Solubility and Miscibility for the Mixture of (Ethyl Fluoride + Polyol Ester Oil)

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Vapor−liquid equilibrium (VLE) data of lubricating oil + refrigerant mixtures are necessary for the design and simulation of the refrigeration system. In this paper, the saturated vapor pressure data and VLE data of different mass fractions of the mixture (ethyl fluoride (HFC-161) + polyol ester oil (POE)) in the temperature range from (253 to 333) K were measured by a single-phase cycle method. Throughout the observation of the overall experiment, there was no stratification and no sediment generation, and the color of liquid had no change in the equilibrium cell before and after the experiment. The above-mentioned content suggested that the different ratios of HFC-161 and lubricating oil POE could be miscible. Meanwhile, the saturated vapor-pressure data of the mixture (HFC-161 + POE) revealed that POE had a very small effect on the saturated vapor pressure of the mixture (almost negligible) when the mass fraction of lubricating oil was less than 0.1 of the mixture; POE had a bigger effect on the saturated vapor pressure of the mixture when there was more oil in the mixture. In addition, using the nonrandom two-liquid (NRTL) model and the Wilson model, VLE experimental data were correlated, and the results showed that they had a good agreement with correlated results, to the average and maximum of relative pressure deviations. The results derived from the NRTL model were better than those derived from the Wilson model.

Introduction

Ethyl fluoride (HFC-161) is an environmentally friendly refrigerant that is not destructive to the ozone layer and has a low global-warming potential. It has a very high cooling capacity, relatively high volume cooling capacity, and excellent energy efficiency ratio. At fixed operating conditions, HFC-161 can achieve the same cooling capacity and save energy, conserving global resources and energy, which are becoming increasingly important. Thus, HFC-161 offers tangible economic and social benefits, while minimizing the greenhouse effect on the earth. However, this refrigerant is considered flammable. Refrigerant mixtures using HFC-161 are considered to be new and promising alternative refrigerants.[1,2] So when it comes to environmental protection and conservation of energy, we propose a new type of refrigerant mixtures with HFC-161 and others which have significant advantages. There are some key technology barriers to be surmounted before using such systems, such as refrigerant−lubricant compatibility.[3] Because some lubricating oil inevitably may migrate from the compressor to other parts of the system, such as the evaporator, condenser, expansion device, piping, and so on, thus the presence of the lubricant oil would considerably affect the system performance. Therefore, the purpose of this work is focused on the solubility and miscibility of the mixture (HFC-161 + polyol ester oil (POE)), it will have a scientific and engineering value to promote the new type of environmentally friendly refrigerants.

Experiment

Apparatus. A schematic of the experimental equipment in this work is shown in Figure 1, very similar to the one described in detail by He et al.[4,5] It consists of a stainless steel equilibrium cell with its volume of 80 mL fitted with a motor stirrer coupled to an external drive. A visual observation of the solution in the cell can be made to observe the phase behavior inside it. The cell is thermostatted in a bath, fitted with glass windows, and insulated with polyurethane foam. A circulation loop from vapor to liquid phase is used to accelerate the equilibration by a vapor pump. The temperature was measured with a platinum resistance thermometer (model WZP-II) with a total uncertainty of ± 15 mK. The pressure in the equilibrium cell was measured by a pressure transducer (model PMP4010 from DRUCK, England) and differential pressure null transducer (model 1151DP, from Xi'an Instrument Factory, China). The total uncertainty in pressure measurement is ± 0.0016 MPa. The sample mass was determined with the electronic scales (model: BS4000S, from Beijing Sartorius Limited Co., accuracy: 0.01 g).

Materials. The sample of HFC-161, provided by Zhejiang Lantian Environmental Protection Co., Ltd. (FLTCO), has a mass fraction purity of > 0.9974 with the principal impurities of ethylene and isobutane. It is used without further purification.

The lubricating oil POE (SUNICE T-68) used was bought from SUNOCO Co.; its molecule structure is branch-chain type, and its ISO viscosity grade is VG-68. The typical properties were shown in Table 1. The lubricants were dried to less than 30 ppm before use by a vacuum dehydration unit.

Procedure. The system was first evacuated to remove inert gases. The lubricating oil was weighed into the cell; the entire system was evacuated, and the desired amount of refrigerant was then charged into the cell. The amount of charge was such that 80 % to 90 % of the cell's volume was filled with liquid. Vapor space corrections were therefore negligible. The composition charged into the cell was therefore the composition of the liquid. The entire assembly was positioned on top of a stir plate and submerged in a thermostatted bath. The system was stirred continuously and allowed to equilibrate for an hour before taking measurements. At low temperatures and high concentrations of lubricant, they required a longer time for equilibrium. After the equilibrium, the data (temperature, pressure, and mass fraction of HFC-161 in the liquid phase) were recorded. The

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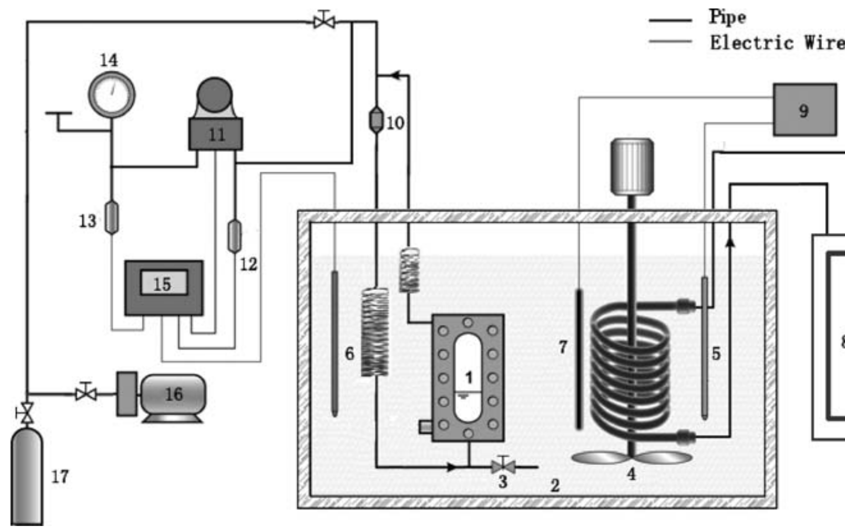

Figure 1. Schematic diagram of the experimental apparatus. 1, equilibrium cell; 2, thermostated bath; 3, valve; 4, stirrer; 5, platinum resistance thermometer; 6, calibrated platinum resistance thermometer; 7, heater; 8, refrigeration system; 9, temperature control instrument; 10, circulation pump; 11, differential-pressure sensor; 12, 13, pressure sensor; 14, piston pressure gauge; 15, data collecting system; 16, vacuum pump; 17, sample.

Table 1. Typical Properties of the Lubricating Oil POE

property	tested method	SUNICE T-68
ρ (288.15 K)/g·cm^{-3}	ASTM D 1250	0.960
Chroma ASTM	ASTM D 1500	L0.5
kinematic viscosity at 313.15 K/mm^2·s^{-1}	ASTM D 445	66.6
kinematic viscosity at 373.15 K/mm^2·s^{-1}	ASTM D 445	8.22
closed flash point/K	ASTM D 92	527.15
pour point/K	ASTM D 97	233.15
total acid number/mg KOH·g^{-1}	ASTM D 974	0.01
$10^6 w$ (H_2O)	ASTM D 4928	35
volume resistance point at 298.15 K/cm	ASTM D 1169	$5.0 \cdot 10^{14}$

vapor pressure of the mixture (refrigerant (1) + oil (2)) was determined from $w_1 = 0$ to 0.90 and (253 to 343) K.

Analysis of the Experimental Uncertainty. In this paper, the experiment uncertainty may be caused by the main factors, such as temperature measurement uncertainty, pressure measurement uncertainty, reagents' purity uncertainty, the liquid component measurement uncertainty, and so on.

Temperature Measurement Uncertainty. In this experiment, the temperature was measured by the secondary W2PB-2 standard platinum resistance thermometers with an uncertainty of ± 0.01 K and data collection instrument for Keithley2010 (7-bit). In the experiment, uneven fluctuations were less than ± 10 mK·h^{-1}; temperature fluctuations are less than ± 5 mK in 30 min in the relatively short time. The total uncertainty in temperature measurement was less than ± 15 mK.

Pressure Measurement Uncertainty. The pressure was measured with a pressure transducer (model PMP4010 from DRUCK, England) and differential pressure null transducer (model 1151DP, from Xi'an Instrument Factory, China). The total uncertainty in pressure measurement was estimated to be ± 0.0016 MPa.

Component Measurement Uncertainty. In this paper, the mass of the mixture (refrigerant and lubricating oil) was determined by weighing the lubricating oil and refrigerant in electronic scales (model: BS4000S, from Beijing Sartorius (Sartorius) Limited Co., its full scale: 4010 g, and its uncertainty: 0.01 g), respectively.

The mass fraction of refrigerant in the liquid phase is as follows:

$$w_R = \frac{m_R - m_{V,R}}{m_R + m_{OIL} - m_{V,R}} \tag{1}$$

where m_{OIL} is the mass of lubricating oil, m_R is the additive refrigerant mass, and $m_{V,R}$ is the vapor-phase refrigerant mass in the equilibrium cell.

The masses m_{OIL} and m_R were determined on an electronic scale; its uncertainty is 0.01 g. The mass of refrigerant in the vapor phase is obtained by the following equation:

$$m_{V,R} = \rho V \tag{2}$$

where ρ is the refrigerant density in the vapor phase, obtained by REFPROP,[6] and the vapor-phase refrigerant volume V consists of two parts, stainless steel pipe volume V_1 and the upper vapor space volume V_2 in the equilibrium cell. In this paper, by measurement, the vapor measurement uncertainty of the total volume is ± 1.15 cm^3, and the total uncertainty of w_R is ± 0.002.

Theory

The equation-of-state approach is difficult for polar substance and macromolecular compound electrolyte systems. The lubricating oil is usually a macromolecular compound, whereas HFC-161 is a polar molecule. Making matters more challenging, the equation of state requires detailed thermophysical data (for example critical temperature, critical pressure, and so on) which are difficult to know. Therefore, the activity coefficient method is chosen to deal with vapor−liquid equilibrium (VLE) data of the mixture (refrigerants + lubricating oil) in this paper.

There are a lot of activity coefficient models. Common activity coefficient models are the Wohl model,[7] Van Laar model,[8] Flory−Huggins model,[9] Wilson model,[10] Heil model,[11] NRTL model (nonrandom two-liquid),[12] UNIQUAC model (universal quasi-chemical model),[13] and their modified models. However, every model cannot correlate all VLE data of the mixture (refrigerants + lubricating oil). Moreover, despite its simple form, the Van Laar model is rarely used to correlate these data, whereas the UNIFAC model contains functional

Table 2. Experimental and Calculated Results by Wilson and NRTL Models for the Mixture (HFC-161 (1) + POE (2))

			NRTL model			Wilson model		
T/K	w_1	p/Pa	p_{calc}/Pa	$100((p - p_{calc})/p)$	$y_{1,calc}$	p_{calc}/Pa	$100((p - p_{calc})/p)$	$y_{1,calc}$
253.15	0.1204	116500	109812	5.7409	0.9426	109680	5.8544	0.9415
	0.1981	135000	143164	−6.0475	1.0605	143641	−6.4008	1.0640
	0.3295	176000	174823	0.6689	0.9933	175149	0.4833	0.9952
	0.4300	189900	188305	0.8400	0.9916	188467	1.6865	0.9831
	0.5274	196700	196765	−0.0328	1.0003	196834	−3.6516	1.0365
	0.6157	203900	202062	0.9013	0.9910	202090	0.8876	0.9911
	0.7362	210200	207038	1.5041	0.9850	207044	1.5017	0.9850
	0.7917	210700	208736	0.9320	0.9907	208738	0.9312	0.9907
	0.8891	211400	211090	0.1466	0.9985	211090	0.1467	0.9985
258.15	0.1200	136500	140523	−2.9472	1.0295	129464	5.1547	0.9485
	0.1977	168300	173733	−3.2284	1.0323	172010	−5.9825	1.0598
	0.3289	212200	208858	1.5750	0.9843	211867	0.1568	0.9984
	0.4298	231300	225531	2.4941	0.9751	228603	1.1659	0.9883
	0.5272	241700	236499	2.1520	0.9785	238848	1.1798	0.9882
	0.6155	244800	243548	0.5116	0.9949	245143	−0.1399	1.0014
	0.7362	250800	250222	0.2306	0.9977	250963	−0.0649	1.0006
	0.7916	253300	252470	0.3276	0.9967	252926	0.1479	0.9985
	0.8891	256000	255538	0.1807	0.9982	255662	0.1321	0.9987
263.15	0.1194	159600	153928	3.5542	0.9645	150113	5.9442	0.9406
	0.1973	193400	204678	−5.8312	1.0583	203692	−5.3215	1.0532
	0.3283	253900	252510	0.5476	0.9945	255292	−0.5481	1.0055
	0.4295	277400	272991	1.5893	0.9841	277053	0.1251	0.9987
	0.5271	293800	285704	2.7558	0.9724	289885	1.3325	0.9867
	0.6153	298900	293605	1.7716	0.9823	297252	0.5515	0.9945
	0.7361	302400	301014	0.4585	0.9954	303383	−0.3252	1.0033
	0.7916	304100	303521	0.1903	0.9981	305226	−0.3701	1.0037
	0.8891	307200	306986	0.0698	0.9993	307612	−0.1341	1.0013
268.15	0.1188	188200	181168	3.7364	0.9626	176018	6.4731	0.9353
	0.1968	229600	241500	−5.1831	1.0518	241020	−5.4331	1.0543
	0.3276	301400	301709	−0.1025	1.0010	304515	−1.0336	1.0103
	0.4292	330200	328521	0.5086	0.9949	331743	−0.4673	1.0047
	0.5268	356300	344811	3.2245	0.9678	347717	2.4090	0.9759
	0.6152	361000	354373	1.8358	0.9816	356778	1.1696	0.9883
	0.7361	361600	362228	−0.1737	1.0017	363938	−0.6467	1.0065
	0.7915	362800	364438	−0.4516	1.0045	365861	−0.8436	1.0084
	0.8890	366300	367006	−0.1926	1.0019	367884	−0.4325	1.0043
273.15	0.1181	219500	211371	3.7034	0.9630	204816	6.6900	0.9331
	0.1962	269800	286945	−6.3545	1.0635	282625	−5.4176	1.0542
	0.3267	354900	356070	−0.3296	1.0033	359451	−1.2824	1.0128
	0.4289	391000	385428	1.4251	0.9857	393085	−0.5332	1.0053
	0.5266	422700	403267	4.5974	0.9540	412858	2.3284	0.9767
	0.6150	430900	414312	3.8497	0.9615	424141	1.5685	0.9843
	0.7359	432100	424636	1.7274	0.9827	433142	−0.2411	1.0024
	0.7914	434500	428132	1.4657	0.9853	435610	−0.2555	1.0026
	0.8890	436000	432978	0.6931	0.9931	438544	−0.5835	1.0058
278.15	0.1173	254500	249398	2.0047	0.9800	243930	4.1531	0.9585
	0.1956	322200	337018	−4.5989	1.0460	333539	−6.8351	1.0684
	0.3258	415200	417721	−0.6072	1.0061	416158	−0.2306	1.0023
	0.4283	459200	452504	1.4582	0.9854	451659	1.6423	0.9836
	0.5263	493200	473698	3.9542	0.9605	473237	4.0477	0.9595
	0.6148	506000	486806	3.7933	0.9621	486552	3.8436	0.9616
	0.7358	508700	499052	1.8966	0.9810	498956	1.9155	0.9808
	0.7913	509300	503190	1.1996	0.9880	503136	1.2104	0.9879
	0.8889	511700	508918	0.5436	0.9946	508905	0.5462	0.9945
283.15	0.1161	292800	283442	3.1960	0.9680	280880	4.0711	0.9593
	0.1949	373100	390333	−4.6188	1.0462	386490	−6.4418	1.0644
	0.3247	482600	486684	−0.8462	1.0085	483815	−0.2518	1.0025
	0.4278	534800	528166	1.2404	0.9876	526300	1.5893	0.9841
	0.5261	572100	553193	3.3049	0.9670	552063	3.5024	0.9650
	0.6146	588100	568568	3.3211	0.9668	567905	3.4340	0.9657
	0.7357	593500	582913	1.7838	0.9822	582648	1.8285	0.9817
	0.7910	594900	587734	1.2045	0.9880	587580	1.2304	0.9877
	0.8888	597500	594443	0.5116	0.9949	594405	0.5181	0.9948
288.15	0.1150	333500	320588	3.8718	0.9613	310047	7.0324	0.9297
	0.1941	424900	447450	−5.3070	1.0531	437238	−5.3839	1.0538
	0.3235	556300	561619	−0.9561	1.0096	563007	−1.2056	1.0121
	0.4272	619600	611409	1.3220	0.9868	620562	−0.1553	1.0016
	0.5257	666500	641302	3.7806	0.9622	654483	1.8030	0.9820
	0.6143	679200	659619	2.8830	0.9712	673890	0.7819	0.9922
	0.7354	691800	676631	2.1926	0.9781	689481	0.3352	0.9966
	0.7909	692600	682345	1.4807	0.9852	693758	−0.1672	1.0017
	0.8887	694700	690229	0.6435	0.9936	698693	−0.5748	1.0057

Table 2. Continued

			NRTL model			Wilson model		
T/K	w_1	p/Pa	p_{calc}/Pa	$100((p - p_{calc})/p)$	$y_{1,calc}$	p_{calc}/Pa	$100((p - p_{calc})/p)$	$y_{1,calc}$
293.15	0.1142	378700	381591	−0.7635	1.0076	368523	2.6875	0.9731
	0.3219	638100	649555	−1.7952	1.0180	653657	−2.4381	1.0244
	0.4266	714200	706824	1.0328	0.9897	716450	−0.3150	1.0031
	0.5254	756300	741019	2.0205	0.9798	752475	0.5057	0.9949
	0.6149	776300	762129	1.8255	0.9817	773008	0.4241	0.9958
	0.7349	794100	781415	1.5974	0.9840	789305	0.6038	0.9940
	0.7907	795800	788012	0.9787	0.9902	794005	0.2255	0.9977
	0.8887	800200	797095	0.3880	0.9961	799588	0.0765	0.9992
298.15	0.1129	426800	406787	4.6891	0.9531	401732	5.8734	0.9413
	0.1916	532300	564995	−6.1422	1.0614	562730	−7.7407	1.0774
	0.3203	727600	720970	0.9112	0.9909	720228	1.0132	0.9899
	0.4259	805200	795829	1.1638	0.9884	795293	1.2304	0.9877
	0.5204	851600	839717	1.3954	0.9860	839282	1.4465	0.9855
	0.6129	875800	869315	0.7405	0.9926	868996	0.7769	0.9922
	0.7341	901400	895264	0.6808	0.9932	895099	0.6990	0.9930
	0.7901	903600	903870	−0.0299	1.0003	903766	−0.0183	1.0002
	0.8887	917900	915401	0.2722	0.9973	915371	0.2755	0.9972
303.15	0.1121	478400	455749	4.7348	0.9527	444622	7.0607	0.9294
	0.1904	596600	629494	−5.5136	1.0551	628323	−7.1127	1.0711
	0.3185	824000	807884	1.9559	0.9804	812062	1.4488	0.9855
	0.4251	904900	898473	0.7102	0.9929	902315	0.2857	0.9971
	0.5174	952200	951266	0.0981	0.9990	954025	−0.1916	1.0019
	0.6122	989100	989131	−0.0031	1.0000	990820	−0.1739	1.0017
	0.7329	1014500	1021365	−0.6767	1.0068	1022079	−0.7471	1.0075
	0.7890	1023800	1032056	−0.8064	1.0081	1032475	−0.8473	1.0085
	0.8886	1043700	1046264	−0.2457	1.0025	1046368	−0.2556	1.0026
308.15	0.1105	533500	510619	4.2888	0.9571	481812	9.6885	0.9031
	0.1890	654600	693420	−5.9304	1.0593	692629	−5.8095	1.0581
	0.3162	911900	888627	2.5522	0.9745	907058	0.5310	0.9947
	0.4223	1009000	996278	1.2608	0.9874	1015105	−0.6050	1.0061
	0.5158	1058400	1063809	−0.5111	1.0051	1078652	−1.9134	1.0191
	0.6103	1109200	1113273	−0.3672	1.0037	1123242	−1.2660	1.0127
	0.7319	1139100	1156790	−1.5530	1.0155	1161445	−1.9616	1.0196
	0.7882	1158200	1171148	−1.1180	1.0112	1173997	−1.3639	1.0136
	0.8884	1184700	1189867	−0.4362	1.0044	1190621	−0.4998	1.0050
313.15	0.1087	591100	565029	4.4105	0.9559	517812	10.8911	0.8911
	0.1873	733000	768764	−4.8791	1.0488	757801	−4.8134	1.0481
	0.3123	1019800	979564	3.9455	0.9605	1004604	1.4901	0.9851
	0.4200	1116900	1104730	1.0896	0.9891	1136087	−1.7179	1.0172
	0.5140	1169900	1185981	−1.3746	1.0137	1213222	−3.7030	1.0370
	0.6077	1243700	1247149	−0.2774	1.0028	1266929	−1.8677	1.0187
	0.7307	1285500	1303942	−1.4346	1.0143	1313848	−2.2052	1.0221
	0.7870	1296400	1322716	−2.0299	1.0203	1328970	−2.5123	1.0251
	0.8873	1339100	1347073	−0.5954	1.0060	1348819	−0.7258	1.0073
318.15	0.1067	650300	626959	3.5893	0.9641	549946	14.2452	0.8575
	0.1855	801100	856296	−6.8900	1.0689	821289	−4.3436	1.0434
	0.3076	1108700	1076073	2.9428	0.9706	1102377	1.4591	0.9854
	0.4171	1228000	1214442	1.1041	0.9890	1262608	−2.8183	1.0282
	0.5119	1296800	1308355	−0.8911	1.0089	1356721	−4.6207	1.0462
	0.6064	1378400	1383563	−0.3745	1.0037	1422576	−3.2048	1.0320
	0.7293	1450000	1457671	−0.5290	1.0053	1479632	−2.0435	1.0204
	0.7856	1460600	1483412	−1.5618	1.0156	1497966	−2.5583	1.0256
	0.8869	1504900	1517631	−0.8460	1.0085	1521985	−1.1353	1.0114
323.15	0.1044	713800	713891	−0.0127	1.0001	595266	16.6061	0.8339
	0.3029	1222900	1179705	3.5321	0.9647	1218000	0.4007	0.9960
	0.4144	1341900	1328248	1.0174	0.9898	1407606	−4.8965	1.0490
	0.5090	1429200	1432387	−0.2230	1.0022	1517093	−6.1498	1.0615
	0.6044	1531100	1522351	0.5714	0.9943	1594820	−4.1617	1.0416
	0.7276	1630600	1617505	0.8031	0.9920	1661662	−1.9049	1.0190
	0.7839	1650500	1652641	−0.1297	1.0013	1683055	−1.9724	1.0197
	0.8864	1692100	1701594	−0.5611	1.0056	1711239	−1.1311	1.0113
328.15	0.1018	779500	803786	−3.1156	1.0312	626382	19.6431	0.8036
	0.2986	1342200	1346619	−0.3293	1.0033	1326872	1.1420	0.9886
	0.4119	1458000	1509875	−3.5579	1.0356	1553220	−6.5308	1.0653
	0.5062	1557100	1619613	−4.0147	1.0401	1682973	−8.0838	1.0808
	0.6027	1705500	1715312	−0.5753	1.0058	1777167	−4.2021	1.0420
	0.7263	1824000	1816217	0.4267	0.9957	1857666	−1.8457	1.0185
	0.7827	1836200	1853847	−0.9611	1.0096	1883336	−2.5670	1.0257
	0.8853	1890200	1906996	−0.8886	1.0089	1916869	−1.4109	1.0141
333.15	0.0987	845600	857088	−1.3585	1.0136	643262	23.9284	0.7607
	0.2936	1456200	1461806	−0.3850	1.0038	1424981	1.4672	0.9853
	0.4091	1575800	1651000	−4.7722	1.0477	1697340	−7.7129	1.0771
	0.5029	1695300	1777156	−4.8284	1.0483	1852490	−9.2721	1.0927
	0.6008	1875800	1891598	−0.8422	1.0084	1968807	−4.9583	1.0496
	0.7247	2035400	2013625	1.0698	0.9893	2067580	−1.5810	1.0158
	0.7813	2047500	2060065	−0.6137	1.0061	2099101	−2.5202	1.0252
	0.8846	2111700	2126588	−0.7050	1.0071	2140004	−1.3403	1.0134

groups; as lubricating oil is usually in the mixture, it hardly was used in this field.

Martz et al.[14] compared the six activity coefficient models based on the concept of local mole fraction, including Wilson, Heil, NRTL, Tsuboka and Katayama, Wang−Chao, and UNIQUAC models through seven different refrigerant + lubricant (R12 + naphthenic oil, R12 + paraffinic oil, R22 + POE, R134a + polyalkylene glycol oil (PAG), R134a + POE, R125 + POE). The results showed that the correlated results from the Heil model were best.

Wahlstrom and Lennart[15] used the five activity coefficient models to correlate the solubility data for 20 systems of five different hydrofluorocarbons (HFCs) in four different pentaerythritol esters. The five models were the Flory−Huggins, UNIQUAC, Wilson, Heil, and NRTL models. The Flory−Huggins and UNIQUAC models had some difficulties in describing all isotherms with only two parameters, while the Wilson, Heil, and NRTL models all showed a better ability.

Taking into account the above-mentioned comparison and the complexity of different activity coefficient models themselves, the Wilson[10] and NRTL[12] models will be used to correlated the VLE data of the mixture (HFC-161 (1) + POE (2)).

Results and Discussion

Throughout the observation of the overall experiment, there was no stratification and no sediment generation, and the color of liquid had no change in the equilibrium cell before and after the experiment. The above-mentioned content suggested that the different ratios of HFC-161 and lubricating oil POE could be miscible.

HFC-161 and the lubricating oil POE were mixed and placed on the equilibrium cell, where they were held at a constant temperature of 50 °C for four days. Subsequently, the vapor phase of the mixture was analyzed using chromatography (model GC112A from China), and the results showed the HFC-161 had no change over time, suggesting that no chemical reactions occurred. Moreover, the analysis showed there was almost no lubricating oil in the vapor phase of the mixture.

VLE data of the mixture (HFC-161 (1) + POE (2)) in the temperature range of (253 to 333) K were measured, shown in Table 2, where w_1 is the mass fraction of HFC-161 in the liquid phase.

The saturated vapor pressure of the mixture (HFC-161 (1) + POE (2)) varies with the temperature at different mass fractions of HFC-161, as shown in Figure 2. The saturated vapor pressure of the mixture (HFC-161 (1) + POE (2)) varies with the mass fraction of HFC-161 at the same temperature, as shown in Figure 3.

As can be seen from Figures 2 and 3, because of the addition of lubricants, the saturated vapor pressure of the mixture (HFC-161 (1) + POE (2)) is lower than that of pure substance HFC-161 at different temperatures. Especially in the higher temperatures, the deviation is more obvious. For example, saturated vapor pressures of the mixture with $w_1 = 0.5$ are about 0.035, 0.017, and 0.029 lower than those of HFC-161 respectively at the temperatures (263.15, 273.15, and 283.15) K, almost close to the HFC-161 saturated vapor pressure curve; when the temperatures are (313.15, 323.15, and 333.15) K, the relative deviations reached about 14 %, 20 %, and 22 %, respectively. From the above analysis and Figures 2 and 3, it can been seen that in the tested temperature range, POE had a very small effect on the saturated vapor pressure of the mixture (almost negligible) when the mass fraction of lubricating oil is less than 0.1 of the mixture. When w_1 is 0.7, 0.8, and 0.9, respectively, their saturated vapor pressure curves are close to that of HFC-161; when $w_1 = 0.2$ and 0.3, respectively, their saturated vapor pressures are also much lower than that of HFC-161 at $T = 253.15$ K, that is, POE had a bigger effect on saturated vapor pressure of the mixture when there was more oil in the mixture.

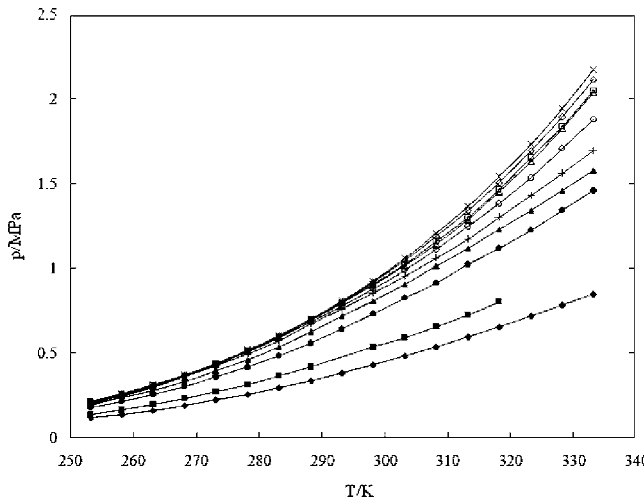

Figure 2. Curve of saturated vapor pressure p versus T for the mixture of (HFC-161 (1) + POE (2)). ◆, $w_1 = 0.12$ (HFC-161); ■, $w_1 = 0.20$; ●, $w_1 = 0.33$; ▲, $w_1 = 0.43$; +, $w_1 = 0.53$; ○, $w_1 = 0.61$; △, $w_1 = 0.74$; □, $w_1 = 0.79$; ◇, $w_1 = 0.89$; ×, $w_1 = 1.00$.

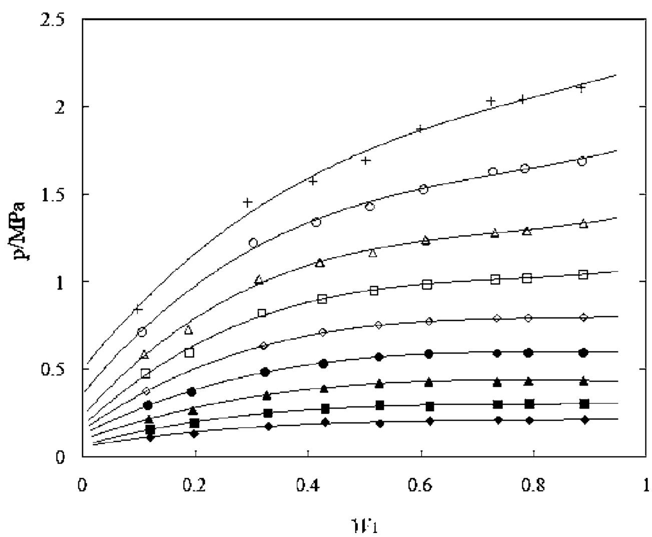

Figure 3. Curve of saturated vapor pressure of the mixture of (HFC-161 (1) + POE (2)) versus the mass fraction of HFC-161. ◆, $T = 253.15$ K; ■, $T = 263.15$ K; ▲, $T = 273.15$ K; ●, $T = 283.15$ K; ◇, $T = 293.15$ K; □, $T = 303.15$ K; △, $T = 313.15$ K; ○, $T = 323.15$ K; +, $T = 333.15$ K; −, calculated value.

In addition, by choosing different activity coefficient models, VLE data were correlated. In the correlation, the necessary conditions can be written between the vapor phase and the liquid phase:

$$y_i p = \gamma_i x_i p_i^s \tag{3}$$

where p is the equilibrium pressure, p_i^s is the saturated pressure of component i, y_i is the vapor mole fraction of component i, (in this paper, assumed $y_1 = 1$), and x_i is the liquid mole fraction of component i.

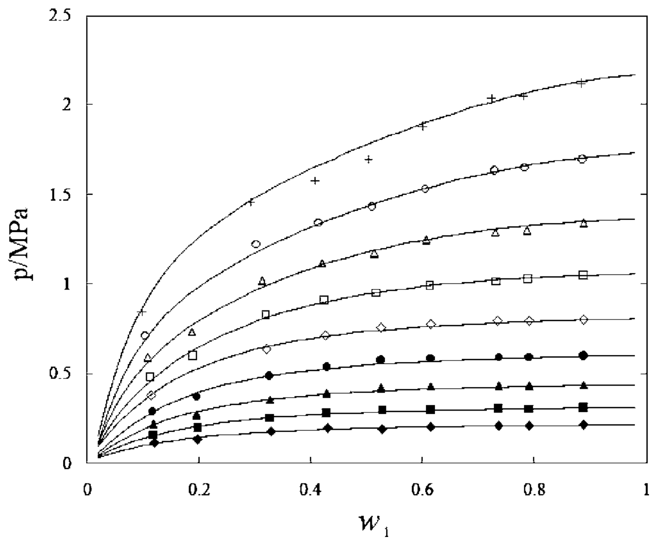

Figure 4. Correlated results with the NRTL model. ◆, $T = 253.15$ K; ■, $T = 263.15$ K; ▲, $T = 273.15$ K; ●, $T = 283.15$ K; ◇, $T = 293.15$ K; □, $T = 303.15$ K; △, $T = 313.15$ K; ○, $T = 323.15$ K; +, $T = 333.15$ K; —, calculated value.

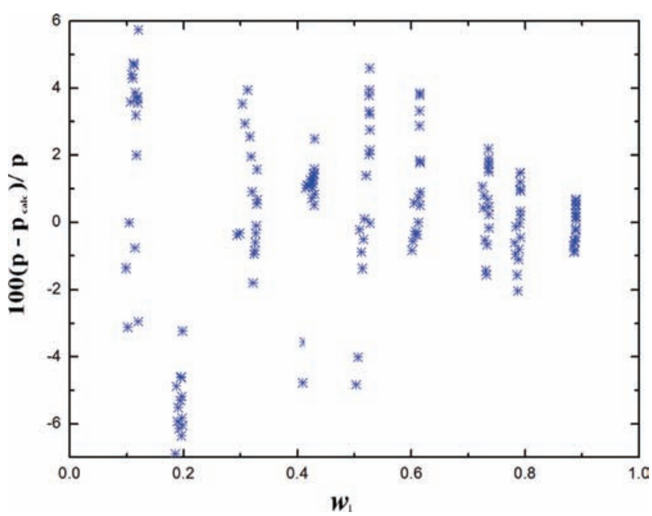

Figure 5. Relative pressure deviation of experimental data from the calculated values with the NRTL model for the mixture (HFC-161 (1) + POE (2)).

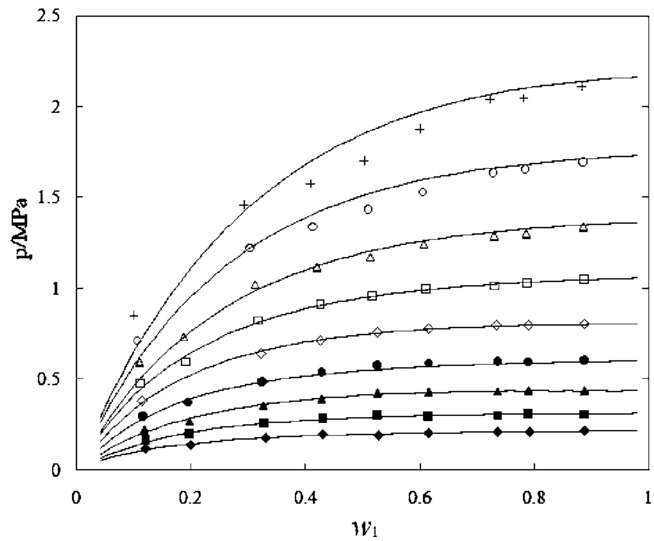

Figure 6. Correlated results with the Wilson model. ◆, $T = 253.15$ K; ■, $T = 263.15$ K; ▲, $T = 273.15$ K; ●, $T = 283.15$ K; ◇, $T = 293.15$ K; □, $T = 303.15$ K; △, $T = 313.15$ K; ○, $T = 323.15$ K; +, $T = 333.15$ K; —, calculated value.

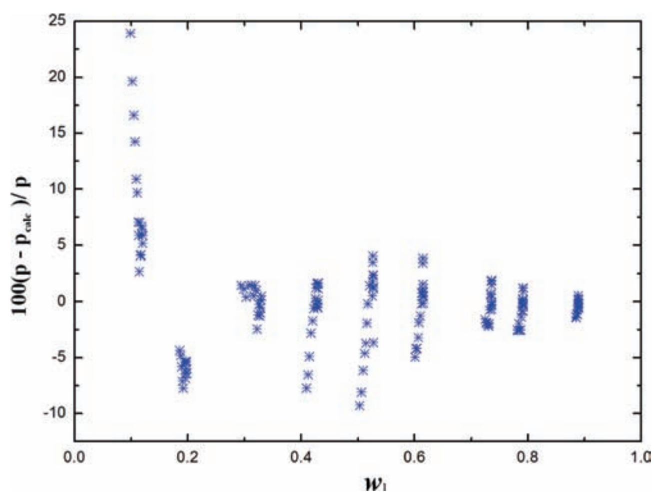

Figure 7. Relative pressure deviation of experimental data from the calculated values with the Wilson model for the mixture (HFC-161 (1) + POE (2)).

The parameters of the activity coefficient models are obtained by minimizing the objective function (OBJ):

$$\mathrm{OBJ} = \frac{\sum_{i=1}^{N_p} \left| \frac{p_{calc} - p}{p} \right|_i}{N_p} \tag{4}$$

where p_i is the experimental pressure, p_{calc} is the calculated pressure, and N_p is the number of experimental points.

Using NRTL and Wilson models, the correlated results of the binary mixture (HFC-161 (1) + POE (2)) are shown in Figures 4 to 7. The average relative pressure deviation and maximum relative pressure deviation are shown in Table 3 [$\delta p = (1/N_p)\sum|((p_{calc} - p)/p)|_i$] and Figures 5 and 7. The interaction parameters of Wilson and NRTL models are given in Table 4 (in the correlation, the molecular weight of HFC-161 is 48.06, and its saturated vapor pressure equation is shown in ref 16; the molecular weight of POE is 697.04 $g\cdot mol^{-1}$).[17]

As can be seen from Figures 4 to 7, correlated results using the NRTL model for the mixture (HFC-161 (1) + POE (2)) are better than those of Wilson; its largest relative deviation of the pressure is close to 6.4 %, but most of relative deviations are within (0 to 2) %. The largest relative deviation of the Wilson model is 23.9 %, and most of deviations are within (0 to 4) %. The reason for this is that the third interaction parameter α exists in the NRTL model.

In addition, the correlation coefficients R and determination coefficients DC of the Wilson model and NRTL model for the mixture (HFC-161 (1) + POE (2)) are obtained, as shown in Table 5.

The correlation coefficient R is calculated

$$R = \frac{\sum_{i=1}^{N_p} (p_i - \bar{p})(p_{calc,i} - \bar{p}_{calc})}{\sqrt{[\sum_{i=1}^{N_p} (p_i - \bar{p})^2][\sum_{i=1}^{N_p} (p_{calc,i} - \bar{p}_{calc})^2]}} \tag{5}$$

where $\bar{p}$ is the average experimental pressure and $\bar{p}_{calc}$ is the average calculated pressure.

Table 3. Average Relative Pressure Deviation and Maximum Relative Pressure Deviation Derived by NRTL Model and Wilson Model

	NRTL		Wilson	
T/K	100 δp	100 δp_{max}	100 δp	100 δp_{max}
253.15	1.8683	6.0475	2.3938	6.4008
258.15	1.5164	3.2284	1.5694	5.9825
263.15	1.8631	5.8312	1.6280	5.9442
268.15	1.7121	5.1831	2.1009	6.4731
273.15	2.6829	6.3545	2.1000	6.6900
278.15	2.2285	4.5989	2.7138	6.8351
283.15	2.2253	4.6188	2.5408	6.4418
288.15	2.4930	5.3070	1.9377	7.0324
293.15	1.3002	2.0205	0.9095	2.6875
298.15	1.7806	6.1422	2.1193	7.7407
303.15	1.6383	5.5136	2.0137	7.1127
308.15	2.0020	5.9304	2.6265	9.6885
313.15	2.2263	4.8791	3.3252	10.8911
318.15	2.0810	6.8900	4.0476	14.2452
323.15	2.1717	5.7353	4.6529	16.6061
328.15	1.7337	4.0147	5.6782	19.6431
333.15	1.8219	4.8284	6.5975	23.9284

Table 4. Interaction Parameters of the Wilson Model and NRTL Model for the Mixture (HFC-161 (1) + POE (2))

	NRTL model			Wilson model	
T/K	α	τ_{12}	τ_{21}	Λ_{12}	Λ_{21}
253.15	−0.5000	−2.1672	0.1953	4.5237	0.2211
258.15	−0.5000	−2.8499	0.7294	5.6076	0.0756
263.15	−0.5000	−2.2089	−7.0600	6.4637	0.0165
268.15	−0.5000	−2.1461	0.2876	6.7474	0.0030
273.15	−0.5000	−2.0829	−0.3536	6.9587	−0.0033
278.15	−0.5000	−2.1461	−0.1777	3.9916	0.5929
283.15	−0.5000	−2.1171	−0.4793	4.1538	0.5438
288.15	−0.5000	−2.2040	−0.7084	7.3281	−0.0031
293.15	−0.4500	−2.3514	0.0182	6.8128	0.0094
298.15	−0.4500	−3.0236	−5.5136	7.2808	0.0308
303.15	−0.4500	−3.4038	−5.9132	6.3691	0.1570
308.15	−0.4500	−4.1234	−6.7265	6.8499	0.1460
313.15	−0.4500	−4.7233	−3.9808	7.9820	0.1253
318.15	−0.4500	−5.6041	−1.2042	8.5269	0.1173
323.15	−0.4000	−7.1094	−3.3835	8.2637	0.1210
328.15	−0.4000	−6.4882	−2.1087	8.8471	0.1130
333.15	−0.4000	−7.4695	−2.0805	9.6767	0.1033

Table 5. Values of the Correlation Coefficient and Determination Coefficient of the Wilson Model and NRTL Model for the Mixture (HFC-161 (1) + POE (2))

	R		DC	
T/K	NRTL	Wilson	NRTL	Wilson
253.15	0.9980	0.9957	0.9930	0.9856
258.15	0.9970	0.9929	0.9947	0.9893
263.15	0.9983	0.9961	0.9954	0.9906
268.15	0.9982	0.9951	0.9941	0.9878
273.15	0.9974	0.9924	0.9943	0.9884
278.15	0.9981	0.9951	0.9928	0.9790
283.15	0.9963	0.9907	0.9941	0.9828
288.15	0.9982	0.9946	0.9956	0.9910
293.15	0.9995	0.9982	0.9987	0.9972
298.15	0.9988	0.9973	0.9952	0.9902
303.15	0.9988	0.9977	0.9956	0.9904
308.15	0.9985	0.9969	0.9960	0.9871
313.15	0.9983	0.9964	0.9949	0.9747
318.15	0.9985	0.9968	0.9926	0.9655
323.15	0.9995	0.9988	0.9899	0.9541
328.15	0.9993	0.9969	0.9915	0.9653
333.15	0.9988	0.9958	0.9890	0.9577

The determination coefficient (DC) is equal to the square of the correlation coefficient, that is

$$\mathrm{DC} = R^2 \tag{6}$$

From Tables 2 and 5, it can be seen that the experimental data have a good agreement with the correlated results obtained by the NRTL and Wilson models. The correlation coefficients and determination coefficients of the NRTL model are bigger (close to 1) than those of Wilson, so the coefficients further indicated that the correlated results by the NRTL model are superior to those of Wilson model.

Conclusions

In this paper, the saturated vapor pressure data and VLE data of nine different mass fractions of the mixture (HFC-161 (1) + POE (2)) in the temperature range of (253 to 333) K were measured by single-phase cycle method. Throughout the observation of overall experiment, there was no stratification and no sediment generation, and the color of the liquid had no change in the equilibrium cell before and after the experiment. The above-mentioned content suggested that the different ratios of HFC-161 and lubricating oil POE could be miscible. Meanwhile, saturated vapor pressure data of the mixture (HFC-161 (1) + POE (2)) revealed that POE had a very small effect on the saturated vapor pressure of the mixture (almost negligible) when lubricating oil was less than 10 % of the mixture; POE had a bigger effect on the saturated vapor pressure of the mixture when there was more oil in the mixture. Using the NRTL model and the Wilson model, experimental data were correlated, and the results showed that, to the average and maximum of relative pressure deviations, the results derived from considering the effects of temperature on the energy parameters were better than those derived from not considering the effects of temperature on the energy parameters. Moreover, the results showed that the NRTL activity coefficient model provided better results than Wilson model.

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