one –CH(OH)– in addition. This –OH is very accessible and establishes stable linking. That could be the reason why the solubility of D-mannose does not fall steeply when a small amount of ethanol is added.

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Viscosities of Trichloroethylene with Ketones and 1,4-Dioxane at 298.15, 308.15, and 318.15 K

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Viscosity data for the binary liquid mixtures of trichloroethylene with methyl ethyl ketone, diethyl ketone, methyl isobutyl ketone, cyclohexanone, and 1,4-dioxane have been determined at 298.15, 308.15, and 318.15 K. The deviation in viscosity has been calculated by using the relation $\Delta \ln \eta = \ln \eta_{mix} - (x_1 \ln \eta_1 + x_2 \ln \eta_2)$ and studied as a function of composition and temperature. In the systems trichloroethylene with methyl ethyl ketone, diethyl ketone, and methyl isobutyl ketone the deviation in viscosity is positive, and the quantity is negative in the remaining systems at the three temperatures. The results have been analyzed in the light of the viscosity relations proposed by Hildebrand and Kosanovich.

Introduction

The evaluation and prediction of viscosities of binary liquid mixtures as a function of composition and temperature are of theoretical and practical importance, but very little data are available. Here, we have reported the viscosities for the binary systems of trichloroethylene with methyl ethyl ketone, diethyl ketone, methyl isobutyl ketone, cyclohexanone, and 1,4-dioxane measured at 298.15, 308.15, and 318.15 K. These systems have been selected with a view to study the effect of molecular structure on the transport property. The viscosity relation proposed by Hildebrand (*1*) and Hildebrand and Lamoreaux (*2*) for pure components and the viscosity relation proposed by Cullilan and Kosanovich (*3*) for binary mixtures have been used to analyze the experimental data.

Experimental Section

The viscosities of pure liquids and liquid mixtures were measured with an Ostwald viscometer and the values were accurate to 0.5%. Densities for the pure components were measured with a bicapillary pycnometer, and densities for mixtures were obtained from excess volume, V^E, data (*4*) by using the relation

$$\rho = \frac{x_1M_1 + x_2M_2}{x_1v_1 + x_2v_2 + V^E} \quad (1)$$

Density values in both the cases were accurate to $\pm 5 \times 10^{-5}$ g·cm^{-3}.

Trichloroethylene (BDH) and cyclohexanone (BDH) were dried over anhydrous sodium sulfate for 2 days and fractionally distilled. 1,4-Dioxane was dried with anhydrous magnesium sulfate and refluxed with sodium; then the sample was fractionally distilled. Methyl ethyl ketone (BDH), diethyl ketone (Fluka), and methyl isobutyl ketone (BDH) were purified by the methods described earlier (*5–7*). The purity of the chemicals was ascertained by comparing the density and boiling point data with literature values (*8*, *9*). The measured values of density and boiling point are presented in Table I along with the literature values.

Table I. Boiling Points and Densities of the Pure Components at 298.15 K

	boiling point, K		density, g·cm^{-3}	
compound	present work	lit. (*8*, *9*)	present work	lit. (*8*, *9*)
trichloroethylene	360.00	360.34	1.454 70	1.451 40[a]
methyl ethyl ketone	352.60	352.79	0.799 50	0.799 70
diethyl ketone	375.00	375.14	0.809 60	0.809 45
methyl isobutyl ketone	389.40	389.65	0.796 53	0.796 10
cyclohexanone	428.70	428.80	0.942 01	0.942 07
1,4-dioxane	374.00	374.47	1.027 70	1.027 97

[a] At 303.15 K.

Results

Density and viscosity results determined at the three temperatures are given in Table II. The deviations in viscosities are calculated by using the relation

$$\Delta \ln \eta = \ln \eta_{mix} - (x_1 \ln \eta_1 + x_2 \ln \eta_2) \quad (2)$$

where x_1 and x_2 are mole fractions and η_1 and η_2 are viscosities of pure components 1 and 2. The values of $\Delta \ln \eta$ are accurate to ± 0.005. $\Delta \ln \eta$ as a function of mole fraction are represented graphically in Figures 1–5 and the data also included in Table II.

The deviations in viscosities are fitted to an empirical equation of the form

$$\Delta \ln \eta = x_1x_2[A_0 + A_1(x_1 - x_2) + A_2(x_1 - x_2)^2] \quad (3)$$

The values of the constants A_0, A_1, and A_2 are obtained by the method of least squares and are given in Table III along with the standard deviation $\sigma(\Delta \ln \eta)$.

According to Hildebrand (*1*), the fluidity, ϕ, of a liquid depends on the ratio of free volume $(V - V_0)$ to intrinsic volume,

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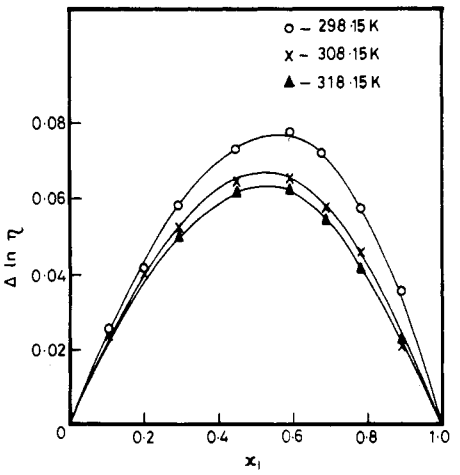

Figure 1. Excess viscosities versus mole fraction for trichloroethylene + methyl ethyl ketone.

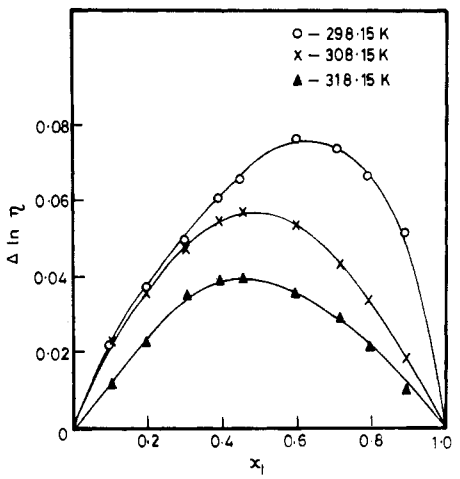

Figure 2. Excess viscosities versus mole fraction for trichloroethylene + diethyl ketone.

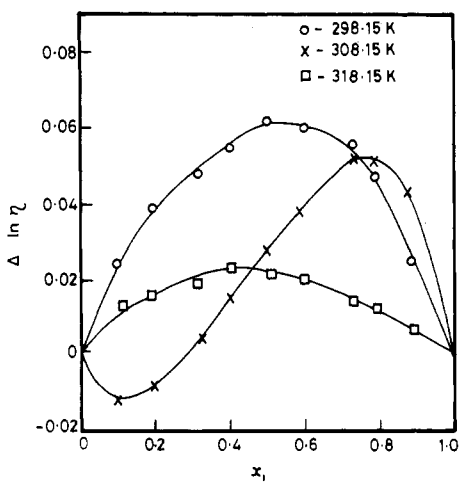

Figure 3. Excess viscosities versus mole fraction for trichloroethylene + methyl isobutyl ketone.

V_0, the molar volume at which the fluidity is zero. The relation is represented as

$$\phi = 1/\eta = B(V - V_0)/V_0 \qquad (4)$$

where the proportionality parameter, B, is a measure of the capacity of the molecules to absorb externally imposed momentum (*3*). Cullilan and Kosanovich (*3*) have proposed eq 4 even for binary mixtures so that V and ϕ in the equation are molar volume and fluidity of the binary mixture, respectively.

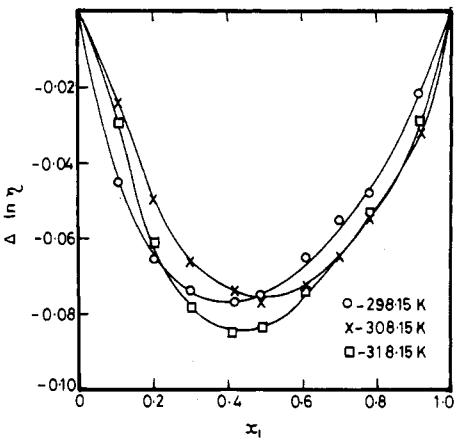

Figure 4. Excess viscosities versus mole fraction for trichloroethylene + cyclohexanone.

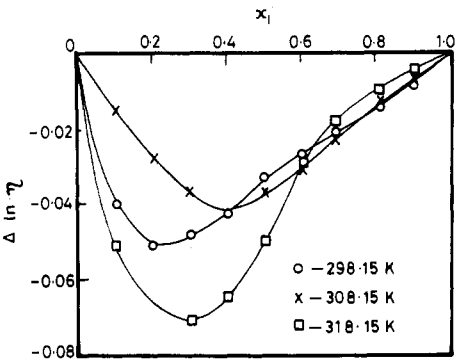

Figure 5. Excess viscosities versus mole fraction for trichloroethylene + 1,4-dioxane.

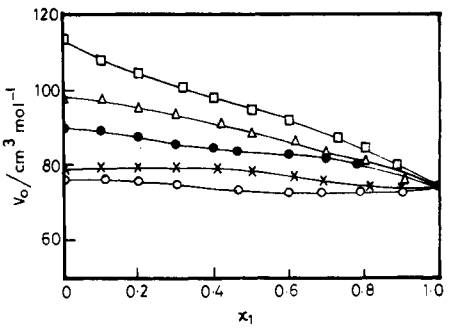

Figure 6. Mole fraction versus V_0 for trichloroethylene + methyl ethyl ketone (O); + diethyl ketone (●); + methyl isobutyl ketone (□); + cyclohexanone (△); + 1,4-dioxane (×).

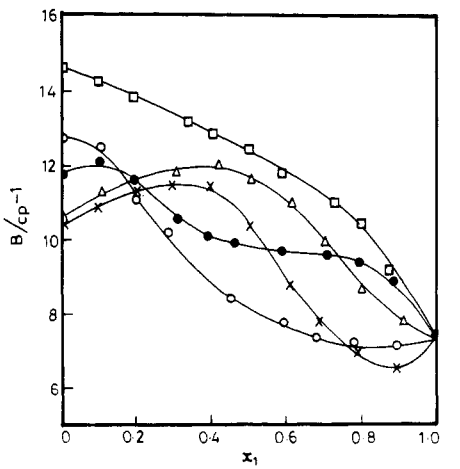

Figure 7. Mole fraction versus B for trichloroethylene + methyl ethyl ketone (O); + diethyl ketone (●); + methyl isobutyl ketone (□); + cyclohexanone (△); + 1,4-dioxane (×).

Table II. Mole Fraction of Trichloroehtylene, x_1, Densities, ρ, Viscosities, η, and Deviation in Viscosity $\Delta \ln \eta$

T, K	x_1	ρ, g·cm^{-3}	η, cP	$\ln \eta$	$\Delta \ln \eta$
	Trichloroethylene + Methyl Ethyl Ketone				
298.15	0.0000	0.799 50	0.408	0.896	
	0.1126	0.873 26	0.439	−0.823	0.026
	0.2042	0.934 87	0.463	−0.770	0.041
	0.2941	0.996 11	0.489	−0.715	0.058
	0.4591	1.108 56	0.532	−0.631	0.073
	0.5988	1.202 00	0.570	−0.562	0.077
	0.6807	1.255 58	0.582	−0.541	0.072
	0.7837	1.321 77	0.598	−0.513	0.057
	0.8997	1.395 44	0.614	−0.488	0.035
	1.0000	1.454 70	0.618	−0.481	
308.15	0.0000	0.789 50	0.373	−0.987	
	0.1126	0.863 65	0.402	−0.911	0.024
	0.2042	0.924 04	0.426	−0.853	0.041
	0.2941	0.983 31	0.449	−0.799	0.053
	0.4591	1.091 94	0.491	−0.711	0.065
	0.5988	1.183 59	0.523	−0.648	0.066
	0.6807	1.237 11	0.539	−0.618	0.058
	0.7837	1.304 14	0.558	−0.583	0.046
	0.8997	1.379 19	0.574	−0.555	0.021
	1.0000	1.443 67	0.588	−0.530	
318.15	0.0000	0.779 00	0.351	−1.047	
	0.1126	0.852 21	0.379	−0.969	0.026
	0.2042	0.911 90	0.401	−0.913	0.039
	0.2941	0.970 56	0.422	−0.862	0.049
	0.4591	1.078 15	0.462	−0.773	0.062
	0.5988	1.169 01	0.494	−0.705	0.063
	0.6807	1.222 08	0.508	−0.677	0.055
	0.7837	1.288 50	0.525	−0.644	0.041
	0.8997	1.362 93	0.544	−0.609	0.022
	1.0000	1.426 80	0.557	−0.585	
	Trichloroethylene + Diethyl Ketone				
298.15	0.0000	0.809 60	0.460	−0.776	
	0.1037	0.868 23	0.483	−0.729	0.021
	0.1997	0.924 24	0.507	−0.679	0.037
	0.3082	0.989 57	0.528	−0.637	0.047
	0.3915	1.041 21	0.549	−0.600	0.060
	0.4564	1.082 34	0.557	−0.584	0.057
	0.5979	1.174 79	0.592	−0.523	0.076
	0.7166	1.255 36	0.612	−0.492	0.073
	0.7989	1.312 91	0.622	−0.474	0.066
	0.8910	1.379 01	0.630	−0.462	0.051
	1.0000	1.454 70	0.618	−0.481	
308.15	0.0000	0.799 72	0.422	−0.862	
	0.1037	0.857 46	0.447	−0.805	0.023
	0.1997	0.912 74	0.467	−0.761	0.035
	0.3082	0.977 35	0.491	−0.712	0.048
	0.3915	1.028 49	0.506	−0.677	0.055
	0.4564	1.069 27	0.518	−0.657	0.054
	0.5979	1.161 03	0.543	−0.610	0.053
	0.7166	1.241 03	0.559	−0.581	0.043
	0.7989	1.298 14	0.564	−0.567	0.029
	0.8910	1.363 74	0.575	−0.527	0.019
	1.0000	1.443 67	0.588	−0.530	
318.15	0.0000	0.790 03	0.397	−0.925	
	0.1037	0.847 27	0.413	−0.885	0.004
	0.1997	0.902 03	0.434	−0.836	0.021
	0.3082	0.965 97	0.456	−0.785	0.035
	0.3915	1.016 56	0.471	−0.752	0.039
	0.4564	1.056 88	0.481	−0.732	0.037
	0.5979	1.147 56	0.504	−0.686	0.035
	0.7166	1.226 60	0.521	−0.652	0.029
	0.7989	1.283 03	0.531	−0.632	0.021
	0.8910	1.347 81	0.541	−0.614	0.007
	1.0000	1.426 80	0.557	−0.585	
	Trichloroethylene + Methyl Isobutyl Ketone				
298.15	0.0000	0.796 53	0.542	−0.613	
	0.1088	0.850 36	0.564	−0.574	0.025
	0.1998	0.898 17	0.578	−0.548	0.039
	0.3286	0.970 48	0.593	−0.522	0.048
	0.4037	1.015 31	0.603	−0.505	0.055
	0.5018	1.077 07	0.616	−0.484	0.062
	0.5921	1.137 33	0.621	−0.488	0.061
	0.7362	1.241 01	0.631	−0.460	0.056
	0.7986	1.289 08	0.630	−0.462	0.046
	0.8859	1.359 94	0.624	−0.471	0.025
	1.0000	1.454 70	0.618	−0.481	
308.15	0.0000	0.787 02	0.505	−0.683	
	0.1088	0.840 37	0.508	−0.677	−0.011
	0.1998	0.887 65	0.516	−0.661	−0.008
	0.3286	0.959 09	0.533	−0.629	0.003
	0.4037	1.003 39	0.546	−0.605	0.016
	0.5018	1.064 48	0.561	−0.578	0.028
	0.5921	1.124 17	0.574	−0.555	0.038
	0.7362	1.227 02	0.595	−0.519	0.052
	0.7986	1.274 73	0.600	−0.510	0.051
	0.8859	1.345 02	0.605	−0.502	0.044
	1.0000	1.443 67	0.588	−0.530	
318.15	0.0000	0.777 57	0.447	−0.805	
	0.1088	0.830 28	0.464	−0.768	0.013
	0.1998	0.877 04	0.475	−0.744	0.017
	0.3286	0.947 71	0.490	−0.713	0.019
	0.4037	0.991 54	0.500	−0.693	0.023
	0.5018	1.051 93	0.510	−0.673	0.021
	0.5921	1.110 92	0.519	−0.655	0.020
	0.7362	1.212 51	0.533	−0.629	0.014
	0.7986	1.259 64	0.539	−0.617	0.012
	0.8859	1.329 11	0.547	−0.603	0.007
	1.0000	1.426 80	0.557	−0.585	
	Trichloroethylene + Cyclohexanone				
298.15	0.0000	0.942 01	1.819	0.598	
	0.1122	0.993 62	1.589	0.463	−0.045
	0.2059	1.037 91	1.365	0.311	−0.065
	0.3057	1.086 38	1.215	0.194	−0.074
	0.4263	1.146 86	1.069	0.067	−0.077
	0.4987	1.184 18	0.988	−0.012	−0.075
	0.6177	1.247 16	0.883	−0.124	−0.065
	0.7064	1.295 33	0.803	−0.219	−0.055
	0.7889	1.340 92	0.739	−0.302	−0.048
	0.9152	1.411 80	0.666	−0.406	−0.021
	1.0000	1.454 70	0.618	−0.481	
308.15	0.0000	0.933 52	1.516	0.416	
	0.1122	0.984 44	1.339	0.292	−0.023
	0.2059	1.028 24	1.174	0.160	−0.050
	0.3057	1.076 25	1.062	0.060	−0.066
	0.4263	1.136 00	0.944	−0.057	−0.074
	0.4957	1.171 25	0.878	−0.130	−0.076
	0.6177	1.234 64	0.789	−0.239	−0.073
	0.7064	1.281 88	0.723	−0.324	−0.065
	0.7889	1.326 55	0.680	−0.385	−0.055
	0.9152	1.396 20	0.618	−0.481	−0.031
	1.0000	1.443 67	0.588	−0.530	
318.15	0.0000	0.924 22	1.311	0.271	
	0.1122	0.974 58	1.158	0.146	−0.029
	0.2059	1.017 86	1.034	0.034	−0.061
	0.3057	1.065 20	0.933	−0.069	−0.079
	0.4263	1.124 09	0.835	−0.180	−0.085
	0.4957	1.158 80	0.791	−0.234	−0.084
	0.6177	1.221 24	0.719	−0.330	−0.072
	0.7064	1.267 69	0.672	−0.397	−0.064
	0.7889	1.311 64	0.633	−0.457	−0.052
	0.9152	1.380 14	0.582	−0.541	−0.029
	1.0000	1.426 80	0.557	−0.585	
	Trichloroethylene + 1,4-Dioxane				
298.15	0.0000	1.027 70	1.149	0.139	
	0.1027	1.073 13	1.036	0.035	−0.039
	0.2015	1.117 03	0.963	−0.037	−0.051
	0.3002	1.160 88	0.909	−0.095	−0.048
	0.4090	1.209 01	0.854	−0.157	−0.043
	0.5020	1.249 82	0.814	−0.205	−0.033
	0.6078	1.295 72	0.767	−0.265	−0.027
	0.6921	1.331 83	0.732	−0.312	−0.021
	0.8076	1.380 53	0.685	−0.378	−0.015
	0.9058	1.421 23	0.649	−0.432	−0.008
	1.0000	1.454 70	0.618	−0.481	
308.15	0.0000	1.017 04	0.969	−0.031	
	0.1027	1.061 95	0.907	−0.098	−0.015
	0.2015	1.105 38	0.852	−0.160	−0.028
	0.3002	1.148 79	0.804	−0.218	−0.037
	0.4090	1.196 59	0.757	−0.278	−0.042

Table II (Continued)

T, K	x_1	ρ, g·cm^{-3}	η, cP	ln η	Δ ln η	T, K	x_1	ρ, g·cm^{-3}	η, cP	ln η	Δ ln η
	0.5020	1.236 77	0.727	−0.318	−0.037		0.3002	1.135 85	0.726	−0.320	−0.071
	0.6078	1.282 12	0.693	−0.366	−0.032		0.4090	1.182 71	0.690	−0.371	−0.069
	0.6921	1.317 74	0.670	−0.400	−0.023		0.5020	1.222 42	0.673	−0.396	−0.050
	0.8076	1.365 73	0.640	−0.446	−0.012		0.6078	1.267 14	0.653	−0.426	−0.030
	0.9058	1.405 80	0.613	−0.489	−0.006		0.6921	1.302 33	0.635	−0.454	−0.018
	1.0000	1.443 67	0.588	−0.530			0.8076	1.349 83	0.605	−0.503	−0.009
318.15	0.0000	1.005 31	0.901	−0.104			0.9058	1.389 48	0.586	−0.534	−0.005
	0.1027	1.050 09	0.815	−0.205	−0.050		1.0000	1.426 80	0.557	−0.585	
	0.2015	1.093 08	0.764	−0.269	−0.068						

Table III. Least-Squares Parameters and Standard Deviation

T, K	A_0	A_1	A_2	τ ln η
Trichloroethylene + Methyl Ethyl Ketone				
298.15	0.2986	0.0771	0.0299	0.001
308.15	0.2703	0.0016	−0.0431	0.001
318.15	0.2496	−0.0010	−0.0040	0.002
Trichloroethylene + Diethyl Ketone				
298.15	0.2699	0.1689	0.1683	0.002
308.15	0.2225	−0.0300	−0.0166	0.002
318.15	0.1620	−0.0119	−0.0803	0.001
Trichloroethylene + Methyl Isobutyl Ketone				
298.15	0.2451	0.0230	0.0291	0.003
308.15	0.1097	0.3308	0.0859	0.003
318.15	0.0818	−0.0308	0.0349	0.001
Trichloroethylene + Cyclohexanone				
298.15	−0.2970	0.1096	−0.1078	0.004
308.15	−0.3052	−0.0633	−0.0213	0.004
318.15	−0.3336	0.0005	−0.0098	0.006
Trichloroethylene + 1,4-Dioxane				
298.15	−0.1367	0.1942	−0.1913	0.002
308.15	−0.1598	0.0777	0.0666	0.004
318.15	−0.1953	0.3100	−0.1553	0.003

Hafez and Hartland (*10*) have analyzed their results of binary mixtures using eq 4.

The parameters B and V_0 for pure components and for mixtures at a fixed mole fraction are obtained by solving eq 4 for the three temperatures by the method of least squares. The values of B and V_0 are plotted as a function of mole fraction in Figures 6 and 7.

Discussion

The data included in Table I and in Figures 1–5 show that the deviation in viscosity is positive for the systems trichloroethylene with methyl ethyl ketone, diethyl ketone, and methyl isobutyl ketone and the property is negative for the systems trichloroethylene with cyclohexanone and 1,4-dioxane. The algebraic values of Δ ln η may be represented in the following order: cyclohexanone < 1,4-dioxane < methyl isobutyl ketone < diethyl ketone < methyl ethyl ketone. This order is not parallel with the molar polarizabilities of noncommon components and this may be ascribed to the influence of molecular structure of ketones on viscosity. A similar behavior in viscosity was observed earlier (*7*, *11*) for systems of methyl ethyl ketone and methyl isobutyl ketone with substituted benzenes.

The sign and magnitude of Δ ln η depend on the combined effect of the factors such as molecular size, shape and intermolecular forces. The positive values of Δ ln η suggest that the viscosity of the mixture is higher than that of the pure components and hence the fluidity of the mixture is low. This indicates the presence of specific interaction such as the formation of a charge-transfer complex between unlike molecules. Further, the hydrogen atom of trichloroethylene acts as an electron acceptor and it may be involved in the formation of hydrogen bond with n-electrons of noncommon components. Specific interactions of a similar type have been observed earlier from thermodynamic data for binary systems containing trichloroethylene with noncommon components acts as electron donors (*12*, *13*). The negative values of Δ ln η in the systems trichloroethylene with cyclohexanone and 1,4-dioxane may suggest that the mutual loss of specific interactions in like molecules outweigh over the specific interactions between unlike molecules. The values of Δ ln η are decreasing with increase of temperature in all the systems.

The data presented in Figures 6 and 7 reveal that the values of V_0 and B are varying nonlinearly with respect to mole fraction in all the systems. This shows that the values of the parameters V_0 and B depend on the composition and nature of the chemical species in the binary mixture.

Registry No. Trichloroethylene, 79-01-6; methyl ethyl ketone, 78-93-3; diethyl ketone, 96-22-0; methyl isobutyl ketone, 108-10-1; cyclohexanone, 108-94-1; 1,4-dioxane, 123-91-1.

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