Oxygen Diffusivities in Organic Liquids at 293.2 K

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Oxygen diffusivities in pure and mixed organic liquids were determined in a polarographic diffusion cell at 293.2 K. The results were compared to some widely applied correlations. An empirical relation with the liquid viscosity to the power of $-{}^2/_3$ is suggested.

The diffusivity D_L of gaseous reactant in the liquid phase is one of the key parameters in gas/liquid mass-transfer operations. A recent study on the volumetric mass-transfer coefficients ($k_L a$) for oxygen in bubble columns with organic liquids (1) was the incentive for this investigation. When correlating the $k_L a$ values with the operating conditions and the liquid properties, the influence of the diffusivity estimates turned out to be rather strong. There are only three experimental oxygen diffusivities at higher temperatures reported by Krieger (2). The predictions of the various suggested correlations often differ by more than a factor of 2. Therefore, our own measurements were carried out.

Experimental Section

The oxygen diffusivity was studied in a polarographic diffusion cell similar to the one applied by Akita (3) to aqueous electrolyte solutions. It consisted of a conventional oxygen electrode (WTW EO-90) and a cap made of poly(tetrafluoroethylene) (PTFE) (Figure 1). The cell was placed in a jacketed glass vessel kept at the temperature of 293.2 ± 0.1 K. The air in the vessel was saturated with vapor (pressure p_L) from the lagoon on the top of the cap. The diffusion path was defined by a removable glass tube with 2.2-mm inner diameter and 9.5-mm height. The dimensions were adjusted to the high values of the oxygen transmissibility (ratio of D_L to Henry's constant H_L) encountered in organic liquids but could easily be modified by using a different glass tube. To protect the PTFE membrane of the electrode, a layer of the same material was sintered onto the bottom of the glass tube. The reproducibility was considerably improved by defining the gas-side surface of the liquid layer with a PTFE membrane, thus avoiding variation of the meniscus. The reading of the oxygen electrode was recorded on a chart recorder. Usually a steady value was reached after 6-12 h. However, in some cases the reading kept on decreasing for days (alcohols, nitrobenzene) or suddenly dropped to zero (carbon tetrachloride). No data are reported for these liquids. There were 11 pure organic liquids and 7 organic mixtures that could be studied. The chemicals were obtained from Merck at the highest available purity except for ligroin (alkanes with bp range of 373-413 K). The viscosities of the liquids were measured with capillary viscometers. More experimental details were described elsewhere (4).

The steady reading of the electrode is proportional to the diffusional flow of oxygen (N). The units of N may be arbitrary.

Table I. Oxygen Diffusivities in Pure Organic Liquids and Liquid Viscosities at 293.2 K

liquid	$10^9 D_L$, m²/s	$10^3 \mu_L$, Pa s
acetone	6.68	0.327
	5.80	
	5.08	
benzene	3.46	0.652
n-butyl acetate	3.22	0.732
cyclohexane	3.29	0.977
decalin	1.60	2.56
1,2-dichloroethane	2.67	0.820
1,4-dioxane	1.92	1.303
	1.97	
	2.01	
ethyl acetate	3.46	0.455
ethylbenzene	2.94	0.669
toluene	4.38	0.590
m-xylene	3.63	0.620

As outlined by Akita (3), the concept of resistances-in-series leads to the equation

$$N = \frac{(P_{baro} - p_L)0.2094}{A + B\dfrac{H_L D_W}{D_L H_W}} \tag{1}$$

where

$$A = \frac{h_{M1} H_{M1}}{D_{M1} a_{M1}} + \frac{h_{M2} H_{M2}}{D_{M2} a_{M2}} + \frac{h_E H_E}{D_E a_E} \tag{2}$$

and

$$B = \frac{h_L H_W}{a_L D_W} \tag{3}$$

It was not necessary to know the individual heights (h) and cross sectional areas (a) of the various sections (indices: E, electrolyte; M1, M2, membranes; L, organic liquid; W, water). Only the effective values of A and B were determined by calibration. From the reading of N_A with moist air in the diffusion path, one obtains

$$A = \frac{(P_{baro} - p_W)0.2094}{N_A} \tag{4}$$

and from the reading of N_W in an additional run with water, it follows

$$B = \frac{(P_{baro} - p_W)0.2094}{N_W} - A \tag{5}$$

The calibration was repeated regularly to track the slow decrease in electrode sensitivity. From the steady reading of N_L with an organic liquid in the diffusion path, the parameter group $(D_L/D_W)(H_W/H_L)$ can be evaluated from eq 1. The diffusion coefficients D_L were calculated by introducing the experimental Henry's constants reported separately (5) and the value of D_W = 2.1 × 10⁻⁹ m²/s (6).
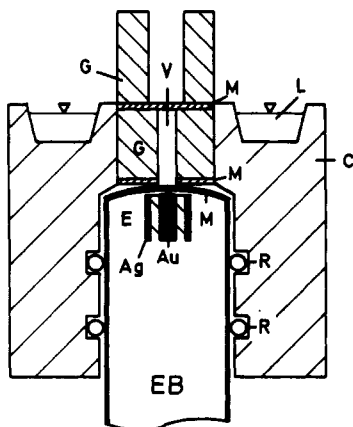
Figure 1. Diffusion cell: Ag, Ag anode; Au, Au cathode; C, PTFE cap; E, electrolyte solution; EB, electrode body; G, glass tube; L, liquid lagoon; M, membrane; R, ring gasket; V, liquid-filled volume.

Table II. Oxygen Diffusivities in Mixed Organic Liquids and Liquid Viscosities at 293.2 K

liquid 1/liquid 2	$x_2{}^a$	$10^9 D_L$, m²/s	$10^3 \mu_L$, Pa s
ligroin (bp, 373–414 K)		3.29	0.538
benzene/cyclohexane	0.069	3.61	0.634
toluene/ethanol	0.050	5.00	0.568
toluene/ethanol	0.136	5.13	0.587
toluene/ethanol	0.280	4.57	0.616
toluene/ethanol	0.550	4.30	0.731
toluene/ethanol	0.735	4.00	0.861

$^a x_2$ = mole fraction.

The accuracy of the evaluated diffusivities decreases at higher transmissibilities because of the nonlinear dependence of D_L/H_L on N (eq 1). The reproducibility of the results varied correspondingly from ±1% (1,4-dioxane) to ±14% (acetone). A detailed discussion of this trend was given elsewhere (4).

Results and Discussion

The oxygen diffusivities determined in pure and mixed organic liquids are listed in Tables I and II, respectively, together with the liquid viscosities (μ_L). There are no literature data to which the results could be compared. Instead, the deviations of some widely applied correlations from the experimentally determined diffusivities in pure liquids are listed in Table III. The best agreement is observed with the correlations of Scheibel (8) and Reddy and Doraiswamy (9), respectively. Since the deviation is rather systematic in some other cases, the relations were modified with the optimized factors listed in Table III. All modified relations show similar mean relative errors in the range of 17–19%. The error in just optimizing the factor in the Stokes–Einstein relation was in the same range (18%). The improvement by considering the molar volumes or molar weights appears small. More important seems to be that most relations retain the high effect of liquid viscosity of the Stokes–Einstein relation. An exponent of –0.66 is obtained by empirically correlating the oxygen diffusivities in pure liquids with the viscosity:

$$D_L = (2.6 \times 10^{-11}) \mu_L{}^{-2/3} \tag{6}$$

Table III. Comparison of the Experimental Oxygen Diffusivities in Pure Liquids (Table I) to Various Correlations

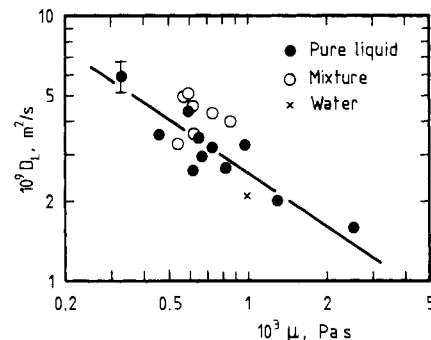| ref	mean relative error, %	
	orig eq	modified eq (factor)
Wilke, Chang (7)	35.1	19.2 (0.84)
Scheibel (8)	27.1	18.0 (1.15)
Reddy, Doraiswamy (9)	28.1	16.7 (1.26)
Lusis, Ratcliff (10)	36.6	17.0 (0.59)
Sovova (11)	66.5	18.5 (0.60)
Diaz et al. (12)	45.1	16.7 (0.69)
$D_L = (2.1 \times 10^{-12}) \mu_L{}^{-1}$		18.1
$D_L = (2.6 \times 10^{-11}) \mu_L{}^{-2/3}$		11.1

Figure 2. Effect of liquid viscosity on the oxygen diffusion coefficient in organic liquids at 293.2 K.

This exponent was also suggested by Herrera (13). Equation 6 describes the experimental data in Table I with 11% mean error (Figure 2). For the toluene/ethanol mixtures also represented in Figure 2, eq 6 is low as for pure toluene but the viscosity effect is similar. The viscosity exponent of $-2/3$ may therefore be a better basis than the Stokes–Einstein relation for any more sophisticated correlation.

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