Third Industrial Fluid Properties Simulation Challenge
State Conditions Transferability Problem

Recommended Bubble Point Pressures for the System Ethanol / 1,1,1,2,3,3,3-Heptafluoropropane

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Primary Source of Recommendation:

All bubble point pressures were determined in a static vapor-liquid equilibrium apparatus at DuPont. The same apparatus and protocols were used to determine the experimental values at 283.17 K provided at http://fluidproperties.org/challenge/third/2006state.html and the benchmark values provided in this document. The benchmark values, with their uncertainties, are provided in Table 2, below.

Experimental Details:

Materials

Anhydrous ethanol (CAS# 64-17-5; purity ≥ 99.5%, 200 proof) was purchased from Quantum Chemicals.

1,1,1,2,3,3,3-heptafluoropropane or HFC-227ea (CAS# 431-89-0; purity >99.999%) was obtained from DuPont.

HFC-227ea was degassed by repeated freeze-pump-thaw cycles using liquid nitrogen to freeze. Ethanol was degassed with the help of an ultrasonic bath at room temperature. Otherwise the samples were used as received.

Apparatus and Procedure

A static vapor-liquid equilibrium (VLE) apparatus was used to measure both isotherms. The idea of the static technique is to maintain the mixture under conditions of temperature and pressure at which liquid and vapor phases coexist, to mix them thoroughly until equilibrium is established, and then to sample and analyze the two phases without disturbing the equilibrium appreciably. In practice the analysis can be difficult, but if overall compositions and cell volumes are known, it is straightforward to use a different technique to determine compositions. Although assumptions are needed about the forms of suitable correlation equations for fugacity and/or activity coefficients, very accurate results are obtainable without the necessity of sampling and analyzing either or both phases.

The pressure is measured with an accuracy of ±0.01 % over the range of pressures measured. The temperature is controlled and measured with an accuracy of ±0.01 K over the range of temperatures measured. Mixtures are prepared by transferring known amounts of the pure components into the evacuated equilibrium cell, which has a total volume of 75 cm^3. The added quantities are determined to ±0.001 g by weighing, which translates into an error of less than 0.01 % in mole fraction. Complete details about the actual apparatus used and data evaluation can be found in the paper by Kao et al. [1].

In Table 1, we provide the experimental results at 283.17 K (10.02 ^{o}C) which had been previously available on the contest web site. In Table 2 we provide the benchmark bubble point pressures and their uncertainties. In Table 3, we provide a more complete set of measurements at 342.13 K (69.98 ^{o}C).

Comparison with Literature and Determination of Uncertainty:

As part of the uncertainty analysis of these measurements, we have compared the pure fluid values with two of the standard sources of vapor pressures for these fluids. DIPPR® 801 [2] lists an uncertainty of their vapor pressure correlation for ethanol and HFC-227ea of < 1% and <5% respectively. REFROPR 7.1 [3] lists an uncertainty of their Helmholtz equation of state model for ethanol and HFC-227ea of 0.5 % and 0.2 % respectively. Table 4 shows these comparisons.

For the bubble point pressure benchmark data, the experimental uncertainties of 0.2% are consistent with uncertainties reported for other carefully-designed apparatus used to measure bubble-point pressures in the 0.2 to 1.2 MPa pressure range [4,5]. These uncertainties consider and propagate the components of uncertainty associated with the purity of the samples used; the uncertainty of the compositions; the measurement uncertainties of temperature and pressure; the theory, calibration, precision, and repeatability of the VLE apparatus; and the comparisons for the pure fluids and for other binary mixtures. From these considerations, we estimate that the combined expanded uncertainty (coverage factor of two, or confidence interval of about 95%) of the bubble point pressure values in Table 2 is 0.2 % for all of the reported values.

References:

[1] C.P. Chai Kao, M.E. Paulaitis, A. Yokozeki., Fluid Phase Equilibria, **127**, 191 (1997).

[2] R.L. Rowley, W.V. Wilding, J.L. Oscarson, N.A. Zundel, T.L. Marshall, T.E. Daubert, R.P. Danner, DIPPR(R) Data Compilation of Pure Compound Properties, Design Institute for Physical Properties, AIChE, New York, NY, (2006).

[3] E.W. Lemmon, M.L. Huber, M.O. McLinden, NIST Standard Reference Database 23, NIST Reference Fluid Thermodynamic and Transport Properties--REFPROP, version 7.1. Standard Reference Data Program, National Institute of Standards and Technology, Gaithersburg, MD, U.S.A. (2006).

[4] N. F. Giles, G. M. Wilson, J. Chem. Eng Data **45,** 146 (2000).

[5] J. D. Olson, International J. Thermophysics **16,** 215 (1995).

Table 1. Experimental Data for the System Ethanol and HFC-227ea: Isotherm I at 283.17 K

Mole Fraction Ethanol	Bubble Point Pressure	
	Pa	psia
0.0	2.801×10^5	40.63
0.0545	2.698×10^5	39.13
0.1123	2.639×10^5	38.28
0.2152	2.561×10^5	37.15
0.3173	2.487×10^5	36.07
0.4137	2.404×10^5	34.87
0.5097	2.297×10^5	33.32
0.6066	2.099×10^5	30.45
0.7328	1.756×10^5	25.466
0.7893	1.485×10^5	21.538
0.8553	1.078×10^5	15.632
0.9001	7.633×10^4	11.071
0.9392	4.784×10^4	6.939
0.9670	2.757×10^4	3.999
1.0	3.075×10^3	0.466

Table 2. Benchmark Bubble Point Pressures for Ethanol and HFC-227ea at 343.13 K

	Problem conditions	
T (K)	Mole Fraction (Ethanol)	P (kPa)
343.13	0.0604	1422 ± 3
343.13	0.1228	1366 ± 3
343.13	0.3314	1222 ± 2
343.13	0.5219	1097 ± 2
343.13	0.7260	885.9 ± 1.8
343.13	0.8547	616.5 ± 1.2
343.13	0.9440	321.5 ± 0.6

Table 3. Experimental Data for the System Ethanol and HFC-227ea: Isotherm II at 343.13 K

Mole Fraction Ethanol	Bubble Point Pressure	
	Pa	psia
0.0	1.487×10^6	215.72
0.0604	1.422×10^6	206.26
0.1228	1.366×10^6	198.12
0.231 1	1.285×10^6	186.31
0.3314	1.222×10^6	177.20
0.4265	1.163×10^6	168.62
0.5219	1.097×10^6	159.15
0.6138	1.018×10^6	147.70
0.7260	8.859×10^5	128.49
0.8029	7.456×10^5	108.14
0.8547	6.165×10^5	89.42
0.9055	4.628×10^5	67.12
0.9440	3.215×10^5	46.63
0.9725	2.025×10^5	29.37
1.0	7.274×10^4	10.55

Table 4. Comparisons for Pure Component Vapor Pressures

Ethanol	**T=283.17 K**	**T=343.13 K**
This Work	0.466 psia	10.55 psia
REFPROP 7.1	0.456 psia	10.45 psia
DIPPR® 801	0.458 psia	10.49 psia
HFC-227ea		
This Work	40.63 psia	215.72 psia
REFPROP 7.1	40.65 psia	215.70 psia
DIPPR® 801	40.78 psia	215.78 psia