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Solute Activity Coefficients at Infinite Dilution via Gas-Liquid Chromatography

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Gas-Liquid chromatographic specific retention volumes and solute activity coefficients at infinite dilution in the liquid phase have been measured for 10 nonpolar binary systems (methane through *n*-decane in *n*-hexadecane) and five systems (benzene through *n*-butylbenzene in *n*-hexadecane) with aromatic solutes and nonpolar substrate. All systems were measured at 40°, 70°, and 90° C. All of the solutes are volatile (vapor pressures of pure substances greater than 30 mm. of Hg in all but four cases) while the solvent was nonvolatile (vapor pressure less than 0.4 mm. of Hg) at all operating temperatures. The results allow interpolation of the activity coefficients of *n*-undecane through *n*-pentadecane on the three isotherms.

ACTIVITY coefficients determined in this work by gas-liquid chromatography (GLC) were found to agree well in the cases where comparison with those extrapolated from static measurements in the bulk liquid at well-defined equilibrium conditions were available (*2, 7, 14*). Other workers have found the same result for other systems (*4, 8, 11*).

The following expression developed by Martire (*9*) relates the solute activity coefficient at infinite dilution in the liquid phase (γ_b^∞) to the GLC measured specific retention volume (V_g):

$$\gamma_b^\infty = \frac{RT}{M_a p_b^0 V_g} \tag{1}$$

This relation can be developed using the definitions of the partition coefficient given by Kaiser (*6*) and Burchfield (*3*). Martire (*10*) and Martire and Pollara (*13*) give the following assumptions, implicit and explicit, as being basic in the derivation of Equation 1: both the vapor of the pure solute and the vapor phase above the solution behave ideally; and with the pure solute as the standard state and if x_b is solute mole fraction, then $x_b \rightarrow 1$, $\gamma_b \rightarrow 1$.

The meaning of the specific corrected retention volume is discussed in detail by Littlewood, Phillips, and Price (*8*). To paraphrase (*8*): under constant experimental conditions, the peak maximum for a particular vapor will appear at a characteristic time. This time, the retention time, is a function of the nature of the vapor, the stationary phase, and the column temperature. It is also dependent on experimental parameters such as the gas-flow rate, the dead volume, and the weight of stationary phase. Thus the retention volume V_r must be corrected to eliminate the effects of the experimental parameters. This is accomplished through the use of Equation 2.

EXPERIMENTAL

The experimental procedure was essentially the same as that used by other workers (*7, 10, 11, 13*). Only procedural and equipment differences will be discussed here.

The column was made from ⅛-inch O.D. copper tubing. The packing consisted of a 19.8% by weight stationary liquid phase of *n*-hexadecane on a solid support of 40- to 60-mesh C-22 Firebrick. The column was installed in a Wilkens Aerograph Hi-Fy Model 600-B equipped with a flame ionization detector. Column temperature was measured at six points with copper-constantan thermocouples, and the oven temperature was further monitored by use of a Beckman thermometer.

At thermal equilibrium, oven temperature was maintained to within ±0.3° C. during the course of the day and ±0.1° C. during short measurement periods. Carrier gas (nitrogen) flow rate was measured with a soap-film meter in conjunction with a Heuer stop watch. This watch was 10 seconds full scale and with divisions of 0.1 second. This unit was also used in measuring retention times for the calculation of the retention volume, V_r. The inlet pressure was controlled and measured to within ±3 mm. of Hg by a needle valve and calibrated pressure gauge. The column outlet pressure was always atmospheric. Blended liquid samples

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of 0.1 μl. were injected with a Hamilton 1-μl. syringe and gas samples were injected with a Yale 1-cc. syringe.

DATA REDUCTION

The method of Martire (*10*) and Martire and Pollara (*13*) was used with the equation developed by Littlewood, Phillips, and Price (*8*) or Johns (*5*):

$$V_g = \frac{V_r}{W} \cdot \frac{T}{T_f} \cdot \frac{P_o - P_w}{P_o} \cdot 3/2 \cdot \frac{(P_i/P_o)^2 - 1}{(P_i/P_o)^3 - 1} \tag{2}$$

By combining Equations 1 and 2, γ_b^∞ can be obtained from directly measured and known quantities. The vapor pressures required were obtained from the literature (*1*, *15*).

The substrate used was *n*-hexadecane of purity more than 99.9 mole %.

RESULTS

The values of V_g are presented in Table I. Table II presents the values of the activity coefficients (γ_b^∞) at infinite dilution calculated using the data in Table I. Error analysis indicates that the activity coefficients calculated from Equation 1, with the exception of those for methane thru propane, are good to ±0.008 or better. This is in good agreement with the estimate of ±0.01 by Martire and Pollara (*12*). Figure 1 shows a plot of the normal paraffins activity coefficient at infinite dilution *vs.* carbons in the chain. It also allows interpolation of activity coefficients of *n*-undecane thru *n*-pentadecane in *n*-hexadecane systems which were not determined in this study.

Table I. Specific Retention Volumes, Cc.

	40° C.	70° C.	90° C.
Methane	0.26	0.19	0.15
Ethane	2.24	1.33	0.97
Propane	8.84	4.80	3.35
n-Butane	30.73	13.63	9.75
n-Pentane	100.7	40.45	24.21
n-Hexane	305.8	110.1	63.86
n-Heptane	878.6	277.6	137.3
n-Octane	2599	692.1	327.5
n-Nonane	6925	1685	754.8
n-Decane		3938	1629
Benzene	629.5	217.0	127.6
Toluene	1860	647.5	301.7
Ethyl benzene	5092	1316	638.8
Propyl benzene		2890	1668
n-Butyl benzene		7012	2896

Table II. Solute Activity Coefficients

	40° C.	70° C.	90° C.
Methane	0.7_7	0.7_5	0.7_4
Ethane	0.7_9	0.7_8	0.7_7
Propane	0.82	0.8_1	0.8_0
n-Butane	0.85	0.84	0.83
n-Pentane	0.87_0	0.85_9	0.85_2
n-Hexane	0.89_2	0.88_2	0.87_6
n-Heptane	0.91_1	0.90_3	0.89_8
n-Octane	0.92_9	0.92_3	0.91_9
n-Nonane	0.94_5	0.94_0	0.93_7
n-Decane		0.95_6	0.95_4
Benzene	0.65_0	0.62_0	0.59_0
Toluene	0.67_4	0.64_8	0.62_4
Ethyl benzene	0.69_7	0.67_2	0.65_4
Propyl benzene		0.69_5	0.67_9
n-Butyl benzene		0.71_5	0.70_2

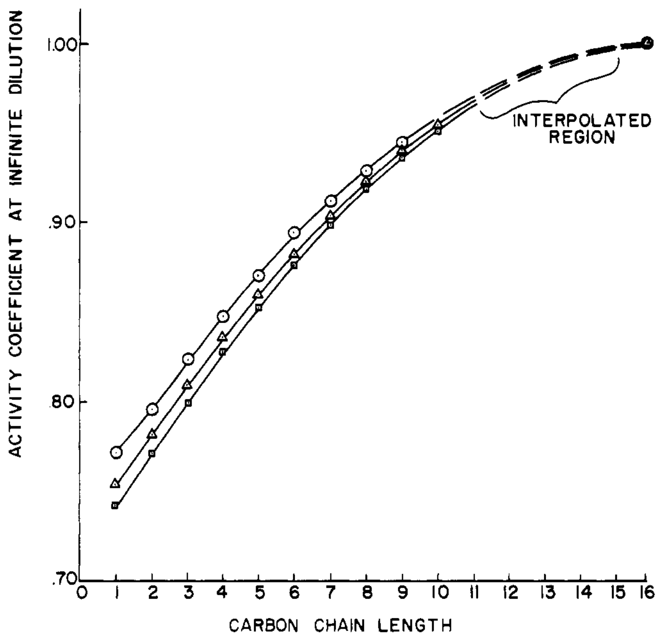

Figure 1. Activity coefficient at infinite dilution vs. carbon chain length for normal paraffin solutes on *n*-hexadecane substrate

○ 40° C.

△ 70° C.

□ 90° C.

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NOMENCLATURE

M_a = Molecular weight of stationary liquid substrate (component *a*)

p_b^0 = Vapor pressure of the pure saturated solute vapor (component *b*) in mm. of Hg abs.

P_i = Column inlet pressure in mm. Hg

P_o = Column outlet pressure in mm. Hg

P_w = Vapor pressure of water at T_f in mm. of Hg abs.

T = Column temperature in ° K.

T_f = Temperature of soap-film meter in ° K.

V_g = Specific corrected retention volume of the solute in cubic centimeters of carrier gas per gram of liquid

V_r = Retention volume of the solute in cubic centimeters of carrier gas measured from the air peak at the temperature T_f

W = Weight of the substrate in grams

x_b = Mole fraction of the solute

γ_b = Activity coefficient of the solute

γ_b^∞ = Activity coefficient of the solute at infinite dilution

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The Reaction of Dioxygen Difluoride with Sulfur Oxides and with Sulfur Oxyfluorides

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Dioxygen difluoride (O_2F_2) is considerably less stable than previously reported. The reaction of O_2F_2 with SO_2 at −160° C. produced mainly F_2SO_2 and lesser amounts of FSO_2OOF and FSO_2OSO_2F. The FSO_2OSO_2F was accounted for by several routes. The F_2SO_2 did not react further with O_2F_2. The reaction of O_2F_2 with the SO_3 produced equimolar amounts of FSO_2OF and $F_2S_2O_6$, which was resistant to further attack of O_2F_2. In contrast to previous attempts to produce SOF compounds by allowing H_2SO_4 to react with fluorinating agents, small amounts of FSO_2OF were formed when O_2F_2 and H_2SO_4 were allowed to react. H_2SO_5 was more reactive toward O_2F_2 than H_2SO_4. The reaction of O_2F_2 and F_2SO produced F_4SO, which did not react further with O_2F_2.

THE CHEMISTRY of dioxygen difluoride (O_2F_2) is unusual since it reacts with most substances at temperatures of −160° C. or below (*12*). Even at these low temperatures, a violent reaction or an explosion occurs when O_2F_2 reacts with any organic material and most inorganic materials containing hydrogen. Many other reactions of O_2F_2 are so violent that simple degradation products result. The reactions of O_2F_2 with various sulfur oxides and with sulfur oxyfluorides can be controlled, and products are formed at −100° C. or lower. Temperatures of 200° to 300° C. are necessary for the formation of these products by conventional fluorination reactions.

RESULTS

Stability of O_2F_2. It was necessary to understand the decomposition of O_2F_2 before studying its chemistry so that decomposition would not be confused with actual reaction. The completeness of a reaction was usually assessed by the disappearance of the red color of the O_2F_2.

O_2F_2 decomposes to oxygen and fluorine, and from all indications to date, it probably decomposes via fluorine atoms. Since fluorine atoms react with most or all of the materials studied, O_2F_2 can act merely as a source of fluorine atoms—i.e., as a simple fluorinating agent. But if the actual chemistry of O_2F_2 is to be determined, the reaction conditions must be those under which O_2F_2 is stable. It is difficult to achieve this ideal situation, since heat released during the reaction serves to decompose the unaltered O_2F_2. However, some success was achieved.

Frisch and Schumacher (*5, 6*) have reported that liquid O_2F_2 decomposes at the rate of 4.3% per day at −78° C. and that its half-life at −50° C. is 220 minutes. The authors found, however, that O_2F_2 is considerably less stable than previously reported and observed a 4% per day decomposition at −160° C. This decomposition was calculated from the average quantities of oxygen and fluorine formed during a 1-day period. Data were not taken over an extended period of time because we did not intend to study the kinetics of decompositions of O_2F_2. Since most of the reactions of O_2F_2 are complete in a matter of seconds or minutes, it was thought that if the reactions were carried out at −160° C. or lower, very little decomposition of O_2F_2 would occur.

Reaction of O_2F_2 with SO_2. The reaction of O_2F_2 with sulfur dioxide (SO_2) at −160° C. was previously studied in detail (*11*). The main reaction is that shown in Equation 1, and two minor products (pyrosulfuryl fluoride, FSO_2OSO_2F, and peroxysulfuryl difluoride, FSO_2OOF) are formed via an OOF intermediate.

$$SO_2 + O_2F_2 \rightarrow F_2SO_2 + O_2 \qquad (1)$$

The main product of this reaction is the same as that reported for the reaction of fluorine with SO_2 (*3*), however pentafluorosulfur hypofluorite was a minor product in the latter reaction.

In further elucidating the chemistry of the SO_2–O_2F_2 system, we found that F_2SO_2 does not react with O_2F_2; actually a stable solution is formed. Its stability is further demonstrated by the facts that F_2SO_2 is stable in the presence of decomposing O_2F_2 (or F atoms) and is also unaffected by passage through a silver difluoride (AgF_2) catalytic reactor with excess fluorine (*3*).

The presence of $F_2S_2O_5$ as a reaction product of O_2F_2 and SO_2 could have occurred by several routes. Photolytic reactions were used to simulate the free-radical conditions caused by the presence of fluorine atoms, and room-temperature reactions were used to simulate the conditions that the products were exposed to during separation. Although peroxysulfuryl difluoride, FSO_2OOF, is quite sta-