

Azeotropic behaviour of (benzene + cyclohexane + chlorobenzene) ternary mixture using chlorobenzene as entrainer at 101.3 kPa

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Abstract

In this paper, the azeotropic behaviour of the (benzene + cyclohexane + chlorobenzene) ternary mixture was experimentally investigated with the aim of enhancing the knowledge for the feasible use of chlorobenzene as an entrainer for the azeotropic distillation of the binary azeotrope. Such a study has not been reported in the literature to the best of the authors' knowledge. (Vapour + liquid) equilibria data for (benzene + cyclohexane + chlorobenzene) at 101.3 kPa were obtained with a Othmer-type ebulliometer. Data were tested and considered thermodynamically consistent. The experimental results showed that this ternary mixture is completely miscible and exhibits an unique binary homogeneous azeotrope, an unstable node at the conditions studied, and the propitious topological characteristics (residual curve map and relative volatility) to be separated. Satisfactory results were obtained for the correlation of equilibrium compositions with the UNIQUAC activity coefficients model and also for prediction with the UNIFAC method. In both cases, low root mean square deviations of the vapour mole fraction and temperature were calculated. The capability of chlorobenzene as a modified distillation agent at atmospheric condition is discussed in terms of the thermodynamic topological analysis. A conceptual distillation scheme with reversed volatility is proposed to separate the azeotropic mixture. In order to reduce the operational cost requirements of the sequence of columns proposed, the range for optimal reflux and the ratio for feed flow conditions were studied.

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1. Introduction

Knowledge of multicomponent (vapour + liquid) equilibrium (VLE) data is important in the design of equipment for separation processes. In addition, this experimental information may be used to test and develop new models for correlation and prediction of thermodynamic properties in multicomponent mixtures. In the last few years, a considerable effort has been developed in the field of phase equilibria and thermodynamic mixing properties. However, the experimental data collections of phase equilibria for ternary or higher order complexity mixtures are still

scarce, mainly due to the high time consuming experimental procedure to obtain a complete description of each mixture of industrial interest.

Separation of the (benzene + cyclohexane) mixture is one of the most challenging processes in chemical engineering, with conventional distillation operations being not practical due to the similar volatilities of the two components at any composition of the mixture and to azeotropic characteristics. In any case, the synthesis, design and optimisation of distillation processes require a reliable knowledge of the phase equilibrium behaviour at the operation conditions.

The principal use of benzene is as chemical raw material in the synthesis of compounds, being also used in the production of drugs, dyes, insecticides, and plastics. Cyclohexane is used in the production of paints and varnishes, as a

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solvent in the plastic industry and for the extraction of essential oils. The importance of cyclohexane lies 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 product stream and needing to be recovered in order to obtain the 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 separation solvent and operating conditions are not properly chosen. Optimising the operating conditions is not a trivial task and contradictory rules of thumb have been found in the literature in this field. For all these reasons, the industry has always been eager to look for a viable alternative to the conventional (benzene + cyclohexane) separation. In any case, a reliable knowledge of the phase equilibrium behaviour is necessary for synthesis, design, and optimisation of any distillation system and for this mixture complete VLE data are not available in the literature.

As an extension of our earlier works concerning (vapour + liquid) or (liquid + liquid) equilibria (VLE or LLE) [2–8], we present new phase equilibria data concerning chlorobenzene as an alternative extractive rectification solvent for the azeotropic mixture (benzene + cyclohexane) at a pressure of 101.3 kPa. No literature data have been made available for this system out of 9 experimental data points gathered in a recent paper [9]. Because experimental data are often not available, at least for process synthesis, group contribution methods may be used for the prediction of the required (vapour + liquid) equilibria. In the past several decades, the group contribution method UNIFAC [10] has become very popular and has thus been integrated in most commercial simulators. This kind of model requires complete and fully updated experimental data in order to compute group interaction parameters and reproduce the behaviour 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 [11] and mole fraction dependence of activity coefficients by UNIQUAC equation [12] are presented. The capability of chlorobenzene as a modified distillation agent at atmospheric pressure is discussed in terms of relative volatility and residual curve maps by means of the thermodynamic topological analysis, a conceptual distillation scheme of reversed volatilities using chlorobenzene as the entrainer being proposed to separate the azeotropic mixture at the studied pressure. Final results show that operating cost requirements of the sequence of columns are directly related to the operational conditions, optimised in terms of reflux and feed flows ratio.

2. Experimental

All chemicals were of Merck's chromatographic grade. Purification was attempted by ultrasonic degassing and drying by molecular sieves (40 nm, 1.6 mm). The mass fraction purity of the materials was checked by gas chromatography and found to be greater than 0.999 for benzene and cyclohexane and 0.990 for chlorobenzene. The maximum water content of the pure liquids was obtained by the coulometry technique being $3.0 \cdot 10^{-2}$, $4.9 \cdot 10^{-3}$, and $3.2 \cdot 10^{-2}$ mass % for benzene, cyclohexane, and chlorobenzene, respectively. Their purity was also checked by determining different physical properties, prior to the experimental work. Densities, refractive index at $T = 298.15$ K, and normal boiling temperatures are close to values found in the literature, as shown in table 1.

The VLE measurements were carried out under an atmosphere of dry nitrogen in a modified all-glass Othmer-type ebulliometer with secondary re-circulation of both phases [8]. Thermal insulation was ensured by means of the whole apparatus having been insulated except in the part corresponding to vapour 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 $(101.3 \pm 9.8 \cdot 10^{-2})$ 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 stabilisation of the boiling temperature. Azeotropic determination was realised by means of consecutive distillation of the vapour condensate fractions, repeatedly through different experimental distillation lines [17], based in the literature azeotropic data, which were gravimetrically prepared. Samples of both liquid and vapour phases were taken at low temperature by a built-in refrigeration device and sealed in ice-cooled graduated test tubes to prevent evaporation leakage. After stabilizing the temperature of the samples by means of a controller bath with a temperature stability of $\pm 10^{-2}$ K, the samples were analysed by measuring their refractive indices and densities at $T = 298.15$ K [15]. Densities of the pure liquid and the mixtures were measured with an Anton Paar DSA-48 densimeter (accuracy of $\pm 10^{-4}$ g · cm⁻³) and refractive indices with an automatic ABBEMAT-HP Dr. Kernchen (accuracy of $\pm 5 \cdot 10^{-5}$) refractometer. Uncertainty for mole fractions was estimated to be $\pm 7 \cdot 10^{-3}$ in both phases. A more detailed description of the experimental procedure can be found in earlier papers.

3. Results and discussion

3.1. Equilibrium equation and activity coefficients

Experimental values of the density (ρ) and refractive index (n_D) at $T = 298.15$ K have been previously

TABLE 1
Summary of molar mass M_w , densities ρ , refractive indices n_D , and normal boiling temperatures T_b of the pure components

Component	$M_w/(\text{g} \cdot \text{mol}^{-1})^a$	ρ (298.15 K)/(g · cm ⁻³)		n_D (298.15 K)		T_b/K	
		exptl.	lit. ^b	exptl.	lit. ^b	exptl.	lit. ^b
Benzene	78.114	0.8736	0.87370	1.49692	1.49792	353.16	353.250
Cyclohexane	84.162	0.7737	0.77389	1.42320	1.42354	353.79	353.888
Chlorobenzene	112.559	1.1008	1.1011 ^c	1.52176	1.52138 ^c	404.92	404.91 ^d

^a Poling et al. [13].

^b TRC Thermodynamic Tables [14].

^c Iglesias et al. [15].

^d Nakanishi et al. [16].

published for this ternary system as a function of x_i [15]. In this work, these physical properties were applied in order to compute mixture composition by application of the corresponding fitting polynomials. The experimental VLE data are given in table 2 with values of the activity coefficients (γ_i) that were computed by means of the following equation:

$$\gamma_i = \phi_i \cdot y_i \cdot P / \{ \phi_i^S \cdot x_i \cdot P_i^S \cdot \exp [v_i^L \cdot (P - P_i^S) / R \cdot T] \}, \quad (1)$$

where the liquid molar volume, v_i^L , was calculated by the Yen and Woods equation [18] and the fugacity coefficients, ϕ_i and ϕ_i^S (the superscript S means saturated conditions), were obtained using a value of the second virial coefficient computed by the Hayden and O'Connell method [19] to characterise the vapour phase deviation from ideal behaviour. The P_i^S is the vapour pressure that was calculated from the Antoine equation:

$$\lg(P/\text{kPa}) = A - \frac{B}{\{(T/\text{K}) + C\}}, \quad (2)$$

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 vapour experimental compositions for the ternary mixture.

3.2. Correlation of the boiling temperature

In order to obtain general parameters of the experimental measurements, the Tamir–Wisniak equation was applied to correlate the boiling temperature [11], which is expressed as follows:

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

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 com-

puted for temperature (as defined by equation (4)) as $\sigma = 0.42$ K

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

In this equation, M is the variable as temperature or vapour phase composition and ND is the number of experimental data points. Figure 2 shows the equilibrium isotherms on the liquid-phase composition diagram calculated from equation (3). The shape of the curves indicates that the system does not exhibit azeotropic behaviour out of the binary range composition of the (benzene + cyclohexane) mixture (unstable node, minimum azeotrope). This is in accordance with previously published data [9,24,25]. The distillation curves show saddle behaviour near pure benzene and pure cyclohexane regions and a stable node trend in the chlorobenzene corner of the Gibbs composition diagram. This type of equilibrium topology without distillation boundaries or any other azeotrope leads to a simple sequence of separation columns [26], usually with more economic distillation schemes in terms of mechanical design and control requirements of the sequence of distillation columns. Comparison of the experimental data obtained in this work with those found in the literature [25] is shown in figure 3.

3.3. Consistency of the VLE data

The thermodynamic consistency of the measured (vapour + liquid) equilibria data have been checked using the McDermott and Ellis method [27] to reject possible inconsistent equilibrium points from the data collection. According to this test, two experimental points (a) and (b) are thermodynamically consistent when:

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

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

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

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 vapour compositions lie between ± 0.001 . However, since the maximum local

TABLE 2
Experimental (vapour + liquid) equilibrium data

T/K	x_1	x_2	y_1	y_2	γ_1	γ_2	γ_3
353.25	1.000	0.000	1.000	0.000	1.000	1.503	1.055
353.89	0.000	1.000	0.000	1.000	1.392	1.000	1.569
404.82	0.000	0.000	0.000	0.000	1.031	1.437	1.000
394.60	0.012	0.111	0.033	0.387	1.025	1.352	1.004
392.41	0.061	0.095	0.160	0.317	1.025	1.362	1.004
388.70	0.108	0.100	0.257	0.302	1.023	1.356	1.005
386.32	0.167	0.083	0.373	0.239	1.022	1.365	1.004
381.19	0.239	0.094	0.469	0.236	1.020	1.353	1.006
375.21	0.393	0.066	0.658	0.144	1.015	1.370	1.008
367.47	0.619	0.038	0.833	0.069	1.008	1.396	1.016
361.84	0.762	0.056	0.870	0.087	1.005	1.393	1.027
358.30	0.839	0.087	0.864	0.120	1.005	1.375	1.036
357.05	0.746	0.193	0.750	0.238	1.018	1.273	1.043
356.77	0.684	0.254	0.689	0.298	1.030	1.225	1.054
357.68	0.586	0.312	0.614	0.364	1.043	1.185	1.066
358.23	0.465	0.410	0.508	0.464	1.069	1.132	1.098
358.86	0.361	0.497	0.412	0.554	1.097	1.095	1.135
359.64	0.269	0.574	0.322	0.639	1.124	1.068	1.174
360.28	0.204	0.628	0.254	0.702	1.145	1.053	1.204
360.57	0.141	0.699	0.181	0.774	1.177	1.036	1.251
361.67	0.062	0.764	0.085	0.863	1.206	1.024	1.294
362.62	0.067	0.720	0.092	0.844	1.179	1.034	1.256
363.66	0.060	0.692	0.083	0.842	1.162	1.041	1.231
365.47	0.050	0.641	0.071	0.833	1.135	1.058	1.190
366.76	0.048	0.600	0.069	0.818	1.116	1.072	1.163
368.72	0.029	0.561	0.044	0.820	1.099	1.088	1.138
369.34	0.025	0.547	0.038	0.817	1.093	1.094	1.129
377.03	0.007	0.372	0.013	0.736	1.046	1.181	1.054
380.62	0.051	0.261	0.099	0.596	1.031	1.245	1.026
379.69	0.126	0.209	0.239	0.476	1.026	1.276	1.019
376.88	0.231	0.166	0.406	0.359	1.022	1.300	1.015
374.70	0.309	0.139	0.512	0.288	1.020	1.316	1.013
372.51	0.388	0.116	0.604	0.229	1.017	1.331	1.013
370.78	0.439	0.108	0.652	0.205	1.015	1.336	1.014
368.86	0.513	0.088	0.721	0.161	1.012	1.351	1.014
366.11	0.576	0.097	0.748	0.163	1.011	1.345	1.018
364.11	0.662	0.077	0.810	0.124	1.008	1.366	1.021
361.66	0.717	0.093	0.817	0.139	1.008	1.356	1.026
361.24	0.670	0.138	0.758	0.198	1.012	1.314	1.029
361.05	0.622	0.181	0.704	0.251	1.018	1.279	1.033
360.97	0.558	0.237	0.635	0.317	1.027	1.237	1.042
361.17	0.497	0.286	0.574	0.375	1.036	1.205	1.052
361.91	0.434	0.323	0.516	0.424	1.044	1.184	1.061
361.75	0.391	0.369	0.468	0.473	1.055	1.158	1.075
362.16	0.304	0.446	0.375	0.561	1.075	1.122	1.103
362.03	0.239	0.524	0.300	0.637	1.100	1.090	1.139
361.85	0.182	0.598	0.234	0.707	1.128	1.065	1.179
362.01	0.131	0.658	0.172	0.768	1.153	1.048	1.215
363.53	0.125	0.610	0.168	0.755	1.128	1.064	1.180
365.11	0.103	0.584	0.143	0.763	1.114	1.074	1.160
366.13	0.101	0.552	0.143	0.751	1.101	1.087	1.140
368.57	0.065	0.520	0.098	0.767	1.087	1.102	1.119
371.05	0.036	0.485	0.056	0.777	1.073	1.120	1.099
374.79	0.067	0.357	0.115	0.669	1.044	1.185	1.052
375.35	0.109	0.304	0.187	0.591	1.036	1.214	1.039
374.44	0.171	0.264	0.284	0.510	1.031	1.236	1.031
372.77	0.249	0.226	0.394	0.426	1.027	1.256	1.026
369.80	0.309	0.235	0.452	0.406	1.028	1.247	1.030
367.17	0.405	0.210	0.549	0.341	1.024	1.260	1.029
364.22	0.561	0.151	0.693	0.233	1.015	1.302	1.025
363.90	0.488	0.219	0.603	0.322	1.024	1.251	1.034
364.04	0.389	0.305	0.489	0.431	1.039	1.197	1.052
364.47	0.293	0.387	0.380	0.533	1.057	1.154	1.076
367.65	0.233	0.360	0.328	0.551	1.049	1.172	1.062

TABLE 2 (continued)

T/K	x_1	x_2	y_1	y_2	γ_1	γ_2	γ_3
366.89	0.185	0.431	0.259	0.626	1.065	1.137	1.087
368.30	0.161	0.419	0.232	0.637	1.061	1.145	1.080
366.92	0.185	0.430	0.259	0.626	1.065	1.137	1.087
365.82	0.200	0.446	0.273	0.625	1.070	1.128	1.095
369.42	0.114	0.439	0.171	0.684	1.064	1.137	1.085
365.37	0.142	0.528	0.195	0.707	1.094	1.094	1.131
363.36	0.296	0.417	0.375	0.549	1.065	1.137	1.089
363.04	0.444	0.281	0.541	0.390	1.035	1.210	1.048
354.88	0.968	0.032	0.955	0.045	1.001	1.461	1.050
354.79	0.946	0.049	0.932	0.067	1.001	1.437	1.046
354.77	0.919	0.068	0.906	0.092	1.002	1.411	1.044
355.03	0.922	0.059	0.915	0.081	1.002	1.421	1.044
355.10	0.915	0.062	0.911	0.085	1.002	1.416	1.043
355.16	0.895	0.074	0.893	0.100	1.003	1.400	1.041
355.08	0.832	0.121	0.832	0.159	1.008	1.344	1.039
354.74	0.783	0.169	0.779	0.211	1.014	1.297	1.041
355.22	0.845	0.108	0.847	0.144	1.006	1.358	1.038
355.26	0.871	0.089	0.872	0.119	1.004	1.381	1.039
355.31	0.863	0.092	0.867	0.124	1.005	1.376	1.039
355.40	0.831	0.113	0.839	0.150	1.007	1.352	1.038
355.58	0.927	0.042	0.934	0.059	1.001	1.439	1.044
355.16	0.806	0.139	0.809	0.180	1.010	1.325	1.039
354.84	0.720	0.217	0.725	0.263	1.022	1.255	1.047
357.36	0.035	0.889	0.049	0.929	1.297	1.005	1.428
356.86	0.020	0.933	0.027	0.958	1.334	1.002	1.482
355.20	0.532	0.374	0.561	0.419	1.060	1.150	1.087
355.15	0.401	0.509	0.441	0.539	1.105	1.088	1.147
355.06	0.356	0.563	0.398	0.584	1.127	1.068	1.177
356.34	0.118	0.810	0.152	0.828	1.251	1.013	1.358
356.52	0.103	0.823	0.135	0.845	1.258	1.012	1.369
357.76	0.060	0.835	0.081	0.888	1.259	1.011	1.371
354.70	0.444	0.480	0.477	0.507	1.095	1.099	1.134
351.44	0.528	0.467	0.533	0.466	1.095	1.101	1.134
351.54	0.561	0.430	0.561	0.437	1.081	1.119	1.116
		$\sigma(T/K)$	$\sigma(y_1)$	$\sigma(y_2)$			$\sigma(y_3)$
UNIQUAC		0.04	0.011	0.016			0.014
UNIFAC		3.90	0.001	0.002			0.003

Temperature T , liquid phase x_i and vapour phase y_i mole fraction, activity coefficient γ_i for {benzene (1) + cyclohexane (2) + chlorobenzene (3)} at 101.3 kPa, and root mean square deviation from the UNIQUAC correlation and the UNIFAC prediction shown in the two last rows.

deviation is not a constant, the expression proposed by Wisniak and Tamir [28] (equation (7)) has been used to compute this quantity:

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

where x and y are molar fraction compositions of both phases as above, t is temperature and a and b subscripts are related to each pair of experimental points of the ternary mixture. In this equation, B_i and C_i are the Antoine constants and Δx , ΔP , and Δt are the uncertainties in the mole fraction, pressure, and temperature which have been

found to be $7.0 \cdot 10^{-3}$, 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, the experimental data gathered in this work are considered to have thermodynamic consistency.

3.4. Correlation of the activity coefficients

Data were regressed to obtain UNIQUAC [12,13] parameters. The vapour phase was modelled by the virial equation with coefficients calculated using the method by Hayden and O'Connell [19]. Fitted values are presented in table 4, while root mean square deviations on T and y_i are shown in table 2, after the experimental data. It is observed that the UNIQUAC activity coefficient model is able to represent (vapour + liquid) equilibria behaviour for the (benzene + cyclohexane + chlorobenzene) mixture.

TABLE 3
Physical properties of the pure components

Compound	P_c/kPa^a	$\text{RD}^a \times 10^{10}/\text{m}$	$\mu^a \times 10^{30}/(\text{C} \cdot \text{m})$	ETA^b	T_c/K^a	Z_c^a	Antoine constants ^c			
							A	B	C	Range T/K
Benzene	4898.051	3.0040	0.00	0.00	562.16	0.271	6.32580	1415.800	-25.122	353.15 to 523.15
Cyclohexane	4075.292	3.2420	0.00	0.00	553.54	0.273	6.24778	1418.380	-19.379	354.15 to 501.15
Chlorobenzene	4520.1 ^b	3.568 ^b	5.837 ^b	0.00 ^b	632.40 ^b	0.268 ^b	6.30963 ^d	1556.60 ^d	-43.15 ^d	347.15 to 429.15

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.

^a Daubert and Danner [20].

^b Prausnitz et al. [21].

^c Gmehling and Onken [22].

^d Riddick et al. [23].

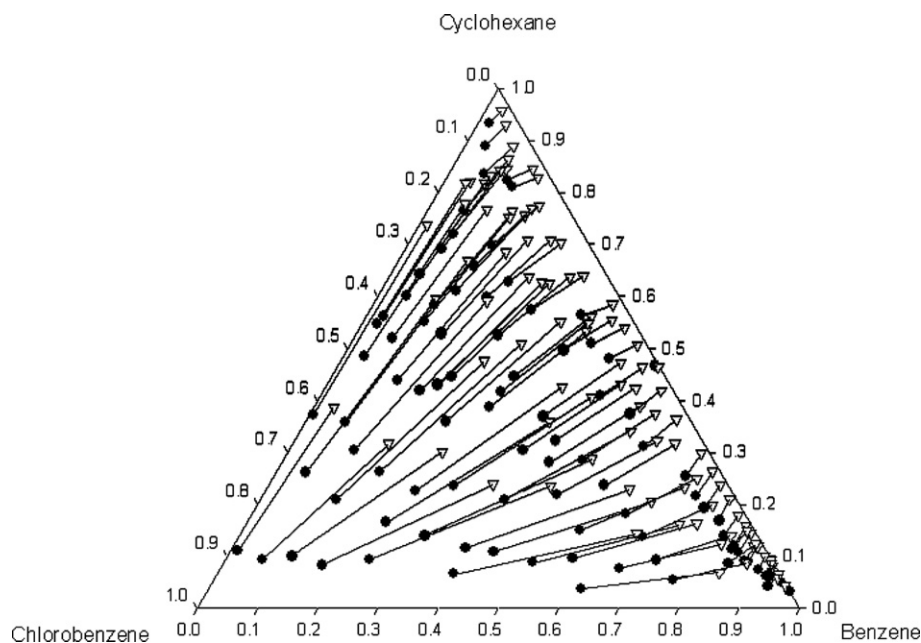


FIGURE 1. Mole fraction (Gibbs) diagram for (benzene + cyclohexane + chlorobenzene) at 101.3 kPa: (●) liquid phase, (▽) vapour phase.

TABLE 4
Parameters of Tamir–Wisniak and UNIQUAC equations for (benzene + cyclohexane + chlorobenzene) at 101.3 kPa

Parameters of Tamir–Wisniak equation			
$A_{12} = -11.4087$	$B_{12} = 7.9353$	$C_{12} = 4.9118$	$D_{12} = 15.4637$
$A_{13} = -17.1981$	$B_{13} = 13.0616$	$C_{13} = 8.9968$	$D_{13} = -6.5181$
$A_{23} = -30.2158$	$B_{23} = 27.9065$	$C_{23} = 20.5659$	$D_{23} = -1.2754$
$E_1 = 23.4313$	$E_2 = -298.349$	$E_3 = 303.7307$	$E_4 = -194.555$
$\sigma = 0.42$			
Parameters of UNIQUAC equation Δu_{ij} ($\text{J} \cdot \text{mol}^{-1}$)			
$\Delta u_{12} = -479.558$	$\Delta u_{13} = 432.994$	$\Delta u_{23} = -335.034$	
$\Delta u_{21} = 443.425$	$\Delta u_{31} = -345.021$	$\Delta u_{32} = 292.738$	

3.5. Behaviour of the azeotrope

In this mixture, only the binary mixture (benzene + cyclohexane) forms a minimum temperature azeotrope under 101.3 kPa, as reported by different authors

[9,24,25]. This was also confirmed in this study by a consecutive distillation of vapour condensate conducted as described in Section 2. After three independent batch distillations starting with different feed compositions, an homogeneous azeotrope was obtained introducing an unstable node character into the ternary mixture. The experimental value and literature data are compared in table 5. It was observed that deviations are less than 0.09 K for temperature values and not more than 0.0114 in molar fraction for benzene, as shown in figure 4.

3.6. Model for VLE prediction

Prediction of (vapour + liquid) equilibria for the ternary system (benzene + cyclohexane + chlorobenzene) at 101.3 kPa has been carried out by means of the UNI-FAC group contribution method [10]. The vapour phase was modelled by the virial equation using the coefficients

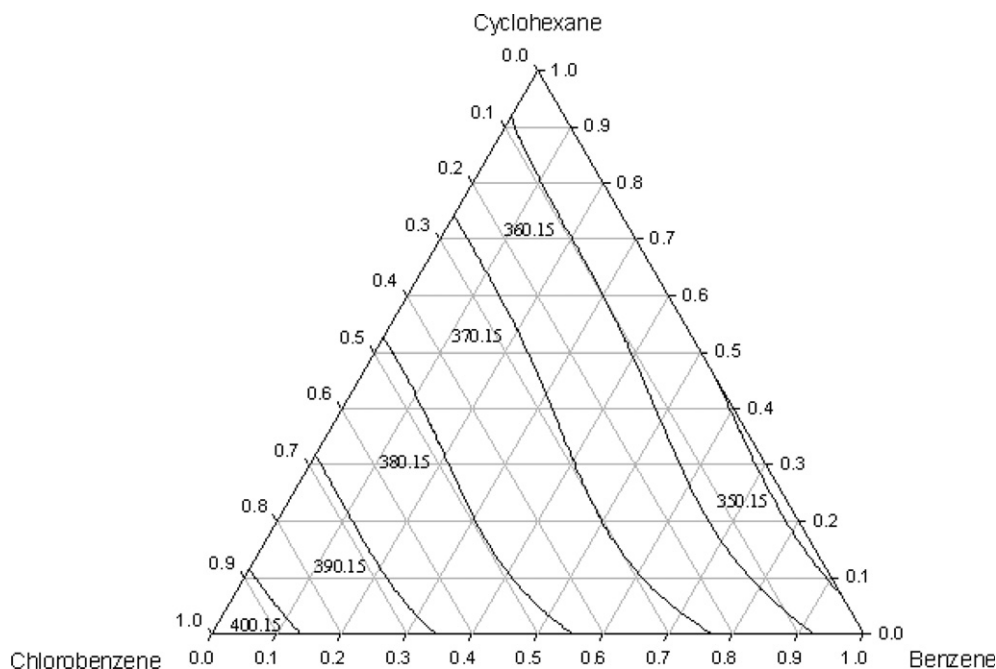


FIGURE 2. Mole fraction (Gibbs) liquid phase diagram for (benzene + cyclohexane + chlorobenzene) at 101.3 kPa calculated using equation (3) with coefficients from table 4. The solid lines are equilibrium isotherms in Kelvin.

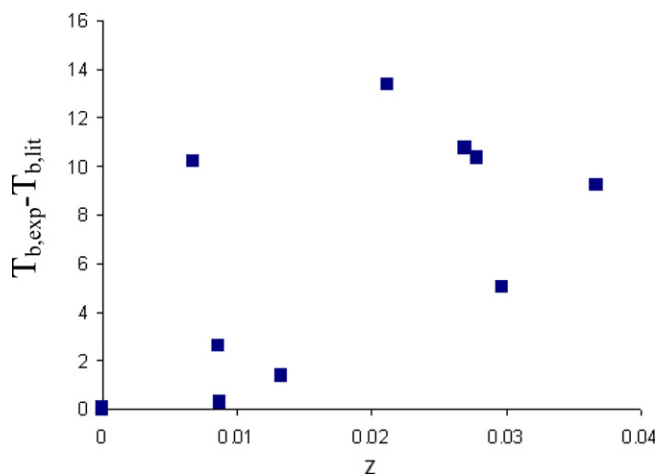


FIGURE 3. Plot of the difference in boiling temperature ($T_{b,exp} - T_{b,lit}$) against z . The z is a function of composition ($z = \prod_i x_i$) and x_i is the molar fraction of the ternary mixture. The literature values are from [9].

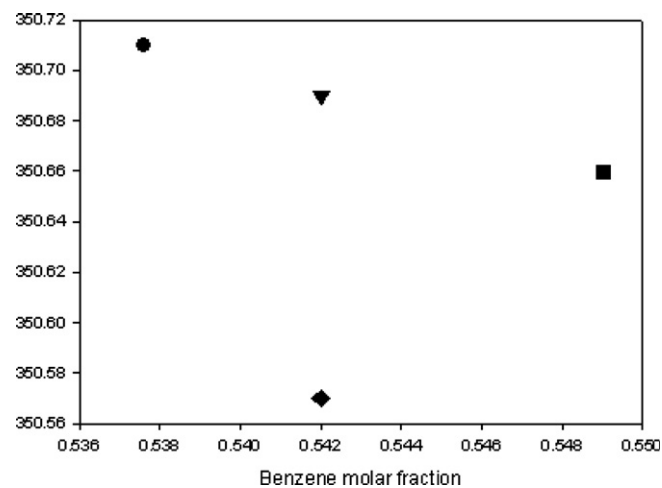


FIGURE 4. Plot of azeotrope temperature against mole fraction benzene for the binary (benzene + cyclohexane) at 101.3 kPa. (●) Horsley [25], (▼) Hiaki *et al.* [24], (◆) Rolemberg and Krähenbühl [9] and (■) experimental data.

TABLE 5
Azeotropic data for the binary mixture (benzene + cyclohexane) at 101.3 kPa

System	x_B	T/K
Benzene + cyclohexane ^a	0.5376	350.71
Benzene + cyclohexane ^b	0.542	350.69
Benzene + cyclohexane ^c	0.542	350.57
Benzene + cyclohexane ^d	0.549	350.66

^a Horsley [25].

^b Hiaki *et al.* [24].

^c Rolemberg and Krähenbühl [9].

^d This work.

calculated by the Hayden and O'Connell method [19]. The group interaction parameters used were taken from Wittig *et al.* [29]. The results are compared with the experimental values, and the root mean square deviations for the temperature $\sigma(T)$ and the composition of the vapour phase $\sigma(y_i)$ are shown in the last row of the table 2. A suitable description of the (vapour + liquid) equilibria behaviour was obtained with the UNI-FAC method owing to the simple topology of the mixture and the common molecular groups enclosed in these solvents.

3.7. Thermodynamic topological analysis

The highly nonlinear (vapour + liquid) equilibrium behaviour of azeotropic or constant-boiling mixtures complicates the further prediction of the sequence of feasible separation columns. 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 constant-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, one has also 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 predict qualitatively the feasible separations for multicomponent azeotropic mixtures. An available tool is the *thermodynamic topological analysis* that provides an efficient way for the preliminary analysis of nonideal distillation problems and for synthesising qualitatively the sequences of separation columns. This theoretical tool is based on the classical works of Schreinemakers and Ostwald [30], 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 vaporisation with reflux). The reason for this renewed interest is the realisation that, in spite of the advances in phase equilibrium calculations and simulations, there is a need for simpler tools to find the limitations and possibilities in modified distillation. The 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 [31]. These allow one to determine the thermodynamic possibilities and boundaries of the separation attending to the nature and behaviour of the mixture. After computing the feasible separation processes, one can synthesise 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. 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 (see equation (8)) between two components, and hence their boiling points

$$\alpha_{ij} = \frac{y_i}{x_i} \bigg/ \frac{y_j}{x_j} \quad (8)$$

It indicates how easy or difficult a particular separation route will be and is a useful procedure to establish the flow sheet of the feasible sequence of separation columns (the order of recovery of the components). Thus if the relative volatility between two components is close to one, it is an indication that they have very similar vapour 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 [32]. Figure 5 presents the relative volatility map for the (benzene + cyclohexane + chlorobenzene) mixture. Two regions of different volatility types are observed in this map. In one of them, benzene is more volatile than cyclohexane and in the other 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).

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 [26]. For the azeotropic or extractive distillation, the azeotropic temperature and composition provide 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 modelling the liquid phase and the virial equation for representing the vapour phase (figure 6). Following the procedure of constructing a residual curve map, one stable node, N1, representing chlorobenzene, two saddle points, S1 and S2, representing benzene and cyclohexane, and one unstable node, N2, representing the binary azeotrope, were found in the Gibbs phase diagram. The azeotropic data of the unstable node were confirmed from the present experimental work and literature. No distillation boundaries are drawn and only a unique feasible distillation region was obtained. The process design of this separation scheme of the (benzene + cyclohexane) with chlorobenzene as the entrainer could be developed completely in the residual curve map. The process scheme developed from the thermodynamic topologi-

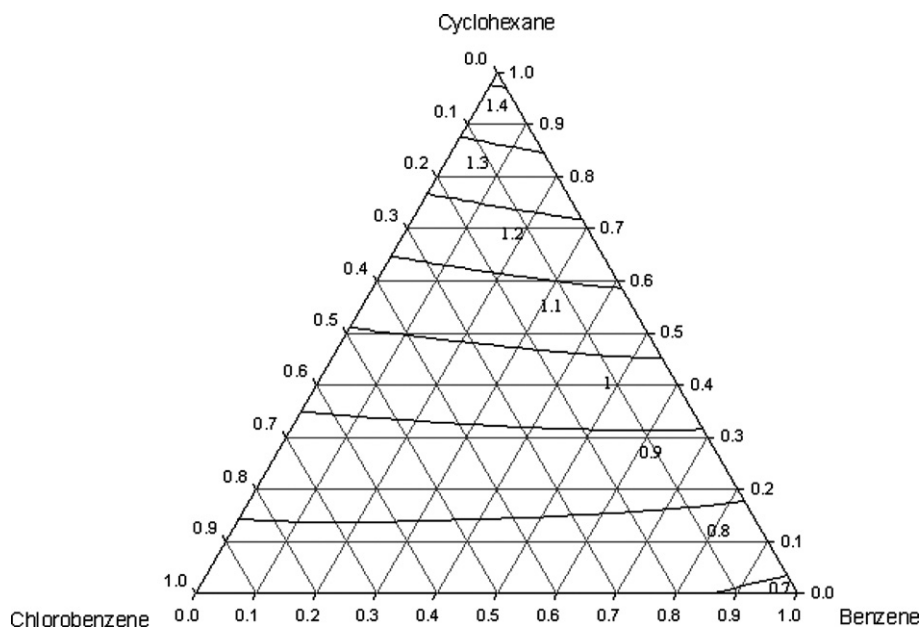


FIGURE 5. Mole fraction (Gibbs) diagram with isolines of relative volatility (adimensional) for (benzene + cyclohexane + chlorobenzene) at 101.3 kPa derived from the experimental data.

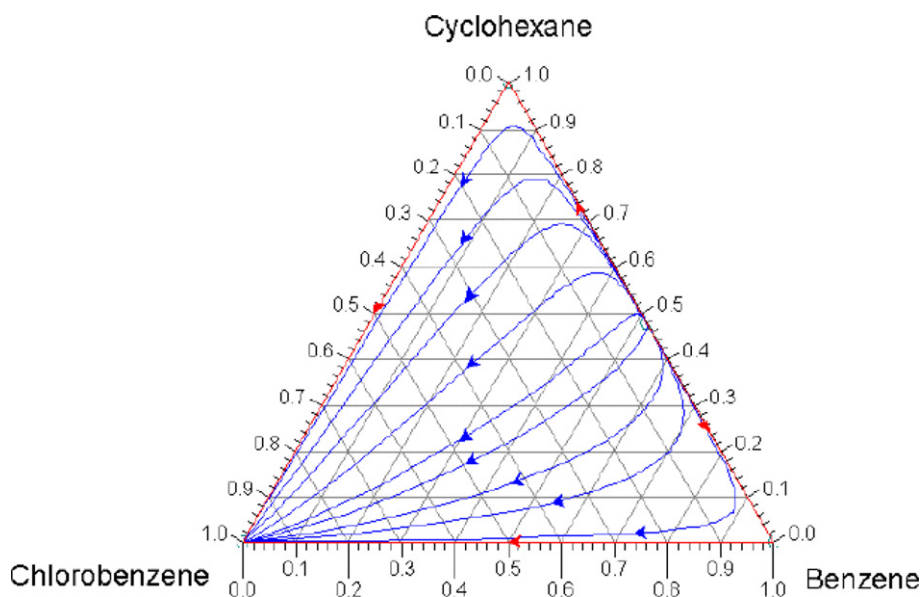


FIGURE 6. Mole fraction (Gibbs) diagram to show the residual curve map for (benzene + cyclohexane + chlorobenzene) at 101.3 kPa by the UNIFAC method (○, azeotrope; →, residue curve).

cal analysis is shown in figure 7a. The capability of the solvent (chlorobenzene) to extract selectively benzene is high. This fact is due to polar interactions between the ring Π -electrons of aromatic molecules of similar molecular volume. In accordance with the relative volatilities obtained from in these calculations, a reverse sequence in extractive rectification is necessary, *i.e.*, the first column operating with cyclohexane as head product and the second column having benzene as head product in the sequence. Furthermore, the position of the isoline $\alpha_{BC} = 1$ with respect to

the (cyclohexane + chlorobenzene) mixture makes it necessary that a relatively high concentration of the solvent in the extraction column be used in order to obtain high purity separations [32]. Despite high requirements of solvent in the extractive column (at least 0.482 in molar fraction of chlorobenzene in the azeotropic feed plate), promising results in the use of chlorobenzene as an entrainer in (benzene + cyclohexane) separation is expected based on the experimental (vapour + liquid) equilibria data obtained in this paper.

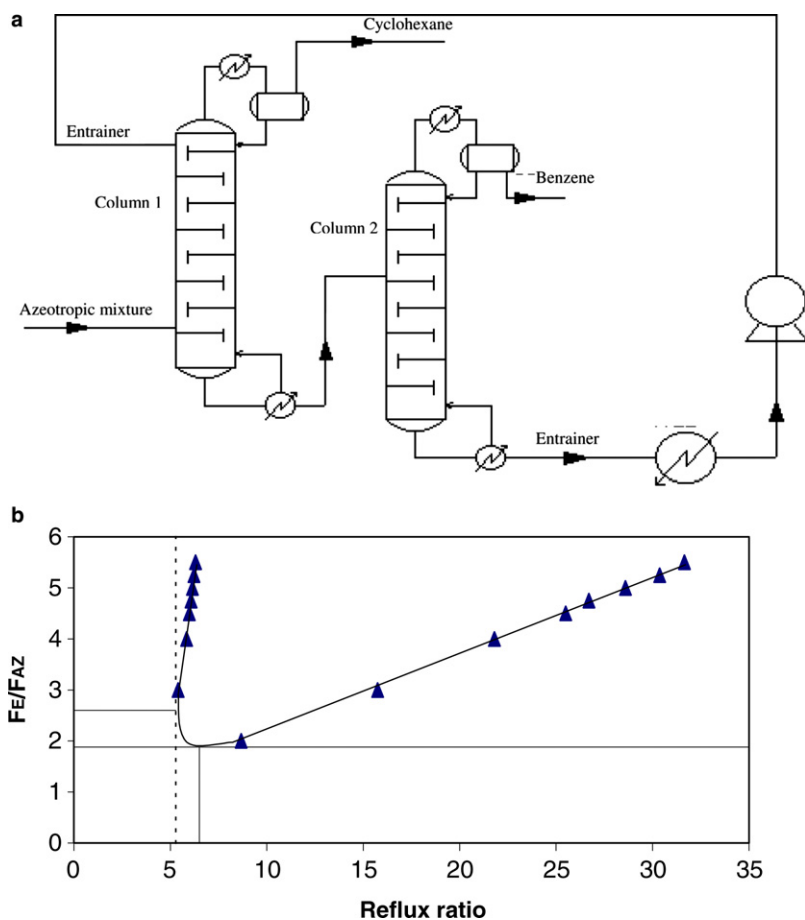


FIGURE 7. (a) Reversed sequence of extractive columns and (b) plot of F_E/F_{AZ} (molar relationship between the entrainer feed and the benzene + cyclohexane feed) against reflux ratio to show operativity limit curve for the extractive column for (benzene + cyclohexane + chlorobenzene) at 101.3 kPa by the UNIFAC method (see the double tangency on each axis).

A conceptual process, regardless of the economic consideration, was then analysed by simulation based on the phase equilibrium behaviour and the relative volatility/residual curve maps of the ternary mixture. To the best of our knowledge for chlorobenzene, such a study has not been reported in the literature.

3.8. Process simulation

In this work, HYSYS (HYPROTECH) is used to simulate the distillation process in steady state. The standard HYPROTECH database applied to the thermophysical data was used for determining the required property data

TABLE 6

Column specifications for simulation of the extractive distillation for the (benzene + cyclohexane + chlorobenzene) mixture at 101.3 kPa

Thermodynamic package: UNIQUAC vapour model: Redlich–Kwong

Extractive column

Top zone (chlorobenzene feed)	7 trays	T feed chlorobenzene	349.64 K
Extraction zone (azeotropic mixture feed)	37 trays	T feed azeotropic mixture of (benzene + cyclohexane)	349.64 K
Stripping zone	46 trays	Cyclohexane fraction (head)	0.98
Total	90 trays	Cyclohexane fraction (bottoms)	$1.00e^{-9}$

Solvent recovery column

Number of trays	11	Benzene fraction (head)	0.99
Inlet stream	Bottoms	Chlorobenzene fraction (bottoms)	0.99

Optimum operative range in column 1 to obtain $x_{\text{cyclohexane}} = 0.98$

Entrainment feed ratio	1.88 to 2.60
Reflux ratio	5.28 to 6.30

of the chemicals involved in this study. The model selected to describe the phase equilibria was UNIFAC/Redlich-Kwong EOS. The HYSYS design specification tool was applied to ensure that cyclohexane compositions at the top of the column were at a specified level. Heat losses, Murphree efficiencies, and other characteristics were assigned for the entire column for increased precision (see table 6 for details). In each simulation, the process was represented by two columns. The temperatures of both feeds were set to the azeotropic boiling temperature of the streams. To develop the process, model parameters such as reflux ratio, flow feed ratio, and size of the extractive section were varied until pure components were obtained in outlet streams. Firstly, simulations for simple (benzene + cyclohexane) mixture were developed. The extraction column was sized and divided into three segments, top (above entrainer feed), extraction (between feed), and stripping sections. The plant was configured to have 90 stages in the extractive column (7 + 37 + 46 stages, from top to bottom) and 11 stages in the solvent recovery column. The Murphree efficiencies (deviation of ideal separation capability of a theoretical stage into a distillation column) of the distillation stages were assumed to be equal to one in the whole column. Initially, flow products were configured at the top and at the bottom of each column. Using these settings, the reflux rate and the feed ratio were examined for the impact on the cyclohexane concentration in the first column top product stream. The design specifications were set as to achieve a concentration of 98% of cyclohexane at the top of the extractive column and a concentration of 98% of benzene at the top of the recovery column. The simulation considering only the (benzene + cyclohexane) feed revealed that the cyclohexane concentration in the top product could not be achieved. Only the composition of the azeotrope was obtained. This simplified model was then altered to take into account the influence of the entrainer and the complete sequence of solvent recovery. Starting with a greater content of chlorobenzene, the desired product concentration could easily be obtained with an adequate adjustment of the distribution of stages between the two volatility zones. A scheme of the sequence of the columns is shown in figure 7a. After including the second column, which was fed with the bottom stream from the first one, the initial design of the complete sequence was obtained. The basic specifications of the simulated columns are presented in table 6. In the simulation, feed flow and reflux ratios were varied in order to obtain the range of operating conditions that provide the desired outlet streams specifications. These results are shown in figure 7b. The optimum range of operating conditions was computed from the limiting cases and is also indicated in figure 7b.

4. Conclusions

In this study, the (vapour + liquid) equilibria behaviour of the (benzene + cyclohexane + chlorobenzene) ternary

mixture was experimentally investigated with the aim of testing the feasibility of using chlorobenzene as an entrainer to the azeotropic distillation. The experimental results show that this ternary mixture is completely miscible and it exhibits an unique binary homogeneous azeotrope as an unstable node under the conditions studied. The ternary (vapour + liquid) equilibrium has been modelled using a correlation model (UNIQUAC) and a predictive method (UNIFAC). The capability of chlorobenzene as modified distillation agent at atmospheric pressure is discussed in terms of relative volatility and residual curve maps (thermodynamic topological analysis). A conceptual distillation scheme based on the reversed volatility observed when chlorobenzene is used as entrainer is proposed to separate the azeotropic mixture. Based on the results, the following conclusions can be drawn: (i) the UNIQUAC model represents an adequate procedure for fitting (vapour + liquid) equilibrium data for this ternary mixture; (ii) the group contribution method UNIFAC can be used for modelling the system when experimental data are not available as for example, at other low pressures, for multicomponent predictions with analogous chemicals; (iii) the study performed here represents a new experimental contribution and an alternative procedure for feasible separation of the azeotropic mixture (benzene + cyclohexane) by modified distillation.

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