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Solubility of HFC32, HFC125, HFC134a, HFC143a, and HFC152a in a Pentaerythritol Tetrapentanoate Ester

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Solubilities of five different hydrofluorocarbons (HFCs) in a pentaerythritol tetrapentanoate ester (95% purity) have been measured at temperatures between 303.15 and 363.15 K and pressures between 0.05 and 1.9 MPa. Henry's constant and the activity coefficient for HFCs at infinite dilution were derived for measurements below 0.26 MPa. The measurements were made with an isochoric method with an uncertainty of less than 2% for Henry's constant and less than 3% at high pressure. Within the investigated temperature range, solubilities for HFCs decrease in the following order: HFC152a > HFC134a > HFC32 > HFC125 > HFC143a. The experimental data have been correlated with a Flory−Huggins model with an extended temperature dependence, which is able to describe the data with a deviation from measured data of less than 2%.

Introduction

Restriction on the use of chlorofluorocarbons as working fluids in heat pumps and refrigeration systems has led to the use of hydrofluorocarbons (HFCs) as alternatives. However, to use HFCs as working fluids, a compressor oil that is compatible with HFCs needs to be found. Important factors for selection of a successful compressor oil are viscosity and lubricity, which are dependent on the working fluid's solubility in the compressor oil. Knowledge of solubility is also required to understand the influence on heat transfer in the working fluid system's evaporator and condenser or when the working fluid's oil-separation system is to be sized.

In the literature polyalkylene glycols (PAG) and pentaerythritol tetraalkyl esters (POE) are frequently discussed as likely compressor oils for the more environmentally safe working fluids, but data about these systems are scarce. Solubility measurements have previously been carried out by Thomas and Pham (1992) for HFC134a in different PAG oils; Takaishi and Oguchi (1993, 1995) for HFC32 and HFC134a in a POE oil; Grebner and Crawford (1993) for HFC134a in an ester oil and a PAG oil; Henderson (1994) for HFC32, HFC134a, HFC125, HFC143a, and HFC152a in different POE oils; Martz et al. (1996) for HFC134a and HFC125 in a POE oil; and Cavestri et al. (1994) for HFC134a in POE and PAG oils. All authors, except the last one, have also correlated their data using models that can accurately describe the solubility of the specific system measured. However, these authors did not describe whether the oils consist of mixtures of different oil molecules or give the structure of the oil molecules. It is therefore difficult to use those correlation models for a mixture which has not yet been measured, for example when a mixture with a new possible compressor oil is investigated. Experimental investigations are time-consuming and thus expensive. New thermodynamic tools that can predict the behavior of a mixture of HFCs and compressor oils will be very useful in the search for successful compressor oils.

As far as we know, no one has measured the solubility of HFCs in a compressor oil consisting of only one substance with a known structure. Such measurements are very valuable in the evaluation and development process of a predictive model. Therefore we have made measurements of the solubility of five different HFCs in a pentaerythritol tetrapentanoate ester. These measurements are the beginning of a series of measurements with different pentaerythritol esters of known structure.

Experimental Section

Isochoric Technique. The experimental technique is an isochoric one where the amount of gas absorbed in a known quantity of liquid solvent is calculated from the pressure change in a gas system of known volume, observed during the absorption of the gas. The experimental equipment together with calibration and calculations is thoroughly described in Wahlström and Vamling (1997a).

The apparatus consists of three sections (Figure 1): (1) a liquid-bath thermostat 1 containing the equilibrium cell with a magnetic stirrer; (2) another liquid-bath thermostat 2 with a gas bottle of calibrated volume; (3) an air-bath thermostat with a pressure transmitter and connections between sections 1 and 2 and to gas storage and a vacuum pump.

The pure solvent was first degassed and weighed before the equilibrium cell was placed into the liquid-bath thermostat 1. The gas was fed into the evacuated gas system, the gas bottle located in the liquid-bath thermostat 2, and the connection tubes located in the air-bath thermostat. The temperature was maintained the same in the air bath and in the liquid bath, and the pressure was recorded. After the interconnecting valve was opened, the gas was admitted into the cell and absorbed by the stirred solvent. The progress of absorption was indicated by the decrease of the pressure. When the pressure remained constant, equilibrium was reached. The next step was to change the temperature for the equilibrium cell. When the pressure again became constant, a new equilibrium point had been reached. The measurements for one pressure level were finished when all the desired temperatures were reached.

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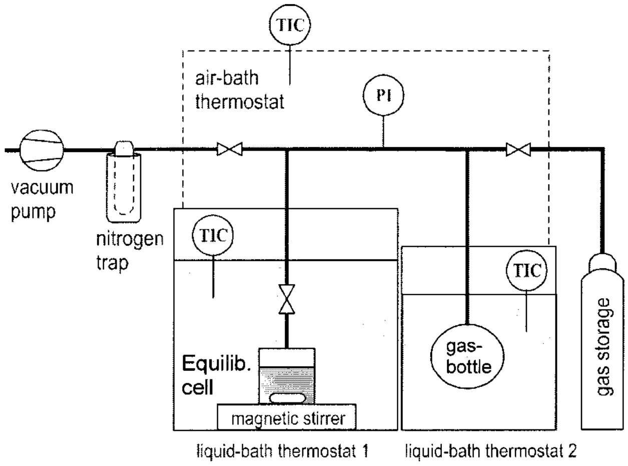

Figure 1. Solubility apparatus.

Then the procedure described above was repeated for the next pressure level.

The density of the solute was determined with an Anton Paar DMA 602 vibrating tube densitometer, described by Wimby and Berntsson (1994). The tube was filled at 20 EC with degassed solute, and then the temperature was increased to the desired temperatures. Ethanol and twice-distilled water were used as calibration liquids.

Calculation of Absorbed Gas. The mole fraction x_1 of absorbed gas (1) in the solvent (2) is calculated according to

$$x_1 = \frac{n_1}{n_1 + n_2} \tag{1}$$

where n_2, the number of moles of the solvent, is calculated from the mass. The number of moles of gas absorbed in the solvent is calculated from

$$n_1 = \left[\frac{V_{\text{gas syst}}}{v_1^{\text{v}}(T_{\text{beg.}}, P_{\text{beg.}})} - \frac{V_{\text{gas syst}}}{v_1^{\text{l}}(T_{\text{equilib gas syst}}, P)} + \frac{V_{2,\text{cell}} - V_{\text{cell}}}{v_1^{\text{v}}(T,P)}\right] \Big/ \left[1 - \frac{v_{\text{abs gas}}}{v_1^{\text{v}}(T,P)}\right] \tag{2}$$

where $V_{\text{gas syst}}$ and V_{cell} are the volume of the gas system (sections 2 and 3) and the volume of the cell (section 1), respectively. The volume $V_{2,\text{cell}}$ of the solvent in the cell is calculated from its mass and measured density. The molar volume v_1^{v} of the gas in the vapor phase at different conditions is calculated with Refprop6 (McOLinden et al., 1998), where T and P are the conditions of the cell at equilibrium, $T_{\text{beg.}}$ and $P_{\text{beg.}}$ are the conditions at sections 2 and 3 at the beginning of the measurement, and $T_{\text{equilib gas syst}}$ is the temperature in sections 2 and 3 at equilibrium. The volume $v_{\text{abs gas}}$ of the absorbed gas in the solvent is calculated as the liquid molar volume of the gas at equilibrium conditions T and P, if liquid exists during those conditions; otherwise, as the liquid molar volume at the bubble point at equilibrium temperature T, unless T is above the critical temperature. Then it is calculated as the partial molar volume in the liquid phase at infinite dilution according to Brelvi and O'Connell (1972).

Henry's constant of a solute (1) in a solvent (2) is calculated according to the equation

$$\text{He1,2} = \lim_{x_1 \to 0}\left(\frac{f_1^{\text{l}}}{x_1 \exp(\bar{v}_1^{\infty}(P - P_2^{\text{sat.}})/RT)}\right) \tag{3}$$

where x_1 is the amount of absorbed gas in the solvent, calculated from the drop of pressure in the gas system of known volume and temperature. The exact amount of gas in the system is determined with the equation of state used in the Refprop6 program (McLinden et al., 1998). The exponential term is called the Poynting correction and takes into account that the liquid is at equilibrium pressure P, different from the saturation pressure of the solvent, $P_2^{\text{sat.}}$. The factor $\bar{v}_1^{\infty}$ is the partial molar volume in the liquid phase at infinite dilution, which is calculated according to Brelvi and O'Connell (1972). Taking into account the equilibrium condition, the liquid-phase fugacity can be written as

$$f_1^{\text{l}} = f_1^{\text{v}} = \varphi_1^{\text{v}} y_1 P \tag{4}$$

Since the solvents have negligible vapor pressures, the mole fraction y_1 of the gas in the vapor phase is taken to equal unity. The gas-phase fugacity coefficient φ_1^{v} is calculated with the equation of state used in Refprop6.

The activity coefficient for the solute at infinite dilution is calculated with

$$\gamma_1^{\infty} = \frac{\text{He}_{1,2}}{(f_1^{\text{l}})^*} \tag{5}$$

The fugacity $(f_1^{\text{l}})^*$ of a pure condensed component 1 at T and P is obtained with

$$(f_1^{\text{l}})^* = P_1^{\text{sat.}}\,\varphi_1^{\text{sat.}}\,\exp\left(\frac{v_1^{\text{l}}(P - P_1^{\text{sat.}})}{RT}\right) \tag{6}$$

It is equal to $P_1^{\text{sat.}}$, the saturation pressure of component 1 at T, with two corrections. First, the fugacity coefficient $\varphi_1^{\text{sat.}}$ corrects for deviations of the saturated vapor from ideal-gas behavior, calculated with Refprop6. Second, the Poynting correction takes into account that the liquid is at equilibrium pressure P, different from the saturation pressure, $P_1^{\text{sat.}}$. The molar volume v_1^{l} of solute in the liquid phase is also calculated with the equation of state used in Refprop6.

Uncertainty. The uncertainty of each experimental quantity is given in Wahlström and Vamling (1997a), and the total uncertainty of measurement is estimated to be less than 2% at low pressure (Henry's constant) and less than 3% at high pressure. For the density measurements the uncertainty in the temperature reading was ± 0.05 °C and the uncertainty of the measured densities is estimated to be less than 0.1%.

Chemicals. The purity according to the manufacturers is 99.9% for all HFCs. All HFCs are supplied by DuPont de Nemours, Dordrecht Works, The Netherlands, except HFC134a which is supplied by ICI Chemicals & Polymers Ltd., Runcorn, Cheshire, U.K.

The pentaerythritol tetrapentanoate ester, $C(CH_2OCOCH_2CH_2CH_2CH_3)_4$, was synthesized by a reaction between a carboxylic acid and an alcohol catalyzed by an acid. The method used is basically the same as the one used by Black and Gunstone (1990) except that the raw product was vacuum-distilled instead of separated by chromatography and that *p*-xylene was used as a solvent instead of *m*-xylene. Pentaerythritol (Aldrich 98%, 0.64 mol, 89 g) was mixed with valeric acid (Aldrich 99%, 2.82 mol, 310 mL), *p*-toluensulfonic acid (40 mmol, 7.6 g), and 160 mL of *p*-xylene in a 1000 mL round flask. A Dean and Stark apparatus was filled with *p*-xylene, and the mixture was reflux-boiled until no more water was trapped in the Dean and Stark trap (this took about 3.5 h). The reaction product was cooled and mixed with diethyl ether into a 2 L separating funnel. The mixture was washed twice with 5% NaOH, twice with water, and once with NaCl. Thereafter the solution was dried with Na_2SO_4 and the solvent was removed with a cyclic evaporator. The small amount of *p*-xylene left in the raw product was removed in the subsequent vacuum distillation at 0.08 mbar and 190−205 EC. The product was a 274 g slightly yellow oil (90% exchange). The distilled product was analyzed by ^{1}H NMR, ^{13}C NMR, and IR spectroscopies, and the purity was estimated to be better than 95%.

Correlation of Experimental Data. Within the investigated temperature range, it was found that Henry's constant on a logarithmic scale versus the reciprocal temperature $1/T$ is practically a straight line. Therefore we have correlated the experimental data with the equation

$$\ln \mathrm{He}_{1,2} = \ln \mathrm{He}_{1,2}^{\mathrm{ref}} + B\left(\frac{1}{T} - \frac{1}{T^{\mathrm{ref}}}\right) \tag{7}$$

where $\mathrm{He}_{1,2}^{\mathrm{ref}}$ is Henry's constant at a reference temperature T^{ref} (333.15 K) and the slope of the line is represented by the parameter B.

Our previous research (Wahlström and Vamling, 1997b) has shown that the Flory−Huggins model can describe similar systems well, and thus we have chosen to correlate the experimental data with that model. The basic equation to represent vapor−liquid equilibria is the equality of fugacities, where the vapor-phase fugacity is calculated with eq 4 and the liquid-phase fugacity is calculated with

$$f_1^{1} = (f_1^{1})^* x_1 \gamma_1 \tag{8}$$

The fugacity $(f_1^{1})^*$ of a pure condensed component 1 at T and P is calculated according to eq 6, and x_1 is the liquid fraction of component 1. For HFCs above their critical temperature no liquid phase exists, and therefore it is necessary to estimate the fugacity, $(f_1^{1})^*$. Chappelow and Prausnitz (1974) gave an equation for extrapolation of the fugacity for ethane, propane, and butane, also used satisfactorily by Stelmachowski and Ledakowicz (1993). The extrapolation was represented with four coefficients, but in this work we have only used the first two coefficients as in

$$\ln (f_1^{1})^* = C_1 + \frac{C_2}{T} \tag{9}$$

The coefficients C_1 and C_2 are determined for each P by using the fugacities calculated with eq 6 for reduced temperatures 0.93 and 0.96.

The deviation from ideality in eq 8 is expressed by an activity coefficient in the liquid phase, γ_1, which is obtained from an excess Gibbs energy model. Here we use the Flory−Huggins model (Prausnitz et al., 1986). For a mixture of fluids that have no difference in molecular interactions or in free volume but have flexible molecules that differ significantly in size, Flory and Huggins independently derived an expression for the activity coefficient

$$\ln \gamma_1 = \ln\left(1 - \left(1 - \frac{1}{r}\right)\Phi_2^*\right) + \left(1 - \frac{1}{r}\right)\Phi_2^* + \chi(\Phi_2^*)^2 \tag{10}$$

The segment fraction Φ_2^* of sites occupied by the solvent is

$$\Phi_2^* = \frac{r x_2}{x_1 + r x_2} \tag{11}$$

where r is the number of segments in a solvent molecule.

The last term in this expression is added to the activity coefficient to apply the Flory−Huggins theory to a real polymer solution, that is, a solution which has differences in molecular interactions. The dimensionless parameter is given in terms of the interchange energy by

$$\chi = w^0/kT \tag{12}$$

where k is Boltzmann's constant and w^0 is the interchange energy between solute molecules and solvent segments. Previous work (Wahlström and Vamling, 1997b) has shown that the temperature representation can be improved if an interchange energy parameter, w^1, is introduced besides the interchange energy parameter w^0. Equation 12 will then be extended to

$$\chi = \frac{w^0}{kT}\left(1 + \frac{w^1}{T}\right) \tag{13}$$

The empirical parameters w^0, w^1, and r were fitted to the experimental data by regression, performed by minimization of the sum of squares

$$\mathrm{SS} = \sum_{i=1}^{N_p}\left(1 - \frac{P_{\mathrm{calc},i}}{P_{\mathrm{expt},i}}\right)^2 \tag{14}$$

where P_{calc} is the calculated pressure, P_{expt} is the experimental pressure, and N_p is the number of experimental points. The result of the parameter estimation may be expressed as a relative deviation of the calculated equilibrium pressures for each mixture. The relative deviation DP (%) is calculated with

$$\mathrm{DP} = \left[\sum_{i=1}^{N_p}\left|\frac{P_{\mathrm{calc},i} - P_{\mathrm{expt},i}}{P_{\mathrm{expt},i}}\right|\right]/N_p \tag{15}$$

Results

The experimental solubilities for the five HFCs in a pentaerythritol tetrapentanoate ester are presented in Tables 1−5. Measurements were made at four temperatures. Each temperature Henry's constant has been derived for points with equilibrium pressures below 0.26 MPa. For the mixtures of HFC125, HFC134a, and HFC32 three points of different equilibrium pressure were used for the derivation at each temperature, while only two points were used for the mixtures of HFC143a and HFC152a due to some experimental problems with leaks. These values were then fitted to eq 7, and the resulting parameters are given in Table 6 together with their 95% confidence interval. The representation can be seen in Figure 2 where the derived experimental Henry's constants are plotted on a logarithmic scale versus the reciprocal temperature $1/T$ together with the calculated Henry's constants from eq 7. Comparison of Henry's constant at the reference temperature (Table 6) shows that the solubilities for HFCs in pentaerythritol tetrapentanoate ester decrease in the following order: HFC152a > HFC134a > HFC32 > HFC125 > HFC143a.

Values for the activity coefficient at infinite dilution are given in Table 7. The activity coefficient has not been derived for temperatures where the solute is above its critical temperature.

Table 1. Mole Fraction Solubility of HFC32 in Pentaerythritol Tetrapentanoate

T/K	P/MPa	x	T/K	P/MPa	x
303.17	0.0711	0.0734	343.18	0.1072	0.0523
303.13	0.0937	0.0955	343.12	0.1415	0.0690
303.15	0.1238	0.1216	343.10	0.1844	0.0894
303.16	0.4078	0.3307	343.17	0.6253	0.2547
303.16	0.5830	0.4290	343.14	0.8948	0.3373
303.15	0.7947	0.5243	343.11	1.2485	0.4304
303.15	1.0738	0.6335	343.15	1.6178	0.5041
323.28	0.0903	0.0620	363.22	0.1226	0.0440
323.24	0.1189	0.0812	363.20	0.1612	0.0588
323.27	0.1560	0.1042	363.34	0.2095	0.0769
323.29	0.5237	0.2911	363.23	0.7140	0.2227
323.26	0.7510	0.3814	363.24	1.0153	0.2993
323.27	1.0375	0.4770	363.36	1.4276	0.3884
323.27	1.3827	0.5687	363.25	1.7949	0.4461

Table 2. Mole Fraction Solubility of HFC125 in Pentaerythritol Tetrapentanoate

T/K	P/MPa	x	T/K	P/MPa	x
303.15	0.0731	0.0675	323.27	1.3920	0.6141
303.16	0.0991	0.0896	343.16	0.1119	0.0444
303.14	0.1372	0.1265	343.17	0.1525	0.0587
303.16	0.2590	0.2222	343.15	0.2139	0.0841
303.14	0.3688	0.3163	343.15	0.6055	0.2238
303.14	0.5309	0.4208	343.15	0.8740	0.3062
303.15	0.6858	0.5206	343.16	1.1990	0.4004
303.15	0.9926	0.6805	343.16	1.6970	0.5192
323.27	0.0936	0.0551	363.17	0.1268	0.0363
323.26	0.1281	0.0725	363.23	0.1732	0.0475
323.26	0.1787	0.1033	363.26	0.2437	0.0684
323.29	0.3385	0.1823	363.28	0.6931	0.1862
323.26	0.4953	0.2687	363.27	0.9985	0.2563
323.26	0.7169	0.3627	363.16	1.3860	0.3414
323.27	0.9611	0.4627	363.25	1.8970	0.4317

Table 3. Mole Fraction Solubility of HFC134a in Pentaerythritol Tetrapentanoate

T/K	P/MPa	x	T/K	P/MPa	x
303.14	0.0515	0.0907	343.15	0.0939	0.0662
303.15	0.0902	0.1551	343.16	0.1679	0.1151
303.14	0.1321	0.2219	343.27	0.2254	0.1554
303.15	0.1765	0.2737	343.15	0.3326	0.2095
303.16	0.2727	0.3962	343.16	0.5239	0.3130
303.14	0.3258	0.4593	343.14	0.6451	0.3734
303.15	0.4583	0.5942	343.15	0.8953	0.4760
323.26	0.0731	0.0781	363.24	0.1129	0.0558
323.26	0.1296	0.1348	363.26	0.2031	0.0973
323.11	0.1815	0.1877	363.25	0.2615	0.1275
323.28	0.2556	0.2418	363.19	0.4046	0.1779
323.27	0.3997	0.3562	363.21	0.6350	0.2708
323.26	0.4854	0.4190	363.25	0.7914	0.3264
323.26	0.6835	0.5414	363.26	1.0650	0.4079

The experimental points were correlated with the Flory–Huggins model with an extended temperature dependence. In Table 8 the number of points, the specific parameters w^0, w^1, r, and the relative deviation DP of calculated and experimental pressures are given for the different mixtures. The representation can be seen in Figures 3–7, where experimental and calculated pressures are plotted versus composition of HFCs in pentaerythritol tetrapentanoate ester, for various temperatures.

The experimental densities at various temperatures for the pentaerythritol tetrapentanoate ester are presented in Table 9 and depicted in Figure 8, together with data measured on the same substance by Kishore and Shobha (1992).

Discussion

The mixtures examined in this work are all only slightly nonideal since the activity coefficients at infinite dilution are around unity. In the temperature range measured in this work HFC32 shows a negative deviation from Raoult's law while HFC143a has a positive deviation.

Table 4. Mole Fraction Solubility of HFC143a in Pentaerythritol Tetrapentanoate

T/K	P/MPa	x	T/K	P/MPa	x
303.15	0.0877	0.0630	343.16	0.1216	0.0440
303.18	0.1525	0.1059	343.15	0.2119	0.0748
303.16	0.4084	0.2541	343.17	0.5729	0.1808
303.17	0.5525	0.3375	343.17	0.7953	0.2514
303.14	0.6900	0.4058	343.12	1.0133	0.3073
303.13	0.8557	0.4855	343.13	1.2738	0.3716
303.15	1.1403	0.6239	343.17	1.6965	0.4604
323.27	0.1060	0.0526	363.21	0.1352	0.0370
323.28	0.1846	0.0889	363.25	0.2350	0.0636
323.27	0.4988	0.2137	363.24	0.6339	0.1531
323.27	0.6867	0.2903	363.25	0.8838	0.2172
323.25	0.8691	0.3533	363.19	1.1292	0.2664
323.24	1.0906	0.4249	363.18	1.4093	0.3269
323.27	1.4762	0.5377	363.23	1.8427	0.3907

Table 5. Mole Fraction Solubility of HFC152a in Pentaerythritol Tetrapentanoate

T/K	P/MPa	x	T/K	P/MPa	x
303.16	0.0585	0.1167	343.15	0.1101	0.0883
303.15	0.0770	0.1532	343.15	0.1441	0.1186
303.16	0.1552	0.2900	343.17	0.2958	0.2357
303.15	0.2158	0.3764	343.15	0.4174	0.3097
303.15	0.2681	0.4497	343.16	0.5405	0.3820
303.15	0.3800	0.5824	343.17	0.7473	0.4845
323.26	0.0844	0.1023	363.26	0.1346	0.0753
323.26	0.1103	0.136	363.23	0.1758	0.1026
323.28	0.2250	0.2636	363.22	0.3635	0.2083
323.26	0.3157	0.3445	363.24	0.5144	0.2744
323.25	0.4009	0.4183	363.26	0.6753	0.3434
323.26	0.5647	0.5387	363.24	0.9043	0.4264

Table 6. Number of Points and Specific Parameters with Their 95% Confidence Interval for Calculating Henry's Constant with Equation 7, at Temperatures between 303 and 363 K, for HFCs in Pentaerythritol Tetrapentanoate

solute	N_p	$\mathrm{He}^{\mathrm{ref}}_{1,2}$/MPa	B/K
HFC32	12	1.710 ± 0.016	−1873 ± 47
HFC125	12	2.050 ± 0.023	−2167 ± 56
HFC134a	12	1.138 ± 0.011	−2300 ± 48
HFC143a	8	2.332 ± 0.020	−1750 ± 42
HFC152a	8	0.979 ± 0.017	−2277 ± 86

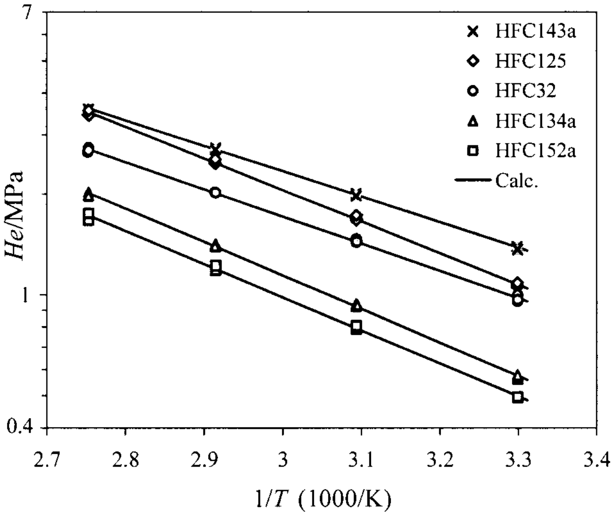

Figure 2. Henry's constant versus temperature for different HFCs in pentaerythritol tetrapentanoate.

The experimental points were correlated both with the Flory–Huggins model according to eq 12, w^0 and r being

Table 7. Activity Coefficient at Infinite Dilution for HFCs in Pentaerythritol Tetrapentanoate

	T/K			
solute	303.2	323.2	343.2	363.2
HFC32	0.67	0.68	0.71	
HFC125	0.93	1.04		
HFC134a	0.88	0.91	0.95	1.01
HFC143a	1.29	1.30	1.39	
HFC152a	0.84	0.86	0.88	0.91

Table 8. Number of Points, Specific Parameters for the Flory–Huggins Model with Extended Temperature Dependence, and the Relative Deviation DP for HFCs Dissolved in Pentaerythritol Tetrapentanoate

solute	N_p	w^0k^{-1}/K	w^1/K	r	DP/%
HFC32	28	806	−197	9.78	1.35
HFC125	30	967	−262	3.47	1.46
HFC134a	28	878	−221	6.17	1.91
HFC143a	28	849	−183	5.28	1.95
HFC152a	24	482	−204	4.62	1.94

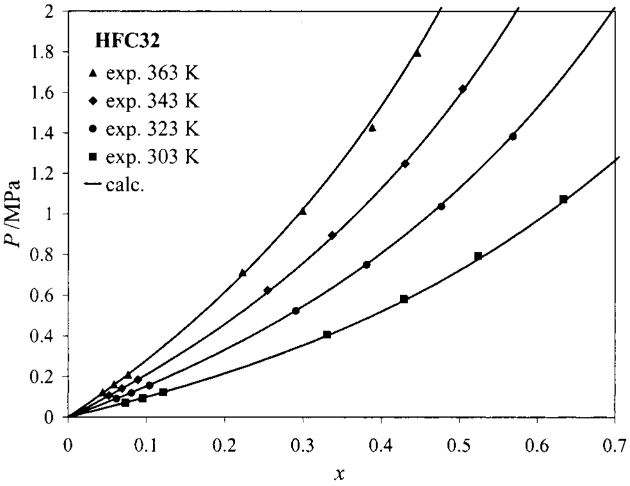

Figure 3. Experimental and Flory–Huggins-calculated pressures versus mole fraction composition for HFC32 in pentaerythritol tetrapentanoate at various temperatures.

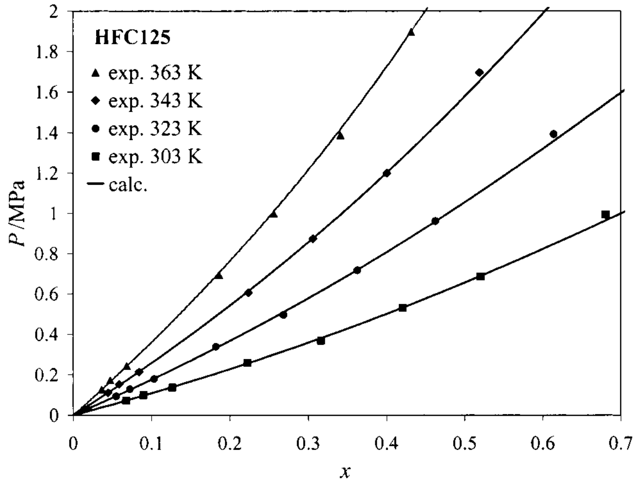

Figure 4. Experimental and Flory–Huggins-calculated pressures versus mole fraction composition for HFC125 in pentaerythritol tetrapentanoate at various temperatures.

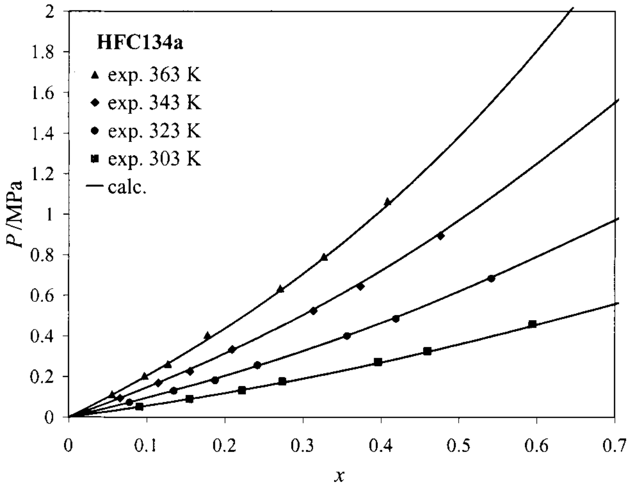

Figure 5. Experimental and Flory–Huggins-calculated pressures versus mole fraction composition for HFC134a in pentaerythritol tetrapentanoate at various temperatures.

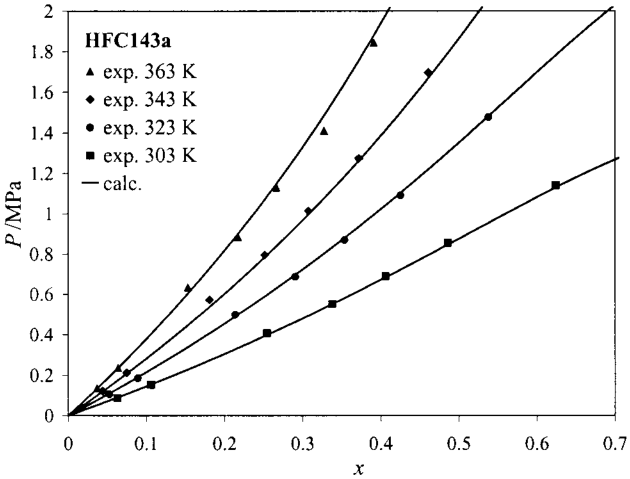

Figure 6. Experimental and Flory–Huggins-calculated pressures versus mole fraction composition for HFC143a in pentaerythritol tetrapentanoate at various temperatures.

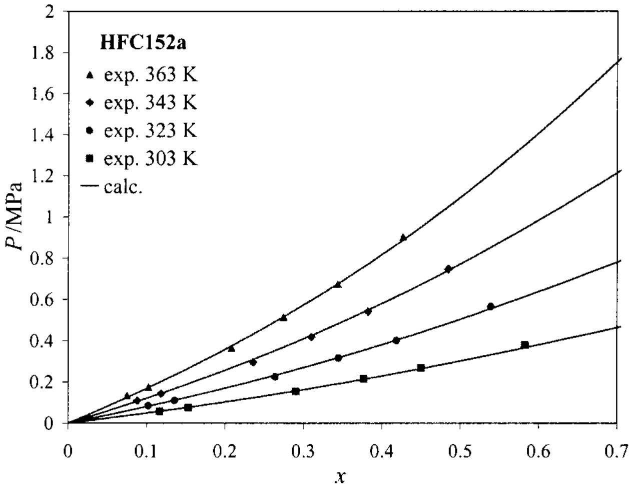

Figure 7. Experimental and Flory–Huggins-calculated pressures versus mole fraction composition for HFC152a in pentaerythritol tetrapentanoate at various temperatures.

regressed for each mixture while w^1 is set equal to zero, and with the Flory–Huggins model according to eq 13, w^0, w^1, and r being all regressed simultaneously for each mixture. The representation of experimental points was highly improved when the extended temperature dependence was introduced.

Comparison of the densities measured in this work and the results of Kishore and Shobha (1992) shows that the

Table 9. Density of Pentaerythritol Tetrapentanoate Ester at Various Temperatures

T/K	density/(kg·m^{-3})	*T*/K	density/(kg·m^{-3})
298.22	1015.0	338.24	983.1
303.13	1011.2	342.85	979.8
308.20	1007.3	347.96	976.1
313.85	1002.4	352.98	972.5
318.02	999.3	358.59	967.9
323.16	995.2	363.33	964.4
328.23	991.2	363.33	964.4
333.09	987.3		

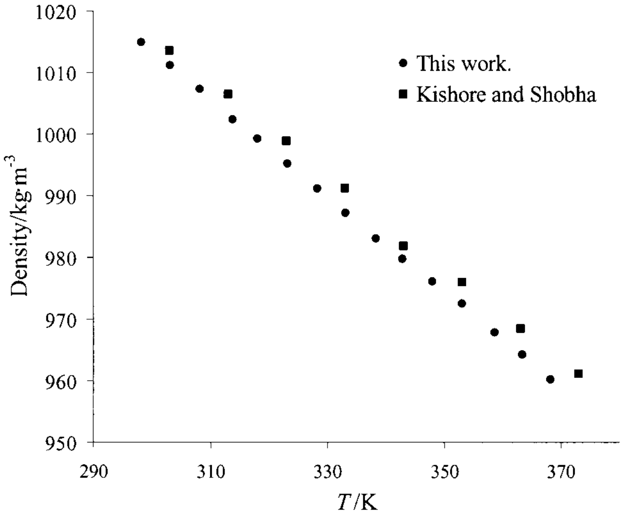

Figure 8. Comparison of experimental densities of pentaerythritol tetrapentanoate versus temperature between this work and Kishore and Shobha (1992).

deviation between the data is around 0.4%. This is a little above the combined margins of error since the uncertainty of the equipment used in this work is 0.1% while the uncertainty of the equipment used by Kishore and Shobha is 0.2%. An explanation of the deviation between the two works might be that the syntheses of the esters are slightly different and therefore the byproduct may be different. The purity of the esters may also be different; in this work the purity is more than 95% while Kishore and Shobha have not mentioned the exact purity. Another factor that may influence the measured values is how well the esters are degassed before the measurements.

Conclusions

The solubilities of five binary systems of five HFCs in a pentaerythritol tetrapentanoate ester have been measured with an isochoric method. Correlation with the Flory−Huggins model with extended temperature dependence shows that the theory is able to describe these kinds of mixtures with a deviation from measured data of less than 2%.

Henry's constant has been derived for low-pressure measurements and within the investigated temperature range the logarithm of Henry's constant versus the inverse temperature forms a straight line for all HFCs. Solubilities for HFCs decrease in the following order: HFC152a > HFC134a > HFC32 > HFC125 > HFC143a.

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Literature Cited

Black, K. D.; Gunstone, F. D. The Synthesis and Spectroscopic Properties of Some Polyol Esters and Ethers. *Chem. Phys. Lipids* **1990**, *56*, 169−173.

Brelvi, S. W.; O'Connell, J. P. Corresponding States Correlations for Liquid Compressibility and Partial Molar Volumes of Gases at Infinite Dilution in Liquids. *AIChE J.* **1972**, *18*, 1239−1243.

Cavestri, R. C.; Munk, J.; Menning, M. Solubility, Viscosity, and Density Measurements of Refrigerant-Lubricant Mixtures. *Proceedings of the Annual Meeting of ASHRAE Transactions*, June 25−29, 1994, Orlando, FL; ASHRAE: Atlanta, GA, 1994; Vol. 100, pp 220−238.

Chappelow, C. C.; Prausnitz, J. M. Solubilities of Gases in High-Boiling Hydrocarbon Solvents. *AIChE J.* **1974**, *20*, 1097−1104.

Grebner, J. J.; Crawford, R. R. Measurement of Pressure-Temperature-Concentration Relations for Mixtures of R-12/Mineral Oil and R-134a Synthetic Oil. *Proceedings of the 1993 Winter Meeting of ASHRAE Transactions*, Jan 23−27, 1993, Chicago, IL; ASHRAE: Atlanta, GA, 1993; Vol. 99, pp 387−396.

Henderson, D. R. *Solubility, Viscosity and Density of Refrigerant/Lubricant Mixtures*; Final Technical Report; Spauschus Associates, Inc.: Eagle's Landing, Stockbridge, GA, 1994.

Kishore, K.; Shobha, H. K. Structural Dependence of Density in High Molecular Weight Esters. *J. Chem. Eng. Data* **1992**, *37*, 371−376.

Martz, W. L.; Burton, C. M.; Jacobi, A. M. Local Composition Modeling of the Thermodynamic Properties of Refrigerant and Oil Mixtures. *Int. J. Refrig.* **1996**, *19*, 25−33.

McLinden, M. O.; Lemmon, E. W.; Klein, S. A.; Peskin, A. P. Refprop6 (Computer Program for Thermodynamic and Transport Properties of Refrigerants and Refrigerant Mixtures); NIST Standard Reference Database23, Version 6.0; National Institute of Standards and Technology: Washington, DC, 1998.

Prausnitz, J. M.; Lichtenthaler, R. N.; Gomes de Azevedo, E. *Molecular* Thermodynamics of Fluid-Phase Equilibria, 2nd ed.; PTR Prentice-Hall Inc: Englewood Cliffs, NJ, 1986.

Stelmachowski, M.; Ledakowicz, S. Prediction of Henry's Constants by the UNIFAC-FV Model for Hydrocarbon Gases and Vapors in High-Boiling Hydrocarbon Solvents. *Fluid Phase Equilib.* **1993**, *90*, 205−217.

Takaishi, Y.; Oguchi, K. Solubility of the Solutions of HFC-134a and Polyolester Based Oil. *Proceedings of the IIR Conference*, May 12−14, 1993, Ghent, Belgium; 1993; International Institute of Refrigeration: Paris, France, Commission B1/2, pp 141−148.

Takaishi, Y.; Oguchi, K. Solubility of R-32 and Polyolester Lubricant Mixtures. *Proceedings of the 19th International Congress of Refrigeration*, Aug 20−25, 1995, The Hague, The Netherlands; 1995; International Institute of Refrigeration: Paris, France, Commission B1, pp 568−574.

Thomas, R. H. P.; Pham, H. T. Solubility and Miscibility of Environmentally Safer Refrigerants/Lubricants Mixtures. *ASHRAE Trans. Symp.* **1992**, *5*, 783−788.

Wahlström, Å.; Vamling, L. The Solubility of HFC125, HFC134a, HFC143a, and HFC152a in *n*-Eicosane, *n*-Hexadecane, *n*-Tridecane and 2,6,10,14-Tetramethylpentadecane. *Can. J. Chem. Eng.* **1997a**, *75*, 544−550.

Wahlström, Å.; Vamling, L. Prediction of Solubility for HFC Working Fluids in Model Substances for Compressor Oils. *Can. J. Chem. Eng.* **1997b**, *75*, 551−561.

Wimby, M.; Berntsson, T. Viscosity and Density of Aqueous Solutions of LiBr, LiCl, $ZnBr_2$, $CaCl_2$, and $LiNO_3$. 1. Single Salt Solutions. *J. Chem. Eng. Data* **1994**, *39*, 68−72.

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