J. Chem. Eng. Data **1982**, *27*, 321-324

Excess Volumes and Isentropic Compressibilities of 2,5,8-Trioxanonane–*n*-Heptane Mixtures[†]

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Measurements of excess volume and ultrasonic speed were carried out for mixtures of 2,5,8-trioxanonane (($CH_3OCH_2CH_2)_2O$) with *n*-heptane at 298.15 K over the entire mole fraction range including the region of high dilution of the ether. From these results, isentropic compressibilities, excess isentropic compressibilities, partial molar excess volumes, and partial molar excess isentropic compressibilities were calculated. A qualitative discussion of the results is presented.

Studies of the thermodynamic properties of polyethers and of their mixtures with other molecular species are of importance from the point of view of providing information about the variation of these properties with the number and positions of the oxygen atoms in the polyether. Such information is needed to develop and evaluate group contribution models for systems involving polyethers. Nevertheless, there have been relatively few studies of the volumetric properties of binary mixtures of aliphatic polyethers with *n*-alkanes, apart from the investigations of acetal–heptane systems by Meyer et al. (*1*) and measurements of the excess volumes of mixtures of 2,5-dioxahexane with *n*-alkanes by Treszczanowicz (*2*).

In the present paper, experimental measurements of excess volumes and ultrasonic speeds are reported for mixtures of 2,5,8-trioxanonane (diglyme) with *n*-heptane at 298.15 K. Isentropic compressibilities are derived from the results.

Experimental Section

Materials. In the course of the present work, samples of 2,5,8-trioxanonane from two different sources were employed without further purification. Sample A (UCB, Belgium; labeled highest purity) was used for the dilatometric measurements, and sample B (Aldrich Chemical Co., labeled 99%) for the ultrasonic determinations. The *n*-heptane (Phillips Petroleum Co., pure grade) was further purified by GLC in a column containing 10% by mass OV-17 on Chromosorb P. Densities of the components were determined in an Anton Paar densimeter with an accuracy of $\pm 2 \times 10^{-5}$ g cm^{-3}. Refractive indices for sodium light were determined within $\pm 3 \times 10^{-5}$ in a Bausch & Lomb refractometer. Both measurements were made at 298.15 ± 0.01 K; the results are listed in Table I together with some values from the literature (*3*, *4*).

Dilatometric Measurements. Molar excess volumes, $V^E{}_m$, were determined at 298.15 K and atmospheric pressure in a successive dilution micrometer syringe dilatometer. The apparatus and procedure have been described previously (*5*). The dilatometer was immersed in a water bath controlled to better than ±0.002 K; the absolute temperature was determined to ±0.01 K (IPTS-68) with a calibrated Hewlett-Packard quartz thermometer. The errors of the ether mole fraction, x_1, and of $V^E{}_m$ are estimated to be less than 5×10^{-5} and $0.0003 + 0.001|V^E{}_m|$ cm^3 mol^{-1}, respectively.

Measurements of Ultrasonic Speeds. Ultrasonic speeds, u, for 2-MHz waves were determined at 298.15 K by using the successive dilution cell and pulse-echo-overlap technique described previously (*6*, *7*). Calibration of the cell was based on the value 1496.739 m s^{-1} for the speed of ultrasound in water at 298.15 K (*8*). The error of the relative ultrasonic speeds is estimated to be less than 0.2 m s^{-1}, and their reproducibility was about 0.02 m s^{-1}. The error of the mole fractions is less than 1×10^{-4}.

Table I. Densities, ρ^*, and Indices of Refraction, n_D, for the Component Liquids at 298.15 K

		ρ^*, g cm^{-3}		n_D	
component		obsd	lit.	obsd	lit.
2,5,8-trioxanonane[a]	A	0.940 93	0.944 0[b]	1.406 27	1.404 3[b]
	B	0.939 72		1.406 06	
n-heptane		0.679 55	0.679 46[c]	1.385 13	1.385 11[c]

[a] Sample A used for dilatometric measurements, and sample B for ultrasonic measurements. [b] Reference *3*. [c] Reference *4*; see Table 23-2-(1.101)-a dated October 31, 1977.

Results

The experimental values of $V^E{}_m$ and u are given in Tables II and III, where x_1 is the mole fraction of 2,5,8-trioxanonane. Isentropic compressibilities, κ_S, and excess isentropic compressibilities, $\kappa_S{}^E$, are also listed in Table III. These were calculated from the relations

$$\kappa_S = [\textstyle\sum x_i V^*{}_i + V^E{}_m]/(u^2 \textstyle\sum x_i M_i) \qquad (1)$$

$$\kappa_S{}^E = \kappa_S - \kappa_S{}^{id} \qquad (2)$$

where $V^*{}_i$ is the molar volume and M_i the molar mass of component i, and $\kappa_S{}^{id}$ is the isentropic compressibility for the corresponding ideal mixture. Values of $\kappa_S{}^{id}$ were calculated from the equation (*9*)

$$\kappa_S{}^{id} = \textstyle\sum \phi_i [\kappa_S{}^*{}_i + TV^*{}_i (\alpha^*{}_i)^2 / C_p{}^*{}_i] - T(\textstyle\sum x_i V^*{}_i)(\textstyle\sum \phi_i \alpha^*{}_i)^2 / \textstyle\sum x_i C_p{}^*{}_i \qquad (3)$$

where ϕ_i is the volume fraction of i in the mixture referred to the unmixed state, T is the temperature, and $\kappa_S{}^*{}_i$, $\alpha^*{}_i$, and $C_p{}^*{}_i$ are respectively the isentropic compressibility, the isobaric thermal expansivity, and the molar isobaric heat capacity for pure component i. At 298.15 K, values of $C_p{}^*{}_1 = 278.5$ J K^{-1} mol^{-1} and of $\alpha^*{}_1 = 1.060$ kK^{-1} were obtained respectively by determining the volumetric heat capacity of 2,5,8-trioxanonane with a Picker flow calorimeter (*10*) and by measuring the density at various temperatures with an Anton Paar densimeter. For *n*-heptane, values of $C_p{}^*{}_2 = 224.71$ J K^{-1} mol^{-1} (*10*) and $\alpha^*{}_2 = 1.256$ kK^{-1} (*11*) were adopted from the literature.

The results for $V^E{}_m$ and $\kappa_S{}^E$ are plotted in Figures 1 and 2. Several different forms of smoothing equations were investigated. The best overall fit for both excess properties was obtained with the form

$$X^E = x_1(1 - x_1) \sum_{j=1}^{n} a_j x_1{}^{(j-1)/2} \qquad (4)$$

where X^E represents either $V^E{}_m$ or $\kappa_S{}^E$. Values of the coefficients, a_j, and the standard deviation, σ, obtained from least-squares analyses in which all points were weighted equally

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0021-9568/82/1727-0321$01.25/0

Table II. Experimental Results for the Molar Excess Volumes, V^E_m, of 2,5,8-Trioxanonane–n-Heptane Mixtures at 298.15 K

x_1	V^E_m, cm^3 mol^{-1}	x_1	V^E_m, cm^3 mol^{-1}	x_1	V^E_m, cm^3 mol^{-1}	x_1	V^E_m, cm^3 mol^{-1}
0.004 15	0.0229	0.139 26	0.5624	0.420 24	0.9154	0.754 54	0.6127
0.014 87	0.0800	0.161 12	0.6204	0.443 01	0.9156	0.778 17	0.5678
0.020 07	0.1065	0.183 71	0.6731	0.472 68	0.9104	0.804 12	0.5160
0.025 95	0.1357	0.209 20	0.7252	0.505 06	0.9005	0.836 13	0.4457
0.033 18	0.1707	0.236 03	0.7721	0.535 57	0.8838	0.864 97	0.3776
0.041 22	0.2082	0.260 46	0.8080	0.567 31	0.8609	0.891 59	0.3109
0.049 57	0.2455	0.284 35	0.8376	0.600 12	0.8311	0.914 40	0.2506
0.059 28	0.2871	0.313 48	0.8668	0.635 66	0.7926	0.932 29	0.2014
0.070 14	0.3312	0.346 04	0.8908	0.672 77	0.7445	0.947 56	0.1585
0.082 10	0.3771	0.371 99	0.9041	0.702 24	0.7013	0.961 51	0.1174
0.097 65	0.4331	0.398 41	0.9124	0.731 50	0.6537	0.971 63	0.0873
0.116 64	0.4953						

Table III. Experimental Results for the Ultrasonic Speeds, u, Isentropic Compressibilities, κ_S, and Excess Isentropic Compressibilities $\kappa_S{}^E$, of 2,5,8-Trioxanonane–n-Heptane Mixtures at 298.15 K

x_1	u, m s^{-1}	κ_S, TPa^{-1}	$\kappa_S{}^E$, TPa^{-1}	x_1	u, m s^{-1}	κ_S, TPa^{-1}	$\kappa_S{}^E$, TPa^{-1}
0.000 00	1129.81	1152.84	0.00	0.405 20	1157.05	960.00	−2.79
0.001 84	1129.74	1152.28	0.25	0.415 42	1158.19	954.92	−2.83
0.005 35	1129.72	1150.98	0.50	0.416 09	1158.29	954.54	−2.87
0.005 82	1129.74	1150.74	0.48	0.462 27	1164.43	930.33	−4.09
0.009 79	1129.74	1149.22	0.72	0.466 51	1164.98	928.16	−4.14
0.011 77	1129.77	1148.41	0.79	0.495 67	1169.19	912.78	−4.86
0.013 74	1129.76	1147.67	0.93	0.506 91	1170.89	906.83	−5.14
0.015 72	1129.78	1146.87	1.01	0.542 47	1176.41	888.05	−5.87
0.017 70	1129.77	1146.14	1.15	0.551 37	1177.87	883.30	−6.08
0.019 68	1129.80	1145.32	1.22	0.570 05	1180.98	873.39	−6.44
0.020 23	1129.77	1145.17	1.31	0.582 85	1183.12	866.65	−6.61
0.024 62	1129.81	1143.40	1.50	0.633 64	1192.28	839.62	−7.40
0.029 58	1129.88	1141.37	1.68	0.702 08	1205.68	803.38	−7.85
0.034 52	1129.92	1139.39	1.91	0.781 72	1223.15	761.23	−7.73
0.039 48	1130.01	1137.33	2.07	0.861 23	1242.28	719.84	−6.28
0.040 05	1129.97	1137.20	2.20	0.900 95	1252.50	699.44	−5.03
0.044 44	1130.07	1135.32	2.29	0.905 92	1253.80	696.91	−4.84
0.049 39	1130.16	1133.25	2.44	0.915 83	1256.45	691.85	−4.48
0.054 33	1130.28	1131.14	2.56	0.925 75	1259.09	686.84	−4.04
0.059 28	1130.39	1129.04	2.68	0.935 67	1261.80	681.78	−3.64
0.064 24	1130.51	1126.92	2.80	0.940 63	1263.13	679.31	−3.39
0.069 21	1130.65	1124.76	2.88	0.945 59	1264.50	676.80	−3.17
0.074 14	1130.77	1122.67	3.03	0.950 55	1265.85	674.32	−2.91
0.079 10	1130.93	1120.48	3.08	0.955 50	1267.24	671.81	−2.69
0.084 05	1131.08	1118.32	3.17	0.960 46	1268.63	669.32	−2.44
0.089 01	1131.27	1116.08	3.18	0.965 42	1270.01	666.84	−2.17
0.093 97	1131.43	1113.90	3.26	0.970 37	1271.39	664.37	−1.90
0.098 92	1131.60	1111.71	3.32	0.975 33	1272.79	661.90	−1.63
0.138 61	1133.32	1093.64	3.46	0.980 29	1274.21	659.42	−1.36
0.178 31	1135.58	1074.85	3.07	0.982 27	1274.80	658.40	−1.28
0.217 41	1138.23	1055.89	2.45	0.984 25	1275.36	657.43	−1.16
0.218 06	1138.30	1055.52	2.39	0.986 23	1275.92	656.45	−1.03
0.257 84	1141.52	1035.70	1.42	0.990 19	1277.00	654.54	−0.75
0.294 17	1144.76	1017.44	0.53	0.992 18	1277.58	653.54	−0.64
0.297 64	1145.15	1015.58	0.34	0.994 16	1278.12	652.59	−0.48
0.337 50	1149.20	995.16	−0.80	0.996 14	1278.66	651.64	−0.34
0.357 27	1151.26	985.13	−1.20	0.998 12	1279.20	650.69	−0.18
0.337 38	1153.67	974.54	−1.95	1.000 00	1279.68	649.83	0.00

are given in Table IV. The curves in Figures 1 and 2 were calculated from eq 4 with these coefficients.

Partial molar excess volumes, V^E_i, and partial molar excess isentropic compressibilities, $K_S{}^E{}_i$, defined by

$$K_S{}^E{}_i = -(\partial V^E{}_i/\partial p)_{T,S} = K_S{}^E{}_m + (1 - x_i)(\partial K_S{}^E{}_m/\partial x_i)_{T,p} \tag{5}$$

where

$$K_S{}^E{}_m = (\sum x_i V^*{}_i + V^E{}_m)\kappa_S{}^E + V^E{}_m \kappa_S{}^{id} \tag{6}$$

are plotted in Figures 3 and 4. For the most part, these were calculated by differentiating the representations of $V^E{}_m$ and $\kappa_S{}^E$ by eq 4. However, these representations are unsuitable for use at high dilutions of ether since they imply an infinite limiting slope of the partial molar quantity at $x_1 = 0$. The simple polynomial

$$X^E = \sum_{j=1}^{n} a_j x_1{}^j \tag{7}$$

was fitted to the $V^E{}_m$ results for $x_1 < 0.1$ and to the $\kappa_S{}^E$ results for $x_1 < 0.05$. The values of the coefficients a_j are given in Table IV. Equation 7 was used to calculate $V^E{}_i$ and $K_S{}^E{}_i$ for $x_1 < 0.015$.

Table IV. Coefficients, a_j, and Standard Deviation, σ, for Representations of V^E_m and $\kappa_S{}^E$ by Eq 4 and 7

	V^E_m, cm^3 mol^{-1}		$\kappa_S{}^E$, TPa^{-1}	
	eq 4	eq 7[a]	eq 4	eq 7[b]
a_1	5.4870	5.5635	91.3603	73.702
a_2	1.1089	−13.125	−231.2427	504.63
a_3	−13.8760	16.066	425.3937	
a_4	16.079		−1120.120	
a_5	−5.637		1367.578	
a_6			−602.488	
σ	0.0003	0.00006	0.063	0.057

[a] Fitted for $x_1 < 0.1$, used for $x_1 < 0.015$. [b] Fitted for $x_1 < 0.05$, used for $x_1 < 0.015$.

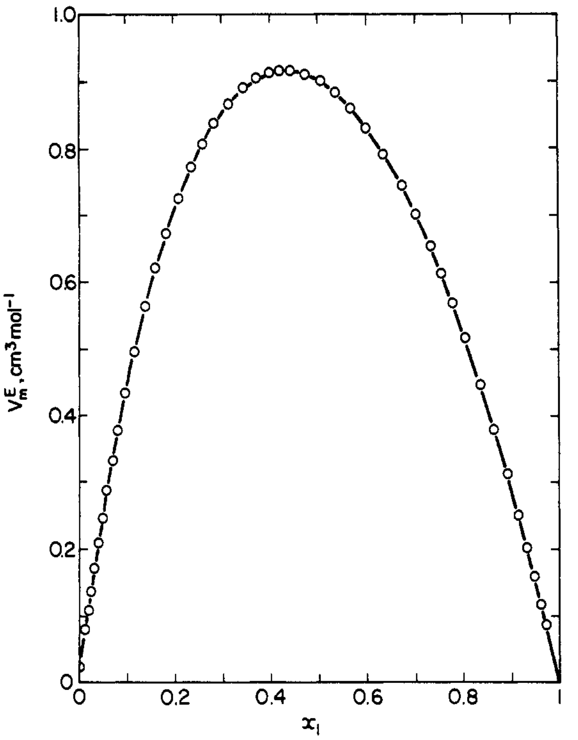

Figure 1. Molar excess volumes of 2,5,8-trioxanonane (1)–*n*-heptane (2) mixtures at 298.15 K. Points are experimental results. Curves are least-squares representations of results by eq 4.

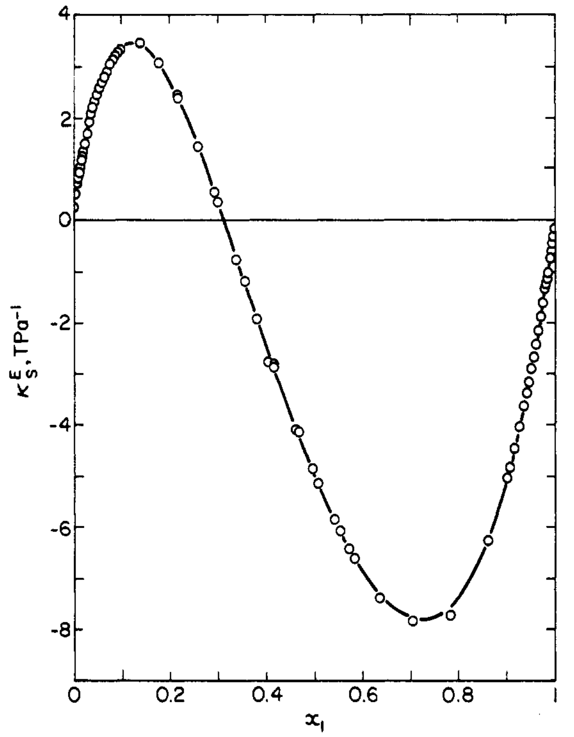

Figure 2. Excess isentropic compressibilities of 2,5,8-trioxanonane (1)–*n*-heptane (2) mixtures at 298.15 K. Points are experimental results. Curves are least-squares representations of results by eq 4.

Discussion

The molar excess volume of 2,5,8-trioxanonane–*n*-heptane mixtures at 298.15 K is positive throughout the mole fraction range and its variation is roughly symmetric about the maximum value 0.916 cm^3 mol^{-1} occurring at $x_1 \approx 0.434$. This behavior is similar to the high positive values of V^E_m found for acetal-heptane mixtures (*1*) and for 2,5-dioxahexane with *n*-heptane and *n*-octane (*2*) for which maxima exceeding 1 cm^3 mol^{-1} are observed. Thus, it appears that positive contributions to V^E_m due to disruption of molecular order in the pure state of the polyether and of the *n*-alkane predominate over negative contributions due to differences in the characteristic temperatures of the components. However, the sigmoid curve and the small magnitude of $\kappa_S{}^E$ indicate that the departure of the isentropic compressibility from ideal behavior is relatively small or,

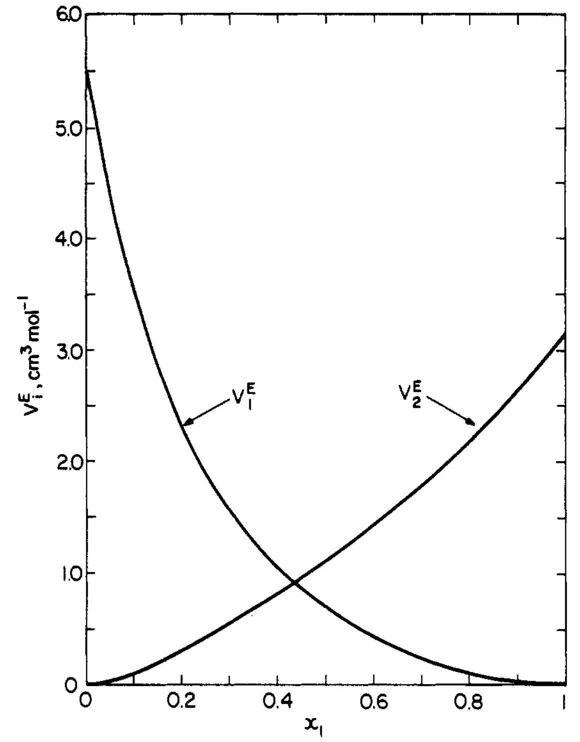

Figure 3. Partial molar excess volumes of components in 2,5,8-trioxanonane (1)–*n*-heptane (2) mixtures at 298.15 K.

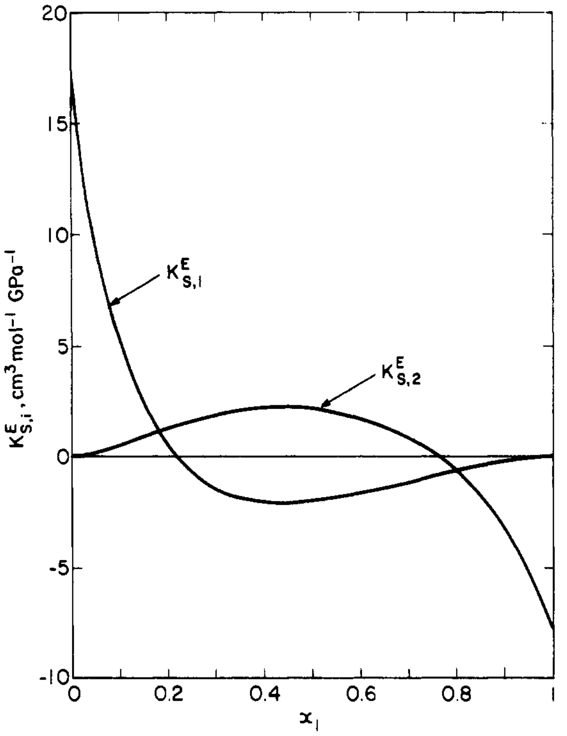

Figure 4. Partial molar excess isentropic compressibilities of components in 2,5,8-trioxanonane (1)–*n*-heptane (2) mixtures at 298.15 K.

in other words, that the curve for V^E_m is relatively insensitive to isentropic variations of pressure.

The molar excess volumes of monoether–alkane mixtures, as exemplified by the recent results for di-*n*-butyl ether–*n*-hexane (*12*), are generally lower than for polyether–alkane mixtures, indicating a closer balance between positive and negative contributions. Previously it was suggested (*13*) that a weak hydrogen bond is formed between the nonbonded electron pairs of an etheric oxygen atom in one molecule and a hydrogen atom of an α-situated CH_2 or CH_3 group in a second ether molecule and that in a polyether the strong inductive effect of several oxygen atoms weakens the C–H bond and enhances the hydrogen bonding. This picture is consistent with the relatively high enthalpies of vaporization of polyethers in comparison to their alkane homomorphs and also with the relatively large deviations of polyether–alkane mixtures from Raoult's law (*13*). In contradistinction, the inductive effect in monoethers is quite weak. Their enthalpies of vaporization are nearly the same as those of their respective alkane homomorphs, and the excess Gibbs energies of monoether–alkane mixtures exhibit only small deviations from ideality (*13*). The larger molar excess volumes of polyether–alkane mixtures compared to those of monoether–alkane mixtures are also understandable on this basis. However, the present results for V^E_1 and $K_S{}^E{}_1$ at low x_1 do not show any signs of the behavior which characterizes the results for the alcohol–alkane systems (*14*, *15*) where self-association through hydrogen bonding is undoubtedly of importance.

Acknowledgment

We are indebted to Mr. P. J. D'Arcy for technical assistance during this investigation.

Glossary

a_j	coefficient in either eq 4 or eq 7
$C_p{}^*{}_i$	molar heat capacity of pure component i at constant pressure, J K^{-1} mol^{-1}
$K_S{}^E{}_i$	partial molar excess isentropic compressibility of component i in mixture, cm^3 mol^{-1} GPa^{-1}
$K_S{}^E{}_m$	molar quantity related to the isentropic compressibility by eq 6
M_i	molar mass of component i
n	number of coefficients in either eq 4 or eq 7
T	thermodynamic temperature, K
u	speed of ultrasound, m s^{-1}
$V^E{}_i$	partial molar excess volume of component i in mixture, cm^3 mol^{-1}
$V^*{}_i$	molar volume of pure component i, cm^3 mol^{-1}
$V^E{}_m$	molar excess volume, cm^3 mol^{-1}
X^E	typical excess thermodynamic function
x_i	mole fraction of component i

Greek Letters

$\alpha^*{}_i$	isobaric thermal expansivity of pure component i, kK^{-1}
κ_S	isentropic compressibility, TPa^{-1}
$\kappa_S{}^E$	excess isentropic compressibility, TPa^{-1}
$\kappa_S{}^{id}$	isentropic compressibility of corresponding ideal mixture
$\kappa_S{}^*{}_i$	isentropic compressibility of pure component i, TPa^{-1}
ρ^*	density of pure component, g cm^{-3}
σ	standard deviation for least-squares fit
ϕ_i	volume fraction of i, in terms of the unmixed components

Subscripts

1	component 1, trioxanonane
2	component 2, *n*-heptane

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Received for review September 22, 1981. Accepted April 5, 1982.

Solubility of Gases in Liquids. 14. Bunsen Coefficients for Several Fluorine-Containing Gases (Freons) Dissolved in Water at 298.15 K

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Bunsen coefficients of six Freon gases, of sulfur hexafluoride, and of argon dissolved in water were measured at 298.15 K. Two modifications of Scholander's microgasometric apparatus were used, and details of a new improved version are given.

Introduction

Despite continued concern about the effects of Freon gases on the environment, few reliable data exist concerning the solubility of these substances in water. The main reason for the paucity of data is the exceedingly small solubility of Freons in water. Yet accurate solubility values need to be known for appropriate modeling and calculation of the long-term fate of Freons. Accordingly, the Bunsen coefficients α of Freon-11

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0021-9568/82/1727-0324$01.25/0