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M. B. King[a]; T. R. Bott[a]; M. J. Barr[a]; R. S. Mahmud[a]; N. Sanders[b]
[a] Department of Chemical Engineering, University Of Birmingham, Birmingham, England [b] Cadbury-Schweppes Reading, England

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Equilibrium and Rate Data for the Extraction of Lipids Using Compressed Carbon Dioxide

M. B. KING, T. R. BOTT, M. J. BARR, and R. S. MAHMUD

DEPARTMENT OF CHEMICAL ENGINEERING
UNIVERSITY OF BIRMINGHAM
BIRMINGHAM B15 2TT, ENGLAND

N. SANDERS

CADBURY-SCHWEPPES
READING, ENGLAND

ABSTRACT

Equilibrium data are given for the solubilities in compressed CO_2 of the lipid components in freshly ground rape seed and of glycerol trioleate (a typical constituent of rape oil) at pressures up to 200 bar and temperatures 25 to 75C. Continuous flow tests in which a bed of ground rape seed was contacted with a stream of liquid CO_2 at 25C and varied flow conditions are also reported. The results are collated in terms of an empirical mass transfer coefficient. A sharp change took place in the lipid concentration in the extractant stream leaving the bed when about 65% of the available oil had been extracted. This, and changes in the composition of the extract, are discussed, together with the use of this type of data for design purposes.

1. INTRODUCTION

Work is being carried out in a number of research centres to investigate the potential of extraction operations both with supercritical compressed gases and with marginally subcritical solvents.

The advantages to be gained by operating with near-critical solvents have been outlined in previous publications (see; e.g. ref. 1). Very briefly these include the following:

(1) Virtually no solvent residue is left in the product.

(2) By careful design, the solvent recovery step can be made to require less energy than is the case with normal liquid extraction.

(3) A wider range of solvents can be used than in normal liquid extraction. Compressed carbon dioxide, for example, can be used. This solvent, which has the advantages of being non-flammable and also non toxic in small amounts, is of particular interest to the food industry (2).

(4) By control of pressure, a range of selectivities and dissolving power can be obtained with a given solvent at given temperature (3). Fractionation operations based on this effect are very possible developments in the future (4).

(5) Because of the diffusivity and viscosity behaviour of near-critical solvents it is anticipated that they should give better penetration into pores and matrices, and hence faster and more efficient extraction from fixed beds and columns than do normal liquid solvents. Firm evidence for good mass transfer rates in operating equipment is as yet scarce, being largely confined to observations on the extractions of coal (5).

A few commercial extraction units utilising near-critical solvents are in operation. For example;

1. The extraction of hops with both subcritical and supercritical carbon dioxide. (A fairly recent development is the reported use of a hop-extraction plant off-season for the extraction of spices (6).)

2. The de-caffeination of coffee using supercritical carbon dioxide.

3. For many years the de-asphalting of petroleum has been carried out by extraction with marginally subcritical propane.

However, it must be said that the number of plants coming into operation is not yet commensurate with the degree of interest and research activity. At Birmingham we believe that this is due in large part to the absence of sufficient design data to enable reliable preliminary costings to be made. Some work which we are carrying out to provide such data is described in this paper.

2. EQUIPMENT

The equipment used to determine the equilibrium data and also the rate of mass transfer data reported below is shown in Fig. 1. This equipment is a substantial development of that used in previous studies (7,8,9,1). It is intended primarily for tests on solutes of low volatility and it consists of a contactor cell (volume approximately 500 cm^3), an equilibrium sampling cell(s) (volume 37.49 cm^3) an air-driven pump and a sample collection system. The pump may be used both to raise the system pressure and to recirculate extractant through the contactor cell when required (7). The material to be extracted is contacted with the extractant (in this case compressed carbon dioxide) in the stainless steel cylinder A which is inserted in the contactor cell. This material may either be a granular solid or a liquid. In the former case a gauze base is screwed to the stainless steel cylinder A. A bed of the solids is contained in the lower part of this cylinder which is 23 cm high and has an internal diameter of 4.4 cm. The bottom rim is pressed firmly on to the floor of the contactor cell by a spring-loaded top which is compressed as the lid of the cell is bolted down, thus preventing the extractant from by-passing the bed. The top of the cylinder is packed with knitmesh to prevent the transport of fine material in the solvent stream.

When a liquid is to be extracted, a stainless steel base with a pipe 2 cm long and 0.3 cm in diameter is screwed into the bottom of the cylinder A (in place of gauze bottom previously used) and the glass vapour/liquid or liquid/liquid contactor shown in Fig. 2 is lowered on to this base with the stainless pipe projecting up into the central glass tube of the contactor into which it is sealed. The region between the top of the contactor and the top of the cylinder is packed with knitmesh and the basket lowered into the contactor cell as before. The pear shaped glass plug D in Fig. 2 acts as a pressure-relief valve and prevents the glass unit C from shattering if the liquid contained in it freezes. This can happen when emptying the equipment.

The rectangular region shown within broken lines on Fig. 1 is contained within an air bath. Further control of the temperature of flowing liquid streams is provided by the line preheater H' and a temperature control jacket which surrounds the sampling cell(s) (see below). The line preheater controls the temperature of the fluid stream entering the extraction cell. It consists of a water bath with an immersed coil through which this stream flows. The bath heater is controlled by a thermocouple positioned at point X. This thermocouple is encased in a stainless steel finger which protrudes into the flowing stream. Similar temperature sensors are located within the contactor cell and at points 1, 2, 3 and 4 in the solvent stream.

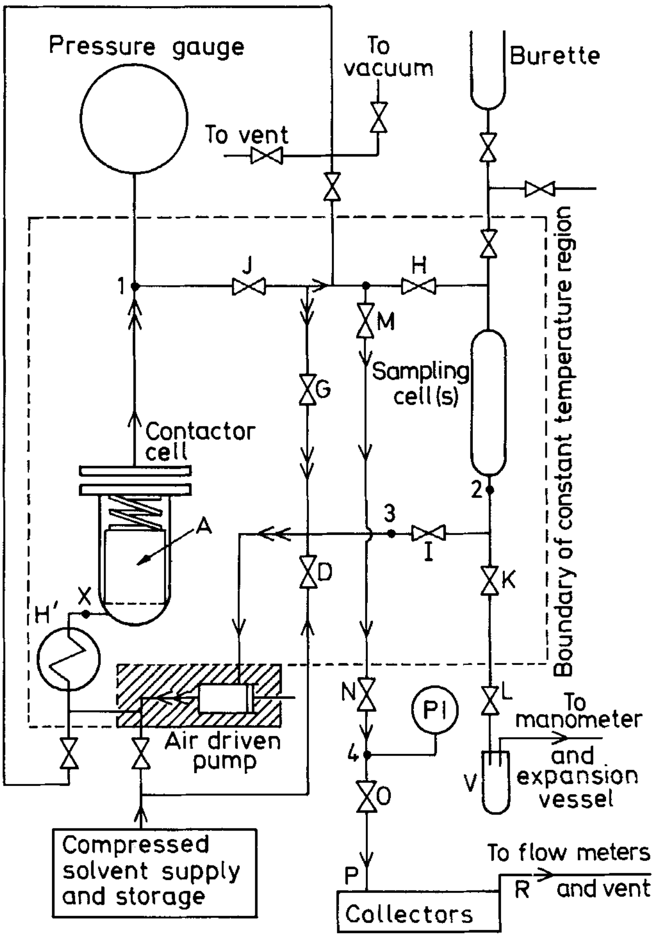

Fig. 1. Equipment for measuring extraction rates and equilibrium solubilities for solids and liquids of low volatility dissolved in near-critical solvents.

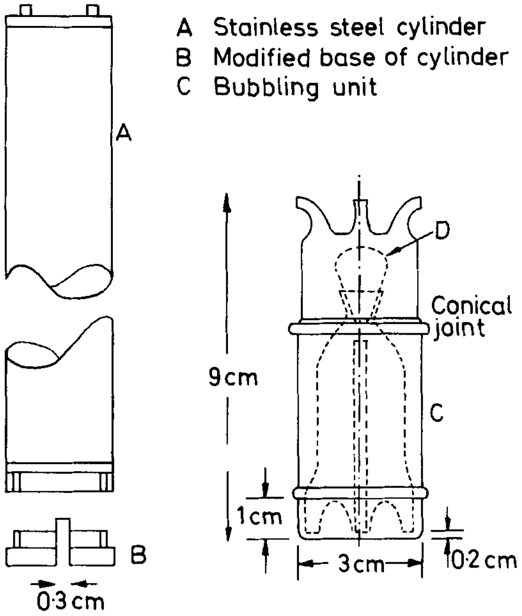

Fig. 2. Contactor used for determinations of the solubility of liquid glycerol trioleate in compressed carbon dioxide (for dimensions of cylinder see text).

2.1 Recirculation tests to determine equilibrium solubilities

When determining equilibrium data the extractant phase is recirculated through the material in the contactor cell until equilibrium has been achieved under controlled conditions of temperature and pressure (7).

In practice this was normally found to require a recirculation period of about twenty minutes for the systems studied. (Tests carried out at a set of progressively increasing recirculation periods indicated that no appreciable change in the composition of the extractant phase took place when the recirculation time was increased beyond this value.) After achieving equilibrium, a sample of the recirculating phase is isolated in the sampling cell (s) and the contents are analysed. Recirculation may either be via valve G (as indicated by double arrows on Figure 1) or via the sample cell (s). If recirculation has been via G, the cell (s) is evacuated and a sample of the recirculated phase is allowed to flow slowly into it. If recirculation has been via (s), all that is required is to close valves H and I. Having isolated the sample, valves K and L are cautiously opened and the extractant contained in (s) (in this case CO_2) is allowed to expand via glass receivers into a previously evacuated vessel of known volume (7). The amount of CO_2 in the sample is determined from the pressure rise. The amount of solute is determined by washing all deposited droplets from (s) and connecting piping into the vessel V with a suitable volatile solvent, evaporating off the solvent and weighing. This procedure gives the equilibrium amount of materials of negligible volatility (such as natural oils) present in the extractant. In the present work equilibrium concentrations (C*) were obtained for the lipid components in compressed carbon dioxide contacted with rape seed. Tests were also carried out in which liquid glycerol trioleate was equilibriated with compressed carbon dioxide at a series of temperatures and pressures.

2.2 "Once through" Extraction tests to determine loadings as a function of residence time and flow velocity through bed

When determining the approach to equilibrium achieved under varied flow conditions, extractant at the appropriate temperature and pressure is continuously injected at X, passes through the contactor cell where it makes a single contact with the material to be extracted and then flows down the line M N O P R as indicated by single arrows on Figure 1. Pressure let-down takes place at valves N and O. The product collects in the collectors below O and is weighed at intervals. The small amount of heavy component left in line N O P at the end of each interval is allowed for by washing this section of line with volatile solvent into a small receiver, evaporating and weighing. The average loading over each interval is calculated from the solvent gas passed in that interval and the product collected.

Provision is made for heating the piping between valves N and O. When carbon dioxide is used as solvent it is usually desirable to maintain the pressure in this section of line somewhat above its (inconveniently high) triple-point pressure and also to apply sufficient heat to prevent the formation of solid CO_2 at the expansion valves, thus avoiding irregularities in flow.

This form of equipment is intended primarily for the study of the extraction of lipid materials of very low volatility from oil-bearing seeds. These seeds normally contain some water and the collectors consist of a horizontal flow section at normal temperature, where sufficient residence time is allowed for the collection of more than 95% of the lipid droplets, followed by a series of collectors maintained at -80°C in which water collects. The efficiency of collection was assessed by mass balance between the oily extract collected and the weight loss (on a water-free basis) of the contents of the extractor.

A series of flow tests of this type was carried out for the extraction of ground rape seed with marginally subcritical carbon dioxide at 25°C and 70 bar. In these, as in the equilibrium tests, "low" erucic acid varieties of seed were used. These were ground until the bulk of the material lay in the size range 500 to 600 microns. Some widening of the particle size distribution took place during the extraction operation.

The temperature was measured to within ±0.1°C and remained steady during the tests to within ±0.3°C. Pressure was measured to within ±0.2% and remained steady to within ±1%. Results obtained by M. J. Barr with this equipment are discussed below.

3. RESULTS AND DISCUSSION

3.1 Extraction and equilibrium tests with rape seed at 25°C and 70 bar

The top curve in Fig. 3 gives the equilibrium loading of lipid materials in carbon dioxide at various stages during the extraction process. These data were obtained by stopping the extraction process and recirculating carbon dioxide through the bed as described in section 2.1.

Consideration of the accuracy with which the amount of heavy component in the sample bomb could be weighed and other factors, indicates that these equilibrium loadings are subject to a worst error of about ±6%.

The lower 3 curves in Figure 3 were obtained from "once through" extraction tests. They show the concentration (or "loading") of oily extract in the stream leaving the top of the contactor as a function of the percentage of the oil in the seed which has been extracted. These loadings are average values over the interval between the % extraction shown and that corresponding to the previous point in the series (or, in the case of the first point, for a % extraction of zero). Consideration of the accuracy of the integrating flow meter used to measure the amount of solvent gas passed and of the accuracy with the product collected over a given interval could be weighed suggests that these average loadings are subject to a worst error of about ±3%. The results shown are for a superficial flow velocity (v) of about 0.08 cm/sec and a series of "empty tower" residence times (τ). (τ was varied by carrying out tests at a series of bed heights for a given flow rate of CO_2. It is given by τ = (volume of bed)/(volumetric flow rate of compressed solvent). The superficial flow velocity v is given by v = (volumetric flow rate of compressed solvent)/(cross section area of bed). τ and v are considered to be subject to worst errors of ±6% and ±4% respectively.

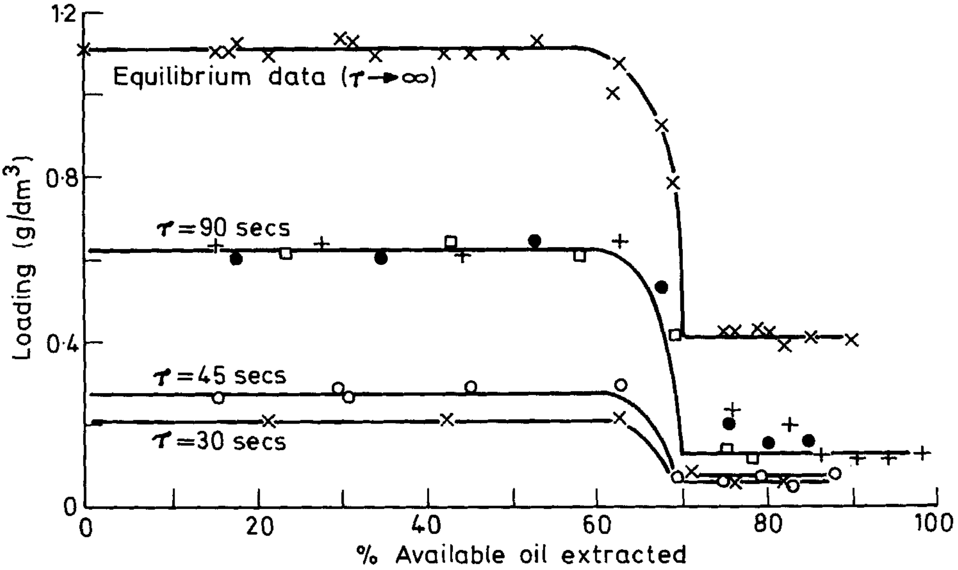

Fig. 3. Equilibrium loadings and loadings at stated residence times (τ) as function of % available oil extracted. (The flow tests were carried out at a superficial velocity of 0.08 cm/sec.) The extraction temperature and pressure were 25°C and 70 bar.

The total oil content of the seed (required in calculating the % oil extracted) was obtained by extracting the seed for 8 hours in a high pressure soxhlet extractor. A value of 39.7% was obtained in this way, which is a typical figure for rape seed.

It is seen that both the equilibrium loadings and those obtained under the above flow conditions remain substantially constant until the % oil extracted exceeds about 65%. A sharp fall then takes place in both the above loadings. Similar results were obtained under other flow conditions. A similar fall in loading has been observed by other workers (4, 10, 11, 12, 13) though they worked only under non-equilibrium conditions. Some of these workers interpret the sharp fall as being due to a progressive increase as extraction proceeds in the lengths of the diffusion paths by which the oil reaches the surfaces of the seed particles. However according to this simple diffusional picture (which neglects changes in composition of the extracted material) the equilibrium loading might be expected to remain constant during the extraction process. Figure 3 shows that this is not the case and that, in fact, the equilibrium loading mirrors that obtained under flow conditions. Extraction appears to take place in two fairly distinct stages with a sharp demarcation between them. The equilibrium loading C^* under the conditions studied is about 1 g/dm^3 in the first stage and about 0.4 g/dm^3 in the second stage. This suggests that the oil may be present in two forms, a "free" form the extraction of which is completed at the end of the first stage, and a second form which is in some way "bound". It is quite possible that the composition of the extract may be different in the two stages. Limited confirmation of this is contained in Table 1.

This table shows 'FAME' analyses giving the major fatty acid groups present in the extract obtained in two cases. The first of these is for the seed used throughout this work. The second, for comparison, is for a seed with a rather higher erucic content which was used in earlier tests. It is seen that, in both cases, a fairly sharp increase takes place in the erucic content at about the degree of extraction (65%) at which the change in loading takes place.

"Iatroscan" tests were carried out to determine the relative amounts of mono-, di- and tri-glycerides and of free fatty acids in the extracts. Mono- and di-glycerides were virtually absent for extraction less than 82% though small amounts (usually less than 5%) were found at higher levels of extraction. Free fatty acids were present to some degree at all stages of extraction, though at extractions below about 90% the average content did not exceed about 3%. However at very high levels of extraction (greater than 90%) the free fatty acid content increased markedly. Some increase in free fatty acid content has also been observed by Friedrich (2) towards the end of his extractions of Soybeans. The reason for this is not altogether clear but may be connected with some breakdown of the triglycerides at the end of the test.

Determinations were also made of the nitrogen content of seed extracted to varying degrees using the macro-Kjeldhal method (14). These revealed a small but significant decrease in nitrogen content during extraction from 3.61% initially to 2.98% by weight finally. A likely source for the nitrogen lies in the protein content of the seed. Lipo-proteins are known to be present in the membranes surrounding the oil-droplets in the seed (15). In the belief that slight transfer of hydrophobic lipoprotein into the oily part of the extract might be taking place. Folin-Lowrey (16) tests for protein have been initiated and have so far proved positive. This was not the case with a hexane extract.

3.2 Mass Transfer Coefficients

If the rate of transport of solute from an element of the solid bed to the extractant may be written in the form:

TABLE 1

Major Fatty Acid Composition (% w/w) of extracts from "low" erucic rape seed (Seed 1) under conditions illustrated in Fig. 3 Data for a higher erucic seed (Seed 2) are included for comparison in the lower part of the table.
(Seed 1 was the seed used in the remainder of this paper.)

% Available Oil Extracted	ACID GROUPS					
	Palmitic (16:0)	Stearic (18:0)	Oleic (18:1)	Linoleic (18:2)	Linolenic (18:3)	Erucic (22:1)
	SEED 1					
21	4.46	1.59	67.81	13.95	2.48	0.05
42	5.63	1.25	67.65	15.79	3.42	0.08
62	5.55	1.30	65.31	18.56	6.41	0.08
65	5.18	1.50	65.07	16.51	5.76	0.08
71	4.64	0.70	63.78	17.01	5.55	0.16
76	5.11	1.71	62.44	20.08	5.99	0.17
82	1.17	*	*	*	*	0.19
	SEED 2					
29	9.4	1.7	62.7	*	3.9	5.5
46	7.8	1.4	60.9	12.6	5.2	5.7
62	6.0	0.7	54.2	23.7	8.4	6.5
69	4.2	1.2	50.0	17.8	10.6	13.4
75	4.5	1.2	51.2	19.2	11.3	10.2
82	4.7	1.2	46.9	16.5	11.8	17.2

*Chromatographic resolution inconclusive

$$N = (\text{effective area for mass transfer}) \times (C^* - C) \times k_c \quad (1)$$

and conditions are such that k_c and C^* are constant up the bed, the dependence of solute concentration on residence time in the bed under conditions of "plug flow" is given by

$$(C_T/C^*) = 1 - \exp(-k_c a\tau) \quad (2)$$

where

N is the mass of solute extracted in unit time in the element of the tower.

C is the concentration of solute in the solvent within this element, expressed as mass of solute per unit volume of solvent.

C^* is the equilibrium value of C.

C_T is the concentration of solute in the solvent stream leaving the extraction tower.

a is the interfacial area for mass transfer per unit volume of bed.

τ is the "empty tower" residence time.

k_c is an arbitrarily defined mass transfer coefficient.

The mechanism of mass transfer from the bed of solids is probably complex, involving diffusion through pores in the solid as well as across a boundary film of solvent (10). Nevertheless, if Eq. (1) is empirically valid, $k_c a$ should provide a convenient measure of the rate of mass transfer. If this is the case and $k_C a$ is independent of residence time, a plot of $\ln(1-C_T/C^*))$ as a function of τ should be linear for a given solvent velocity. Figures 4 and 5 show such plots for the first and second periods of extraction respectively. The superficial velocity of the solvent is 0.08 cm/sec in each case. Since extraction must be zero for zero residence time these plots have been drawn to pass through the origin. Points shown as ringed crosses are derived from values of C_T taken from the curves shown in Fig. 3. The points shown as crosses are from additional single observations of C_T (Table 2). C^* is taken in every case from the curve in Fig. 3. Systematic deviation from linearity is not apparent in either figure indicating that equations 1 and 2 satisfactorily represent the mass transfer rate in both extraction periods.

The results of earlier tests (17) are also satisfactorily represented by Equation 2. For a given solvent at given

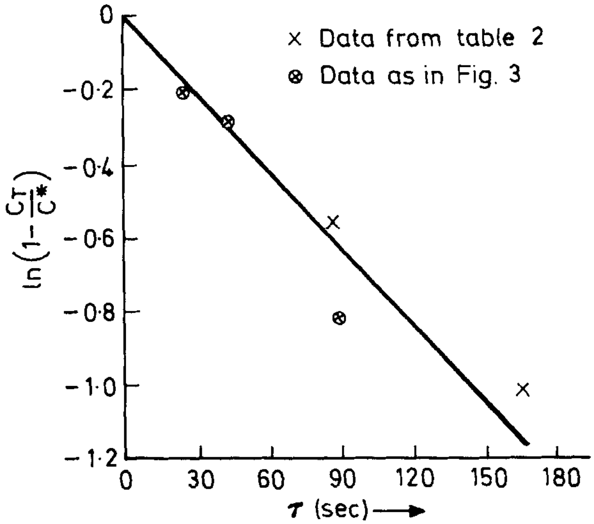

Fig. 4. Period 1. k_ca = (-slope) = 0.0087 sec^{-1}. v = 0.08 cm/sec.

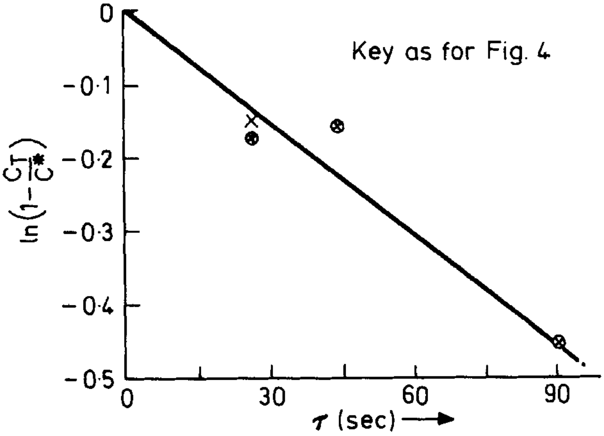

Fig. 5. Period 2. k_ca = (-slope) = 0.0050 sec^{-1}. v = 0.08 cm/sec.

temperature and pressure, the parameter $k_c a$ would be expected to depend on the nature of the bed and on the superficial flow velocity (v) of solvent.

If $k_c a$ can be established as a function of these parameters the design of larger scale plant from laboratory tests should be facilitated. Tests were therefore carried out in which flow velocity was varied. The results are shown in Table 2. It appears that, within the scatter, $k_c a$ in the first period is an increasing function of solvent velocity.

3.3 Equilibrium loadings for rape seed compared with equilibrium solubilities of glycerol trioleate in compressed CO_2

Determinations were made of the equilibrium loading of lipid material in carbon dioxide contacted with freshly ground rape seed as a function of temperature and pressure (Fig. 6). These loadings agree well with data for Soya bean oil obtained by Quirin (18).

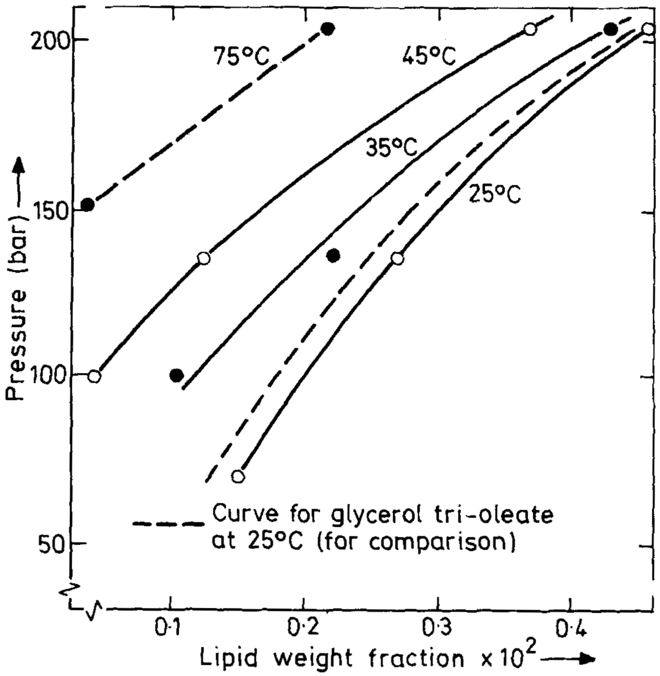

Fig. 6. Equilibrium loading of lipid material in CO_2 extract of fresh ground rape seed as function of pressure and temperature.

TABLE 2

Data used in establishing k_ca as a function of solvent velocity (Extraction conditions: 25°C, 70 bar. In these calculations C^* in periods 1 and 2 is taken as 1.11 and 0.41 g/dm^3 respectively. The values of (k_ca) shown are considered to be subject to a worse error of about ±10%).

Extraction period	C_T (g/dm^3)	v (cm/sec)	τ (sec)	k_ca (sec^{-1})
1	0.150	0.038	56	0.0026
1	0.271[1]	0.047	81	0.0035
2	0.138[2]	0.047	79	0.0053
1	0.669	0.052	144	0.0064
1	0.275	0.052	42	0.0068
1	0.704	0.078	173	0.0058
1	0.475	0.08	91	0.0062
1	-	0.08	-	0.0087[3]
2	-	0.08	-	0.0050[4]
1	0.594	0.11	70	0.011
1	0.718	0.121	62	0.017

1. Average of four determinations at % extraction <65%
2. Average of two determinations at % extraction >65%.
3. From Fig. 3 and 4.
4. From Fig. 3 and 5.

Similar determinations were made for carbon dioxide equilibrated with liquid glycerol trioleate. (Glycerol trioleate is a typical constituent of rape seed oil.) In this case the glycerol trioleate was placed in the contactor shown in Fig. 2 and equilibrium was achieved by recirculating carbon dioxide through it. The glycerol trioleate used was of 98% purity initially. Samples of the extracts and residues from these tests were analysed to confirm that decomposition was negligible.

The results are given in Fig. 7. It is seen that the equilibrium loadings for glycerol trioleate are about 20% lower than for the rape seed. This difference is significant (the equilibrium loadings shown are believed to be accurate within a worst error of ±6%). It probably arises from the fact that, although the initial rape extract consists predominantly of triglycerides, only about 68% of the acid groups present are oleic groups (see Table 1). Exact correspondence with the behaviour of

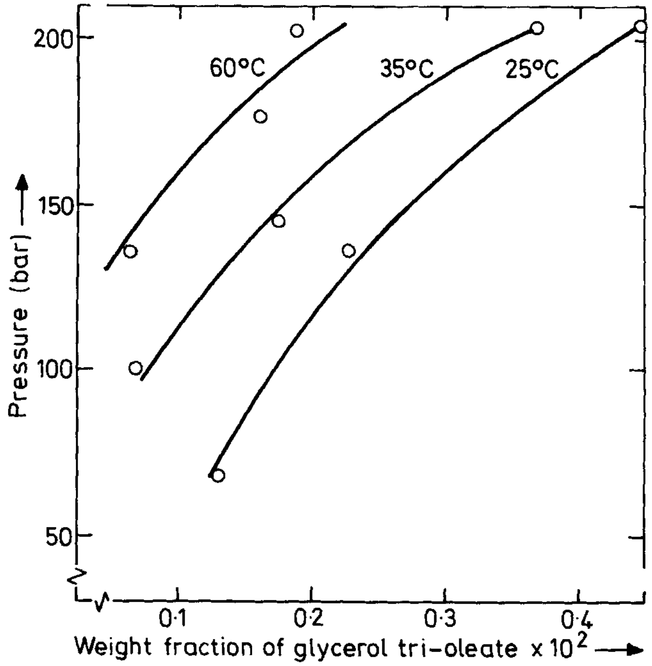

Fig. 7. Solubility of liquid glycerol trioleate in compressed carbon dioxide as function of pressure and temperature

glycerol trioleate would not therefore be expected. Furthermore, as noted in Section 3.1, small amounts of free fatty acids were detected in the rape seed extract. These extract considerably more readily than do the corresponding glycerides.

It may be seen from Figs. 6 and 7 that in the range covered by these tests lipid solubility in compressed carbon dioxide at given pressure decreases with increase in temperature. This is typical of the behaviour of solutes of low volatility at pressures extending over a limited range above the critical pressure of the compressed extractant. Soy bean oil, for example, shows this behaviour in compressed carbon dioxide at pressures up to about 250 bar (18) while the extract from Pinex wood chips shows it at pressures up to about 185 bar (8). At higher pressures, solubility in these cases increases with increasing temperature at given pressure. The exact interpretation of this behaviour is complex. In essence however it may be regarded as due to the competing effects of the reduction in solvent density and the increase in solute volatility which accompany the temperature rise. Decreasing solvent density decreases the probability of a given solute molecule in the extractant phase interacting with a solvent molecule, tending to decrease solubility (7). Increasing solute volatility, on the other hand, increases the escaping tendency of the solute from the condensed phase thus tending to increase solubility. At the pressures and temperatures considered in the present paper solvent density decreases comparatively rapidly with isobaric increase in temperature and it is the effect of this factor on solubility which predominates. At higher pressures than these the influence of temperature on density becomes less marked and an increase in solubility with temperature would be anticipated, as in the case of Soy bean oil (18).

4. CONCLUSIONS

1. In our tests on the extraction of rape seed with liquid carbon dioxide we find that, for a constant extractant flow rate, the oil content of the extract phase following a single contact with the seed bed remains approximately constant until about 60 or 70% of the oil present has been extracted. With further extraction of oil, the oil content of the extract phase (i.e. the "loading") falls sharply. The equilibrium loading behaves in a rather similar way, suggesting that the effect is more probably due to the presence of the oil in two forms than to diffusional effects. There is evidence that the change in loading is associated with some change in composition of the extract: the analyses reported in Table 1 show a marked increase in the content of the Erucic acid group at the higher levels of extraction.

2. Values of the mass transfer parameter $k_c a$ (defined in Eq. 1) range between 0.3×10^{-2} sec^{-1} and 1.7×10^{-2} sec^{-1} for the conditions we have studied. This parameter is not significantly

dependent on residence time but appears to be an increasing function of solvent velocity. Knowledge of this empirically defined parameter should facilitate scale-up calculations, though further work is required to establish its practical utility in representing the complex phenomena involved in the extraction of natural products.

3. Equilibrium loadings in the first extraction period agree quite closely with solubility data for glycerol trioleate, which is a typical constituent of rape seed oil.

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