Materials. Degassed, distilled water was used. The propyne was a technical grade (95%) supplied by the Air Reduction Co. and further purified by fractionation by the Phillips Petroleum Co. A mass spectrometer analysis of the purified propyne showed the purity to be 99.99 mole %.

DISCUSSION OF RESULTS

The experimental data are given in Table I and in Figure 1, where the solubility is shown as a function of the total pressure of the system. The smoothed data given in Table II were taken from the pressure-composition figures and plotted on a temperature-composition diagram in Figure 2. Figure 2 shows that propyne does not exhibit the minimum solubility phenomena in this pressure and temperature range.

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Solubilities of Various Hydrocarbons in Methanol

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IN STUDIES of complexes of urea and thiourea with various hydrocarbons (*14*) it was necessary to know the solubilities of these hydrocarbons in methanol. A literature search showed that data on the solubilities of hydrocarbon-methanol systems were lacking for all but a few hydrocarbons. Because reliable data concerning the solubility parameter of methanol could not be found, even estimation of the desired information was prevented. Therefore, solubilities and critical solution temperatures of a number of hydrocarbons in methanol have been determined.

As a result of these investigations, a value is given for the solubility parameter of methanol ($\delta = 12.4$) considered sufficiently reliable that the solubilities of hydrocarbons other than those studied here may be estimated. This value is in fair agreement with empirically predicted values, but in poor agreement with the values derived from heat of vaporization and vapor pressure data.

Data are also presented which indicate that the solubility parameter of 2,2,4-trimethylpentane is 7.45 rather than 6.82 and that of 2,2,5-trimethylhexane is 7.50 rather than 7.04. Other information derived from these solubility studies is reported and discussed.

EXPERIMENTAL

Reagents. The hydrocarbons and methanol (Table I) were carefully checked for purity, and were used as received, or purified as described below. A Cary Model 11 recording spectrophotometer was used to scan the spectrum from 300 $m\mu$ to 205 $m\mu$ for these materials, unless otherwise stated. Gas-liquid partition chromatographic analyses were obtained on a 14-foot tri-(*m*-tolyl) phosphate column in a Fisher-Gulf Model 160 partitioner. From the information obtained, and the refractive indices taken with an Abbe refractometer, conservative estimates of the impurity levels were made.

Ultraviolet analysis of *n*-pentane (technical grade) indicated the absence of unsaturated compounds. Gas chromatographic analysis and ultraviolet absorption revealed a minor trace of benzene as impurity, estimated to be less than 0.05 mole %. Ultraviolet analysis of *n*-hexane indicated that unsaturated compounds were absent. Gas chromatographic analysis showed no impurities; the maximum impurity was estimated to be 0.05 mole %. Ultraviolet analysis of *n*-heptane indicated approximately 0.8 mole % of impurity, probably unsaturated in nature. *n*-Octane (practical grade) was purified by passage through short columns of silica gel (Davison, No. 12) until the unsaturated compounds were removed. The resulting material, after purification, contained an estimated maximum impurity of 0.2 mole %.

n-Nonane contained small amounts of unsaturated impurities. The *n*-decane contained some unidentified unsaturated material, the maximum impurity was estimated to be about 0.5 mole %. 2,2-Dimethylbutane contained some unsaturated compounds, the maximum impurity being estimated from ultraviolet spectra to be 0.1 mole %. Ultraviolet analysis of 2,3-dimethylbutane indicated a trace of benzene and approximately 1.5 mole % of unsaturated impurities. Unsaturated compounds were present in 3-methylheptane to about 0.3 mole % as determined by

Table I. Refractive Indices of Hydrocarbons Used

Hydrocarbon	Source[a]	Refractive Index: Exptl.	Refractive Index: Literature
n-Pentane	EOC	1.3583	1.35748 (2)
n-Hexane	FC	1.3794	1.37486 (2)
n-Heptane	EOC	1.3879	1.38764 (2)
n-Octane	EOC	1.3975	1.39745 (2)
n-Nonane	MCB	1.40545	1.40549 (2)
n-Decane	MCB	1.4116	1.4120 (*3, 4*)
3-Methylpentane	MCB	1.3762	1.3764 (*4*)
2,2-Dimethylbutane	MCB	1.36885	1.36876 (2)
2,3-Dimethylbutane	MCB	1.37500	1.37495 (2)
3-Methylheptane	MCB	1.3984	1.39495 (2)
2,2,4-Trimethylpentane	EOC	1.39145	1.39145 (2)
2,2,5-Trimethylhexane	MCB	1.3997	1.3996 (2)
Cyclopentane	MCB	1.4046	1.40645 (2)
Methylcyclopentane	MCB	1.4100	1.4097 (2)
Cyclohexane	MCB	1.4259	1.42623 (2)
Methylcyclohexane	MCB	1.42315	1.42312 (2)

[a] EOC, Eastman Organic Chemicals; FC, Fisher certified; MCB, Matheson, Coleman, and Bell.

Table II. Solubilities of Hydrocarbons in Methanol at Various Temperatures

Hydrocarbon	Solubility, G. Hydrocarbon/100 Ml. CH_3OH at ° C.							
	5	10	15	20	25	30	35	40
Pentane	62.0	81	Misc.	Misc.	Misc.	Misc.	Misc.	Misc.
Hexane	32.4	37.0	42.7	49.5	60.4	83	Misc.	Misc.
3-Methylpentane	38.9	45.0	53.0	65	91	Misc.	Misc.	Misc.
2,2-Dimethylbutane	59	80	Misc.	Misc.	Misc.	Misc.	Misc.	Misc.
2,3-Dimethylbutane	49.5	59.3	76	170	Misc.	Misc.	Misc.	Misc.
Heptane	18.1	20.0	22.5	25.4	28.7	32.7	37.8	45.0
Octane	12.2	13.6	15.2	16.7	18.4	20.6	23.0	26.0
3-Methylheptane	15.4	17.0	19.0	21.2	24.2	27.4	31.4	36.5
2,2,4-Trimethylpentane	24.9	27.9	31.4	35.3	40.2	46.0	56.0	76
Nonane	8.4	9.5	10.5	11.6	12.9	14.2	15.5	17.0
2,2,5-Trimethylhexane	16.2	17.9	20.0	22.1	24.7	28.0	31.6	36.0
Decane	6.2	6.8	7.4	8.1	8.9	9.8	10.9	12.0
Cyclopentane	68	86	140	Misc.	Misc.	Misc.	Misc.	Misc.
Methylcyclopentane	38.0	41.5	50.0	59.5	74	110	Misc.	Misc.
Cyclohexane	...	...	34.4	38.4	43.5	50.3	60	74
Methylcyclohexane	26.9	29.8	33.2	37.2	42.2	48.8	57.5	70.9

ultraviolet analysis. Ultraviolet analyses of 2,2,4-trimethylpentane showed unsaturated material to be absent, and the maximum impurity was estimated to be less than 0.1 mole %. Purification allowed a reduction of the maximum impurity to a level of less than 0.04 mole %.

Ultraviolet analysis of 2,2,5-trimethylhexane indicated about 0.2 mole % of impurities of an unsaturated nature. Cyclopentane analyses were not performed, because the refractive index indicated acceptable purity. Methylcyclopentane (99%) was observed to contain approximately 0.02 mole % of benzene and about 1 mole % of unidentified unsaturated compounds which render methylcyclopentane somewhat more soluble in methanol. Spectroquality cyclohexane contained no unsaturated material and the maximum impurity was estimated to be 0.02 mole %. No ultraviolet or gas chromatographic analyses were made of spectroquality methylcyclohexane.

Methanol (E.I. du Pont de Nemours & Co.) was employed in these investigations. Reproducible results could be obtained only after careful distillation, at a high reflux ratio and low throughput, through a 6-foot column, 1-inch in diameter, packed with 3/16-inch ceramic beads, or a 3-foot column packed with 0.16 × 0.16 inch Type 316 stainless steel protruded packing (H.E.T.P. $\cong$ 0.5 inch for methanol). The product so obtained had an $n^{20}_D = 1.3293$ [(*21*) 1.3290], and gave results identical to those obtained using methanol (MCB spectro grade) which had been additionally purified by distillation from magnesium (*2*), observed $n^{20}_D = 1.3289$. This purified methanol had a boiling point of 64.6° C. (corrected) and a freezing point of −99° C. [literature values (*21*) are 64.7° and −97.8° C., respectively.]

Solubility Measurements. Solubilities of various hydrocarbons in methanol were determined by the isoplethal or synthetic method (*1*). Samples of known composition of solute and solvent were heated and/or cooled and the temperature of phase transitions was noted. In general, the phase transition most reproducible and easily observed, and therefore chosen, was the unmixing temperature (cloud point) obtained when a miscible solution was cooled until the finely dispersed solute was just no longer completely miscible. The solubility curves so obtained for these binary systems (Figures 1 to 3) were prepared by plotting the unmixing temperature-composition data.

RESULTS

Table II lists solubility values and Table III the critical solution temperatures (C.S.T.) observed in these studies. For comparison, critical solution temperatures observed by others (*3, 5, 6, 12, 13, 16–20*) are also given. It is estimated that temperature measurements are accurate to within ±0.2° C. and that solubilities are accurate to ±2% of the value.

Table III. Critical Solution Temperatures of Hydrocarbons in Methanol

Hydrocarbon	C.S. T., ° C.		References
	This work	Previous work	
Pentane	14.25	14.75	(*3*)
Hexane	33.2	34.5, 35, 32, 36.55, 34.8, 42.85, 42.6, 43.8, 42.0, 34.50	(*3, 5, 6, 12, 16–19, 20*)
3-Methylpentane	27.2		
2,2-Dimethylbutane	14.2		
2,3-Dimethylbutane	20.4		
Heptane	51.2	51.0, 51.5, 51	(*3, 5, 20*)
2,2,3-Trimethylbutane	...	28.2	(*20*)
Octane	65.7	66.7	(*20*)
3-Methylheptane	60.2		
2,2,4-Trimethylpentane	43.0	42.5, 43	(*3, 5, 20*)
2,2,5-Trimethylhexane	57.5		
Cyclopentane	16.6		
Methylcyclopentane	32.1		
Cyclohexane	45.75	45.60 45.85, 45, 46[illegible]	(*3, 5, 13, 17, 20*)
Methylcyclohexane	46.0	44.5, 47	(*5, 20*)

DISCUSSION

Hildebrand (*7–10*) has combined the Flory-Huggins equation, entropy correction

$$R \ln x_2 = R\,[\ln \phi_2 + (1 - V_2/V_1)\,\phi_1] \qquad (1)$$

with the heat term, given by the Van Laar–Hildebrand-Scatchard equation for a regular solution as

$$\ln a_2 = \ln x_2 + [(V_2\phi_1^2/RT)(\delta_1 - \delta_2)^2] \qquad (2)$$

to obtain

$$RT \ln (a_2/\phi_2) = V_2\phi_1^2(\delta_1 - \delta_2)^2 + RT\,\phi_1[1 - (V_2/V_1)] \qquad (3)$$

where the first term on the right incorporates the heat of mixing and the second term the entropy of mixing; a = activity, V = molal volume, δ = solubility parameter, ϕ = volume fraction, and x = mole fraction. Subscripts 1 and 2 refer to methanol solvent, and hydrocarbon solute, respectively.

Hildebrand and Scott (*11*) give the relation

$$RT_c = \frac{2x_1x_2V_1^2V_2^2}{(x_1V_1 + x_2V_2)^3}\,(\delta_1 - \delta_2)^2 \qquad (4)$$

If $V_1 = V_2$ and $x_1 = x_2 = 0.5$, then

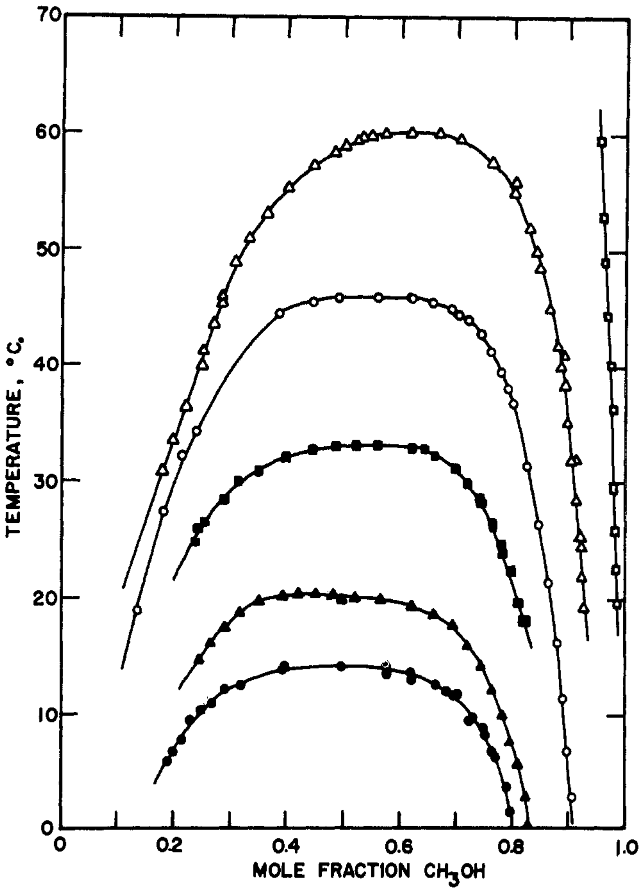

Figure 1. Solubilities of hydrocarbons in methanol

● 2,2-Dimethylbutane	▲ 2,3-Dimethylbutane
■ *n*-Hexane	○ *n*-Decane
△ 3-Methylheptane	□ Methylcyclohexane

$$2RT_c = V(\delta_1 - \delta_2)^2 \tag{5}$$

where T_c is the consolute temperature in ° K. and R is the gas constant. Hildebrand and Scott (*11*) note that if $V_1 = V_2$, Equation 5 may be used to give approximate values, if one takes $V = \frac{1}{2}(V_1 + V_2)$.

Values of V_2 and ΔH_v for the various hydrocarbons have been taken from the C-461 Tables (*15*) and values of δ_2 have been calculated from the relation given by Hildebrand:

$$\delta_2 = [(\Delta H_v - RT)/V_2]^{1/2} \tag{6}$$

Hildebrand (*8*) has already noted that the uncertainty is expected to be 0.2 to 0.3, even for $V_1 \gg V_2$.

Equation 3 at 25° C. and Equation 4 at the critical solution temperatures have been utilized in calculations of the solubility parameter of methanol, and the data are summarized in Table IV. To compare calculations for *n*-nonane and *n*-decane with Equation 4, the solute activity was approximated as unity for *n*-nonane and *n*-decane when using Equation 3. From Table IV, $\delta_1 = 12.4$. Equations 3 and 4 give better, more consistent results than the more approximate Equation 5 for the solubility of these hydrocarbons in methanol. From calculations using Equations 3 and 4 it was observed that $\Delta\delta$ decreases as the carbon chain length of the hydrocarbon increases, as pointed out by Hildebrand and Scott (*11*).

If $\delta_2 = 7.45$ is chosen for 2,2,4-trimethylpentane, as proposed by Hildebrand (*10*), the agreement is much better (Table IV). This suggests that $\delta_2 = 7.50$ for 2,2,5-trimethylhexane, rather than $\delta_2 = 7.04$.

Using the various relationships given by Hildebrand and Scott (*11*) for estimating δ_1, and $\Delta H_v = 9.11$ kcal. per mole (calorimetric) and 8.28 kcal. per mole (approx.), $P_c = 78.67$ atm., $a = 9.523$ liter atm. per mole (*15*), and $\gamma = 22.0$ dynes per cm. for methanol, values of 14.5, 13.8, 11.1, 11.9

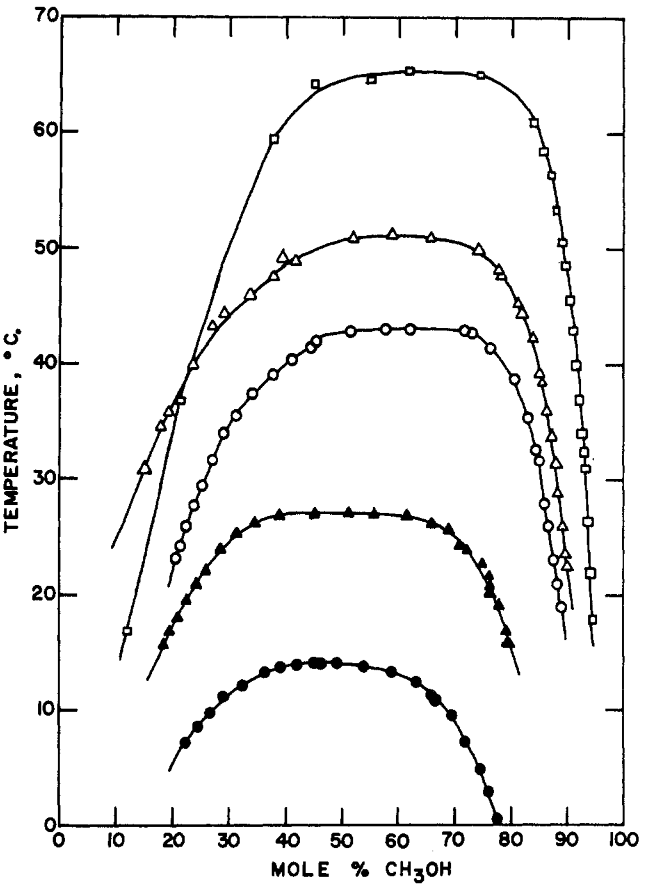

Figure 2. Solubilities of hydrocarbons in methanol

● *n*-Pentane	▲ 3-Methylpentane	
○ 2,2,4-Trimethylpentane	△ *n*-Heptane	□ *n*-Octane

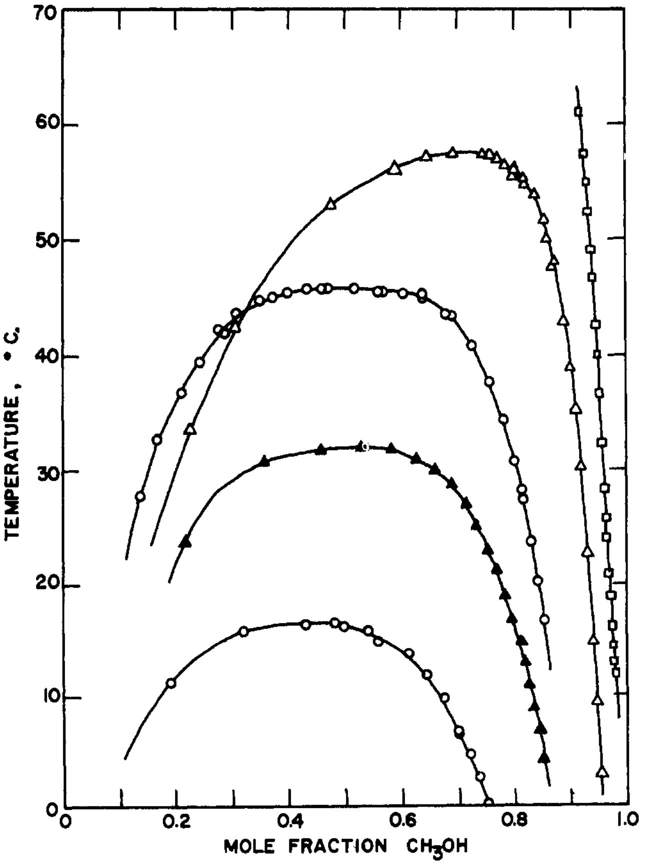

Figure 3. Solubilities of hydrocarbon in methanol

● Cyclopentane	▲ Methylcyclopentane
○ Cyclohexane	△ 2,2,5-Trimethylhexane
□ *n*-Nonane	

Table IV. The Solubility Parameter of Methanol

			Using Equation 3 at 25° C.				Using Equation 4 at C.S.T.			
Solute	V_2	δ_2	ϕ_2	ϕ_2'	$(\delta_1 - \delta_2)$	δ_1	t_c, ° C.	x_2^c	$(\delta_1 - \delta_2)$	δ_1
n-Pentane	116.1	7.02	...	...	...	...	14.25	0.52	5.11	12.13
n-Hexane	131.6	7.27	0.480	0.910	5.28	12.55	33.2	0.45	4.84	12.11
3-Methylpentane	130.6	7.14	0.580	0.877	5.48	12.62	27.2	0.50	4.18	12.32
2,2-Dimethylbutane	133.7	6.72	...	...	...	...	14.2	0.50	5.08	11.80
2,3-Dimethylbutane	131.2	6.97	...	...	...	...	20.4	0.54	5.38	12.35
n-Heptane	147.5	7.45	0.297	0.967	4.91	12.36	51.2	0.39	4.60	12.05
2,2,3-Trimethylbutane	146.1	6.96	...	...	...	...	28.2	0.4	4.50	11.46*
2,2,3-Trimethylbutane	146.1	(7.40)[a]	...	...	...	...	28.2	0.4	4.50	11.90
n-Octane	163.5	7.56	0.208	0.956	4.70	12.26	65.7	0.38	4.65	12.21
3-Methylheptane	162.8	7.41	0.257	0.961	4.79	12.20	60.2	0.38	4.62	12.03
2,2,4-Trimethylpentane	166.1	6.82	0.369	0.937	4.95	11.77	43.0	0.37	4.42	11.24*
2,2,4-Trimethylpentane	166.1	(7.45)[a]	0.369	0.937	4.95	12.40	43.0	0.37	4.42	11.87
n-Nonane[b]	179.7	7.65	0.153	...	4.70	12.35	...	...	...	...
2,2,5-Trimethylhexane	182.4	7.04	0.260	0.957	4.74	11.78	57.5	0.28	3.92	10.96*
2,2,5-Trimethylhexane	182.4	(7.50)[a]	0.260	0.957	4.74	12.24	57.5	0.28	3.92	11.42
n-Decane[b]	194.9	7.75	0.109	...	4.64	12.39	...	...	...	...
Cyclopentane	94.7	8.10	...	...	...	...	16.6	0.58	5.44	13.54*
Methylcyclopentane	113.1	7.85	0.499	0.904	5.36	13.21*	32.1	0.48	4.97	12.82*
Cyclohexane	108.7	8.21	0.360	0.950	5.15	13.36*	45.75	0.50	5.23	13.44*
Methylcyclohexane	128.3	7.84	0.354	0.942	5.03	12.87*	46.0	0.45	4.94	12.78*
Av. (omitting* values) ± std. dev.						12.37 ± 0.13				12.03 ± 0.22
Av., all values ± std. dev.						12.57 ± 0.42				12.15 ± 0.67
ΔH_v calculation						14.5				14.5

[a] Estimated to give better agreement with experimental results.

[b] Assumed $a_2 = 1$. Table V indicates this assumption is not unreasonable.

Table V. Calculated Activities of Saturated Solutions of Some Saturated Hydrocarbons in Methanol at 25° C.

Hydrocarbon	X_2	a_2
Hexane	0.221	0.72
3-Methylpentane	0.300	0.67
Heptane	0.104	0.94
Octane	0.061	1.09
3-Methylheptane	0.079	1.19
2,2,4-Trimethylpentane	0.125	0.81
Nonane	0.039	1.13
2,2,5-Trimethylhexane	0.072	1.11
Decane	0.025	1.04

(14.2), and 10, respectively, were calculated for δ_1. The average of these is 12.6. The value of (14.2) was calculated by using the empirical factor 1.2, as suggested by Hildebrand and Scott to obtain better agreement. The immediate observation is that, other than giving rough values, these values of δ_1 from the above approximate relations would be of little use for calculations of solubilities and/or consolute temperatures, although the value of 11.9 and the average of 12.6 are in fair agreement with the value of 12.4, considered to be a "best value" from experimental data. Certainly, 14.5 for δ_1 is too large.

The critical solution temperature and the solubility curves of *n*-pentane and 2,2-dimethylbutane are very nearly identical. Although the δ_2 values differ by more than 0.3, the difference in V_2 (about 17) apparently offsets this change in δ_2, or the δ_2 of 2,2-dimethylbutane is too low. The value of δ_1 calculated for 2,2-dimethylbutane in Table IV appears to favor the latter explanation—i.e., a better value of δ_2 would be about 7.0 for 2,2-dimethylbutane.

From the data of Table IV, with the use of Equation 4, C.S.T. values of approximately 80° and 95° C. are estimated for *n*-nonane and *n*-decane, respectively.

In view of the paucity or nonexistence of data for activities of methanol solutions of hydrocarbons, we have calculated such values for the saturated hydrocarbons investigated, using Equation 3, the solubility data presented herein, and the value of 12.4 for δ_1. The results of these calculations presented in Table V, are only approximate, but should be useful until more accurate values are reported.

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