Thermophysical Properties of 2,2,2-Trifluoroethanol + Tetraethylene Glycol Dimethyl Ether

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Isothermal P,x data from 303.15 K to 423.15 K, liquid densities from 283.15 K to 423.15 K, and dynamic viscosities from 343.15 K to 393.15 K for the binary system 2,2,2-trifluoroethanol + tetraethylene glycol dimethyl ether were measured. The vapor−liquid equilibrium (VLE) data were measured using a static apparatus. VLE data were correlated by the five-parameter NRTL equation, while density and kinematic viscosity data were correlated with temperature and liquid composition using empirical equations. The viscosity data used in the correlation cover the range of 293.15−393.15 K. VLE data indicate that this binary system exhibits large negative deviations from Raoult's law. These mixtures present large exothermic excess molar enthalpies. The excess molar enthalpy calculated using the Gibbs−Helmholtz equation and the NRTL parameters was compared with experimental data existing in the literature.

Introduction

Organic fluid mixtures such as tetraethylene glycol dimethyl ether (2,5,8,11,14-pentaoxapentadecane, TEGDME or E181) with 2,2,2-trifluoroethanol (TFE) (Bockelmann and Renz, 1983; Seher and Stephan, 1983; Stephan and Hengerer, 1993; Coronas et al., 1996) and poly(ethylene glycol) 250 dimethyl ether (PEGDME 250), or TEGDME or glycerol with methanol (Stüven, 1989; Boer et al.,1994; Herraiz et al., 1996) have been suggested as working pairs in absorption heat pumping systems. Such mixtures are noncorrosive, are completely miscible over a wide temperature range, are thermally stable up to temperatures above 200 °C (Seher and Stephan, 1983), and can be used at low working pressures. Also, poly(ethylene glycol) dimethyl ether has been proved successful for scrubbing waste air and gas streams containing different organic substances because of its low vapor pressure, low viscosity, and good dissolving power for many organic substances, acid gases, and even inorganic compounds.

This work is a continuation of our study on new working fluid pairs for consideration in absorption cycles for refrigeration and for upgrading waste heat to a useful higher temperature level.

The vapor−liquid equilibrium (VLE) for the TFE + TEGDME system was reported by Seher and Stephan (1983) only at 725 Torr, while Krumbeck and Schulz (1989) measured excess enthalpy in the range of 298.15 K to 448.15 K. López et al. (1997) determined also excess enthalpy at 298.15 K and atmospheric pressure using a Calvet calorimeter. Stephan and Hengerer (1993) determined liquid densities and dynamic viscosities in the range of 293.15 K to 346.25 K using an aerometer and a falling-ball viscometer, respectively. Olivé et al. (1994, 1995) measured density at 303.15 K and atmospheric pressure with a vibrating-tube densitometer and kinematic viscosities using a Schott-Geräte capillary viscometer in the range 283.15−333.15 K. Svejda et al. (1990) reported excess volumes in the range 293.15−313.15 K, isothermal compressibilities at 0.1−10 MPa and 293.15 K, and excess enthalpy at 293.15 K and atmospheric pressure using a Picker calorimeter. Olivé (1998) reported excess volumes and viscosities from 283.15 K to 393.15 K and 293.15 to 393.15 K, respectively.

To complete the thermophysical properties of this system over a wide temperature range, we reported the vapor−liquid equilibria from 303.15 K to 423.15 K at 10 K intervals and pressures up to 1 MPa, liquid densities from 283.15 K to 423.15 K, and liquid dynamic viscosities from 340.15 K to 393.15 K.

Experimental Section

Materials. TFE (Solvay Fluor und Derivate GMBH, 99.9+%) and tetraethylene glycol dimethyl ether $CH_3O(CH_2CH_2O)_4CH_3$ (Aldrich, 99+%) were used without further purification, but they were thoroughly degassed by several freezing and thawing cycles, and stored over type 4A molecular sieves.

Apparatus. The total vapor pressures of the TFE + TEGDME binary mixtures were measured by a static method (Pemberton and Mash, 1978; Chaudhari et al., 1995). The apparatus was described in Esteve et al. (1995). It consists of an equilibrium cell, a double-walled thermostat bath with a 25 L capacity filled with silicon oil (Baysilone M-20 from Bayer), a differential pressure null transducer (DPT) (Ruska Model 2439-702), a precise pressure controller (Ruska Model 3891-801), and a Haake proportional temperature controller for the bath. The measuring systems are a digital pressure gauge (Ruska Model 6242), a Pt100 platinum resistance thermometer, and a Mettler electronic balance with an accuracy of ±0.1 mg for weighing the pure components. The temperature in the bath was controlled to better than ±0.01 K up to 373.15 K and ±0.02 K above 373.15 K, and the accuracy of liquid mole fraction is better than ±0.0001. The accuracy of the measurements was 0.013 kPa for pressures lower than 130 kPa and 0.20 kPa for pressures up to 1 MPa, and the overall reproducibility of the pressure measurement was estimated better than 0.05 kPa and 0.3 kPa, respectively.

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Table 1. Experimental Vapor Pressure and Liquid Mole Fraction and Estimated Vapor Mole Fraction and Activity Coefficient of TFE for the System TFE (1) + TEGDME (2) at Different Temperatures

P/kPa	x_1	y_1(calc)	γ_1	P/kPa	x_1	y_1(calc)	γ_1	P/kPa	x_1	y_1(calc)	γ_1
				T = 303.15 K							
0.135	0.0836	0.9987	0.1282	0.887	0.3967	0.9999	0.1758	3.191	0.7128	0.9999	0.3539
0.280	0.1595	0.9994	0.1396	1.163	0.4817	0.9999	0.1919	5.239	0.8064	0.9999	0.5148
0.475	0.2397	0.9997	0.1574	1.540	0.5564	0.9999	0.2204	8.074	0.8851	1.0000	0.7239
0.671	0.3209	0.9998	0.1683	2.231	0.6406	0.9999	0.2767	11.51	0.9619	1.000	0.9512
				T = 313.15 K							
0.254	0.0836	0.9976	0.1411	1.553	0.3948	0.9998	0.1834	5.891	0.7127	0.9999	0.3831
0.521	0.1595	0.9989	0.1521	2.196	0.4827	0.9999	0.2110	9.379	0.8064	0.9999	0.5392
0.823	0.2397	0.9994	0.1603	2.948	0.5563	0.9999	0.2467	13.79	0.8852	0.9999	0.7410
1.212	0.3210	0.9996	0.1695	4.212	0.6406	0.9999	0.3069	19.88	0.9619	1.0000	0.9552
				T = 323.15 K							
0.469	0.0837	0.9960	0.1591	2.794	0.3974	0.9996	0.2000	10.39	0.7128	0.9999	0.4111
0.913	0.1595	0.9981	0.1627	3.987	0.4826	0.9998	0.2273	16.11	0.8064	0.9999	0.5646
1.469	0.2398	0.9989	0.1742	5.199	0.5563	0.9999	0.2656	23.45	0.8852	0.9999	0.7546
2.083	0.3205	0.9994	0.1856	7.443	0.6406	0.9999	0.3310	32.87	0.9619	1.0000	0.9567
				T = 333.15 K							
0.798	0.0837	0.9937	0.1714	4.789	0.5557	0.9993	0.2142	17.20	0.7128	0.9999	0.4320
1.584	0.1595	0.9971	0.1789	6.615	0.4826	0.9996	0.2471	26.19	0.8064	0.9999	0.5824
2.425	0.2399	0.9983	0.1857	8.867	0.5562	0.9998	0.2885	38.20	0.8852	0.9999	0.7682
3.492	0.4799	0.9989	0.1963	12.61	0.6406	0.9999	0.3540	52.17	0.9619	1.0000	0.9601
				T = 343.15 K							
1.308	0.0837	0.9903	0.1839	7.893	0.3972	0.9990	0.2338	27.44	0.7128	0.9999	0.4531
2.526	0.1596	0.9954	0.1872	10.89	0.7826	0.9994	0.2670	41.33	0.8064	0.9999	0.6007
4.033	0.2397	0.9974	0.1990	14.43	0.5563	0.9997	0.3084	59.38	0.8852	0.9999	0.7790
5.790	0.3209	0.9984	0.2141	20.38	0.6406	0.9999	0.3747	80.02	0.9619	1.0000	0.9619
				T = 353.15 K							
2.065	0.0837	0.9861	0.1962	12.60	0.3971	0.9986	0.2528	42.68	0.7128	0.9999	0.4731
4.041	0.1593	0.9935	0.2028	17.35	0.4826	0.9992	0.2881	63.41	0.8064	0.9999	0.6222
6.291	0.2397	0.9963	0.2140	22.83	0.5563	0.9996	0.3297	89.31	0.8852	0.9999	0.7976
9.226	0.3209	0.9978	0.2305	31.68	0.6406	0.9998	0.3949	119.0	0.9619	1.0000	0.9667
				T = 363.15 K							
3.106	0.0837	0.9803	0.2048	19.28	0.3972	0.9981	0.2715	63.78	0.7128	0.9999	0.4954
6.049	0.1594	0.9907	0.2113	26.28	0.4826	0.9990	0.3072	93.76	0.8064	0.9999	0.6395
9.785	0.2397	0.9949	0.2281	34.74	0.5563	0.9994	0.3500	130.5	0.8852	0.9999	0.8057
14.15	0.3209	0.9967	0.2482	48.02	0.6406	0.9997	0.4170	172.1	0.9619	0.9999	0.9674
				T = 373.15 K							
4.643	0.0846	0.9737	0.2267	28.53	0.3972	0.9974	0.2870	94.71	0.7128	0.9998	0.5153
9.187	0.1595	0.9878	0.2295	39.27	0.4826	0.9985	0.3255	135.6	0.8064	0.9999	0.6597
14.48	0.2397	0.9931	0.2417	41.21	0.5563	0.9991	0.3696	186.5	0.8852	0.9999	0.8218
20.93	0.3209	0.9958	0.2614	70.35	0.6406	0.9996	0.4368	243.0	0.9619	0.9999	0.9713
				T = 383.15 K							
6.702	0.0835	0.9657	0.2303	41.50	0.3972	0.9966	0.3049	131.7	0.7128	0.9997	0.5355
13.20	0.1594	0.9840	0.2416	56.32	0.4826	0.9980	0.3428	190.4	0.8064	0.9999	0.6770
21.12	0.2397	0.9911	0.2590	73.58	0.5563	0.9988	0.3874	259.3	0.8852	0.9999	0.8316
30.55	0.3209	0.9946	0.2800	100.1	0.6406	0.9994	0.4562	334.5	0.9619	0.9999	0.9728
				T = 393.15 K							
10.31	0.0836	0.9595	0.2647	57.60	0.3972	0.9955	0.3204	180.7	0.7128	0.9996	0.5508
18.68	0.1594	0.9793	0.2563	78.45	0.4826	0.9974	0.3584	261.4	0.8064	0.9999	0.6916
29.49	0.2397	0.9882	0.2711	102.1	0.5563	0.9984	0.4024	352.7	0.8852	0.9999	0.8414
42.74	0.3209	0.9929	0.2941	138.1	0.6406	0.9992	0.4715	450.6	0.9619	0.9999	0.9747
				T = 403.15 K							
14.21	0.08358	0.9494	0.2778	79.13	0.3972	0.9943	0.3375	244.6	0.7128	0.9995	0.5690
25.53	0.1594	0.9738	0.2679	107.2	0.4827	0.9966	0.3762	350.9	0.8064	0.9999	0.7069
40.27	0.2397	0.9851	0.2845	139.5	0.5563	0.9980	0.4207	468.8	0.8852	0.9999	0.8506
59.10	0.3209	0.9910	0.3098	187.6	0.6406	0.9990	0.4897	594.8	0.9619	0.9999	0.9764
				T = 413.15 K							
18.69	0.0836	0.9366	0.2829	106.4	0.3942	0.9930	0.3548	325.5	0.7128	0.9994	0.5894
34.48	0.1594	0.9382	0.2822	144.2	0.4827	0.9958	0.3955	461.5	0.8065	0.9998	0.7230
54.43	0.2397	0.9819	0.3004	187.0	0.5563	0.9975	0.4415	611.5	0.8852	0.9999	0.8599
78.97	0.3209	0.9890	0.3260	250.0	0.6406	0.9987	0.5112	770.9	0.9619	0.9999	0.9780
				T = 423.15 K							
25.36	0.0836	0.9250	0.3031	139.3	0.3973	0.9913	0.3715	422.9	0.7128	0.9992	0.6067
45.35	0.1594	0.9610	0.2945	190.1	0.4827	0.9948	0.4139	596.0	0.8064	0.9998	0.7369
72.24	0.2397	0.9776	0.3123	245.3	0.5563	0.9968	0.4603	789.5	0.8852	0.9999	0.8683
103.5	0.3209	0.9864	0.3402	327.4	0.6406	0.9984	0.5296	982.2	0.9619	0.9999	0.9796

Table 2. Parameters of NRTL Equation, Root-Mean-Square Deviations (RMSD), and the Variance (*s*) for the TFE + TEGDME System[a]

$C_{12}{}^{C}$/J mol^{-1}	$C_{12}{}^{T}$/J mol^{-1} K^{-1}	$C_{2}{}^{C}$/J mol^{-1}	$C_{21}{}^{T}$/J mol^{-1} K^{-1}	α_{12}	RMSD *P*/kPa	RMSD *T*/K	RMSD x_1	*s*
−1134.4	29.266	−5801.5	−3.349	0.67	0.17	0.01	0.0014	19.52

[a] RMSD $X = [[\sum^{N}_{i=1}(X_{\mathrm{exp}} - X_{\mathrm{calc}})_i{}^2)]/N]^{1/2}$.

Liquid densities were measured using a vibrating densimeter (Anton Paar DMA 602H-DMA60). They were determined at atmospheric pressure for the temperature range of 283.15 K to 333.15 K, and at a pressure of 1.5 MPa for higher temperatures in order to avoid the vaporization of TFE. The pressure of the system was applied with a high-pressure generator from High Pressure Equipment Company (HiP Model 50-6-15). The vacuum of the system was achieved using a vacuum pump (Telstar Type 80/70). The temperature in the vibrating tube was measured by a thermometer (Anton Paar MKT 100) with a micro RTD probe calibrated in the temperature working range, having an accuracy of ±0.01 K. The overall accuracy of density measurements was $\pm 2 \times 10^{-5}$ g cm^{-3}. The experimental uncertainty for densities is about 0.000 20 g cm^{-3}.

Liquid dynamic viscosities from 343.15 K to 393.15 K were obtained with a Haake falling-ball viscometer (Hoeppler) with a thermostated bath (CT 1450/2) and six different standard balls, applied for different measuring ranges. The bath was filled with silicon oil Baysilone M-20. The temperature in the jacket around the measuring tube was determined by a thermometer (Anton Paar MKT 100) with an accuracy of ±0.01 K. The accuracy estimated for the viscosity measurements was about 0.75% at 343.15 K and 1.7% at 393.15 K.

Procedure. The experimental procedure for VLE measurement, which included the load of the sample, the measurement of the vapor pressure, and the calculation accurately of the cell volume, was described by Esteve et al. (1995). Data reduction from the initial composition of the sample and measured vapor pressure and temperature was described by Herraiz et al. (1998). In this approach, a polynomial Redlich−Kister equation for the Gibbs free energy of the liquid phase was assumed and the corresponding parameters were obtained by fitting *P*,*x* data at each temperature.

The experimental procedure for density measurement was already reported by Conesa et al. (1998). For viscosity measurement, the dynamic viscosities of water at temperatures between 323.15 K and 373.15 K at 10 K intervals from the CRC Handbook (1990−91) were used for calibrating the Haake falling-ball viscometer. The dynamic viscosities of TEGDME from 343.15 K to 393.15 K, measured by Conesa et al. (1998) with an Ubbelohde-type glass capillary tube viscometer (Schott-Geräte AVS 310), were used to check the Haake falling-ball viscometer and experimental procedure. The relative deviation between our experimental viscosities and those from Conesa et al. (1998) is within ±1.5%.

Results and Data Reduction

Vapor Pressure Data. The vapor pressure correlations from Chaudhari et al. (1995) for TFE and TEGDME were used. For TFE, the critical temperature, volume, and pressure have been taken from Sauermann et al. (1993) and the acentric factor from Ioannidis et al. (1997). The physical properties at the critical state for TEGDME have been taken from Bokelmann et al. (1983). The liquid molar volumes for each compound were calculated from the density−temperature correlations (Sauermann et al., 1993; Conesa et al.,1998).

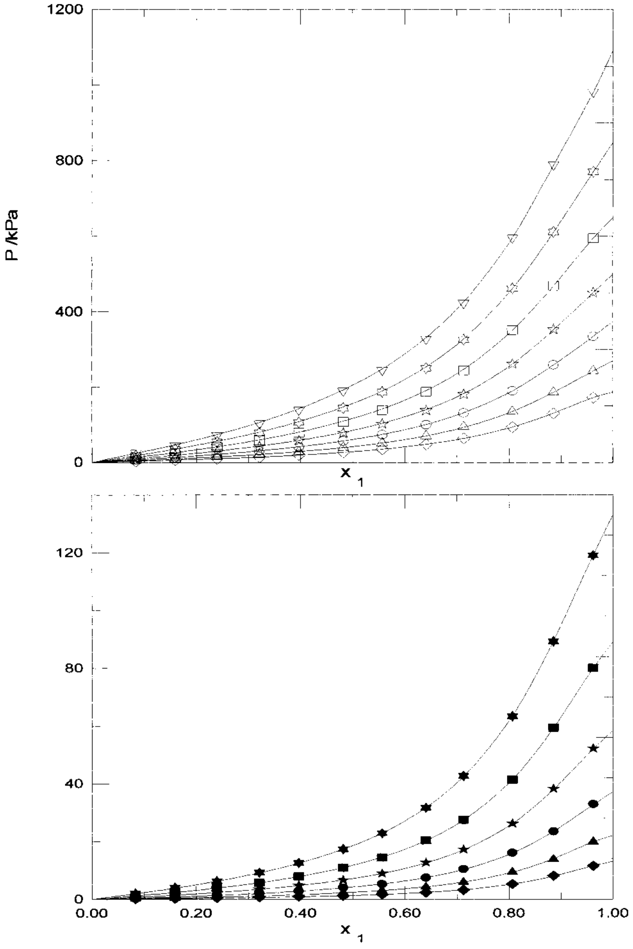

Figure 1. Experimental vapor pressures of TFE (1) + TEGDME (2) at different temperatures and correlation with NRTL equation: ◆, 303.15 K; ▲, 313.15 K; ●, 323.15 K; ★, 333.15 K; ■, 343.15 K; ✸, 353.15 K; ◇, 363.15 K; △, 373.15 K; ○, 383.15 K; ☆, 393. 15 K; □, 403.15 K; ✡, 413.15 K; ▽, 423.15 K; —, calculated by NRTL equation.

Vapor−liquid equilibrium data for TFE + TEGDME are given in Table 1. The activity coefficients included in this table were obtained using the Redlich−Kister equation for the excess Gibbs free energy with the parameters obtained at each temperature. *P*,*T*,*x* data were correlated by the temperature-dependent five-parameter NRTL equation

$$\ln \gamma_i = x_j{}^2\left[\tau_{ji}\left(\frac{G_{ji}}{x_i + x_jG_{ji}}\right)^2 + \frac{\tau_{ij}G_{ij}}{(x_j + x_iG_{ij})^2}\right]$$

where

$$\tau_{ij} = C_{ij}/RT$$

$$G_{ij} = \exp(-\alpha_{ij}\tau_{ij})$$

$$C_{ij} = C_{ij}{}^{C} + C_{ij}{}^{T}(T - 273.15)$$

The vapor-phase behavior was calculated from the virial equation of state truncated at the second virial coefficient,

Table 3. Experimental Liquid Densities for TFE (1) + TEGDME (2)

x_1	ρ/kg·m^{-3}	x_1	ρ/kg·m^{-3}	x_1	ρ/kg·m^{-3}	x_1	ρ/kg·m^{-3}
283.15 K and 101.33 kPa							
0.0000	1020.48	0.4184	1094.06	0.7851	1231.18	0.9490	1354.65
0.1112	1035.67	0.4873	1112.11	0.8335	1261.54	0.9777	1383.42
0.1422	1040.34	0.5513	1131.27	0.8610	1280.63	1.0000	1408.21
0.2815	1064.36	0.6072	1150.28	0.8962	1307.92		
0.3027	1068.50	0.6671	1173.60	0.9308	1337.77		
0.3744	1083.71	0.7026	1189.01	0.9470	1352.93		
293.15 K and 101.33 kPa							
0.0000	1011.27	0.3906	1077.10	0.7969	1225.34	0.9508	1341.02
0.0486	1017.50	0.4923	1102.75	0.8520	1260.44	0.9751	1364.74
0.1190	1027.33	0.5999	1136.29	0.8705	1273.65	1.0000	1390.91
0.2150	1042.49	0.7051	1178.07	0.8999	1296.44		
0.2935	1056.71	0.7589	1204.25	0.9199	1313.21		
303.15 K and 101.33 kPa							
0.0000	1002.11	0.3524	1058.49	0.6484	1142.42	0.9013	1283.03
0.0499	1008.42	0.4055	1070.17	0.7023	1164.59	0.9211	1299.22
0.1007	1015.33	0.4536	1081.78	0.7531	1188.55	0.9474	1322.35
0.1499	1022.49	0.5017	1094.52	0.7975	1212.59	0.9540	1328.37
0.2006	1030.44	0.5511	1108.98	0.8521	1246.80	1.0000	1373.82
0.3023	1048.45	0.6018	1125.48	0.8760	1263.69		
313.15 K and 101.33 kPa							
0.0000	992.70	0.4187	1062.77	0.7993	1200.51	0.9497	1308.75
0.0525	999.25	0.4853	1079.29	0.8284	1217.71	1.0000	1356.41
0.1109	1007.12	0.5483	1097.04	0.8601	1238.35		
0.1756	1016.66	0.6196	1120.29	0.8880	1258.24		
0.2547	1029.67	0.6919	1148.11	0.9092	1274.51		
0.3230	1042.34	0.7479	1173.47	0.9303	1291.80		
323.15 K and 101.33 kPa							
0.0000	983.23	0.3584	1039.00	0.7944	1184.21	0.9435	1286.96
0.0385	987.90	0.4691	1064.09	0.8039	1189.48	0.9573	1298.77
0.0687	991.74	0.5683	1091.63	0.8280	1203.53	0.9730	1312.65
0.1231	999.09	0.6033	1102.85	0.8750	1233.96	1.0000	1338.11
0.1889	1008.80	0.6578	1122.19	0.9100	1259.70		
0.2943	1026.55	0.7458	1159.49	0.9314	1276.83		
333.15 K and 101.33 kPa							
0.0000	974.24	0.5010	1061.55	0.7997	1173.81	0.9749	1297.01
0.0988	986.45	0.6004	1090.51	0.8498	1202.86	1.0000	1319.58
0.2006	1017.18	0.6490	1107.22	0.9000	1236.79		
0.2968	1001.07	0.6990	1126.49	0.9247	1255.44		
0.4030	1038.22	0.7570	1152.11	0.9500	1275.79		
343.15 K and 1.5 MPa							
0.0000	965.01	0.3904	1025.08	0.7479	1134.84	0.9448	1253.66
0.0572	971.76	0.4662	1042.01	0.8226	1172.43	1.0000	1299.89
0.1346	981.86	0.5747	1071.05	0.8527	1189.98		
0.2243	995.03	0.6392	1091.79	0.9012	1221.45		
0.3197	1011.27	0.7084	1117.79	0.9208	1235.50		
353.15 K and 1.5 MPa							
0.0000	955.52	0.4644	1030.40	0.7565	1125.13	0.9464	1237.40
0.0955	966.90	0.5659	1056.57	0.7665	1129.81	0.9721	1256.88
0.1617	975.71	0.5711	1058.18	0.8483	1172.19	1.0000	1279.15
0.3505	1006.52	0.6426	1080.57	0.8860	1195.31		
0.4491	1026.95	0.6908	1098.01	0.8870	1.19598		
363.15 K and 1.5 MPa							
0.0000	946.26	0.3744	1000.82	0.7070	1091.72	0.9525	1222.89
0.0545	952.51	0.3781	1001.52	0.7571	1112.24	1.0000	1258.04
0.1258	961.36	0.4805	1023.51	0.8421	1153.97		
0.1579	965.62	0.5046	1029.37	0.8840	1178.22		
0.2638	981.29	0.5853	1050.99	0.8960	1185.56		
373.15 K and 1.5 MPa							
0.0000	936.99	0.4474	1004.91	0.8275	1130.56	0.9853	1225.26
0.0833	946.48	0.5082	1019.00	0.8695	1152.52	1.0000	1235.17
0.1890	960.22	0.5732	1035.73	0.8940	1166.62		
0.2726	972.69	0.6099	1046.28	0.9306	1189.12		
0.3519	986.15	0.7174	1082.43	0.9578	1206.96		
383.15 K and 1.5 MPa							
0.0000	927.68	0.3725	979.33	0.7771	1092.31	1.0000	1210.96
0.1005	939.00	0.4901	1003.32	0.8343	1118.11		
0.1483	944.89	0.5907	1028.64	0.8749	1138.82		
0.2416	957.82	0.6497	1046.09	0.9038	1154.33		
0.3201	970.24	0.7660	1087.81	0.9658	1190.01		

Table 3 (Continued)

x_1	ρ/kg·m^{-3}	x_1	ρ/kg·m^{-3}	x_1	ρ/kg·m^{-3}	x_1	ρ/kg·m^{-3}
393.15 K and 1.5 MPa							
0.0000	918.42	0.2758	953.29	0.6279	1027.89	1.0000	1186.71
0.0872	928.11	0.3518	965.67	0.7004	1050.64		
0.1328	933.56	0.4179	977.90	0.7994	1087.91		
0.1862	940.31	0.4804	990.71	0.8851	1127.40		
0.2387	947.76	0.5629	1010.24	0.9374	1155.44		
403.15 K and 1.5 MPa							
0.0000	909.90	0.3028	948.47	0.6011	1008.61	0.9018	1118.79
0.0758	918.55	0.3968	964.42	0.7008	1038.58	1.0000	1163.97
0.2010	934.08	0.5069	985.98	0.8039	1076.12		
413.15 K and 1.5 MPa							
0.0000	900.80	0.3028	938.00	0.6011	995.77	0.9018	1098.30
0.0758	908.96	0.3968	953.45	0.7008	1024.55	1.0000	1135.21
0.2010	924.05	0.5069	974.24	0.8039	1059.74		
423.15 K and 1.5 MPa							
0.0000	891.70	0.3028	927.43	0.6011	983.02	0.9018	1076.72
0.0758	899.29	0.3968	942.32	0.7008	1010.17	1.0000	1103.92
0.2010	913.93	0.5069	962.32	0.8039	1042.47		

Table 4. Parameters of Liquid Density Correlation for TFE (1) + TEGDME (2) in the Temperature Range of 283.15 K to 423.15 K

a_1	a_2	a_3	a_4	a_5	s/kg·m^{-3}
0.002 672 9	$4.086\,0 \times 10^{-5}$	$-2.370\,7 \times 10^{-7}$	$1.348\,67 \times 10^{-4}$	$-1.062\,61 \times 10^{-5}$	0.78

estimated from the correlation of Tsonopoulos (1974). The parameters were fitted using the maximum likelihood principle (Prausnitz et al., 1980) in order to minimize the function

$$s = \sum_N \left[\frac{(P_{\text{calc}} - P_{\text{exp}})^2}{\sigma_P} + \frac{(T_{\text{calc}} - T_{\text{exp}})^2}{\sigma_T} + \frac{(x_{\text{calc}} - x_{\text{exp}})^2}{\sigma_x} \right]$$

where P is the pressure, T the temperature, and x the liquid mole fraction of TFE. The standard deviations σ_P, σ_T, and σ_x for P, T, and x were taken as 0.05 kPa for pressures less than 130 kPa and 0.3 kPa for pressures up to 1 MPa, 0.02 K, and 0.0005, respectively.

The fitting parameters and root-mean-square deviations in P,T,x are given in Table 2. The experimental vapor pressure data for all the isotherms are plotted in Figure 1 along with the data calculated using the five-parameter NRTL equation for comparison. From this figure, it can be seen that the agreement between experimental and calculated values from NRTL equation is excellent.

The experimental vapor pressures of Seher and Stephan (1983) are lower than the values calculated by the five-parameter NRTL model, and have an average relative deviation of 4.6% from our calculated data.

Experimental excess molar enthalpy data for the TFE + TEGDME system from Krumbeck and Schulz (1989) were accurately correlated by Coronas et al. (1996) as a function of the mixture composition and the temperature in the range 298.15 K to 448.15 K. In this temperature range these mixtures present large exothermic excess enthalpies and asymmetrical $H^{\text{E}}(x_1)$ curves with the maximum located in the TFE-rich region. The maximum values of the experimental excess molar enthalpy increase with the temperature from 3897.6 J mol^{-1} at 298.15 K to 5388.52 J mol^{-1} at 448.15 K. Nevertheless, the excess molar enthalpy calculated using the Gibbs−Helmholtz equation and the NRTL parameters is always higher and does not correctly predict the dependence on temperature. The root-mean-square relative deviation between experimental and calculated data varies from 59% at 293.15 K to 9.6% at 363.15 K.

Densities. Experimental liquid density data at atmospheric and 1.5 MPa pressures are listed in Table 3. The influence of pressure on liquid density is very small under a 1.5 MPa pressure, and was neglected in this work. All experimental density data were correlated with temperature and the concentration of TFE, by the empirical equation of Kumar and Koganti (1997)

$$\rho/\rho_2 = 1 + \text{aa}C_1 + \text{bb}C_1^{3/2}$$

where

$$\text{aa} = a_1 + a_2(T/K - 273.15) + a_3(T/\text{K} - 273.15)^2$$

$$\text{bb} = a_4 + a_5(T/\text{K} - 273.15)$$

$$C_1 = \frac{x_1\rho}{x_1M_1 + x_2M_2}$$

ρ and ρ_2 are the liquid density of the mixture and TEGDME, respectively, at temperature T, C_1 is the mole concentration in TFE in mol dm^{-3}, and x_1 and x_2 are the mole fraction of TFE and TEGDME, respectively. The liquid density of TEGDME was calculated using the correlation of Conesa et al. (1998).

The parameters a_i are summarized in Table 4 together with the standard deviation of the density correlation over a wide temperature range. Comparing with literature experimental density data of the studied mixture, our data agreed very well with those of Svejda et al. (1990) with a deviation less than 0.1%, but are in only fair agreement with those of Stephan and Hengerer (1993) by a maximum deviation of 0.5%. Figure 2 shows the variation of the liquid density with composition and temperature. From this figure, it can be seen that the liquid densities of the TFE + TEGDME system increase with the mole fraction of TFE at each temperature. Also, excess volumes of the TFE + TEGDME system determined from our density data show an S-shape at lower temperatures, while all are negative at temperatures above 303.15 K (Olivé, 1998).

Viscosities. Experimental dynamic viscosity data from 343.15 K to 393.15 K are listed in Table 5. Olivé et al.

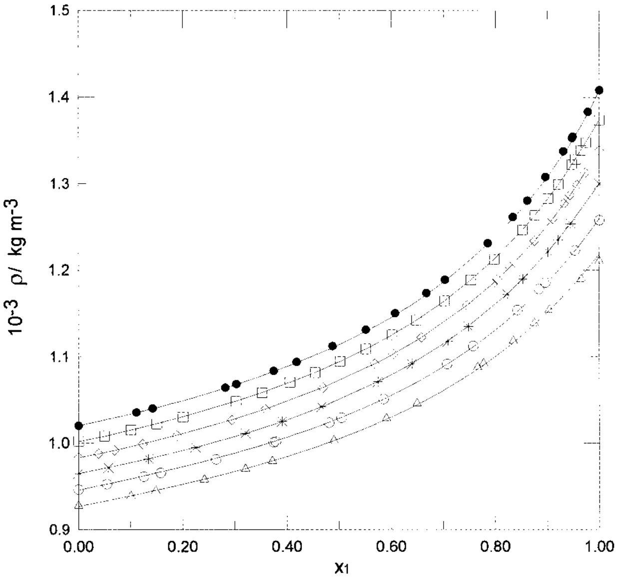

Figure 2. Experimental and calculated liquid densities for TFE + TEGDME at different temperatures: ●, 283.15 K; □, 303.15 K; ◇, 323.15 K; ∗, 343.15 K; ○, 363.15 K; △, 383.15 K; —, calculated by the equation of Kumar and Koganti (1997).

Table 5. Experimental Dynamic Viscosities of TFE (1) + TEGDME (2)

x_1	η/mPa s	x_1	η/mPa s
	343.15 K		
0.0000	1.4222	0.5982	1.2381
0.0986	1.3910	0.6988	1.1894
0.2009	1.3673	0.8000	1.1000
0.3022	1.3441	0.8456	1.0549
0.4005	1.3225	0.9002	0.9773
0.4860	1.3020	1.0000	0.6712
	353.15 K		
0.0000	1.2355	0.5982	1.0626
0.0986	1.2057	0.6988	1.0209
0.2009	1.1822	0.8000	0.9456
0.3022	1.1629	0.8456	0.9009
0.4005	1.1411	0.9002	0.8354
0.4860	1.1097	1.0000	0.5616
	363.15 K		
0.0000	1.0954	0.5982	0.9263
0.0986	1.0670	0.6988	0.8897
0.2009	1.0351	0.8000	0.8143
0.3022	1.0115	0.8456	0.7740
0.4005	0.9988	0.9002	0.7146
0.4860	0.9662	1.0000	0.4762
	373.15 K		
0.0000	0.9623	0.5990	0.7992
0.1005	0.9339	0.7009	0.7629
0.1947	0.9127	0.7512	0.7403
0.3002	0.8852	0.8002	0.7140
0.4002	0.8680	0.9008	0.6081
0.5141	0.8314	1.0000	0.4044
	383.15 K		
0.0000	0.8590	0.5990	0.7107
0.1005	0.8380	0.7009	0.6726
0.1947	0.8174	0.7512	0.6554
0.3002	0.7882	0.8002	0.6322
0.4002	0.7743	0.9008	0.5292
0.5141	0.7406	1.0000	0.3570
	393.15 K		
0.0000	0.7712	0.5990	0.6303
0.1005	0.7568	0.7009	0.5925
0.1947	0.7382	0.7512	0.5777
0.3002	0.7092	0.8002	0.5582
0.4002	0.6984	0.9008	0.4599
0.5141	0.6625	1.0000	0.3071

(1994) presented the composition dependence of the kinematic viscosities of the studied system at 303.15 K using the equations of McAllister-2 parameters, McAllister-3 parameters (McAllister, 1960), Stephan and Heckenberger (1989), and Soliman and Marshall (1990). The Stephan and Heckenberger correlation was found to be the best for the system TFE + TEGDME.

Table 6. Parameters of the Kinematic Viscosity Correlation of TFE (1) + TEGDME (2) in the Temperature Range of 293.15 K to 393.15 K

A_0	$A_1 \times 10^3$	B_0	$s \times 10^6$/m^2·s^{-1}
1.023 67	−1.534 68	−0.886 19	0.031

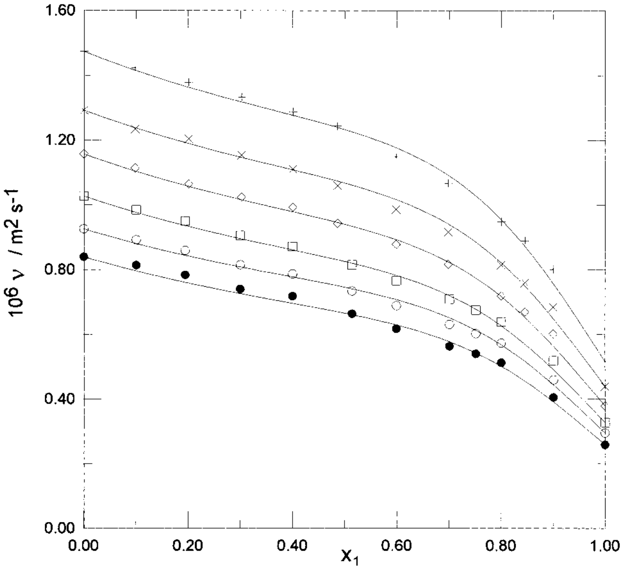

Figure 3. Experimental and calculated kinematic viscosities for TFE + TEGDME at different temperatures: +, 343.15 K; ×, 353.15 K; ◇, 363.15 K; □, 373.15 K; ○, 383.15 K; ●, 393.15 K; —, calculated by the equation of Stephan and Heckenberger (1989).

Kinematic viscosity data were calculated from our density correlation and measured dynamic viscosity data. The new kinematic viscosities in the range 343.15−393.15 K together with kinematic viscosity data in the range 293.15−333.15 K, measured by Olivé et al. (1994, 1995), were fitted by the equation of Stephan and Heckenberger (1989) using linear temperature functions for the binary interaction parameters. This equation was written as

$$\ln \nu = x_1 \ln \nu_1 + x_2 \ln \nu_2 + \ln\left[1 + \frac{x_1 x_2}{A + B{x_1}^2}\right]$$

$$A = A_0 + A_1(T/\mathrm{K} - 273.15)$$

where x_1 and x_2 are the mole fractions of TFE and TEGDME, respectively. The parameters A_0, A_1, and B of this equation are summarized in Table 6 with the standard deviation, which is also very small. Figure 3 shows the variation of the kinematic viscosities with composition in the temperature range of 343.15 K to 393.15 K. Viscosity hardly decreases with composition at TFE mole fraction less than 0.6 for any temperature, while viscosity decreases sharply with composition at TFE mole fraction greater than 0.6, especially at low temperatures.

Conclusion

In this paper, VLE data for TFE + TEGDME from 303.15 K to 423.15 K over the entire composition range were presented. The five-parameter NRTL temperature-dependent equation was used to fit them with a satisfactory accuracy. These data indicate that this binary system has large negative deviations from Raoult's law. The logarithm of activity coefficients of TFE becomes more negative with the decrease of temperature and increase of the mole fraction of TEGDME. This behavior is due to the fact that there are pronounced interactions between the −OH group in the TFE and the oxygen atom in the ether. Taking into account that an exothermic behavior favors absorption process, we conclude that the mixtures of poly(ethylene glycol) dimethyl ethers with TFE could be very interesting for their use in absorption machines.

Liquid densities of TFE + TEGDME system from 283.15 K to 423.15 K were reported in this paper. The empirical correlation of Kumar and Koganti (1997) was applied to fitting them with a very small standard deviation. The comparison between our data and literature data existing below 346.25 K showed that our density data are in good agreement with literature data. Excess volumes of TFE + TEGDME obtained from measured densities show an S-shape at lower temperature, while all are negative at temperatures above 303.15 K.

Also, new experimental viscosity data were measured in the temperature range 343.15 K to 393.15 K at intervals of 10 K. The correlation equation proposed by Stephan and Heckenberger (1989) with linear temperature functions for the binary interaction parameters was used to represent the temperature and concentration dependence of kinematic viscosities for this binary mixture. It results in very small correlation deviations in a wide temperature range of 283.15 K to 393.15 K for both our viscosity data and those from Olivé et al. (1994, 1995).

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