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Excess Volumes and Isentropic Compressibilities of Mixtures of 1,2-Dichlorobenzene + Isopropyl Alcohol, + Isobutyl Alcohol, and + Isopentyl Alcohol at 303.15 K

Vadlamoodi C. Kumar, Bojja Sreenivasulu, and Puligundla R. Naidu*

Department of Chemistry, University College, Sri Venkateswara University, Tirupati 517502, India

Excess volume and deviation in isentropic compressibility were measured for mixtures of 1,2-dichlorobenzene with isopropyl alcohol, isobutyl alcohol, and isopentyl alcohol at 303.15 K. Excess volume exhibits inversion in sign in the three mixtures. This is similar to the trend between excess volume and composition observed in the mixtures of 1,2-dichlorobenzene with 1-propanol, 1-butanol, and 1-pentanol. However, the negative excess volume becomes dominant in mixtures of 1,2-dichlorobenzene with isopropyl alcohol and isobutyl alcohol. Deviation in isentropic compressibility is negative over the whole range of composition and is similar to that observed for the mixtures of 1,2-dichlorobenzene with the corresponding 1-alkanols. However, a large negative deviation is observed in mixtures of 1,2-dichlorobenzene with the isoalcohols.

Introduction

Excess volumes (V^E) and isentropic compressibilities (K_S) for binary mixtures of 1,2-dichlorobenzene with 1-butanol and 1-pentanol are reported in the literature (*1*, *2*). While V^E exhibited inversion in sign, deviation in isentropic compressibility was negative throughout the whole range of composition. We report here new experimental excess volumes and deviations in isentropic compressibilities for mixtures of 1,2-dichlorobenzene with isopropyl alcohol, isobutyl alcohol, and isopentyl alcohol. The results have been compared with those of the three corresponding 1-alcohols. The comparison was made to study the effect of branching of an alcohol on the two properties. The experimental data for the mixture 1,2-dichlorobenzene + 1-propanol needed for the comparison were also determined in the present investigation.

Experimental Section

Excess volumes were measured directly by using the dialatometer described by Rao and Naidu (*3*). The mixing cell contained two bulbs of different capacities which were connected through a U tube with mercury to separate the two components. One end of the bulb was fitted with a capillary (1-mm i.d.), and the other end of the second bulb was fitted with a ground-glass stopper. The excess volumes were accurate to ±0.003 $cm^3 \cdot mol^{-1}$.

Isentropic compressibilities were computed from measured sound speed data and densities evaluated from excess volumes. The ultrasonic sound speed was measured with a single-crystal interferometer at 4-MHz frequency, and the data were accurate to ±0.15%. All the measurements were made at constant temperature, employing a thermostat that could be maintained to ±0.01 K. The density was computed from the measured excess volume using the relation

$$\rho_{1,2} = \frac{x_1 M_1 + x_2 M_2}{V^\circ + V^E} \tag{1}$$

where M, $\rho_{1,2}$, V°, and x represent the molecular weight, density, molar volume of the ideal mixture, and mole fraction of the mixture, respectively.

Table I. Densities (ρ) of Pure Components at 303.15 K

component	$\rho/(g \cdot cm^{-3})$ lit.	$\rho/(g \cdot cm^{-3})$ present study
1,2-dichlorobenzene	1.299 22	1.299 19
1-propanol	0.796 00	0.796 02
isopropyl alcohol	0.776 90	0.776 85
isobutyl alcohol	0.794 37	0.794 35
isopentyl alcohol	0.801 79	0.801 78

Table II. Mole Fraction of 1,2-Dichlorobenzene (x_1), Excess Volumes (V^E) for the Binary Mixtures of 1,2-Dichlorobenzene with 1-Propanol and Isoalcohols at 303.15 K

x_1	$V^E/(cm^3 \cdot mol^{-1})$	x_1	$V^E/(cm^3 \cdot mol^{-1})$
	1,2-Dichlorobenzene + 1-Propanol		
0.0663	−0.084	0.4918	−0.048
0.2341	−0.146	0.5946	0.005
0.3334	−0.125	0.7062	0.047
0.4329	−0.080	0.8450	0.059
	1,2-Dichlorobenzene + Isopropyl Alcohol		
0.0824	−0.173	0.5066	−0.120
0.2005	−0.264	0.6126	−0.038
0.3142	−0.253	0.7219	0.028
0.4650	−0.159	0.8312	0.064
	1,2-Dichlorobenzene + Isobutyl Alcohol		
0.1074	−0.155	0.6322	−0.043
0.1791	−0.207	0.7419	0.008
0.2950	−0.215	0.7857	0.028
0.3887	−0.177	0.8547	0.035
0.4829	−0.132		
	1,2-Dichlorobenzene + Isopentyl Alcohol		
0.1164	−0.135	0.5741	−0.064
0.1975	−0.168	0.6878	−0.007
0.2923	−0.174	0.7695	0.020
0.3896	−0.147	0.8791	0.041
0.5037	−0.094		

Purification of Materials

All the materials were purified by the methods described by Riddick and Bunger (*4*). 1,2-Dichlorobenzene (S. D. Fine Chemicals) was passed through alumina in a 30 × 2 cm column and fractionally distilled. All alcohols were dried by re-

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* To whom correspondence should be addressed.

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Table III. Standard Deviation $\sigma(V^E)$ and Values of Constants in Equation 1

system	$a_0/(cm^3 \cdot mol^{-1})$	$a_1/(cm^3 \cdot mol^{-1})$	$a_2/(cm^3 \cdot mol^{-1})$	$\sigma(V^E)/(cm^3 \cdot mol^{-1})$
1,2-dichlorobenzene + 1-propanol	−0.1687	1.0945	−0.3017	0.002
1,2-dichlorobenzene + isopropyl alcohol	−0.5015	1.7079	−0.4634	0.006
1,2-dichlorobenzene + isobutyl alcohol	−0.4816	1.2500	−0.2567	0.004
1,2-dichlorobenzene + isopentyl alcohol	−0.3969	1.0659	−0.1083	0.005

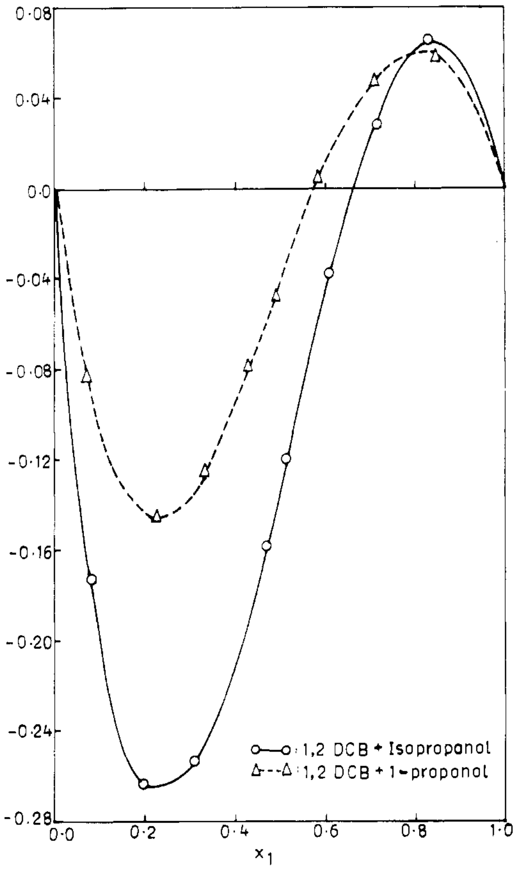

Figure 1. Mole fraction of 1,2-dichlorobenzene with isoalcohols or 1-alcohols. V^E plotted against the mole fraction (x_1) of 1,2-dichlorobenzene with isopropyl alcohol and 1-propanol at 303.15 K.

fluxing with fused calcium oxide and finally distilled using a fractionating column.

The purity of the sample was checked by comparing the measured density of the compounds with those reported in the literature (*4*, *5*). Densities were determined with a bicapillary type pycnometer, which offered an accuracy of 2 parts in 10^5. The measured densities and those reported in the literature are given in Table I.

Results and Discussion

Experimental results for excess volumes of mixtures of 1,2-dichlorobenzene with 1-propanol, isopropyl alcohol, isobutyl alcohol, and isopentyl alcohol are included in Table II. The results are also graphically presented along with those for the mixture of the common component with the corresponding 1-alkanols in Figures 1–3. Experimental V^E data have been reduced using the polynomial

$$V^E/x_1x_2 = [a_0 + a_1(x_1 - x_2) + a_2(x_1 - x_2)^2] \qquad (2)$$

where x_1, x_2 denote mole fractions of components 1 and 2 and a_0, a_1, a_2 are constants. The values of the constants obtained by the least-squares method are given in Table III, along with the standard deviation $\sigma(V^E)$.

Table IV. Volume Fractions (ϕ_1), Densities (ρ), Sound Velocities (u), Isentropic Compressibilities (K_S), and the Deviations in Isentropic Compressibilities (ΔK_S) of 1,2-Dichlorobenzene with 1-Propanol and Isoalcohols at 303.15 K

ϕ_1	$\rho/(g \cdot cm^{-3})$	$u/(m \cdot s^{-1})$	K_S/TPa^{-1}	$\Delta K_S/TPa^{-1}$
	1,2-Dichlorobenzene + 1-Propanol			
0.0000	0.796 02	1219	845	
0.0962	0.845 33	1221	793	−17
0.3142	0.955 75	1228	694	−36
0.4284	1.013 03	1229	654	−35
0.5336	1.065 43	1231	619	−31
0.5919	1.094 40	1232	602	−27
0.6873	1.141 79	1235	574	−20
0.7827	1.189 31	1241	546	−13
0.8909	1.243 63	1249	515	−5
1.0000	1.299 19	1266	480	
	1,2-Dichlorobenzene + Isopropyl Alcohol			
0.0000	0.776 85	1138	994	
0.1161	0.839 30	1156	892	−42
0.2684	0.919 89	1174	789	−67
0.4012	0.989 25	1185	720	−68
0.5597	1.071 02	1200	648	−58
0.6003	1.091 77	1203	633	−52
0.6981	1.141 95	1215	593	−42
0.7915	1.189 97	1227	558	−29
0.8781	1.234 77	1244	523	−20
1.0000	1.299 19	1266	480	
	1,2-Dichlorobenzene + Isobutyl Alcohol			
0.0000	0.794 35	1173	915	
0.1273	0.860 03	1194	816	−44
0.2092	0.901 90	1201	769	−55
0.3366	0.966 38	1201	717	−52
0.4354	1.015 92	1200	684	−42
0.5310	1.063 81	1204	648	−36
0.6758	1.135 97	1214	597	−24
0.7771	1.186 56	1228	559	−18
0.8164	1.206 18	1232	546	−14
0.8770	1.236 72	1242	524	−10
1.0000	1.299 19	1266	480	
	1,2-Dichlorobenzene + Isopentyl Alcohol			
0.0000	0.801 78	1214	846	
0.1194	0.862 22	1220	779	−23
0.2021	0.903 68	1225	737	−35
0.2983	0.951 64	1227	698	−39
0.3965	1.000 30	1226	665	−36
0.5109	1.056 79	1229	626	−33
0.5811	1.091 45	1233	603	−30
0.6939	1.147 02	1239	568	−24
0.7746	1.186 84	1243	545	−18
0.8821	1.240 10	1251	515	−8
1.0000	1.299 19	1266	480	

Experimental sound speed (u) data and density (ρ) computed from measured excess volume data are presented in columns 3 and 2, respectively, of Table IV. Isentropic compressibility K_S and deviation in isentropic compressibility ΔK_S are calculated using the equations

$$K_S = U^{-2}\rho^{-1} \qquad (3)$$

$$\Delta K_S = K_S - \phi_1 K_{S_1} - \phi_2 K_{S_2} \qquad (4)$$

$$\phi_1 = \frac{x_1 V_1^\circ}{x_1 V_1^\circ + x_2 V_2^\circ} \qquad (5)$$

$$\phi_2 = 1 - \phi_1$$

where K_S, K_{S_1}, and K_{S_2} represent isentropic compressibilities

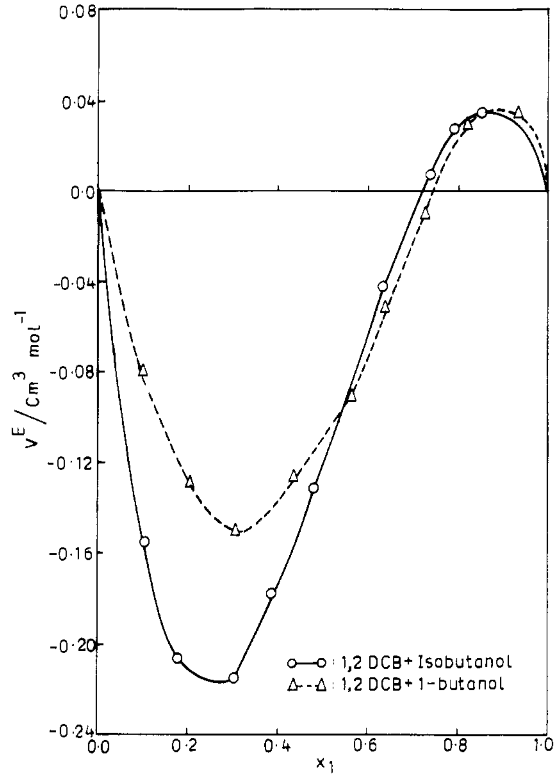

Figure 2. Mole fraction of 1,2-dichlorobenzene with isoalcohols or 1-alcohols. V^E plotted against the mole fraction (x_1) of 1,2-dichlorobenzene with isobutyl alcohol and 1-butanol at 303.15 K.

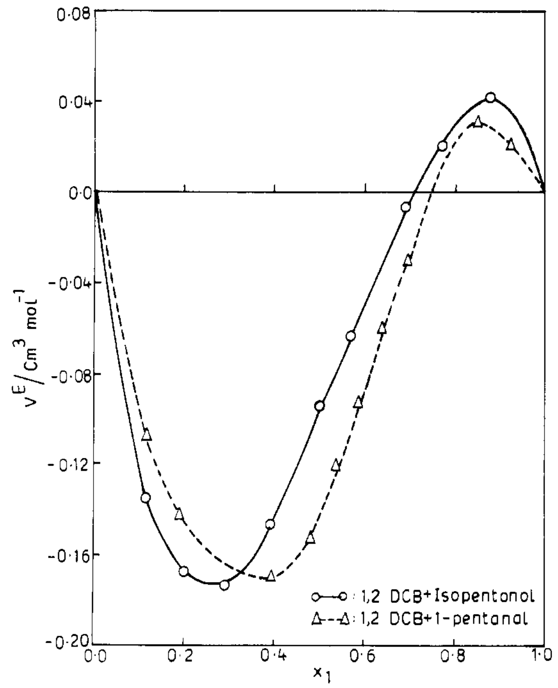

Figure 3. Mole fraction of 1,2-dichlorobenzene with isoalcohols or 1-alcohols. V^E plotted against the mole fraction (x_1) of 1,2-dichlorobenzene with isopentyl alcohol and 1-pentanol at 303.15 K.

of a mixture and the pure components 1 and 2, respectively. ϕ_1 and ϕ_2 denote volume fractions of the components. The values of K_S and ΔK_S are included in columns 4 and 5 of Table IV. The results are graphically represented along with those for mixtures of 1,2-dichlorobenzene with 1-propanol, 1-butanol, and 1-pentanol in Figure 4.

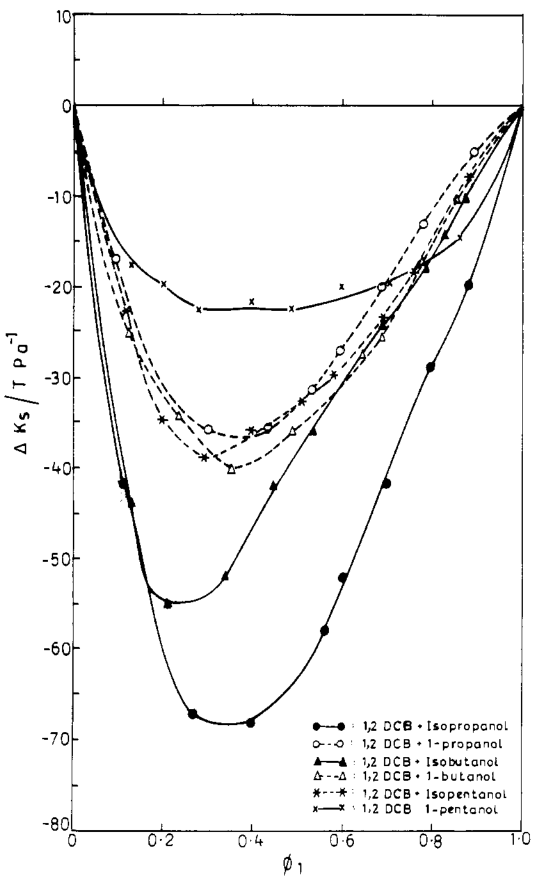

Figure 4. Volume fraction of 1,2-dichlorobenzene with isoalcohols or 1-alcohols. ΔK_S plotted against the volume fraction (ϕ_1) of 1,2-dichlorobenzene with isopropyl alcohol, isobutyl alcohol, and isopentyl alcohol and with 1-propanol, 1-butanol, and 1-pentanol at 303.15 K.

Table V. Standard Deviation $\sigma(\Delta K_S)$ and Values of Constants in Equation 6

system	b_0/TPa^{-1}	b_1/TPa^{-1}	b_2/TPa^{-1}	$\sigma(\Delta K_S)$/ TPa^{-1}
1,2-dichlorobenzene + 1-propanol	−131.0	92.0	12.6	0
1,2-dichlorobenzene + isopropyl alcohol	−248.0	153.0	−80.2	1
1,2-dichlorobenzene + isobutyl alcohol	−153.0	199.0	−170.0	2
1,2-dichlorobenzene + isopentyl alcohol	−140.0	94.1	−26.0	2

These results also have been fitted into an empirical equation of the form

$$\Delta K_S/\phi_1\phi_2 = [b_0 + b_1(\phi_1 - \phi_2) + b_2(\phi_1 - \phi_2)^2] \quad (6)$$

The numerical values of the constants b_0, b_1, and b_2 are included in Table V, along with the standard deviation $\sigma(\Delta K_S)$.

The results in Table II show that V^E exhibits inversion in sign in the three binary mixtures. However it remains negative over a large range of composition. The curves in Figures 1–3 show that replacement of 1-propanol and 1-butanol by the corresponding isoalcohols leads to a more negative value of V^E. However the replacement of 1-pentanol by isopentyl alcohol does not change the value of V^E to a significant extent.

The deviation in the isentropic compressibility ΔK_S is negative over the whole range of composition. The curves in Figure 4 indicate that deviation becomes more negative in mixtures of 1,2-dichlorobenzene with the three isoalcohols.

Registry No. 1,2 DCB, 95-50-1; isopropyl alcohol, 67-63-0; isobutyl alcohol, 78-83-1; isopentyl alcohol, 123-51-3.

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Vapor–Liquid Coexistence Curve and the Critical Parameters of 1-Chloro-1,1-difluoroethane (HCFC-142b)

Seisho Tanikawa, Jun Tatoh, Yukishige Maezawa,* 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

Vapor–liquid coexistence curve near the critical point of 1-chloro-1,1-difluoroethane (HCFC-142b) was measured by a visual observation of the meniscus in an optical cell. Saturation densities including 13 saturated-vapor and 18 saturated-liquid densities were obtained in the range of temperature from 354 K to the critical temperature, corresponding to the density range from 181 to 947 kg/m^3. The experimental errors in temperature and density were estimated to be within ±10 mK and between ±0.09 and ±0.53%, respectively. Not only the level where the meniscus disappeared but also the intensity of the critical opalescence were considered for the determination of the critical temperature and density as 410.29 ± 0.02 K and 446 ± 3 kg/m^3, respectively. The critical exponent, β, was also determined to be 0.339 ± 0.002. A saturated-vapor/saturated-liquid density correlation was developed on the basis of the present measurements.

Introduction

HCFC-142b (1-chloro-1,1-difluoroethane) is one of the environmentally acceptable refrigerants. A binary mixture of HCFC-22 (chlorodifluoromethane) + HCFC-142b has the possibility of becoming a promising substitute for CFC-12 (dichlorodifluoromethane). We have already reported the critical parameters of several CFC-alternative refrigerants, i.e., HFC-152a (*1*), HFC-134a (*2*), and HCFC-123 (*3*). This paper reports the measured vapor–liquid coexistence curve in the critical region, the experimentally determined critical temperature, density, and exponent, and a saturation density correlation for HCFC-142b.

Experimental Section

A visual observation apparatus, originally built by Okazaki et al. (*4*) and redesigned by Tanikawa et al. (*3*), was used for all measurements. The apparatus and procedure have been reported in detail in our previous publications (*3–6*).

Temperature measurements were performed by using a standard platinum resistance thermometer, and measured temperatures were converted into two different temperature scales of IPTS-68 and ITS-90. All the descriptions given in figures and correlations in the present paper are exclusively dependent on the temperature scale of IPTS-68. The thermometer was put in the vicinity of optical cell at the same level in the bath.

Table I. Saturated-Vapor Densities ρ'' of HCFC-142b[a]

T_{68}/K (T_{90}/K)	ρ''/(kg/m^3)	T_{68}/K (T_{90}/K)	ρ''/(kg/m^3)
395.833 (395.802)	181.3 ± 1.0[b]	408.991 (408.958)	326.3 ± 0.3[b]
399.071 (399.039)	202.8 ± 0.8[b]	409.956 (409.922)	365.5 ± 0.6*[b]
402.747 (402.714)	232.8 ± 0.9[b]	410.232 (410.198)	389.1 ± 0.4*[b]
404.660 (404.627)	252.4 ± 0.4[b]	410.295 (410.261)	412.8 ± 0.8*[b]
405.739 (405.706)	266.9 ± 0.5[b]	410.292 (410.258)	438.0 ± 0.4*[c]
408.218 (408.185)	308.5 ± 0.3[b]	410.293 (410.259)	442.0 ± 0.7*[b]
408.693 (408.660)	318.3 ± 0.5[b]		

[a] Values marked with asterisks are from points at which critical opalescence was observed. [b] Sample with 99.8 mass % purity was used. [c] Sample with 99.9 mass % purity was used.

Table II. Saturated-Liquid Densities ρ' of HCFC-142b[a,d]

T_{68}/K (T_{90}/K)	ρ'/(kg/m^3)	T_{68}/K (T_{90}/K)	ρ'/(kg/m^3)
410.282 (410.249)	446.0 ± 0.4*[c]	403.306 (403.274)	670.8 ± 0.9[b]
410.283 (410.250)	446.8 ± 0.4*[b]	398.562 (398.530)	718.5 ± 0.6[b]
410.290 (410.255)	453.6 ± 0.5*[c]	396.188 (396.157)	738.2 ± 0.7[b]
410.281 (410.248)	473.3 ± 0.5*[b]	391.694 (391.664)	770.2 ± 1.9[b]
410.222 (410.188)	493.5 ± 1.1*[b]	387.434 (387.405)	796.9 ± 1.1[b]
409.645 (409.612)	546.0 ± 0.5[b]	382.291 (382.263)	825.1 ± 1.7[b]
408.450 (408.417)	584.9 ± 1.5[b]	376.617 (376.590)	853.8 ± 0.8[b]
407.686 (407.652)	603.4 ± 1.0[b]	369.842 (369.813)	884.1 ± 1.2[b]
406.465 (406.432)	626.4 ± 1.3[b]	353.548 (353.527)	947.4 ± 0.9[b]

[d] See Table I for footnotes *a–c*.

The experimental uncertainty in temperature was estimated to be within ±10 mK as the sum of 2 mK, the precision of the thermometer; 1 mK, the precision of the bridge; and 7 mK, the possible temperature fluctuation of the silicone oil in the bath. The value of the resistance measured with our thermometer at the triple point of water altered by 0.000 03 Ω. The uncertainty in density was estimated to be between ±0.09%, which is considered to be due to the uncertainties of the cell volumes and the sample mass, and ±0.53%, which includes the uncertainty of the expansion factor. The purities of the two samples furnished by manufacturers were 99.8 and 99.9 mass %.

Results

The saturated-vapor densities were measured at temperatures above 396 K (0.965 in reduced temperature) and at densities between 181 kg/m^3 (0.407 in reduced density) and 442 kg/m^3, whereas the saturated-liquid densities were measured above 354 K (0.862) and between 446 and 947 kg/m^3 (2.124). The experimental results including 13 saturated-vapor and 18 saturated-liquid densities are listed in Tables I and II.

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* To whom correspondence should be addressed.

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