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TERNARY PHASE EQUILIBRIA OF THE ISO-PROPANOL+WATER+CARBON DIOXIDE SYSTEM AT HIGH PRESSURE

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Abstract–Ternary phase diagrams are presented for the system: iso-propanol(IPA)+water+carbon dioxide at temperatures from 15 to 70 °C and pressures from 7 to 17 MPa. The distribution coefficients of IPA between the dense phase carbon dioxide and water changed dramatically with temperature and pressure. In the vicinity of the critical point, distribution coefficients was low, yet at liquid-like densities carbon dioxide had a high affinity for IPA. Selectivity reversal was observed at differing pressures. High selectivity of CO_2 for IPA was achieved in the near-critical liquid and in supercritical carbon dioxide at high pressure.

Key words : Phase Equilibria, Iso-Propanol, Carbon Dioxide, Water, Supercritical Fluid Extraction

INTRODUCTION

Extraction of alcohols from aqueous solutions, such as those produced from fermentation broths, has long been of interest in chemical and food engineering. In general, separation employs the traditional methods of distillation and liquid extraction, both of which are energy intensive and inefficient when a pure alcohol is required. Near- and supercritical fluid extraction is an alternative separation technique rapidly gaining favour in the food industry. In particular, the technique has the potential to split azeotropes and otherwise recover alcohols from aqueous solutions.

The popularity of supercritical fluids stems in part from their unusual properties. Specifically, properties can often be finely tuned to give good separations so leading to improved separation efficiency, reduced energy requirements and easier handling. With such advantages, attention to supercritical fluid technology is increasing.

In aqueous alcohol extraction a good solvent displays high capacity for alcohol and good rejection of water. Capacity is characterised by solubility, whereas selectivity (reflected in the distribution coefficient) determines ease of extraction [Chrastil, 1982; Hemmaplardh et al., 1972].

Experience shows that in the vicinity of the critical point the distribution coefficient often changes greatly with only slight changes in pressure and temperature. Thus to fully understand solvent behaviour it is necessary to study distribution coefficients under these conditions and with care.

Several studies have reported on ethanol dehydration with dense phase (liquid and supercritical) carbon dioxide [McHugh et al., 1981; Paulaitis et al., 1985; DiAndreth and Paulaitis, 1988; Lim and Lee, 1994; Adrian et al., 1996]. Magashi and Wilkinson [1990] studied the recovery of wine flavour components with liquid carbon dioxide at 6.0 MPa and temperatures between 0 °C and 20 °C. They found that the yield of extract increased when the ratio of solvent to feed was above 4 and extraction of volatile flavours from wine distillate was more economical than from wine.

Chun and Wilkinson [1995, 1996], and Chun et al. [1995] measured the mass transfer of lower primary alcohols (C_1 to C_4) from water to carbon dioxide in a spray column at 25 °C to 45 °C and 7 to 15 MPa. They found that the mass transfer efficiency of dense carbon dioxide was more than double that of a conventional liquid solvent.

Studies such as the above were limited to rather narrow ranges of temperature and pressure. The purpose of this work, therefore, was to extend the range of conditions for phase equilibria on the system IPA+water+carbon dioxide.

EXPERIMENTAL

There are several accepted techniques for measurement of high pressure phase equilibria. Each has strengths and weaknesses. Fig. 1 shows the phase equilibrium apparatus used here. The well-established flow technique was used, as shown in Fig. 1. The apparatus incorporates a view cell for phase separation and visualisation.

The cell was mounted vertically in a constant temperature air chamber where the large heat capacity kept thermal fluctuations within the cell to less than the limit of measurement ±0.02 °C. High purity cylinder carbon dioxide was chilled to −15 °C before being pumped to the cell. The reagent-grade IPA+water (Milli-Q) solution was delivered by a second high pressure metering pump.

The two streams were mixed and brought to temperature using a length of crimped, coiled tube. Equilibrium between the phases was confirmed by runs at different flow rates and by

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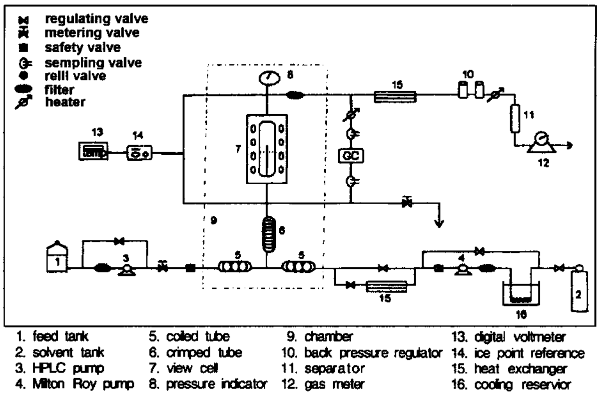

Fig. 1. Phase equilibrium apparatus.

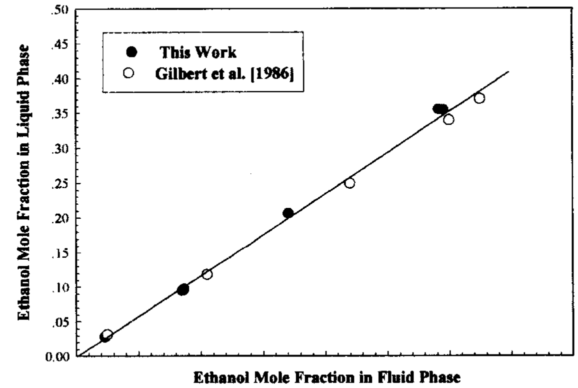

Fig. 2. Phase equilibrium at temperature, 35 °C and pressure, 10.34 MPa.

comparison with published data on ethanol+water+CO_2 [Gilbert et al., 1986] (vide Fig. 2).

Phase separation occurred in the view-cell which was also used to check on the interface level and freedom from entrainment. The phases left the equilibrium cell via insulated lines

Table 1. Equilibrium tie line data for : IPA-water-carbon dioxide at various pressures and temperatures

Light phase mole fraction			Heavy phase mole fraction			Distribution coefficient		Selectivity
y_{IPA}	y_{H2O}	y_{CO2}	x_{IPA}	x_{H2O}	x_{CO2}	m_s	m_w	λ
				T=15 °C, P=10.34 MPa				
0.0042	0.0035	0.9923	0.0111	0.9645	0.0244	0.164	0.0016	105.1
0.0080	0.0034	0.9886	0.0200	0.9539	0.0261	0.177	0.0016	112.6
0.0230	0.0054	0.9716	0.0469	0.9263	0.0269	0.229	0.0027	83.4
0.0903	0.0217	0.8880	0.0908	0.8827	0.0265	0.499	0.0123	40.5
0.1344	0.0427	0.8229	0.1169	0.8483	0.0349	0.609	0.0266	22.9
0.1489	0.0523	0.7988	0.1289	0.8318	0.0394	0.627	0.0341	18.4
				T=25 °C, P=6.89 MPa				
0.0016	0.0181	0.9803	0.0116	0.9744	0.0140	0.059	0.0080	7.4
0.0032	0.0153	0.9815	0.0245	0.9616	0.0139	0.058	0.0071	8.3
0.0116	0.0074	0.9809	0.0663	0.9134	0.0203	0.085	0.0040	21.5
0.0780	0.0227	0.8992	0.1178	0.8632	0.0191	0.348	0.0138	25.2
0.1666	0.0644	0.7690	0.2795	0.5906	0.1299	0.439	0.0803	5.5
0.1984	0.0867	0.7149	0.3300	0.3699	0.3001	0.531	0.2069	2.6
				T=25 °C, P=8.27 MPa				
0.0043	0.0059	0.9898	0.0094	0.9716	0.0190	0.196	0.0026	74.4
0.0099	0.0061	0.9841	0.0187	0.9614	0.0199	0.231	0.0028	83.6
0.0319	0.0063	0.9618	0.0463	0.9372	0.0165	0.316	0.0031	102.0
0.0865	0.0208	0.8928	0.0783	0.9019	0.0198	0.537	0.0112	48.0
0.1972	0.0938	0.7091	0.3075	0.4846	0.2079	0.521	0.1572	3.31
0.1879	0.0834	0.7287	0.2957	0.5116	0.1927	0.502	0.1289	3.9
				T=35 °C, P=8.27 MPa				
0.0021	0.0169	0.9810	0.0105	0.9702	0.0194	0.087	0.0076	11.49
0.0048	0.0210	0.9742	0.0230	0.9598	0.0172	0.093	0.0097	9.52
0.0130	0.0132	0.9737	0.0660	0.9176	0.0164	0.095	0.0070	13.67
0.0159	0.0058	0.9783	0.1272	0.8394	0.0334	0.069	0.0038	18.20
0.0109	0.0050	0.9841	0.1051	0.8690	0.0258	0.054	0.0030	18.00
0.0299	0.0124	0.9578	0.3168	0.4536	0.2296	0.080	0.0230	3.46
0.0512	0.0147	0.9341	0.3089	0.3056	0.3856	0.557	0.2534	2.200
				T=40 °C, P=10.34 MPa				
0.0052	0.0059	0.9889	0.0072	0.9725	0.0202	0.310	0.0026	118.9
0.0353	0.0104	0.9543	0.0421	0.9381	0.0198	0.384	0.0051	75.9
0.1033	0.0533	0.8434	0.1101	0.8504	0.0395	0.501	0.0335	15.0
0.1890	0.0830	0.7281	0.2147	0.6409	0.1444	0.604	0.0888	6.80
0.2111	0.1166	0.6723	0.2336	0.5322	0.2342		0.1675	4.13
0.2961	0.2933	0.4106	0.2178	0.1223		1.465	2.5829	0.57

Table 1. continued

Light phase mole fraction			Heavy phase mole fraction			Distribution coefficient		Selectivity
y_{IPA}	y_{H2O}	y_{CO2}	x_{IPA}	x_{H2O}	x_{CO2}	m_s	m_w	λ
T=45 °C, P=12.41 MPa								
0.0056	0.0101	0.9843	0.0095	0.9695	0.0210	0.2557	0.0045	56.8
0.0121	0.0093	0.9786	0.0152	0.9647	0.0201	0.3458	0.0042	82.0
0.0411	0.0116	0.9473	0.0403	0.9385	0.0212	0.4655	0.0057	82.2
0.1211	0.0379	0.8410	0.0825	0.8884	0.0291	0.7260	0.0211	34.4
0.1561	0.0611	0.7829	0.1033	0.8587	0.0380	0.7851	0.0370	21.2
0.2023	0.0999	0.6979	0.1114	0.8513	0.0373	0.9624	0.0622	15.5
0.2998	0.3450	0.3552	0.1252	0.8285	0.0463	1.4707	0.2558	5.8
T=65 °C, P=13.79 MPa								
0.0052	0.0202	0.9746	0.0064	0.9759	0.0176	0.348	0.0089	39.1
0.0147	0.0141	0.9712	0.0172	0.9643	0.0185	0.374	0.0064	58.4
0.0310	0.0164	0.9527	0.0347	0.9455	0.0198	0.405	0.0078	51.6
0.0536	0.0161	0.9303	0.0564	0.9205	0.0231	0.448	0.0083	54.2
0.0961	0.0341	0.8698	0.2797	0.4782	0.2421	0.278	0.0576	4.8
0.1578	0.0655	0.7767	0.2831	0.2227	0.4943	0.532	0.2805	1.9
T=65 °C, P=17.23 MPa								
0.0137	0.0140	0.9723	0.0113	0.9691	0.0196	0.525	0.0063	84.0
0.0185	0.0139	0.9676	0.0156	0.9646	0.0198	0.519	0.0063	82.4
0.1835	0.0865	0.7300	0.0858	0.8730	0.0411	1.085	0.0503	21.6
0.1595	0.0678	0.7727	0.0783	0.8891	0.0326	1.007	0.0377	26.7
0.2583	0.1870	0.5547	0.0925	0.8689	0.0386	1.478	0.1139	13.0
T=70 °C, P=13.79 MPa								
0.0126	0.0151	0.9722	0.0182	0.9639	0.0179	0.305	0.0069	44.2
0.0148	0.0152	0.9700	0.0194	0.9628	0.0178	0.336	0.0069	48.3
0.0652	0.0211	0.9138	0.1628	0.7623	0.0749	0.241	0.0167	14.5
0.0642	0.0215	0.9143	0.1600	0.7671	0.0730	0.240	0.0168	14.3
0.0619	0.0220	0.9161	0.1418	0.7971	0.0610	0.251	0.0159	15.8
0.0697	0.0227	0.9076	0.3003	0.4346	0.2652	0.196	0.0440	4.5
0.0684	0.0228	0.9088	0.3000	0.4333	0.2667	0.192	0.0444	4.3
T=70 °C, P=17.23 MPa								
0.0074	0.0156	0.9769	0.0061	0.9747	0.0192	0.524	0.0069	76.1
0.0104	0.0186	0.9710	0.0084	0.9725	0.0190	0.534	0.0082	64.7
0.0374	0.0175	0.9451	0.0274	0.9518	0.0209	0.610	0.0082	74.4
0.0630	0.0213	0.9157	0.0447	0.9313	0.0240	0.650	0.0105	61.6
0.1174	0.0432	0.8395	0.0654	0.9047	0.0299	0.864	0.0230	37.6
0.1536	0.0658	0.7805	0.0809	0.8824	0.0367	0.949	0.0373	25.5
0.3014	0.4672	0.2314	0.0993	0.8674	0.0333	1.907	0.3383	5.6

with minimal pressure drop. This ensured integrity of the phase compositions by preventing phase separation in the sample lines. Tests showed this arrangement, operated with care, achieved reliable results.

The interface level in the cell was controlled by manual adjustment of the metering valve. Pressure was set by the back-pressure regulator and measured by a precision Bourdon tube gauge to ±70 kPa (calibrated at the operating pressure). The exit streams were analysed by in-line sampling and direct injection into a gas chromatograph equipped with a short column and TCD. The TCD responded to all components of the mixture and had more than adequate sensitivity for the purpose. The chromatograph was calibrated at pressure against standard mixtures. Streams were sampled at 10 minutes intervals, with steady-state being achieved within ~45 minutes.

RESULTS AND DISCUSSION

Although ternary mixtures present more difficulties in interpreting phase behaviour than binary systems, much can be inferred about them from their related binary mixtures. In alcohol+water+carbon dioxide mixtures, two completely miscible components, alcohol and water are separated by the largely immiscible solvent, carbon dioxide. When an alcoholic solute is extracted from water, small amounts of the water are inevitably coextracted into the solvent.

The separability of alcohol from water by a solvent is conveniently expressed by the selectivity, λ, defined as :

$$\lambda=\frac{m_s}{m_w}$$

Where m_s and m_w are the distribution coefficients based on mass concentration of IPA in CO_2 (solvent) and water respectively. Fugacity coefficients can also be used to express the distribution coefficient between phases for each component, thus :

$$m_i=\frac{y_{wi}}{x_{wi}}=\frac{\varphi_i^L}{\varphi_i^V}$$

Data for the present system were obtained in the ranges of temperature 15 to 70 °C and pressure 7 to 17.23 MPa, chosen to span the CO_2 critical zone. The data were summarized in

Table 1. Results are discussed in terms of distribution coefficients, selectivity and ternary phase diagrams. The density of carbon dioxide was obtained from the IUPAC tables [Angus et al., 1976] interpolated using a localised Peng-Robinson equation of state [Peng and Robinson, 1976].

Fig. 2 shows data for ethanol+water+CO_2 at 35 °C, 10.32 MPa obtained with the present set-up, comparing favourably with those of Gilbert et al. [1984]. In Fig. 4 the data on the IPA+water+CO_2 system at 40 °C compare very favourably with that of Paulaitis et al. [1983].

1. Distribution Coefficients

Fig. 3 presents selected isotherms at various pressures. Generally, the solubility of IPA was greater in the aqueous than CO_2 phase. However at 70 °C and 17.23 MPa, more IPA dissolved in the dense gas phase; a behaviour only partly explained by pressure (Compare Fig. 9, 10).

Fig. 5 shows the variation of distribution coefficient with CO_2 density where coefficients generally increased with increasing density. However there were exceptions. In the case of the 25 °C isotherm, a decrease was observed at high pressure when the solvent density exceeded ~850 kg/m^3 (i.e., redecued density, ρ_{r,CO_2} >1.8). Again, at 65 °C the distribution coefficient decreased only slightly at the low pressure end when solvent densities fell below ~400 kg/m^3 (ρ_{r,CO_2}< 0.85).

In the design of extraction processes, solvent selectivity is perhaps of even greater significance than solvent capacity. The sensitivity of selectivity to conditions is particularly evident in the near-critical liquid region where solvent compressibility is high.

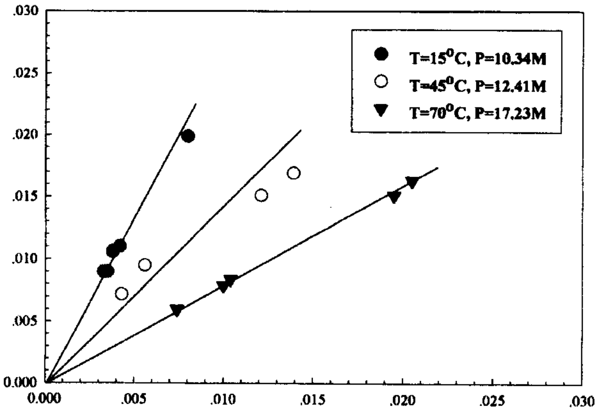

Fig. 3. Equilibrium isotherms for IPA-water-CO_2.
(The 'fluid' phase is CO_2 rich, 'liquid' is H_2O rich)

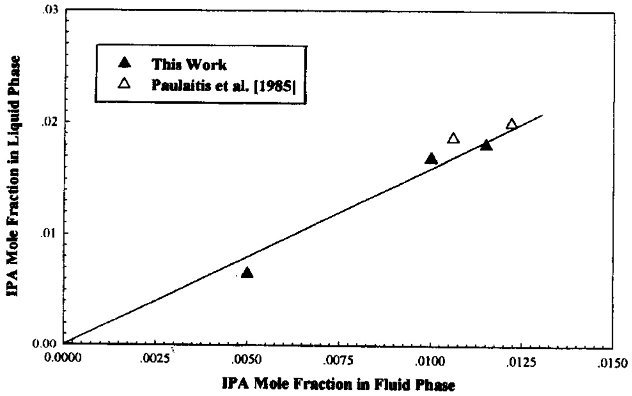

Fig. 4. Comparison of equilibrium data at 40°C and 10.34 MPa.
(The 'fluid' phase is CO_2 rich, 'liquid' is H_2O rich)

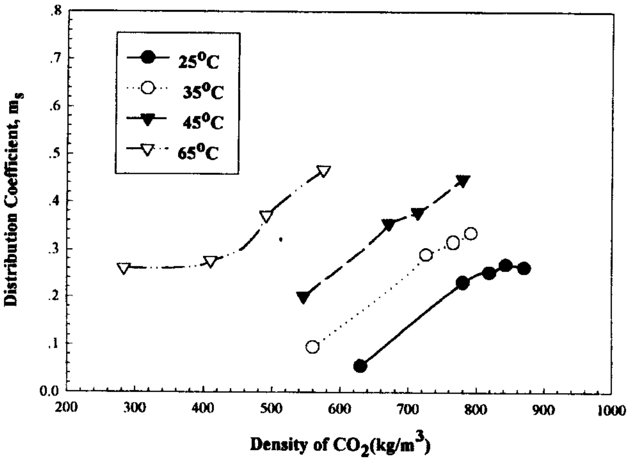

Fig. 5. Distribution coefficient of IPA in the system : IPA-water-CO_2.

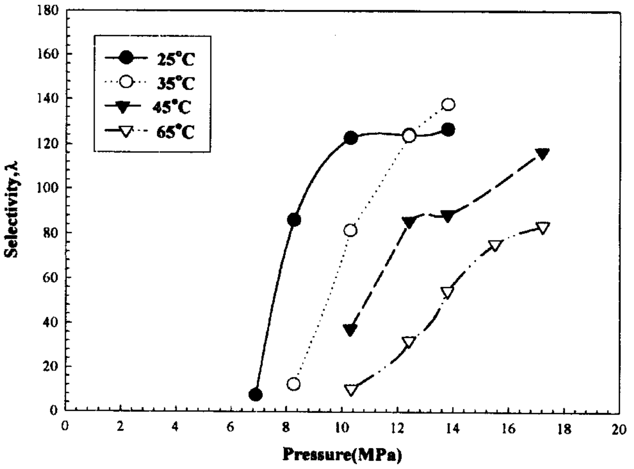

Fig. 6. Selectivity of CO_2 for IPA in H_2O as a function of pressure.

Fig. 6 shows the dependence of solvent selectivity, λ, on pressure and temperature. Generally selectivity increased with pressure and decreased with temperature. In the case of the 25 and 35 degree isotherms, it is interesting to note the selectivity cross-over at high pressure. This is related to the well-known solubility cross-over effect observed in some solid+CO_2 binaries.

2. Phase Diagrams ; IPA+Water+CO_2

Fig. 7 to 10 are representative of phase behaviour at 25 °C, 35 °C and 70 °C. Full experimental data are given in the tables. At 25 °C (Fig. 7) the IPA solute generally favoured the aqueous phase except between 0.0396 and 0.20698 mass fraction IPA. At these conditions the loading of IPA and water in the light (CO_2) phase, and of CO_2 in the dense phase, were less than 20 and 9 mole % respectively.

The selectivity of the solvent for IPA over water decreased with increasing dilution of the solvent. At 35 °C (Fig. 8) the tie lines largely inclined towards the CO_2 rich phase when the

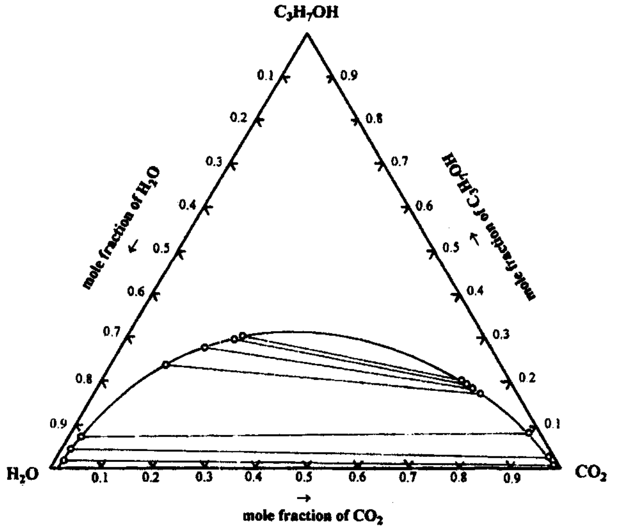

Fig. 7. Phase equilibrium tie lines at T=25 °C and P=8.27 MPa.

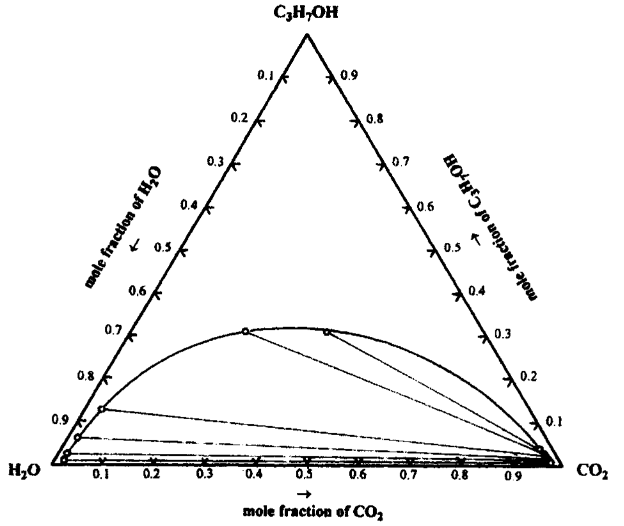

Fig. 8. Phase equilibrium tie lines at T=35 °C and P=8.27 MPa.

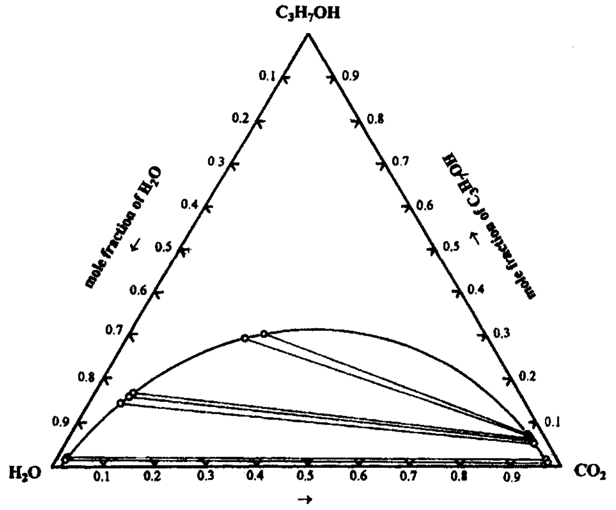

Fig. 9. Phase equilibrium tie lines at T=70 °C and P=13.79 MPa.

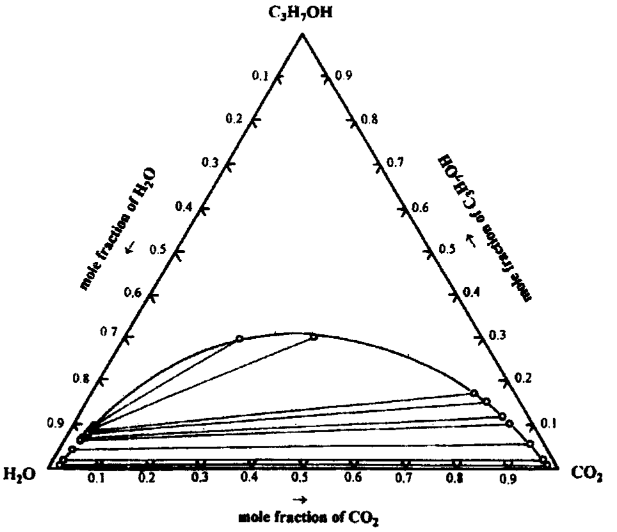

Fig. 10. Phase equilibrium tie lines at T=70 °C and P=17.23 MPa.

loading of IPA in the solvent was less than 5 mole %. The weak solvating power of the CO$_2$ is attributed to its low density of 560 kg/m^3 (ρ_{r,CO_2}= 1.195).

The phase behaviour at 70 °C, and at 13.79 and 17.23 MPa is shown in Figs. 9 and 10. Interestingly, selectivity reversed between these two pressures. The reason for this is unclear, but the observation clearly demonstrates not only the strong influence of pressure on solubility in the supercritical state but also the scrupulous care in interpolating limited data.

CONCLUSIONS

Phase equilibria and distribution coefficients are reported for IPA+water+carbon dioxide. In the vicinity of the critical point distribution coefficients are low, but at liquid-like densities, the carbon dioxide becomes a much stronger solvent for the alcohol. High selectivity for IPA is experienced in near-critical liquid and in supercritical carbon dioxide at high pressure.

This ternary system unusual phase behavior. For distribution coefficients less than 0.35 the tie lines incline toward the carbon dioxide-rich phase, while at higher distribution coefficients the tie lines slope toward the water-rich phase. Thus IPA can be made to favour either the water or carbon dioxide phase as desired, depending on the conditions selected for extraction.

ACKNOWLEDGEMENT

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NOMENCLATURE

m : distribution coefficient based on mass [-]

Greek Letters

β : extraction factor [-]
φ : fugacity coefficient [-]
λ : selectivity [-]

ρ : density [kg·m^{-3}]

Superscripts

L : liquid phase
V : gas or vapour phase

Subscripts

c : critical condition
i : component no.
IPA : iso-propanol
r : reduced condition
s : solute, alcohol
w : carrier, water

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