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Measurements of *PVTx* Properties for the R 22 + R 114 System

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The *PVTx* properties for the R 22 + R 114 system have been measured by the constant-volume method coupled with several isothermal expansion procedures. The results for five different compositions of 0, 20, 30, 50, and 75 wt % R 22 cover the range of temperatures 283–443 K and the range of pressures 0.13–9.11 MPa, which corresponds to the density variation from 94 to 1104 kg/m^3. The experimental uncertainties of the temperature, pressure, density, and mass fraction measurements were estimated to be no greater than 10 mK, 2.0 kPa, 0.09%, and 0.12%, respectively. The dew and bubble points and the interaction virial coefficients of the present system were determined. The critical locus is also illustrated.

As a part of our current research projects on the thermodynamic properties of refrigerant mixtures, we have measured the *PVTx* properties of the R 22 + R 114 system. The present R 22 + R 114 system is of particular interest as one of the promising working mediums for refrigeration and heat pump cycles. No experimental data, however, of the thermodynamic properties for this system have been available up to now. This paper reports the *PVTx* measurements for five different compositions of 0, 20, 30, 50, and 75 wt % R 22 in the range of temperatures 283–443 K and the range of pressures 0.13–9.11 MPa, which covers the density range 94–1104 kg/m^3. The dew and bubble points, critical locus, and interaction virial coefficients of this system are also reported. The purity of each component supplied was 99.99 wt % R 22 (chlorodifluoromethane, $CHClF_2$) and 99.94 wt % R 114 (dichlorotetrafluoroethane) being an isomeric blend of 95% $CClF_2CClF_2$ + 5% CCl_2FCF_3.

Experimental Section

The *PVTx* measurements of this work have been made by the constant-volume method coupled with several isothermal expansion procedures for a mixture of a certain fixed composition. The apparatus and experimental procedure used here are essentially the same as those used by Takaishi et al. (*1*, *2*) in similar measurements for the R 12 + R 22 system. The sample cell of 268.434 ± 0.006 cm^3 inner volume and the expansion cell of 55.583 ± 0.007 cm^3 were spherical in shape and made of 304 stainless steel. The prescribed quantity of each pure component was prepared by weighing the mass of the sample on a chemical balance with a sensitivity of 2 mg. The samples thus prepared were then supplied one by one into the sample cell immersed in liquefied nitrogen. The mass fraction of the sample mixture in the sample cell was determined to be the ratio of the mass of each component to that of the mixture with an uncertainty of no greater than 0.12%.

The sample cell assembled with the expansion cell and a differential pressure detector was then immersed into a thermostated fluid bath. The bath-fluid temperature was controlled within a fluctuation of ±5 mK by using a stirrer and electric heaters. After the thermal equilibrium between the sample and bath fluid was confirmed, the temperature of the bath fluid was measured with a 25-Ω platinum resistance thermometer (Chino: Model R800-1) with a precision of 5 mK on IPTS-68 by a Mueller-type bridge (Shimadzu: Model BD-100). The uncertainty of the sample temperature measurements was less than 10 mK. The pressure of the sample was transmitted to nitrogen gas. The pressure of the sample was balanced with that of nitrogen by means of the differential pressure detector with a sensitivity of 0.1 kPa. We measured the pressure of nitrogen gas thus transmitted with two different pressure gages: an air-piston pressure gage (Ruska: Model 2465) with an effective piston area of 0.083 917 1 ± 0.000 006 6 cm^2 for pressures below 4 MPa and an oil-operated dead-weight pressure gage (Futaba: Model TL-2) with 1.000 42 ± 0.000 20 cm^2 for those above 4 MPa. The uncertainty of the sample pressure measurements was less than 0.6 kPa for pressures below 4 MPa and less than 2.0 kPa for those above 4 MPa.

The density of the sample initially in the sample cell at a certain temperature and pressure was determined to be the ratio of the mass of the sample to the inner volume of the sample cell adjusted to account for the volume variation due to elevated temperature and pressure. After the *PVT* measurements along the initial isochore were completed for a prescribed temperature range, the sample within the sample cell was expanded into the preevacuated expansion cell under a homogeneous state. Throughout the expansion procedure, the bath-fluid temperature was controlled within a fluctuation of ±10 mK and both the sample cell and the expansion cell were rocked by a rocking device to ensure homogeneity of the sample density and composition within these two vessels. Then the *PVT* measurements were continued along the newly obtained isochore for a mixture of the same fixed composition. Repeating these procedures, we obtained a set of *PVT* data for the mixture of fixed composition along several isochores by a single charge of the sample. Because of the possible accumulation of uncertainty in the density measurements due to repeating the expansion procedures, we did not repeat the

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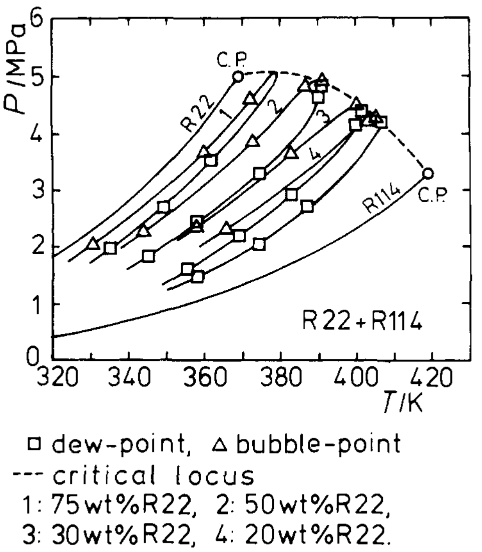

Figure 1. Dew and bubble point curves and the critical locus for the R 22 + R 114 system.

expansion procedures more than 4 times. We estimated the uncertainty in the density measurements to be less than 0.09%, which consists of that due to the measurement of the inner volume of the sample cell, 0.01%, that due to the mass measurements, 0.06%, and that due to the expansion procedures, 0.005%, per each procedure.

Results

Experimental results of the *PVTx* measurements for five different compositions of 0, 20, 30, 50, and 75 wt % R 22 are tabulated in Table I. Because the results of the measurements for 100 wt % R 22 were reported in a previous publication (*2*), we did not repeat the measurements for this composition in the present work. The values with an asterisk in Table I are those measured at a state of vapor-liquid coexistence. The values of density and mass fraction in the two-phase region given in Table I are only nominal. The results cover the range of temperatures 283–443 K and the range of pressures 0.13–9.11 MPa, which corresponds to the density variation from 94 to 1104 kg/m^3.

The composition dependence of the *PVT* surface for the R 22 + R 114 system was analyzed on the basis of these results. Thirty isochores were examined graphically with respect to their curvature on a pressure–temperature diagram and the dew and bubble points for each composition were determined as tabulated in Table II. Molar masses of 86.469 g/mol for R 22 and 170.922 g/mol for R 114 were used for converting mass fraction into mole fraction. The mole fraction of each composition is also shown in Table II. The uncertainty of the dew and bubble point temperatures is estimated to be 0.5 K, although the uncertainty of those near the critical point is 2–3 K due to the very small change in slope of the isochore. The critical locus on a pressure–temperature diagram for the present system was found as shown in Figure 1. The coexistence-state surface near the critical point is projected onto a density–mole fraction diagram in Figure 2, where several lines of constant temperature and constant pressure are illustrated.

The second virial coefficients for the mixture components were determined by fitting the present results for densities up to 205 kg/m^3 to the virial equation of state truncated at the third term. For the component R 114, the second virial coefficient was determined by fitting the *PVT* data of the present work, those measured by McHarness cited in the literature (*3*), and those by Wilson and Hules (*4*). The second virial coefficients thus determined are in good agreement with the experimental data of Bottomley and Nairn (*5*) with an average deviation of 0.44%. Using these second virial coefficients for R 114 thus obtained with those for R 22 proposed by Kagawa et al. (*6*), we calculated the interaction virial coefficients for the present R 22 + R 114 system and tabulated them in Table III. The uncertainty of the tabulated values is no greater than 2%.

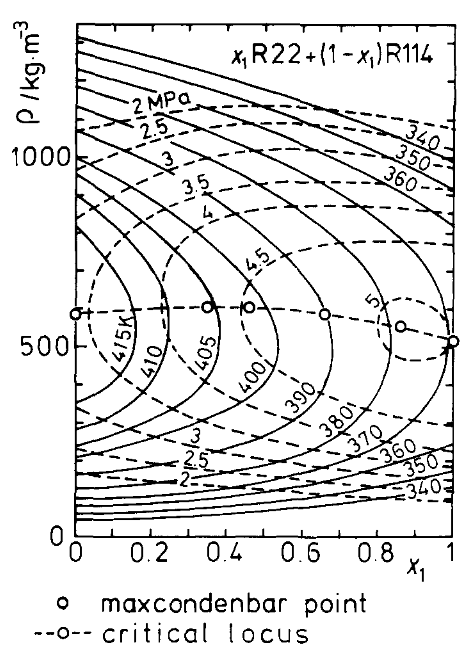

Figure 2. Projection of the coexistence-state surface in the critical region onto a density–mole fraction diagram for the R 22 + R 114 system.

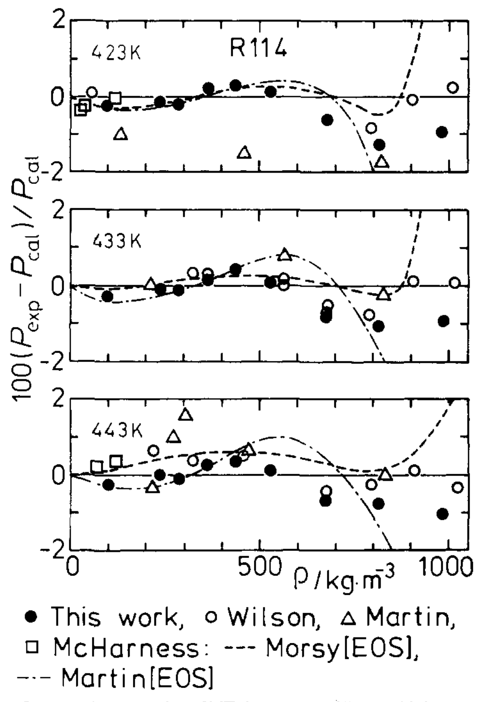

Figure 3. Comparison of the *PVT* data with Wilson–Hules equation of state for R 114 along the 423, 433, and 443 K isotherms.

Discussion

The present results of the *PVT* properties for R 114 were compared with the available experimental data (*3*, *4*) and some of the equations of state (*3*, *4*, *7*). Typical comparisons are shown in Figure 3, where the pressure deviations of the experimenal data from the pressure values calculated by the Wilson–Hules equation of state (*4*) are plotted. In this figure the pressure deviations of the values calculated by two equa-

Table I. Experimental *PVTx* Data for the R 22 + R 114 System[a,b]

T, K	P, MPa	ρ, kg/m^3
(A) 0 wt % R 22 + 100 wt % R 114		
373.180	1.3264	98.52
383.356	1.3923	98.47
393.337	1.4557	98.43
403.271	1.5171	98.38
413.379	1.5791	98.33
423.325	1.6390	98.28
433.356	1.6988	98.23
443.300	1.7580	98.18
283.168	0.1289	237.32*
288.335	0.1545	237.26*
293.691	0.1858	237.21*
299.642	0.2250	237.14*
303.235	0.2518	237.10*
308.119	0.2918	237.05*
313.671	0.3433	236.99*
318.366	0.3922	236.94*
323.360	0.4494	236.89*
328.650	0.5165	236.83*
333.702	0.5875	236.77*
338.936	0.6682	236.72*
343.305	0.7417	236.67*
349.145	0.8491	236.60*
353.956	0.9455	236.55*
368.514	1.2895	236.38*
373.916	1.4386	236.32*
383.154	1.7097	237.11*
408.148	2.5682	236.81
413.147	2.6851	236.76
423.157	2.8795	236.64
433.153	3.0634	236.52
443.137	3.2458	236.40
393.147	2.0665	286.06*
413.167	2.8314	285.77
423.158	3.1016	285.63
433.161	3.3362	285.49
443.163	3.5682	285.34
409.053	2.7510	360.97*
417.194	3.1205	360.82
419.168	3.1874	360.79
423.203	3.3213	360.71
433.199	3.6403	360.53
443.134	3.9520	360.35
408.289	2.7182	435.73*
415.186	3.0552	435.57*
417.173	3.1599	435.53*
419.184	3.2537	435.49
423.162	3.4228	435.40
433.204	3.8330	435.17
443.154	4.2269	434.95
413.148	2.9480	525.81*
416.132	3.1032	525.73*
418.173	3.2119	525.68*
420.202	3.3199	525.62
423.158	3.4764	525.54
433.158	3.9856	525.27
443.157	4.4942	525.00
411.131	2.8520	675.51*
414.179	3.0054	675.41*
417.189	3.1642	675.30*
418.173	3.2184	675.27*
419.153	3.2771	675.23
423.208	3.5467	675.09
433.132	4.2425	674.74
443.142	4.9622	674.39
407.009	2.6575	815.54*
413.174	2.9549	815.28*
415.184	3.0615	815.20*
417.167	3.2418	815.11
419.192	3.4366	815.03
423.148	3.8211	814.86
433.159	4.8251	814.42
443.147	5.8546	813.98
388.174	1.8888	985.30*
399.145	2.3064	984.77*
401.096	2.3879	984.67*
413.199	4.1833	984.02
423.192	5.8003	983.48
433.150	7.4441	982.94
443.135	9.1092	982.38
(B) 20 wt % R 22 + 80 wt % R 114		
293.172	0.3934	94.94*
323.155	0.7786	94.81*
355.066	1.4002	94.66*
356.981	1.4479	94.66*
359.009	1.4762	94.65
360.847	1.4910	94.64
363.087	1.5089	94.63
373.082	1.5851	94.58
383.359	1.6590	94.54
393.625	1.7308	94.49
403.096	1.7959	94.45
413.172	1.8647	94.40
423.029	1.9309	94.35
433.204	1.9985	94.30
382.466	1.8943	114.11
293.200	0.4177	138.32*
323.173	0.8257	138.13*
371.160	1.9722	137.82*
372.546	2.0160	137.81*
374.592	2.0485	137.79
376.560	2.0729	137.78
379.406	2.1070	137.76
383.579	2.1543	137.73
393.507	2.2697	137.67
403.094	2.3772	137.60
413.145	2.4851	137.53
423.240	2.5929	137.46
432.950	2.6954	137.40
293.178	0.4347	201.53*
323.175	0.8766	201.25*
384.798	2.6099	200.66*
387.223	2.7035	200.63
389.043	2.7399	200.62
391.006	2.7769	200.60
393.742	2.8258	200.57
403.407	3.0016	200.47
413.478	3.1830	200.37
423.393	3.3551	200.27
433.013	3.5194	200.18
293.179	0.4712	488.54*†
323.196	0.9769	487.87*†
394.071	3.4861	486.20*†
397.373	3.6627	486.12*†
401.741	3.9076	486.01*†
405.904	4.1388	485.91*†
411.873	4.4638	485.76†
394.817	3.5952	586.84*†
398.725	3.8120	586.72*†
402.840	4.0664	586.60*†
407.150	4.3441	586.47†
413.292	4.7600	586.28†
423.429	5.4543	585.98†
293.175	0.4759	711.77*†
323.193	0.9927	710.79*†
392.959	3.5540	708.40*†
396.467	3.7821	708.27*†
399.470	3.9795	708.16*†
401.420	4.1082	708.10*†
404.204	4.3153	707.99†
407.394	4.5752	707.88†
413.167	5.0901	707.66†
423.237	6.0268	707.29†
293.169	0.4705	1104.53*
323.167	0.9859	1103.02*
362.601	2.1834	1100.96*
366.360	2.4585	1100.75
368.764	3.0996	1100.60
372.953	4.2201	1100.34
382.997	6.8965	1099.71
(C) 30 wt % R 22 + 70 wt % R 114		
293.184	0.4729	95.01*
323.168	0.9283	94.88*
343.954	1.3467	94.79*
349.513	1.4774	94.77*
352.140	1.5441	94.76*
354.356	1.5840	94.75
368.295	1.6972	94.68
373.427	1.7370	94.66
383.454	1.8135	94.61
393.345	1.8874	94.57
403.417	1.9616	94.52
413.616	2.0360	94.47
423.153	2.1049	94.43
382.777	2.0687	114.21
293.176	0.5108	138.43*
323.169	0.9990	138.24*
361.248	1.9435	138.00*
367.407	2.1363	137.95*
369.250	2.1890	137.94
373.386	2.2433	137.91
383.202	2.3666	137.85
393.335	2.4886	137.78
403.423	2.6085	137.71
413.262	2.7229	137.65
423.315	2.8383	137.58
422.088	3.2344	166.07
293.175	0.5292	201.69*
323.176	1.0591	201.42*
363.307	2.1732	201.03*
373.585	2.5541	200.93*
375.156	2.6135	200.92*
383.697	2.9288	200.83
393.158	3.1172	200.74
403.107	3.3105	200.64
412.779	3.4946	200.54
423.193	3.6870	200.44
293.162	0.5349	372.30*
323.158	1.1190	371.78*
393.395	3.7925	370.53*
397.345	3.9919	370.46*
402.862	4.2600	370.36
413.200	4.7025	370.16
422.944	5.1089	369.98
383.291	3.3723	447.48*
393.550	3.9136	447.24*
395.400	4.0126	447.20*
397.256	4.1335	447.16*
398.220	4.1958	447.14*
403.276	4.4750	447.02
413.170	5.0007	446.80
422.728	5.5010	446.58
293.168	0.5533	542.43*
323.166	1.1482	541.68*
373.038	2.9175	540.39*
383.602	3.4437	540.11*
388.234	3.6968	539.98*
393.369	4.0000	539.84*
398.157	4.3009	539.71*
403.296	4.6436	539.57
412.945	5.2848	539.30
423.460	5.9892	539.01
373.539	3.0719	910.57*
379.237	3.3958	910.31*
381.348	3.5103	910.21*
383.466	3.6300	910.12*
388.252	4.4095	909.88
389.207	4.5656	909.84
393.289	5.2488	909.63
402.634	6.8439	909.17
412.282	8.7264	908.68
293.172	0.5627	1103.25*
323.176	1.1751	1101.74*
355.587	2.2669	1100.05*
356.388	2.2985	1100.01*
357.261	2.3326	1099.96*
358.335	2.5474	1099.90
363.296	3.9842	1099.59
373.287	6.9103	1098.95
(D) 50 wt % R 22 + 50 wt % R 114		
293.177	0.6414	100.29*
323.149	1.2226	100.16*
333.032	1.4499	100.11*
339.190	1.6132	100.08*
341.540	1.6764	100.07*
343.738	1.7975	100.06*
347.266	1.8440	100.04
353.521	1.9161	100.01
363.820	2.0153	99.96
373.517	2.1078	99.92
383.347	2.2004	99.87
403.318	2.3815	99.77
413.322	2.4715	99.72
423.310	2.5601	99.67
293.173	0.6615	140.37*
323.152	1.4094	140.18*
353.142	2.2247	139.98*
356.114	2.3491	139.96*
357.157	2.3670	139.95*
358.155	2.3938	139.95
363.147	2.4979	139.91
373.148	2.6488	139.85
383.163	2.7928	139.78
393.157	2.9278	139.71
403.150	3.0697	139.64
413.153	3.2045	139.57
423.153	3.3380	139.50
293.179	0.6766	204.51*
323.158	1.3703	204.23*
353.152	2.3914	203.94*
363.140	2.7906	203.85*
365.138	2.8767	203.83*
366.133	2.9222	203.82*
367.159	2.9678	203.81*
368.137	3.0096	203.80*
369.078	3.0594	203.79*
371.166	3.1396	203.77*
373.161	3.2152	203.75*
374.100	3.2654	203.74*
375.202	3.2941	203.72
377.131	3.3423	203.71
380.142	3.4118	203.68
383.123	3.4811	203.65
393.093	3.7088	203.55
403.170	3.9330	203.44
383.001	4.1856	393.15*
387.273	4.4546	393.07*
388.169	4.5103	393.05*
389.105	4.5647	393.03
393.888	4.8287	392.94
403.190	5.3136	392.75
413.090	5.8195	392.55
423.020	6.3195	392.35
293.173	0.6900	476.58*
323.159	1.4396	475.93*
383.302	4.3054	474.54*
388.124	4.6389	474.42*
389.387	4.7269	474.39*
390.444	4.8029	474.37*
391.251	4.8576	474.35
393.183	4.9858	474.30
403.288	5.6478	474.06
413.191	6.2892	473.82
423.233	6.9389	473.57
293.192	0.6916	575.25*
323.136	1.4469	574.46*
373.312	3.7575	573.07*
382.819	4.3776	572.80*
385.235	4.5489	572.73*
387.464	4.7193	572.66*
389.215	4.8586	572.61*

Table I (Continued)

T, K	P, MPa	ρ, kg/m^3	T, K	P, MPa	ρ, kg/m^3	T, K	P, MPa	ρ, kg/m^3	T, K	P, MPa	ρ, kg/m^3
391.217	5.0183	572.55	323.151	1.4643	1101.98*	374.658	2.3972	95.89	361.009	3.4750	203.66*
393.138	5.1731	572.49	340.158	2.1073	1101.10*	383.524	2.4883	95.84	363.344	3.5497	203.64
403.110	5.9931	572.20	341.146	2.1550	1101.05*	393.625	2.5907	95.80	373.783	3.8481	203.54
413.360	6.8513	571.89	342.184	2.1943	1101.00*	403.341	2.6883	95.75	383.962	4.1216	203.44
423.341	7.6860	571.59	343.140	2.2381	1100.94*	413.630	2.7908	95.70	363.182	3.8923	753.72*
293.171	0.6942	694.34*	344.162	2.3568	1100.88	423.372	2.8867	95.66	368.928	4.3279	753.51*
323.152	1.4530	693.39*	345.167	2.6973	1100.82	293.196	0.7995	140.23*	374.266	4.8823	753.30
363.203	3.2030	692.05*	346.153	3.0348	1100.76	323.170	1.6432	140.04*	378.838	5.5501	753.12
373.674	3.8292	691.69*	353.154	5.4397	1100.31	339.348	2.2633	139.93*	383.523	6.2516	752.94
383.055	4.4919	691.37*	363.128	8.8947	1099.65	346.831	2.5944	139.88*	393.337	7.7645	752.54
392.931	5.4548	691.02	(E) 75 wt % R 22 + 25 wt % R 114			349.781	2.6941	139.86	352.755	3.2089	910.19*
402.979	6.5580	690.65	293.186	0.7873	96.25*	351.090	2.7134	139.86	355.533	3.3837	910.07*
413.154	7.7065	690.28	323.127	1.5758	96.12*	362.969	2.9303	139.78	358.438	3.5791	909.94*
423.136	8.8479	689.91	331.296	1.8415	96.08*	373.387	3.1174	139.71	361.715	4.1067	909.78
293.182	0.6981	899.83*	333.628	1.9094	96.07*	383.658	3.2766	139.64	362.943	4.3811	909.72
323.157	1.4624	898.59*	335.019	1.9593	96.07*	393.234	3.4312	139.57	373.789	6.9369	909.17
371.254	3.7485	896.51*	336.809	1.9816	96.06	403.565	3.5957	139.50	293.172	0.8243	1101.72*
372.175	3.8092	896.47*	339.109	2.0098	96.05	413.699	3.7544	139.43	323.166	1.7339	1100.20*
373.170	3.9273	896.42	343.676	2.0640	96.03	423.236	3.9026	139.36	328.893	1.9704	1099.91*
375.179	4.2932	896.32	353.658	2.1751	95.98	293.179	0.8065	204.32*	330.891	2.1665	1099.80
376.194	4.4800	896.27	363.389	2.2795	95.94	323.172	1.6844	204.04*	332.795	2.9458	1099.67
383.193	5.8487	895.93				353.245	3.0342	203.74*	333.991	3.4381	1099.59
393.183	7.7279	895.44				359.076	3.3440	203.68*	343.917	7.5460	1098.93
293.174	0.6889	1103.50*									

[a] Values with an asterisk were measured at a state of vapor–liquid coexistence. The values of density and mass fraction in this state are only nominal. [b] Values with a cross are data for a mixture of 21.03 wt % R 22 + 78.97 wt % R 114.

Table II. Dew and Bubble Points for the R 22 + R 114 System[a]

compn of R 22		dew point			bubble point		
w_1, wt %	x_1, mol %	T, K	P, MPa	ρ, kg/m^3	T, K	P, MPa	ρ, kg/m^3
20.00	33.07	358.0	1.47	94.6	365.8	2.30	1100.9
		374.2	2.05	137.8	403.3	4.21	708.1†
		387.0	2.70	200.6	405.9	4.26	586.6†
		406.4	4.20	485.9†			
30.00	45.86	354.1	1.58	94.7	357.8	2.36	1099.9
		369.0	2.19	137.9	383.8	3.65	910.1
		383.0	2.92	200.9	401.4	4.52	539.8
		399.8	4.14	370.5			
		401.4	4.38	447.2			
50.00	66.41	344.8	1.81	100.1	343.9	2.26	1100.9
		357.8	2.42	140.0	373.0	3.85	896.4
		374.4	3.28	203.7	386.8	4.82	691.2
		389.5	4.62	393.0	391.0	4.92	572.6
		390.7	4.82	474.4			
75.00	85.57	335.1	1.96	96.1	330.5	2.04	1099.8
		348.6	2.68	139.9	360.0	3.67	909.8
		361.4	3.51	203.6	372.3	4.58	753.4

[a] Values with a cross are data for a mixture of 21.03 wt % R 22 + 78.97 wt % R 114 (34.49 mol % R 22 + 65.51 mol % R 114).

Table III. Interaction Virial Coefficients for the R 22 + R 114 System

T, K	B_{11}, cm^3/mol	B_{22}, cm^3/mol	B_{12}, cm^3/mol
330	-281	-642	-394
340	-261	-599	-366
350	-244	-560	-342
360	-228	-524	-319
370	-213	-492	-299
380	-200	-462	-281
390	-187	-435	-265
400	-176	-410	-250
410	-166	-386	-236
420	-156	-365	-224
430	-147	-345	-213
440	-138	-327	-202

tions of state (EOS) (*3*, *7*) from those by the Wilson–Hules equation of state are also depicted. Our results are in good agreement with the experimental data of McHarness cited in the literature (*3*) and of Wilson and Hules (*4*), whereas those of Martin (*3*) deviate from our results with a considerable scatter of about ±1.5%. The sample of R 114 used by Martin contained 5% CCl_2FCF_3 as our sample did. Wilson and Hules, however, used a sample of 93.0% $CClF_2CClF_2$ + 7.0% CCl_2FCF_3. Examining more precisely, one finds that the data of Wilson and Hules for densities up to 675 kg/m^3 deviate from our results within a pressure deviation of ±0.2%, but the pressure values of their data for densities greater than 800 kg/m^3 are systematically higher than those of our results by 0.5–1.0%. Wilson and Hules used two different constant-volume apparatuses, one for low-density measurements and the other for high densities. They claimed that the uncertainty in pressure for low-density measurements was less than 0.1%, whereas that for high densities was 0.2%.

Although Martin (*3*) as well as Morsy (*7*) correlated his equation of state on the basis of the experimental data of Martin (*3*) and those of McHarness cited in the literature (*3*), the calculated values agree with our results for densities up to 700 kg/m^3 within a pressure deviation of ±1%. At the present stage, however, the equation of state proposed by Wilson and Hules (*4*) describes quite reasonably the *PVT* surface of our results. However, the equation of ref *4* has defects in the critical region as they stated.

The shape of dew and bubble point curves of the present R 22 + R 114 system shown in Figure 1 is much wider than that of the R 12 + R 22 system shown in a previous publication (*2*). The maximum pressure difference between dew and bubble points at a given temperature is about 0.72 MPa for the mixture of 30 wt % R 22 + 70 wt % R 114 at 376 K. The critical locus is convex with a maximum pressure corresponding to a critical pressure of the mixture of around 75 wt % R 22 + 25 wt % R 114. This trend of the critical locus is in contrast to that for the R 12 + R 22 system (*8*) for which the pressure decreases with increasing temperature. There is a similar difference concerning the composition dependence in the shape of the coexistence-state surface in the critical region. The surface for the R 22 + R 114 system is shaped like a ridge, while that for the R 12 + R 22 system is shaped like a saddle as shown in a previous publication (*8*).

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Glossary

B_{11}	second virial coefficient for R 22, cm^3/mol
B_{22}	second virial coefficient for R 114, cm^3/mol
B_{12}	interaction virial coefficient, cm^3/mol
CP	critical point
P	pressure, MPa
P_{calcd}	pressure value calculated by Wilson–Hules equation of state (*4*), MPa
P_{exptl}	pressure value of experimental data, MPa
T	temperature, K
w_1	mass fraction of R 22
x_1	mole fraction of R 22
ρ	density, kg/m^3

Registry No. Freon 22, 75-45-6; Freon 114, 76-14-2.

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Excess Volumes of Nitrobenzene with Alkyl-Substituted Chloroethanes at 303.15 and 313.15 K

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Excess volumes of nonelectrolyte solutions of nitrobenzene with 1,2-dichloroethane, 1,1,1-trichloroethane, and 1,1,2,2-tetrachloroethane were measured at 303.15 and 313.15 K by using a dilatometer and are reported in this paper.

Introduction

In view of their probable value in the systematic analysis of the behavior of substances, experimental excess volumes of nitrobenzene with 1,2-dichloroethane, 1,1,1-trichloroethane, and 1,1,2,2-tetrachloroethane have been undertaken and are reported in this paper. These measurements were made as part of a continuing project on the thermodynamic and physical properties of nonelectrolyte solutions (*1–4*).

Experimental Section

The excess volumes have been determined at 303.15 and 313.15 K by using a single composition per loading type dilatometer described by Rao and Naidu (*5*). The excess volumes are accurate to ±0.003 cm^3 mol^{-1}. The dilatometer was standardized with a cyclohexane–benzene system at 298.15 K. The measured excess volumes for the standard system are in good agreement with the earlier values reported (*6*).

Purification of Materials. Nitrobenzene (BDH) was dried over anhydrous calcium chloride for 2 days and the dried sample was distilled by using a 1-m fractionating column under reduced pressure. 1,2-Dichloroethane (BDH) was washed with a dilute solution of potassium hydroxide and then with water. It was dried over phosphorus pentoxide and distilled in a fractionating column. The fraction of the second distillation was collected and stored in an amber-colored bottle.

1,1,1-Trichloroethane (Koch-light Laboratories) was washed with concentrated sulfuric acid and then with 10% sodium chloride solution. It was dried over calcium chloride and distilled in a fractionating column. The middle fraction was collected and stored.

During the distillation 0.5 g of phenol was added as a stabilizer.

1,1,2,2-Tetrachloroethane (BDH) was stirred with concentrated sulfuric acid at 80 °C for 10 min. The discolored acid was removed and again 25 mL of the acid was added. The liquid was then washed with water, dried over potassium carbonate, and distilled under vacuum.

During the distillation about 0.5 g of phenol was added as a stabilizer.

The purity of the compounds was checked by densities, refractive indices, and boiling points. The densities were measured with a bicapillary pyconometer. The densities are accurate to 5 parts in 10^5. The refractive indices were measured with an Abbe refractometer which gave an accuracy of ±0.0002.

The boiling points were measured with a Swietoslawaki type ebulliometer which gave an accuracy of ±0.1 °C. The measured values are presented in Table I along with the literature values (*7*, *8*).

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