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Liquid–liquid equilibria for ternary systems acetic acid + n-butyl acetate + hydrocarbons at 293.15 K

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A B S T R A C T

Liquid–liquid equilibrium data for acetic acid + n-butyl acetate + hydrocarbons ternary systems at $T = 293.15$ K are reported in this work. The effect of hydrocarbon chain length on liquid–liquid equilibrium is determined and discussed. Aliphatic hydrocarbons such as hexadecane, dodecane and decane were particularly investigated. The organic chemicals (esters and hydrocarbons) were quantified by gas chromatography using a flame ionization detector while acetic acid was quantified by titration with sodium hydroxide. Experimental tie-line data for the ternary mixtures were correlated using Othmer–Tobias, Bachman and Hand correlations in order to show the reliability of the experimental results. Finally, these experimental data were correlated with the UNIQUAC model. It appeared that this model provides a good correlation of the solubility curve with these three hydrocarbons.

Keywords:

Liquid–liquid equilibrium data
Ternary mixture
Hydrocarbons
UNIQUAC model

1. Introduction

Low molecular weight esters are most commonly synthesized by direct esterification of carboxylic acids with alcohols in presence of acid catalysts by either a batch or a continuous process [1–4]. Esters are essential for the fragrance and flavouring industry. n-butyl acetate (BA) is a widely known ester used as a solvent in the production of lacquers for example, but more commonly as a synthetic apple flavouring used in food industry [5]. Production of BA increased in the last decade because its low toxicity and low environmental impact compared with other esters [6].

Industrially, the most commonly used separation processes for such equilibrium-limited reversible reactions is reactive distillation [7,8]. Nevertheless, in the case of butyl acetate, distillation is high-energy consuming due to low relative volatilities between the carboxylic acid and the ester. Indeed, the boiling points of acetic acid (118 °C) and butyl acetate (126 °C) are relatively close, and thus separation by distillation require a higher number of stage and reflux ratio in comparison to other esters. With the increasing price of energy, alternative separation techniques have to be considered, in order to reduce the energy consumption associated with the separation of the components. In this study, we focus on liquid–liquid extraction of the principal product, n-butyl acetate (BA) from the remaining reactant, acetic acid (AA), these mixture being a single homogeneous phase. This technique is of considerable economic

importance in the chemical industry and may be considered either at the end of the reaction or during the reaction in order to shift the equilibrium. The nature of solvent naturally influences the equilibrium characteristics of BA extraction from AA solutions. Previous works give some data on phase equilibrium for systems such as acetic acid and butan-1-ol [9] or ternary systems with acetic acid, water and esters [10] or alcohols [11–13]. In this study, aliphatic hydrocarbons (HCs), from hexane (C6) to hexadecane (C16), were used as organic solvent. Some liquid–liquid equilibrium (LLE) data for such ternary systems AA–BA–HC were obtained at $T = 293.15$ K, under atmospheric pressure.

First of all, mutual solubility of AA and HCs were studied in order to determine suitable solvents for liquid–liquid extraction of BA in excess of AA. LLE results for the ternary systems AA + BA + HC presenting a biphasic area are given in this work. Moreover, to show the consistency of our experimental results, tie-line data were correlated using Othmer–Tobias, Bachman and Hand correlations. Finally, experimental ternary diagrams were compared with data calculated with the UNIQUAC model. This model may provide a good correlation of the solubility curve with the hydrocarbons of interest.

2. Experimental

2.1. Materials

All chemicals (n-butyl acetate, glacial acetic acid, hexane C6, octane C8, decane C10, dodecane C12 and hexadecane C16) were purchased from Sigma–Aldrich. They were of guaranteed reagent

Table 1Compositions of initial mixtures, experimental tie-lines, solute distribution ratios, D and selectivity, S for ternary systems [AA + BA + HC] at $T = 293.15$ K.

Initial composition			AA-rich phase			HC-rich phase			D	S
w_{AA}	w_{BA}	w_{HC}	w_{AA}	w_{BA}	w_{HC}	w_{AA}	w_{BA}	w_{HC}		
Octane										
0.500	0.000	0.500	0.747	0.000	0.253	0.266	0.000	0.734	–	–
0.495	0.010	0.495	–	–	–	–	–	–	–	–
Decane										
0.500	0.000	0.500	0.846	0.000	0.154	0.217	0.000	0.783	–	–
0.490	0.020	0.490	0.811	0.030	0.159	0.252	0.017	0.731	0.577	1.714
0.480	0.040	0.480	0.748	0.058	0.194	0.288	0.038	0.674	0.656	1.626
0.475	0.050	0.475	0.713	0.069	0.218	0.316	0.047	0.637	0.688	1.768
0.470	0.060	0.470	0.655	0.081	0.264	0.359	0.064	0.577	0.800	1.462
0.462	0.075	0.463	–	–	–	–	–	–	–	–
Dodecane										
0.500	0.000	0.500	0.881	0.000	0.119	0.153	0.000	0.847	–	–
0.487	0.025	0.488	0.855	0.044	0.101	0.175	0.020	0.805	0.451	2.206
0.474	0.050	0.476	0.806	0.079	0.115	0.192	0.039	0.769	0.490	2.055
0.462	0.075	0.463	0.761	0.105	0.134	0.219	0.061	0.720	0.581	2.018
0.450	0.100	0.450	0.699	0.131	0.170	0.258	0.091	0.651	0.696	1.889
0.437	0.125	0.438	0.594	0.155	0.251	0.333	0.120	0.547	0.775	1.383
0.425	0.150	0.425	–	–	–	–	–	–	–	–
Hexadecane										
0.500	0.000	0.500	0.948	0.000	0.052	0.098	0.000	0.902	–	–
0.475	0.050	0.475	0.872	0.083	0.045	0.110	0.030	0.860	0.357	2.821
0.450	0.100	0.450	0.765	0.167	0.068	0.128	0.065	0.807	0.391	2.328
0.425	0.150	0.425	0.705	0.219	0.076	0.129	0.100	0.771	0.460	2.520
0.400	0.200	0.400	0.583	0.272	0.145	0.187	0.167	0.646	0.614	1.913
0.387	0.225	0.388	0.521	0.290	0.189	0.222	0.208	0.570	0.716	1.683
0.375	0.250	0.375	0.433	0.289	0.278	0.292	0.239	0.469	0.826	1.222
0.362	0.275	0.363	–	–	–	–	–	–	–	–

grade and their purities are reported by the supplier to be higher than 99%. They were used without any further purification as no impurities were detected using gas chromatography with a flame ionization detector (GC-FID). The amount of water in acetic acid was determined using a Karl–Fisher apparatus (831 KF Coulometer, Metrohm), this value being of 396 \pm 54 ppm.

2.2. Procedure

Ternary mixtures of known composition (AA + BA + HC) were precisely prepared in closed vials and mixed during at least 3 h at 293.15 K. The accuracy of the temperature is 1 K. The total weight of each sample was approximately 40 g. When the thermodynamic equilibrium was achieved, the system separated into two liquid phases that became transparent with a well-defined interface. After this decantation, the lower phase containing mainly AA and the remaining HC-rich upper phase were successively collected and weighted. After separation, samples of both phases were still transparent and were carefully analyzed to determine their compositions in order to build the LLE tie-lines.

2.3. Analysis methods

Ternary mixtures were analyzed by gas chromatography (GC) using an Agilent Technologies apparatus (6890N Network GC System) coupled to a flame ionization detector (FID) in order to determine BA and HC amounts. Separation was carried out with a capillary column (HP-FFAP column, 50 m, 0.32 mm, 0.50 μ m) from Agilent J&W GC Columns. The chromatograph was equipped with an automatic split injector and the injections (0.5 μ L) were performed with a split ratio of 100. The carrier gas was helium and the column head pressure was adjusted to 15 psi. Injector temperature was 220 $^{\circ}$ C. Temperature in the oven was held 14 min at 90 $^{\circ}$ C, then ramped to 200 $^{\circ}$ C at 10 $^{\circ}$ C min $^{-1}$ and finally held 5 min at 200 $^{\circ}$ C. The total running time was 30 min. The temperature of the detector (FID) was 250 $^{\circ}$ C. Each sample was analyzed three times and the values of mass fractions given in this paper are the average of

the three injections. The uncertainty is $u(w) = 0.001$, which corresponds to the maximum standard deviation calculated. AA could also be quantified by GC-FID but results are less reliable.

That is why an automatic titrator (751 GPD Titrino, Metrohm) was used to determine the quantity of AA in each sample. We verified that no hydrolysis of BA occurs during the titration with sodium hydroxide (0.1 M), with standard mixtures of AA and BA over the whole range of composition. The pH of the solution was measured throughout the titration thanks to an electrode, accuracy being more important with an electrode than an indicator. The endpoint corresponds to a sudden change in the measured pH, and then the

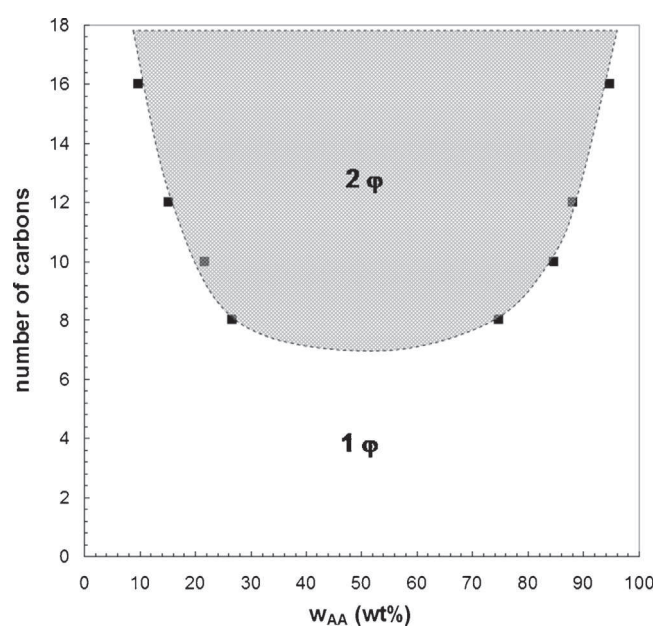


Fig. 1. Plot of mutual solubilities of acetic acid with different hydrocarbons from octane to hexadecane at 293.15 K (marked area is biphasic).

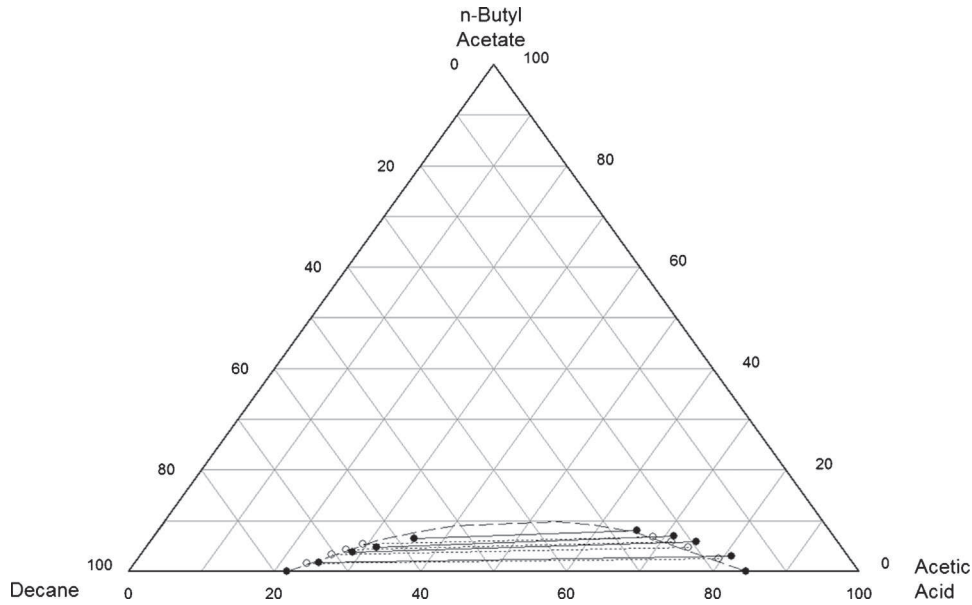


Fig. 2. Ternary diagram for LLE of [AA + BA + decane] at $T = 293.15\text{ K}$; ($\cdots\circ\cdots$) UNIQUAC tie-line data, (---) UNIQUAC solubility curve, (—●—) experimental tie-line data.

equivalence point allows the determination of AA amount in the sample.

3. Results and discussion

3.1. LLE experimental results

First of all, miscibility of acetic acid with hydrocarbons was determined. It was noticed that AA and hexane were miscible in all proportions whereas AA and all the other hydrocarbons present an incomplete mutual solubility. The results are reported in Table 1 (lines with a butyl acetate mass fraction w_{BA} equal to zero) and represented in Fig. 1. It is experimentally shown that the biphasic area is larger when the hydrocarbon chain length increases. Concerning the system AA+BA+C8, as it can be noticed in Table 1, with only 1% of BA ($w_{BA} = 0.01$), the mixture is monophasic, which means that the biphasic area of this system is very small. That is

why we did not represent a phase diagram of this system. The LLE diagrams for the other ternary systems with each hydrocarbon are plotted in Figs. 2–4. Because (HC + AA) is a liquid pair that is partially miscible and the two other liquid pairs (BA + AA) and (BA + HC) are completely miscible, the ternary systems behave as type-I LLE [14].

In order to evaluate the extracting capability of the hydrocarbon solvent for the separation of the ester from acidic solutions, the selectivity (S) and solute distribution ratio (D) were calculated from experimental data according to following Eqs. (1)–(2):

$$S = \frac{w_{BA}^{HC} \times w_{AA}^{AA}}{w_{BA}^{AA} \times w_{AA}^{HC}} \quad (1)$$

$$D = \frac{w_{BA}^{HC}}{w_{BA}^{AA}} \quad (2)$$

where w is the mass fraction, subscripts BA and AA refer respectively to n-butyl acetate and acetic acid, and superscripts HC

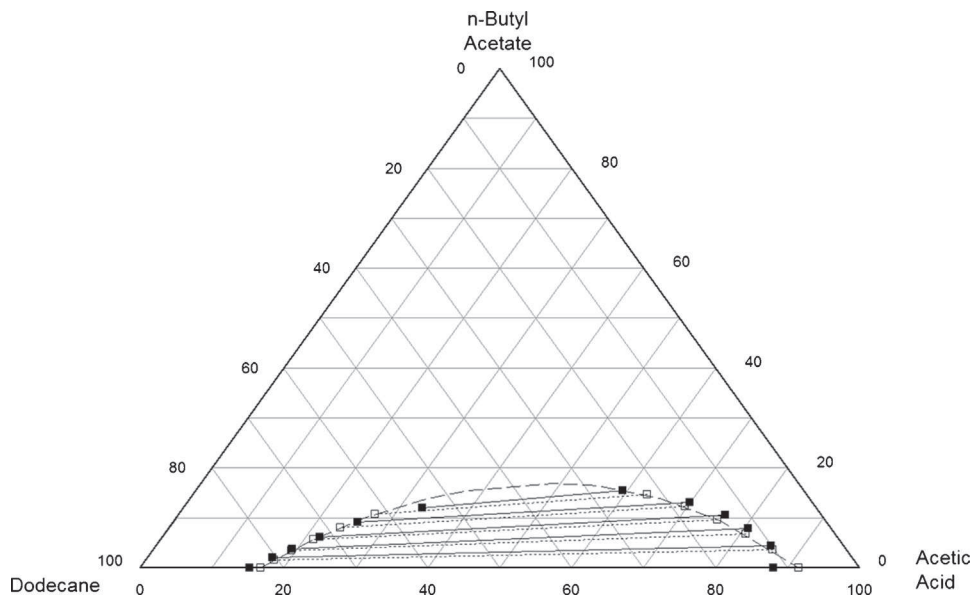


Fig. 3. Ternary diagram for LLE of [AA + BA + dodecane] at $T = 293.15\text{ K}$; ($\cdots\square\cdots$) experimental solubility curve, (---) UNIQUAC solubility curve, (—■—) experimental tie-line data.

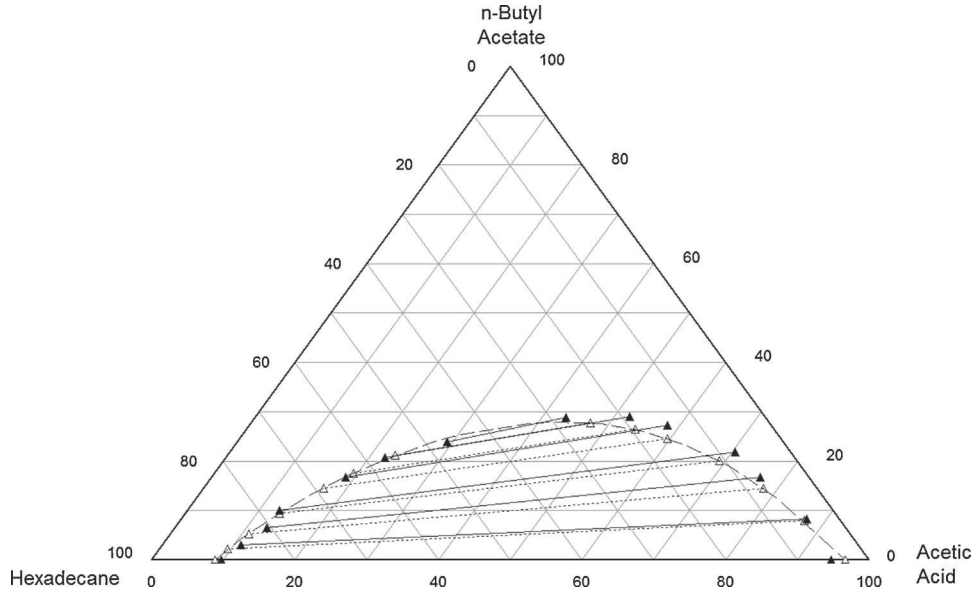


Fig. 4. Ternary diagram for LLE of [AA + BA + hexadecane] at $T = 293.15$ K; ($\cdots\triangle\cdots$) experimental solubility curve, (—) UNIQUAC solubility curve, ($-\triangle-$) experimental tie-line data.

and AA represent the hydrocarbon-rich phase and the AA-rich phase, respectively. Values of S and D are reported in Table 1. These parameters are widely used for evaluating the solvent (HC) efficiency in unit operations such as liquid–liquid extraction. The distribution coefficient is related to the extracting capacity of BA in the HC and determines the amount of HC needed for the extraction process, while the selectivity is related to the number of stages needed in the separation process. Theoretically, higher selectivity corresponds to fewer stages required for a given separation process and a higher distribution coefficient corresponds to a lower amount of solvent needed for a given separation, and consequently a smaller apparatus and lower operating costs. The selectivity as a function of solute distribution ratios for the three studied ternary systems is plotted for all initial compositions and particularly for an initial composition of $w_{BA} = 0.05$ in Fig. 5.

As it was expected, the selectivity decreases with the solute distribution ratio, which involves a compromise between these two parameters, i.e. between the size of the apparatus and the amount of solvent needed. No significant differences are observed between the three hydrocarbons. Nevertheless, as the biphasic area becomes larger when the length of hydrocarbon increases, hexadecane may be an appropriate solvent for this liquid–liquid extraction in order to collect an extract with higher purity.

3.2. Consistency of tie-line data

In this work, the Othmer–Tobias correlation [15] (Eq. (3)), the Bachman correlation [16] (Eq. (4)) and the Hand correlation [17] (Eq. (5)) were used to ensure the quality of the obtained experimental tie-line data:

$$\ln \left(\frac{1 - w_{HC}^{HC}}{w_{HC}^{HC}} \right) = A + B \ln \left(\frac{1 - w_{AA}^{AA}}{w_{AA}^{AA}} \right) \quad (3)$$

$$w_{BA}^{HC} = A' + B' \frac{w_{BA}^{HC}}{w_{AA}^{AA}} \quad (4)$$

$$\ln \left(\frac{w_{BA}^{AA}}{w_{AA}^{AA}} \right) = A'' + B'' \ln \left(\frac{w_{BA}^{HC}}{w_{HC}^{HC}} \right) \quad (5)$$

where w is the mass fraction, subscripts BA, HC and AA refer respectively to n-butyl acetate, hydrocarbon and acetic acid, and superscripts HC and AA represent the hydrocarbon-rich phase and the AA-rich phase, respectively; A , B , A' , B' , A'' and B'' , the parameters of the Othmer–Tobias correlation, the Bachman correlation and the Hand correlation, respectively. The correlation parameters and the correlation factor R^2 values were determined by a partial least-squares regression. The correlated results are reported in Table 2. The Othmer–Tobias, Bachman and Hand plots are also shown in Figs. 6–8, respectively, for the three investigated systems with decane, dodecane and hexadecane. As seen from Table 2 and Figs. 6–8, the closeness of the correlation factor R^2 to unity and the linearity of the plot reveal the high degree of consistency of measured LLE data in this study.

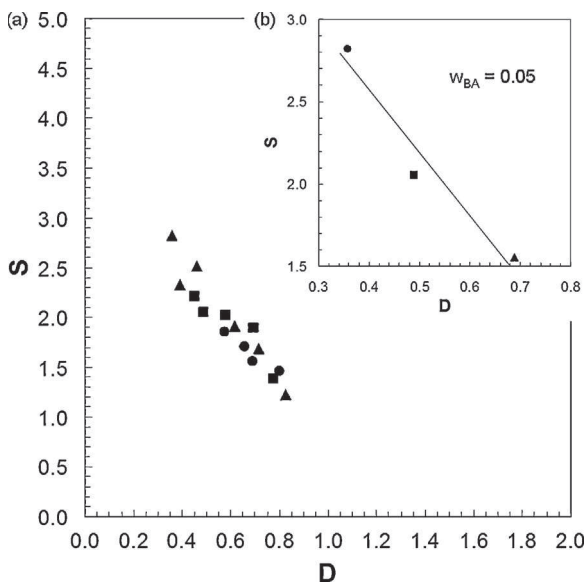


Fig. 5. (a) Selectivity S as a function of solute distribution ratio D for the three systems [AA + BA + HC] with HC: (\bullet) decane, (\blacksquare) dodecane, (\blacktriangle) hexadecane; (b) example for initial composition $w_{BA} = 0.05$.

Table 2
Constants of Othmer–Tobias, Bachman and Hand equations system.

Hydrocarbon	Othmer–Tobias correlation			Bachman correlation			Hand correlation		
	A	B	R ²	A'	B'	R ²	A''	B''	R ²
Decane	0.258	0.892	0.995	0.002	0.656	0.992	-0.332	0.785	0.994
Dodecane	0.145	0.919	0.995	0.007	0.594	0.981	-0.220	0.727	0.994
Hexadecane	-0.246	0.907	0.966	0.023	0.435	0.961	0.159	0.707	0.982

3.3. Correlation model

Experimental data are thus correlated with the excess Gibbs free energy model UNIQUAC [18]. The expression of the activity coefficient of the compound *i* is given in the following Eq. (6):

$$\ln \gamma_i = \ln \frac{\phi_i}{x_i} + 1 - \frac{\phi_i}{x_i} - \frac{z}{2} \left(\ln \frac{\phi_i}{\theta_i} + 1 - \frac{\phi_i}{\theta_i} \right) + q_i \left[1 - \ln \left(\sum_{j=1}^N \theta_j \tau_{ji} \right) - \sum_{j=1}^N \frac{\theta_j \tau_{ji}}{\sum_{k=1}^N \theta_k \tau_{kj}} \right] \quad (6)$$

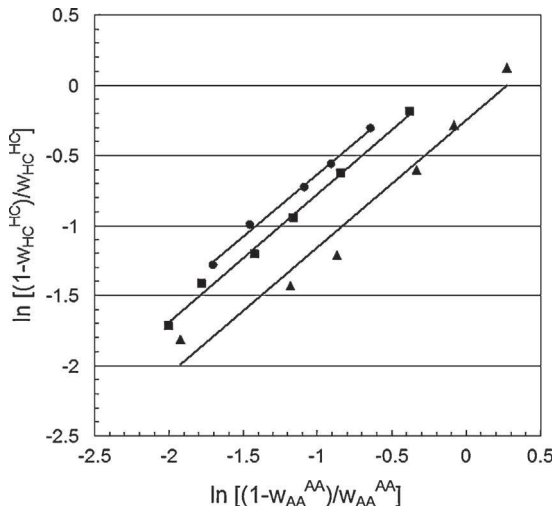


Fig. 6. Othmer–Tobias plot for the [AA+BA+HC] ternary systems at $T=293.15$ K with HC: (●) decane, (■) dodecane, (▲) hexadecane.

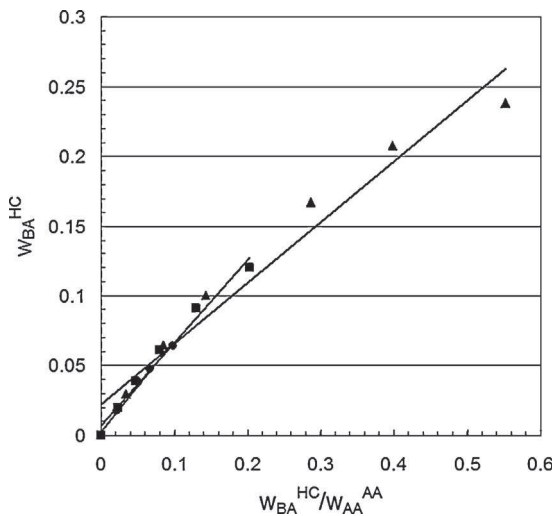


Fig. 7. Bachman plot for the [AA+BA+HC] ternary systems at $T=293.15$ K with HC: (●) decane, (■) dodecane, (▲) hexadecane.

Table 3
Structural parameters of the UNIQUAC model.

Compound	r (m ² /kmol)	q (m ³ /kmol)
Acetic acid	5.180×10^8	0.0333
n-Butyl acetate	1.049×10^9	0.0732
Decane	1.504×10^9	0.1092
Dodecane	1.774×10^9	0.1296
Hexadecane	2.314×10^9	0.1706

Table 4
Optimized UNIQUAC binary parameters.

Pair	B_{ij} (K)	B_{ji} (K)
AA+BA	29.006	80.708
AA+C10	-18.535	-270.071
AA+C12	-26.558	-270.500
AA+C16	-14.638	-333.271
BA+C10	50.602	42.413
BA+C12	16.526	54.114
BA+C16	8.937	35.641

with:

$$\phi_i = \frac{x_i r_i}{\sum_{j=1}^N x_j r_j} \quad (7)$$

$$\theta_i = \frac{x_i q_i}{\sum_{j=1}^N x_j q_j} \quad (8)$$

$$z = 10(\text{coordination number}) \quad (9)$$

$$\tau_{ij} = \exp \left(\frac{B_{ij}}{T} \right) \quad (10)$$

where x stands for the molar fraction, N the number of components, T the temperature (K) and B_{ij} an empirical asymmetric binary interaction parameter. The pure compound structural parameters r and

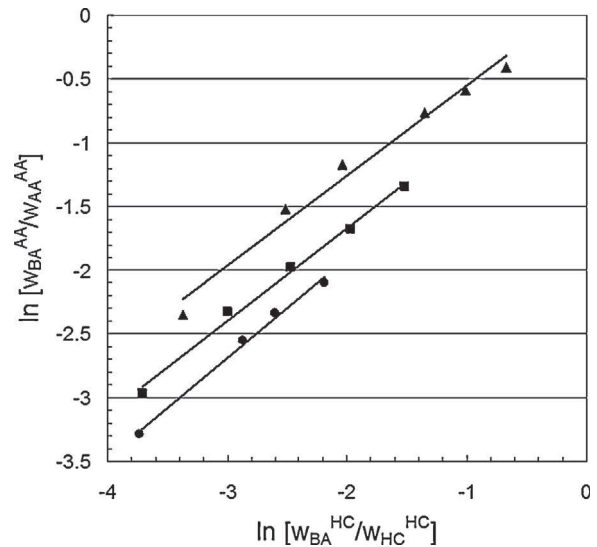


Fig. 8. Hand plot for the [AA+BA+HC] ternary systems at $T=293.15$ K with HC: (●) decane, (■) dodecane, (▲) hexadecane.

Table 5
Calculated tie-lines with the UNIQUAC model (mass fractions).

Initial composition			AA-rich phase			HC-rich phase			rmsd (%)
w_{AA}	w_{BA}	w_{HC}	w_{AA}	w_{BA}	w_{HC}	w_{AA}	w_{BA}	w_{HC}	
Decane									
0.500	0.000	0.500	0.846	0.000	0.154	0.217	0.000	0.783	2.45
0.490	0.020	0.490	0.796	0.025	0.180	0.236	0.016	0.748	
0.480	0.040	0.480	0.743	0.047	0.210	0.261	0.034	0.705	
0.475	0.050	0.475	0.715	0.058	0.227	0.277	0.043	0.680	
0.470	0.060	0.470	0.684	0.068	0.248	0.295	0.053	0.652	
Dodecane									
0.500	0.000	0.500	0.915	0.000	0.085	0.168	0.000	0.832	2.14
0.487	0.025	0.488	0.861	0.036	0.103	0.179	0.016	0.805	
0.474	0.050	0.476	0.808	0.068	0.124	0.193	0.035	0.772	
0.462	0.075	0.462	0.754	0.097	0.149	0.213	0.056	0.731	
0.450	0.100	0.450	0.697	0.123	0.180	0.238	0.080	0.682	
0.437	0.125	0.438	0.632	0.146	0.222	0.273	0.107	0.619	
Hexadecane									
0.500	0.000	0.500	0.967	0.000	0.033	0.088	0.000	0.912	2.65
0.475	0.050	0.475	0.870	0.080	0.050	0.095	0.022	0.883	
0.450	0.100	0.450	0.780	0.146	0.074	0.109	0.053	0.838	
0.425	0.150	0.425	0.692	0.201	0.107	0.131	0.094	0.775	
0.400	0.200	0.400	0.597	0.246	0.157	0.167	0.146	0.687	
0.387	0.225	0.388	0.542	0.264	0.194	0.194	0.176	0.630	
0.375	0.250	0.375	0.474	0.277	0.249	0.234	0.212	0.554	

q (van der Waals area and van der Waals volume, respectively) are extracted from the DIPPR database [19] and are reported in Table 3. The interaction binary parameters B_{ij} are simultaneously adjusted to reproduce the experimental mutual solubilities of the ternary systems investigated. The objective function (OF) minimized in order to determine optimal parameters is given by Eq. (11):

$$OF = \sum_{i=1}^M \sum_{j=1}^N \left(1 - \frac{K_{ij}^{\text{exp}}}{K_{ij}^{\text{calc}}} \right)^2 \quad (11)$$

where M is the number of experimental data and N the number of components. K_{ij} is the molar distribution ratio of the compound j for the i th experiment, defined by Eq. (12):

$$K_{ij} = \frac{x_{ij}^{\text{AA}}}{x_{ij}^{\text{HC}}} \quad (12)$$

where x denotes the molar fraction, and the superscripts AA and HC stand for the acetic acid-rich phase and hydrocarbon-rich phase, respectively. Optimized binary parameters B_{ij} are reported in Table 4.

To evaluate the model performance for each system studied, a root-mean square deviation (rmsd) between the experimental and calculated compositions in both phases is calculated using Eq. (13):

$$\text{rmsd} = 100 \cdot \sqrt{\frac{\sum_{i=1}^M \sum_{j=1}^N (x_{ij}^{\text{AA,exp}} - x_{ij}^{\text{AA,calc}})^2 + (x_{ij}^{\text{HC,exp}} - x_{ij}^{\text{HC,calc}})^2}{2MN}} \quad (13)$$

Calculated values as well as rmsd are reported in Table 5. The model results are found in well agreement with experimental values, with a maximal rmsd of 2.65% for the AA + BA + C16 mixture. Our values of rmsd are similar to values of previous works on ternary systems [20,21].

4. Conclusion

Liquid-liquid equilibrium (LLE) data for the systems acetic acid + n-butyl acetate + hydrocarbons were determined at 293.15 K and atmospheric pressure. As it was shown that hexane and acetic acid were miscible in all proportions, ternary mixtures were not feasible. Nevertheless, all the other investigated systems from octane to hexadecane formed a type-I phase diagram of LLE. The two-phase region increased with increasing the hydrocarbon chain length for the ternary systems studied. Moreover, consistency of

experimental data has been shown using Othmer-Tobias, Bachman and Hand correlations. In general, experimental data could be properly correlated using an UNIQUAC model. The phase diagrams of the systems acetic acid + n-butyl acetate + hydrocarbons can be used in liquid-liquid extraction practice and as reference data.

List of symbols

A, B	Othmer-Tobias correlation constants
A', B'	Bachman correlation constants
A'', B''	Hand correlation constants
B_{ij}	UNIQUAC binary interaction parameter
C6	hexane
C8	octane
C10	decane
C12	dodecane
C16	hexadecane
D	solute distribution ratio (in mass)
M	number of experimental data
N	number of components
K	molar distribution ratio
OF	objective function
q	molecular pure compound structural parameter, van der Waals volume (m^3/kmol)
r	molecular pure compound structural parameters, van der Waals area, (m^2/kmol)
R^2	Othmer-Tobias, Bachman, Hand correlation coefficients
rmsd	root mean square deviation
S	selectivity
T	temperature (K)
w	concentration in mass fraction
x	concentration in mole fraction

Superscripts

AA	acetic acid-rich phase
HC	hydrocarbon-rich phase

Subscripts

AA	acetic acid
BA	n-butyl acetate
HC	hydrocarbon
i	experiment
j	compound

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