries among azeotropes leads to complex sequences of separation columns [27], with necessary azeotrope recycle, difficult control policy and expensive installation costs for the sequence of distillation columns.

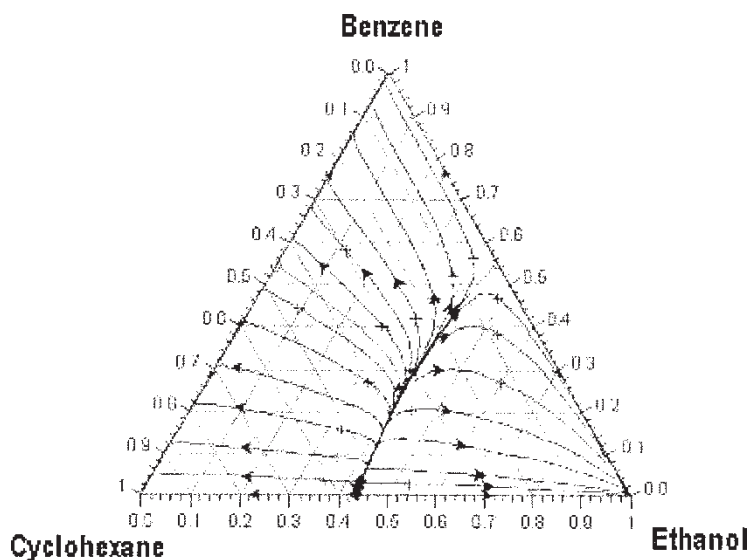


Figure 5. Residual curve map for ethanol + benzene + cyclohexane at 101.3 kPa by UNIFAC method.

4. Conclusions

In this study, the azeotropic behavior of the ethanol + benzene + cyclohexane ternary mixture was experimentally investigated for feasibility using ethanol as an entrainer to the azeotropic distillation of the binary azeotrope. The experimental results showed that this ternary mixture is completely miscible and exhibits three binary homogeneous azeotropes as saddle points at the studied conditions, and a ternary minimum azeotrope with a unstable node trend. The ternary vapor–liquid equilibrium has been modeled using a correlating model (UNIQUAC) and a predictive model (UNIFAC). The capability of ethanol as modified distillation agent at atmospheric condition was discussed in terms of relative volatility and residual curve maps (Thermodynamic topological analysis). Based on the results, the following conclusions can be drawn: (i) the UNIQUAC model represents an adequate procedure for fitting VLE data of this kind of ternary mixtures; (ii) group contribution model UNIFAC model can be used for modeling and cases in which no experimental data is available (close different pressures, multicomponent predictions with analogous chemicals, etc.); and (iii) the study reported here represents a new experimental contribution and ethanol is not a feasible entrainer for separating benzene + cyclohexane owing to the complex residue curve maps with three different distillation zones for the ternary mixture, leading to a scheme with at least three columns and difficult operation.

Acknowledgments

M. Iglesias would like to thank the support of the Chemical Engineering Post-graduation Program of Federal University of Bahia during his stay at Salvador-Bahia, Brasil.

S. Mattedi would like to acknowledge the support of the Chemical Engineering Department of the ETSEQ – Universitat Rovira I Virgili during her stay at Tarragona–Spain.

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