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R. J. Lahiere[a]; J. L. Humphrey[a]; J. R. Fair[a]
[a] Department of Chemical Engineering, the University of Texas at Austin, Austin, Texas

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Mass Transfer in Countercurrent Supercritical Extraction

R. J. LAHIERE, J. L. HUMPHREY, and J. R. FAIR

DEPARTMENT OF CHEMICAL ENGINEERING
THE UNIVERSITY OF TEXAS AT AUSTIN
AUSTIN, TEXAS 78712

ABSTRACT

This paper addresses problems and background information associated with the design of sieve-tray extraction colums operating in the supercritical solvent region. An appropriate mass transfer model is selected, and the needs and sources of basic data are reviewed. The model is executed for both conventional and supercritical extraction cases. Comparisons for both cases are made against measured data. It is concluded that stage efficiencies for the supercritical case are superior, largely due to favorable transport properties.

INTRODUCTION

For several years industry has been considering supercritical fluid extraction (SFE) as a candidate for many separation applications. Principal reasons for the interest are high selectivity, ease of solute-solvent separation, low operating temperature, and possible nontoxicity of the solvent. These indicated advantages are especially true when carbon dioxide is the solvent, and most of the reported work in SFE has involved this solvent. There is another possible advantage of operating with a supercritical solvent: high rates of mass transfer because of favorable transport properties. This advantage is relatively unexplored, and represents the topic of the present paper.

Most of the reported studies of SFE have dealt with the thermodynamic behavior of supercritical fluid (SCF) mixtures, mainly in solid-fluid systems (1, 2). Equations of state have been used to predict solid-SCF equilibria fairly successfully (1, 3, 4). However, liquid-SCF equilibria appear more relevant to chemical process applications, but a proportionately smaller amount of work appears to have been directed toward this area.

As mentioned, mass transfer behavior of SFE systems has received very little attention. It is clear that for the economical scaleup and design of commercial SFE systems involving multistage contacting more attention must be given to this mass transfer issue. As is the case for conventional extraction, absorption and distillation carried out in staged or continuous countercurrent equipment, the efficiency of mass transfer in a SFE contactor will depend on phase flow rates, degree of loading (with respect to throughput capacity), and system properties. The objective of this work is to elucidate the effects of these sets of parameters on the mass transfer performance of small, column-type SFE contactors.

PREVIOUS WORK

It has been a general expectation that SFE extractors should give favorable mass transfer rates compared with extractors for conventional conditions, because of higher diffusion coefficients and lower viscosities (5, 6). However, one work has shown that the augmented mass transfer flux under SFE conditions depends on solubility enhancement (7).

In one mass transfer study Brunner used supercritical carbon dioxide to separate an aqueous 10 wt. % solution of ethanol in a spray column (8). The effects of pressure, temperature and solvent/feed ratio on the mass transfer rate were examined. Mass transfer coefficients almost two orders of magnitude greater than those in conventional liquid extraction were reported. An uncertainty in the coefficients was recognized and was attributed to the specification of characteristic length and to the problem of calculating diffusion coefficients in the supercritical solvent.

Experiments to determine separation efficiencies of different packings in a 2.54 cm. extraction column were performed by Peter and Tiegs (9). This study showed that a separation of a mixture of glycerides of oleic acids, with carbon dioxide as the supercritical component and acetone as an entrainer, could be made most efficiently with wire spirals and with a gauze-type (Sulzer) structured packing. At the upper loading limit an efficiency of 3.5 theoretical stages per meter of packing height was achieved.

In an investigation conducted by Critical Fluid Systems, Inc., mass transfer efficiency was measured for an alcohol-water separation using near-critical carbon dioxide in a 100 cm. diameter sieve tray column (10, 11). Optimum solvent/feed ratios for the extracted compounds (ethanol, isopropanol, sec-butanol) were determined. However, the main objective of the work was to evaluate the economics of the pilot-plant operation as a whole and not the efficiency of the column, and no mass transfer data per se were determined.

Another pilot scale study involved use of liquid carbon dioxide at 60 atmospheres and ambient temperature as the solvent (12). A 4 cm. diameter Scheibel column was used to extract 12 model compounds (such as ethanol, ethyl acetate, 1-hexanol and citronellal) from water. Emphasis was placed on the recovery of each constituent as a function of feed rate, feed composition and agitator rate.

MASS TRANSFER MODELS

A large amount of effort has gone into the analysis of mass transfer efficiency of sieve tray extractors. Predictive models have been made by Skelland and Conger (13), Treybal (14, 15) and Pilhofer (16). A review of these models was provided by Fair et al. (17). More recently Rocha et al. (18) have presented an improved efficiency model, based on a comprehensive data bank from literature sources as well as a large amount of their own data. The data cover extractor diameters up to 22.2 cm. diameter and a variety of extraction systems; in all cases the operating pressure was atmospheric.

The Rocha model considers mass transfer between phases to occur in four discrete steps: drop formation, hole jetting, drop rise (or fall) and drop coalescence. The contribution of drop rise is isolated from the "end effects" (formation, jetting and coalescence) which are consolidated into a single contribution.

The general form of the model is:

$$E_{md} = \frac{1.1\ K_{fd}A_{fd} + K_{rd}A_{rd}}{Q_d\rho_d/M_d + 0.5K_{rd}A_{rd} + 0.1K_{fd}A_{fd}} \tag{1}$$

where E_{md} = tray efficiency (Murphree), fractional

Q_d = volumetric flow rate of dispersed phase, cm^3/sec

K_{fd} = overall mass transfer coefficient for drop formation, based on dispersed phase, gm-moles/(sec-cm^2)

K_{rd} = overall mass transfer coefficient for drop rise or fall, based on dispersed phase

A = interfacial area, based on the equivalent overall mass transfer coefficient, cm^2/cm^3

ρ_d = density of the dispersed phase, gm/cm^3

M = molecular weight of the dispersed phase, gm/gm-mole

The overall mass transfer coefficients in Equation 1 are determined from individual phase mass transfer coefficients by the two-film model as follows:

$$\frac{1}{K_{id}} = \frac{1}{k_{id}} + \frac{m_{dc}}{k_{ic}} \tag{2}$$

where m_{dc} = slope of the equilibrium curve (mole fraction of solute dispersed phase)/(mole fraction of solute in continuous phase)

k = individual film coefficient, gm-moles/(sec-cm^2)

i = f, for drop formation

i = r, for drop rise or fall

and the second subscript terms d and c refer to the dispersed and continuous phases.

The approach is modular in that various correlations can be used to predict values of the individual film coefficients. Rocha et al. selected a special set of correlations, and that set will be used in the analysis given in the present paper. The important property variables are density, viscosity, diffusivity and interfacial tension. A particularly important grouping of flow and property variables is the dimensionless Weber number:

$$We = \frac{U_o^2 \rho_d d_o}{\sigma} \tag{3}$$

where U_o = linear velocity of dispersed phase through the holes

ρ_d = density of the dispersed phase

d_o = hole diameter

σ = interfacial tension

High values of the Weber number tend to give higher values of tray efficiency.

EXPERIMENTAL WORK

For the present analysis the primary source of experimental data is the work of Moses and de Filippi (11). As mentioned earlier, the work was carried out in a 10 cm. sieve tray column with supercritical carbon dioxide as the solvent and with alcohols extracted from a water solution. A flow diagram of the test equipment is shown in Figure 1. The main components of the system include the sieve tray extraction column, a distillation column and a vapor recompression cycle. The column was of stainless steel and was 2.0 m. overall height. Characteristics of the trays are given in Table 1.

The sieve trays were assembled on threaded rods which were passed through the center bore of the column to place the trays in their correct position. The tray bundles consisted of four trays spaced 36.0 cm. apart or eight trays spaced 18.0 cm. apart. A teflon/stainless steel layered sieve tray design was recommended to enable proper operation of the holes. Details of the tray design are shown in Figure 2. For some runs the diameter of the downcomer was varied from top to bottom to accommodate varying flow rates.

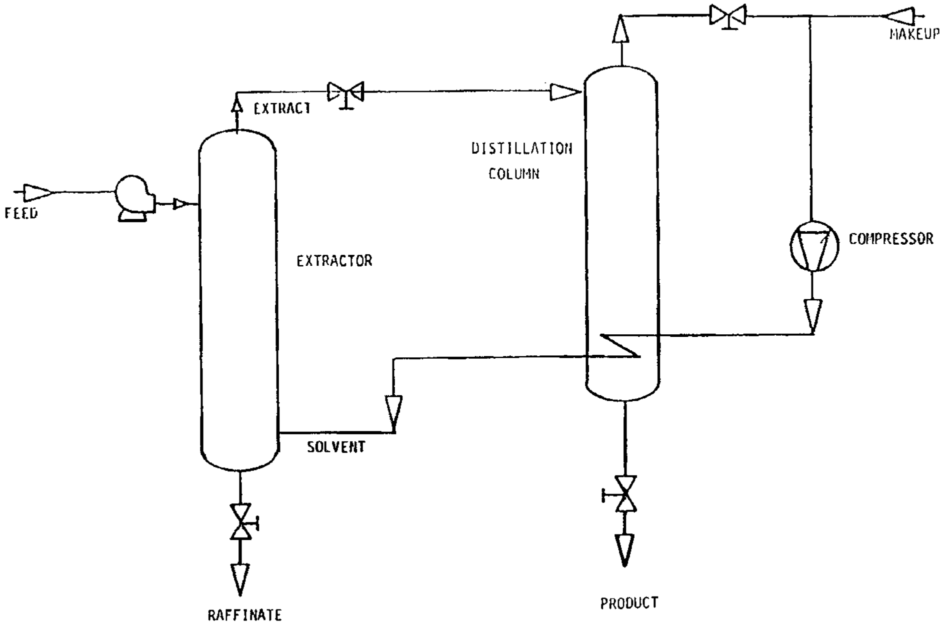

Figure 1. Simplified flow diagram of Moses/de Filippi test unit (11)

Table 1

DIMENSIONS OF SIEVE TRAYS (1)

Column inside diameter, cm.	10
Hole diameter, cm	0.32
Holes per tray	88
Downcomer diameter (circular), cm	0.6 - 2.8
Downcomer length, cm	15.2
Tray spacing, cm	18, 36

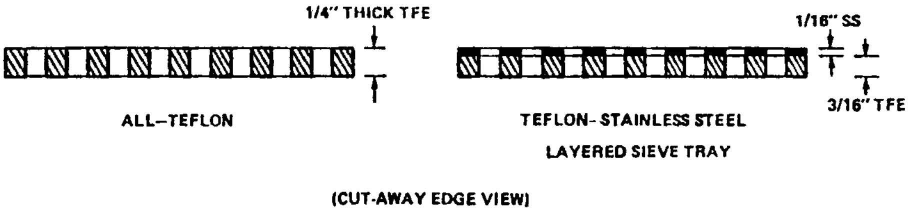

Figure 2. Sieve tray construction (11).

Table 2

EXPERIMENTAL SYSTEMS AND CONDITIONS

Solvent	Carbon dioxide
Solutes	Ethanol, isopropanol
Carrier	Water
Temperatures, ^{o}C	18 - 30
Critical temperature of CO_2, ^{o}C	31.05
Pressure, atm	82
Critical pressure of CO_2, atm	72.8

The distillation column was a 10 cm. diameter vessel, 1.5 m. tall. It included a stripping section only and was used to recover extracted solute from the solvent. A reboiler, consisting of four heat exchanger coils, provided the energy for the stripping.

For operation, the feed consisted of a 10 wt % solution of ethanol or isopropanol in water. (Some experiments were also performed with sec-butanol, but are not within the scope of the present paper.) The operating temperature range was 18 to 30° C and the operating pressure was 82 atmospheres absolute. Since the extractions were performed at ambient temperature, below the critical temperature of carbon dioxide but pressure was maintained above the critical pressure of carbon dioxide, the solvent was regarded as being in the critical, rather than the supercritical, state. The experimental conditions are summarized in Table 2.

DATA REDUCTION

Equilibrium information for the Moses and de Filippi work was taken from the graphical presentations of Francis (19) and thus may incorporate some error. Distribution coefficients on a molar basis were reported as 0.25 and 0.65 for the ethanol and isopropanol systems, respectively. A Kremser-type analysis was performed to generate a relationship between solvent/feed ratio, solute recovery and theoretical stages, and the experimental results were superimposed on a graphical representation of this relationship. The results are shown in Figures 3 and 4. In these figures, x_f and x_r refer to solute mass fraction in the feed and raffinate streams, respectively.

By interpolation, stage efficiencies can be deduced from the plotted results. Because of errors in interpolation plus likely errors in the distribution coefficients, the deduced stage efficiencies are thought not to be more accurate than +15% (i.e., +1.15 times the deduced value of the efficiency).

COMPARISON OF EXPERIMENTAL AND CALCULATED RESULTS

The model of Rocha et al. (18) was applied to the raw data of Moses and de Filippi, and the overall efficiency results were deduced by the present authors. Physical properties used in the modeling work are shown in Table 3. Diffusion coefficients in the critical fluid phase were estimated using the Wilke-Chang equation (24), assuming 15% overprediction with this method. The 15% correction factor was based on a study of measured diffusion coefficients in supercritical fluids (25).

A reasonable estimate of the aqueous phase diffusion coefficient was obtained by using the value of this property at atmospheric pressure (26) and incorporating a Stokes-Einstein correction for solvent viscosity (24).

A comparison between experimental and calculated overall efficiencies is presented in Figure 5 for the carbon dioxide/isopropanol/water system. The model underpredicts efficiency by about 20%. One possible reason for this error is that the interfacial tension used was that of carbon dioxide/water; the influence of isopropanol solute was neglected. The presence of solute would lower the interfacial tension and thus increase the efficiency. Interfacial tension data for the three component system under supercritical conditions are not available.

A similar comparison for the supercritical carbon dioxide extraction of ethanol from water is shown in Figure 6. In this case, the experimental efficiencies are overpredicted by about 40%. Again, the influence of solute on the carbon dioxide/water interfacial tension was neglected, but the effect should be less than for the isopropanol case.

The validity of the distribution coefficients should also play a role in the accuracy of the deduced efficiencies. One would expect that the bulk of the mass transfer resistance would lie in the

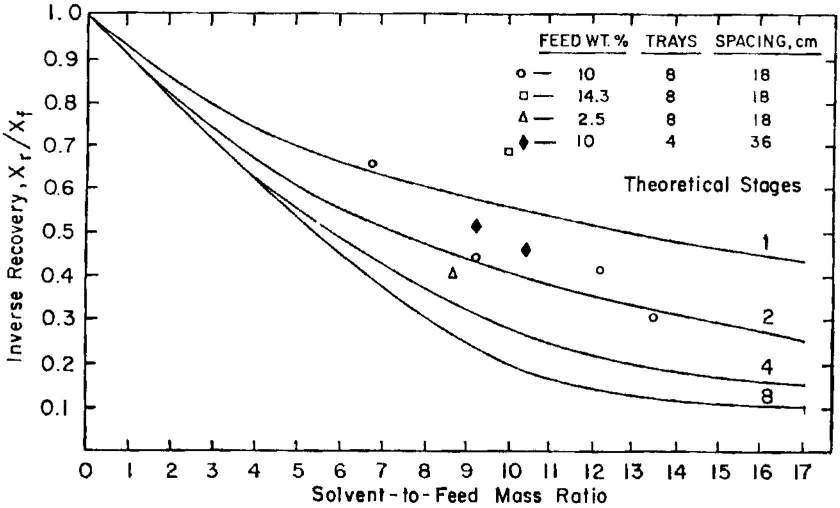

Figure 3. Inverse recovery vs. solvent/feed mass ratio, ethanol solute (11).

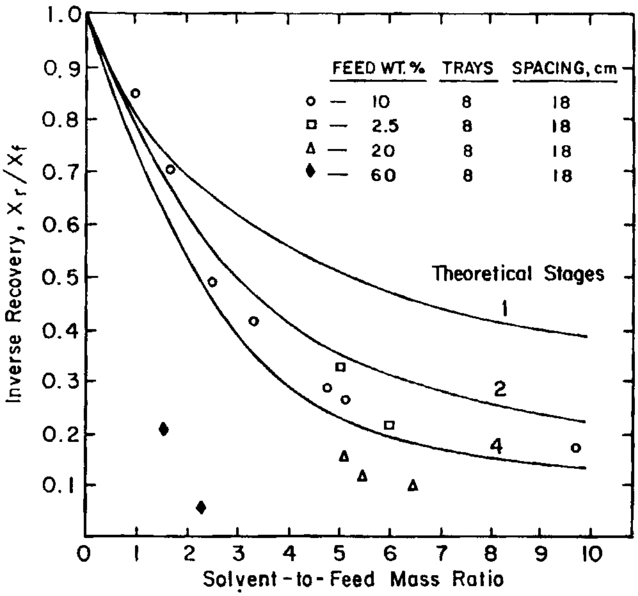

Figure 4. Inverse recovery vs. solvent/feed mass ratio, isopropanol solute (11). Eight trays at 18 cm. spacing.

Table 3

PHYSICAL PROPERTIES OF CO_2/ALCOHOL/WATER SYSTEMS

(82 atm and 25° C)

Distribution coefficient (molar basis),				
Ethanol solute			0.25	(11)
Isopropanol solute			0.65	(11)

	Dispersed Phase		Continuous Phase	
Density, g/cm^3	0.774	(20)	0.997	(21)
Viscosity, cp	0.067	(22)	0.890	(23)
Diffusion coefficient, cm^2/s (ethanol solute)	$1.62(10^{-4})$	(24, 25)	$1.34(10^{-5})$	(26)
Diffusion coefficient, cm^2/s (isopropanol solute)	$1.36(10^{-4})$	(24, 25)	$1.13(10^{-5})$	(26)
Interfacial tension, dynes/cm	23	(27)	23	(27)

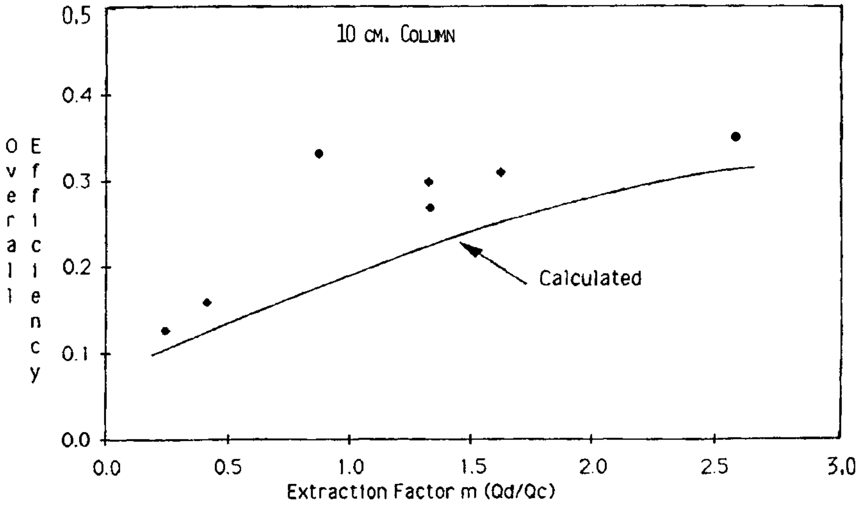

Figure 5. Comparison of Experimental (11) and Calculated Results: $CO_2/IPA/H_2O$

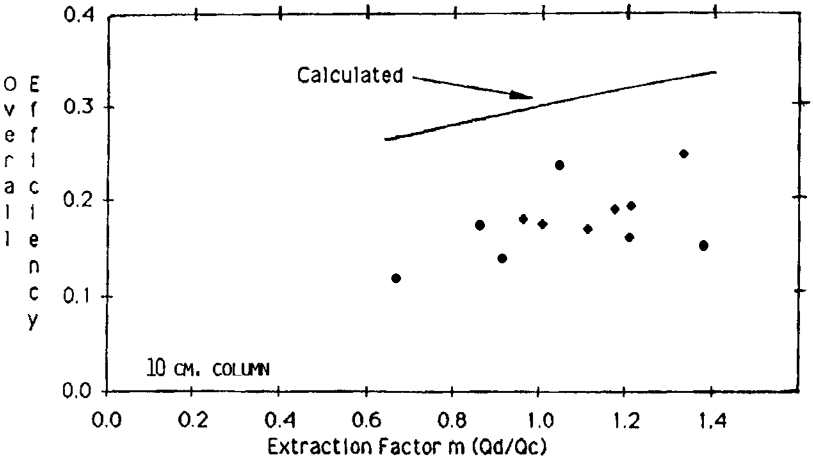

Figure 6. Comparison of experimental (11) and calculated results: $CO_2/EtOH/H_2O$.

aqueous phase, because of its significantly lower diffusivity and higher viscosity. However, the model predicted that 75% of the resistance to mass transfer was in the supercritical fluid phase, suggesting inaccuracies in the distribution coefficients.

Figures 5 and 6 show efficiencies in the range of 30% for the isopropanol system and 18% for the ethanol system. The transport, surface and equilibrium properties of the systems must be compared to explain the difference. In these figures, the extraction factor is defined as $m_{de}Q_d/Q_c$, where m_{dc} and Q_d are as defined earlier and Q_c is the volumetric flow rate of the continuous phase.

It was shown in Table 3 that the diffusion coefficients for ethanol in carbon dioxide and in water are greater than those for isopropanol in carbon dioxide and in water. This is the reverse of the indicated efficiencies, again suggesting inaccuracies in interfacial tension and distribution coefficient values used in the model. Much more work on the properties of supercritical extraction systems will be needed before such anomalies exhibited here can be resolved.

COMPARISON OF SUPERCRITICAL CONTACTOR DEVICES

Several types of contacting devices operating with supercritical solvents are compared in Figure 7. The volumetric efficiency was used to make the comparisons. This parameter combines mass transfer efficiency with throughput capacity, and for a tray-type device is:

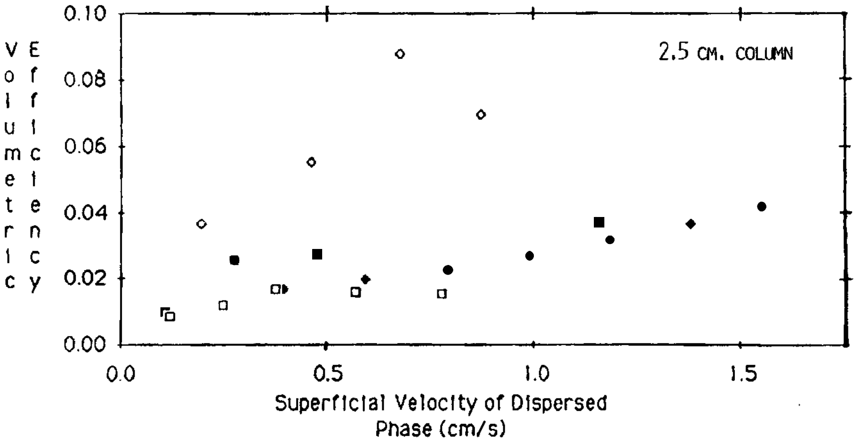

Figure 7. Comparison of countercurrent contactors operating with supercritical solvents.

Legend: ● sieve trays; ◇ wire spirals; ■ Sulzer; □ Raschig rings

$$\text{Volumetric Efficiency (V.E.)} = \frac{(U_c + U_d)\ E_o}{H_t} \tag{4}$$

where U_c and U_d are superficial velocities of the continuous and dispersed phases, E_o is an overall efficiency, approximately equal to the stage efficiency E_{md} and H_t is the tray spacing. For a packed column Equation 4 converts to:

$$\text{Volumetric Efficiency (V.E.)} = \frac{(U_c + U_d)}{\text{HETS}} \tag{5}$$

where HETS is the height equivalent to a theoretical stage.

The data for the sieve trays were computed with the model of Rocha et al. (18) for the carbon dioxide/ethanol/water system at 100 atm and 35° C, while packing data were taken from the work of Peter and Tiegs (9) and are for the separation of a mixture of glycerides and oleic acids. It is recognized that the latter data are not necessarily equivalent in terms of transport properties, and represent a system with an inherently lower mass transfer capability. If such a difference is recognized, the Figure 7 shows that packings known for high efficiency in distillation service, such as wire spirals and Sulzer structured packing, indeed have indicated high efficiencies for supercritical fluid extraction services.

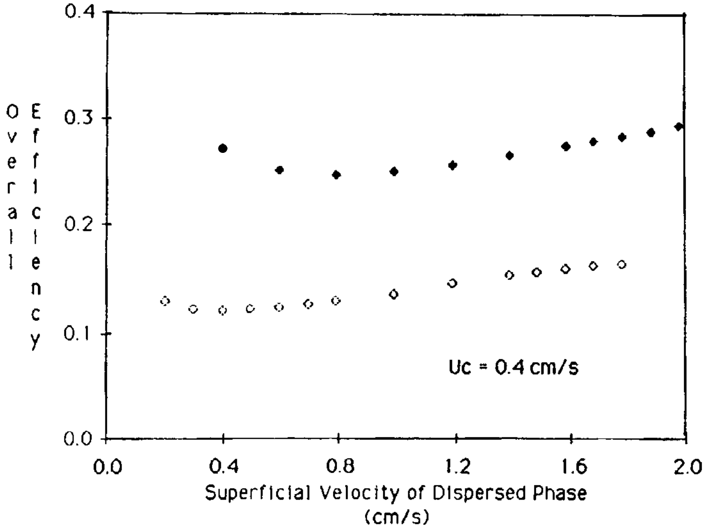

Figure 8. Comparison of supercritical and liquid extraction: calculated values, sieve trays. (10 cm. column)

COMPARISONS OF SUPERCRITICAL AND CONVENTIONAL EXTRACTION

Overall efficiencies for supercritical and "conventional" liquid extraction systems were computed by use of the Rocha et al. model. The SFE system was carbon dioxide/ethanol/water at 100 atm. and 35^{o} C, and the conventional system was toluene/acetone/water at atmospheric pressure and ambient temperature. These systems were compared because they both have interfacial tensions in the range of 22 - 25 dynes/cm., and the aqueous phase diffusion coefficients for ethanol and acetone should be about the same.

As Figure 8 shows, extraction efficiencies in the supercritical case are some 90% greater than those for the conventional case. The major contributor to the enhancement for SFE appears to be the dispersed phase diffusion coefficient, estimated as 2.1 (10^{-4}) cm/sec. for SFE and 2.6 (10^{-5}) cm/sec. for the conventional case. Also, the viscosity of the SFE dispersed phase is an order of magnitude less than that for the conventional dispersed phase (toluene). The transport property advantage of the supercritical system appears to be real.

SUMMARY AND CONCLUSIONS

The mass transfer aspects of countercurrent supercritical extraction have been examined with the aid of a model developed for conventional liquid-liquid extraction. The model predicted published SFE efficiency data with an accuracy of about ± 40%. The discrepancy was attributed more to inaccurate values of the distribution coefficient and the interfacial tension than to a basic lack of applicability of the model.

Comparisons of several contacting devices, operating under SFE conditions, were made using volumetric efficiency as a parameter. Those packings known to give high efficiency in distillation service were found to give very good efficiencies in SFE service.

The mass transfer model was used to compare predicted efficiencies for SFE with those of conventional extraction. It appears that as much as 90% greater efficiencies might be expected for SFE, and this enhancement is due primarily to more favorable viscosities and diffusion coefficients.

A design routine for SFE processes can be envisioned in which the physical and geometric properties of the system are optimized over a range of temperatures, pressures and compositions. With further development of mechanistic mass transfer models coupled with improved methods for predicting equilibrium and transport properties, much pilot plant scaleup work might be obviated.

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