Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

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Online publication date: 24 February 2003

To cite this Article Jiménez, Laureano and Costa-López, José(2003) 'Solvent Selection for a Reactive and Extractive Distillation Process by Headspace Gas Chromatography', Separation Science and Technology, 38: 1, 21 — 37
To link to this Article: DOI: 10.1081/SS-120016696
URL: http://dx.doi.org/10.1081/SS-120016696

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SEPARATION SCIENCE AND TECHNOLOGY
Vol. 38, No. 1, pp. 21–37, 2003

Solvent Selection for a Reactive and Extractive Distillation Process by Headspace Gas Chromatography

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ABSTRACT

The aim of this study is to determine the best solvent for the transesterification of the methanol and methyl acetate azeotropic mixture with n-butanol using the extractive and reactive distillation technology. A preliminary selection according to heuristics and physical properties was completed. Selectivity at infinite dilution for 40 systems was measured using headspace gas chromatography. This criteria help to cluster solvents into groups, but a definitive selection cannot be made. To consider the industrial application, the importance of *peripheral* properties was discussed. In addition, reactive and nonreactive residue curve maps analysis was made to reject those promising solvents without any feasible separation sequence (distillation boundary). Taking into

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DOI: 10.1081/SS-120016696 0149-6395 (Print); 1520-5754 (Online)

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account all these considerations, n-alkanes, alkilbenzenes, and, in particular, o-xylene were found to be the best alternatives.

Key Words: Headspace gas chromatography; Solvent selection; Selectivity; Reactive distillation; Extractive distillation.

INTRODUCTION

Volatile Organic Carbon legislation has affected the traditional market of many byproducts that were sold as solvents. The manufacture of poly-(vinyl alcohol) (PVA) is one of the processes in which some changes are due in the near future. PVA consumption increased at an overall rate of almost 2% annually between 1992 and 1998, indicating that most of the applications are mature. Overall expenditure is forecast to remain relatively stable during 1999–2003, although the average growth in the adhesives market is over 2% annually.[1]

In the PVA process, the main byproduct is an azeotropic mixture of methanol (MeOH) and methyl acetate (MeAc). This mixture has been sold for years to the paint, lacquers, and varnishes industries, where it was used as a solvent. Nowadays, it is used to produce dilute acetic acid with a relatively high capital cost (sulfuric acid is used as catalyst) and a high energetic cost.[2,3] As a marketing opportunity, a *reactive and extractive distillation process* with butanol (BuOH) was designed, thus integrating the process with MeOH reuse and high purity butyl acetate (BuAc) production. To date, oxygenated solvents are the biggest beneficiaries of the move away from hazardous solvents. The equilibrium conversion (Eq. 1) for the stoichiometric feed ratio ranged from 30% to 37%.

$$MeAc + BuOH \leftrightarrow BuAc + MeOH \tag{1}$$

Carrying out reactive extractive distillation experiments or even rigorous process simulation and cost estimation for all the possible solvents is expensive, tedious, and inefficient. Therefore a preliminary selection, based upon well-known rules of thumb and physical properties, was performed. The difference in boiling point is the universal data that qualify or disqualify a solvent: This difference should be large enough to ensure that the solvent remains in the reaction zone and that its presence in the distillate is minimum, but not so large to unnecessarily increase the energy needs in the solvent recovery system. Several investigations[4] pointed out the use of low boiling-points solvents in the so-called *reverse extractive distillation*, but as the amount of solvent has to be increased enormously to ensure a significant liquid

concentration and the enthalpy of vaporization affects the energy balance, such processes will only be competitive when there is no high-boiling solvent available.[5]

The widely accepted criterion for solvent selection is the selectivity at infinite dilution (S_{ij}^{∞}). The higher the selectivity, the better the solvent. In the literature, Momoh[6] asserts that, for extractive distillation, results from S_{ij}^{∞} do not match with the ones from rigorous modeling and costing analysis. The influence of the solvent recovery system and the recycle streams, not considered in the S_{ij}^{∞} analysis, would be able to explain most of the differences. As a conclusion, we can state that good, average, and bad solvents perform similarly, although the ranking with both methods does not match.

To obtain experimental S_{ij}^{∞} values we require a method that is rapid, that does not depend on a particular expression for Gibbs free energy, that does not involve chemical analysis of mixtures in highly diluted regions, and that does not require extrapolation from concentrated to infinite dilution regions. Experimental measurements[4,7] that fulfil these requirements are generally done in four ways: differential ebulliometry, gas/liquid elution chromatography, headspace chromatography, and static total pressure. Differential ebulliometers measure isobaric changes in the boiling point of a solvent when small, known amounts of solute are added in one of the chambers. Gas/liquid elution chromatographic needs a specific column for each solvent and a complex signal analysis over time. Headspace chromatography allows automatic vapor-phase sampling from a system in which equilibrium has been reached. The static total pressure method measures the vapor pressure, a trouble-free variable; the major drawback is that it requires that all samples are thoroughly degassed. Overall, the last method is the most accurate technique for very volatile systems, while for mixtures, differential ebulliometry is the preferred method.

Headspace gas chromatography has a number of operational advantages. First, the solvent does not need to be degassed nor must more volatile impurities be removed, and therefore, sample preparation is minimized. Second, the sensitivity, accuracy, reproducibility, precision and detection capabilities of chromatographic systems are such that work is performed at regions where Henry's Law is accurately obeyed. Third, the separations, even to study simultaneously several solutes, is generally trivial for modern gas chromatographs (GC). Fourth, the analysis time is reduced due to on-line coupling to a GC. The disadvantages of headspace are the relatively high investment required, some matrix effects, and carry-over problems. This technique is routinely applied to trace-components analysis of blood, food, fragrances, residual solvents, and environmental samples. Typically it is used for complex samples, because regardless of its nature, the apparatus is exposed only to a clean gas phase.

Measurement Principles

Since we ensure that the liquid and vapor phases are in equilibrium, we can state that

$$\phi_i \cdot y_i \cdot P \equiv \gamma_i \cdot x_i \cdot f_i^{oL} \tag{2}$$

where ϕ is the fugacity coefficient, P is the total pressure, γ is the activity coefficient and f^{oL} is the pure component liquid fugacity at standard conditions. The subscripts correspond to the component, and y and x are the mole fractions in the vapor and liquid phase, respectively.

The ϕ_i definition considering the virial equation of state truncated after the second term is given by

$$\phi_i = \frac{n_i \cdot R \cdot T}{V} \cdot \exp\left(\frac{2}{\upsilon} \cdot \sum_j y_i \cdot B_{ij}\right) \tag{3}$$

where V is the volume, n is the number of mols, υ is the specific volume (V/n_t), and B_{ij} is the virial coefficient for the i–j pair. At low or moderate pressures, the fugacity is essentially the partial pressure and the correction factor becomes unity. Consequently, the exponential terms in Eq. 3 not only tend to cancel each other but also are virtually one. Thus, making the appropriate substitutions the relative volatility equation can be easily arranged to a simple and practical expression.

$$\alpha_{ij} \equiv \frac{y_i/x_i}{y_j/x_j} = \frac{\gamma_i/p_i}{\gamma_j/p_j} \tag{4}$$

where α is the relative volatility.

Since the components are relatively nonvolatile, the influence of the solvent is usually quantified in terms of the selectivity (S_{ij}), which is defined as the ratio of the relative volatility of the two key components with solvent (superscript S) compared to the case without solvent presence. To contrast among different solvents, it is a common practice to consider the situation of infinite dilution conditions (superscript ∞).

$$S_{ij}^{S,\infty} = \frac{\gamma_{ij}^{S,\infty}}{\gamma_{ij}^{\infty}} \tag{5}$$

For a multicomponent system, in which several objectives coexist (e.g., no BuAc or BuOH should be obtained by top, no MeOH or MeAc should be obtained by bottom, no solvent should be in the distillate), the geometric mean ($S_m^{S,\infty}$) of the key systems involved is used.

EXPERIMENTAL

Materials and Apparatus

All chemicals used were purchased in the highest available quality (HPLC grade or spectrophotometer quality), preserved over 3 Å-molecular sieves (Union Carbide, Fluka AG, Buchs, Switzerland), and used without further purification. The purity was checked with GC.

A HP-7694 Headspace Sampler (Hewlett-Packard Instrument Co., Palo Alto, CA) on-line coupled with the HP-5890 Series II GC equipped with a flame ionization detector was used. The signal was processed in a HP-3365 Chemstation. The capillary column was a NWCOTT fused silica coating CP-WAX 52-CB (50-m, 0.32-mm internal diameter Catalogue 007773 Crompack). In both, the GC and the headspace systems, the carrier gas was controlled by an electronic pressure control system. A schematic diagram of the experimental set-up is shown in Fig. 1.

The experimental apparatus has two lines, one for the GC and the other for the headspace. Helium always flows from the headspace through the

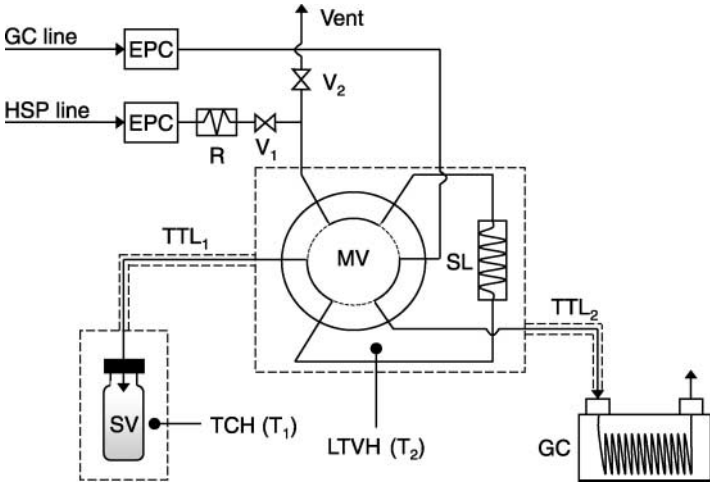

Figure 1. Dual-channel for the experimental set-up: GC line, gas chromatograph line; HSP line, headspace line; EPC, electronic pressure controller; R, flow restrictor; V_i, valve ($i = 1, 2$); MV, multiposition valve; SL, sample loop; TTL, thermostated transfer line ($i = 1, 2$); SV, sample vial; LTVH, liquid-thermostated valve holder (T_2); and TCH, thermostated cell holder (T_1, $T_2 > T_1$). Dashed lines indicate thermostatic sections.

heated transfer line into the GC injection port. In the standby mode, the sample loop, sample line, and sampling needle are flushed continuously. To sample, the dosage needle pierces the septum, and the carrier gas from the headspace line pressurizes the headspace vial (this pressure is completely independent of the column head pressure). Next, V_2 is opened and the compressed gas in the sample vial vents through the sample loop. Subsequently, valve V_1 is closed and the gas sample loop is placed in series with the GC line. Immediately the contents are delivered through the heated transfer line direct into the GC without splitting.

The main advantages of the pressure-loop system are that it can be thermostated to high temperatures and that the fixed volume of the sample loop improves the run-to-run reproducibility. The major disadvantage is that it may cause ghost peaks due to carryover from previous analysis.

Sample Preparation

Samples were prepared by successive dilutions from gravimetrically standard solutions. Weighing accuracy was better than 0.01%. Aliquots of the solutions were added by syringe and the vials were immediately sealed with a teflon-coated silicone–rubber septum and aluminum/nickel crimped caps. The signal was related to composition through calibration curves. The error, due to all instrumental and calibration uncertainties, was checked in a set of analysis at 1:1000 dilution level to be within an accuracy of 1.32% and a standard deviation of 0.0106.

Experimental Procedure

Optimum values for all the operational features were investigated.[8] Even in highly diluted conditions, excellent repeatability is possible because of the inherent precision of the valve and loop sampling system and the accurately thermostated sample chamber. For a dilution of up to 1:1000 (Fig. 2a) the selectivity remains constant, and the standard deviation is within the analytical error. The optimum liquid mixture in the vial (Fig. 2b) has to satisfy that a) there is enough vapor-phase to obtain a sample and perform the analysis, and b) the liquid volume is big enough to consider that the composition has not changed significantly. The ratio liquid:vapor phase used was 1. Equilibrium time of 45 minutes (Fig. 2c) before injection was considered to be sufficient to reach vapor–liquid equilibrium (VLE), even for highly viscous systems. The analyses were run with the cell-holder thermostated at 328.15 K and 378.15 K

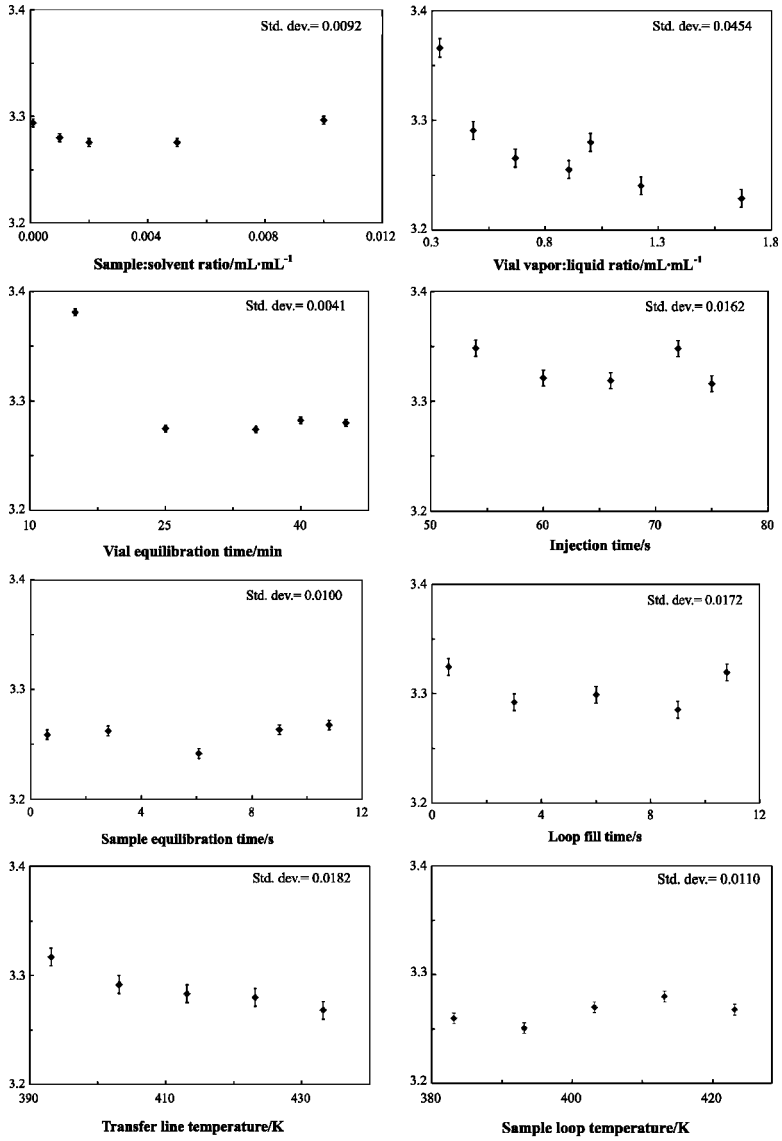

Figure 2. Effect of the headspace operational parameters in the selectivity of BuOH + BuAc in cumene (1:1000) at 353.15 K. (a) Sample:solvent ratio, mL mL^{-1}; (b) vial vapor:liquid ratio, mL mL^{-1}; (c) vial equilibration time, min; (d) injection time, s; (e) sample equilibration time, s; (f) loop fill time, s; (g) transfer line temperature, K; (h) sample loop temperature, K.

for MeOH + MeAc and BuOH + BuAc, respectively. This temperature is a reasonable compromise between the need of high sensitivity (achieved at high temperatures) and the requirements for maximum safety (samples should not be stored above the boiling point). Before describing the quantitative results of the study, the pneumatic timing steps of the system were assessed.[9,10] Vial pressurization time was 10 seconds to ensure that the sample loop was completely filled (ΔP is the driving force). Loop fill time (Fig. 2d) and vent time were set to 6 seconds, which is sufficient to purge the sample loop and allow the line to reach atmospheric pressure. Adequate purging guards against sample carryover. After waiting for 9 seconds for the sample loop equilibration time (Fig. 2e), the sample is injected throughout 60 seconds (Fig. 2f). To prevent condensation, adsorption, minimize band broadening, and avoid ghost peaks, the transfer lines are thermostated at high temperatures. Final values selected for the sample loop temperature and the transfer line temperature were 403.15 K and 423.15 K, respectively (Fig. 2g and 2h).

The GC temperature profile for the MeOH + MeAc + solvent system was 4.7 min at 333.15 K, 15 K min^{-1} to 458.15 K and 1 min at 458.15 K, while for the BuOH + BuAc + solvent it was 5.5 min at 368.15 K, 15 K min^{-1} to 473.15 K, and 0.5 min at 473.15 K.

RESULTS AND DISCUSSION

Problem Statement

Previous results from process modeling predict a poor reagent contact in the reaction area of the reactive distillation, due to the high difference in boiling point (390.9 K for BuOH and 330.4 K for MeAc). To formulate all practicable distillation sequences for the four-component separation system, an accurate analysis of the nonreactive residue curve maps was performed. Residue curve maps (RCM) are built based solely on the system physical properties: VLE, liquid–liquid equilibrium and solubility data. In a nonreactive mixture the temperature always increases along a residue curve line, and the singular points are either nodes (stable or unstable) or saddles. Singular points are azeotropes or pure components, and they can be linked by distillation boundaries.[11] It has been demonstrated that curved distillation boundaries can be crossed; alternatively, boundaries can be shifted when the operating conditions (e.g., pressure) change. This information allows us to assign the system topology for the whole composition space and develop strategies to achieve the desired target, making RCM a very useful technique for process synthesis. Thus, an evaluation of multicomponent azeotropic data

was performed using a continuation method. AspenSplit™ (Aspen Technology, Cambridge, MA) was used to perform all calculations and data analysis. The quaternary nonreactive system has two binary azeotropes that give rise to a distillation surface boundary (BuOH and BuAc are the stables nodes, while the MeOH + MeAc azeotrope is the unstable node) as stated in Fig. 3. Any of the four feasible distillations sequences detected lead to the desired product separation.[12,13] Although the composition of the MeOH + MeAc azeotrope is sensitive to pressure, no viable strategy for pressure swing distillation was discovered. In addition, no practical cross-boundary strategy was found.

Most separation processes that, like this one, had disadvantageous separation factors require external agents. In this case the entrainer has two different objectives: to influence the activity coefficients of the components to a different extent (extractive section of the distillation column) and to enhance the reagents contact efficiency in the reaction section of the unit. The question behind this problem is how we can find out which solvents enable the separation of the given multicomponent system.

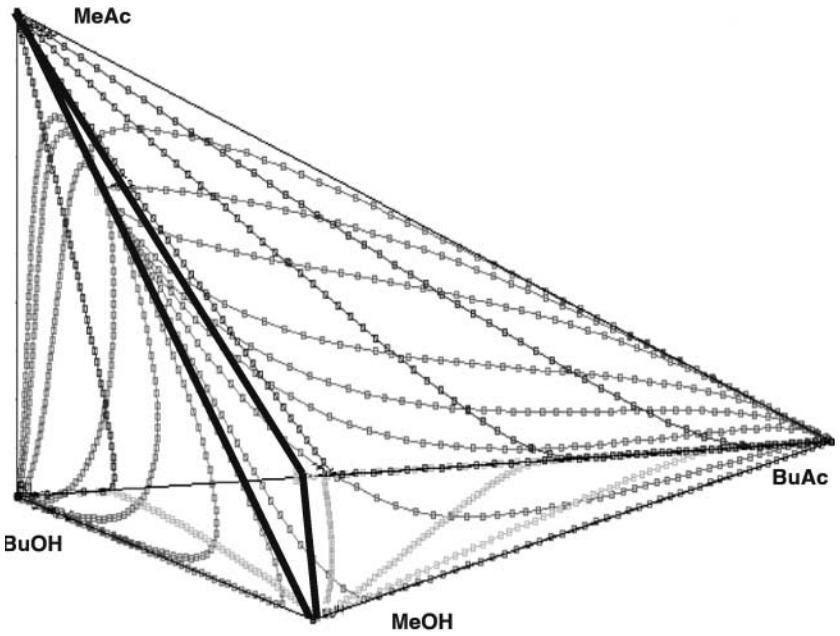

Figure 3. Nonreactive residue curve map for MeOH + MeAc + BuOH + BuAc at 101.3 KPa.

Preliminary Solvent Screening

As it was stated, VLE thermodynamic models can predict γ_{ij}^{∞} with a reasonable accuracy. It is worth mentioning that, as the number of functional groups is much smaller than the number of potential solvents, group contribution methods (e.g., UNIFAC) are preferred to activity coefficient models (e.g., NRTL, UNIQUAC) during the preliminary phases of development of any project. γ_{ij}^{∞} values were estimated using UNIFAC modified by Gmehling et al. at Dortmund University.[14] UNIFAC-Dortmund differs from classical UNIFAC only in the combinatorial term and in the temperature dependence of the group interaction parameter.

Preliminary solvent screening was made with the help of the vast Dortmund Data Bank and the integrated software package (DDBST™ GmbH, Oldenburg, Germany). Due to software limitations,[5] only binary systems were checked: MeOH + MeAc (initial problem); MeOH + BuOH (key components if no conversion is achieved in the reactive and extractive distillation unit); MeOH + BuAc (key components to separate if total conversion is reached); and BuOH + BuAc (separation in the solvent recovery system). To perform the analysis, azeotropic data were prioritized over the infinite dilution data, as they are more accurate. No restriction about the entrainer solubility (homogeneous or heterogeneous) or the number and type of azeotropes (pressure maximum or minimum) was considered. For azeotropic systems, the criteria used were a minimum difference in boiling point of 25 K, a separation factor at infinite dilution higher than 1.5 or lower than 1/1.5, and a melting point lower than 20 K. DDBST™ provides a large number of feasible solvents (Table 1). It is noteworthy that this list contains some solvents of practical importance that cannot be described by any group contribution method (e.g., sulfolane). UNIFAC-Dortmund was used to compute the solvents without experimental data available. By referring to the total number of solvents this double-checking strategy adds nine additional solvents. When the type of azeotrope formed is a key result, the conclusion

Table 1. Number of feasible solvents retrieved from DDBST™.

	Experimental	UNIFAC-Dortmund	Misclassified
MeOH + MeAc	22	25	7
MeOH + BuOH	53	37	9
MeOH + BuAc	10	15	1
BuOH + BuAc	7	6	4
Total	75	64	20

seems to be that DDBST™ provides poor results, as 26% of the solvents were misclassified (i.e., UNIFAC-Dortmund predict one homogeneous and one heterogeneous azeotrope whereas data from the Dortmund Data Base states that both are homogeneous). This apparent inadequate performance is due to the complex structure of certain solvents, where the prediction capabilities of group contribution methods have shortcomings (e.g., α, β-di-halogens, α-dialkenes, α-dialcohols). On the contrary, UNIFAC-Dortmund estimations exhibit good accuracy for alkilbenzenes components.

The large amount of possible solvents leads to further selection within the list of promising solvents. The additional criteria were based upon heuristics such as the industrial applicability, effect in VLE, chemical stability, ratio solvent/feed or solubility. Usually, there is no solvent that matches all these characteristics. Therefore, compromise solutions—using cost analysis[15] and further constraints based on physical properties[16,17] such as latent heat, melting point, density, and viscosity—were considered.

Selectivity at Infinite Dilution

Selectivity at infinite dilution for MeOH + MeAc (328.15 K) and BuOH + BuAc (373.15 K) are compiled in Table 2. The binary samples were measured simultaneously in a single run. For the systems including MeOH + MeAc, there is somewhat more scatter to the data. We suspect that this higher random error is due to the higher volatility, which results in a larger uncertainty in the liquid composition. The analysis of the data reveals that for the BuOH + BuAc system, the selectivity values remain almost constant, except for those solvents that have a poor performance. The MeOH + MeAc system behavior is different, and there are significant differences among solvents.

Concerning the industrial application, we reject the halogenated solvents, for the higher toxicity and the high possibility to contaminate the MeOH with hydrogen chloride due to decomposition reactions. The $S_m^{S,\infty}$ profile helps to group solvents into categories: good, average, and bad performance, but no final assertion can be made. By taking into account all this information, a detailed evaluation of the solvent information in the reactive RCM was performed for the best potential separating agents. The experimental conclusion was that the best solvents for this process are the alkilbenzenes (xylenes, toluene, and mesitylene) and n-alkanes (n-heptane and n-decane).

The five-dimension space analysis for the nonreactive mixture reveals that for n-heptane, p-xylene, and toluene there are two different distillation regions in the RCM, thus leading to complex separation strategies that involve

Table 2. $S_{ij}^{S,\infty}$ Experimental values of the binary system in the presence of the solvent.

Solvent	MeOH + MeAc	BuOH + BuAc
Tetrachloroethylene	9.37	3.96
Toluene	6.52	4.85
n-heptane	6.39	3.99
o-xylene	5.56	4.58
α-pinene	5.08	4.97
β-pinene	5.11	4.70
Hexadecane	6.83	3.44
Mesitylene	4.42	4.10
p-xylene	3.75	4.67
m-xylene	4.19	3.77
Decahydronaphtalene	3.71	4.19
n-decane	3.54	4.11
Ethylbenzene	3.57	4.06
Cumene	3.54	4.02
Chlorobenzene	2.62	4.68
p-dichlorobenzene	4.49	2.64
Sulfolane	3.60	1.71
Nitrobenzene	3.85	0.848
o-dichlorobenzene	3.18	0.517
N,N-dimetylformamide	1.76	0.735

high reflux ratios to cross distillation boundaries. In these three cases the unstable nodes are the BuOH and the solvent, while the stable node is the MeOH + MeAc azeotrope. The other promising solvents have just one distillation region. For these solvents cost, availability, inflammability, and toxicity will be considered for the final evaluation.

Solvent Performance

Several authors have transferred the RCM concept to reactive distillation by overlaying a chemical reaction, either assuming chemical equilibrium[18] or applying rate equations and homogeneously catalyzed kinetics expression.[19] To maintain the visualization capabilities of reactive RCM for the five-component system a set of transformed mole compositions, X_i and

Y_i, (Eq. 6) will be used.[20]

$$X_i = \frac{x_i - \upsilon_i^T \cdot (\upsilon_{\text{Ref}})^{-1} \cdot x_{\text{Ref}}}{1 - \upsilon_{TOT}^T \cdot (\upsilon_{\text{Ref}})^{-1} \cdot x_{\text{Ref}}} \quad (i = 1, \ldots, C - R) \tag{6}$$

where υ_i^T is the row vector of the stoichiometric coefficients for component i in each of the R reactions, x_{Ref} is the vector of mole fractions of the R reference components in the liquid phase, and C is the number of components. These new variables behave in a similar way as mole fractions in nonreactive mixtures and can be thought of as reaction-invariant compositions. Transformed composition variables also satisfy the following relationships.

$$\sum_{i=1}^{C-R} X_i = 1; \quad \sum_{i=1}^{C-R} Y_i = 1 \tag{7}$$

Hence, we can represent multicomponent systems in a lower-dimensional composition space (C − R − 1 degrees of freedom). For example, in a quaternary mixture with just one chemical reaction, all residue curve lines collapse.

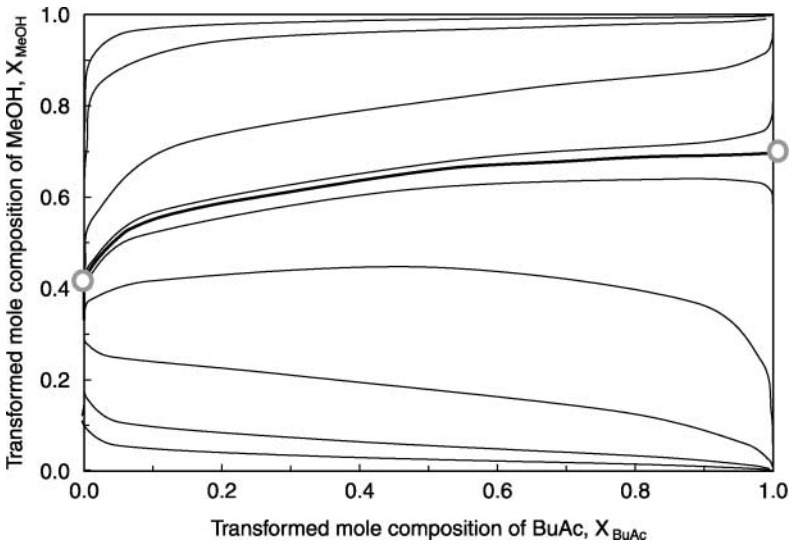

Figure 4. Reactive RCM in transformed mole composition for the transesterification of MeAc with BuOH using o-xylene as entrainer at 101.3 KPa.

The computation of reactive RCM in transformed composition is described in detail elsewhere[20] and any further explanation is unnecessary. Calculations were done with AspenPlus™ (Aspen Technology, Cambridge, MA).

Reactive RCM analysis for the most promising alternatives was carried out. To compute the transformed mole composition, BuOH was selected as the reference component. For example, the reactive RCM using o-xylene as solvent is shown in Fig. 4. The *reactive boundary* generates two different regions, but fortunately, the working conditions, even during start-up and shut down, lie far off and there is no need to consider a boundary-crossing strategy.

CONCLUSIONS

This work shows the synergic combination of computer-aided process engineering tools (AspenSplit™, DDBST™ and AspenPlus™) and experimental work (headspace). The computational methods used for solvent selection were complementary: in the limits of the thermodynamic models, data are retrieved from the experimental data bank; and in the case where no data is available, physical property estimation provides the results.

The headspace technique was used for a rapid, precise, and accurate measurement of the selectivity at infinite dilution. Since the determination in ternary or higher-order systems has no additional difficulties, other than the preparation of dilute solutions, headspace is a fast method for screening solvents for azeotropic and/or extractive distillation.

The use of graphical tools, such as RCM, provides key insights into the problem. For instance, it is possible to detect whether a specific solvent reaches the desired product separation by determining the product composition regions for a given feed composition, the azeotropes introduced, and the presence of distillation boundaries.

No solvent reaches all the objectives and constraints, but pondering all considerations, n-alkanes and alkilbenzenes were found to be the best. A fine analysis led us to select o-xylene as the best entrainer for the extractive and reactive distillation.

SYMBOLS

Symbols

B	second virial coefficient
BuAc	butyl acetate

BuOH	butanol
C	number of components
f	pure component liquid fugacity
GC	gas chromatography
MeAc	methyl acetate
MeOH	metanol
n	number of moles, mol
p	partial pressure, Pa
P	total pressure, Pa
PVA	poly-(vinyl alcohol)
R	ideal gas constant, $8.31441\,J\,mol^{-1}\,K^{-1}$ or number of reactions
RCM	residue curve map
S_{ij}	selectivity of ith versus jth component
T	temperature, K
V	volume, m^3
VLE	vapor liquid equilibrium
x, y	liquid and vapor mole fractions
X, Y	transformed liquid and vapor mole fractions (Eq. 6)
α	relative volatility
γ	activity coefficient
ϕ	fugacity coefficient
υ	molar volume, $m^3\,mol^{-1}$ or row vector of stoichiometric coefficients

Subscripts and Superscripts

i, j	i^{th}/j^{th} component
L	liquid phase
o	standard conditions
Ref	reference component
S	in presence of solvent
t	total
∞	infinite dilution conditions

ACKNOWLEDGMENTS

The authors would like to thank Cervezas Damm s.a. (Barcelona, Spain), Aspen Technology (Cambridge, MA), and DDBST GmbH (Oldenburg, Germany) for providing the necessary facilities. One of the authors

(L. Jiménez) gratefully acknowledges the financial support from Fundación Caja de Madrid.

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Received September 2001
Revised April 2002