Vapor−Liquid Equilibria of the Perfluoromethyl Vinyl Ether and Chlorotrifluoroethylene System

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Isothermal vapor−liquid equilibrium (VLE) data for the perfluoromethyl vinyl ether + chlorotrifluoroethylene system were measured in a vapor−liquid equilibrium still with a vapor recycling system at four temperatures from (267.67 to 282.62) K. The uncertainty of the temperature was ± 0.01 K, and the accuracy of the pressure was ± 0.05 %. The experimental data were correlated with the NRTL equation and the Wilson equation. The calculated results agree well with the experimental data. Azeotropic VLE behaviors can be observed at certain compositions from the experimental data.

Introduction

Perfluoromethyl vinyl ether is the first important monomer for a perfluoroelastomer and possibly will become an important new type of monomer for modified fluororubber and fluoroplastics.[1,2]

In our synthetic route, many byproducts are generated and can be removed by distillation. Chlorotrifluoroethylene is the main product among these byproducts and made up about 10∼20 %. Vapor−liquid equilibria (VLE) data are necessary for developing a distillation process and for designing a distilling tower. However, these data are very scarce, and it is necessary to determine them experimentally.

Experimental Section

Chemical. Perfluoromethyl vinyl ether (mole fraction $x > 99.9$ %) and chlorotrifluoroethylene ($x > 99.8$ %) were supplied by the Chenguang Research Institute of Chemical Industry, China National Blue Star Co. All materials were checked by gas chromatography and used without further purification.

Apparatus. The VLE measurements were performed in a recirculation cell. This apparatus is similar to that described in previous documents.[3] The cell is made of 316L stainless steel (internal volume of about 200 mL), which was immersed inside a cryostat filled with a glycol + water solution. The temperature of the cryostat was controlled by a low-temperature thermostat (Shanghai Hengping Instrument and Meter, model DC3006). The fluctuation of the cryostat temperature was less than ± 0.01 K. An electromagnetic pump was used to recirculate the vapor phase to mix with the liquid phase in the cell to accelerate the thermodynamic equilibrium process.

A platinum resistance thermometer calibrated with a standard thermometer was inserted into the liquid phase in the cell to measure the phase equilibrium temperature. The uncertainty of the temperature was ± 0.01 K. The pressure was measured by a calibrated high-accuracy pressure transducer (Tianshui Huatian Microelectronics Co., model LYB501B), which had an accuracy of ± 0.05 %. The compositions of the liquid and vapor phases were analyzed by a gas chromatograph (model Beifen SQ206). The gas chromatograph was calibrated with gas mixtures of known compositions that were prepared gravimetrically by an electronic balance (uncertainty of ± 0.0001 g), and the uncertainty of the composition was about ± 0.001 in mole fraction. The leakage test for the experimental apparatus had been done. Also, the experimental system had been tested and verified by measuring the vapor pressure of chlorotrifluoroethylene[4] and VLE data of the ethane + propane system[5,6] (the maximum and average derivations from the literature are 0.7 % and 0.4 % for the vapor pressure of chlorotrifluoroethylene and 1.5 % and 1.1 % for the VLE data).

Experimental Procedure[7]

VLE Data Measurement. As described above, the apparatus system was first evacuated to remove the remaining gas in the equilibrium cell and recirculation loop, and then the cryostat was cooled. Meanwhile, a certain amount of the pure perfluoromethyl vinyl ether from a pressured feed cylinder was charged to the cell. After the desired temperature was reached and maintained constant for an hour, the pressure of the cell was measured. A proper amount of chlorotrifluoroethylene (to ensure that the level of the liquid inside the cell was much higher than the entry of the liquid sampling capillary) was recharged to the cell from the feed cylinder. After the vapor phase was recirculated for at least 2 h and the fluctuation of the pressure was maintained at less than ± 0.05 % for half an hour, the equilibrium was confirmed to be established. The pressure in the cell was measured. After sweeping the sampling lines, we opened the outlet valve for the vapor phase or liquid phase and then immediately closed the valve, so the sample of the vapor or liquid phase was withdrawn (about 0.15 mL each time). At least three samples of both the vapor and liquid phase were analyzed by the gas chromatograph. If the difference of the measuring value among the three samples was less than 1 %, the average value was recorded. The interval of every two sampling processes was about 0.5 h. The pressure drop caused by the vapor sampling process was less than 0.05 KPa, and the pressure would reinstate soon due to vapor recirculation.

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10.1021/je7001144 CCC: $37.00

Table 1. VLE Data for the Perfluoromethyl Vinyl Ether (1) + Chlorotrifluoroethylene (2) System

experimental data			calculated data (NRTL model)				calculated data (Wilson model)			
P_{exptl}/kPa	$x_{1,\text{exptl}}$	$y_{1,\text{exptl}}$	$y_{1,\text{calcd}}$	Δy	P_{calcd}/kPa	ΔP/kPa	$y_{1,\text{calcd}}$	Δy	P_{calcd}/kPa	ΔP/kPa
$T = 267.67$ K										
222.4	1.0000	1.0000	1.0000	0.0000	222.4	0.0	1.0000	0.0000	222.4	0.0
227.5	0.8805	0.8580	0.8609	0.0029	228.3	0.8	0.8614	0.0034	228.4	0.9
233.5	0.7812	0.7440	0.7454	0.0014	233.9	0.4	0.7499	0.0027	234.3	1.8
239.2	0.6812	0.6403	0.6359	−0.0045	237.6	−1.6	0.6417	−0.0013	238.7	0.5
244.1	0.5866	0.5428	0.5394	−0.0034	242.6	−1.5	0.5464	0.0014	244.7	1.6
251.3	0.4241	0.3965	0.3927	−0.0037	248.9	−2.4	0.3940	−0.0024	249.7	−1.6
255.2	0.3075	0.2941	0.2930	−0.0011	254.2	−1.0	0.2933	−0.0008	254.5	−0.7
256.6	0.2327	0.2270	0.2302	0.0032	260.3	3.7	0.2300	0.0029	260.0	3.4
256.5	0.1933	0.1953	0.1970	0.0016	258.7	2.2	0.1966	0.0013	258.2	1.7
255.4	0.1426	0.1533	0.1526	−0.0007	254.3	−1.1	0.1523	−0.0010	253.7	−1.7
252.5	0.0658	0.0790	0.0778	−0.0012	248.7	−3.8	0.0779	−0.0010	249.1	−3.3
248.0	0.0000	0.0000	0.0000	0.0000	248.0	0.0	0.0000	0.0000	248.0	0.0
$T = 272.54$ K										
264.7	1.0000	1.0000	1.0000	0.0000	264.7	0.0	1.0000	0.0000	264.7	0.0
271.6	0.8821	0.8605	0.8600	−0.0004	271.5	−0.1	0.8602	−0.0002	271.5	−0.1
277.7	0.7810	0.7450	0.7463	0.0012	278.1	0.5	0.7474	0.0024	278.6	1.0
285.7	0.6633	0.6151	0.6196	0.0046	287.8	2.1	0.6214	0.0063	288.6	2.9
291.8	0.5729	0.5278	0.5289	0.0012	292.4	0.6	0.5308	0.0030	293.4	1.6
298.4	0.4454	0.4134	0.4121	−0.0013	297.5	−0.9	0.4094	−0.0040	295.5	−2.9
302.6	0.3452	0.3262	0.3258	−0.0004	302.2	−0.4	0.3171	−0.0090	294.2	−8.4
305.3	0.2504	0.2432	0.2460	0.0028	308.8	3.5	0.2457	0.0025	308.5	3.2
305.1	0.2050	0.2088	0.2079	−0.0009	303.8	−1.3	0.2075	−0.0013	303.2	−1.9
303.2	0.1489	0.1581	0.1594	0.0013	305.7	2.5	0.1590	0.0009	305.0	1.8
298.9	0.0672	0.0803	0.0799	−0.0003	297.5	−1.4	0.0801	−0.0002	298.0	−0.9
294.4	0.0000	0.0000	0.0000	0.0000	294.4	0.0	0.0000	0.0000	294.4	0.0
$T = 277.45$ K										
313.2	1.0000	1.0000	1.0000	0.0000	313.2	0.0	1.0000	0.0000	313.2	0.0
321.3	0.8869	0.8589	0.8649	0.0060	323.6	2.3	0.8648	0.0064	323.7	2.2
327.5	0.7900	0.7587	0.7574	−0.0012	326.8	−0.6	0.7565	−0.0002	327.4	−0.9
337.9	0.6500	0.6147	0.6088	−0.0059	334.3	−3.6	0.6069	−0.0041	335.6	−4.3
345.3	0.5535	0.5156	0.5132	−0.0024	343.7	−1.6	0.5128	−0.0006	344.8	−1.9
353.1	0.4352	0.4024	0.4047	0.0023	355.1	2.1	0.4047	0.0035	356.1	2.0
358.6	0.3205	0.3021	0.3062	0.0041	363.4	4.8	0.3051	0.0043	363.7	3.5
361.4	0.2482	0.2347	0.2431	0.0084	374.2	12.9	0.2435	0.0080	376.6	13.7
361.4	0.1911	0.2002	0.1962	−0.0040	354.2	−7.2	0.1950	−0.0043	353.6	−9.4
359.0	0.1402	0.1601	0.1515	−0.0086	348.4	−10.6	0.1508	−0.0088	347.8	−12.3
353.9	0.0696	0.0814	0.0825	0.0011	358.6	4.8	0.0824	0.0012	359.2	4.3
347.8	0.0000	0.0000	0.0000	0.0000	347.8	0.0	0.0000	0.0000	347.8	0.0
$T = 282.62$ K										
367.3	1.0000	1.0000	1.0000	0.0000	367.3	0.0	1.0000	0.0000	367.3	0.0
376.7	0.8930	0.8685	0.8711	0.0026	377.9	1.2	0.8699	0.0029	378.0	0.6
386.4	0.7720	0.7411	0.7364	−0.0047	383.7	−2.7	0.7361	−0.0036	384.5	−2.6
394.3	0.6810	0.6477	0.6399	−0.0078	389.6	−4.7	0.6403	−0.0063	390.5	−4.5
401.9	0.6005	0.5617	0.5581	−0.0035	399.3	−2.5	0.5601	−0.0019	400.5	−1.1
414.1	0.4465	0.4204	0.4149	−0.0055	408.7	−5.4	0.4150	−0.0044	409.7	−5.4
421.5	0.3390	0.3188	0.3214	0.0025	424.9	3.4	0.3211	0.0028	425.3	3.1
424.7	0.2609	0.2595	0.2555	−0.0040	418.2	−6.5	0.2548	−0.0041	417.9	−7.8
424.5	0.2142	0.2122	0.2165	0.0042	433.0	8.5	0.2158	0.0039	432.3	7.1
420.8	0.1526	0.1650	0.1635	−0.0015	417.1	−4.1	0.1630	−0.0018	416.3	−5.2
414.1	0.0703	0.0828	0.0836	0.0008	418.0	3.1	0.0835	0.0009	418.5	3.7
408.1	0.0000	0.0000	0.0000	0.0000	408.1	0.0	0.0000	0.0000	408.1	0.0

After the measurement at one concentration was finished, this procedure was repeated at another concentration by adding chlorotrifluoroethylene to the equilibrium cell. At last, after evacuating the equilibrium cell and recirculation loop, more chlorotrifluoroethylene was charged to measure its vapor pressure. So the phase envelope curve at one temperature was obtained.

Correlations

The experimental results for vapor−liquid equilibrium were correlated with the NRTL[8,9] equation and the Wilson[10] equation.

The vapor pressure of the binary system was less than 4.5 atm, so the vapor phase could be approximately regarded as an ideal gas; thereby, the activity coefficients, γ_i, of the components were calculated from

$$\gamma_i = \frac{y_i P}{x_i P_i^0} \tag{1}$$

where x_i and y_i are the liquid and vapor mole fractions in equilibrium; P is the total pressure; and P_i^0 is the vapor pressure of pure component i.

For the binary system, the NRTL equation has the following form

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

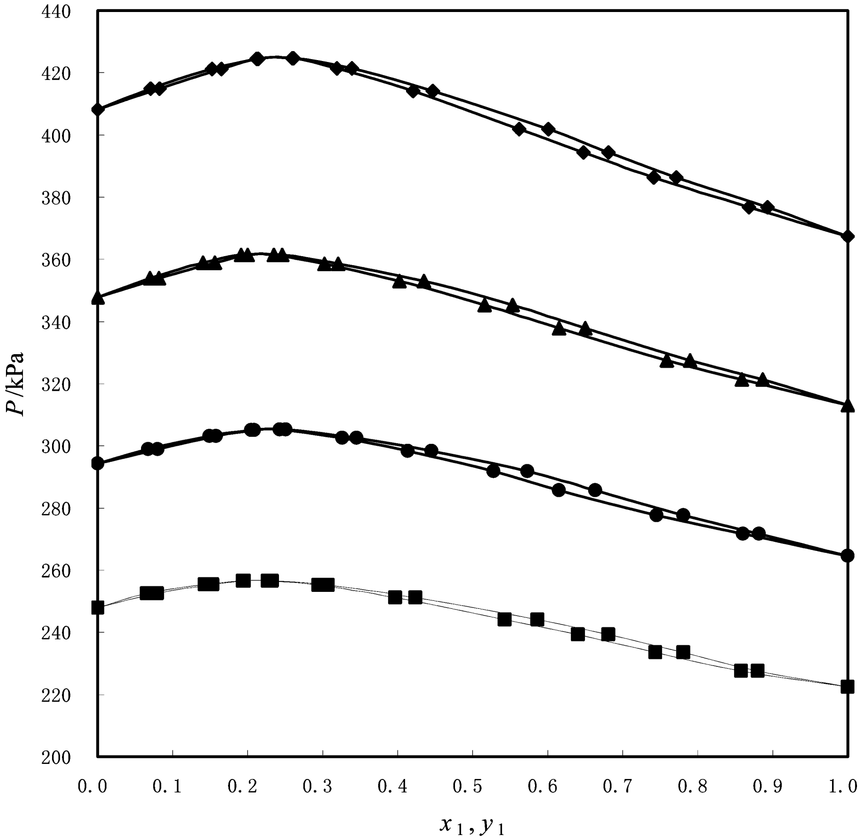

Figure 1. Vapor−liquid equilibrium for the perfluoromethyl vinyl ether (1) + chlorotrifluoroethylene (2) system at different temperatures: ■, 267.67 K; ●, 272.54 K; ▲, 277.45 K; ◆, 282.62 K.

where

$$\tau_{ji} = \Delta g_{ji} = (g_{ji} - g_{ii})/RT \tag{3}$$

$$G_{ji} = \exp(-a_{ji}\tau_{ji}) \tag{4}$$

In the NRTL model, a_{ij}, Δg_{ij}, and Δg_{ji} are adjustable parameters and can be regressed from the experimental data.

The Wilson equation has the following form

$$\ln \gamma_i = -\ln(x_i + \Lambda_{ij}x_j) + x_j\left[\frac{\Lambda_{ij}}{x_i + \Lambda_{ij}x_j} - \frac{\Lambda_{ji}}{x_j + \Lambda_{ji}x_i}\right] \tag{5}$$

where

$$\Lambda_{ij} = \frac{V_j^l}{V_i^l}\exp[-\lambda_{ij}/RT] \tag{6}$$

Here Λ_{ij} and Λ_{ji} are the Wilson equation parameters. λ_{ij} and λ_{ji} are adjustable parameters and can be regressed from the experimental data.

The parameter estimation of the two equations was based on the iterative solution, using the maximum likelihood regression of the objective function, Q_i, with the activity coefficients obtained from the consistency test as experimental values

$$Q_i = \sum_{i=1}^{n}\left(\frac{\gamma_{\text{exptl}} - \gamma_{\text{calcd}}}{\gamma_{\text{exptl}}}\right)^2 \tag{7}$$

where γ_{exptl} and γ_{calcd} are the experimental activity coefficients and the calculated ones, respectively.

Results and Discussion

In this work, the $P-T-x-y$ data of the perfluoromethyl vinyl ether + chlorotrifluoroethylene system were measured at four temperatures (267.67 K, 272.64 K, 277.66 K, 282.64 K). These data are presented in Table 1 and plotted in Figure 1.

Table 2. Maximum and Average Deviations and Maximum and Average Relative Errors of Calculated Values from the Experimental Data for the Vapor-Phase Composition

	NRTL model		Wilson model	
T	max relative error	av relative error	max relative error	av relative error
K	%	%	%	%
266.67	1.52	0.74	1.39	0.70
272.54	1.15	0.45	2.79	0.82
277.45	3.58	1.41	3.75	1.53
282.62	2.03	1.01	1.81	0.98

In the NRTL model, the two adjustable parameters Δg_{ij} and Δg_{ji} were regressed as functions of temperature as follows

$$\Delta g_{ij}/\text{J}\cdot\text{mol}^{-1} = 5705.2 - 8.0219(T/\text{K}) - 399\,354(K/\text{T}) \tag{8}$$

$$\Delta g_{ji}/\text{J}\cdot\text{mol}^{-1} = -3089.5 - 5.4572(T/\text{K}) + 183\,143(K/\text{T}) \tag{9}$$

The third parameter a_{ij} of the NRTL model was regarded as a numerical constant, and its value was 0.54 for the binary system.

In the Wilson model, the two adjustable parameters λ_{ij} and λ_{ji} were regressed as functions of temperature

$$\lambda_{ij}/\text{J}\cdot\text{mol}^{-1} = -477.9 + 23.953(T/\text{K}) - 0.05039(T/\text{K})^2 \tag{10}$$

$$\lambda_{ji}/\text{J}\cdot\text{mol}^{-1} = -177.3 - 9.6591(T/\text{K}) + 0.02328(T/\text{K})^2 \tag{11}$$

The VLE data at four temperatures were calculated with the models and the functions presented above and compared with the experimental data, which can be found in Table 1. The maximum and average relative deviations of vapor-phase compositions for both models are shown in Table 2. The average deviation is 0.90 % for the NRTL model and 1.01 % for the Wilson model. It indicates that the calculations with the two models are satisfactory. Experimental behavior ($P-x-y$ data) is shown in Figure 1. Azeotropic behaviors can be observed from the figure. The perfluoromethyl vinyl ether + chlorotrifluoroethylene system could be regarded as a pressure maximum (or positive) azeotrope.

Conclusions

Isothermal VLE data for the perfluoromethyl vinyl ether + chlorotrifluoroethylene system were measured at four temperatures. The NRTL and Wilson models were used to correlate experimental data. The predicted VLE data are in good agreement with the experimental data. According to the results, azeotropic behaviors could exist in the binary system.

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Received for review March 5, 2007. Accepted April 27, 2007.

JE7001144