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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To cite this Article Momoh, S. O.(1991) 'Assessing the Accuracy of Selectivity as a Basis for Solvent Screening in Extractive Distillation Processes', Separation Science and Technology, 26: 5, 729 — 742

To link to this Article: DOI: 10.1080/01496399108049911

URL: http://dx.doi.org/10.1080/01496399108049911

SEPARATION SCIENCE AND TECHNOLOGY, 26(5), pp. 729–742, 1991

Assessing the Accuracy of Selectivity as a Basis for Solvent Screening in Extractive Distillation Processes

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Abstract

An important parameter for consideration in the screening of solvents for an extractive distillation process is selectivity at infinite dilution. The higher the selectivity, the better the solvent. This paper assesses the accuracy of using selectivity as a basis for solvent screening in extractive distillation processes. Three types of binary mixtures that are usually separated by an extractive distillation process are chosen for investigation. Having determined the optimum solvent feed rate to be two times the feed rate of the binary mixture, the total annual costs of extractive distillation processes for each of the chosen mixtures and for various solvents are carried out. The solvents are ranked on the basis of the total annual cost (obtained by design and costing equations) for the extractive distillation processes, and this ranking order is compared with that of selectivity at infinite dilution as determined by the UNIFAC method. This matching of selectivity with total annual cost does not produce a very good correlation.

1. INTRODUCTION

The separation of close-boiling components by an ordinary distillation process usually results, apart from control problems, in high capital and energy costs. The alternative process of extractive distillation has to be used. An extractive distillation process (EDP) is generally defined as "a distillation in the presence of a substance which is a relatively nonvolatile compared to the components to be separated and which, therefore, is charged continuously near the top of the distilling (extraction) column so that an appreciable concentration is maintained on all plates of the column" (*1*). In the presence of the solvent, the relative volatility of the components to be separated increases, thereby making the otherwise difficult separation an easy one and hopefully leading to a reduction in the overall cost of the process. Therefore, at the heart of an extractive distillation process is the selection of a solvent capable of enhancing the relative volatility of the two key components to be separated.

Traditionally, the screening of such solvents is done by ranking the solvents in the order of their selectivity at infinite dilution (*2–5*). Selectivity at infinite dilution is therefore an important parameter for consideration in the screening of solvents for an extractive distillation process. This is usually defined (*4*) as γ_i/γ_j, where γ_i and γ_j are the activity coefficients of components *i* and *j* at infinite dilution in the solovent. (See Appendix A for the derivation.)

Over the years, numerous articles have appeared in the literature on various aspects of the extractive distillation process. The experimental works include those of Drickamer and Hummel (*6*), Dunn et al. (*7*), and Halslund (*8*). These dealt with the study of composition temperature profiles and product composition boundaries. The theoretical studies have mainly centered around methods of predicting the vapor–liquid equilibrium (VLE) data, chemistry action of solvents, with a few articles on column and column sequence design. Notable among the theoretical and design studies are the works of Gerster et al. (*3*), Gerster (*9*), Tassios (*10*), Kyle and Leng (*2*), Kolbe et al. (*4*), Bastos et al. (*5*), Benedict and Rubin (*1*), Hess et al. (*11*), Deal and Derr (*12*), Hanson and Van Winkle (*13*), Null et al. (*14*), Eckert et al. (*15*), Thomas et al. (*16, 17*), Dongen et al. (*18*), Levy et al. (*19*), Doherty and Caldarola (*20*), Sucksmith (*21*), and Kumar et al. (*22*). Fahim et al. (*23*) suggested a computational method based on energy requirement for the selection of the best solvent for liquid–liquid extraction of aromatics from hydrocarbons.

When solvents are ranked in the order of selectivity, the solvent with the highest selectivity is always considered to be the most promising solvent for a given separation. In other words, the solvent with the highest selectivity has the greatest potential, among others, in enhancing the relative volatility of the key components to be separated. This may indicate that, in economic terms, the use of the solvent with the highest selectivity will always give the lowest total annual cost (TAC) of the extractive distillation process (the extraction and the recovery columns taken together). How correct is this assertion or how does the order of solvents ranked on the basis of total annual cost of EDP vary with the order based on the selectivity of the solvents being considered? And what is the minimum selectivity required for an extractive process to be cheaper than using an ordinary distillation process if possible?

In spite of the volume of work that has been done on the screening of solvents for an extractive distillation process by using selectivity at infinite dilution, the issues raised above are yet to be investigated. This, then, is the focus of this paper. Investigating these issues will provide an opportunity to assess the accuracy of the use of selectivity as a basis for solvent screening in an extractive distillation process.

The structure of the paper is as follows: Using a test mixture of *n*-butane/*trans*-2-butene/acetone, we first determine the optimum solvent feed rate for use in the optimum design of an extractive distillation process. For further analysis, three different types of binary mixtures that are usually separated by an extractive distillation process are chosen for investigation. The selectivities of many solvents capable of enhancing the relative volatilities of the chosen mixtures are determined by using the UNIFAC (UNIQUAC functional-group activity coefficients) (*24*) group method for predicting activity coefficients of component mixtures. The TAC of the EDP is calculated for each of the three different types of binary mixtures by using the various solvents. The solvents are then ranked in the order of their selectivity at infinite dilution for each of the mixtures. This ranking is compared with that obtained for the TAC of the EDP for each of the mixtures and solvents. This is followed by a discussion of the results and our conclusions.

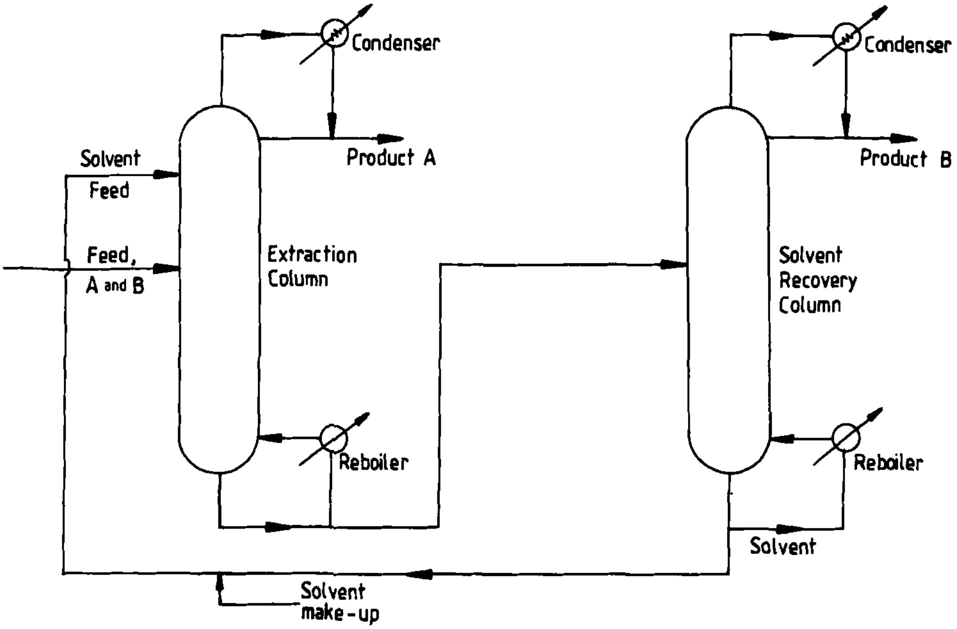

FIG. 1. Typical extractive distillation process.

2. OPTIMUM SOLVENT FEED RATE

A fundamental flow sheet for accomplishing an EDP is shown in Fig. 1. The solvent is added at the top of the first column. The solvent is usually fed a few stages below the top plate in order to reduce the solvent concentration in the ascending vapor to a negligible amount before the overhead product is withdrawn.

The solvent feed rate is generally a compromise between improved separability with increasing solvent concentration and increasing cost of solvent recovery at increased flow rate. An increase in feed rate increases the relative volatility of the components to be separated, thus decreasing the number of plates required. The solvent recovery costs, the initial solvent cost, and the reboiler steam requirements are bound to increase at the higher solvent rate. These factors have to be balanced to yield an optimum solvent feed rate.

Some workers (*25*, *26*) have used a solvent feed rate of about two times the feed rate of the mixture to be separated. Knickle (*27*) suggested three times the feed rate of the components. In the work of Kumar et al. (*22*) an exceptionally high solvent rate was used; 0.85 to 0.90 mol fraction of solvent concentration at the solvent feed plate. This amounts to about 5 to 9 times the feed rate of the components.

We note that these values of optimum solvent rate were arbitrarily picked. In this paper, however, the determination of the optimum solvent feed rate is obtained on the basis of the economic design of the process. As far as we know, this is the first attempt in this direction. The capital and the operating costs for an EDP are determined as explained later. This is done for the test case of a mixture of *n*-butane/*trans*-2-butene with acetone as the solvent. The solvent feed rate is varied from 50 to 500 kmol/100 kmol of the feed rate of the key components (*n*-butane/*trans*-2-butene). Three levels of concentration are examined. These are 25/75, 50/

TABLE 1
The Optimum Solvent Feed Rate for the *n*-Butane/*trans*-2-Butene/Acetone Extractive Distillation Process[a]

Solvent feed rate (kmol/h)	25/75 kmol of A and B	50/50 kmol of A and B	75/25 kmol of A and B
50	1,214,838	1,363,128	1,496,938
100	1,056,369	1,162,803	1,256,066
200	990,286	1.074,161	1,141,773
300	1,010,741	1,091,297	1,152,759
400	1,074,988	1,152,980	1,204,275
500	1,134,438	1,227,878	1,271,732

[a] A = *n*-Butane, B = *trans*-2-butene.

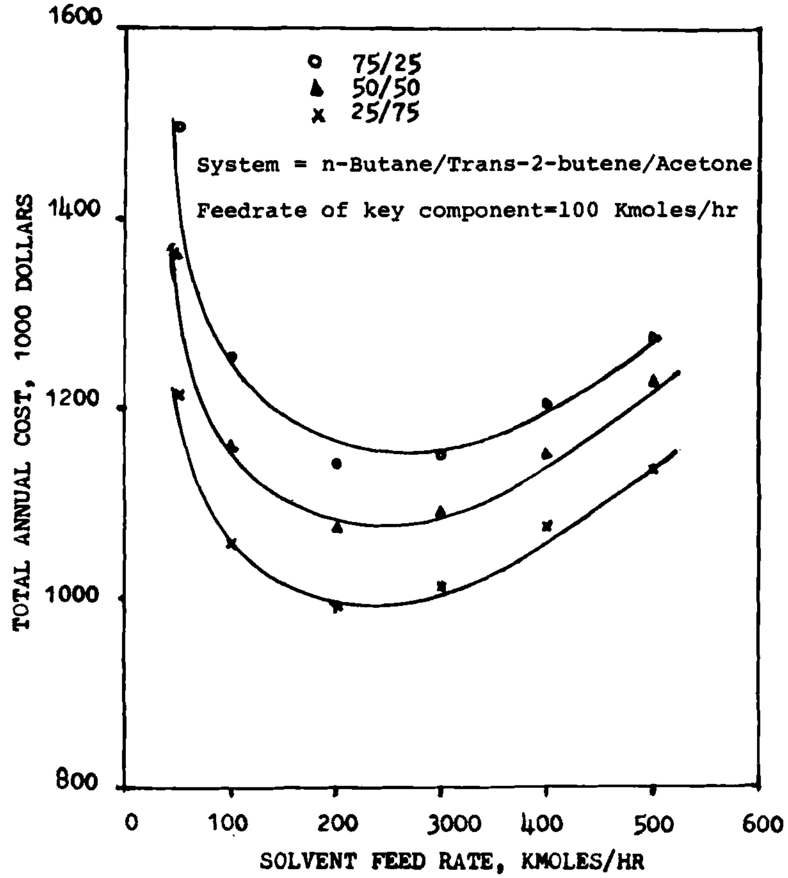

FIG. 2. Optimum solvent rate for extractive distillation.

50, and 75/25. For example, 25/75 means 25 kmol *n*-butane to 75 kmol *trans*-2-butene. The results are given in Table 1 and displayed in Fig. 2.

3. ECONOMIC EVALUATION OF THE EXTRACTIVE DISTILLATION PROCESS FOR THE COMPARISON OF SOLVENTS

The economic evaluations were carried out by using many different solvents for separating three different binary mixtures: 2-methyl-butene/isoprene (Mixture A), *n*-butane/*trans*-2-butene (Mixture B), and *n*-hexane/benzene (Mixture C). For each case we did a complete design and costing of the process by using our cost estimating computer programs. The UNIFAC method was used to establish the VLE data for the components. By using the same UNIFAC-predicted VLE data in both the complete costing and in the determination of the selectivity at infinite dilution, a valid comparison of solvent ranking in terms of the TAC and selectivity at infinite dilution is possible. The design calculation steps made use of known equations and a rigorous method of Naptitali and Sandholm (*28*) to obtain the number of plates, column height and diameter, and the heat loads at the condensers and reboilers. Then the heat transfer areas of the condensers and reboilers were obtained. All these were used to obtain the capital and the energy (or operating) costs of the extractive distillation process. The capital costs involve two columns, two condensers, and two reboilers. The energy costs include the cost of the condensers' cooling water and the reboilers' steam cost. Other necessary details on the sizing and costing equations are given in the works of Momoh (*29*) and Fredenslund et al. (*30*).

The cost of the solvents is assumed constant at the optimum solvent feed rate and therefore not considered in the calculation of the TAC. The optimum solvent rate is taken from the results obtained in Section 2 above, and it is two times the feed rate of the key component. The heat transfer duty of the solvent cooler (if any) and the cost of solvent are always considered negligible compared to the steam and cooling water costs (*22*). The entering feed stream to the extraction column is taken to be 50/50 molar composition of any key component mixtures.

4. RESULTS, DISCUSSIONS, AND CONCLUSIONS

4.1. Tables and Figures

Table 1 shows the tabulated results for the determination of the optimum solvent feed rate using *n*-butane/*trans*-2-butene/acetone as a test mixture. The results are displayed in Fig. 2 for the three levels of concentration.

Figures 3, 4, and 5 and Tables 2, 3, and 4 show, respectively, the ranking of solvent selectivity at infinite dilution with the TAC of the EDP for 2-methyl-1-butene/isoprene, *n*-butane/*trans*-2-butene, and *n*-hexane/benzene mixtures for the various potential solvents.

4.2. Optimum Solvent Feed Rate

For the three levels of concentrations of the components shown in Fig. 2, the optimum solvent feed rate lies between 200 and 300 kmol/h per 100 kmol/h of the feed rate of the key components. That is, the optimum solvent feed rate is two or three times the feed rate of the key component mixtures. This happens to be in agreement with values that have been suggested by rules of thumb in the literature (*25–27*). A solvent feed rate

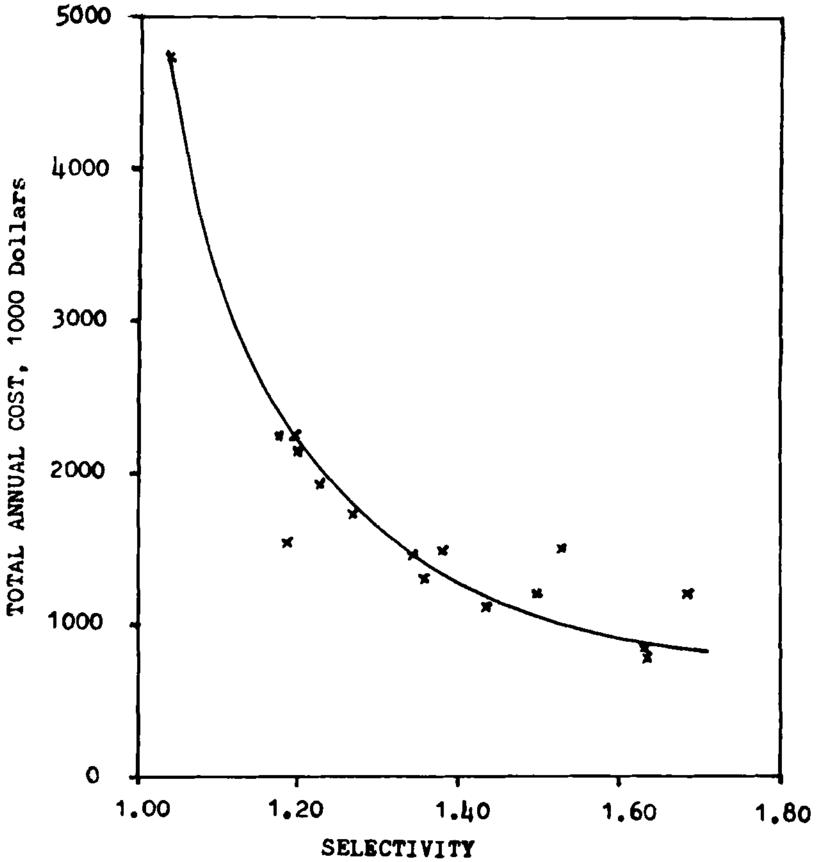

FIG. 3. The effect of solvent selectivity on the total annual cost of an extractive distillation operation (2-methyl-1-butene/isoprene).

of two times the feed rate of the key components is considered appropriate for further analysis. This keeps the solvent recovery cost in the second column to a minimum.

4.3. Selectivity and the Total Annual Cost

In general, the results in Tables 2, 3, and 4, as displayed in Figs. 3, 4, and 5, show that as the solvent selectivity increases, the total annual cost of the EDP decreases. The reason for this is given later.

For the binary Mixture A (Table 2), the best solvent in terms of the TAC is next to the best in terms of solvent selectivity at infinite dilution.

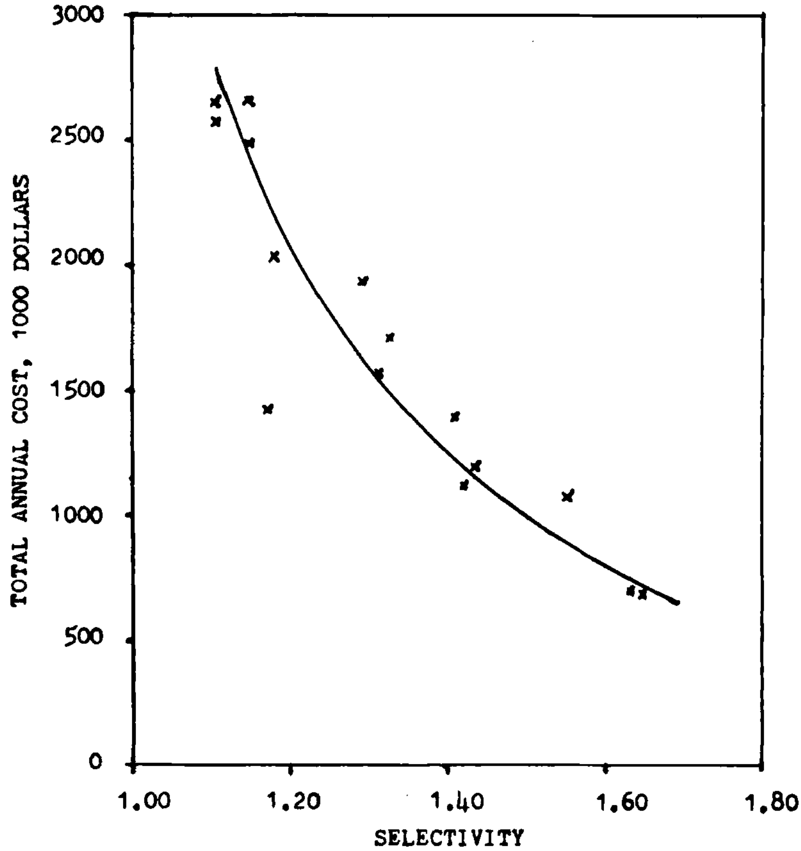

FIG. 4. The effect of solvent selectivity on the total annual cost of an extractive distillation operation (*n*-butane/*trans*-2-butene).

But for binary Mixtures B and C, the best solvent in terms of selectivity is also the best in terms of TAC (Tables 3 and 4). It is also observed that the ranking of solvents on the basis of selectivity and TAC is best for Mixtures B and C. The ranking is not good for Mixture A. There is no apparent reason that can be adduced for this behavior. For example, for Mixtures B and C the same first three solvents are obtained when the various solvents are ranked in terms of TAC and in terms of solvent selectivity, whereas this is not so for the case of Mixture A. For all cases the order of solvents when ranked on the basis of TAC is not the same throughout as when ranked on the basis of selectivity. This means that, in general, the matching of selectivity with the TAC for the solvents used in the EDP

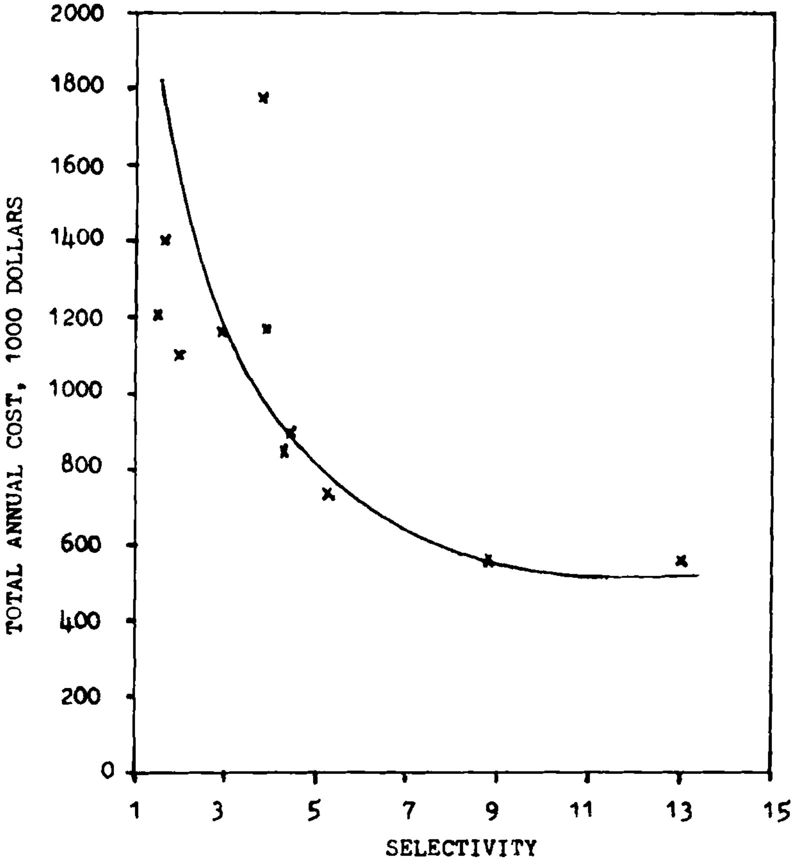

FIG. 5. The effect of solvent selectivity on the total annual cost of an extractive distillation operation (*n*-hexane/benzene).

of each of the three test mixtures is not perfect. This suggests how good or accurate the use of selectivity as a basis for screening solvents in an EDP is.

Now, coming back to the nature of the curves of TAC versus selectivity at infinite dilution. As stated above, an increase in selectivity leads to a decrease in the TAC of the EDP. The decrease is sharp at lower selectivity, but the slope of the curve flattening at higher selectivity is about 1.40 for 2-methyl-1-butene/isoprene, about 9.0 for *n*-hexane/benzene, and 1.60 for *n*-butane/*trans*-2-butene mixtures. The reason for the shape of the curve is clear. Higher selectivity yields higher relative volatility. A higher selectivity therefore results in a smaller reflux ratio and fewer equilibrium num-

TABLE 2
Relationship between TAC and Selectivity at Infinite Dilution (S^{∞}) for 2-Methyl-1-butene/Isoprene

Solvent	TAC in dollars[a]	Order	S	Order
Nitromethane	769,306	1	1.6339	2
Acetonitrile	847,002	2	1.6319	3
Propionitrile	1,124,459	3	1.4323	6
Dimethylacetamide	1,198,127	4	1.4945	5
Methanol	1,204,804	5	1.6839	1
Butyronitrile	1,297,594	6	1.3545	7
Morpholine	1,450,704	7	1.3408	9
Methyl ethyl ketone	1,480,248	8	1.3770	8
Acetone	1,504,035	9	1.5266	4
Ethylene chlorohydrin	1,533,817	10	1.1854	14
Cyclopentanone	1,722,085	11	1.2665	10
Methyl isobutyl ketone	1,917,681	12	1.2237	11
Cyclohexanone	2,144,885	13	1.1976	12
Diethyl ketone	2,237,229	14	1.1760	15
Ethyl butyrate	2,247,301	15	1.1954	13
Tetrahydrofuran	4,742,780	16	1.0374	16

[a] The total annual cost for the ordinary distillation process is $3,276,024.

TABLE 3
Relationship between TAC and Selectivity at Infinite Dilution (S^{∞}) for *n*-Butane/*trans*-2-Butene

Solvent	TAC in dollars[a]	Order	S	Order
Nitromethane	682,607	1	1.6456	1
Acetonitrile	701,752	2	1.6310	2
Acetone	1,074,161	3	1.5501	3
Butyronitrile	1,124,365	4	1.4197	4
Methyl ethyl ketone	1,196,157	5	1.4342	5
Morpholine	1,395,364	6	1.4084	6
Ethyl butyrate	1,421,495	7	1.1683	11
Methyl isobutyl ketone	1,566,696	8	1.3124	8
Styrene	1,710,129	9	1.3265	7
Cyclohexanone	1,936,142	10	1.2902	9
Toluene	2,038,691	11	1.1796	10
Ethylbenzene	2,485,082	12	1.1488	13
1-Butanol	2,571,445	13	1.1060	15
2-Butanol	2,651,390	14	1.1062	14
Tetrahydrofuran	2,654,324	15	1.1489	12

[a] The total annual cost for the ordinary distillation process is $10,820,431.

TABLE 4
Relationship between TAC and Selectivity at Infinite Dilution (S^{∞}) for *n*-Hexane/Benzene

Solvent	TAC in dollars[a]	Order	*S*	Order
Dimethylsulfoxide	563,200	1	13.0703	1
Dimethylformamide	568,304	2	8.8296	2
Furfuran	740,255	3	5.2960	3
Phenol	845,267	4	4.3250	5
Aniline	897,585	5	4.4680	4
Styrene	1,100,363	6	1.9900	9
Pyridine	1,159,731	7	2.9462	8
Nitromethane	1,168,126	8	3.9211	6
Ethylbenzene	1,206,677	9	1.5115	11
Toluene	1,398,022	10	1.6508	10
Propionitrile	1,777,788	11	3.8253	7

[a] The total annual cost for the ordinary distillation process is $899,249.

ber of plates required for the given separation in the extraction column. A lower reflux rate corresponds to a lower vapor flow rate and a thinner column. This could result in an overall decrease in the cost of the utilities used, and they do constitute the major cost of an EDP. The change in the TAC resulting from a change in selectivity is higher at low selectivity than at high selectivities. As selectivity increases to very high values, the TAC is controlled mainly by the almost constant cost of the recovery column.

The TAC of using an ordinary distillation process (without a solvent) to separate the three test mixtures is obtained, and the values are indicated in the footnotes of Tables 2, 3, and 4. These values are $3,276,024, $10,820,431, and $899,249, respectively, for Mixtures A, B, and C. This implies that any solvent whose use in an EDP gives a TAC smaller than that for the ordinary distillation process is a good solvent for separating the particular given mixture. Such solvents represent improvements in the TAC of separation by an EDP over the ordinary distillation process. For example, when all solvents (except the last one) listed in Table 2 are added to the 2-methyl-1-butene/isoprene mixture, they are capable of making the EDP cheaper than the ordinary distillation process for separating the mixture. Of course, the smaller the TAC of the EDP, the better the solvent. In other words, when solvents are ranked in the order of increasing TAC, the solvents that are high in the ranking table are the most likely choices for use in the EDP.

If a very good correlation or matching between the TAC and selectivity were obtained, it would then be possible to state conclusively the minimum selectivity required of a solvent for an EDP to be cheaper than using an ordinary distillation process for these test cases. It is observed that for the binary Mixtures A, B, and C, the minimum selectivity required of a solvent to guarantee that the TAC of the resulting EDP is smaller than the TAC of the ordinary distillation process is about equal or greater than 1.1760, 1.1060, and 4.3250 (Tables 2, 3, and 4), respectively.

Most of the analyses reported here are on the basis of an equal molar composition of the original binary component mixture in the feed. The trends and patterns of the results are not likely to be affected by using other feed concentrations.

In conclusion, we observe that selectivity at infinite dilution is still a useful but not necessarily always accurate tool in screening solvents for an EDP. Matching selectivity with the total annual cost does not produce a very good correlation. This may not be too surprising. Choosing solvents on the basis of selectivity alone tends to emphasize the cost of the extraction column in which the difficult separation takes place, whereas the cost in the second column (i.e., the solvent recovery column) is sometimes significant and may control the cost of the process in some case. This will be the subject of a future paper.

APPENDIX A: DERIVATION OF SELECTIVITY AT INFINITE DILUTION

Quantitatively, selectivity is defined as the ratio of the relative volatilities of the key components in a mixture, which are to be separated, in the presence of a solvent to their relative volatilities before the addition of a solvent (*31*). Thus, for key components i, j, and solvent s, selectivity S_{ij} is

$$S_{ij} = \frac{\alpha_{ijs}}{\alpha_{ij}} \tag{1}$$

But

$$\alpha_{ij} = \frac{\gamma_i f_i^\circ \theta_j}{\gamma_i f_j^\circ \theta_i} \tag{2}$$

At low to moderate pressures and temperatures, the standard state fugacity, f_i°, can be approximated by the pure-component vapor pressure, p_i°, and the rate of the vapor-phase fugacity coefficient, θ, is usually close to 1.0. Equation (2) becomes

$$\alpha_{ij} = \frac{\gamma_i p_i^\circ}{\gamma_j p_j^\circ} \tag{3}$$

As the activity coefficients depend on the phase compositions, and the role of the solvent tends to increase with an increase in its concentration, it is common practice to consider the situation of infinite dilution. Then the definition of selectivity at infinite dilution becomes, from Eq. (3):

$$S_{ij}^{\infty} = \gamma_i^{\infty}/\gamma_j^{\infty} \tag{4}$$

NOMENCLATURE

γ	liquid-phase activity coefficient
α	relative volatility
S	selectivity
f	standard state fugacity
θ	vapor-phase fugacity coefficient
p	pure component vapor pressure
EDP	extractive distillation process
TAC	total annual cost of an EDP

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Received by editor April 4, 1990