ments in the literature that water is strongly hydrogen-bonded to siloxanes, as for example, the explanation given for the strong adsorption of water on glass (*7*). Contrast this value of 0.2 kcal./mole for E_H in dimethylsiloxanes with the value of 2.26 kcal./mole observed for diethyl ether (*1*). This low value, however, observed for E_H-siloxane is in accordance with previous observations on the weak basicity of the siloxane bond in organosiloxanes (*5*).

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Derivatives of o-Hydroxy- and o-Mercaptothioanisole

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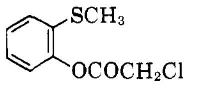
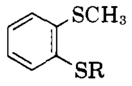
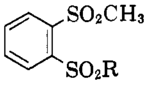
SEVERAL NEW and readily accessible derivatives of *o*-hydroxy- (I) and *o*-mercaptothioanisole (II) have been prepared (Table I). Conversion of *o*-aminothioanisole into I (*4*) was achieved by diazotization followed by hydrolysis (*5*). Reaction of I with chloroacetyl chloride (*2*) afforded 2-(2′-chloroacetoxy)phenylmethyl sulfide (III) in good yield.

o-Mercaptothioanisole was prepared by the general procedure described by Livingstone (*6*) and by Gordella and Passerini (*3*), with one exception; the intermediate xanthate ester was reduced with lithium aluminum hydride (*1*) instead of hydrolyzed with potassium hydroxide. The method involving reduction gave yields of 30–31%, which compares favorably with the 21% yield reported for potassium hydroxide hydrolysis (*6*). The disulfide of II (*7*) as well as some nitrophenyl derivatives (*3*) have been reported. Compounds IVa and IVb were prepared by allowing II to react with benzyl chloride and phenacyl chloride, respectivly, in hot sodium ethoxide solution. Oxidation of IVa and IVb with 30% hydrogen peroxide in glacial acetic acid led to the disulfonyl compounds Va and Vb, respectively. When II was warmed to 80° with phenylisocyanate, phenylisothiocyanate or α-naphthylisocyanate, and then cooled, the corresponding urethan derivatives IVc, IVd and IVf were obtained in good yields. The diphenylcarbamoyl ester (IVe) was also prepared.

Table I. Properties of Derivatives of o-Hydroxy- and o-Mercaptothioanisole


III


IV


V

Compound		R	Name	% Yield	M.P.[a]	Recryst. Solvent	Sulfur Anal. Calcd.	Sulfur Anal. Found
III			2-(2′-Chloroacetoxy)phenylmethyl sulfide	75	94–95	EtOH	14.8	14.7[b]
IV	a	$C_6H_5CH_2$	2-Benzylmercaptomethylmercaptobenzene	75	80–81	CH_3OH	26.0	25.9
	b	$C_6H_5COCH_2$	ω-(2-Methylmercaptophenylmercapto)acetophenone	80	81	CH_3OH	23.4	23.4
	c	C_6H_5NHCO	S-(2-Methylmercaptophenyl)-*N*-phenylthiocarbamate	60	133.5–135	$CHCl_3$–(hex.)	23.3	23.1
	d	C_6H_5NHCS	2-Methylmercaptophenyl-*N*-phenyldithiocarbamate	64	109.5–111	Abs. alc.	33.0	33.3
	e	$(C_6H_5)_2NCO$	S-(2-Methylmercaptophenyl)-*N*, N-diphenylthiocarbamate	44	123–124	$CHCl_3$–(hex.)	18.2	18.2
	f	α-$C_{10}H_7NHCO$	S-(2-Methylmercaptophenyl)-*N*-α-naphthylthiocarbamate	60	169.5–171	$CHCl_3$–(hex.)	19.7	19.5
V	a	$C_6H_5CH_2$	2-Benzylsulfonylmethylsulfonylbenzene	65	169.5–171	$EtOH$–H_2O	20.7	20.5
	b	$C_6H_5COCH_2$	ω-(2-Methylsulfonylphenylsulfonyl)acetophenone	59	143–144.5	CH_3OH	19.0	18.9

[a] Melting points are corrected; [b] *Anal.* Calcd: C, 49.9; H, 4.2. Found: C, 50.2; H, 4.4.

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Diffusion Coefficients in Hydrocarbon Systems

The *n*-Butane–*n*-Decane System in the Liquid Phase

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Measurements of the Chapman-Cowling diffusion coefficient were carried out at pressures up to 600 p.s.i.a. at temperatures between 220° and 340° F. in the liquid phase of the *n*-butane–*n*-decane system. The Chapman-Cowling diffusion coefficient yielded much smaller variations with state than did the Fick diffusion coefficients. The relationships between these two types of coefficients are included.

EXPERIMENTAL INFORMATION available concerning the molecular transport of the lighter hydrocarbons in the liquid phase of binary hydrocarbon systems indicates that there is a significant variation in the Chapman-Cowling diffusion coefficient (*2*) for a particular binary system with changes in state. As a result of this variation it is desirable to carry out experimental investigations to establish the value of the Chapman-Cowling diffusion coefficient over the range of conditions of industrial interest. The current investigation relates to the molecular transport in the liquid phase of the *n*-butane-*n*-decane system at pressures up to nearly 600 p.s.i.a. in the temperature interval between 220° and 340° F.

METHODS AND EQUIPMENT

The experimental approach involved the introduction of *n*-butane in the gas phase at a known rate into an isochoric chamber containing a heterogeneous mixture of *n*-butane and *n*-decane. Initially, this binary mixture was brought to physical equilibrium by mechanical agitation. After quiescent conditions had been obtained, the pressure was increased a predetermined amount by addition of *n*-butane. The quantity of the lighter hydrocarbon required to maintain the system under isobaric conditions at the newly established elevated pressure was determined as a function of time.

The equipment has been described (*10, 12*). Small vertical tubes were provided in the lower part of the isochoric vessel to decrease the influence of local accelerations upon the molecular transport. The temperature was determined by a strain-free, platinum resistance thermometer (*4*) and was known relative to the international platinum scale within 0.02° F.

Pressure was measured by a balance involving a piston-sleeve combination and was known within 0.1 p.s.i.a. or 0.05 per cent, whichever was the larger measure of uncertainty. Isobaric conditions were maintained by means of a manostat (*15*). The *n*-butane was introduced in the liquid phase by an injector (*10*). Liquid *n*-butane was evaporated by passage through a conditioning coil of small dimensions located in the oil bath surrounding the isochoric vessel. Physical values of the position of the injector were recorded automatically as a function of time. The rate of introduction of *n*-butane was controlled from an analog output of the manostat. Variations in pressure during a set of diffusion measurements were not more than 0.05 p.s.i.a. No difficulties were experienced from the evaporation of the *n*-butane in the conditioning coil prior to its introduction into the diffusion vessel.

Methods of analysis used in other studies (*8*) were applied in the resolution of the experimental data. From the assumption of local equilibrium (*3*) at the gas-liquid interface, the following expression may be derived (*8*) to establish the Chapman-Cowling diffusion coefficient:

$$D_{Ckj} = \left[\frac{\pi \underline{m}_{kc}^{2}}{4A_{i}^{2}\theta(\sigma_{kb} - \sigma_{kbo})^{2}}\right]\left[1 - \frac{\bar{V}_{kl}^{*}(\sigma_{kb} - \sigma_{kd})}{1 - \bar{V}_{kl}^{*}\sigma_{kd} - \bar{V}_{jl}^{*}\sigma_{jd}}\right]^{2} \qquad (1)$$

In the foregoing expression the asterisks indicate values of the quantity in question for the conditions existing in the liquid phase at bubble point during a particular set of isobaric, isothermal measurements. The effect of hydrodynamic velocity (*10*) and the change in volume of the liquid phase were taken into account. Equation 1 is limited to a system where the state of the liquid phase at the interface is established from its prevailing temperature and pressure. Measurements obtained at physical equilibrium (*9, 11*) were employed to evaluate the partial volumetric data in the liquid and gas phases.