Ultrasonic Speeds in the Liquid Phase of the Azeotropic Mixture Refrigerant R502 under High Pressures

Toshiharu Takagi* and Hiroshi Teranishi

Department of Chemistry, Faculty of Engineering and Design, Kyoto Institute of Technology, Matsugasaki, Sakyoku, Kyoto 606, Japan

The ultrasonic speeds in the liquefied fluorocarbon azeotropic mixture refrigerant R502 were measured over the ranges of temperatures from 283.15 to 323.15 K and pressures from near-saturated vapor pressure to about 50 MPa by using a sing-around technique operated at a frequency of 2 MHz. The results, which showed smooth change with pressure for each isotherm, were used to estimate the values at the saturated liquid. The isentropic compressibilities were determined from experimental values. These results indicated a strong dependence on pressure in the region of pressures near saturated vapor and at higher temperatures.

Introduction

In previous papers, we reported the ultrasonic speeds in the liquid phase of fluorocarbon refrigerants: dichlorotetrafluoroethane R114 (*1*) and bromotrifluoromethane R13B1 (*2*) measured under several conditions of temperature and pressure. These results provided some information about the properties of each compound having different characteristics as fluorocarbon refrigerants. This paper presents, as one of a program on the ultrasonic speed for compressed refrigerants, new experimental data on the azeotropic mixture refrigerant R502 of monochlorodifluoromethane R22 and monochloropentafluoroethane R115, which were measured at temperatures every 5 K from 283.15 to 323.15 K under pressures from near-saturated vapor pressure to about 50 MPa. From the results, the isentropic compressibilities were determined. The values of density required in the way of calculation were used from the data reported elsewhere. The temperature and pressure effects of these quantities including data in the saturation line are examined.

Experimental Section

Material. The azeotropic mixture refrigerant R502 of monochlorodifluoromethane $CHClF_2$ (R22) and monochloropentafluoroethane $CClF_2CF_3$ (R115) was supplied by Daikin Kogyo Co. The purity of sample was better than 99.9 wt % and the concentration at azeotropic point was 49.2 wt % (R22)/50.8 wt % (R115) as measured by GLC.

Apparatus. The method used for measurements of ultrasonic speed was a sing-around technique with a fixed-path ultrasonic interferometer of 2 MHz, similar to that described previously (*1*). The temperature was estimated by a T-type thermocouple within ±0.03 K. The pressures were observed with a precise Bourdon gauge up to 5 MPa and a strain gauge up to 200 MPa. The maximum estimated error of pressure was ±0.015 MPa in the range up to 5 MPa and ±0.13 MPa above 5 MPa up to 50 MPa. In the vicinity of saturated vapor pressure, the measurements were carried out at narrower pressure intervals than those in the upper pressure region. The reliability of this apparatus was confirmed by measuring the speed in liquid benzene to be less than ±0.13% under the present conditions (*1*).

Results and Discussion

The experimental results of ultrasonic speed u in the liquid phase of azeotropic mixture refrigerant R502 at several temperatures T and pressures p are listed in Table I. These results at each temperature increase monotonously with rise of pressure, as illustrated graphically in Figure 1. For each temperature the variations in speed u with pressure p were used to determine, by the method of least squares, the coefficients in the polynomial equation

$$u/(\mathrm{m\cdot s^{-1}}) = \sum_{i=0}^{4} a_i (p/\mathrm{MPa})^i \qquad (1)$$

The values of the coefficients a_i are listed in Table II, together with the percentage root-mean-square deviations δ_{rms}, and the maximum deviations δ_{max}. The full line indicated in Figure 1 was calculated from the above equation. The larger deviation from the smoothing curve occurs chiefly in the near-saturation-pressure line, and it shows a tendency to increase with rise of temperature.

From the coefficients, the ultrasonic speeds u_{p_s} in the liquid phase at saturated vapor pressure p_s were estimated by an extrapolation of eq 1. The results are also listed in Table I with the p_s value calculated from the equation reproted in ref *3*. The u_{p_s} values, which can be drawn by a smoothing curve with temperature T as shown in Figure 2, are expressed as a function of T (in K) in the equation

$$u_{p_s}/(\mathrm{m\cdot s^{-1}}) = 493.44 - 4.039(T - 283.15) - 14.582 \times 10^{-3}(T - 283.15)^2 + 9.5724 \times 10^{-5}(T - 283.15)^3 \qquad (2)$$

The coefficients in the equation were obtained by the method of least squares. This equation is found to reproduce the above extrapolated data with a mean error of ±0.24% and a maximum error of ±0.31%.

The results at p_s and p thus obtained are found to have clearly a large difference with the temperature and pressure from those for R114 and R13B1 described in our previous papers (*1*, *2*). The critical temperatures T_c for R114, R13B1, and R502 are 418.95, 340.15, and 355.35 K (*3*), respectively. For example, at 3 MPa the absolute u value and its pressure dependence $(\partial u/\partial p)_T$ for R502 at 313.15 K show higher values 382.5 $\mathrm{m\cdot s^{-1}}$, 15.55 $\mathrm{m\cdot s^{-1}\cdot MPa^{-1}}$, than those for R13B1, 328.34 $\mathrm{m\cdot s^{-1}}$, 13.08 $\mathrm{m\cdot s^{-1}\cdot MPa^{-1}}$, at 298.15 K, which is nearly the same as the reduced temperature $T_r(=T/T_c)$. However, the $(\partial u/\partial p)_T$ values for R502 decrease sharply with rise of temperature. From these facts, it is suggested that the speed in R502 may have a very low value at temperatures near the critical point.

From the measurement of speed in R13B1 (*2*), a large absorption of acoustic wave, which is well-known to occur in the region near vapor–liquid transition (*4*, *5*), was observed, and therefore the experimental u value has a relatively large irregularity. In the present refrigerant R502 the large absorption of acoustic wave such as shown in R13B1 was not observed though the measurement was carried out at the same temperature range. Therefore the present results of speed are considered to be more reliable than those for R13B1. The probable uncertainty on the u values including those in the

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Table I. Ultrasonic Speed u, Density ρ, and Isentropic Compressibility κ_S at Several Pressures p

p/MPa	u/m·s^{-1}	ρ^a/kg·m^{-3}	κ_S/TPa^{-1}	p/MPa	u/m·s^{-1}	ρ^a/kg·m^{-3}	κ_S/TPa^{-1}	p/MPa	u/m·s^{-1}	ρ^a/kg·m^{-3}	κ_S/TPa^{-1}
283.15 K											
0.773^b	494.4^c	1282^d	319	4.51	534.2	1303	268	31.3	720.0	1408	136
1.27	499.6	1283	312	7.5	562.3	1319	239	33.3	730.8	1414	132
1.70	504.4	1286	305	10.1	584.6	1332	219	37.6	752.1	1426	123
2.19	509.8	1289	298	14.2	615.2	1349	195	43.1	777.7	1440	114
2.65	514.8	1292	291	18.7	646.3	1367	175	48.2	799.6	1452	107
3.06	519.1	1294	286	23.1	674.3	1383	158	51.0	811.4	1458	104
3.44	523.1	1297	281	25.3	687.2	1390	152				
3.80	526.9	1299	277	27.1	697.4	1396	147				
288.15 K											
0.890^b	470.5^c	1262^d	357	8.3	549.4	1321	250	32.4	710.4	1416	139
1.49	478.4	1278	341	10.6	569.2	1333	231	33.8	717.7	1420	136
2.08	484.6	1282	331	13.7	594.0	1348	210	37.3	735.4	1430	129
2.47	488.3	1285	326	18.6	629.3	1369	184	38.7	742.4	1434	126
3.25	496.8	1291	313	21.7	649.3	1380	171	42.2	759.3	1444	120
4.05	507.6	1296	299	24.4	666.0	1390	162	45.7	775.2	1453	114
4.57	513.4	1299	292	29.7	696.2	1408	146	50.5	794.5	1464	108
293.15 K											
1.019^b	453.2^c	1237^d	393	9.3	544.3	1294	260	33.1	706.1	1390	144
1.41	457.5	1240	385	12.1	568.8	1308	236	37.6	729.0	1403	134
1.50	459.2	1241	382	15.3	594.2	1324	213	41.5	748.3	1414	126
2.66	473.9	1250	356	18.2	615.1	1336	197	44.3	761.7	1421	121
3.51	484.5	1257	339	21.1	634.7	1348	184	47.4	775.1	1429	116
5.2	503.1	1269	311	24.8	658.6	1362	169	50.5	788.8	1437	111
7.0	521.9	1280	286	29.0	683.1	1377	155				
298.15 K											
1.162^b	430.1^c	1216^d	444	9.1	523.1	1274	286	27.4	659.5	1358	169
1.62	435.7	1218	432	11.2	542.7	1286	264	31.2	681.6	1371	157
1.93	440.3	1221	422	12.1	550.3	1291	255	35.1	703.0	1383	146
2.60	449.5	1226	403	17.5	593.6	1318	215	40.0	727.7	1398	135
3.64	462.2	1235	378	20.2	613.1	1330	200	44.4	749.1	1410	126
4.38	471.7	1241	362	23.4	634.5	1343	185	47.2	762.2	1417	121
6.7	498.4	1258	319	24.2	639.1	1346	181	51.3	779.8	1427	115
303.15 K											
1.318^b	407.5^c	1192^d	505	6.8	480.2	1238	350	24.7	629.8	1334	189
2.05	418.5	1196	477	9.5	509.3	1257	306	29.0	656.6	1350	170
3.34	436.5	1209	434	12.4	536.7	1275	272	34.7	689.3	1369	153
4.91	457.9	1223	389	15.1	559.6	1290	224	37.9	709.4	1379	144
5.96	470.3	1232	367	19.7	595.2	1313	215	43.8	734.6	1397	132
308.15 K											
1.490^b	386.8^c	1166^d	573	9.4	489.1	1237	337	37.1	688.0	1365	154
1.97	393.1	1168	553	12.4	519.1	1258	295	40.7	706.8	1376	145
2.37	399.7	1173	533	14.5	537.7	1270	272	43.4	720.7	1384	139
2.76	406.2	1178	514	17.9	566.1	1289	242	46.1	733.1	1391	133
3.51	417.4	1186	483	21.5	592.6	1306	218	49.6	749.8	1401	126
4.66	432.9	1198	445	25.7	621.3	1324	195				
7.0	462.2	1219	384	33.4	667.8	1353	165				
313.15 K											
1.576^b	359.6^c	1141^d	677	20.0	567.7	1286	241	39.7	689.9	1363	154
2.45	374.1	1148	622	21.9	581.3	1295	228	41.4	699.2	1368	149
3.62	391.5	1163	560	24.3	598.1	1306	214	43.7	710.6	1375	143
4.02	397.7	1168	541	26.0	609.9	1313	204	45.8	721.2	1382	139
4.36	403.6	1172	523	29.3	630.7	1327	189	48.7	734.3	1389	133
8.8	461.7	1215	386	32.4	649.6	1338	177	49.5	738.6	1392	131
15.8	533.8	1263	277	34.6	662.4	1346	169				
18.6	556.9	1279	252	37.0	675.3	1354	161				
318.15 K											
1.880^b	339.1^c	1111^d	782	18.0	536.7	1258	276	35.1	652.4	1333	176
3.92	373.1	1139	630	20.0	552.4	1268	258	38.4	671.0	1345	165
5.1	393.6	1155	558	22.6	572.9	1282	237	42.3	691.4	1357	154
7.7	431.0	1183	454	26.1	597.1	1298	216	45.0	705.3	1366	147
10.1	459.9	1204	392	29.5	619.0	1312	198	49.3	726.0	1378	137
13.5	496.2	1230	330	32.5	637.7	1324	185				
323.15 K											
2.101^b	314.7^c	1082^d	933	11.8	462.3	1200	390	34.4	636.2	1318	187
2.51	322.5	1088	883	15.1	495.1	1223	333	38.3	658.1	1332	173
2.86	329.1	1095	843	18.0	521.6	1242	295	42.5	681.2	1346	160
4.17	353.3	1117	717	20.5	542.6	1257	270	45.6	697.1	1356	151
5.9	382.7	1141	598	23.7	566.9	1273	244	49.7	716.6	1368	142
8.9	425.5	1173	470	30.0	609.4	1301	207				

[a] Reference *8*. [b] p_{sat}. [c] Extrapolated. [d] Reference *10*.

Table II. Coefficients a_i of Eq 1, Root-Mean-Square δ_{rms},[a] and Maximum Deviation δ_{max}

T/K	a_0	a_1	$-a_2$	$10^3 a_3$	$-10^5 a_4$	δ_{rms}/%	δ_{max}/%
283.15	485.69	11.514	0.208 79	3.238	2.195	0.041	0.10
288.15	459.51	12.645	0.260 26	4.362	3.102	0.063	0.21
293.15	439.75	13.470	0.286 23	4.788	3.360	0.051	0.16
398.15	413.75	14.409	0.315 83	5.230	3.588	0.052	0.13
303.15	386.62	16.445	0.459 13	9.860	8.699	0.056	0.18
308.15	363.10	16.535	0.399 18	6.922	4.905	0.084	0.21
313.15	332.30	17.984	0.438 23	7.307	4.950	0.046	0.15
318.15	303.66	19.856	0.528 55	9.299	6.549	0.086	0.21
323.15	270.70	22.259	0.648 12	11.992	8.732	0.095	0.16

[a] δ_{rms} (%) $= 100\{1/n\sum[(u_{exptl} - u_{calcd})/u_{calcd}]^2\}^{1/2}$, where n is the number of points.

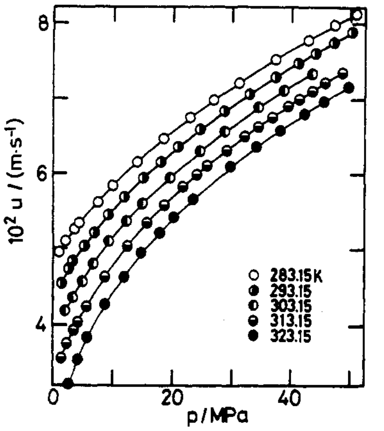

Figure 1. Pressure dependence of ultrasonic speed u in the liquid phase of refrigerant R502.

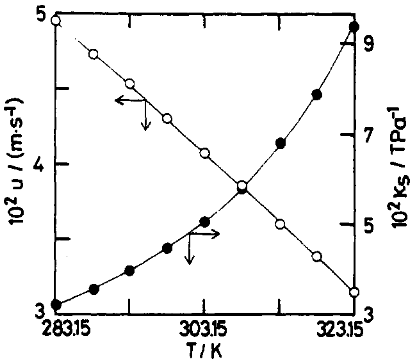

Figure 2. Temperature dependence of ultrasonic speed u and isentropic compressibility κ_S in the saturated liquid phase of refrigerant R502.

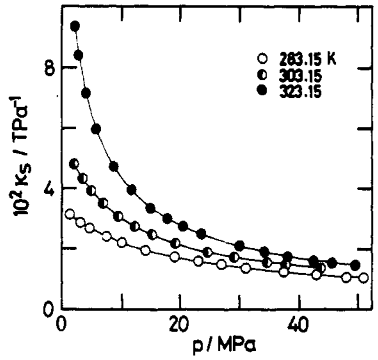

Figure 3. Pressure dependence of isentropic compressibility κ_S in the liquid phase of refrigerant R502.

saturation line is ±0.34% in the range up to 5 MPa and ±0.23% above 5 MPa.

The development of the ultrasonic method of studying fluids has made it possible to determine the isentropic compressibility κ_S by use of the thermodynamic formula

$$\kappa_S = (\rho \cdot u^2)^{-1} \qquad (3)$$

In this calculation, the values of density $\rho(=1/V$; V, specific volume) are required. For R502 the experiment on pVT properties and the formulation of the equation of state have previously been studied in wide ranges of temperature and pressure (*3*, *6*, *7*). But many of those are investigations in the gas phase, and thus precise pVT data for liquefied refrigerant R502 are rarely reported, especially experimental data.

Recently Makita and his co-workers (*8*) measured the pVT values for R502 at four temperatures and about 10 points of pressure in the range of present experimental work by using a high-pressure buret method. They reported the pVT values for organic liquids measured by the same instrument to be less than ±0.1% (*9*). These experimental results were indicated by the Tait equation. Therefore the density at arbitrary conditions can be estimated as each Tait parameter is shown by a smoothed curve with temperature. And so, by combining their pVT values with the experimental ultrasonic speeds u, the isentropic compressibilities κ_S were obtained by eq 3, and the results are also listed in Table I with the densities derived at each condition corresponding to that of the experimental u value. Also the saturated liquid densities were obtained from the equation reported by Okada (*10*). His data agreed well with those reported by Martin and Downing (*6*) within ±0.1%. The uncertainty of κ_S values at p and p_s thus obtained is better than ±1.5%. Figure 3 shows the values at three isotherms of 283.15, 303.15, and 323.15 K as a function of pressure. As can be seen in this figure, the values at 283.15 K, which is the lowest temperature in this work, decrease slightly at first, and while in the high-pressure region those are almost constant with pressure. On the other hand, the values in the high-temperature region are found to show a rapidly decreasing tendency with pressure: the initial value at 323.15 K reduces by half with a pressure change of only about 8 MPa. But in the right-hand side the slope exhibits a nearly same pressure variation with that at 283.15 K.

The isentropic compressibility at the saturation line is also presented in Figure 2. With rise of temperature, the values rise gently in the vicinity of room temperature; however, those at the higher temperature region indicate a large temperature effect. It is suggested that the values will approach a very high value as the temperature in the fluid approaches the critical value, as it should be predictable from the curves of speed vs. pressure behavior showed in Figure 3.

As described above, it is found that the isentropic compressibility, which can be estimated accurately from the speed, shows large temperature and pressure dependence compared with those for ultrasonic speed, and therefore its effect upon pressure and temperature is extremely useful to determine the properties of fluorocarbon refrigerants.

Registry No. R502, 39432-81-0.

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Isothermal Vapor–Liquid Equilibria for the *n*-Hexane–Cyclohexane–Tetralin System

Katsuji Noda,* Mitsuhisa Ohashi, and Kiyoharu Ishida

Department of Chemical Engineering, Shizuoka University, Hamamatsu 432, Japan

Total pressure data are presented for the ternary *n*-hexane–cyclohexane–tetralin system and for binary mixtures composed of its constituents at 283.15 K. Experimental total pressures are compared with values calculated by the Wilson equation and good agreement between calculated and experimental values is obtained. Selectivity of tetralin for separating *n*-hexane and cyclohexane is discussed.

Introduction

Vapor–liquid equilibrium data are useful not only for the design of separation processes but also for the study of the properties of solutions of liquid mixtures. It is also important to know the behavior of solutions for systems which are difficult to separate by distillation.

This paper presents the total pressures for the binary systems *n*-hexane–cyclohexane, *n*-hexane–tetralin, and cyclohexane–tetralin and for the ternary *n*-hexane–cyclohexane–tetralin system at 283.15 K.

Some works have been published on the vapor–liquid equilibria for the *n*-hexane–cyclohexane system (*1–4*). Li et al. (*1*) have reported the total pressure data for the *n*-hexane–cyclohexane system at 0–25 °C. However, the data for other binary systems and for the ternary system at low pressure are hardly available in the literature.

Data for the binary systems are correlated by the Wilson equation, and the predicted values for the ternary system are calculated by using the binary parameters and compared with observed values.

Experimental Section

The total pressures are measured by the static method, and the experimental apparatus and procedure were similar to those of the previous paper (*5*). Pressure measurements were made with a Zimmerli manometer and a cathetometer and are reproducible to within ±50 Pa. The equilibrium cell was immersed in a water bath and controlled by a thermostat with a cooling unit. The temperature of the water bath was determined by using a mercury-in-glass thermometer which was calibrated with a standard one in the National Research Laboratory of Metrology, Japan, and maintained within ±0.02 K.

The liquid mole fraction was evaluated from the total (liquid + vapor) weight of each material and their respective material balance in the liquid and vapor phases. The compositions of the vapor phases were first calculated from Raoult's law and then by the iterative calculation procedure discussed later, until successive iterations yielded almost the same values ($\Delta x < 0.0001$). The amount of tetralin in the vapor phase could be neglected because of the very low concentrations in the range of this experiment. The liquid compositions were estimated within ±0.001.

Commercially available guaranteed-reagent *n*-hexane and cyclohexane were used after further purification in a laboratory distillation column where only the middle half of the distillate was recovered. Spectrograde tetralin (Nakarai Chemicals, Ltd.) was used with no further purification. The boiling points of distilled *n*-hexane and cyclohexane agreed with literature values, and the vapor pressures of *n*-hexane and cyclohexane at 293.15 K are 16 150 Pa (16 165 Pa (*6*), 16 145 Pa (*7*)), and 10 330 Pa (10 336 Pa (*6*)), and the densities (in g cm^{-3}) of *n*-hexane, cyclohexane, and tetralin at 293.15 K are 0.6591 (0.659 37 (*8*)), 0.7787 (0.778 55 (*8*)), and 0.9698 (0.9702 (*8*)), respectively.

Results and Discussion

The equilibrium equation for each component i containing a vapor phase and a liquid phase, both at the same temperature T and total pressure P, is

$$\phi_i y_i P = \gamma_i x_i \phi_i^{s} P_i^{s} \exp\{(P - P_i^{s})v_i/RT\} \qquad (1)$$

where ϕ_i is the vapor-phase fugacity coefficient, γ_i is the liquid-phase activity coefficient, P_i^{s} is the pure-component vapor pressure, and v_i is the pure-component saturated liquid volume. The fugacity coefficient ϕ_i is given by

$$\ln \phi_i = \frac{2}{v}\sum_{j=1}^{N} y_j B_{ij} - \ln z \qquad (2)$$

To correlate the vapor–liquid equilibrium data, it is necessary to evaluate the liquid activity coefficients. From many expressions, the Wilson equation (*9*) was used. The excess Gibbs free energy is given by

$$\frac{g^{E}}{RT} = -\sum_{i=1}^{N} x_i \ln \left[\sum_{j=1}^{N} x_j \Lambda_{ij}\right] \qquad (3)$$

The liquid activity coefficient is expressed in the form of

$$\ln \gamma_i = 1 - \ln \left[\sum_{j=1}^{N} x_j \Lambda_{ij}\right] - \sum_{k=1}^{N} \frac{x_k \Lambda_{ki}}{\sum_{j=1}^{N} x_j \Lambda_{kj}} \qquad (4)$$

where

$$\Lambda_{ij} = \frac{v_j}{v_i} \exp[-(\lambda_{ij} - \lambda_{ii})/RT] \qquad (5)$$