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

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

Tracy Park, Timothy R. Rettich, Rubin Battino,* Dennis Peterson, and Emmerich Wilhelm[†]
Department of Chemistry, Wright State University, Dayton, Ohio 45435

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

[†] Visiting Associate Professor of Chemistry from Institut für Physikalische Chemie, Universität Wien, A-1090 Wien, Austria.

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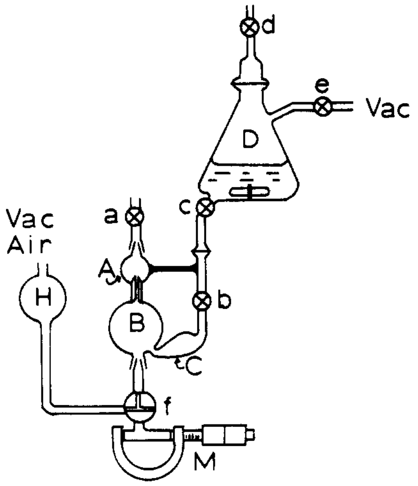

Figure 1. Schematic presentation of the new modified Scholander microgasometric apparatus. For details see text.

(CCl_3F), Freon-12 (CCl_2F_2), Freon-13 ($CClF_3$), Freon-14 (CF_4), Freon-116 (C_2F_6), Freon-C318 (c-C_4F_8), and sulfur hexafluoride dissolved in pure water at 298.15 K were measured at a total pressure of about 100 kPa. Two modifications of Scholander's microgasometric apparatus (*1*) were used in the experiment. The value of α for argon in water was also measured as a check on the modifications.

The results of Parmelee (*2*), though of poor precision, are the only available data for Freon-12 and Freon-13 in water. Reliable measurements concerning Freon-14 and sulfur hexafluoride are due to Ashton et al. (*3*). More recently, Freon-14 was included in a study by Wen and Muccitelli (*4*), which also contains the only available data for Freon-116 and Freon-C318 in water. The Bunsen coefficient for argon in water was taken from a review by Wilhelm et al. (*5*). No solubility data could be found for Freon-11 in water.

Materials

Freon-11 (99.9 mol % minimum purity), Freon-12 (99.0%), Freon-13 (99.0%), Freon-116 (99.6%), and SF_6 (99.9%) were supplied by the Matheson Gas Co. Freon-14 (99.7%) was from Air Products. Freon-C318 (99.9%) was from Union Carbide. Argon (99.998%) was from Airco, Inc. Freon-11 is a liquid at room temperature. A vapor sample was obtained by placing some Freon-11 in an exhaustively purged vessel, warming in hot water, and then sampling via a syringe through a side arm.

The water used was house "distilled" (reverse osmosis) water, which was passed through ion-exchange columns until its specific resistance was 5×10^6 Ω cm or better.

Apparatus

Two different versions of the Scholander microgasometric apparatus were housed in an air bath with temperature controlled to better than ±0.05 K. The main advantage of the air bath over a water bath (as used in previous studies involving a modified Scholander apparatus) is that the air bath accommodates the entire microgasometric apparatus, including the micrometer buret and the mercury reservoir. The first version used was the Scholander apparatus as modified by Steen (*6*), Douglas (*7*), and finally Weiss (*8*). The procedure for degassing the distilled water, storing it, and transferring it to the microgasometric apparatus was described by Douglas (*7*), as was the procedure for calculation of the Bunsen coefficient.

The second version is depicted in Figure 1. The design includes a more efficient method of degassing and transferring water to the microgasometric apparatus. Shown in Figure 1 are a 4-mL compensation chamber (A), a 10-mL equilibration chamber (B), and an 8-mL side arm (C). The ground-glass joint above A is inverted relative to Scholander's original design, in order to prevent grease from contaminating A and the rest of the system. High-vacuum Rotaflow valves a and b open to the atmosphere and an O-ring joint, respectively. Via this O-ring joint the microgasometric apparatus is connected to the degassing flask (D). Valves c–e are Rotaflow valves used to control the degassing and transfer of water, and f is a three-way glass stopcock for transferring mercury. Because of the greater amount of mercury required by the new design, a larger mercury reservoir (H) is used. The micrometer buret portion (M) of the apparatus remains unchanged from the original design.

Table I. Bunsen Coefficient (α) at 298.15 K for Six Freons, Sulfur Hexafluoride, and Argon Dissolved in Water[a]

	α	SD	no. of measurements
Freon-11 (CCl_3F)			
exptl	0.249 1	1.7	3
Freon-12 (CCl_2F_2)			
exptl	0.065 72	1.0	5
lit. (*2*)	0.051		
Freon-13 ($CClF_3$)			
exptl	0.017 71	1.7	5
lit. (*2*)	0.02		
Freon-14 (CF_4)			
exptl	0.004 751	2.1	5
lit. (*3*)	0.004 738		
lit. (*4*)	0.004 62		
Freon-116 (C_2F_6)			
exptl	0.001 206	6.4	3
lit. (*4*)	0.001 26		
Freon-C318 (c-C_4F_8)			
exptl	*0.002 689*	1.9	3
lit. (*4*)	0.002 65		
SF_6			
exptl	*0.005 440*	1.3	3
lit. (*3*)	0.005 451		
argon			
exptl	0.031 22	1.6	5
exptl	*0.031 05*	0.8	3
lit. (*5*)	0.031 21		

[a] For each set of measurements the standard deviation is given in percent, i.e., SD = $100\sigma/\alpha$.

The procedure for degassing and transferring distilled water in the new design is as follows. With no water in the system the mercury level is lowered to f, which is then closed along with a, d, and e. The entire system up to valve f is then evacuated, f is opened, and the mercury is allowed to rise to just above valve c, which is then closed. Water is then added to D and degassed by the method of Battino et al. (*9*). Valve f is opened to the mercury reservoir and c is opened, allowing the water to flow into C. Valves b and c are closed, and the entire apparatus is removed from the vacuum line. The mercury is removed from A by opening a until the mercury level falls to the top of the capillary tubing between A and B. The excess mercury is removed and A is half-filled with distilled water. The microgasometric apparatus is then transferred to the air bath and the gas sample is introduced by the method described by Douglas (*7*). The cap for A is replaced, and, after the temperature stabilizes, the procedure of Douglas (*7*) is subsequently followed. With either version 30 min to 2 h was required to reach equilibrium conditions.

Results and Discussion

Values of the experimental Bunsen coefficients at 298.15 K are shown in Table I, along with literature values for comparison. Experimental results which were obtained with the newly designed apparatus are italicized. The significantly larger uncertainty of the results for Freon-116 is a consequence of its extremely small solubility, which is close to the limit of the apparatus.

No significant difference was observed in the precision or accuracy of the results obtained by the two methods. However, the new version has several advantages over the Douglas version. The main advantage is that degassed water is transferred directly to the side arm of the microgasometric apparatus without the use of an intermediate transfer vessel or syringe. The risk of contamination by air is thereby practically excluded. The new method also allows continuous monitoring of the degassing process. Finally, the high-vacuum Rotaflow valve seals off the degassed water in the side arm from atmospheric contamination better than the Teflon plug used in the Douglas system.

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Viscosities and Densities at 298.15 K for Mixtures of Methanol, Acetone, and Water

Katsuji Noda,* Mitsuhisa Ohashi, and Kiyoharu Ishida

Department of Chemical Engineering, Shizuoka University, Hamamatsu 432, Japan

Viscosities and densities at 298.15 K are presented for the ternary methanol–acetone–water system and the binary mixtures composed of its constituents. The obtained data are correlated by using the McAllister equation of the four-body interactions.

Introduction

The viscosities of liquid mixtures are required for many practical problems concerning heat transport, mass transport, and fluid flow. Many viscosity–composition curves are not always simple functions of the compositions. The deviation from ideality is especially large for the systems including hydrogen bonds.

In this study, the viscosities and the densities at 298.15 K are determined for the binary methanol–acetone, acetone–water, and water–methanol systems and for the ternary methanol–acetone–water system. The viscosities of the binary systems are correlated by using the McAllister equation of the four-body interactions (*1*). This equation is expanded to the ternary system and used to correlate the data.

Experimental Section

Viscosities and densities were measured with an Ostwald-type viscometer and a 10-mL pycnometer, respectively. These are calibrated by using deionized distilled water. This equipment was immersed in a water bath at 298.15 ± 0.05 K. The estimated uncertainties in these measurements are ±0.002 μm^2 s^{-1} in viscosities and ±0.2 kg m^{-3} in densities. Methanol and acetone used in this experiment were chromato-grade reagents purchased from Wako-Pure Chemicals, Japan. As the physical properties for the pure liquids listed in Table I are consistent with values in the literature within the experimental error, these chemicals were used without further purifications.

Results and Discussion

Experimental viscosities and densities for the binary and ternary liquid mixtures are presented in Tables II and III.

Table I. Physical Constants of Pure Compounds at 298.15 K

	methanol	acetone
viscosity, mPa s	0.542 (this work)	0.301 (this work)
	0.541 (*3*)	0.302 (*2*)
	0.5445 (*4*)	0.304 (*4*)
density, kg m^{-3}	786.7 (this work)	784.7 (this work)
	786.9 (*3*)	784.3 (*2*)
	786.64 (*4*)	784.4 (*4*)
	786.53 (*5*)	785.01 (*5*)

Table II. Viscosity and Density Data for the Binary Systems at 298.15 K

x_1	viscosity, μm^2 s^{-1}	density, kg m^{-3}	x_1	viscosity, μm^2 s^{-1}	density, kg m^{-3}
Methanol (1) + Acetone					
0.0	0.384	784.7	0.3551	0.431	788.6
0.1219	0.415	786.3	0.4628	0.440	789.7
0.2100	0.413	787.2	0.6406	0.477	790.5
0.2292	0.418	787.5	0.7026	0.499	790.5
0.2781	0.419	788.0	0.7901	0.535	790.1
0.2939	0.421	788.0	0.8780	0.589	789.4
0.2977	0.418	787.9	1.0	0.689	786.7
0.3077	0.420	788.4			
Methanol (1) + Water					
0.0	0.893	997.1	0.4856	1.505	884.5
0.0507	1.126	983.4	0.5542	1.396	869.9
0.1125	1.385	966.9	0.7133	1.149	837.7
0.1411	1.480	960.2	0.8040	0.992	821.0
0.2276	1.657	941.1	0.8345	0.952	816.0
0.2927	1.683	925.7	0.9140	0.825	800.1
0.4198	1.593	898.4			
Acetone (1) + Water					
0.0583	1.239	974.2	0.5266	0.764	848.1
0.1460	1.454	943.9	0.6181	0.613	832.1
0.2056	1.393	925.0	0.7699	0.489	810.1
0.3020	1.211	897.8	0.8195	0.474	804.0
0.4597	0.869	861.4			

Several empirical and semiempirical relations have been used to represent the dependence of the viscosities on the compo-

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