ρ_{ij} = coefficient as defined by $G_{ij} = \rho_{ij} \exp(-\alpha_{ij} \tau_{ij})$
τ_{ij} = coefficient as defined by $\tau_{ij} = (g_{ij} - g_{jj})/RT$
ϕ_1 = volume fraction of alcohol monomer
ϕ_{OB} = volume fraction of hydrocarbon at free state
ϕ = volume fraction
ψ_i = vapor phase fugacity coefficient of component i
ψ_i^s = vapor phase fugacity coefficient of pure component i at system temperature and P_i^s

Subscripts

A = alcohol
AB = alcohol-hydrocarbon complex formation
B = hydrocarbon
i = component

Superscripts

o = properties of a pure substance in its particular reference state
E = excess property
L = liquid
V = vapor

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Liquid-Phase Diffusion Coefficients for Dissolved Gases: Systems Chlorine–Carbon Tetrachloride and Hydrogen Chloride–Ethylene Glycol

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A steady-state diaphragm cell method has been used to measure the liquid-phase diffusion coefficients of chlorine in carbon tetrachloride and hydrogen chloride in ethylene glycol. In the chlorine–carbon tetrachloride system, it is shown that the Wilke-Chang equation correlates the experimental values very closely.

Experimental data on the liquid-phase diffusion coefficients of dissolved gases are sparse, especially for systems in which the gas solubility is high. The theoretical interpretation of gas absorption rates in such cases has therefore often had to rely on diffusivity values predicted by one of the many correlations available in the literature. This paper reports measured values for two such high-solubility systems which have not been previously investigated.

Experimental

The technique employed is a steady-state diaphragm cell method first described by Tham et al. *(4)*. In brief, the apparatus consists of two chambers, each of volume 500 cm^3, separated by a vertical sintered-glass diaphragm of 9-cm diam and mean pore size 5 μ. In one chamber, the liquid solvent is kept saturated by a continuous stream of solute gas, while diffused solute is continually stripped from solvent in the other chamber by a stream of nitrogen. When steady state is attained, a direct measure of the diffusion rate is obtained by determining the total amount of solute gas in the nitrogen stream in a known time. Hydrogen chloride and chlorine are absorbed in $N/10$ sodium hydroxide and 10 wt % potassium iodide solutions, respectively. Subsequent titrations are reproducible to ±0.05 ml. The diffusion coefficient may then be calculated by applying a cell constant found from experiments using N/10 potassium chloride solution, a substance whose diffusion coefficient is well established *(2)*. The diffusion cell is completely immersed in a water bath which is thermostatically controlled to ±0.05°C. Measurements were taken at 5°C intervals in the range 25–45°C.

Flow rates of approximately 30 ml/min of presaturated gas ensure that good liquid mixing is obtained in the cell compartments, effectively eliminating the possibility of density-induced streaming through the vertical diaphragm. Careful balancing of the pressure drop in the gas exit lines ensures that pumping effects are also negligible. This technique, which has been shown to produce results equivalent to those from the usual diaphragm cell *(4)*, has several advantages. It does not require handling of liquids containing dissolved gas, and an experiment may be completed in about 2 hr. Also, since measurement is not made until steady state is reached, adsorp-

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Table I. Experimental Results

Temp, °C	Satn concn of solute, gm/cm^3	Diffusion flux through diaphragm, gram/hr	Diffusion coeff $D \times 10^5$, cm^2/sec
	Chlorine–carbon tetrachloride		
25	0.130	0.305	2.88
30	0.115	0.299	3.17
35	0.104	0.283	3.34
40	0.091	0.267	3.61
45	0.079	0.249	3.86
	Hydrogen chloride–ethylene glycol		
25	0.370	0.0485	0.161
30	0.358	0.0510	0.175
35	0.348	0.0573	0.202
40	0.336	0.0654	0.239
45	0.325	0.0742	0.280

tion of the diffusing gas on the diaphragm is not a problem.

The gases used were obtained from ICI Ltd. The minimum purities were 99.9% for chlorine and 99.6% for hydrogen chloride. Carbon tetrachloride and ethylene glycol were supplied by Fisons Ltd. with specified purities of 99.98% and 99.7% respectively. Full experimental details are available in ref. *3*.

Results and Discussion

Diffusion fluxes and coefficients, together with the corresponding temperatures and concentrations are listed in Table I. Each value of D is the mean of three determinations which had a maximum deviation of less than 0.5%.

The coefficients measured by this technique are necessarily integral values for a concentration range from effectively zero to the saturation value. A disadvantage of this characteristic is that there is a fixed relationship between the solute concentration and temperature, which means that their separate effects on the diffusion coefficient cannot be evaluated. However, there appears to be no reason why this could not be overcome by operating the equipment at several different pressures for each temperature.

Table II. System Chlorine–Carbon Tetrachloride

Temp, °C	μ, cP	$D \times 10^5$ (exptl), cm^2/sec	$D\mu/T \times 10^8$	$D \times 10^5$ (Eq 1), cm^2/sec
25	0.95	2.88	9.18	2.80
30	0.89	3.17	9.31	3.03
35	0.84	3.34	9.11	3.27
40	0'79	3.61	9.11	3.53
45	0.75	3.86	9.11	3.78

For the chlorine–carbon tetrachloride system, which exhibits an almost ideal solubility relationship, the parameter $D\mu/T$ is virtually constant, as suggested by the Stokes-Einstein equation. The empirical correlation of Wilke and Chang *(5)* also requires this parameter to be constant

$$D = 7.4 \times 10^{-8}\, T \frac{(\phi M)^{0.5}}{\mu V^{0.6}} \qquad (1)$$

Using their recommended value of $\phi = 1.0$ for carbon tetrachloride, the above equation gives a good prediction of the measured diffusion coefficients, as shown in Table II.

This agreement is perhaps surprising, since the Wilke-Chang correlation is only claimed to be valid for predicting diffusion coefficients at infinite dilution, which certainly does not correspond to the experimental conditions in this study.

In the case of the hydrogen chloride–ethylene glycol system, the parameter $(D\mu/T)$ varies by about 15% in the range 25–45°C, a not unexpected result in view of the complex hydrogen bonding which occurs *(1)*.

Nomenclature

D = diffusion coefficient, cm^2/sec
M = molecular weight of the solvent
V = molar volume of the solute, cm^3/g-mol
T = absolute temperature, K
μ = viscosity of solvent, cP
ϕ = association factor in Wilke-Chang correlation

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