J. Chem. Eng. Data 1991, 36, 156-159

Isobaric Heat Capacity Data for Liquid HCFC-123 ($CHCl_2CF_3$, 2,2-Dichloro-1,1,1-trifluoroethane)

Shinsuke Nakagawa,* Haruki Sato, and Koichi Watanabe

Department of Mechanical Engineering, Faculty of Science and Technology, Keio University, 3-14-1, Hiyoshi, Kohoku-ku, Yokohama 223, Japan

The isobaric heat capacity, C_p, of liquid 2,2-dichloro-1,1,1-trifluoroethane ($CHCl_2CF_3$, HCFC-123), which is a promising alternative to CFC-11, has been measured by using flow calorimetry. The values of 80 C_p have been determined in the range of temperatures from 275.65 to 440 K and pressures from 0.5 to 3.2 MPa, respectively. The overall uncertainties of the determined C_p values are concluded to be less than ±0.4% for temperatures below 420 K, ±0.5% at 430 K, ±0.8% at 440 K, respectively. The C_p data have been correlated with a function of temperature and pressure within ±0.4%, and the C_p of saturated liquid, C_p', have been derived from the correlation.

Introduction

The fully halogenated chlorofluorocarbons (CFCs) have been widely used as a blowing agent, a cleaning agent, or a working fluid for heat-pumping and refrigeration systems. But there is concern for their ozone-depletion and global-warming potential so that many CFC alternatives have been suggested. HCFC-123 ($CHCl_2CF_3$), which has small ozone-depletion potential, is promised as one of alternatives to replace CFC-11 (CCl_3F). This paper reports the isobaric heat capacity data of liquid HCFC-123 and a correlation for the heat capacity of compressed and saturated liquid. The purity of the sample HCFC-123 used in the measurements was 99.82 wt %.

Experimental Section

The detailed description regarding the flow calorimeter has been reported in our previous papers (*1*–*3*). Measurements for another alternative refrigerant, HFC-134a (CF_3CH_2F), have already been reported by the present authors (*4*). The special features of our apparatus are its highly adiabatic performance, the flow stability of the sample liquid in the closed circulation system, and the reliability of automatic measurements of the mass-flow rate. The isobaric heat capacity, C_p, is defined as follows:

$$C_p = \dot{Q}/(\dot{m}\,\Delta T) \tag{1}$$

Flow calorimetry consists of three simultaneous measurements: measurement of energy, $\dot{Q}$, supplied by a microheater to the flowing sample liquid; measurement of the temperature increment, ΔT, which is the temperature difference, $T_{out} - T_{in}$, of sample liquid before and after heating by the microheater; and measurement of the mass-flow rate, $\dot{m}$. The reliability of this apparatus was confirmed by measuring the C_p values of water. The systematic errors were not found, and the standard deviation from the equation of state developed by Sato et al. (*5*) was 0.34%.

Results

Measurements were performed at temperatures from 275.65 to 440 K and pressures from 0.5 to 3.2 MPa. All measured values are listed in Table I. The table includes the measured pressure, P, measured temperature, T, energy supplied to the sample fluid, $\dot{Q}$, temperature increment, ΔT, mass-flow rate, $\dot{m}$, and measured heat capacity, C_p. Note that the measured temperature T_{68} is assigned to the temperature of the arithmetic mean of T_{in} and T_{out} on the basis of the International Practical Temperature Scale of 1968 (IPTS-68).

In order to know the effect of heat loss on measured C_p values, data at various mass-flow rates are plotted against the inverse mass-flow rates in Figure 1. Measurements were performed at a state, i.e., at a certain temperature and pressure, selecting two different mass-flow rates. It was confirmed from Figure 1 that the measured C_p values do not depend on the mass-flow rates. Thus, it was concluded that the effect of heat loss is small enough to not necessarily be compensated for. The temperature increment has to be small enough so as to produce no difference between the average of the C_p values at inlet and outlet temperatures, C_p(av), and the true C_p value at a given temperature. The measurements in the temperature range from 275.65 to 420 K were performed with the temperature increment 5 K, while the measurements at 430 K were performed with about 3 K of ΔT and 1.6 K for the measurements at 440 K, respectively. The unsmoothed experimental data are summarized in Table I. We confirmed that the difference between C_p(av) and the true C_p was within ±0.1% by examining the data with a developed correlation given as a function of temperature and pressure. After we corrected the C_p values that were measured at the same temperatures and pressures but mass-flow rates to those at nominal temperatures and pressures with the aid of developed correlation, we determined the C_p values at nominal temperatures and pressures as arithmetic means of those at the same temperatures and pressures but mass-flow rate. In Table II, 80 C_p values at nominal temperatures and pressures are listed. The uncertainties of the measurements are ±8 mK in temperature increment, ±0.01% in energy supplied, ±0.3% in mass-flow rate, ±11 mK in temperature, and ±3 kPa in pressure, respectively. The overall uncertainties of the determined C_p values summarized in Table II is concluded to be less than ±0.4% for temperatures below 420 K, ±0.5% for those at 430 K, and ±0.8% for those at 440 K, respectively. The C_p values were correlated with the following temperature and pressure function.

$$C_p/R = a + bP_r^{0.5} + cP_r \tag{2}$$

$$a = 0.06718(1 - T_r)^{-2} - 0.3756(1 - T_r)^{-1} + 27.24 - 12.98(1 - T_r)^{0.5}$$

$$b = 6.215 \times 10^{-7}(1 - T_r)^{-5} - 0.001719(1 - T_r)^{-3} - 0.6750(1 - T_r)$$

$$c = -0.01581(1 - T_r)^{-2} + 0.5316(1 - T_r)$$

where $P_r = P/P_c$, $T_r = T/T_c$, $R = R_0/M$, and C_p is given in kJ/(kg·K), P in MPa, and T in K. The critical pressure, P_c, is 3.6655 MPa, which has been reported by Piao et al. (*6*). The critical temperature, T_c, is 456.86 K, which has been reported by Tanikawa et al. (*7*). The universal gas constant R_0 = 8.31451 J/(mol·K) and molar mass M = 152.93 g/mol.

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* To whom correspondence should be addressed.

0021-9568/91/1736-0156$02.50/0

Table I. Measured Isobaric Heat Capacity of HCFC-123

P, MPa	T, K	$\dot{Q}$, J/s	ΔT, K	$\dot{m}$, g/s	C_p, kJ/(kg·K)
0.500	275.64	0.8177	4.998	0.1623	1.008
0.503	275.65	0.5649	5.009	0.1123	1.004
1.004	275.65	0.8150	5.000	0.1627	1.002
1.004	275.65	0.5629	5.013	0.1123	1.000
1.501	275.65	0.8167	5.005	0.1631	1.000
1.501	275.65	0.5629	5.004	0.1127	0.998
2.002	275.66	0.8168	5.016	0.1625	1.002
2.001	275.66	0.5625	5.019	0.1123	0.998
2.499	275.65	0.8160	5.009	0.1631	0.999
2.500	275.66	0.5648	5.018	0.1129	0.997
3.000	275.65	0.8172	5.006	0.1631	1.001
2.998	275.68	0.5709	5.070	0.1128	0.998
0.501	300.01	0.8453	5.020	0.1635	1.030
0.503	300.00	0.5835	5.011	0.1130	1.030
1.002	300.00	0.8401	5.010	0.1631	1.029
1.000	300.00	0.5803	5.009	0.1126	1.029
1.502	300.00	0.8389	5.003	0.1632	1.027
1.500	299.99	0.5787	4.998	0.1129	1.026
2.000	300.00	0.8399	5.006	0.1632	1.028
1.999	300.00	0.5806	5.009	0.1131	1.025
2.505	300.00	0.8394	5.008	0.1636	1.025
2.506	299.99	0.5812	5.000	0.1136	1.023
3.001	300.00	0.8432	5.013	0.1641	1.025
2.999	300.00	0.5826	5.027	0.1133	1.023
0.504	310.00	0.8498	5.004	0.1625	1.045
0.504	310.00	0.5867	4.994	0.1123	1.047
1.002	310.01	0.8528	5.027	0.1627	1.043
1.003	310.00	0.5898	5.006	0.1129	1.044
1.505	310.00	0.8489	5.008	0.1624	1.044
1.505	310.00	0.5882	4.998	0.1125	1.046
2.005	309.99	0.8475	4.992	0.1628	1.043
2.005	310.01	0.5876	5.005	0.1125	1.044
2.503	310.01	0.8485	5.013	0.1622	1.044
2.503	310.01	0.5854	5.006	0.1121	1.043
3.004	310.01	0.8506	5.009	0.1629	1.043
3.002	310.00	0.5879	4.994	0.1129	1.043
0.505	320.01	0.8637	5.020	0.1620	1.062
0.507	320.00	0.5970	4.996	0.1125	1.062
1.000	320.00	0.8622	5.000	0.1626	1.061
1.002	320.00	0.5971	5.009	0.1122	1.062
1.504	320.00	0.8573	4.998	0.1618	1.060
1.504	320.00	0.5927	4.996	0.1118	1.061
2.001	320.00	0.8598	5.003	0.1628	1.056
2.001	320.00	0.5958	4.997	0.1128	1.057
2.501	320.01	0.8623	5.013	0.1630	1.055
2.500	320.01	0.5975	5.018	0.1127	1.056
2.998	320.00	0.8719	4.996	0.1656	1.054
3.001	320.00	0.6086	5.003	0.1156	1.052
0.502	330.00	0.8731	5.000	0.1623	1.076
0.503	330.00	0.6064	5.002	0.1123	1.080
1.003	330.00	0.8717	5.002	0.1622	1.074
1.001	330.01	0.6065	5.019	0.1122	1.077
1.505	330.00	0.8713	5.004	0.1628	1.070
1.503	330.00	0.6035	4.996	0.1125	1.073
2.002	330.00	0.8702	5.008	0.1622	1.072
2.004	330.00	0.6030	4.999	0.1123	1.074
2.496	330.01	0.8785	5.019	0.1631	1.073
2.496	330.02	0.6108	5.039	0.1130	1.073
2.999	330.00	0.8707	5.012	0.1626	1.068
3.003	330.00	0.6173	4.997	0.1154	1.070
0.603	339.99	0.8845	5.001	0.1621	1.091
1.004	340.00	0.8862	5.012	0.1624	1.089
1.501	340.01	0.8872	5.014	0.1626	1.088
2.001	340.00	0.8861	5.008	0.1633	1.083
2.503	340.00	0.8857	5.010	0.1632	1.083
3.001	340.00	0.8991	5.010	0.1660	1.081
0.702	350.00	0.9048	5.011	0.1631	1.107
1.002	349.99	0.9049	5.005	0.1628	1.111
1.502	350.00	0.9045	5.019	0.1633	1.104
2.003	349.99	0.9004	4.993	0.1633	1.104
2.499	350.00	0.9000	5.018	0.1634	1.098
3.001	350.00	0.9127	5.001	0.1662	1.098
0.802	360.00	1.0182	5.020	0.1791	1.133
0.802	360.00	0.8290	5.011	0.1462	1.132
1.002	360.00	1.0179	5.021	0.1794	1.130
1.002	359.99	0.8266	5.005	0.1461	1.131
1.502	359.99	1.0142	5.026	0.1792	1.126
1.503	360.00	0.8263	5.008	0.1464	1.127
2.000	360.00	1.0127	5.016	0.1799	1.122
2.000	360.00	0.8241	5.017	0.1461	1.124
2.499	359.99	1.0059	5.002	0.1798	1.119
2.499	360.00	0.8230	5.017	0.1462	1.122
2.998	360.00	0.9117	5.013	0.1634	1.113
1.003	370.00	1.0376	5.021	0.1799	1.149
1.003	370.00	0.8431	5.017	0.1463	1.149
1.502	370.00	1.0336	5.017	0.1799	1.145
1.502	370.00	0.8403	5.017	0.1465	1.143
2.005	370.02	1.0303	5.036	0.1798	1.138
2.010	370.01	0.8308	5.013	0.1457	1.137
2.500	370.00	1.0305	5.034	0.1805	1.134
2.498	370.00	0.8347	5.017	0.1467	1.134
3.000	369.99	1.0369	5.012	0.1829	1.131
2.998	369.99	0.8440	5.003	0.1490	1.132
1.200	380.01	1.0537	5.040	0.1777	1.176
1.199	379.97	0.8588	4.983	0.1463	1.178
1.499	379.99	1.0538	5.025	0.1789	1.172
1.500	380.00	0.8604	5.015	0.1462	1.173
2.000	380.01	0.8603	5.020	0.1473	1.164
2.003	380.02	1.0530	5.040	0.1794	1.165
2.502	380.02	1.0535	5.057	0.1800	1.157
2.500	380.00	0.8546	5.035	0.1469	1.155
2.997	380.00	1.0556	5.030	0.1821	1.152
2.996	379.99	0.8630	5.009	0.1494	1.154
1.501	390.01	1.0921	5.035	0.1797	1.207
1.501	390.01	0.8870	5.033	0.1458	1.208
1.999	390.00	1.0825	5.032	0.1796	1.198
1.999	390.01	0.8840	5.030	0.1470	1.196
2.502	390.01	1.0801	5.051	0.1801	1.187
2.497	390.02	0.8788	5.052	0.1463	1.189
2.998	390.00	1.0855	5.034	0.1828	1.180
2.997	390.00	0.8858	5.033	0.1489	1.182
1.702	400.00	1.1314	5.045	0.1804	1.243
1.703	400.01	0.9217	5.041	0.1468	1.245
1.997	400.00	1.1203	5.043	0.1800	1.234
1.998	399.99	0.9101	5.010	0.1467	1.238
2.501	400.00	1.1119	5.045	0.1802	1.223
2.498	400.00	0.9065	5.040	0.1469	1.224
3.002	399.98	0.9095	4.991	0.1497	1.217
3.004	399.99	1.0975	5.034	0.1793	1.216
1.903	410.02	1.1799	5.074	0.1788	1.300
1.903	410.01	0.9648	5.054	0.1462	1.305
1.998	410.01	1.1765	5.055	0.1796	1.296
1.998	410.02	1.1765	5.063	0.1794	1.295
1.998	410.01	1.1765	5.039	0.1803	1.295
1.998	410.01	0.9609	5.039	0.1473	1.294
1.998	410.01	0.9609	5.039	0.1471	1.296
1.998	410.01	0.9609	5.041	0.1470	1.297
2.501	410.00	1.1624	5.064	0.1802	1.274
2.499	410.01	0.9468	5.057	0.1465	1.278
3.000	410.00	1.1560	5.041	0.1829	1.254
3.000	410.00	1.1560	5.043	0.1829	1.253
3.000	410.01	0.9519	5.060	0.1496	1.257
2.302	420.02	1.2465	5.070	0.1791	1.373
2.499	420.00	1.2308	5.044	0.1795	1.359
2.994	420.01	1.2071	5.048	0.1801	1.328
3.194	420.00	1.1950	5.045	0.1800	1.316
3.200	420.01	1.3089	5.069	0.1960	1.317
2.701	430.00	0.8112	3.055	0.1799	1.476
2.803	429.98	0.8031	3.050	0.1797	1.465
2.999	429.99	0.7953	3.055	0.1802	1.445
3.193	429.99	0.7795	3.045	0.1802	1.421
3.196	429.99	0.8469	3.046	0.1956	1.421
3.000	440.02	0.4887	1.582	0.1793	1.723
3.199	440.01	0.4665	1.577	0.1800	1.644
3.200	440.01	0.5043	1.570	0.1953	1.644

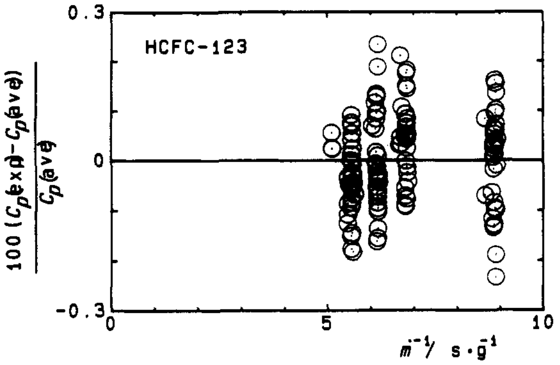

Figure 1. Reproducibility in C_p measurements at various mass-flow rates. C_p(exp) denotes the measured value, whereas C_p(av) is the averaged value.

Table II. Isobaric Heat Capacity of HCFC-123

P, MPa	T, K	C_p, kJ/(kg·K)	P, MPa	T, K	C_p, kJ/(kg·K)
0.500	275.65	1.006	0.800	360.00	1.132
1.000	275.65	1.001	1.000	360.00	1.130
1.500	275.65	1.000	1.500	360.00	1.127
2.000	275.65	1.000	2.000	360.00	1.123
2.500	275.65	0.998	2.500	360.00	1.120
3.000	275.65	1.000	3.000	360.00	1.113
0.500	300.00	1.030	1.000	370.00	1.149
1.000	300.00	1.029	1.500	370.00	1.144
1.500	300.00	1.027	2.000	370.00	1.138
2.000	300.00	1.027	2.500	370.00	1.134
2.500	300.00	1.024	3.000	370.00	1.131
3.000	300.00	1.024	1.200	380.00	1.177
0.500	310.00	1.046	1.500	380.00	1.173
1.000	310.00	1.043	2.000	380.00	1.164
1.500	310.00	1.045	2.500	380.00	1.156
2.000	310.00	1.043	3.000	380.00	1.153
2.500	310.00	1.043	1.500	390.00	1.208
3.000	310.00	1.043	2.000	390.00	1.197
0.500	320.00	1.062	2.500	390.00	1.188
1.000	320.00	1.061	3.000	390.00	1.181
1.500	320.00	1.060	1.700	400.00	1.244
2.000	320.00	1.056	2.000	400.00	1.236
2.500	320.00	1.056	2.500	400.00	1.223
3.000	320.00	1.053	3.000	400.00	1.216
0.500	330.00	1.078	1.900	410.00	1.303
1.000	330.00	1.076	2.000	410.00	1.296
1.500	330.00	1.071	2.500	410.00	1.276
2.000	330.00	1.073	3.000	410.00	1.255
2.500	330.00	1.073	2.300	420.00	1.373
3.000	330.00	1.069	2.500	420.00	1.359
0.600	340.00	1.091	3.000	420.00	1.328
1.000	340.00	1.089	3.200	420.00	1.316
1.500	340.00	1.088	2.700	430.00	1.476
2.000	340.00	1.083	2.800	430.00	1.465
2.500	340.00	1.083	3.000	430.00	1.445
3.000	340.00	1.081	3.200	430.00	1.421
0.700	350.00	1.107	3.000	440.00	1.723
1.000	350.00	1.111	3.200	440.00	1.644
1.500	350.00	1.104			
2.000	350.00	1.104			
2.500	350.00	1.098			
3.000	350.00	1.098			

Table III. Isobaric Heat Capacity of Saturated Liquid HCFC-123

P, MPa	T, K	C_p', kJ/(kg·K)	P, MPa	T, K	C_p', kJ/(kg·K)
0.037	275.65	1.006	0.580	360.00	1.132
0.044	280.00	1.012	0.733	370.00	1.154
0.067	290.00	1.024	0.914	380.00	1.180
0.098	300.00	1.036	1.127	390.00	1.211
0.139	310.00	1.050	1.374	400.00	1.252
0.193	320.00	1.064	1.659	410.00	1.308
0.261	330.00	1.079	1.987	420.00	1.392
0.347	340.00	1.095	2.363	430.00	1.527
0.452	350.00	1.112	2.792	440.00	1.800

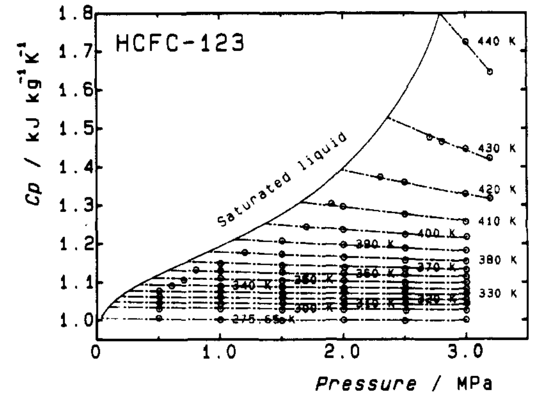

Figure 2. Experimental data and the correlation for isobaric heat capacity of liquid HCFC-123.

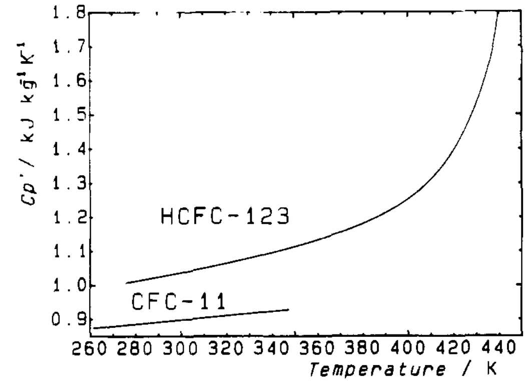

Figure 3. Comparison of isobaric heat capacity of saturated liquid HCFC-123 with that of CFC-11 (8).

Equation 2 is effective in a temperature range between 275.65 and 440 K. This correlation reproduces the measured C_p data within ±0.4%. Saturated liquid C_p data in Table III were also derived by substituting vapor pressures calculated from eq 3,

$$\ln (P/P_c) = (A\tau + B\tau^{1.2} + C\tau^2 + D\tau^3)/(1 - \tau) \quad (3)$$

$$\tau = 1 - T/T_c$$

$$A = -7.87576 \qquad B = 1.45751$$

$$C = 0.520220 \qquad D = -3.47970$$

developed by Piao et al. (6), into eq 2. The measured C_p values for the compressed liquid and the isotherms, as well as the saturation curve calculated from eq 2, are shown on a C_p–P diagram in Figure 2.

Discussion

Since no measured C_p values nor equations of state that are effective in the liquid phase have been available for HCFC-123 at present, we cannot compare our data with another source. As shown in Figure 1, the reproducibility of our measurements was better than ±0.3% and our correlation can reproduce our data within ±0.4%. No constrained behavior beyond the experimental error was observed in our measurements.

For practical applications, when the C_p' values of HCFC-123 are compared with those of CFC-11 (8), the C_p' of HCFC-123 is larger than that of CFC-11 by about 10%, as shown in Figure 3.

Conclusion

The C_p values of hydrofluorocarbon HCFC-123 were measured at 80 state points in the liquid phase, covering temperatures from 275.65 to 440 K and pressures from 0.5 to 3.2 MPa with the uncertainty of ±0.4% for the data below 420 K, ±0.5% for the data at 430 K, and ±0.8% for the data at 440 K, respectively. These C_p data were correlated as a function of temperature and pressure, and saturated liquid C_p' values were derived from the correlation.

Acknowledgment

We acknowledge the assistance of Hideo Miyahara in the present measurements. We are also grateful to Asahi Glass Company, Tokyo, for kindly furnishing the sample of HCFC-123.

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Received for review July 24, 1990. Accepted November 26, 1990. The financial support from the Tokyo Electric Power Co., Inc., is greatly appreciated.

Vapor–Liquid Equilibrium Determination by Total Pressure Measurements for Three Binary Systems Made of 1,2-Dimethoxyethane with Toluene, Methylcyclohexane, or (Trifluoromethyl)benzene

Kazunori Aizawa and Masahiro Kato*

Department of Industrial Chemistry, Faculty of Engineering, Nihon University, Koriyama, Fukushima 963, Japan

Total vapor pressures were measured for the three binary systems made of 1,2-dimethoxyethane with toluene, methylcyclohexane, or (trifluoromethyl)benzene (benzotrifluoride) at 350 K. Densities of the mixtures were measured at 298.15 K. The vapor–liquid equilibria were correlated by using the Wilson equation.

Introduction

Vapor–liquid equilibria (VLE) are required for engineering use such as in the design and operation of distillation equipment. In the present study, isothermal total pressures P were measured by the ebulliometric method for the three binary systems made of 1,2-dimethoxyethane with toluene, methylcyclohexane, or (trifluoromethyl)benzene (benzotrifluoride) at 350 K. The densities of these mixtures were measured at 298.15 K, and the molar excess volumes V^E were calculated.

Experimental Section

The experimental apparatus previously reported by Kato et al. (*1*, *2*) was modified in the present study, as shown in Figure 1. The ebulliometer E has been described by Kato et al. (*3*). The liquid volume in the ebulliometer is about 25 cm^3.

At the start of an experiment, a solution of desired composition was prepared by mixing each pure substance, which was weighed by use of syringes and an automatic balance, similarly to the procedures of the previous works (*3*, *4*). The reproducibility of the composition was within ±0.001 mole fraction. Cocks K_1, K_2, and K_3 and solenoid valve V were opened, and K_4 and K_5 were closed. The system pressure was reduced by the vacuum pump near to the total pressure of the desired boiling point temperature. Next, cocks K_2 and solenoid valve V were closed, and the temperature was kept constant by use of the Williams (*5*) two-liquid manostat with a precision of ±0.01 mmHg. The upper layer of the manostat is dibutyl phthalate, and the lower layer is ethylene glycol saturated with sodium nitrite. The prepared solution was then boiled. The temperature was controlled to the desired temperature by reducing the pressure.

After attainment of steady state, the total pressure was measured with a Ruska 3850 quartz Bourdon gage with a precision of ±0.02 mmHg. The experimental temperature was measured at 350 K with a Hewlett-Packard 2804A quartz thermometer calibrated at the triple point of water in a reference cell. The reproducibility of the thermometer temperature measurements was ±0.01 K. The densities of the binary liquid mixtures were determined at 298.15 K with an Anton Paar DMA48 digital density meter with a precision of ±0.0001 g/cm^3.

Toluene was a special grade reagent supplied by Wako Pure Chemical Industries Ltd. 1,2-Dimethoxyethane, methylcyclohexane, and (trifluoromethyl)benzene were special grade reagents supplied by Tokyo Kasei Kogyo Co., Ltd. Toluene and methylcyclohexane were used without further purification. (Trifluoromethyl)benzene and 1,2-dimethoxyethane were further purified by distillation in an Oldershaw distillation column with 30 plates. The physical properties of the materials used are listed in Table I.

Results

The experimental total pressures P for the three binary systems at 350 K are given in Table II and Figure 2. The experimental densities ρ for the three binary mixtures at 298.15 K are shown in Table III. Figure 3 shows the molar excess liquid volumes V^E calculated from

$$V^E = V - (x_1V_1 + x_2V_2) \qquad (1)$$

and correlated with the following equation:

$$V^E = x_1x_2[\alpha + \beta(x_1 - x_2)] \qquad (2)$$