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Solubility of HFCs in Pentaerythritol Tetraalkyl Esters

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The solubilities of difluoromethane (HFC32), 1,1,1,2,2-pentafluoroethane (HFC125), 1,1,1,2-tetrafluoroethane (HFC134a), 1,1,1-trifluoroethane (HFC143a), and 1,1-difluoroethane (HFC152a) in pentaerythritol tetranonanoate, pentaerythritol tetra-2-ethylbutanoate, and pentaerythritol tetra-2-ethylhexanoate have been measured at temperatures between 303 and 363 K and pressures between 0.07 and 2.1 MPa. Henry's constant and the activity coefficient for HFCs at infinite dilution were derived for measurements below 0.34 MPa. The measurements were made by an isochoric method with an uncertainty of <2% for Henry's constant and <3% at high pressure. Within the investigated temperature range, solubilities for HFCs in pentaerythritol tetraalkyl esters 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 <2.7%.

Introduction

The Montreal protocol has regulated the production of chlorofluorocarbons and hydrochlorofluorocarbons, and this has led to the use of hydrofluorocarbons (HFCs) as working fluids in heat pumps and refrigeration systems. However, since HFCs have a different influence on compressor oils, new oils that are compatible with HFCs need to be found. For commercial applications, polyalkylene glycol (PAG), alkylbenzene (AB), and polyol ester (POE) have frequently been suggested as likely alternatives while mineral oils have been found to be unacceptable (Short and Rajewski, 1996). POEs have been found to have favorable properties compared to those of PAGs. They are less hygroscopic, have higher miscibilities, and are miscible with mineral oils (Thomas and Pham, 1992; Short and Cavestri, 1992). Therefore, we have chosen in this work to consider one type of POEs, namely pentaerythritol tetraalkyl esters (PEs).

To minimize costly experimentation in the search for suitable compressor oils for different applications, new thermodynamic tools that can predict the behavior of HFCs and different kinds of PEs would be very useful. Viscosity and lubricity are very important factors for a successful compressor oil, and these factors are dependent on the solubility of the working fluid in the compressor oil. Knowledge of the solubility of HFCs in PEs is therefore very important in the evaluation of new thermodynamic models.

Solubility measurements have previously been carried out for HFCs in different POE oils by Takaishi and Oguchi (1993, 1995), Grebner and Crawford (1993), Cavestri et al. (1994), Henderson (1994), and Martz et al. (1996). However, these authors did not describe the exact structure of the oil molecules or whether the oils consist of mixtures of different oil molecules. It is therefore difficult to use those data in the evaluation and development of a predictive model for solubility of HFCs and compressor oils.As far as we know, no one has reported the solubility of HFCs in different compressor oils consisting of only one substance with a known structure. Therefore, we have made measurements of the solubility of five different HFCs in three different PEs. The PEs consist of a nucleus which has four equal alkyl chains. The nuclei are the same in all three PEs, and the four alkyl chains are one linear one and two different branched ones for each PE, respectively; see Figure 1. Together with data from another linear pentaerythritol tetraalkyl ester with known structure (Wahlström and Vamling, 1999), these series of data can be used as a basis for evaluation of predictive thermodynamic tools.

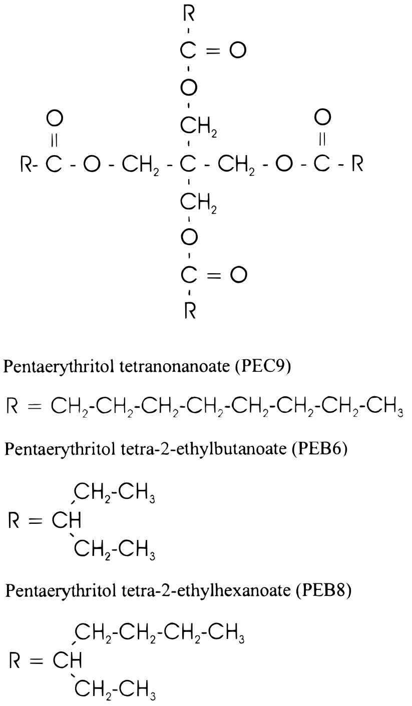

Figure 1. Chemical structures for the different PEs. All PEs consist of the same nucleus with four equal alkyl chains R.

Experimental Methods

Isochoric Technique. The experimental technique is an isochoric one where the amount of gas absorbed in a

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Table 1. Mole Fraction Solubility of HFC32 in PEC9

T/K	P/MPa	x	T/K	P/MPa	x
303.13	0.2033	0.1877	343.24	0.2525	0.1264
303.14	0.2174	0.1973	343.24	0.2702	0.1324
303.09	0.2339	0.2097	343.20	0.2904	0.1417
303.18	0.3783	0.2988	343.25	0.5197	0.2236
303.19	0.7137	0.4635	343.25	0.9458	0.3485
303.15	0.8820	0.5314	343.21	1.2496	0.4244
303.15	1.2908	0.6622	343.21	1.7887	0.5343
323.07	0.2310	0.1532	363.22	0.2693	0.1061
323.08	0.2469	0.1612	363.21	0.2877	0.1116
323.03	0.2658	0.1715	363.20	0.3096	0.1189
323.10	0.4550	0.2583	363.23	0.5731	0.1959
323.10	0.8445	0.4026	363.23	1.0235	0.3051
323.07	1.0836	0.4759	363.12	1.3810	0.3836
323.06	1.5792	0.5968	363.11	1.9372	0.4856

Table 2. Mole Fraction Solubility of HFC125 in PEC9

T/K	P/MPa	x	T/K	P/MPa	x
303.15	0.0928	0.0787	343.25	0.1295	0.0532
302.91	0.1021	0.0867	343.23	0.1422	0.0592
303.11	0.2462	0.2033	343.20	0.3093	0.1225
302.91	0.3729	0.2861	343.23	0.5168	0.1924
302.91	0.4993	0.3611	343.23	0.6556	0.2365
302.88	0.9493	0.5715	343.23	1.4358	0.4333
302.88	1.2951	0.6985	343.24	1.9431	0.5328
323.09	0.1115	0.0656	363.22	0.1442	0.0435
323.08	0.1226	0.0725	363.33	0.1579	0.0489
323.05	0.2826	0.1569	363.16	0.3290	0.0972
323.08	0.4537	0.2345	363.32	0.5651	0.1593
323.08	0.5913	0.2913	363.32	0.7018	0.1927
323.07	1.2093	0.4919	363.27	1.5910	0.3736
323.08	1.6548	0.6017	363.28	2.1035	0.4582

Table 3. Mole Fraction Solubility of HFC134a in PEC9

T/K	P/MPa	x	T/K	P/MPa	x
303.15	0.1038	0.1622	343.25	0.1630	0.1138
303.14	0.1186	0.1843	343.26	0.1806	0.1269
303.16	0.1677	0.2499	343.25	0.2387	0.1629
303.14	0.3326	0.4146	343.24	0.5558	0.3143
302.90	0.4160	0.4917	343.23	0.7163	0.3852
302.91	0.4743	0.5399	343.23	0.7811	0.4067
302.90	0.6056	0.6480	343.23	1.0700	0.5155
323.09	0.1348	0.1370	363.22	0.1863	0.0949
323.11	0.1514	0.1542	363.24	0.2035	0.1060
323.10	0.2071	0.2031	363.22	0.2622	0.1332
323.09	0.4503	0.3646	363.23	0.6417	0.2696
323.07	0.5746	0.4395	363.33	0.8312	0.3355
323.07	0.6433	0.4749	363.31	0.8830	0.3450
323.07	0.8616	0.5864	363.31	1.2183	0.4482

Table 4. Mole Fraction Solubility of HFC143a in PEC9

T/K	P/MPa	x	T/K	P/MPa	x
303.16	0.1353	0.1020	343.21	0.1728	0.0718
303.15	0.1741	0.1269	343.24	0.2118	0.0863
303.09	0.2667	0.1910	343.18	0.3186	0.1269
303.01	0.3975	0.2571	343.23	0.5236	0.1846
303.00	0.9242	0.5031	343.23	1.1982	0.3719
303.04	0.9392	0.5104	343.21	1.2994	0.3892
303.03	1.3353	0.6642	343.20	1.8465	0.5068
323.08	0.1557	0.0854	363.24	0.1876	0.0606
323.09	0.1950	0.1044	363.22	0.2249	0.0727
323.03	0.2964	0.1545	363.13	0.3356	0.1068
323.07	0.4668	0.2176	363.33	0.5688	0.1593
323.07	1.0857	0.4308	363.31	1.2811	0.3217
323.07	1.1426	0.4450	363.33	1.4194	0.3419
323.07	1.6501	0.5780	363.33	1.9742	0.4461

Table 5. Mole Fraction Solubility of HFC152a in PEC9

T/K	P/MPa	x	T/K	P/MPa	x
303.15	0.1131	0.2286	343.26	0.1693	0.1579
303.11	0.1190	0.2361	343.21	0.1780	0.1627
303.11	0.1335	0.2604	343.21	0.2001	0.1815
303.17	0.1821	0.3276	343.26	0.3139	0.2578
303.18	0.3287	0.5096	343.26	0.5638	0.4072
303.16	0.3418	0.5214	343.22	0.6276	0.4348
303.16	0.4642	0.6481	343.25	0.8665	0.5472
323.10	0.1438	0.1909	363.24	0.1891	0.1317
323.05	0.1513	0.1970	363.20	0.1996	0.1342
323.05	0.1699	0.2185	363.17	0.2238	0.1512
323.09	0.2492	0.2930	363.22	0.3722	0.2245
323.09	0.4519	0.4607	363.21	0.6539	0.3591
323.09	0.4856	0.4810	363.22	0.7507	0.3893
323.09	0.6704	0.6034	363.22	1.0220	0.4893

Table 6. Mole Fraction Solubility of HFC32 in PEB6

T/K	P/MPa	x	T/K	P/MPa	x
323.11	0.1180	0.0817	343.27	0.8317	0.3311
323.11	0.1495	0.1024	343.28	1.1018	0.4039
323.10	0.1621	0.1112	343.28	1.5808	0.5127
323.11	0.3624	0.2243	363.25	0.1552	0.0577
323.11	0.7130	0.3807	363.23	0.1971	0.0726
323.11	0.9282	0.4548	363.28	0.2115	0.0776
323.11	1.3377	0.5716	363.22	0.4792	0.1646
343.28	0.1382	0.0683	363.22	0.9242	0.2893
343.26	0.1753	0.0859	363.25	1.2414	0.3607
343.24	0.1894	0.0923	363.25	1.7605	0.4613
343.27	0.4261	0.1915			

Table 7. Mole Fraction Solubility of HFC125 in PEB6

T/K	P/MPa	x	T/K	P/MPa	x
323.11	0.1404	0.0934	343.24	0.9374	0.3598
323.04	0.1519	0.1022	343.22	1.1996	0.4321
323.07	0.1686	0.1132	343.25	1.5109	0.5149
323.09	0.4006	0.2434	363.28	0.1868	0.0603
323.09	0.7709	0.4272	363.23	0.2058	0.0665
323.11	0.9592	0.5004	363.21	0.2281	0.0744
323.11	1.2094	0.5898	363.24	0.5534	0.1615
343.25	0.1658	0.0750	363.22	1.0590	0.2996
343.19	0.1819	0.0820	363.24	1.3842	0.3666
343.24	0.2019	0.0913	363.27	1.7228	0.4385
343.22	0.4858	0.1985			

Table 8. Mole Fraction Solubility of HFC134a in PEB6

T/K	P/MPa	x	T/K	P/MPa	x
323.13	0.1106	0.1282	343.25	0.5702	0.3552
323.09	0.1144	0.1315	343.27	0.5817	0.3652
323.11	0.1275	0.1466	343.26	0.8401	0.4790
323.11	0.2619	0.2767	363.29	0.1657	0.0886
323.10	0.4333	0.4036	363.22	0.1741	0.0923
323.12	0.4489	0.4178	363.24	0.1909	0.1031
323.11	0.6320	0.5349	363.24	0.4073	0.2034
343.29	0.1407	0.1065	363.23	0.6887	0.3082
343.25	0.1464	0.1105	363.25	0.6914	0.3139
343.27	0.1615	0.1232	363.24	1.0126	0.4198
343.28	0.3401	0.2382			

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 is thoroughly described by Wahlström and Vamling (1997a) while the calculations of absorbed gas, Henry's constant, and the activity coefficient at infinite dilution are described by Wahlström and Vamling (1999). The uncertainty of each experimental quantity is given by Wahlström and Vamling (1997a), and the total uncertainty of each measurement is estimated to be <2% at low pressure (Henry's constant) and <3% at high pressure.

Density Measurements. The densities of the PEs were determined with an Anton Paar DMA 602 vibrating tube densitometer, described by Wimby and Berntsson (1994). The tube was filled at 20 °C with degassed PE, and then the temperature was increased to the desired temperature. Ethanol and double-distilled water were used as calibration liquids. The uncertainty in the temperature reading was ±0.05 °C, and the uncertainty of the measured densities is estimated to <0.1%.

Table 9. Mole Fraction Solubility of HFC143a in PEB6

T/K	P/MPa	x	T/K	P/MPa	x
323.09	0.1651	0.0861	343.27	0.9292	0.3080
323.08	0.1707	0.0886	343.26	1.2634	0.3967
323.12	0.2202	0.1119	343.27	1.7884	0.5178
323.12	0.4173	0.2025	363.23	0.2089	0.0577
323.12	0.8163	0.3615	363.22	0.2158	0.0595
323.11	1.0780	0.4537	363.25	0.2718	0.0747
323.11	1.5164	0.5882	363.25	0.5253	0.1452
343.26	0.1894	0.0699	363.26	1.0124	0.2625
343.24	0.1955	0.0723	363.25	1.4050	0.3452
343.29	0.2490	0.0910	363.24	1.9669	0.4499
343.29	0.4769	0.1711			

Table 10. Mole Fraction Solubility of HFC152a in PEB6

T/K	P/MPa	x	T/K	P/MPa	x
323.13	0.0964	0.1256	343.29	0.3793	0.2978
323.13	0.1023	0.1345	343.28	0.5036	0.3766
323.12	0.1091	0.1447	343.28	0.7400	0.5021
323.14	0.2937	0.3387	363.28	0.1446	0.0915
323.12	0.3809	0.4173	363.29	0.1489	0.0964
323.12	0.5506	0.5485	363.28	0.1689	0.1064
343.29	0.1219	0.1074	363.27	0.4537	0.2585
343.28	0.1273	0.1142	363.26	0.6157	0.3394
343.26	0.1407	0.1244	363.27	0.9074	0.4513

Table 11. Mole Fraction Solubility of HFC32 in PEB8

T/K	P/MPa	x	T/K	P/MPa	x
303.16	0.1346	0.1305	343.26	0.1818	0.0922
303.10	0.1466	0.1426	343.21	0.2001	0.0997
303.17	0.1551	0.1510	343.27	0.2112	0.1069
303.14	0.3901	0.3292	343.13	0.5588	0.2424
303.12	0.5202	0.3951	343.14	0.7593	0.3043
303.12	0.7677	0.5157	343.12	1.1742	0.4224
303.16	1.1357	0.6416	343.16	1.6146	0.5120
323.10	0.1590	0.1105	363.20	0.2005	0.0779
323.03	0.1748	0.1198	363.20	0.2207	0.0840
323.11	0.1847	0.1276	363.21	0.2332	0.0904
323.24	0.4827	0.2828	363.23	0.6214	0.2090
323.22	0.6488	0.3477	363.23	0.8490	0.2695
323.22	0.9870	0.4679	363.21	1.3344	0.3822
323.27	1.4121	0.5755	363.25	1.7624	0.4586

Table 12. Mole Fraction Solubility of HFC125 in PEB8

T/K	P/MPa	x	T/K	P/MPa	x
303.11	0.1322	0.1321	343.22	0.1880	0.0846
303.11	0.1508	0.1468	343.20	0.2138	0.0943
303.14	0.1605	0.1577	343.24	0.2286	0.1019
303.16	0.4732	0.4003	343.16	0.7314	0.2951
303.15	0.7054	0.5314	343.17	1.1890	0.4109
303.15	1.0272	0.6812	343.16	1.6389	0.5208
323.07	0.1620	0.1066	363.21	0.2075	0.0689
323.04	0.1841	0.1190	363.15	0.2368	0.0759
323.08	0.1973	0.1275	363.20	0.2527	0.0829
323.26	0.6157	0.3446	363.26	0.8208	0.2544
323.26	0.9660	0.4724	363.29	1.3647	0.3514
323.25	1.3836	0.6048	363.23	1.8071	0.4393

Table 13. Mole Fraction Solubility of HFC134a in PEB8

T/K	P/MPa	x	T/K	P/MPa	x
303.14	0.0901	0.1515	343.15	0.1080	0.0791
303.16	0.1110	0.1881	343.26	0.1453	0.1043
303.14	0.2142	0.3244	343.12	0.1903	0.1357
303.13	0.3224	0.4475	343.15	0.3841	0.2529
303.16	0.5389	0.6530	343.13	0.5871	0.3533
323.24	0.0873	0.0952	343.15	1.0257	0.5334
323.09	0.1183	0.1275	363.22	0.1269	0.0653
323.24	0.1521	0.1610	363.21	0.1675	0.0855
323.24	0.3007	0.2895	363.23	0.2243	0.1133
323.23	0.4580	0.4022	363.24	0.4607	0.2191
323.25	0.7952	0.5997	363.23	0.6999	0.3057
363.22	1.2047	0.4637			

Table 14. Mole Fraction Solubility of HFC143a in PEB8

T/K	P/MPa	x	T/K	P/MPa	x
303.11	0.1475	0.1113	343.22	0.1893	0.0773
303.13	0.1568	0.1156	343.23	0.2000	0.0810
303.14	0.1665	0.1216	343.25	0.2133	0.0843
303.13	0.5577	0.3651	343.15	0.7920	0.2793
303.13	0.8017	0.4888	343.12	1.1496	0.3774
303.15	1.1591	0.6482	343.16	1.6783	0.4959
323.05	0.1688	0.0941	363.22	0.2059	0.0646
323.07	0.1785	0.0985	363.21	0.2173	0.0680
323.08	0.1901	0.1030	363.22	0.2320	0.0700
323.23	0.6854	0.3190	363.24	0.8787	0.2445
323.23	0.9975	0.4292	363.25	1.2687	0.3321
323.27	1.4727	0.5676	363.23	1.8150	0.4322

Table 15. Mole Fraction Solubility of HFC152a in PEB8

T/K	P/MPa	x	T/K	P/MPa	x
303.11	0.0751	0.1576	343.21	0.1242	0.1163
303.18	0.0842	0.1739	343.26	0.1388	0.1294
303.18	0.1007	0.2053	343.26	0.1681	0.1534
303.19	0.2618	0.4544	343.31	0.4371	0.3435
303.16	0.4006	0.5865	343.15	0.7368	0.4817
323.04	0.1000	0.1367	363.18	0.1451	0.0990
323.10	0.1116	0.1516	363.29	0.1626	0.1100
323.12	0.1347	0.1794	363.26	0.1971	0.1307
323.14	0.3552	0.3999	363.31	0.5015	0.2930
323.28	0.5739	0.5388	363.24	0.8732	0.4221

Chemicals. The HFCs used are difluoromethane (HFC32), 1,1,1,2,2-pentafluoroethane (HFC125), 1,1,1,2-tetrafluoroethane (HFC134a), 1,1,1-trifluoroethane (HFC143a), and 1,1-difluoroethane (HFC152a), and the purity according to the manufacturers is 99.9% for all of them. 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 three different PEs are pentaerythritol tetranonanoate PEC9, pentaerythritol tetra-2-ethylhexanoate PEB6, and pentaerythritol tetra-2-ethylbutanoate PEB8. Figure 1 shows the chemical structure for each PE. The pentaerythritol tetraalkyl esters were 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 solvent instead of *m*-xylene.

For synthesis of PEC9, pentaerythritol (Aldrich 98%, 0.70 mol, 97 g) was mixed with nonanoic acid (Aldrich 96%, 3.08 mol, 560 mL), *p*-toluenesulfonic acid (8.4 g), and 175 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 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 0.1 mbar and 200−220 °C. The product was 440 g of 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 >95%.

The synthesis of PEB6 was performed in the same way except that pentaerythritol (Aldrich 98%, 1.0 mol, 139 g) was mixed with 2-ethylbutanoic acid (Aldrich 99%, 4.4 mol, 560 mL), *p*-toluenesulfonic acid (12 g), and 100 mL of *p*-xylene in a 1000 mL round flask. The mixture was reflux-boiled for 4 days and vacuum-distilled at 0.08 mbar and 190−200 °C. The product was 415 g of a yellow-brown oil which crystallized (79% exchange, melting point 37−39 °C). The purity was estimated to be >95%.

The synthesis of PEB8 was also performed in the same way as that for PEC9 that pentaerythritol (Aldrich 98%, 0.80 mol, 111 g) was mixed with 2-ethylhexanoic acid (Aldrich 99%, 3.52 mol, 570 mL), *p*-toluenesulfonic acid (9.6 g), and 200 mL of *p*-xylene in a 1000 mL round flask. The mixture was reflux-boiled for 6 days and vacuum-distilled at 0.08 mbar and 200−230 °C. The product was 430 g of a slightly yellow oil (84% exchange). The purity was estimated to be >90% regarding tetraesters. The product probably contains small amounts of di- and triesters (5−10%).

Correlation of Experimental Data

All experimental data are correlated with an extended Flory−Huggins-based model, which is thoroughly described by Wahlström and Vamling (1999). Briefly, the model is based on equality of vapor and liquid fugacities. The deviation from ideality in the vapor phase is described with a gas-phase fugacity coefficient calculated with an equation of state. In the liquid phase the activity coefficient expression derived by Flory and Huggins is used:

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

where

$$\Phi_2^* = \frac{rx_2}{x_1 + rx_2} \qquad (2)$$

and where r is the number of segments in a PE molecule. Here x_1 is the mole fraction of the HFC and x_2 is the mole fraction of the PE. Previous work (Wahlström and Vamling, 1997b) has shown that, by introducing an extra temperature dependence in the expression for the χ parameter, the representation of experimental data can be improved. The χ parameter is then given by

$$\chi = \frac{w^0}{kT}\left(1 + \frac{w^1}{T}\right) \qquad (3)$$

where k is Boltzmann's constant and w^0 and w^1 are related to the interchange energy between a HFC molecule and a PE segment.

The model contains three empirical parameters, w^0, w^1, and r, which were simultaneously regressed for each mixture to fit the experimental data. The result of the parameter estimation is expressed as the relative deviation DP of the calculated equilibrium pressures, as described by Wahlström and Vamling (1999).

We have also correlated the low-pressure experimental data with the equation

$$\ln \mathrm{He}_{1,2} = \ln \mathrm{He}_{1,2}^{\mathrm{ref}} + B\left(\frac{1}{T} - \frac{1}{T^{\mathrm{ref}}}\right) \qquad (4)$$

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.

Results

The experimental solubilities for the 15 mixtures of five different HFCs in three different PEs are presented in Tables 1−15. Measurements were made at four temperatures for PEC9 and PEB8 mixtures and at three temperatures for PEB6 mixtures, since PEB6 is solid at 303 K. Henry's constant has been derived for three different measurements at each temperature with equilibrium pressures below 0.34 MPa, except for the HFC134a + PEB8 mixture at 303 K, where only two different measurements are used. The representation can be seen in Figures 2−4, where the derived experimental Henry's constants are plotted on a logarithmic scale versus the reciprocal temperature 1/*T*. It was found that within the investigated

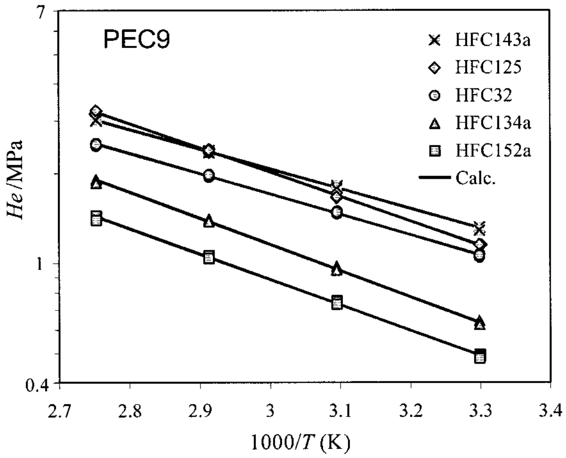

Figure 2. Henry's constant versus temperature for HFCs in PEC9.

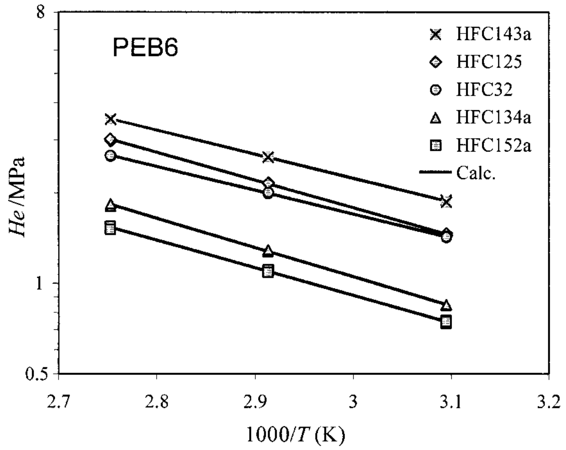

Figure 3. Henry's constant versus temperature for HFCs in PEB6.

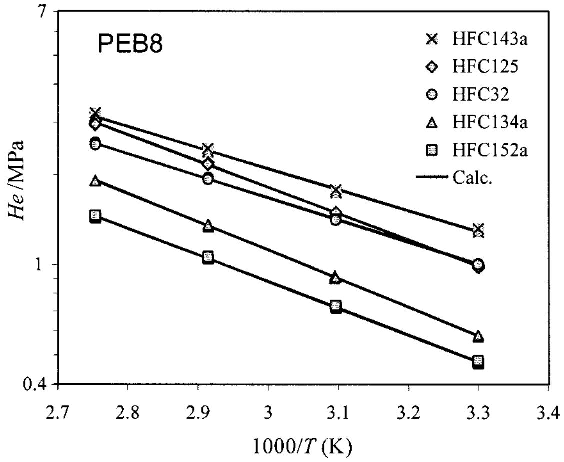

Figure 4. Henry's constant versus temperature for HFCs in PEB8.

Table 16. Number of Points and Specific Parameters with Their 95% Confidence Intervals for Calculating Henry's Constant with Eq 4 for HFC−PE Mixtures[a]

mixture	Np	$He_{1,2}^{ref}$/MPa	B/K
HFC32 + PEC9	12	1.704 ± 0.014	−1568 ± 39
HFC125 + PEC9	12	2.015 ± 0.017	−1880 ± 41
HFC134a + PEC9	12	1.155 ± 0.011	−2017 ± 47
HFC143a + PEC9	12	2.067 ± 0.014	−1523 ± 33
HFC152a + PEC9	12	0.882 ± 0.009	−1958 ± 52
HFC32 + PEB6	9	1.696 ± 0.008	−1821 ± 29
HFC125 + PEB6	9	1.779 ± 0.012	−2119 ± 42
HFC134a + PEB6	9	1.048 ± 0.009	−2240 ± 52
HFC143a + PEB6	9	2.231 ± 0.010	−1841 ± 29
HFC152a + PEB6	9	0.909 ± 0.009	−2114 ± 64
HFC32 + PEB8	12	1.666 ± 0.008	−1701 ± 25
HFC125 + PEB8	12	1.805 ± 0.014	−2027 ± 37
HFC134a + PEB8	11	1.112 ± 0.005	−2193 ± 24
HFC143a + PEB8	12	2.087 ± 0.025	−1616 ± 60
HFC152a + PEB8	12	0.873 ± 0.006	−2051 ± 31

[a] For PEC9 and PEB8 mixtures the parameters are derived at temperatures between 303 and 363 K, and for PEB6 mixtures at temperatures between 323 and 363 K

Table 17. Activity Coefficients at Infinite Dilution for HFCs in PEs

	T/K			
mixture	303.1	323.1	343.2	363.2
HFC32 + PEC9	0.73	0.70	0.69	
HFC125 + PEC9	1.00	1.03		
HFC134a + PEC9	0.98	0.94	0.94	0.95
HFC143a + PEC9	1.22	1.17	1.20	
HFC152a + PEC9	0.83	0.79	0.76	0.75
HFC32 + PEB6		0.67	0.70	
HFC125 + PEB6		0.89		
HFC134a + PEB6		0.83	0.87	0.92
HFC143a + PEB6		1.22	1.33	
HFC152a + PEB6		0.80	0.80	0.81
HFC32 + PEB8	0.69	0.67	0.68	
HFC125 + PEB8	0.86	0.91		
HFC134a + PEB8	0.90	0.89	0.91	0.97
HFC143a + PEB8	1.22	1.15	1.22	
HFC152a + PEB8	0.81	0.77	0.76	0.77

Table 18. Number of Measurements, Specific Parameters for the Flory−Huggins Model with Extended Temperature Dependence, and the Relative Deviation DP for HFCs Dissolved in PEC9, PEB6, and PEB8

mixture	Np	$w^0 \cdot k^{-1}$/K	w^1/K	r	DP/%
HFC32 + PEC9	28	839	−158	14.93	1.98
HFC125 + PEC9	28	997	−208	6.91	2.01
HFC134a + PEC9	28	938	−176	10.41	2.08
HFC143a + PEC9	28	817	−152	7.79	2.12
HFC152a + PEC9	28	654	−152	10.03	1.42
HFC32 + PEB6	21	680	−209	7.77	1.30
HFC125 + PEB6	21	993	−271	3.94	1.16
HFC134a + PEB6	21	973	−233	7.03	1.05
HFC143a + PEB6	21	772	−199	4.31	2.68
HFC152a + PEB6	18	491	−205	5.19	0.90
HFC32 + PEB8	28	775	−177	11.58	1.48
HFC125 + PEB8	24	998	−238	5.81	1.85
HFC134a + PEB8	23	808	−203	6.94	1.90
HFC143a + PEB8	24	703	−162	5.76	2.17
HFC152a + PEB8	20	707	−169	9.76	1.92

Table 19. Densities of PEs at Various Temperatures

PEC9		PEB6		PEB8	
T/K	ρ/kg·m^{-3}	T/K	ρ/kg·m^{-3}	T/K	ρ/kg·m^{-3}
298.30	951.3	313.08	978.2	299.26	960.6
303.20	947.9	318.18	974.4	303.16	958.1
307.21	945.2	323.23	970.7	308.04	954.7
318.30	936.4	328.33	967.1	313.14	950.7
323.21	933.0	338.30	960.2	317.98	947.2
328.30	929.4	342.92	957.2	323.17	943.6
338.28	922.5	348.04	953.7	328.19	940.2
342.90	919.6	358.18	946.8	333.32	936.7
348.05	916.3	363.08	943.5	338.16	933.4
358.16	909.4	368.26	939.9	343.19	930.1
363.04	906.0			347.82	927.1
368.20	902.6			352.92	923.8
357.92	920.5				
363.18	917.0				
367.66	914.1				

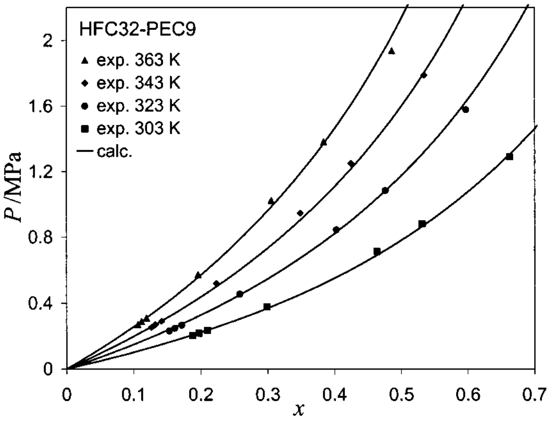

Figure 5. Experimental and Flory−Huggins-calculated pressures versus mole fraction composition for HFC32 in PEC9 at various temperatures.

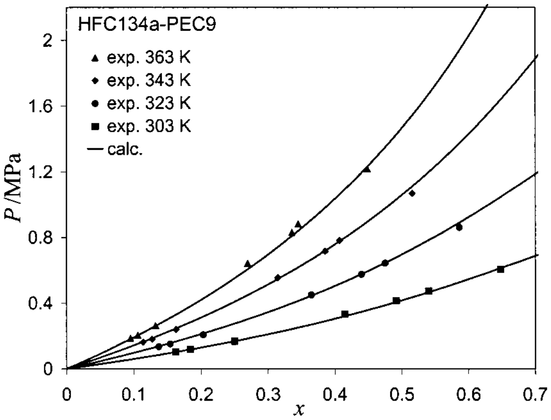

Figure 6. Experimental and Flory−Huggins-calculated pressures versus mole fraction composition for HFC134a in PEC9 at various temperatures.

temperature range a practically straight line is formed. Therefore, the data were fitted to eq 4, and the resulting parameters are given in Table 16 together with their 95% confidence interval. The calculated Henry's constants from eq 4 are also plotted in Figures 2−4. Comparison of Henry's constant at the reference temperature (Table 16) shows that the solubilities for HFCs in PEs decrease in the following order: HFC152a > HFC134a > HFC32 > HFC125 > HFC143a. Values for the activity coefficient at infinite dilution are given in Table 17. The activity coefficient has not been derived for temperatures where the solute is above its critical temperature.

The experimental values were correlated with the Flory−Huggins model with an extended temperature dependence. In Table 18 the number of measurements, the specific parameters w^0, w^1, and r, and the relative deviation DP of calculated and experimental pressures are given for each mixture. Examples of the representation can be seen in Figures 5−9, where experimental and calculated pressures are plotted versus composition of HFCs in PEs, for various temperatures.

The experimental densities at various temperatures for the PEs are presented in Table 19. Our densities for PEC9

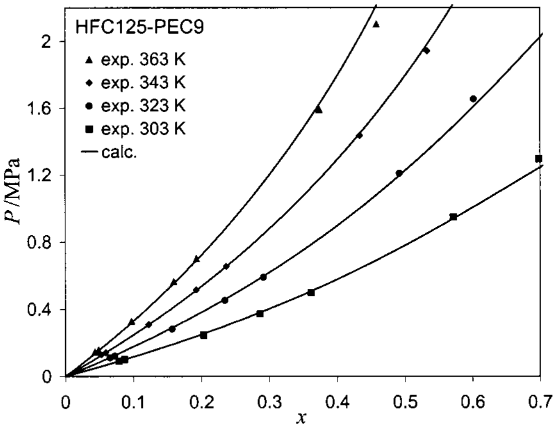

Figure 7. Experimental and Flory–Huggins-calculated pressures versus mole fraction composition for HFC125 in PEC9 at various temperatures.

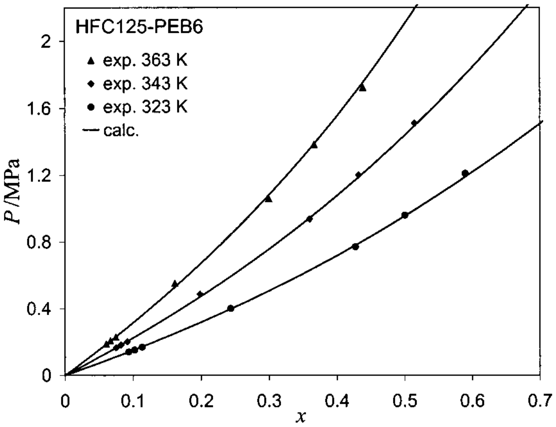

Figure 8. Experimental and Flory–Huggins-calculated pressures versus mole fraction composition for HFC125 in PEB6 at various temperatures.

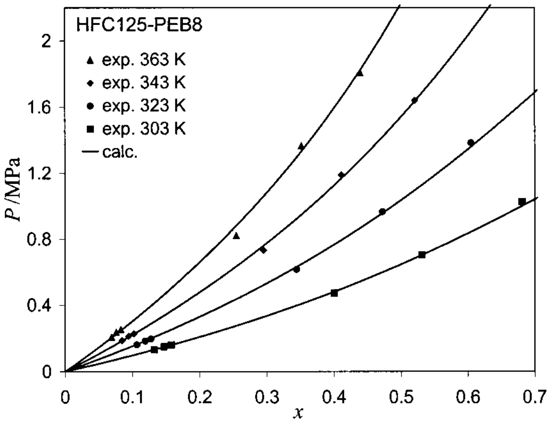

Figure 9. Experimental and Flory–Huggins-calculated pressures versus mole fraction composition for HFC125a in PEB8 at various temperatures.

are compared with measurements made by Kishore and Shobha (1992) in Figure 10. The difference between the densities is <0.6%.

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 studied, HFC32 shows a negative deviation from Raoult's law while HFC143a has a positive deviation.

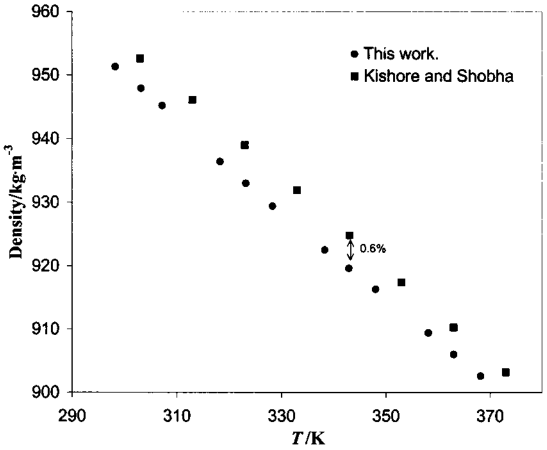

Figure 10. Comparison of experimental densities of PEC9 versus temperature between this work and that of Kishore and Shobha (1992).

Comparison of the densities measured in this work and the results of Kishore and Shobha (1992) shows that the difference between the data is 0.6%. This is 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%. This might depend on the fact that the syntheses of PEC9 are slightly different and therefore the purities and the byproducts may be different. The purity of the PEC9 in this work is >95% while Kishore and Shobha have not stated the purity.

Conclusions

The solubilities of 15 binary systems of five HFCs in three different pentaerythritol tetraalkyl esters have been measured with an isochoric method. 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 mixtures. Solubilities for HFCs in pentaerythritol tetraalkyl esters decrease in the following order: HFC152a > HFC134a > HFC32 > HFC125 > HFC143a.

Correlation with the Flory–Huggins model with extended temperature dependence shows that the theory is able to describe these kinds of mixtures with an uncertainty <2.7%.

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