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Phase equilibrium study for the separation of ethanol–water solution using subcritical and supercritical hydrocarbon solvent extraction

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ABSTRACT

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In order to dehydrate fermented or synthetic crude ethanol, phase equilibria for subcritical and supercritical solvents (CO_2, C_2H_4, C_3H_6, C_3H_8, n-C_4H_{10} and $CO_2 + C_3H_8$) and ethanol aqueous solution (ethanol concentrations of 2–99 wt.%) were measured. For these solvents the selectivity and solubility of ethanol under different conditions were investigated. We confirmed experimentally that ethanol–water solution can be separated completely by supercritical and subcritical propane or proylene solvent extraction, as has been predicted previously using the group contribution equation of state model proposed by Brignole et al. (Brignole, E.A., Skjold-Jorgensen, S. and Fredenslund, A., 1984. Ber. Bunsenges. Phys. Chem., 88: 801. Brignole, E.A., Anderson, P.M. and Fredenslund, A., 1987. Ind. Eng. Chem. Res. 26: 254–261.)

INTRODUCTION

Dehydration of fermented or synthetic crude ethanol (ethanol concentrations of 5–40 wt.%) requires a large amount of energy. In the last 10 years many studies have been made on near-supercritical or supercritical fluid extraction processes that offer the possibility of energy savings.

The CO_2 solvent has been intensively investigated. Nagahama et al. (1988), Furuta et al. (1989) and Brignole et al. (1984, 1987) reported that

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the azeotropic concentration could be broken using CO_2 solvent at 313 K and 3.9–5.8 MPa, 333 K and 10 MPa, and liquid CO_2 (293 K) respectively.

Meanwhile, Inomata et al. (1990) and Abboud et al. (1984) reported that the azeotropic concentration could be broken by addition as entrainers of glycol and 2-ethylhexanol, respectively, into the CO_2 solvent.

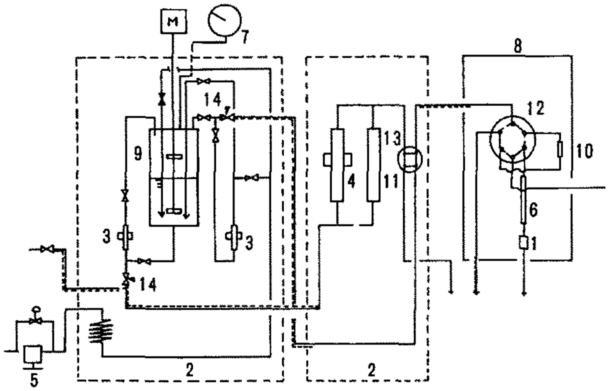
As mentioned above, the CO_2 solvent extraction method can be improved for ethanol selectivity by choosing the optimum temperature, pressure and entrainer. However, the ethanol solubility does not increase significantly. In addition, previous studies have not shown any clear advantage in terms of energy saving in comparison with ordinary distillation.

The solubility of ethanol may be increased by using a hydrocarbon solvent having a high affinity for ethanol, but only a few studies of the extraction using hydrocarbon solvents have been reported. Coenen (1987) extracted fermented alcohol and reported that CO_2 was a better solvent than C_2H_4 and C_2H_6. McHugh et al. (1983) measured phase equilibria for the C_2H_6–C_2H_5OH–H_2O system and estimated its behaviour using the Peng–Robinson equation of state (EOS). (Peng and Robinson, 1976). Although we found no paper describing experiments of ethanol extraction using C_3H_8 as solvent, Brignole et al. (1984, 1987) developed an EOS using the group contribution method applicable to high pressures, determined group parameters, and simulated the ethanol extraction process using C_3H_8 as solvent. They concluded that C_3H_8 is a promising solvent which can save energy and concentrate ethanol up to absolute ethanol, but no one has yet demonstrated this experimentally. Nakayama et al. (1988) used 1,1-difluoroethane (DFE) as solvent, and concluded that this had a higher solubility than CO_2.

On the basis of the above facts, we carried out an experimental investigation of promising solvents by measuring the phase equilibria systematically for aqueous ethanol solution with CO_2, hydrocarbon solvents (C_2H_4, C_3H_6, C_3H_8 and n-C_4H_{10}) and a mixed solvent ($CO_2 + C_3H_8$).

EXPERIMENTAL APPARATUS AND PROCEDURE

The phase equilibrium apparatus (Fig. 1) incorporated the advantages of the static method described by Takishima et al. (1986) and the flow method described by Inomata et al. (1990). The mixture was held in a cell (1.0 l), agitated, and mixed at a specified temperature and pressure. Mixing was then stopped and the gas and liquid phases were slowly circulated using a magnetic pump. The gaseous and liquid phases were withdrawn continuously through a metering valve from the circulation line, at a minimum flow rate, so as not to disturb the phase equilibrium in the cell. The samples were heated to about 150°C and fully gasified at atmospheric pressure. By keeping constant the adsorption equilibria of ethanol and water within the sampling tube, errors due to adsorption of ethanol and water were eliminated. The samples were



1	TCD detector	8	Process gas chromatography
2	Air bath heater	9	Equilibrium cell
3	High pressure magnetic pump	10	Sampler
4	Low pressure magnetic pump	11	Surge tank
5	Solvent feed pump	12	6-way valve
6	Packed column	13	4-way valve
7	Pressure gage	14	Needle valve

Fig. 1. Schematic flow diagram of the apparatus used to measure the high pressure phase equilibria.

analysed using a process gas chromatograph with a Porapak QS 80/100 mesh (4.2 m) and a preset cycle time. The purity of the samples used in these experiments were as follows: CO_2, 99.99 vol.%; C_2H_4, 99.5 vol.%; C_3H_6, 99.8 vol. %; C_3H_8, 98.9 vol.%; n-C_4H_{10}, 98.5 vol.%; ethanol, more than 99.5 vol.%; water, distilled.

RESULTS FOR EXTRACTION OF ETHANOL

CO_2–H_2O system

Figure 2 shows the phase equilibria for the CO_2–H_2O system at 304 K and 3–15 MPa. Both the gas and the liquid phase compositions agree well with the results of Wiebe and Gaddy (1940, 1941) and Takishima et al. (1986).

CO_2–C_2H_5OH–H_2O system

Figures 3 and 4 show the ethanol–water selectivity curves and the solubility of ethanol in the CO_2 phase for the CO_2–C_2H_5OH–H_2O system at 293, 313 and 383 K at 9.905 MPa pressure. The measured data are given in Table 1.

As shown in Fig. 3, the maximum extracted ethanol concentrations (free of CO_2) are 90–92 wt. % at 293 and 313 K, i.e. near the critical temperature of CO_2.

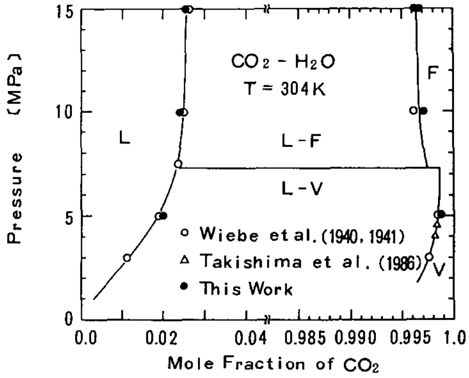


Fig. 2. Phase equilibria for the CO_2–H_2O system at 304 K.

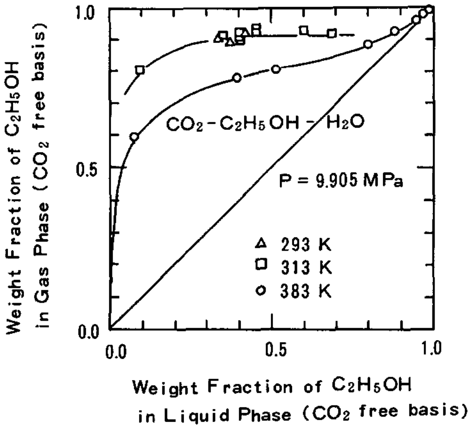


Fig. 3. Ethanol–water selectivity in the CO_2–C_2H_5OH–H_2O system at 9.905 MPa.

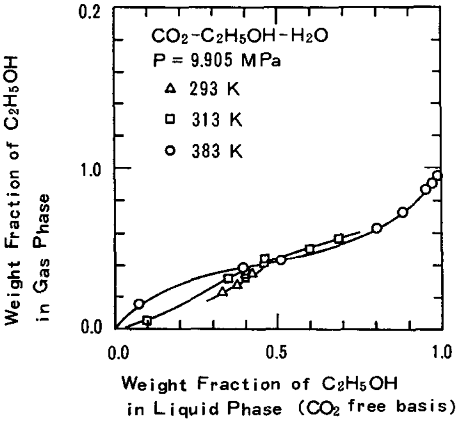


Fig. 4. Solubility of ethanol in the CO_2–C_2H_5OH–H_2O system at 9.905 MPa.

TABLE 1

Phase equilibria for the CO_2–C_2H_5OH–H_2O system at 9.905 MPa

Temperature (K)	Weight fraction[a]					
	Heavy phase			Light phase		
	CO_2	C_2H_5OH	H_2O	CO_2	C_2H_5OH	H_2O
293	NA	0.3300	0.6700	0.9743	0.0235	0.0022
	NA	0.3750	0.6250	0.9684	0.0279	0.0038
	NA	0.4190	0.5810	0.9659	0.0349	0.0028
313	NA	0.1000	0.9000	0.9930	0.0057	0.0013
	NA	0.3500	0.6500	0.9662	0.0312	0.0026
	NA	0.6000	0.4000	0.9443	0.0504	0.0053
	NA	0.6900	0.3100	0.9363	0.0586	0.0051
	NA	0.4000	0.6000	0.9590	0.0378	0.0032
	NA	0.4000	0.6000	0.9595	0.0369	0.0037
	NA	0.4000	0.6000	0.9634	0.0332	0.0034
	0.1161	0.4082	0.4755	0.9527	0.0437	0.0035
	0.1100	0.4113	0.4786	0.9546	0.0420	0.0033
383	0.0337	0.0731	0.8933	0.9744	0.0152	0.0103
	0.0797	0.3711	0.5492	0.9511	0.0383	0.0106
	0.1057	0.4585	0.4358	0.9460	0.0434	0.0106
	0.2146	0.6330	0.1524	0.9286	0.0633	0.0082
	0.2466	0.6670	0.0864	0.9207	0.0733	0.0060
	0.2773	0.6901	0.0326	0.9096	0.0818	0.0033
	0.2847	0.6964	0.0188	0.9069	0.0913	0.0018
	0.2908	0.7031	0.0061	0.9036	0.0958	0.0006

[a] NA, not analysed.

C_3H_8–C_2H_5OH–H_2O system

Figures 5 and 6 show the ethanol–water selectivity, and the solubility of ethanol in the C_3H_8 phase at three temperatures (313, 384 and 403 K) and one pressure (9.905 MPa) for the C_3H_8–C_2H_5–OH–H_2O system. The measured data are given in Table 2.

As shown in Fig. 5, the concentration of extracted ethanol (free of C_3H_8) is higher at lower temperatures, satisfying the specifications of regular ethanol (93.1 wt.% or 95 vol.% of ethanol). However, owing to the high affinity between ethanol and C_3H_8, the mixture became homogeneous when the ethanol concentration (free of C_3H_8) in the liquid phase was increased to about 80–90 wt.%.

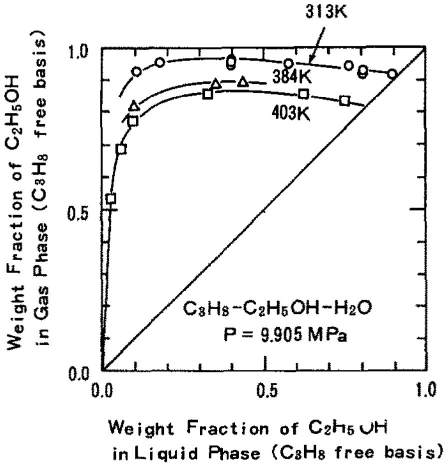


Fig. 5. Ethanol–water selectivity in the C_3H_8–C_2H_5OH–H_2O system at 9.905 MPa.

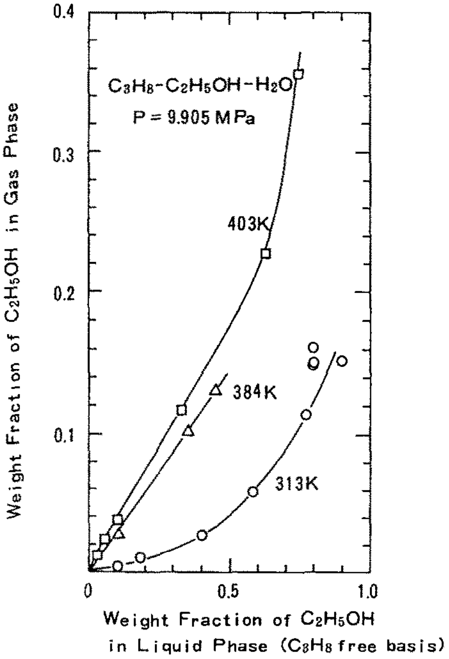


Fig. 6. Solubility of ethanol in the C_3H_8–C_2H_5OH–H_2O system.

As shown in Fig. 6, the solubility of ethanol in the C_3H_8 phase increased remarkably with the ethanol concentration in the liquid phase and with temperature.

C_3H_6–C_2H_5OH–H_2O system

Figures 7 and 8 show the ethanol–water selectivity, and the solubility of

TABLE 2

Phase equilibria for the C_3H_8–C_2H_5OH–H_2O system at 9.905 MPa

Temperature (K)	Weight fraction[a]					
	Heavy phase			Light phase		
	C_3H_8	C_2H_5OH	H_2O	C_3H_8	C_2H_5OH	H_2O
313	NA	0.1032	0.8968	0.9953	0.0043	0.0003
	NA	0.1798	0.8202	0.9882	0.01090	0.0005
	NA	0.4000	0.6000	0.9706	0.0281	0.0013
	NA	0.4000	0.6000	0.9718	0.0271	0.0011
	NA	0.5816	0.4181	0.9384	0.0583	0.0028
	NA	0.8029	0.1971	0.8373	0.1509	0.0117
	NA	0.9000	0.1000	0.8342	0.1523	0.0135
	NA	0.9000	0.1000	0.8340	0.1529	0.0131
	0.00083	0.04435	0.95482	0.99846	0.00131	0.00023
	0.00089	0.07881	0.92030	0.99656	0.00309	0.00034
	0.00102	0.14067	0.85831	0.99374	0.00594	0.00032
	0.00108	0.18455	0.81437	0.99049	0.00912	0.00039
	0.02621	0.52072	0.45307	0.94613	0.05141	0.00245
	0.12870	0.66760	0.20380	0.87910	0.11460	0.00630
	0.20295	0.64101	0.15604	0.83292	0.15398	0.00130
384	NA	0.103	0.897	0.9673	0.0267	0.0060
	NA	0.3467	0.6533	0.8856	0.1021	0.0123
	NA	0.4430	0.5570	0.8528	0.1304	0.0168
403	0.0009	0.0271	0.9720	0.9781	0.0118	0.0101
	0.0013	0.0569	0.9418	0.9651	0.0242	0.0107
	0.0023	0.0985	0.8995	0.9518	0.0374	0.0108
	0.0121	0.3295	0.6585	0.8652	0.1164	0.0184
	0.1046	0.5641	0.3313	0.7357	0.2273	0.0370
	0.2579	0.5551	0.1870	0.5449	0.3573	0.0678

[a] NA, not analysed.

ethanol in the C_3H_6 phase at two temperatures (313 and 403 K) and one pressure (9.905 MPa) for the C_3H_6–C_2H_5OH–H_2O system. The measured data are given in Table 3.

Figure 7 shows that at lower temperatures the extracted ethanol concentration is higher, as observed for the C_3H_8 solvent. The maximum ethanol concentration is about 95 wt.% at 313 K, which satisfies the specification of regular alcohol (95 vol.% or 93.1 wt.%).

As shown in Fig. 8, the concentration of ethanol in the C_3H_6 phase increases with the ethanol concentration in the liquid phase and with temperature. These tendencies are similar to those observed for C_3H_8.

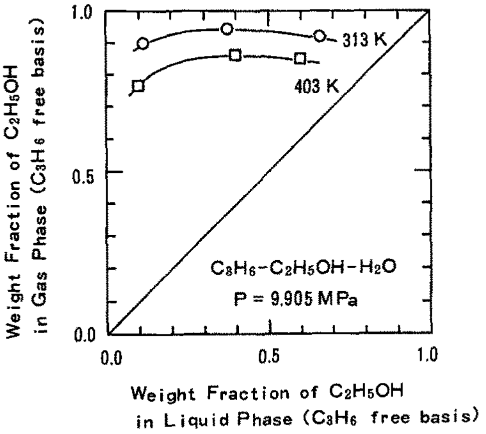


Fig. 7. Ethanol-water selectivity in the C_3H_6-C_2H_5OH-H_2O system at 9.905 MPa.

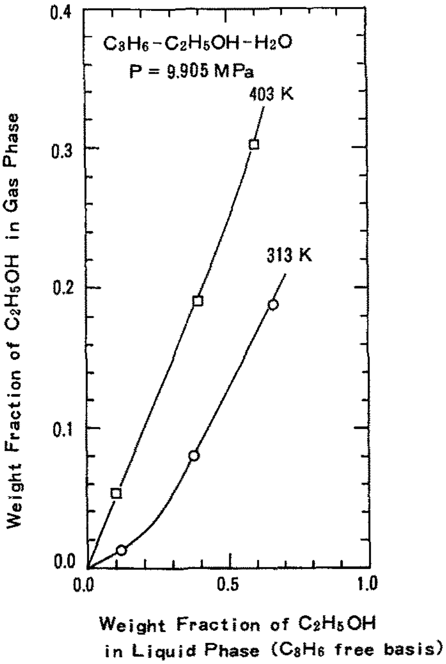


Fig. 8. Solubility of ethanol in the C_3H_6-C_2H_5OH-H_2O system at 9.905 MPa.

n-C_4H_{10}-C_2H_5OH-H_2O *system*

Figure 9 shows the ethanol-water selectivity and the solubility of ethanol in n-C_4H_{10} solvent at a weight fraction of ethanol in the liquid phase (as a solvent-free basis) X_2^* of 0.4, a pressure of 9.905 MPa, and in the temperature range 313-433 K. The measured data are given in Table 4.

TABLE 3

Phase equilibria for the C_3H_6–C_2H_5OH–H_2O system at 9.905 MPa

Temperature (K)	Weight fraction					
	Heavy phase			Light phase		
	C_3H_6	C_2H_5OH	H_2O	C_3H_6	C_2H_5OH	H_2O
313	0.0026	0.1164	0.8810	0.9865	0.0122	0.0013
	0.0115	0.3726	0.6159	0.9148	0.0805	0.0047
	0.0921	0.5974	0.3105	0.7959	0.1877	0.0163
403	0.0054	0.1008	0.8937	0.9307	0.0533	0.0160
	0.0355	0.3815	0.5850	0.7804	0.1897	0.0299
	0.1216	0.5269	0.3515	0.6434	0.3024	0.0542

As shown in Fig. 9, the concentration of ethanol in the n-C_4H_{10} solvent increases with temperature and is a little lower than that in the case of C_3H_8.

C_2H_4–C_2H_5OH–H_2O system

Figure 10 shows the solubility of ethanol in the C_2H_4 phase at 313 K and 9.905 MPa for the C_2H_4–C_2H_5OH–H_2O system. The measured data are given in Table 5.

The solubility of ethanol in the C_2H_4 phase increases with the ethanol concentration in the liquid phase, but is lower than that in the CO_2, C_3H_6, C_3H_8 and n-C_4H_{10} systems.

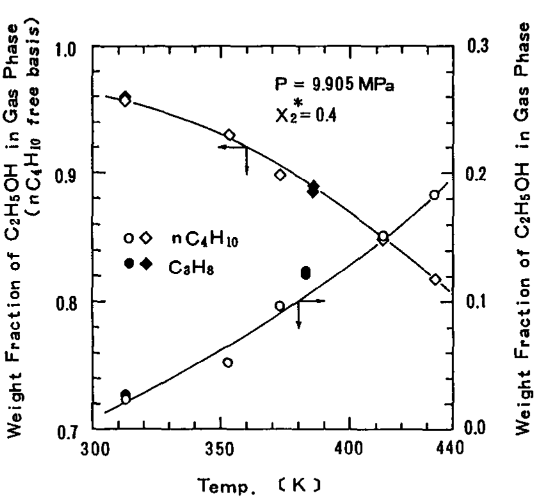


Fig. 9. Effect of temperature on the ethanol–water selectivity and the solubility of ethanol in the n-C_4H_{10}–C_2H_5OH–H_2O system at 9.905 MPa.

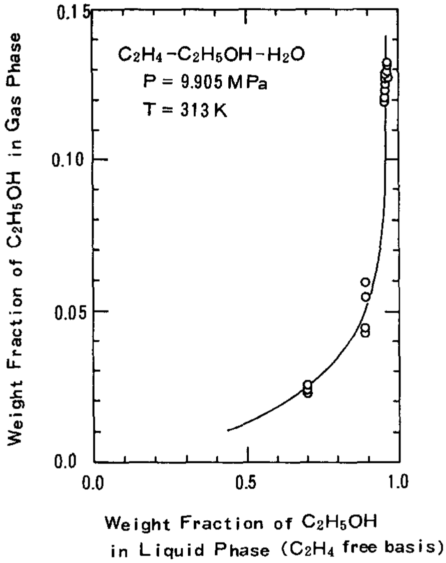


Fig. 10. Solubility of ethanol in the C_2H_4–C_2H_5OH–H_2O system at 9.905 MPa.

TABLE 4

Phase equilibria for the n-C_4H_{10}–C_2H_5OH–H_2O system at 9.905 MPa

Temperature (K)	Weight fraction					
	Heavy phase			Light phase		
	n-C_4H_{10}	C_2H_5OH	H_2O	n-C_4H_{10}	C_2H_5OH	H_2O
313	0.0035	0.3851	0.6114	0.9762	0.0228	0.0010
353	0.0065	0.3680	0.6256	0.9434	0.0526	0.0040
373	0.0119	0.3816	0.6065	0.8914	0.0975	0.0111
413	0.0189	0.3847	0.5964	0.8217	0.1522	0.0261
433	0.0247	0.3847	0.5926	0.7767	0.1826	0.0407

CO_2–C_3H_8–C_2H_5OH–H_2O system

Figures 11–14 show the extracted ethanol concentration for two different ethanol concentrations in the liquid phase ($X_2^* = 0.1$ and 0.4, the weight fraction on a solvent-free basis) as a function of the C_3H_8 concentration in the mixed solvent ($CO_2 + C_3H_8$). The measured data are given in Tables 6 and 7.

These results show that the single solvent (C_3H_8) is better than the mixed solvent ($CO_2 + C_3H_8$).

TABLE 5

Phase equilibria for the C_2H_4–C_2H_5OH–H_2O system at 313 K and 9.905 MPa

Weight fraction [a]					
Heavy phase			Light phase		
C_2H_4	C_2H_5OH	H_2O	C_2H_4	C_2H_5OH	H_2O
NA	0.7018	0.2982	0.9429	0.0235	0.0017
NA	0.7018	0.2982	0.9754	0.0230	0.0017
NA	0.7018	0.2982	0.9744	0.0239	0.0017
NA	0.8891	0.1109	0.9520	0.0428	0.0053
NA	0.8891	0.1109	0.9361	0.0548	0.0094
NA	0.8891	0.1109	0.9322	0.0598	0.0080
NA	0.8891	0.1109	0.9455	0.0448	0.0097
NA	0.9565	0.0435	0.8711	0.1247	0.0042
NA	0.9565	0.0435	0.8767	0.1191	0.0042
NA	0.9565	0.0435	0.8762	0.1208	0.0030
NA	0.9565	0.0435	0.8738	0.1230	0.0032
NA	0.9613	0.0387	0.8655	0.1281	0.0064
NA	0.9613	0.0387	0.8654	0.1288	0.0058
NA	0.9613	0.0387	0.8685	0.1279	0.0036
NA	0.9613	0.0387	0.8737	0.1210	0.0053
NA	0.9651	0.0349	0.8607	0.1325	0.0068
NA	0.9651	0.0349	0.8665	0.1293	0.0042
NA	0.9651	0.0349	0.8625	0.1317	0.0058
NA	0.9651	0.0349	0.8694	0.1269	0.0037

[a] NA, not analysed.

RESULTS FOR THE SEPARATION OF ETHANOL

The experimental results for the extraction of ethanol indicated that C_3H_8, C_3H_6 and n-C_4H_{10} were promising solvents. The usual method of recovery of ethanol from the solvent phase is to lower the pressure (pressure swing). Thus the vapour–liquid equilibria for the separation of ethanol from these solvents were measured and studied.

C_3H_8–C_2H_5OH–H_2O system

Figure 15 shows the pressure effect for the phase equilibria of the C_3H_8–C_2H_5OH–H_2O ternary system at 313 K with $X_2^* = 0.41$ and 0.78. Measured data are given in Table 8.

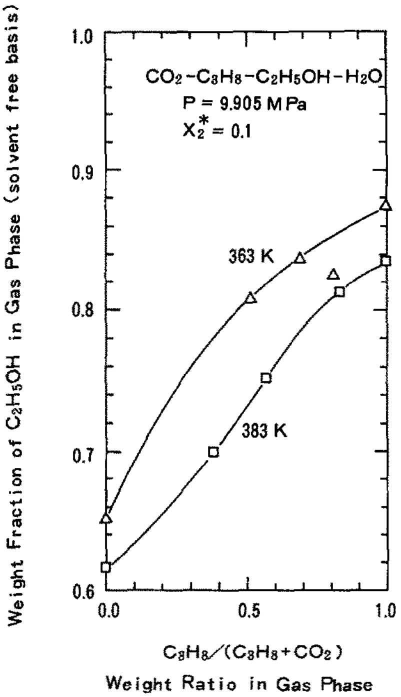


Fig. 11. Ethanol–water selectivity in the CO_2–C_3H_8–C_2H_5OH–H_2O system at $X_2^* = 0.1$, and $P = 9.905$ MPa.

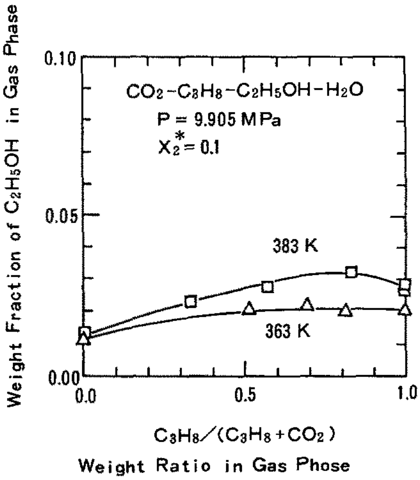


Fig. 12. Solubility of ethanol in the CO_2–C_3H_8–C_2H_5OH–H_2O system at $X_2^* = 0.1$, and $P = 9.905$ MPa.

The weight fraction of ethanol in the gas phase became a minimum at about 1.37 MPa, which is almost equal to the vapour pressure of pure C_3H_8. When the weight fraction of ethanol in the liquid phase is high, for

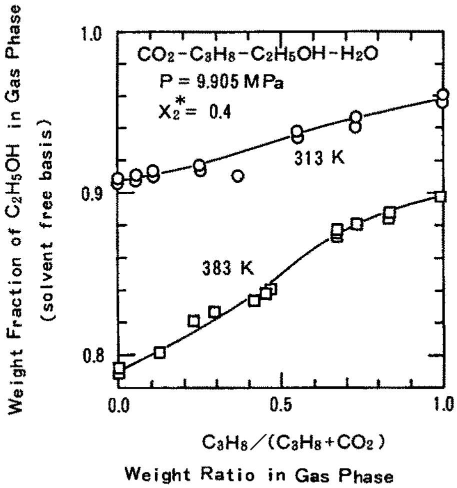


Fig. 13. Ethanol–water selectivity in the CO_2–C_3H_8–C_2H_5OH–H_2O system at $X_2^* = 0.4$, and $P = 9.905$ MPa.

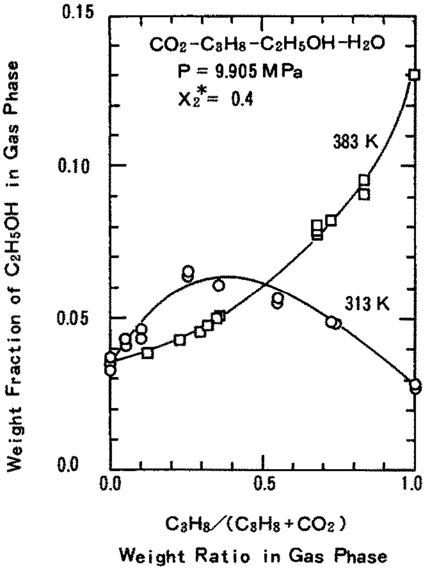


Fig. 14. Solubility of ethanol in the CO_2–C_3H_8–C_2H_5OH–H_2O system at $X_2^* = 0.4$, and $P = 9.905$ MPa.

example 0.78, the ethanol concentration in the vapour phase is about 0.015, and this means that much ethanol may be lost in the vapour phase.

According to these results, as the extracted ethanol concentration from the extractor is about 96 wt.% (solvent free), the loss of ethanol will be even higher.

TABLE 6

Phase equilibria for the CO_2-C_3H_8-C_2H_5OH-H_2O system at $X_2^* = 0.1$ and 9.905 MPa

Temperature (K)	Weight fraction							
	Heavy phase				Light phase			
	CO_2	C_3H_8	C_2H_5OH	H_2O	CO_2	C_3H_8	C_2H_5OH	H_2O
383	0.0362	0.0	0.1007	0.8631	0.9722	0.0	0.0171	0.0107
	0.0235	0.0008	0.1068	0.8690	0.6474	0.3198	0.0229	0.0098
	0.0167	0.0011	0.1068	0.8753	0.4159	0.5479	0.0274	0.0088
	0.0090	0.0012	0.1084	0.8814	0.1614	0.7991	0.0322	0.0074
	0.0	0.0015	0.1044	0.8941	0.0	0.9662	0.0282	0.0056
363	0.0370	0.0	0.0989	0.8643	0.9831	0.0	0.0110	0.0058
	0.0215	0.0007	0.1051	0.8727	0.4775	0.4996	0.0202	0.0048
	0.0160	0.0008	0.1009	0.8823	0.3038	0.6705	0.0215	0.0042
	0.0104	0.0009	0.0973	0.8914	0.1835	0.7921	0.0201	0.0043
	0.0012	0.0007	0.1035	0.8947	0.0044	0.9718	0.0208	0.0030

As mentioned above, the ethanol concentration in the C_3H_8 solvent phase from the extractor can be increased up to about 96 wt.% and so, using ethanol solutions of 95 and 98 wt.%, isothermal vapour-liquid equilibrium data for the solvent-C_2H_5OH-H_2O system were measured at various pressures. The measured data are given in Table 9.

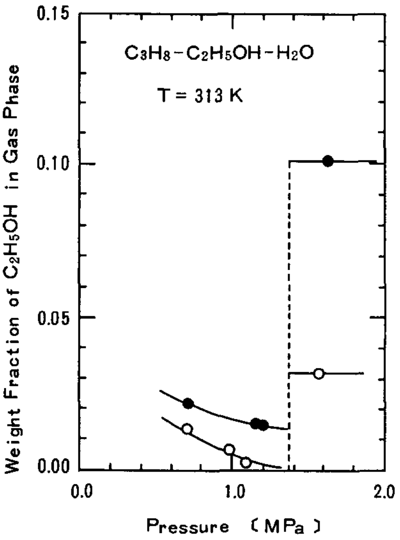


Fig. 15. Solubility of C_2H_5OH in the light phase for solvent separation by pressure swing at 313 K.

TABLE 7

Phase equilibria for the CO_2–C_3H_8–C_2H_5OH–H_2O system at $X_2^* = 0.4$ and 9.905 MPa

Temperature (K)	Weight fraction [a]							
	Heavy phase				Light phase			
	CO_2	C_3H_8	C_2H_5OH	H_2O	CO_2	C_3H_8	C_2H_5OH	H_2O
313	NA	NA	0.4000	0.6000	0.9022	0.0523	0.0413	0.0042
	NA	NA	0.4000	0.6000	0.8975	0.0557	0.0427	0.0041
	NA	NA	0.3800	0.6200	0.8560	0.0968	0.0431	0.0041
	NA	NA	0.3800	0.6200	0.8482	0.1008	0.0466	0.0044
	NA	NA	0.4281	0.5719	0.6998	0.2305	0.0639	0.0058
	NA	NA	0.4281	0.5719	0.6949	0.2344	0.0649	0.0059
	NA	NA	0.4218	0.5719	0.5936	0.3394	0.0610	0.0060
	NA	NA	0.4218	0.5719	0.4211	0.5182	0.0568	0.0040
	NA	NA	0.4218	0.5719	0.4239	0.5176	0.0549	0.0036
	NA	NA	0.4107	0.5893	0.2489	0.7000	0.0483	0.0027
	NA	NA	0.4107	0.5893	0.2566	0.6914	0.0488	0.0031
	NA	NA	0.4000	0.6000	0.0	0.9595	0.0369	0.0037
	NA	NA	0.4000	0.6000	0.0	0.9634	0.0332	0.0034
	0.0	NA	0.4000	0.6000	0.0	0.9706	0.0281	0.0013
384	NA	NA	0.4000	0.6000	0.9473	0.0068	0.0362	0.0068
	NA	NA	0.4000	0.6000	0.9477	0.0067	0.0361	0.0095
	NA	NA	0.4000	0.6000	0.8319	0.1200	0.0385	0.0095
	NA	NA	0.4000	0.6000	0.7295	0.2180	0.0431	0.0094
	NA	NA	0.4000	0.6000	0.6646	0.2801	0.0457	0.0096
	NA	NA	0.4000	0.6000	0.6407	0.3018	0.0480	0.0095
	NA	NA	0.4000	0.6000	0.6067	0.3337	0.0499	0.0097
	NA	NA	0.4000	0.6000	0.6031	0.3368	0.0505	0.0097
	NA	NA	0.4000	0.6000	0.2921	0.6169	0.0797	0.1235
	NA	NA	0.4000	0.6000	0.2928	0.6177	0.0786	0.0109
	NA	NA	0.4000	0.6000	0.2424	0.6638	0.0825	0.0113
	NA	NA	0.4000	0.6000	0.1464	0.7503	0.0912	0.0116
	NA	NA	0.4000	0.6000	0.1469	0.7503	0.0912	0.0116
	NA	NA	0.4000	0.6000	0.0	0.8530	0.1309	0.0161

[a] NA, not analysed.

Figure 16 shows the relative volatility of water and ethanol with respect to C_3H_8 as a function of the C_3H_8 concentration in the liquid phase at 333 K. The relative volatility of water is higher than that of ethanol, and exceeds unity at the higher end of the C_3H_8 concentration in the liquid phase. Therefore, azeotropic distillation using C_3H_8 can separate most of the C_3H_8 and water in the distillate from the top of the tower, and absolute ethanol and a certain amount of recovered C_3H_8 in the liquid phase from the bottom of the tower.

TABLE 8

Phase equilibria for the C_3H_8–C_2H_5OH–H_2O system at 313 K

Pressure (MPa)	Weight fraction[a]					
	Heavy phase			Light phase		
	C_3H_8	C_2H_5OH	H_2O	C_3H_8	C_2H_5OH	H_2O
0.588	NA	0.4099	0.5901	0.9813	0.0135	0.0052
0.971	NA	0.4108	0.5892	0.9923	0.0067	0.0010
1.079	NA	0.4129	0.5871	0.9972	0.0022	0.0007
1.569	NA	0.4007	0.5993	0.9764	0.0317	0.0019
0.686	NA	0.7754	0.2246	0.9733	0.0225	0.0041
1.128	NA	0.7754	0.2246	0.9823	0.0149	0.0028
1.177	NA	0.7754	0.2246	0.9827	0.0146	0.0027
1.618	NA	0.7754	0.2246	0.8902	0.1012	0.0086

[a] NA, not analysed.

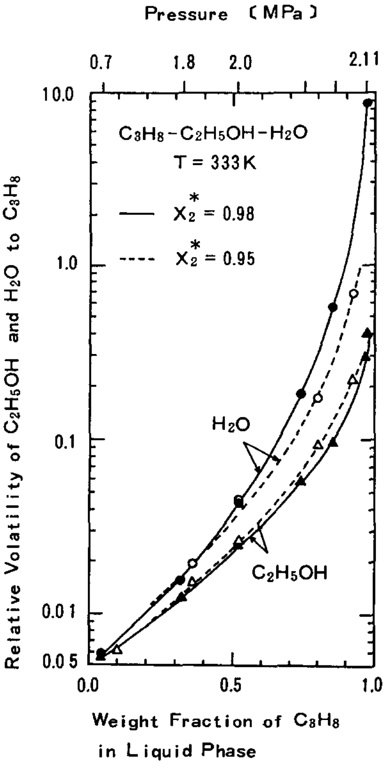


Fig. 16. Relative volatility of C_2H_5OH and H_2O with respect to C_3H_8 for solvent separation as a function of the weight fraction of C_3H_8 in the liquid phase at 333 K.

TABLE 9

Vapour–liquid equilibria for the $C_3H_8(1)-C_2H_5OH(2)-H_2O(3)$ system

Temperature (K)	Pressure (MPa)	Weight fraction										
		Liquid phase			Vapour phase			Equilibrium ratio [a]			Relative volatility with respect to C_3H_8[b]	
		C_3H_8	C_2H_5OH	H_2O	C_3H_8	C_2H_5OH	H_2O	K_1	K_2	K_3	α_{21}	α_{31}
333	1.064	0.1067	0.8442	0.0492	0.9525	0.0451	0.0025	8.927	0.0534	0.0508	0.00598	0.0569
	1.864	0.3700	0.5967	0.0332	0.9746	0.0237	0.0017	2.634	0.0397	0.0512	0.0151	0.0194
	1.986	0.5285	0.4467	0.0527	0.9764	0.0215	0.0021	1.847	0.0481	0.0847	0.0261	0.0458
	1.996	0.8047	0.1841	0.0112	0.9770	0.0206	0.0024	1.214	0.112	0.214	0.0922	0.176
	2.027	0.9234	0.0726	0.0040	0.9800	0.0171	0.0029	1.061	0.236	0.725	0.222	0.683
	0.657	0.0622	0.9090	0.0289	0.9216	0.0759	0.0247	14.820	0.0835	0.0856	0.00563	0.00578
	1.834	0.3206	0.6590	0.0204	0.9739	0.0252	0.00096	3.038	0.0382	0.0470	0.0126	0.0155
	1.971	0.5235	0.4625	0.0141	0.9766	0.0223	0.00115	1.866	0.0482	0.0816	0.0258	0.0437
	2.040	0.7461	0.2477	0.00616	0.9797	0.0188	0.0015	1.313	0.0760	0.0244	0.0579	0.185
	2.089	0.8531	0.1434	0.00358	0.9821	0.0156	0.00231	1.151	0.109	0.645	0.0947	0.560
	2.097	0.9754	0.0243	0.00024	0.9880	0.0099	0.00207	1.013	0.406	0.625	0.401	0.617
363	1.125	0.0538	0.8942	0.0520	0.8483	0.1434	0.0083	15.77	0.160	0.160	0.0102	0.0101
	2.678	0.2236	0.7347	0.0417	0.9286	0.0677	0.0037	4.153	0.092	0.0887	0.0222	0.0214
	3.202	0.4463	0.5239	0.0298	0.9367	0.0597	0.0035	2.099	0.114	0.117	0.0543	0.0560
	3.394	0.5860	0.3920	0.0220	0.9393	0.0570	0.0037	1.603	0.145	0.168	0.0907	0.105
	3.627	0.8605	0.1320	0.0075	0.9483	0.0475	0.0044	1.102	0.360	0.587	0.327	0.532
	3.678	0.9271	0.0693	0.0036	0.9568	0.0392	0.0040	1.032	0.566	1.111	0.548	1.077
	3.698	0.9672	0.0308	0.0020	0.9738	0.0229	0.0034	1.007	0.744	1.700	0.738	1.688
383	1.064	0.0390	0.9054	0.0556	0.6852	0.2972	0.0176	17.57	0.328	0.317	0.0187	0.0180
	2.016	0.1026	0.8452	0.0522	0.8254	0.1652	0.0094	8.045	0.195	0.180	0.0243	0.0224
	3.050	0.1993	0.7542	0.0465	0.8732	0.1202	0.0066	4.381	0.159	0.142	0.0364	0.0324
	4.083	0.3895	0.5747	0.0385	0.8932	0.1013	0.0055	2.293	0.176	0.143	0.0769	0.0623

[a] $K_1 = Y_1/X_1$; $K_2 = Y_2/X_2$; $K_3 = Y_3/X_3$.

[b] $\alpha_{21} = K_2/K_1$; $\alpha_{31} = K_3/K_1$.

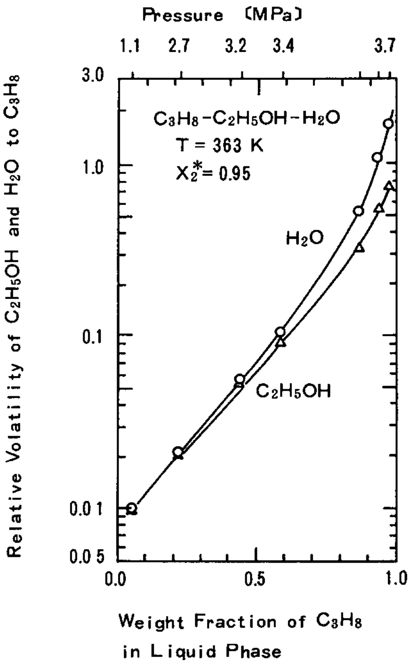


Fig. 17. Relative volatility of C_2H_5OH and H_2O with respect to C_3H_8 for solvent separation as a function of the weight fraction of C_3H_8 in the liquid phase at 363 K.

Brignole et al. (1984, 1987) predicted these phenomena by process simulation using the group contribution EOS method, but the present work appears to be the first in which the phase equilibria were measured and the phenomena were confirmed quantitatively and experimentally.

Figure 16 also shows that if 98 wt.% (propane free) ethanol solution is used, ethanol can be separated more easily from water.

Figures 17 and 18 show the results at 363 K and 383 K respectively. At 363 K, a similar tendency to that seen at 333 K was observed, but at 383 K, which is higher than the critical temperature of C_3H_8 ($T_c = 369$ K), the relative volatilities of water and ethanol reverse, and it became difficult to separate ethanol from C_3H_8 and water.

From these results, we conclude that when the temperature and pressure were lower than the critical points for C_3H_8, most ethanol could be separated from C_3H_8 and dehydrated by the azeotropic distillation method.

A disadvantage of this azeotropic distillation method is the partial resolution of C_3H_8 in absolute ethanol in the liquid phase at the bottom of the tower, and it is necessary to strip C_3H_8 completely from the bottom liquid until its concentration drops below that allowable. However, as the presence of C_3H_8 in the bottom of the separating tower permits a smaller temperature difference between the top and the bottom of the tower, it will be possible to save much energy using the vapour recompression method.

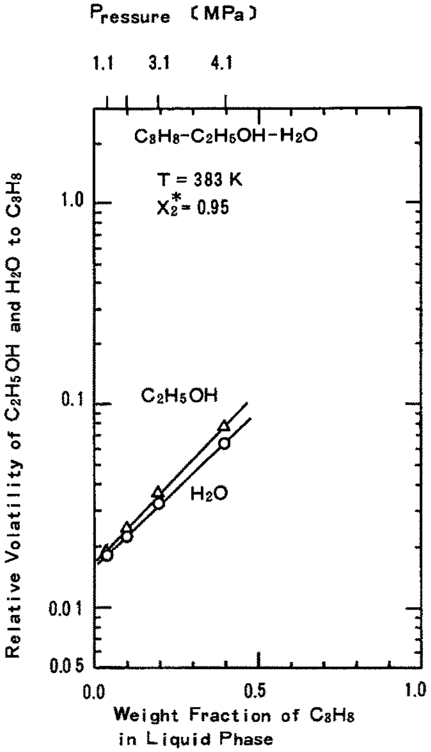


Fig. 18. Relative volatility of C_2H_5OH and H_2O with respect to C_3H_8 for solvent separation as a function of the weight fraction of C_3H_8 in the liquid phase at 383 K.

$C_3H_6-C_2H_5OH-H_2O$ system

The phase equilibria for the 95 wt.% (propylene free) ethanol aqueous solution and the C_3H_6 system were also measured. Figure 19 shows the relationship between the relative volatilities of water and ethanol to that of C_3H_6 and the concentration of C_3H_6 in the liquid phase at 333 K. The measured data are given in Table 10.

The relative volatility of water was greater than that of ethanol and exceeded unity at the higher end of the C_3H_6 concentration in the liquid phase. Therefore it will also be possible to separate ethanol from C_3H_6 and simultaneously to dehydrate ethanol by the azeotropic distillation method as well as C_3H_8 solvent. In the case of C_3H_6, there is a greater difference in the relative volatility between ethanol and water than in the case of C_3H_8.

n-*$C_4H_{10}-C_2H_5OH-H_2O$ system*

The phase equilibria for the 95 wt.% ethanol solution and n-C_4H_{10} system were also measured. Figure 20 shows the relationship between the relative

TABLE 10

Vapour–liquid equilibria for the $C_3H_6(1)$–$C_2H_5OH(2)$–$H_2O(3)$ system at 333.2 K

Pressure (MPa)	Weight fraction									Relative volatility[b] with respect to C_3H_6	
	Heavy phase			Light phase			Equilibrium ratio[a]				
	C_3H_6	C_2H_5OH	H_2O	C_3H_6	C_2H_5OH	H_2O	K_1	K_2	K_3	α_{21}	α_{31}
1.755	0.2379	0.7192	0.0430	0.9710	0.0272	0.0018	4.082	0.0378	0.0417	0.00930	0.0102
2.118	0.3789	0.5858	0.0353	0.9761	0.0221	0.0018	2.576	0.0378	0.0505	0.0147	0.0196
2.256	0.5165	0.4566	0.0269	0.9786	0.0196	0.0019	1.895	0.0429	0.0687	0.0226	0.0363
2.344	0.6876	0.2954	0.0170	0.9806	0.0172	0.0021	1.426	0.0583	0.125	0.0409	0.0879
2.422	0.8993	0.0972	0.0045	0.9846	0.0130	0.0024	1.095	0.134	0.532	0.122	0.486
2.432	0.9000	0.0952	0.0049	0.9864	0.0108	0.0028	1.096	0.114	0.581	0.104	0.531
2.471	0.9456	0.0518	0.0026	0.9883	0.0087	0.0030	1.045	0.167	1.154	0.160	1.104

[a,b] See footnotes to Table 9.

TABLE 11

Vapour–liquid equilibria for the n-C_4H_{10}(1)–C_2H_5OH(2)–H_2O(3) system at 353.2 K

Pressure (MPa)	Weight fraction									Relative volatility[b] with respect to n-C_4H_{10}	
	Liquid phase			Vapour phase			Equilibrium ratio[a]				
	n-C_4H_{10}	C_2H_5OH	H_2O	n-C_4H_{10}	C_2H_5OH	H_2O	K_1	K_2	K_3	α_{21}	α_{31}
0.677	0.1600	0.7939	0.0461	0.8554	0.1167	0.0079	5.346	0.147	0.171	0.858	0.0321
0.971	0.4662	0.5045	0.0293	0.9217	0.0717	0.0066	1.977	0.142	0.225	0.631	0.114
1.049	0.8479	0.1441	0.0080	0.9370	0.0545	0.0085	1.105	0.378	1.0625	0.356	0.961
1.069	0.9127	0.0833	0.0041	0.9505	0.0369	0.0126	0.041	0.443	3.073	0.144	2.951

[a,b] See footnotes to Table 9.

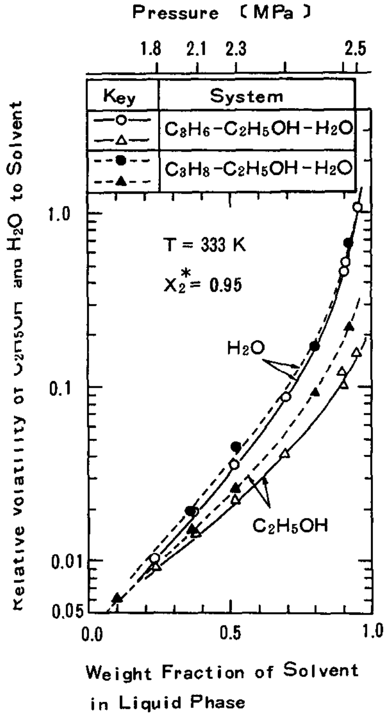


Fig. 19. Comparison of C_3H_6 with C_3H_8 in terms of the relative volatilities of C_2H_5OH and H_2O with respect to C_3H_6 or C_3H_8 for solvent separation as a function of the weight fraction of C_3H_6 or C_3H_8 in the liquid phase at 333 K.

volatilities of water and ethanol to n-C_4H_{10} at 353 K and the n-C_4H_{10} concentration in the liquid phase. The measured data are given in Table 11.

The relative volatility of water is greater than that of ethanol and exceeds unity at the higher end of the n-C_4H_{10} concentration. Therefore it will also be possible to separate almost all the ethanol from n-C_4H_{10} and simultaneously to dehydrate ethanol by the azeotropic distillation method. The difference in the relative volatilities of water and ethanol was also a little greater than that for C_3H_8, so ethanol may be separated more easily from water by using n-C_4H_{10} as solvent.

However, Holderbaum et al. (1991) have recently shown that the vapour–liquid equilibria of the butane–ethanol system shows azeotropic behaviour at all temperatures. Thus butane and ethanol cannot be separated completely by distillation.

CONCLUSIONS

The phase equilibria for the subcritical and supercritical solvents and the C_2H_5OH–H_2O system using CO_2, a light hydrocarbon (C_2H_4, C_3H_6, C_3H_8

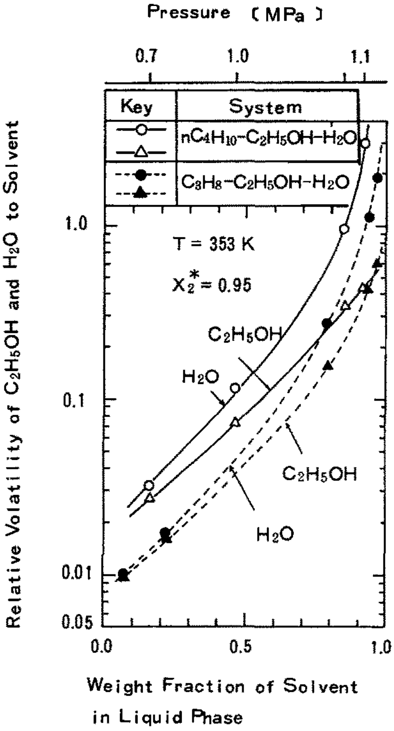


Fig. 20. Comparison of n-C_4H_{10} with C_3H_8 in terms of the relative volatilities of C_2H_5OH and H_2O with respect to n-C_4H_{10} or C_3H_8 for solvent separation as a function of the weight fraction of n-C_4H_{10} or C_3H_8 in the liquid phase at 353 K.

and n-C_4H_{10}), or a mixed solvent ($CO_2 + C_3H_8$) were measured. The experimental results revealed the following facts.

(1) CO_2 could hardly break the azeotropic concentration, even at high temperatures (383 K), and the ethanol solubility in the CO_2 phase did not increase significantly.

(2) C_2H_4 was low in terms of both the selectivity and the solubility of ethanol. It is a poor solvent for extracting ethanol.

(3) C_2H_6 was excluded from this study as the results of previous studies indicate that it is a poor solvent.

(4) C_3H_6, C_3H_8 and n-C_4H_{10} showed almost the same behaviour, with the exception that the vapour–liquid equilibrium of the n-C_4H_{10}–ethanol system shows azeotropic behaviour. Using these solvents, ethanol was concentrated up to about 96 wt.%, which is higher than the specification of regular ethanol (95 vol.% or 93.1 wt.%). Meanwhile, the relative volatilities of water to these solvents were greater than that of ethanol, and exceeded 1.0 at higher solvent concentrations in the liquid phase. Using azeotropic distillation under these conditions, it will be possible to separate most

solvents and water as distillate from the top of the tower and absolute ethanol with dissolved solvent from the bottom.

(5) Comparing C_3H_8 with the mixed solvent ($CO_2+C_3H_8$), C_3H_8 was better than the mixed solvent in terms of both the solubility and the selectivity of ethanol.

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