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Isobaric Ternary Vapor–Liquid Equilibria System: Chloroform–Methanol–Chlorobenzene

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Reliable vapor–liquid equilibrium data obtained with a modified Jones equilibrium still are presented for the ternary system chloroform–methanol–chlorobenzene at 760 ± 1 mmHg total pressure. The experimental data were correlated satisfactorily with Wohl's three-suffix Margules equations using the ternary constant $C = -0.304$. No ternary azeotrope was noticed. It is observed that the binary azeotrope of the chloroform–methanol system is eliminated at 55 mol % composition of chlorobenzene in the liquid phase. The data are found to be thermodynamically consistent.

As a part of continuing study on chlorobenzene as a possible solvent for the separation of azeotropic mixtures, the system chloroform–methanol–chlorobenzene is studied. The investigation is carried out to obtain vapor–liquid equilibrium data for the present system, to examine the effect of the solvent on the azeotropic composition of the binary system chloroform–methanol, to correlate the experimental data, and to observe whether a ternary azeotrope appears for the present system.

Experimental and Analytical Data

The experimental vapor–liquid equilibrium data were obtained at 760 ± 1 mmHg pressure, using a Jones equilibrium still as modified by ward (*10*). The physical properties, refractive index, and specific gravity were used for analysis. The refractive indices were determined at 35 °C and the specific gravities were estimated at 30 °C. If A, B, and C are the three components of a ternary system, then known samples of the three components were taken in conical flasks at various B/(B + C) ratios from 0.1 to 0.9 and varying the concentration of A from O to 100% for each B/(B + C) ratio. These samples were then placed in a constant-temperature bath maintained at 30 ± 1 °C for about 20 min and the specific gravity was determined. The refractive indices of these samples were estimated at 35 ± 1 °C. Refractive indices and specific gravities were plotted against concentration of A for each B/(B + C) ratio and smoothed data of constant refractive index and constant specific gravity were obtained. Using these constant refractive index and constant specific gravity data, a ternary calibration chart was prepared, which was later used for analyzing the unknown samples. This method was applied earlier by Subbarao et al. (*8*). The compositions of the mixtures could be analyzed with an accuracy of x_i ±0.005 mole fraction in all composition ranges and the temperature could be read with an accuracy of ±0.1 °C.

General Operating Principle and a Brief Description of Ward's Modified Still

The general principle of operation is to take the vapors from a boiling solution to a condenser and condensate chamber and to revaporize the condensate and bubble the saturated vapors through the original solution. When equilibrium is reached, the vapors emerging from and bubbling through, will have the same composition, which is indicated by the constancy in the temperature of the boiling liquid.

The equilibrium chamber—main heating chamber—is connected through a vapor tube to the double condenser system to the condensate chamber. The condensate chamber is connected through a three-way stopcock to the flash vaporizer tube which in turn extends almost to the bottom of the equilibrium chamber. The vaporizer tube is provided with a small bend at its end about 5 mm from the side of the equilibrium chamber, which serves as a pool to hold about 2–3 drops of the residual condensate liquid, which ensures against superheating of the vapor returning to the main equilibrium chamber. The lower ends of the equilibrium chamber and condensate chamber are closed by stopcocks, through which the liquid and vapor samples, respectively, are taken for analysis. A thermowell is fitted from the top of the vapor chest in the equilibrium chamber. The vertical condenser, connecting the horizontal main chamber and the condensate chamber, ensures against excessive vapor losses. The top of the condensate chamber is connected to the three-way vaporizer tube. Its chief function is to allow drainage of the vaporizer tube and to maintain equal pressure on both sides during the operation of the still.

Calculations

The activity coefficient data of the experimental runs are calculated by the following equation.

$$\gamma_i = \frac{Z_i P y_i}{P_i^\circ x_i} \tag{1}$$

The vapor-phase nonideality correction factor "Z" is estimated for all the runs, with the relation (*2*)

$$\log Z_i = \frac{(P_i^\circ - P)(V_i - \beta_i)}{2.303RT} \tag{1a}$$

The vapor pressures of the chemicals are obtained at the desired temperatures using Antoine-type vapor pressure equations. The equations used are given below (*1*):

chloroform

$$\log P^\circ = 6.95465 - \frac{1170.966}{t + 226.232} \tag{2}$$

methanol

$$\log P^\circ = 8.08097 - \frac{1582.271}{t + 239.726} \tag{3}$$

chlorobenzene

$$\log P^\circ = 6.97808 - \frac{1431.053}{t + 217.55} \tag{4}$$

The following composition and boiling temperature ranges were covered: $x_1 = 0.021\text{–}0.916$, $x_2 = 0.004\text{–}0.832$, $x_3 = 0.025\text{–}0.960$; temperature (t, °C) = 55.1–110.7 °C. The activity coefficients for the present system were estimated using the following three-suffix Margules equations of Wohl (*13*):

$$\log \gamma_1 = x_2^2[0.37 + 0.72x_1] + x_3^2[0.2 - 0.9x_1] + x_2x_3[0.09 - 0.9x_1 + 0.08x_3 + 0.304(1 - 2x_1)] \tag{5}$$

$$\log \gamma_2 = x_3^2[0.8 + 0.08x_2] + x_1^2[0.73 - 0.72x_2] + x_1x_3[1.37 - 0.72x_2 + 0.9x_1 + 0.304(1 - 2x_2)] \tag{6}$$

$$\log \gamma_3 = x_1^2[-0.25 + 0.9x_3] + x_2^2[0.84 - 0.08x_3] + x_1x_2[0.31 - 0.08x_3 + 0.72x_2 + 0.304(1 - 2x_3)] \tag{7}$$

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Table I. Physical Properties of the Chemicals

chemical	density at 30 °C exptl	density at 30 °C lit.	RT at 30 °C exptl	RT at 30 °C lit.	bp (°C) at 760 ± 1 mmHg pressure exptl	bp (°C) at 760 ± 1 mmHg pressure lit.
chloroform	1.4704	1.4706 (*9*)	1.4395	1.43973 (*9*)	61.20	61.20 (*9*)
methanol	0.7865	0.7867 (*11*)[a]	1.3260	1.3266 (*11*)[a]	64.90	64.75 (*9*)
chlorobenzene	1.0968	1.0954 (*9*)	1.5200	1.5194 (*9*)	131.80	131.75 (*9*)

[a] At 25 °C.

Presentation of Results

Table I (*9*, *11*) compares the physical properties of pure chemicals with literature values. Experimental t-x-y data and a comparison of the calculated and experimental activity

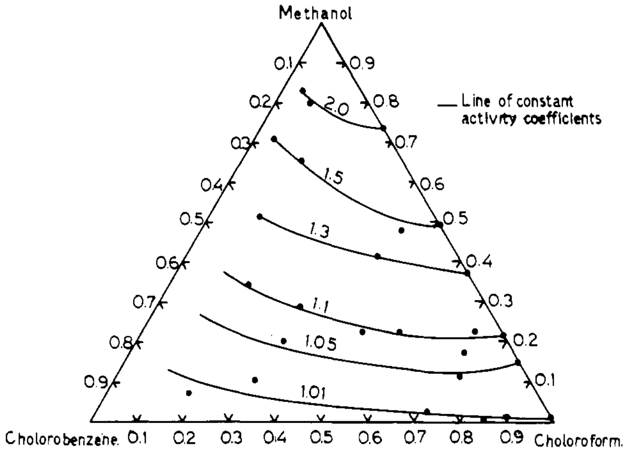

Figure 1. Activity coefficient data for chloroform.

Table II. Vapor-Liquid Equilibrium Data at 760 ± 1 mmHg Total Pressure, with Experimental and Estimated Activity Coefficient Data (System: Chloroform (1)-Methanol (2)-Chlorobenzene (3))

no.	x_1	x_2	y_1	y_2	t, °C	γ_1 (exptl)	γ_1 (calcd)	γ_2 (exptl)	γ_2 (calcd)	γ_3 (exptl)	γ_3 (calcd)
1	0.032	0.008	0.131	0.481	99.50	1.432	1.449	18.173	6.175	1.017	1.001
2	0.035	0.014	0.146	0.340	110.70	1.130	1.439	5.293	6.046	0.972	1.002
3	0.181	0.004	0.481	0.251	93.90	1.066	1.059	20.449	6.692	0.9940	1.037
4	0.716	0.024	0.885	0.077	67.80	1.009	0.925	2.832	3.284	1.135	1.000
5	0.052	0.006	0.153	0.536	98.30	1.059	1.374	28.027	6.255	0.863	1.003
6	0.755	0.007	0.909	0.064	63.70	1.115	0.937	9.454	7.582	1.037	0.959
7	0.890	0.013	0.922	0.070	62.10	1.009	0.985	5.933	6.173	0.805	0.755
8	0.097	0.004	0.242	0.503	93.70	1.006	1.237	45.467	6.409	0.862	1.013
9	0.021	0.022	0.062	0.687	89.60	1.320	1.497	12.871	5.861	0.915	1.001
10	0.239	0.020	0.344	0.546	73.70	0.988	0.985	19.399	6.471	0.916	1.059
11	0.420	0.056	0.512	0.401	69.20	0.954	0.886	5.997	5.995	1.219	1.118
12	0.555	0.031	0.662	0.285	67.70	0.977	0.879	8.148	7.006	0.998	1.109
13	0.650	0.016	0.772	0.173	67.00	0.993	0.899	9.844	7.563	1.320	1.061
14	0.702	0.046	0.774	0.187	64.30	1.002	0.927	4.106	6.187	1.383	1.013
15	0.848	0.007	0.884	0.101	62.40	1.006	0.971	15.710	6.866	0.999	0.826
16	0.053	0.037	0.108	0.727	78.30	1.229	1.379	11.843	5.593	0.943	1.007
17	0.178	0.070	0.255	0.626	72.60	1.015	1.083	6.606	5.131	1.020	1.045
18	0.304	0.108	0.372	0.545	67.60	1.006	0.956	4.485	4.595	1.105	1.108
19	0.402	0.069	0.461	0.470	66.90	0.962	0.895	6.219	5.608	1.049	1.119
20	0.603	0.063	0.664	0.287	65.20	0.973	0.901	4.441	5.865	1.264	1.091
21	0.869	0.024	0.874	0.116	61.40	1.001	0.981	5.477	5.927	0.943	0.787
22	0.047	0.262	0.080	0.806	70.30	1.290	1.485	2.473	2.739	1.168	1.145
23	0.169	0.182	0.221	0.695	67.80	1.068	1.146	3.368	3.420	1.005	1.109
24	0.319	0.203	0.370	0.574	64.60	1.044	1.000	2.822	3.190	1.034	1.200
25	0.466	0.193	0.489	0.472	62.00	1.026	1.042	2.706	3.274	1.123	1.228
26	0.536	0.085	0.570	0.391	63.70	0.985	0.896	4.756	5.285	0.942	1.124
27	0.749	0.071	0.742	0.234	60.50	1.016	1.047	3.868	5.139	1.393	0.963
28	0.878	0.032	0.860	0.134	60.70	0.998	0.985	4.877	5.531	0.691	0.770
29	0.067	0.356	0.102	0.792	67.90	1.239	1.477	1.954	2.121	1.420	1.304
30	0.170	0.346	0.215	0.703	65.70	1.100	1.257	1.942	2.090	1.429	1.357
31	0.313	0.289	0.366	0.579	63.40	1.093	1.075	2.096	2.384	1.281	1.342
32	0.476	0.226	0.504	0.466	60.30	1.093	0.991	2.440	2.859	1.061	1.280
33	0.651	0.113	0.635	0.344	59.80	1.022	0.942	3.672	4.407	0.957	1.081
34	0.824	0.072	0.770	0.221	58.40	1.026	0.984	3.918	4.656	0.988	0.858
35	0.881	0.040	0.858	0.135	59.90	1.019	0.989	4.055	5.214	0.949	0.764
36	0.110	0.513	0.166	0.748	65.10	1.338	1.523	1.427	1.477	1.973	1.799
37	0.184	0.501	0.252	0.682	63.60	1.272	1.142	1.413	1.458	1.926	1.886
38	0.373	0.378	0.438	0.519	60.20	1.216	1.171	1.633	1.800	1.828	1.638
39	0.554	0.224	0.558	0.421	58.60	1.098	1.007	2.382	2.789	1.071	1.268
40	0.743	0.112	0.684	0.305	57.80	1.031	0.977	3.562	4.091	0.888	0.986
41	0.811	0.090	0.747	0.246	58.00	1.025	0.989	3.546	4.254	0.822	0.882
42	0.898	0.057	0.820	0.177	57.80	1.023	0.999	4.062	4.512	0.780	0.734
43	0.039	0.712	0.068	0.841	65.70	1.516	1.883	1.129	1.150	3.084	2.768
44	0.129	0.652	0.203	0.731	63.10	1.486	1.705	1.187	1.179	2.827	2.674
45	0.412	0.416	0.487	0.486	58.20	1.306	1.248	1.503	1.598	1.807	1.832
46	0.723	0.172	0.670	0.321	56.70	1.076	1.021	2.552	3.054	1.051	1.062
47	0.916	0.053	0.845	0.153	58.20	1.019	1.001	3.715	4.469	0.743	0.702
48	0.046	0.832	0.108	0.834	64.00	2.130	2.066	1.024	1.039	4.299	4.146
49	0.078	0.802	0.162	0.786	62.90	1.973	2.011	1.046	1.047	4.100	4.005
50	0.435	0.475	0.536	0.447	56.30	1.449	1.386	1.308	1.369	2.356	2.191
51	0.892	0.083	0.786	0.214	56.70	1.023	1.010	3.492	3.859	0.980	0.747
52	0.721	0.224	0.671	0.324	55.10	1.141	1.083	2.113	2.390	1.193	1.140

Table III. Details of the Consistency Test (3)

no.	x_1	$\log \gamma_1$	$x_1[\log \gamma_{ip} - \log \gamma_{if}]$ (e)	x_2	$\log \gamma_2$	$x_2[\log \gamma_{2p} - \log \gamma_{2f}]$ (e)	x_3	$\log \gamma_3$	$x_3[\log \gamma_{3p} - \log \gamma_{3f}]$
				(a) At 60 ± 2 °C[a]					
1	0.476	0.0386	−0.000 999	0.226	0.3874	+0.002 350	0.298	0.0257	−0.001 221
2	0.554	0.0407	+0.016 176	0.224	0.3770	−0.039 760	0.222	0.0298	+0.009 945
3	0.651	0.0094	+0.022 069	0.113	0.5649	−0.023 786	0.236	−0.0191	−0.026 951
4	0.749	0.0068	−0.000 973	0.071	0.5875	+0.001 079	0.180	0.1440	+0.011 880
5	0.811	0.0107	+0.005 190	0.090	0.5497	−0.013 599	0.099	−0.0851	+0.016 780
6	0.869	0.0004	+0.010 080	0.024	0.7386	−0.003 321	0.107	−0.0255	+0.008 174
7	0.878	−0.0009	−0.006 672	0.032	0.6881	+0.004 179	0.090	−0.1615	−0.000 252
8	0.881	0.0080	−0.007 841	0.040	0.6080	+0.004 724	0.079	−0.0227	−0.002 567
9	0.916	0.0080	0.0000	0.053	0.5700	+0.002 014	0.031	−0.1290	+0.003 295
				(b) At 65 ± 2 °C[b]					
1	0.129	0.1721	+0.005 882	0.652	0.0745	−0.052 094	0.219	0.4513	+0.034 186
2	0.110	0.1265	+0.007 436	0.513	0.1544	−0.038 782	0.377	0.2952	+0.062 846
3	0.184	0.1045	+0.015 658	0.501	0.1501	−0.067 033	0.315	0.2846	+0.044 163
4	0.170	0.0414	+0.011 203	0.346	0.2882	−0.059 269	0.484	0.1550	+0.085 716
5	0.313	0.0386	+0.007 105	0.289	0.3214	−0.046 904	0.398	0.1075	+0.055 919
6	0.319	0.0187	+0.017 672	0.203	0.4505	−0.095 877	0.478	0.0145	+0.041 490
7	0.402	−0.0168	+0.010 170	0.069	0.7937	−0.015 642	0.529	0.0207	+0.021 371
8	0.536	−0.0066	−0.002 626	0.085	0.6772	+0.012 427	0.379	−0.0259	−0.030 737
9	0.603	−0.0119	+0.003 196	0.063	0.6475	+0.001 871	0.334	0.1018	−0.042 652
				(c) At (60–65) ± 2 °C[c]					
1	0.129	0.1721	+0.005 882	0.652	0.0745	−0.052 094	0.219	0.4513	+0.034 186
2	0.110	0.1265	+0.007 436	0.513	0.1544	−0.038 782	0.377	0.2952	+0.062 846
3	0.184	0.1045	+0.015 658	0.501	0.1501	−0.067 033	0.315	0.2846	+0.044 163
4	0.170	0.0414	+0.011 203	0.346	0.2882	−0.059 269	0.484	0.1550	+0.085 716
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9	0.603	−0.0119	−0.027 255 6	0.063	0.6475	+0.018 257 4	0.334	0.1018	−0.017 234 4
10	0.476	0.0386	−0.025 037 6	0.226	0.3874	+0.061 133	0.298	0.0257	+0.021 456
11	0.554	0.0407	+0.016 176	0.224	0.3770	−0.039 760	0.222	0.0298	0.009 945
12	0.651	0.0094	+0.022 069	0.113	0.5649	−0.023 786	0.236	0.0191	−0.026 951
13	0.749	0.0068	−0.000 973	0.071	0.5875	+0.001 079	0.180	0.1440	+0.011 880
14	0.811	0.0107	+0.005 19	0.090	0.5497	−0.013 599	0.099	−0.0851	+0.016 780
15	0.869	0.0004	+0.010 080	0.024	0.7386	−0.003 321	0.107	−0.0255	+0.008 174
16	0.878	−0.0009	−0.006 672	0.032	0.6881	+0.004 179	0.090	−0.1615	−0.000 252
17	0.881	0.0080	−0.007 841	0.040	0.6080	+0.004 724	0.079	−0.0227	−0.002 567
18	0.916	0.0080	0.000	0.053	0.5700	−0.002 014	0.031	−0.1290	+0.003 275

[a] % error = $(e_+ - e_-)/[(e_+ + e_-)/2] \times 100 = 0.010007/0.1229385 \times 100 = 8.14\%$. [b] % error = $(|e_+| - |e_-|)/[(|e_+| + |e_-|)/2] \times 100 = 0.013305/0.4449635 \times 100 = 2.99\%$. [c] % error = $(|e_+| - |e_-|)/[(|e_+| + |e_-|)/2] \times 100 = 0.0454618/0.6269445 \times 100 = 7.251$.

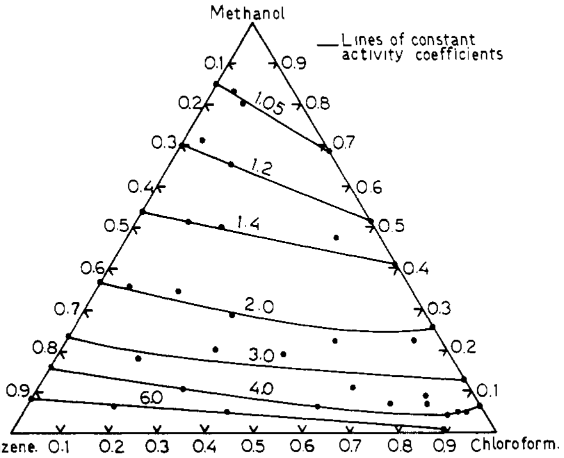

Figure 2. Activity coefficient data for methanol.

coefficient data are presented in Table II. The details of the thermodynamic consistency test using the numerical integration method of Li and Lu (*3*) are presented in Table III.

Activity coefficient data are presented in Figures 1, 2, and 3 for chloroform, methanol, and chlorobenzene, respectively. The *x*–*y* diagram on chlorobenzene free basis is presented in Figure 4.

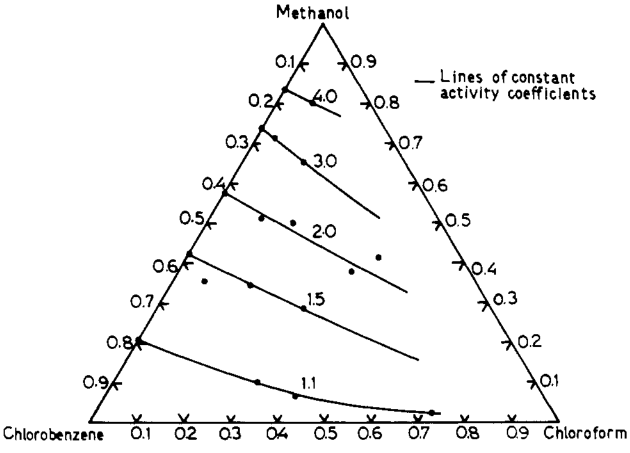

Figure 3. Activity coefficient data for chlorobenzene.

Discussion and Correlation of Results

The application of the ternary Van Laar (*13*), Li and Coull (*4*), or White (*12*) equations to correlate the experimental vapor–liquid equilibrium data is restricted by the condition

$$A_{32}/A_{23} = (A_{31}/A_{13})(A_{12}/A_{21})$$

which is not satisfied in the present case. Therefore, the data

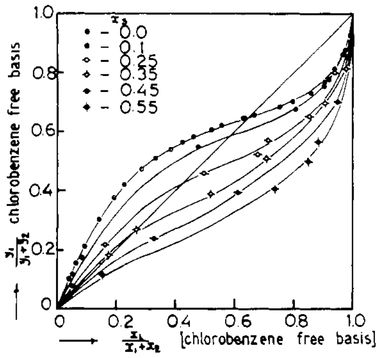

Figure 4. x–y diagram on a chlorobenzene-free basis.

are correlated with Wohl's three-suffix Margules equations (*13*) utilizing six binary constants and one ternary constant. A good agreement is not obtained between the calculated and experimental values, when "C" is assumed to be zero. In order to obtain a more satisfactory fit of the data, about nine values of "C" are computed from experimental ternary measurements using appropriate equations and compositions suggested by Severnes et al. (*7*). They are averaged to give a value of $C = -0.304$ and with this ternary constant a better fit of the data is possible than with those of the ternary constant evaluated from the constituent binary constants, in accordance with Wohl's suggestion (*13*). The binary constants used in the Wohl ternary three-suffix Margules equations are taken from literature and are reproduced with their sources: $A_{12} = 0.37$, $A_{21} = 0.73$ (*5*); $A_{23} = 0.80$, $A_{32} = 0.84$ (*6*); $A_{31} = 0.25$, $A_{13} = 0.2$ (*6*).

The method of Li and Lu (*3*) is used for testing the internal thermodynamic consistency of the present data. The percentage error defined as $(\epsilon_+ - \epsilon_-)/[(\epsilon_+ + \epsilon_-)/2] \times 100$ is 8.14 for the data around 60 ± 2 °C and 2.99 for the data around 65 ± 2 °C. When all the data points in the range 60 ± 2 to 65 ± 2 °C are taken into account, the percentage error was found to be 7.25. According to this method, the data are found to be thermodynamically consistent.

From the equilibrium curve for the system chloroform–methanol drawn on a chlorobenzene-free basis with the percentage composition of chlorobenzene as the parameter, the azeotrope for this system disappeared at 55 mol % liquid-phase composition of chlorobenzene. This is further confirmed by estimating the relative volatility of methanol to chloroform in the presence of a chlorobenzene and chlorobenzene-free composition.

Acknowledgment

The authors are thankful to CSIR for awarding S.R.F. to M.N.R.

Glossary

A_{12}, A_{21}	end values from plot of logarithms of activity coefficients vs. percentage composition for the 1–2 binary
A_{23}, A_{32}	end values from the plot of logarithms of activity coefficients vs. percentage composition for the 2–3 binary
A_{31}, A_{13}	end values from the plot of logarithms of activity coefficients vs. percentage composition for the 1–3 binary
C	ternary constant
P°	pure component vapor pressure
P	total pressure
R	gas constant
t	temperature, °C
T	absolute temperature, K
V	liquid molal volume
x	mole fraction of the component in the liquid phase
y	mole fraction of the component in the vapor phase
Z	correction factor for nonideality in the vapor phase

Greek Symbols

β	second virial coefficient
γ	activity coefficient
δ	density
ϵ	$x_i(\log \gamma_{ip} - \log \gamma_{if})$

Subscripts

1	component chloroform
2	component methanol
3	component chlorobenzene
ip, if	values of the preceding and following points, respectively

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