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High-Pressure Phase Equilibria in Ternary Systems of Propionic Acid and Water with Ethane, SF_6, or Refrigerant 13 ($CClF_3$), 23 (CF_3H), or 116 (C_2F_6)

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Vapor-liquid and liquid-liquid equilibrium compositions are presented for the ternary systems of H_2O and propionic acid with refrigerant 23 (R23; CF_3H), ethane, R13 ($CClF_3$), SF_6, and R116 (C_2F_6) at 313 K, near the critical temperature of each solvent. Equilibria for most systems were determined at 15.0 MPa; the subcritical solvent SF_6 was studied at a pressure just above its vapor pressure at 313 K (4.0 MPa). The distribution coefficient of propionic acid between the solvent phase and the aqueous phase increases with the water solubility of the solvent. Only the fully fluorinated solvents SF_6 and R116 (C_2F_6) are immiscible with propionic acid under the conditions of interest. Where solvent + water binary data are available, the experimental data for the ternary systems were correlated by using a cubic equation of state and a density-dependent mixing rule with model parameters derived from binary data only.

Introduction

Near-critical and supercritical fluid (SCF) solvents have attracted widespread attention for use as extractants and reaction media (*1-4*). Particular interest has centered on the extraction of light organic alcohols from dilute solutions produced by fermentation. Phase equilibrium data are available for systems of ethanol and water with CO_2, ethylene, and ethane (*5-9*) and for systems of isopropyl alcohol and water with CO_2 (*9-12*). Panagiotopoulos and Reid (*1*, *13*) have determined phase equilibria for ternary systems with supercritical CO_2 and acetone or 1-butanol.

The equilibria between aqueous solutions of light organic acids and supercritical and near-critical solvents have been less extensively investigated than those for systems with alcohols. Snedeker (*14*) presented data for the system carbon dioxide + water + acetic acid, and Elgin and Weinstock (*15*) determined equilibria for the systems ethylene + water + acetic acid or propionic acid. Francis (*16*) measured phase equilibria for the system subcritical CO_2 + water + acetic acid. Finally, the authors recently presented data for the ternary systems CO_2 + water + acetic, propionic, and butyric acids (*17*).

The present work arose from efforts to identify solvents suitable for use in the in situ recovery of fermentation products. Selection of solvents for this purpose is constrained both by the phase equilibrium properties of candidate solvents and by their effects on microbial physiology (*18*, *19*), requiring the examination of a wider variety of solvents than has commonly been considered. The present work presents phase equilibrium data for the ternary system of each of the solvents of interest with water and propionic acid at a single, elevated pressure. The experimental pressures were chosen to be above the region of strong pressure dependence of distribution coefficients, so that the data would be indicative of the greatest extraction efficiency that could be achieved with each solvent. The temperature at which these data were collected (313 K) was chosen to allow comparison with existing phase equilibrium data (*15-17*, *20*), and also to be compatible with microbial growth.

Experimental Section

***Equipment and Procedures*.** The experimental apparatus used was a high-pressure visual cell with on-line sampling and chromatographic analysis of both phases, as described in detail elsewhere (*21*). Equilibrium phase compositions were measured with a Sigma 2 gas chromatograph (Perkin-Elmer) fitted with a Porapak Q column (Supelco), using helium as the carrier gas. Samples were injected directly from external recirculation loops into the chromatograph using high-pressure switching valves (Valco).

The relative response factor for carbon dioxide was determined by measuring equilibrium data for mixtures for which data are available in the literature (*22-24*). The response factors for the other gases were determined relative to that for CO_2 by analyzing standard mixtures prepared gravimetrically (*19*) in high-pressure cylinders (Whitey 304L-HDF4; nominal volume 150 mL). An independent control was provided by comparison of the results for some systems with the known behavior of their binary SCF + H_2O system at low concentrations of organic acid, as described previously (*17*, *19*, *21*). The stability of the relative response factors was monitored by periodic injection of reference mixtures. Validation of the experimental procedures and comparisons with literature data are given in detail elsewhere (*19*, *21*).

***Materials*.** Glass-detailed water (Mallinckrodt) and analytical grade propionic acid (Sigma) were used as received. Gas chromatographic analysis of the acid indicated a purity in the 99.5-99.7 wt % range, with water being the major contaminant. Most gases were from Matheson: ethane (CP, 99.0% minimum, typically 99.53%, balance chiefly hydrogen and ethylene), R116 (99.6% minimum, 99.89% typical, balance chiefly C_2F_5H and air), SF_6 (CP 99.8% minimum, 99.9% typical, balance chiefly CF_4 and air), and R13 (99.0% minimum, balance chiefly air). R22 (99.9% minimum) and R23 (98.0% minimum) were from Du Pont. All gases were as received.

Correlation

For the correlation of the experimental results we used a cubic equation of state (EOS) based on the Peng-Robinson form (*1*, *21*), with a density-dependent mixing rule. A detailed discussion of the model used is given in ref 21. The mixing rule involves two interaction parameters per binary system, $k_{12} = k_{21}$ and $\lambda_{12} = -\lambda_{21}$. The second parameter λ_{ij} describes the deviation of the mixture from the quadratic mixing rule at high densities. The equation of state pure component energy and volume parameters a and b were determined for the subcritical components (SF_6, H_2O, and propionic acid) by using a technique proposed by Panagiotopoulos and Kumar (*25*). The parameters

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Table I. Experimental Results for the System R23 + Water + Propionic Acid at 313 K

	liquid phase				SCF phase			
	P_{avg}, MPa	mole fraction			P_{avg}, MPa	mole fraction		
P, MPa		R23	H_2O	acid		R23	H_2O	acid
21.60	21.50	0.012	0.966	0.023	21.78	0.968	0.005	0.027
19.06	22.87	0.011	0.950	0.040	15.26	0.954	0.008	0.037
20.57	21.32	0.014	0.926	0.061	19.82	0.876	0.012	0.111
20.21	20.68	0.012	0.906	0.081	19.74	0.823	0.020	0.157
19.60	16.30	0.026	0.838	0.135	22.90	0.738	0.052	0.204
19.73	21.70	0.055	0.721	0.224	17.75	0.663	0.071	0.264
20.65	23.55	0.074	0.675	0.252	17.75	0.609	0.096	0.294

Table II. Experimental Results for the System Ethane + Water + Propionic Acid at 313 K

	liquid phase				SCF phase			
	P_{avg}, MPa	mole fraction			P_{avg}, MPa	mole fraction		
P, MPa		ethane	H_2O	acid		ethane	H_2O	acid
13.76	13.62	0.005	0.926	0.069	13.98	0.960	0.005	0.034
14.32	14.84	0.006	0.873	0.116	13.55	0.916	0.000	0.068
15.81	15.80	0.011	0.840	0.149	15.82	0.881	0.003	0.114
14.03	14.05	0.021	0.735	0.244	14.00	0.835	0.004	0.158
16.85	16.80	0.044	0.607	0.343	16.92	0.728	0.010	0.252
15.61	15.95	0.060	0.544	0.392	15.28	0.657	0.012	0.326
12.71	12.71	0.054	0.549	0.397				
17.00	17.00	0.077	0.479	0.439				

Table III. Experimental Results for the System R13 + Water + Propionic Acid at 313 K

	liquid phase				SCF phase			
	P_{avg}, MPa	mole fraction			P_{avg}, MPa	mole fraction		
P, MPa		R13	H_2O	acid		R13	H_2O	acid
15.68	16.43	0.004	0.949	0.046	14.94	0.986	0.000	0.014
16.40	17.68	0.002	0.950	0.047	13.85	0.983	0.015	0.002
15.01	15.02	0.002	0.844	0.154	14.99	0.950	0.006	0.044
15.04	15.42	0.002	0.834	0.164	14.79	0.962	0.003	0.034
16.71	16.76	0.005	0.811	0.184	16.52	0.938	0.001	0.061
15.17	15.17	0.005	0.747	0.248				
15.63	16.24	0.012	0.614	0.374	15.23	0.874	0.023	0.104
15.37	15.12	0.014	0.600	0.385	15.62	0.880	0.000	0.120
15.30	15.30	0.022	0.518	0.460	15.31	0.845	0.018	0.137
15.97	16.04	0.023	0.513	0.464	15.91	0.834	0.018	0.148
14.72	14.76	0.035	0.439	0.526	14.67	0.818	0.015	0.167
15.97	15.64	0.050	0.376	0.574	16.30	0.754	0.013	0.233
15.44	15.19	0.079	0.292	0.629	15.56	0.690	0.015	0.295

Table IV. Experimental Results for the System SF_6 + Water + Propionic Acid at 313 K

	liquid phase				SCF phase			
	P_{avg}, MPa	mole fraction			P_{avg}, MPa	mole fraction		
P, MPa		SF_6	H_2O	acid		SF_6	H_2O	acid
4.56	4.60	0.000	0.976	0.024	4.47	0.990	0.010	0.000
4.06	4.06	0.000	0.924	0.075				
4.26	4.26	0.001	0.862	0.138				
4.18	4.24	0.001	0.743	0.256	4.11	0.983	0.009	0.008
4.25	4.28	0.000	0.648	0.347	4.22	0.986	0.007	0.008
4.28	4.36	0.010	0.435	0.556	4.20	0.974	0.000	0.026
4.36	4.99	0.014	0.294	0.692	3.74	0.957	0.000	0.043
4.42	4.82	0.009	0.188	0.804	4.01	0.923	0.000	0.077
4.44	4.49	0.021	0.103	0.876	4.40	0.911	0.000	0.089

Table V. Experimental Results for the System R116 + Water + Propionic Acid at 313 K

	liquid phase				SCF phase			
	P_{avg}, MPa	mole fraction			P_{avg}, MPa	mole fraction		
P, MPa		R116	H_2O	acid		R116	H_2O	acid
14.59	14.56	0.000	0.888	0.112	14.62	0.966	0.018	0.016
16.72	16.52	0.001	0.768	0.232	16.92	0.986	0.000	0.012
15.30	15.82	0.004	0.584	0.413	14.78	0.980	0.000	0.019
15.98	16.84	0.005	0.520	0.475	15.12	0.977	0.000	0.022
16.18	16.48	0.012	0.328	0.660	15.99	0.964	0.000	0.035
15.83	15.79	0.020	0.231	0.748	15.88	0.910	0.003	0.080
14.61	14.55	0.057	0.060	0.884	14.66	0.914	0.000	0.086

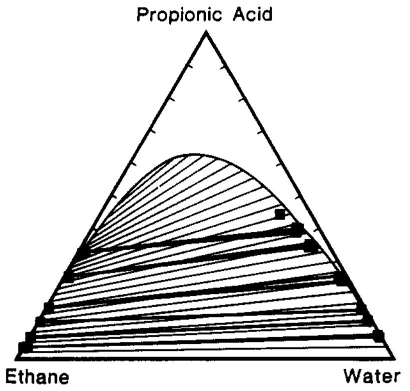

Figure 1. Phase equilibrium behavior of the system water + propionic acid + ethane at 313 K: (■—■) measured tie lines, (—) predicted tie lines.

thus obtained exactly reproduce vapor pressure and liquid density for the components of interest at each temperature. For the supercritical components, the conventional acentric factor correlation (*26*) was used with values for the critical constants taken from Reid et al. (*27*).

Results and Discussion

The experimental equilibrium compositions measured for the five systems are given in Tables I–V. Each line in the tables gives the compositions of the coexisting phases for a different overall system composition; the entries are ordered by increasing acid mole fraction. Data from one to three chromatographic analyses (usually two) at each point were averaged to result in the reported concentration. The average standard deviation (reproducibility) for the set of analyses was ±0.004 in mole fraction with a maximum deviation between duplicate analyses of ±0.02. The absolute accuracy of the results is more difficult to ascertain. If the uncertainties in the relative response factors that may result in systematic errors are included, the accuracy of the results may be estimated to be ±0.006 in mole fraction or ±2% of the value reported, whichever is greater (*19*, *21*).

In working with the highly incompressible systems studied in this work, changes in system pressure produced by alteration of the system configuration for sampling of the different phases were greater than previously observed for more compressible systems (*17*). It is believed that the contribution of pressure variations is less than the stated accuracy of the results, however, based on the weak pressure dependence under similar conditions of the closely related CO_2 + water + propionic acid system (*17*) and other systems described in the literature (*9*, *21*). For example, the distribution coefficient (ratio of acid mole fraction in the SCF phase to that in the aqueous phase) for the CO_2 + water + propionic acid system (*17*) changes by less than 2%/MPa in going from 10.0 to 15.0 MPa. In order to facilitate assessment of the pressure variation associated with each point, the average of the pressures at which each phase was sampled is listed in the table, along with the overall average sampling pressure for the tie line. A full listing of the raw (not averaged) experimental results is available elsewhere (*19*); individual points are shown in Figure 1 to illustrate the high reproducibility of the measurements. Data for the R23 system were collected at 21.0 MPa, as the densities of the liquid and SCF phases in this system are too similar at 15.0 MPa to allow complete separation of the phases for sampling.

The ternary phase equilibrium results for the system of water and propionic acid with ethane are presented as an equilateral triangular diagram in Figure 1. Modified Peng–Robinson EOS predictions also appear in this figure. Prediction of several systems (R23, SF_6, and R116) was hampered by a lack of literature data on the mutual binary solubilities of these SCF with water, which are too low to allow accurate extrapolations to be made from data taken with the equipment used in this work. The pure component and correlation parameters used in prediction are tabulated in Tables VI–VIII.

Table VI. Pure Component Parameters and Physical Property Data Used (Subcritical Components)

component	ρ, kg m^{-3}	P_{VP}, kPa	a, J m^3 mol^{-2}	10^6b, m^3 mol^{-1}
water	992.1	7.38	0.8162	16.07
propionic acid	967.8	1.34	3.534	67.95

Table VII. Pure Component Parameters and Physical Property Data Used (Supercritical Components)

component	T_c, K	P_c, kPa	a, J m^3 mol^{-2}	10^6b, m^3 mol^{-1}
R13	302.0	3870	0.7268	50.478
ethane	305.4	4880	0.5962	40.482

Table VIII. Interaction Parameters

binary system	$k_{12} = k_{21}$	$\lambda_{12} = -\lambda_{21}$, J^2 m^3 mol^{-3}
water (1) + propionic acid (2)	−0.127	1221
ethane (1) + water (2)	0.152	−4016
R13 (1) + water (2)	0.22	−6556
ethane (1) + propionic acid (2)	−0.0062	634
R13 (1) + propionic acid (2)	−0.0487	971

The SCF + water + propionic acid systems change in equilibrium behavior in a regular way with decreasing water solubility of the SCF. The two-phase regions of the less polar SCF systems are more extensive, and follow the (binary) edges of the triangular diagrams more closely, reflecting the lower mutual solubilities of the SCF with water and with propionic acid solutions. The tie lines of the systems involving more polar SCF have a negative slope in going from the SCF-rich to the water-rich phase, implying a more effective extraction of propionic acid from water into the more polar SCF. The fully fluorinated solvents SF_6 and R116 are immiscible with propionic acid at 313 K up to at least 25.0 MPa (*19*). The ternary systems of these solvents resemble the ethane results (Figure 1) in showing an extensive two-phase region, but they also display a region of immiscibility between the SCF and the aqueous phase.

No directly comparable literature results are available for any of the ternary systems studied in this work. A check on the accuracy of the results is provided by the measured concentrations of ethane in the aqueous phase and water in the ethane phase for low acid mole fractions, extrapolated to zero concentration of acid, which agree with the accepted literature values for the ethane + water binary system within the stated accuracy (*28*, *29*). The most closely comparable ternary data are those of Elgin and Wienstock (*15*) on the ethylene + water + propionic acid ternary system at 288 K (T_r = 1.02) and at 3.5 MPa (P_r = 0.69). These results are qualitatively similar to our results for the ethane + water + propionic acid ternary system at 313 K, 15.0 MPa (T_r = 1.02; P_r = 3.07).

Finally, our results may be compared with those of Schmidt (*20*) for the binary solubilities of naphthalene derivatives in SCF solvents at pressures up to 40.0 MPa and at temperatures of 318–328 K. Carbon dioxide and R23 were found to be the most generally effective solvents tested, followed by ethane and ethylene and finally by R13 and SF_6. This ordering, although determined under much different conditions, is in agreement with our observations of relative SCF solvent power for extraction of propionic acid from dilute aqueous solutions.

For practical applications of the phase equilibrium behavior demonstrated here, the crucial parameters are the selectivity of the supercritical fluid phase for the organic compound over water, and the distribution coefficient, or ratio of acid mole fraction in the supercritical fluid phase to that in the aqueous phase. The selectivities observed are very high, being greater than several hundred for low acid mole fractions. As a consequence, substantially dehydrated propionic acid may be obtained from dilute solutions in a single extraction step. Distribution coefficients, by contrast, exhibit a relatively strong dependence on solvent properties. The more polar (i.e., water-soluble) solvents could potentially be useful for the selective extraction of propionic acid from aqueous solutions. Application of the water-immiscible solvents SF_6 and R116 to processing of aqueous solutions, however, would probably be limited to recovery of solutes less polar than propionic acid.

As observed previously (*13*, *17*), the modified Peng-Robinson model was successful in predicting the qualitative characteristics of the experimentally observed behavior for all the cases studied. The quantitative agreement between experimental results and model predictions derived from binary data is good in most cases, with the agreement being closest at low acid mole fractions, closest to the binary data from which the correlation parameters were derived.

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Isobaric Vapor-Liquid Equilibria for the Binary Systems Formed by Acetonitrile and Aromatic Hydrocarbons

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The isobaric vapor-liquid equilibria of the binary systems formed by acetonitrile + benzene, + toluene, + *m*-xylene, + *p*-xylene, or + ethylbenzene were measured at 28.0 and 101.3 kPa. The activity coefficients were correlated by using the NRTL equation.

Introduction

In the framework of an extensive study about the thermodynamic properties of the systems containing acetonitrile and aromatic hydrocarbons (*1-2*), isobaric vapor-liquid equilibria were measured at 28 and 101.3 kPa, for the five binary systems acetonitrile (1) + benzene (2), + toluene (2), + *m*-xylene (2), + *p*-xylene (2), or + ethylbenzene (2). Only partial information concerning these systems is reported in the literature: excess enthalpy data were measured for all the investigated systems (*1*) at 25 and 41.2 °C, and additional data are available for the systems containing benzene, toluene, and ethylbenzene at 25 °C (*3*) and for the systems containing toluene at 48.2 °C (*4*). Isothermal vapor-liquid equilibria are reported for the systems containing benzene (*5-8*) and toluene (*4-5*, *7*, *9*).

Table I. Refractive Indexes *n* and Normal Boiling Points of the Chemicals

chemical	n(D, 20 °C)		normal boiling points/°C	
	this work	lit.[a]	this work	lit.[b]
acetonitrile	1.3420	1.344 11	81.6	81.60
benzene	1.5011	1.501 12	80.1	80.100
toluene	1.4961	1.496 93	110.6	110.625
m-xylene	1.4973	1.497 22	139.0	139.103
p-xylene	1.4958	1.495 82	138.0	138.351
ethylbenzene	1.4959	1.495 88	136.0	136.186

[a] Riddick, J. A.; Bunger, W. B.; Sakano, T. K. In *Organic Solvents*, 4th ed.; Weissberger, A., Ed.; Techniques of Chemistry, Vol. II; John Wiley & Sons: New York, 1986. [b] Dreisbach, R. R. *Physical Properties of Chemical Compounds*; American Chemical Society: Washington, DC, 1955.

Some sets of isobaric vapor-liquid equilibria are available for the systems containing benzene (*5*, *10-12*) and toluene (*4*, *10-11*) and a single set at 101.3 kPa for the systems containing *p*-xylene, and ethylbenzene (*13*), while for the system acetonitrile *m*-xylene no vapor-liquid equilibrium data appear to be reported.

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