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Kassim M. Kassim[a]; Michael B. King[b]
[a] Science Research Council, Baghdad, Iraq [b] Chemical Engineering Department, Birmingham University, Birmingham, England

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Separating Some Crude Oil Products (azeotropic mixture) by Gas Extraction with Carbon Dioxide at Elevated Pressure

KASSIM M. KASSIM

SCIENCE RESEARCH COUNCIL
BAGHDAD, IRAQ

MICHAEL B. KING

CHEMICAL ENGINEERING DEPARTMENT
BIRMINGHAM UNIVERSITY
BIRMINGHAM, ENGLAND

Abstract

The ethanol/octane system has an azeotrope at normal pressure. This renders separation by simple distillation impossible. The system was studied at elevated pressure to see whether it was possible to separate the azeotropic mixture by gas extraction with carbon dioxide. It was found that the ternary had isologous phases with a ratio not very different from that in the azeotrope.

INTRODUCTION

One advantage claimed for extraction operations carried out with supercritical or near-critical extractants is that a higher mass transfer rate may be obtained than with normal liquid extraction. There is evidence that this is the case, but on a large scale is questionable. Gas extraction operations are at present receiving considerable interest. A number of references have appeared (*1–5*) and a special issue of *Separation Science and Technology* (Vol. 17, 1982) was devoted to papers on gas extraction and similar separation processes. A symposium entitled "Chemical Engineering at Supercritical Conditions" was held during the annual meeting of the American Institution of Chemical Engineering at New Orleans in November 1981, and the papers presented at that conference were published in the form of a book (*6*). A meeting of the Science Food Group, Food Engineering Panel, was entirely devoted to the use of compressed carbon dioxide in solvent extraction (*7–12*). Although a very large number of patents involving extractions into supercritical solvents have been filed and approved over the past 10 years (*4*, *5*), there are at present few working processes. One reason for this is probably the absence of suitable equilibrium and rate data upon which feasibility and scale-up calculations can be based. Another reason in some cases may be the failure to understand fully the chemical and physical processes taking place.

Because of the current research activity in this field and the large number of pilot-plant scale tests being carried out, it seems likely that the above limitations will gradually be overcome. As part of this worldwide activity, we are carrying out some studies to enable us to use this process to separate some crude oil products (azeotropic mixture ethanol/octane) by gas extraction with carbon dioxide at high pressure.

EQUIPMENT

A flow diagram of the equipment is given in Fig. 1. This equipment, described previously (*6*), is suitable for determining equilibrium data. The vapor phase is recirculated through the liquid phase contained in the equilibrium cell until equilibrium has been achieved under controlled conditions of temperature and pressure. Samples of the vapor and liquid phases are then valved off into sample bombs whose contents are analyzed.

CALCULATION OF THE COMPOSITION OF THE PHASES IN THE TERNARY SYSTEM CO_2/ETHANOL/OCTANE

The ternary system CO_2/ethanol/octane was studied at constant temperature (75°C) and various pressures. The composition of the equilibrium phases was noted at each pressure. The mole fractions of ethanol in the liquid and vapor phases on a CO_2-free basis were calculated from the equations

$$X_1 = \frac{(n_{X1})^L}{(n_{X1})^L + (n_{X2})^L} = \frac{\bar{R}}{1 + \bar{R}}$$

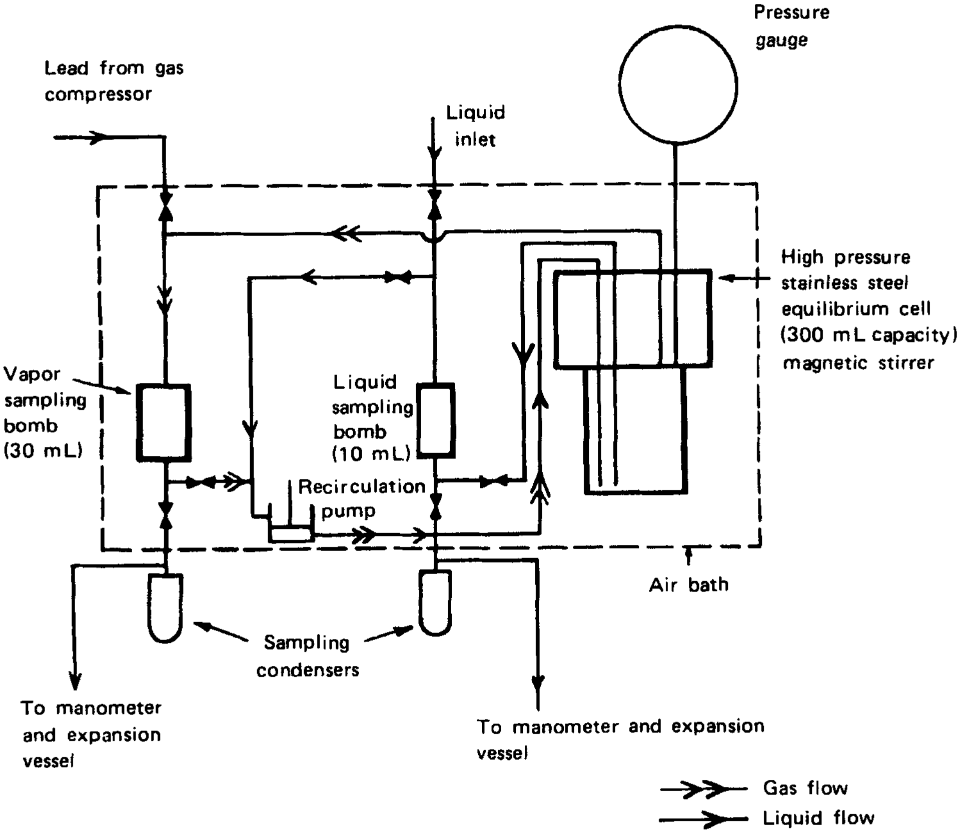

FIG. 1. Equipment for equilibrium determinations in fluid systems.

and

$$Y_1 = \frac{(n_{X1})^G}{(n_{X1})^G + (n_{X2})^G} = \frac{\bar{R}_1}{1 + \bar{R}_1}$$

where $(n_{X1})^L$ = number of moles of ethanol in the liquid phase on a CO_2-free basis
$(n_{X2})^L$ = number of moles of octane in the liquid phase on a CO_2-free basis
$(n_{X1})^G$ = number of moles of ethanol in the vapor phase on a CO_2-free basis
$(n_{X2})^G$ = number of moles of octane in the vapor phase on a CO_2-free basis
$\bar{R} = (n_{X1})^L/(n_{X2})^L$
$\bar{R}_1 = (n_{X1})^G/(n_{X2})^G$

$\bar{R}$ and $\bar{R}_1$ were read directly from the calibration chart when the ratio of the corresponding peak heights obtained from the chromatographic analyses of the liquid and vapor sample bombs were known.

The calculations for the mole fractions of CO_2 in the liquid phase (X) and in the vapor phase (Y) of this system were carried out using the following equations:

$$Y = \frac{(n_Y)^G}{(n_X)^G + (n_Y)^G}$$

and

$$(1 - X) = \frac{(n_X)^L}{(n_Y)^L + (n_X)^L}$$

where $(n_Y)^G$ = number of moles of CO_2 in the vapor sample bomb
$(n_X)^G$ = number of moles of heavy component in the vapor sample bomb
$(n_Y)^L$ = number of moles of CO_2 in the liquid sample bomb
$(n_X)^L$ = number of moles of heavy component in the liquid sample bomb.

The values of $(n_X)^L$ and $(n_X)^G$ were calculated from the following relationships:

$$(n_X)^L \text{ or } (n_X)^G = \frac{\text{weight of extracted heavy components}}{X_A M_A + X_B M_B}$$

where X_A = mole fraction of Component A (ethanol) in the liquid sample bomb (or the vapor sample bomb)
X_B = mole fraction of Component B (octane) in the liquid sample bomb (or the vapor sample bomb)
M_A = molecular weight of Component A (46.07 g)
M_B = molecular weight of Component B (114.23 g)

In the liquid bomb calculations, X_A and X_B were calculated from $\bar{R}$ by using the equations

$$X_A = \frac{\bar{R}}{1+\bar{R}}, \qquad X_B = \frac{1}{1+\bar{R}}$$

CALCULATION OF $(n_Y)^G$ AND $(n_Y)^L$

Deviation from the perfect gas law pressure of about 1 atm may conveniently be expressed by

$$PV = n(RT + B_v P)$$

where P = pressure
V = system volume
n = number of moles of gas
B_v = second virial coefficient

This equation leads directly to the expressions

$$(n_Y)^G = V\left[\frac{P_2}{RT + B_v P_2} - \frac{P_1}{RT + B_v P_1}\right]$$

$$(n_Y)^G = VP_2\left[\frac{1.0 - \left(\frac{P_1}{P_2}\right)\left(\frac{RT + B_v P_2}{RT + B_v P_1}\right)}{(RT + B_v P_2)}\right]$$

for the number of mole of gas in the vapor sample bomb. P_2 and P_1 are the pressures in the expansion system before and after expansion, and V is the volume of the system (34.6302 L).

The number of moles of CO_2 in the liquid sample bomb, $n_Y{}^L$, was calculated by using exactly the same procedure as that given above except that the total volume of the expansion system (V) was taken as 6,6691 L.

RESULTS

The system CO_2/ethanol/octane was studied at four ethanol/octane ratios in the liquid phase at 75°C. The ethanol/octane ratios in the liquid feed to the equipment were as follows:

(1) 25 mol ethanol/75 mol octane
(2) 42.56 mol ethanol/57.44 mol octane
(3) 80.52 mol ethanol/19.48 mol octane
(4) 94.20 mol ethanol/5.8 mol octane

Because the proportion of heavy component extracted into the vapor was comparatively small, the above mole ratios were maintained in the liquid phase of the equipment without appreciable change through the tests. The mole fractions of ethanol in the liquid and vapor phases were calculated on a CO_2-free basis at the pressures studied for each of the above four charges. The mole fractions of CO_2 in the liquid and vapor phases were also calculated.

Figure 2 shows the mole fraction solubilities of CO_2 in the vapor and liquid phases as a function of pressure for the charge of 42.56 mol ethanol/57.44 mol octane. Figure 3 shows the ratio of the mole fraction of ethanol in the vapor phase to the mole fraction of ethanol in the liquid phase as a function of the pressure for these four ethanol/octane mixtures. Figure 4 shows the relative volatility as a function of pressure.

The ethanol/octane system has an azeotrope at a mole fraction of ethanol of 0.8561 at normal pressure. This renders separation by simple distillation impossible. The above tests were carried out to see whether it would be possible to separate the azeotropic mixture by gas extraction. It was found that the ternary system had isologous phases with an ethanol/octane ratio not very different from that in the azeotrope. This may be seen from Figs. 5 and 6. However, it was found that there was a detectable difference between the mole ratio in these phases and that in the normal azeotrope, and also that there was a noticeable change in the composition of these phases with the pressure of the contacting gas (Figs. 5 and 6).

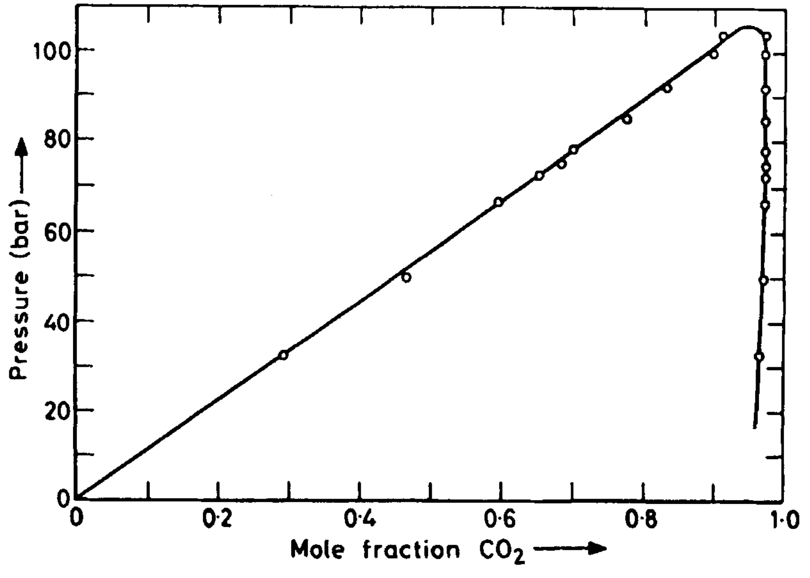

FIG. 2. Mole fraction of CO_2 in the vapor and liquid phases as a function of pressure for the carbon dioxide/ethanol/octane system at 75°C. Mole ratio of octane to ethanol in the liquid phase: 1.35.

DISCUSSION

Data were obtained using four different ethanol/octane feed ratios to the equilibrium cell. The results at 75°C for a charge of 42.5 mol ethanol/ 57.44 mol octane are shown in the form of a pressure/composition diagram in Fig. 2 and for all four charges in triangular diagrams (Figs. 7, 8, and 9). Figure 7 shows the liquid composition of the system as a function of pressure, and it is seen that the saturation curve for the liquid is nearly linear. The data shown for the CO_2/octane system were not obtained in this work but were interpolated from Ref. *13*. The liquid-phase data for the CO_2/ethanol binary have yet to be obtained. Figure 8 shows the vapor composition as a function of pressure at 75°C. Again, the data for the CO_2/octane binary were interpolated from Ref. *13*. Vapor-phase data for the CO_2/ethanol binary system were not obtained in the present work, but some data at gas pressures up to 40 bars were recently obtained by other workers (*14*) for this system at 75°C. These are shown as open circles in Fig. 8, where it is seen that they fit well with data

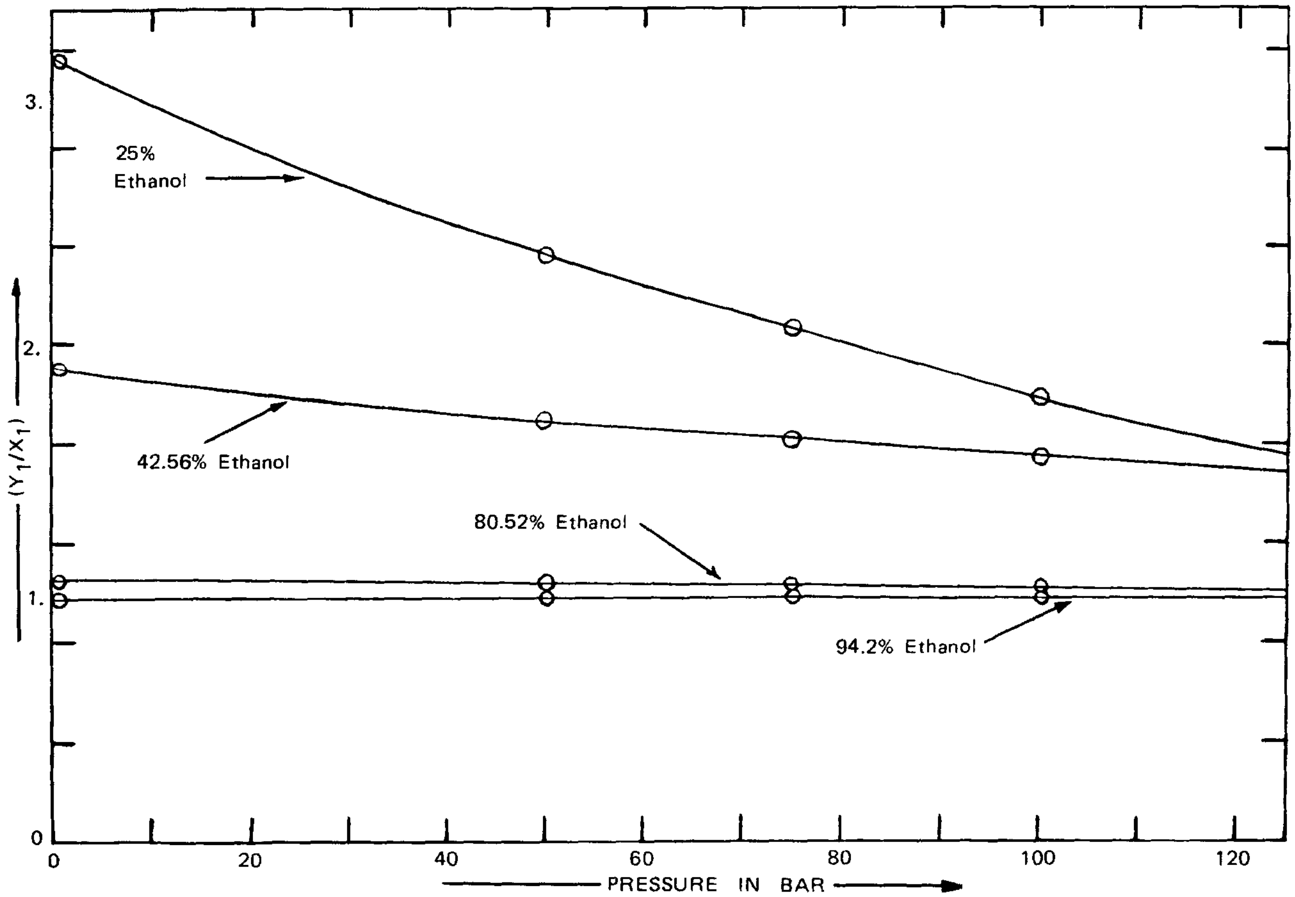

FIG. 3. Ratio of mole fraction of ethanol in the vapor (Y_1) to the mole fraction of ethanol in the liquid (X_1) as a function of pressure at 75°C.

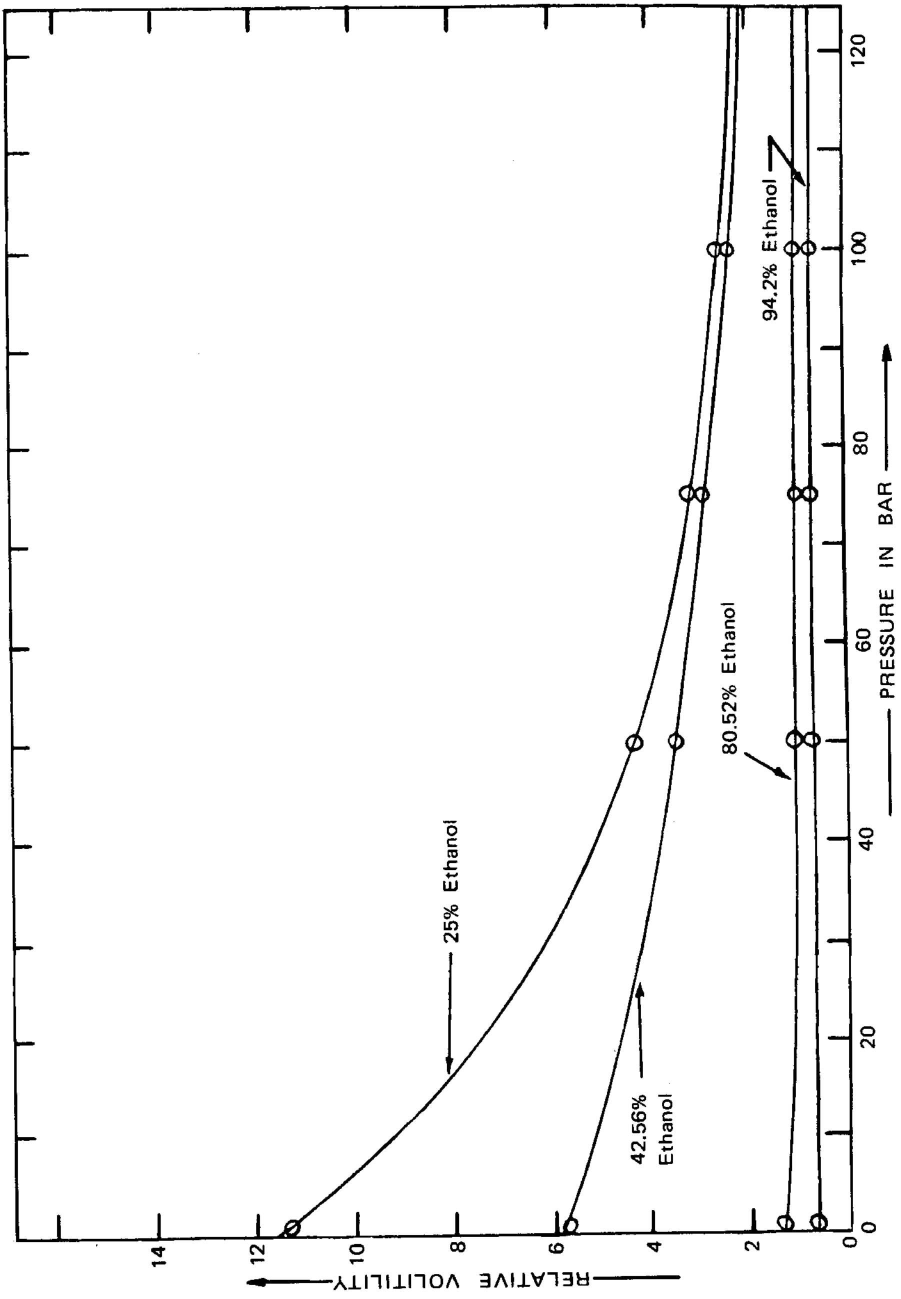

FIG. 4. Relative volatility as a function of pressure at 75°C.

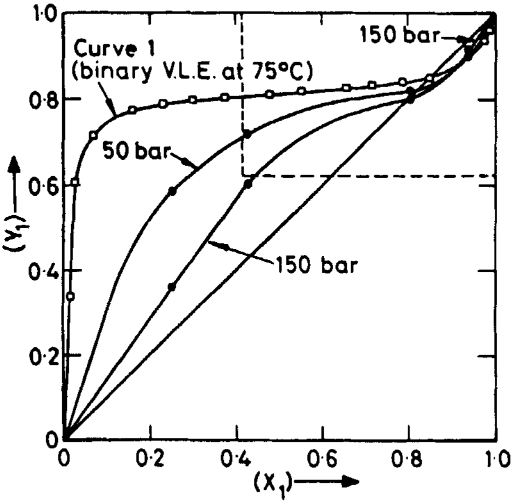

FIG. 5. Mole fractions of ethanol in the vapor and liquid phases (Y_1 and X_1) on a CO_2-free basis at pressures of 150 and 50 bars for the carbon dioxide/ethanol/octane system at 75°C. For comparison, Curve 1 shows the mole fractions of ethanol in the vapor and liquid phases in the ethanol/octane system at 75°C.

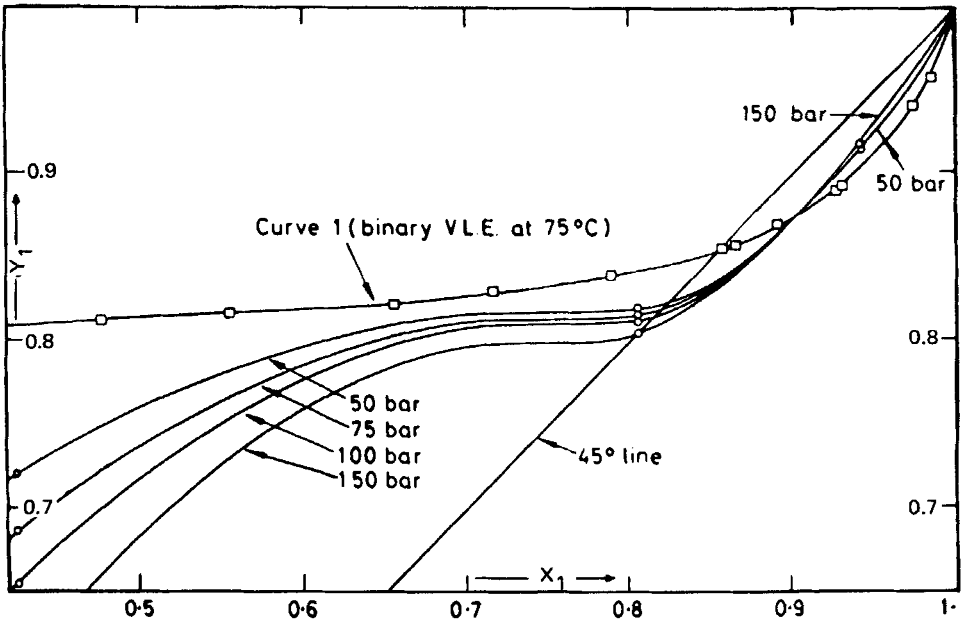

FIG. 6. Enlarged section of the Y_1 versus X_1 diagram for the carbon dioxide/ethanol/octane system at 75°C given in Fig. 5. Additional pressures are shown.

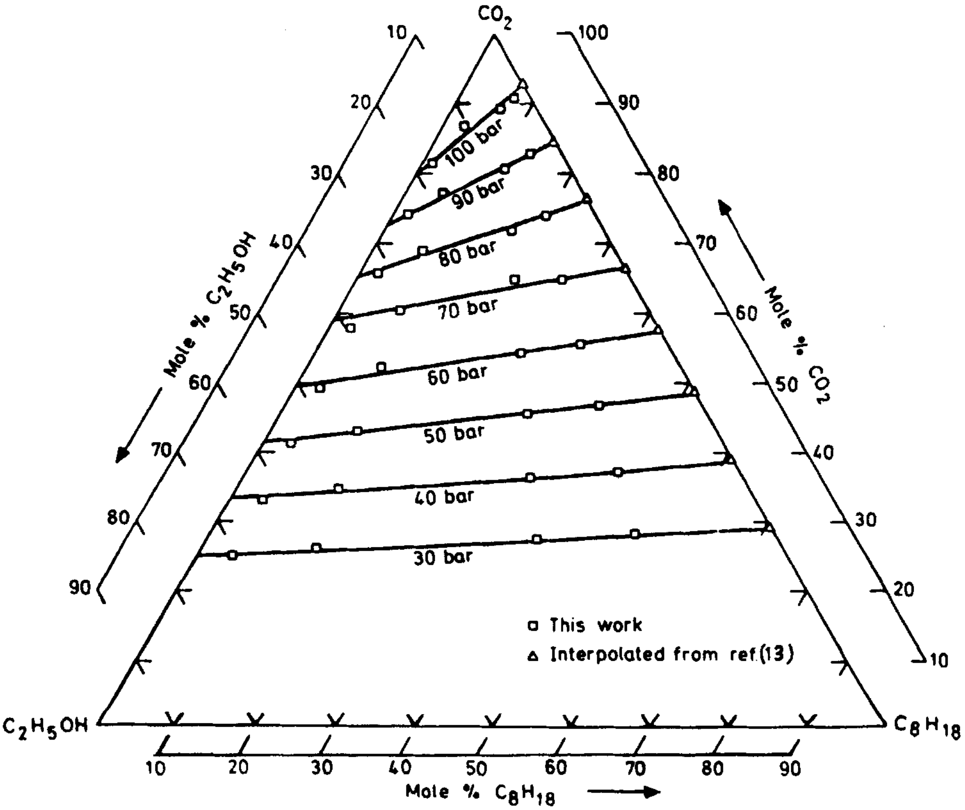

FIG. 7. Liquid compositions for the carbon dioxide/ethanol/octane system as functions of pressure at 75°C.

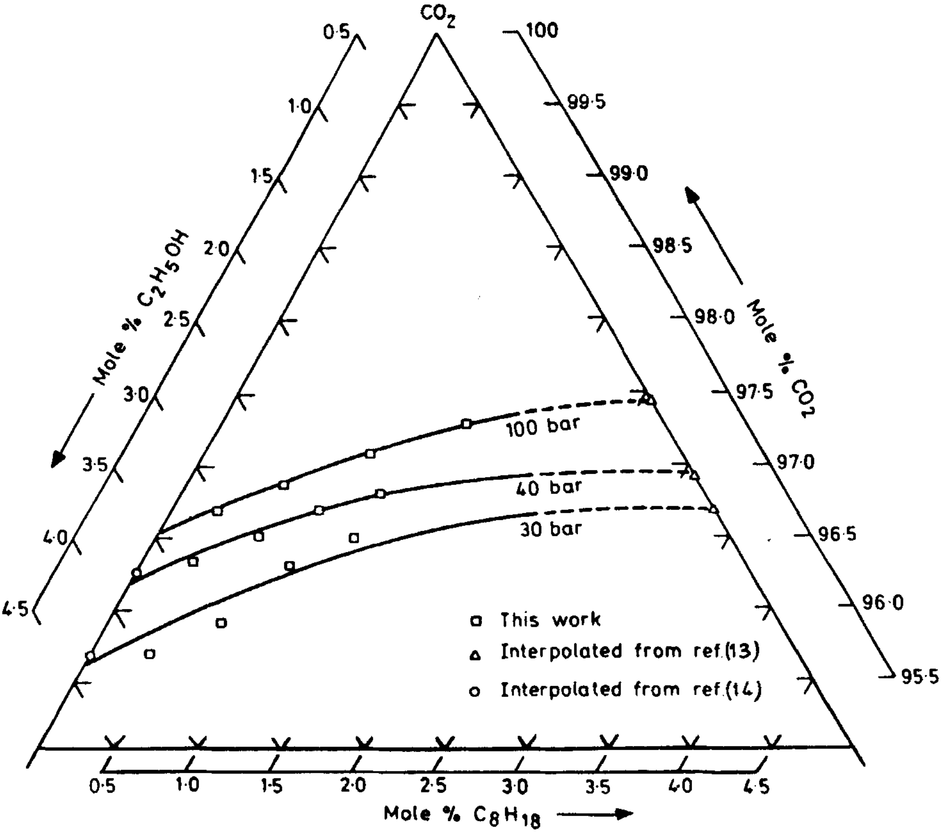

FIG. 8. Vapor compositions for the carbon dioxide/ethanol/octane system as functions of pressure at 75°C.

obtained in the present work for neighboring mixtures. Figure 9 shows the compositions of both the vapor and liquid phases at 75°C and a pressure of 100 bars. The tie lines are also shown in this figure, and it is seen that for an ethanol/octane ratio in excess of 0.224 the octane/ethanol ratio in the vapor phase is greater than that in the liquid phase, while at ethanol/octane ratios less than this, the reverse is true. This situation is analogous to the formation of solutropes which are sometimes encountered in liquid–liquid extraction work. In this case ethanol and octane form a solutrope containing a mole ratio of 0.224 of octane/ethanol when contacted with compressed CO_2 at 75°C and 100 bars. Along the solutrope tie line the mole ratio of octane/ethanol is constant. Gas extraction under these conditions can therefore achieve no change in the octane and ethanol split. As far as it is known, this is the first fully documented example of solutropy occurring in the field of gas extraction.

The composition of the solutrope varies somewhat with pressure. Figure 5 shows the mole fraction of ethanol in the vapor (Y_1) (on a CO_2-free basis) plotted as a function of the mole fraction of ethanol in the liquid (X_1) (on a CO_2-free basis) at pressures of 50, 75, 100, and 150 bars. Plotted on the same diagram are data for the ethanol/octane system at 75°C (*15*). The 45° line is also shown on this diagram, and it is seen that the ethanol/octane binary system shows an azeotrope at an ethanol mole fraction of 0.8561. This azeotrope is rather richer in ethanol than the solutrope obtained with compressed CO_2 at higher pressure (at the solutropic point the X_1–Y_1 curve crosses the 45° line). This is shown more clearly in Fig. 6 which is a section from a large-scale X_1–Y_1 diagram of this system, the section being taken to include the azeotropic and solutropic points. It is seen that as the pressure of the contacting gas increases, the mole fraction of ethanol in the solutrope decreases. The composition of the solutrope is shown as a function of the pressure at 75°C in Table 1. The fact that the solutrope composition at elevated pressure differs from that of the azeotrope at normal pressure indicates that, in principle, it should be possible to separate a mixture of the azeotropic composition (obtained by distillation at normal pressure) by gas extraction. Apart from this possibility, gas extraction seems to have little to offer as a means of separation for this system since the relative volatilities at compositions away from the immediate vicinity of the solutrope become progressively closer to unity as the pressure is raised. This is shown in Fig. 4. These effects are interesting, but it is concluded that gas extraction will not provide an economic way of separating the azeotrope.

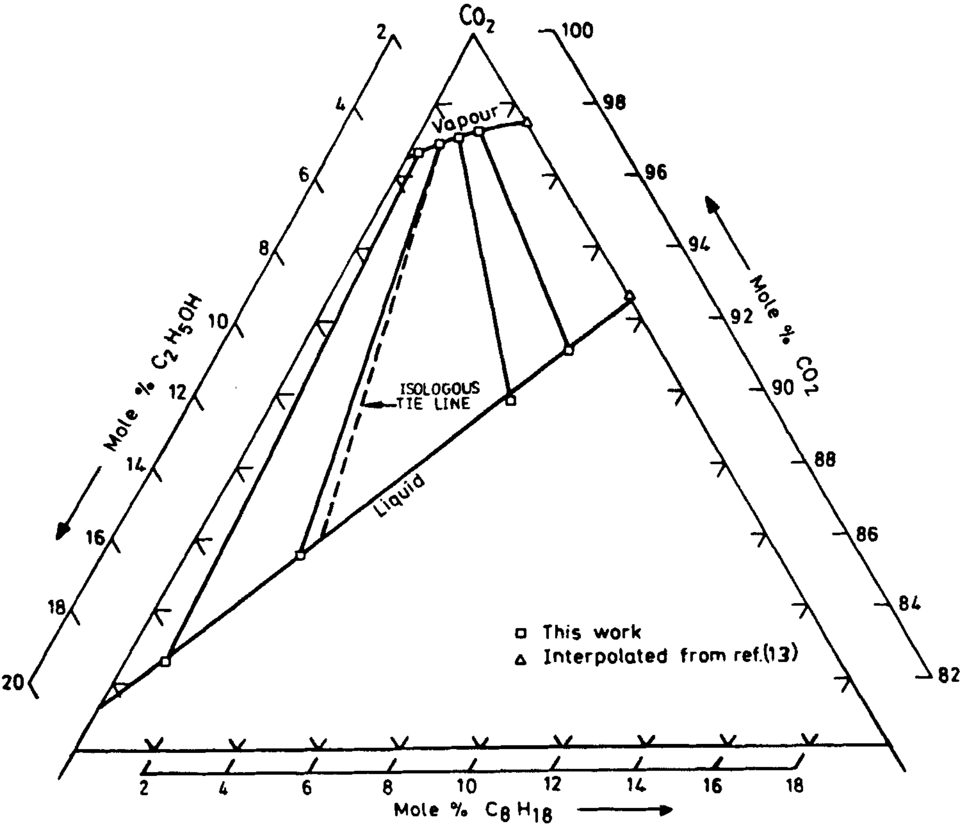

FIG. 9. Vapor and liquid compositions for the carbon dioxide/ethanol/octane system at 100 bars and 75°C.

TABLE 1
Composition of the Solutrope as a Function of Pressure at 75°C

Pressure (bars)	0.937[a]	50.0	75.0	100.0	150.0
Mole fraction of ethanol in the azeotrope (at 0.937 atm) or in the solutrope (at higher pressures)	0.8561	0.8250	0.8201	0.8170	0.8070

[a] The azeotropic pressure at 75°C.

REFERENCES

1. D. F. Williams, *Chem. Eng. Sci.*, *36*, 1769 (1981).
2. G. Brunner and S. Peter, *Chem.-Ing.-Tech.*, *53*, 529 (1981).
3. T. R. Bott, *Chem. Ind.*, p. 228 (1980).
4. L. G. Randall, *Sep. Sci. Technol.*, *17*, 1 (1982).
5. M. B. King and T. R. Bott, *Ibid.*, *17*, 119 (1982).
6. M. B. King, D. A. Alderson, F. H. Fallaha, D. M. Kassim, K. M. Kassim, J. R. Sheldon, and R. S. Mahmud, Paper 31b Delivered at the Symposium on Chemical Engineering at Supercritical Conditions, Held as Part of the 1981 Annual Meeting of the American Institute of Chemical Engineers, New Orleans. Now Available as Chapter 2 in *Chemical Engineering at Supercritical Conditions* (M. E. Paulaitis, J. M. Penninger, R. D. Gray, and P. Davidson, eds.), Ann Arbor Science Publications, Ann Arbor, Michigan, 1983.
7. T. R. Bott, *Chem. Ind.*, p. 394 (1982).
8. H. Brogle, *Ibid.*, p. 385 (1982).
9. R. Volbrecht, *Ibid.*, p. 397 (1982).
10. D. S. Gardner, *Ibid.*, p. 402 (1982).
11. R. P. De Filippi, *Ibid.*, p. 390 (1982).
12. J. P. Calame and R. Steiner, *Ibid.*, p. 399 (1982).
13. D. Alderson, PhD Thesis, University of Birmingham, England, 1975.
14. S. K. Gupta, R. D. Lesslie, and A. D. King Jr., *J. Phys. Chem.*, 77(16) (1973).
15. L. Boublikova and B. C-Y. Lu, *J. Appl. Chem.*, *19* (1969).
16. M. B. King, K. M. Kassim, and H. Al-Najjar, *Chem. Eng. Sci.*, *32*, 1247 (1977).

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