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Vapor + Liquid Equilibrium Measurements and Correlation of the Binary Refrigerant Mixtures Difluoromethane (HFC-32) + 1,1,1,2,3,3-Hexafluoropropane (HFC-236ea) and Pentafluoroethane (HFC-125) + 1,1,1,2,3,3-Hexafluoropropane (HFC-236ea) at 288.6, 303.2, and 318.2 K

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Isothermal vapor–liquid equilibria (VLE) for the binary systems of difluoromethane (HFC-32) + 1,1,1,2,3,3-hexafluoropropane (HFC-236ea) and pentafluoroethane (HFC-125) + 1,1,1,2,3,3-hexafluoropropane (HFC-236ea) were measured at 288.6, 303.2, and 318.2 K using an apparatus in which the vapor phase was recirculated through the liquid. The phase composition at equilibrium was measured by gas chromatography, based on calibration using gravimetrically prepared mixtures. Both systems show a slight deviation from Raoult's law. The uncertainties in pressure, temperature, and vapor- and liquid-phase composition measurements were estimated to be no more than ±1 kPa, ±0.02 K, and ±0.002 mol fraction, respectively. The data were analyzed using the Carnahan–Starling–DeSantis equation of state.

KEY WORDS: Carnahan–Starling–DeSantis equation of state; HFC-125 + HFC-236ea; HFC-32 + HFC-236ea; isothermal vapor–liquid equilibrium; vapor pressures.

1. INTRODUCTION

1,2-Dichlorotetrafluoroethane (CFC-114) is one of the traditional refrigerants for which suitable substitutes have yet to be identified. As part of the

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European Community project of finding a substitute for CFC-114 in high-temperature heat pump applications, several binary and ternary mixtures containing 1,1,1,3,3,3-hexafluoropropane (HFC-236fa) as the basic component were considered, but it was also reported that mixtures containing 1,1,1,2,3,3-hexafluoropropane (HFC-236ea) and 1,1,1,3,3-pentafluoropropane (HFC-245fa) should be studied. No data are currently available for the thermodynamic properties of mixtures containing HFC-236ea. VLE measurements are particularly important for defining the thermodynamic behavior at the saturation boundaries and understanding the molecular interaction between the components. This paper reports on isothermal VLE data for the binary mixtures difluoromethane (HFC-32) + HFC-236ea and pentafluorethane (HFC-125) + HFC-236ea.

2. EXPERIMENTAL

2.1. Materials

HFC-236ea was supplied by Chiminord, Italy. The clear presence of air in the sample was detected by gas chromatography using a thermal conductivity detector (TCD) (5% in the vapor phase and 0.1% in the liquid phase, assessed as a percentage of the area of peaks). No other impurities were detected. To eliminate noncondensable gases, the sample underwent several cycles of freezing with liquid nitrogen, evacuation, thawing, and ultrasound. After this process, no impurities were detected by either the TCD or the flame ionization detector (FID).

HFC-32, with 0.01% impurities (no air) detected by the TCD, was donated by ICI. No impurities were detected by the FID. The sample, nonetheless, underwent the freezing, evacuation, thawing, and ultrasound cycles.

HFC-125, with 0.36% total impurities (CFC-115) detected by the TCD in the liquid phase and 3% (2.4% air) in the vapor phase, was donated by ICI. After the process to eliminate noncondensable gases, no impurities in the liquid phase and 0.03% air (assessed as a percentage of area) in the vapor phase were detected by the TCD; 0.3% impurities (CFC-115) were detected by the FID in both phases.

All samples were used with no further purification.

2.2. Apparatus

The recirculation VLE apparatus and the procedures used in this study have been described in more detail elsewhere [1]. The VLE is reached in a stainless-steel cell of about 50-cm^3 capacity equipped with a magnetic pump. The VLE cell and the magnetic pump were immersed in a thermostatic water bath of about 100-L capacity.

The temperature in the bath was kept stable to within ±1 mK during the measurements by means of a PID-controlled system controlling a heater immersed in the bath. An auxiliary cooler was used to compensate for the heat produced by the PID-controlled system and to maintain the temperature below or near ambient temperature.

The temperature was measured with a 100-Ω platinum resistance thermometer (ISOTECH 909/100), and the uncertainty in temperature measurement was estimated to be ±0.02 K.

Pressure was measured by means of a pressure gauge (Ruska 6000) with a range up to 3500 kPa. A differential pressure cell (Ruska 2413) immersed in the thermostatic bath was used to isolate the chemicals from the quartz sensor of the pressure gauge. The uncertainty in the pressure measurement was estimated to be within ±1 kPa, taking into account the accuracy of the pressure transducer and the stability of the pressure during the measurements.

The composition of the vapor and liquid phases was measured by gas chromatographic analysis. A gas chromatograph (Hewlett–Packard 6890) was connected on-line to the VLE cell. GC analyses were performed using a column 2 m long with an internal diameter of 2.1 mm filled with Porapak T (80/100 mesh) and adopting the following operational parameters: oven temperature, 413 K; nitrogen (carrier) flow rate, 30.5 $\mathrm{cm^3 \cdot min^{-1}}$; and flame ionization detector (FID)—hydrogen flow rate, 40 $\mathrm{cm^3 \cdot min^{-1}}$; and air flow rate, 400 $\mathrm{cm^3 \cdot min^{-1}}$. Under these conditions, the total analysis time was about 5 min. The detector response was carefully calibrated using gravimetrically prepared mixtures. Considering the reproducibility of gas chromatography, the stability of the composition during the measurements, and the uncertainty in calibration, we estimated the accuracy of composition measurements to be within ±0.002 for the mole fraction of both the liquid and the vapor phases.

3. RESULTS AND DISCUSSION

Thirty-one P, x, y equilibrium data (including pure-compound vapor pressures) for the mixture of HFC-32 + HFC-236ea and 29 for the mixture of HFC-125 + HFC-236ea were measured along three isotherms at temperatures of 288.6, 303.2, and 318.2 K. The data are presented in Tables I and II, respectively, while the saturation boundaries are shown in Figs. 1 and 2. Throughout the paper, x and y indicate the liquid and vapor mole fractions, respectively, while P stands for the pressure in kPa.

Table I. Vapor–Liquid Equilibrium Data for the HFC-32 (1) + HFC-236ea (2) System: $\Delta P = 100(P_{\mathrm{cal}} - P_{\mathrm{exp}})/P_{\mathrm{exp}}$, $\Delta y = y_{1,\mathrm{cal}} - y_{1,\mathrm{exp}}$

T_{exp} (K)	P_{exp} (kPa)	$x_{1,\mathrm{exp}}$	$y_{1,\mathrm{exp}}$	P_{cal} (kPa)	$y_{1,\mathrm{cal}}$	$\Delta y \times 10^2$	ΔP
288.54	145.5	0	0	145.0	0		−0.37
288.55	192.9	0.0544	0.2690	195.2	0.2830	1.40	1.17
288.55	236.8	0.1026	0.4246	240.1	0.4371	1.25	1.41
288.55	302.0	0.1720	0.5749	306.0	0.5817	0.68	1.33
288.56	379.9	0.2515	0.6888	383.6	0.6887	−0.01	0.96
288.56	508.5	0.3740	0.7964	508.1	0.7933	−0.31	−0.07
288.55	612.5	0.4678	0.8520	608.8	0.8474	−0.46	−0.61
288.56	618.7	0.4734	0.8541	615.1	0.8501	−0.40	−0.58
288.55	793.3	0.6213	0.9155	786.8	0.9104	−0.51	−0.82
288.55	962.5	0.7562	0.9506	958.9	0.9505	−0.01	−0.37
288.55	1151.7	0.9000	0.9829	1157.5	0.9830	0.01	0.51
288.54	1294.2	1	1	1297.5	1		0.26
303.19	245.2	0	0	244.0	0		−0.48
303.19	371.3	0.0994	0.3789	373.1	0.3838	0.49	0.49
303.19	585.3	0.2546	0.6544	585.2	0.6506	−0.38	−0.01
303.20	806.4	0.4018	0.7856	802.6	0.7800	−0.56	−0.48
303.20	988.7	0.5155	0.8506	984.3	0.8460	−0.46	−0.44
303.19	1190.2	0.6306	0.9006	1183.5	0.8965	−0.41	−0.56
303.19	1431.7	0.7603	0.9427	1429.5	0.9412	−0.15	−0.15
303.19	1741.0	0.9140	0.9814	1748.8	0.9822	0.08	0.45
303.19	1927.7	1	1	1933.4	1		0.30
318.24	395.3	0	0	393.7	0		−0.41
318.24	652.0	0.1437	0.4411	649.8	0.4389	−0.22	−0.34
318.24	929.6	0.2881	0.6507	927.2	0.6454	−0.53	−0.26
318.24	1203.9	0.4168	0.7639	1196.2	0.7569	−0.70	−0.64
318.24	1462.3	0.5292	0.8341	1452.4	0.8267	−0.74	−0.68
318.24	1719.8	0.6337	0.8833	1711.9	0.8778	−0.55	−0.46
318.24	2030.8	0.7515	0.9271	2032.7	0.9251	−0.20	0.09
318.25	2390.0	0.8751	0.9653	2403.2	0.9663	0.10	0.55
318.24	2394.8	0.8776	0.9659	2410.4	0.9670	0.11	0.65
318.24	2795.9	1	1	2803.0	1		0.26

Both mixtures show almost-ideal behavior, with a small negative deviation from Raoult's law. It is worth noting that similar behavior was shown for the mixtures HFC-32 + HFC-236fa and HFC-125 + HFC-236fa [2].

3.1. Pure-Fluid Vapor Pressures

The experimental vapor pressures of the pure compounds measured in this work were compared with data reported in the literature [3–10].

Table II. Vapor–Liquid Equilibrium Data for the HFC-125 (1) + HFC-236ea (2) System: $\Delta P = 100(P_{\text{cal}} - P_{\text{exp}})/P_{\text{exp}}$, $\Delta y = y_{1,\text{cal}} - y_{1,\text{exp}}$

T_{exp} (K)	P_{exp} (kPa)	$x_{1,\text{exp}}$	$y_{1,\text{exp}}$	P_{cal} (kPa)	$y_{1,\text{cal}}$	$\Delta y \times 10^2$	ΔP
288.54	146.3	0	0	145.0	0		−0.91
288.54	272.4	0.1419	0.5145	270.2	0.5152	0.07	−0.81
288.54	371.8	0.2585	0.6734	372.6	0.6823	0.89	0.21
288.54	470.2	0.3715	0.7722	471.7	0.7771	0.49	0.33
288.54	614.1	0.5329	0.8594	614.2	0.8628	0.34	0.02
288.54	726.1	0.6599	0.9078	728.4	0.9098	0.20	0.32
288.54	834.9	0.7771	0.9434	837.2	0.9447	0.13	0.27
288.54	938.3	0.8831	0.9713	940.2	0.9721	0.08	0.20
288.55	1060.0	1	1	1062.6	1		0.24
303.19	245.0	0	0	244.0	0		−0.40
303.18	374.9	0.1059	0.3866	373.1	0.3874	0.08	−0.49
303.18	517.1	0.2226	0.5900	516.1	0.5941	0.41	−0.19
303.19	645.2	0.3274	0.7019	645.8	0.7046	0.27	0.09
303.19	799.0	0.4510	0.7900	800.6	0.7924	0.24	0.20
303.19	947.7	0.5674	0.8499	949.5	0.8523	0.24	0.19
303.19	1110.7	0.6915	0.9006	1113.3	0.9024	0.18	0.24
303.19	1248.0	0.7913	0.9351	1251.0	0.9365	0.14	0.24
303.19	1391.4	0.8884	0.9658	1392.6	0.9668	0.10	0.09
303.19	1568.4	1	1	1569.9	1		0.10
318.24	394.9	0	0	393.7	0		−0.31
318.24	521.6	0.0768	0.2709	519.6	0.2717	0.08	−0.38
318.24	728.7	0.2015	0.5115	726.4	0.5182	0.67	−0.32
318.24	943.9	0.3313	0.6615	945.5	0.6659	0.44	0.17
318.24	1167.8	0.4606	0.7600	1169.3	0.7634	0.34	0.13
318.24	1383.4	0.5820	0.8289	1386.5	0.8313	0.24	0.22
318.24	1605.4	0.7010	0.8828	1609.0	0.8852	0.24	0.22
318.24	1818.3	0.8066	0.9257	1818.5	0.9272	0.15	0.01
318.24	2041.6	0.9097	0.9645	2039.8	0.9658	0.13	−0.09
318.24	2263.3	1	1	2255.5	1		−0.34

To calculate the vapor pressures at our temperatures, the correlations proposed by the authors were used. When a correlation was not proposed [5, 10], data in the literature were regressed with a Wagner equation in the form presented in Ref. 11 using the pure component critical-point parameters given in Table III. The results are shown in Table IV. There is good agreement between our results and data in the literature for both HFC-125 and HFC-236ea. Slightly higher deviations were observed for HFC-32.

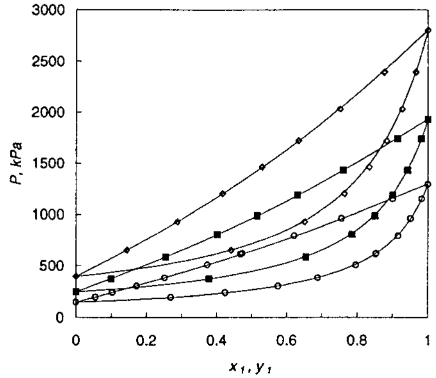

Fig. 1. Vapor–liquid equilibria for HFC-32 (1) + HFC-236ea (2) at $T = 288.55$ K (○), 303.19 K (■), and 318.24 K (◇); (——) CSD EoS fit.

3.2. VLE Data Analysis

For data analysis we considered the Carnahan–Starling–DeSantis (CSD) equation of state (EoS) in the form proposed in Ref. 12 with the van der Waals one-fluid mixing rules. The pure fluid coefficients were taken from Ref. 13 and are given in Table V.

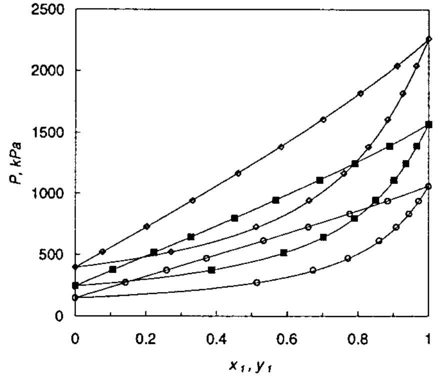

Fig. 2. Vapor–liquid equilibria for HFC-125 (1) + HFC-236ea (2) at $T = 288.54$ K (○), 303.19 K (■), and 318.24 K (◇); (——) CSD EoS fit.

Table III. Critical Parameters for the Pure Compounds

Compound	T_c (K)	P_c (kPa)	Ref. No.
HFC-32	351.255	5782.6	[5]
HFC-125	339.165	3617.3	[5]
HFC-236ea	412.44	3502.0	[3]

The VLE data were reduced using the CSD EoS and minimizing the objective function to optimize the interaction parameter k_{ij}:

$$\mathrm{obf} = \sum_{i=1}^{N_p} (\Delta P/P_{\mathrm{exp}})^2 \tag{1}$$

where N_p is the number of experimental data and $\Delta P = P_{\mathrm{cal}} - P_{\mathrm{exp}}$, where P_{cal} is the saturated pressure calculated from the CSD EoS and P_{exp} is the experimental pressure.

Table IV. Vapor Pressures of Pure Compounds: Comparison Between Experimental Data from This Study and Values Calculated from the Literature: $\Delta P = 100[(P - P_{\mathrm{tw}})/P_{\mathrm{tw}}]$

		T (K)								
		288.6			303.2			318.2		
Fluid	Ref. No.	P (kPa)	$P - P_{\mathrm{tw}}$ (Pa)	ΔP	P (kPa)	$P - P_{\mathrm{tw}}$ (kPa)	ΔP	P (kPa)	$P - P_{\mathrm{tw}}$ (kPa)	ΔP
HFC-32	tw[a]	1294.2			1927.7			2795.9		
	[2]	1295.2	1.0	0.08	1929.5	1.8	0.09	2800.7	4.8	0.17
	[3]	1295.3	1.1	0.09	1929.4	1.7	0.09	2800.1	4.2	0.15
	[4]	1295.1	0.9	0.07	1929.5	1.8	0.09	2800.7	4.8	0.17
	[5]	1296.2	2.0	0.15	1929.9	2.2	0.11	2800.3	4.4	0.16
HFC-125	tw	1060.0			1568.4			2263.3		
	[2]	1060.5	0.5	0.05	1568.4	0.0	0.00	2262.1	−1.2	−0.05
	[4]	1060.7	0.7	0.06	1569.6	1.2	0.08	2265.0	1.7	0.07
	[5]	1058.6	−1.4	−0.13	1568.1	−0.3	−0.02	2264.6	1.3	0.06
	[6]	1060.9	0.9	0.08	1568.3	−0.1	−0.01	2263.3	0.0	0.00
HFC-236ea	tw	146.3			245.0			394.9		
	[2]	145.4	−0.9	−0.62	244.9	−0.1	−0.04	394.7	−0.2	−0.05
	[7]	145.3	−1.0	−0.68	244.7	−0.3	−0.13	394.2	−0.7	−0.17
	[8]	147.5	1.2	0.84	246.8	1.8	0.75	396.2	1.3	0.32

[a] This work.

Table V. Parameters of the CSD EoS, Eq. (1), Taken from Ref. 13 for Data Correlation

	Compound		
Parameter	HFC-32	HFC-125	HFC-236ea
a_0 ($\mathrm{kPa \cdot L^2 \cdot mol^{-2}}$)	1662.2699	3427.9219	5611.9106
a_1 ($\mathrm{K^{-1}}$)	$-2.1975227 \times 10^{-3}$	$-3.1746132 \times 10^{-3}$	$-2.4948509 \times 10^{-3}$
a_2 ($\mathrm{K^{-2}}$)	-1.889027×10^{-6}	$-1.7572861 \times 10^{-6}$	$-1.7370031 \times 10^{-6}$
b_0 ($\mathrm{L \cdot mol^{-1}}$)	7.7987924×10^{-2}	1.4938043×10^{-1}	1.9314696×10^{-1}
b_1 ($\mathrm{L \cdot mol^{-1} \cdot K^{-1}}$)	$-0.75238102 \times 10^{-4}$	$-1.8085107 \times 10^{-4}$	$-1.8123708 \times 10^{-4}$
b_2 ($\mathrm{L \cdot mol^{-1} \cdot K^{-2}}$)	$-0.5301071 \times 10^{-7}$	$-1.1881331 \times 10^{-7}$	$-1.3230688 \times 10^{-7}$

The isotherms were first reduced separately. The results of data reduction are summarized in Table VI. Deviation diagrams for pressure and vapor phase composition are presented in Figs. 3–6. The deviations in both saturated pressure and vapor phase composition for the mixture with HFC-125 are sufficiently small for the data and the adopted model to be considered consistent, although there is a slight systematic deviation for the vapor composition. Higher deviations were observed for the mixture with HFC-32, especially for the isotherm at 288.6 K. However, the S-shaped curves for both pressure and vapor composition deviations suggest that these deviations are due more to the model than to inaccuracy in the experimental data.

The data were also reduced as a set (all three isotherms for each system), assuming simply that k_{ij} is independent of temperature (the results are summarized in Table VII). No practical differences were found with respect to the separate reduction of each isotherm, since the deviations in

Table VI. Results of VLE Data Reduction Using the CSD EoS at $T = 288.6$, 303.2, and 318.2 K[a]

	HFC-32 + HFC-236ea			HFC-125 + HFC-236ea		
T (K)	288.6	303.2	318.2	288.6	303.2	318.2
δP	0.01	0.03	0.10	-0.01	0.01	-0.07
Abs(δP)	0.72	0.34	0.32	0.37	0.22	0.22
Δy	0.0011	-0.0017	-0.0031	0.0031	0.0021	0.0029
Abs(Δy)	0.0048	0.0036	0.0035	0.0031	0.0021	0.0029
k_{12}	-0.0403	-0.0386	-0.0379	0.0050	0.0046	0.0052

[a] $\delta p = (100/N_p) \sum_{i=1}^{N_p} [(P_{\mathrm{cal}} - P_{\mathrm{exp}})/P_{\mathrm{exp}}]_i$; $\mathrm{Abs}(\delta p) = (100/N_p) \sum_{i=1}^{N_p} [|P_{\mathrm{cal}} - P_{\mathrm{exp}}|/P_{\mathrm{exp}}]_i$; $\delta y = [1/(N_p - 2)] \sum_{i=2}^{N_p - 1} (y_{\mathrm{cal}} - y_{\mathrm{exp}})_i$; $\mathrm{Abs}(\delta y) = [1/(N_p - 2)] \sum_{i=2}^{N_p - 1} (|y_{\mathrm{cal}} - y_{\mathrm{exp}}|)_i$.

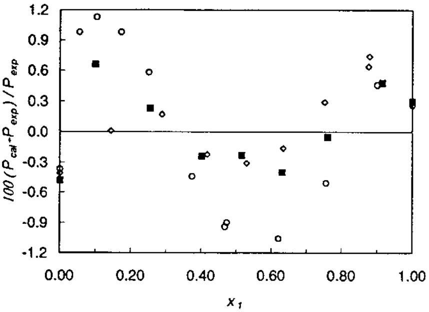

Fig. 3. Deviation plot of saturated pressure for HFC-32 (1) + HFC-236ea (2) at T = 288.55 K (○), 303.19 K (■), and 318.24 K (◇), with the CSD EoS as the baseline.

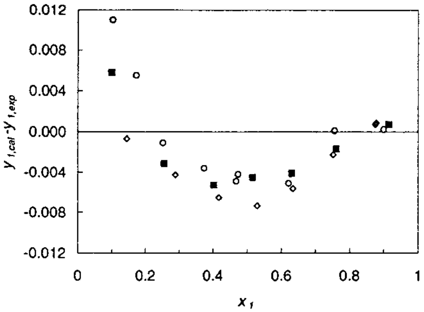

Fig. 4. Deviation plot of vapor phase composition for HFC-32 (1) + HFC-236ea (2) at T = 288.55 K (○), 303.19 K (■), and 318.24 K (◇), with the CSD EoS as the baseline.

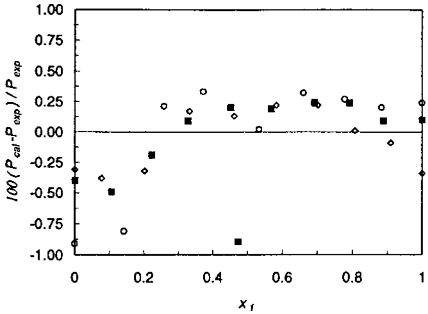

Fig. 5. Deviation plot of saturated pressure deviations for HFC-125 (1) + HFC-236ea (2) at T = 288.54 K (○), 303.19 K (■), and 318.24 K (◇), with the CSD EoS as the baseline.

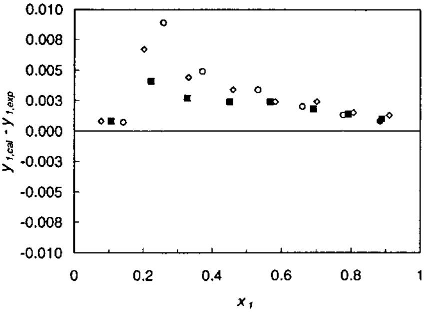

Fig. 6. Deviation plot of vapor phase composition for HFC-125 (1) + HFC-236ea (2) at $T = 288.54$ K (○), 303.19 K (■), and 318.24 K (◇), with the CSD EoS as the baseline.

both pressure and vapor composition are similar. The k_{ij} calculated in this way can be considered a valid average value for each system, independent of temperature.

4. CONCLUSIONS

Both systems considered in this paper show near-ideal thermodynamic behavior at equilibrium, with a small deviation from Raoult's law. The behavior observed here is very similar to that of the related mixtures with HFC-236fa instead of HFC-236ea.

Data reduction with the Carnahan–Starling–DeSantis EoS was satisfactory for the HFC-125 + HFC-236ea system, while higher deviations were found for the HFC-32 + HFC-236ea system, due more to the model than to experimental errors.

Table VII. Results of VLE Data Reduction as a Combined Set Using the CSD EoS

	HFC-32 + HFC-236ea	HFC-125 + HFC-236ea
P	0.02	−0.02
Abs(δP)	0.52	0.27
δy	−0.0010	0.0027
Abs(δy)	0.0043	0.0027
k_{12}	−0.0394	0.0049

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