Interaction of Activated Carbon with Dissolved Oxygen

The sorption of dissolved oxygen on activated carbon was characterized with manometric and packed column apparatus. All carbons tested, granular and powdered, virgin and reactivated, sorbed 150 to 600 μmole of oxygen/g after run times up to 1 700 hr., but still not at equilibrium. The rate data generally conform to a model of sorption limited by intraparticle diffusion. Carboxylic acid groups increase by about 200 μeq/g as a result of dissolved oxygen sorption, which can account for at least 10 to 50% of the oxygen sorbed. Also, about 5% of the sorbed oxygen can be eluted into deoxygenated water.

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SCOPE

Activated carbon treatment of wastewaters usually involves extensive pilot scale development for each new application. Rational methods for process analysis and design are, in practice, limited by factors such as biological growth or changes in the nature of the activated carbon itself in the course of service. This paper is concerned with the latter point, in particular, with changes that result from long-term exposure to dissolved oxygen.

It is well known that activated carbons can sorb oxygen. However, studies since Garten and Weiss (1957) apparently neglect the possibility that dissolved oxygen, like more powerful oxidizing agents, could affect the surface oxide groups and thereby change the sorption characteristics for organic matter. Recent data on organic sorption in the presence of dissolved oxygen suggest that this may occur. (See Supplementary material.)*

Experimental studies were undertaken to determine the rates and extent of dissolved oxygen sorption by activated carbon, without the complications of bacterial growth and poorly characterized organic solutes. This was done with both manometric and packed column apparatus. Also, acidic oxide groups were determined before and after the oxygen sorption.

CONCLUSIONS AND SIGNIFICANCE

All types of activated carbons tested, granular or powdered, virgin or reactivated, sorbed dissolved oxygen. The total sorptions for run times up to 1 700 hr., but still not at equilibrium, are on the order of 150 to 600 μmole/g (10 to 40 mg/g). The rate data generally conform to a model of sorption limited by intraparticle diffusion, with rate factors on the order of 5 to 30 μmole/g-hr.$^{1/2}$ for the characteristic square-root-time dependency of the model. These results provide a base line not available previously for oxygen uptake in the presence of organic solutes, bacterial growth, or catalytic oxidation processes.

Sorption of dissolved oxygen increases acidic surface oxides by about 200 μeq/g. This shows up as increased base sorption capacity, particularly in the pH ranges for carboxylic acid groups. Oxidation reactions are postulated which can account for at least 10 to 50% of the sorbed oxygen. Also, about 5% of the sorbed oxygen can be eluted into deoxygenated water.

SURFACE OXIDES ON ACTIVATED CARBON

Of the various functional groups present on the extended hexagonal microcrystallite lattice of activated carbon, those containing oxygen are particularly important. Oxygen can account for 2 to 25% by weight of an activated carbon, at least half of it being present in the form of surface oxide groups (Boehm et al., 1964). This includes acidic oxides such as carboxyl, phenol, lactone, and quinone, and basic groups such as chromene (benzpyran) and chromenol. The presence of these groups is corroborated by spectroscopic studies and by evidence from methylation and hydrolysis reactions (Snoeyink and Weber, 1967; Mattson and Mark, (1971). For a given activated carbon, the nature and extent of the surface oxide groups depend on its temperature of activation and on its exposure to oxygen during and after activation.

Oxide groups increase the polarity of activated carbon. Thus, sorption of nonpolar species should be impaired as a result of increasing surface oxides, but polar species may be sorbed to a greater or lesser extent, depending on their specific oxide-sorbate interactions. Coughlin (1970) used potassium manganate solution to increase the acidic oxides on a commercial activated carbon from 0.38 to 4.15 meq/g. This lowered both the capacity and the rate of sorption of dextrose, phenol, and sodium benzenesulfonate, but it increased the capacity for urea somewhat. Snoeyink et al. (1974) found that oxidation with aqueous chlorine increased the acidic oxides by as much as 2 meq/g, which decreased the sorption capacity for phenol and nitrophenol by about 50%.

Dissolved oxygen also can affect the surface oxides. Garten and Weiss (1957) established the mechanism of formation of basic oxides by oxidation of chromene groups in acidic solution, with reduction of dissolved oxygen to hydrogen peroxide. However, subsequent investigations apparently have neglected effects of dissolved oxygen on the oxide groups.

APPARATUS

A manometric Biological Oxygen Demand Analyzer (Hach Chemical Co., Model 2737) was used to measure oxygen sorption by slurries of activated carbon and to prepare well-characterized oxidized carbons. It consisted of five bottle-manometer sets like the one shown in Figure 1, with a common motor-belt-pulley arrangement to drive the magnetic stirrers.

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* See paragraph on page 1204.

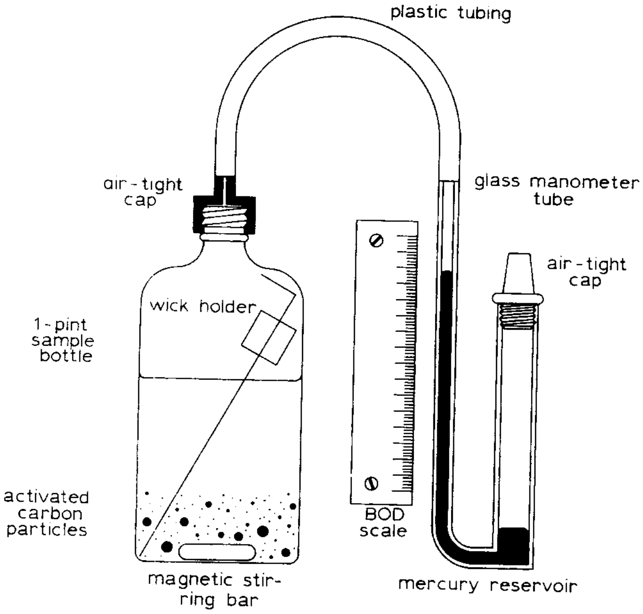

Fig. 1. Manometric apparatus used to study oxygen sorption on activated carbon.

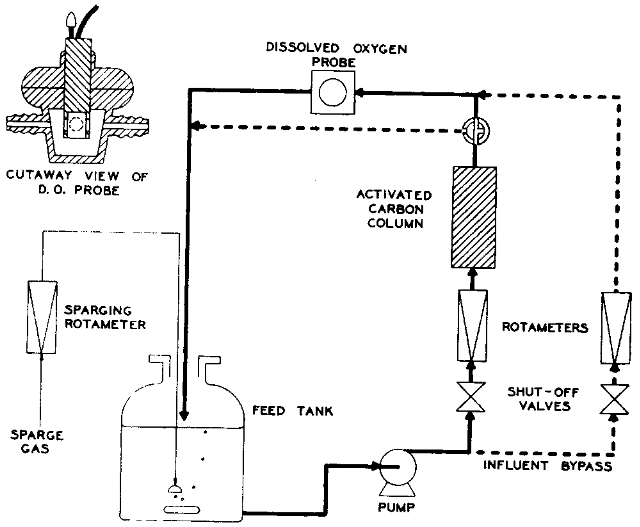

Fig. 2. Schematic flow diagram for column apparatus. Inset shows dissolved oxygen probe mounted in flowthrough port. Dashed lines represent flows used to route the column influent through the probe.

In some runs, the wick contained potassium hydroxide solution to absorb any carbon dioxide evolved owing to biological or chemical oxidations. Oxygen sorption was read directly in units of mg/l uptake on the BOD scale. This gave apparent values for $\bar{c}$ which were then corrected for temperature changes and other experimental deviations. (See Supplementary material for details.)*

Packed column studies were carried out as shown schematically in Figure 2. The apparatus consisted of standard laboratory glass and plastic ware. The activated carbon columns were supported upon glass wool mats or sintered glass plates. A polarographic probe (Yellow Springs, Model 31) was used to measure dissolved oxygen in both the influent and effluent. It was calibrated in place with aerated feed as standard and bypassing of the activated carbon column. Average rates of oxygen sorption were calculated from the concentration differences across the column

$$\bar{r} = \frac{Q}{W}(c_{\text{in}} - c_{\text{out}}) \qquad (1)$$

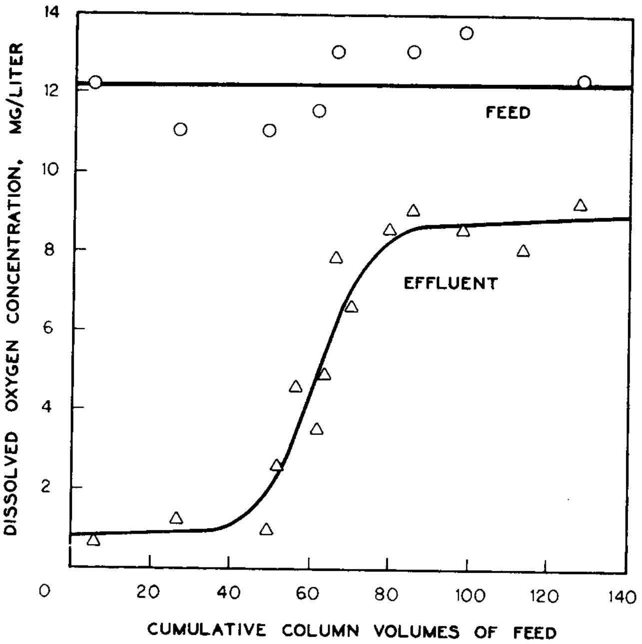

Fig. 3. Sorption of dissolved oxygen in an activated carbon column. 8.9 cm diameter × 26 cm, packed with Filtrasorb 300^{R}. 9 l/hr. flow, 7°C.

or, preferably, from the concentration history by

$$\bar{r} = \frac{Ka}{W}(c^* - c_{\text{in}}) - \frac{V}{W}\frac{dc_{\text{in}}}{dt} \qquad (2)$$

The sparger mass transfer coefficient Ka was evaluated as 47 l/hr. for the usual 1.5 l (STP)/min air flow, via the transient sulfite-oxidation test for rating aerator capacity (Eckenfelder, 1966).

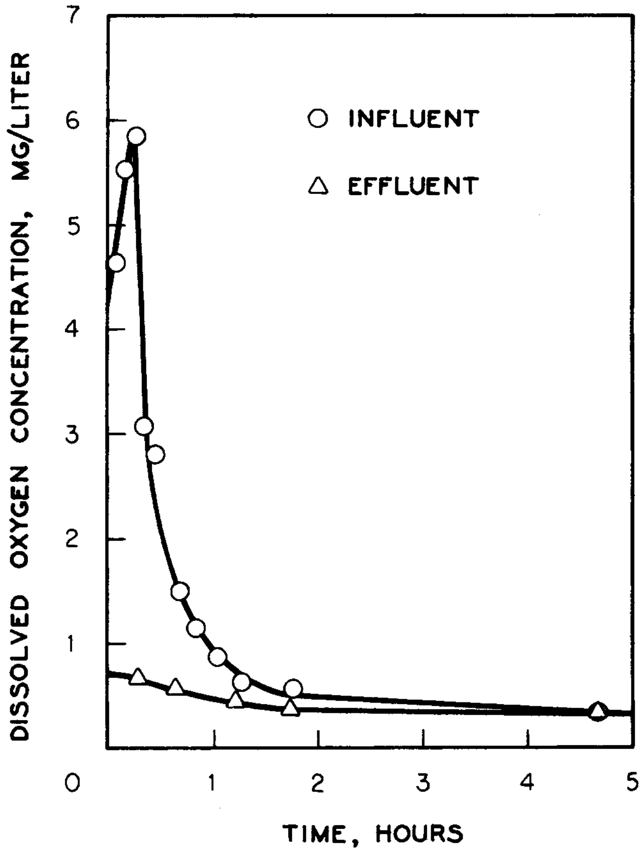

Fig. 4. Elution of oxygen from an activated carbon column. 2.5 cm diameter × 6 cm, packed with Filtrasorb 400^{R} (15g). 2.1 l/hr. flow, 23°C.

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* NAPS No. 02692. See paragraph on page 1204.

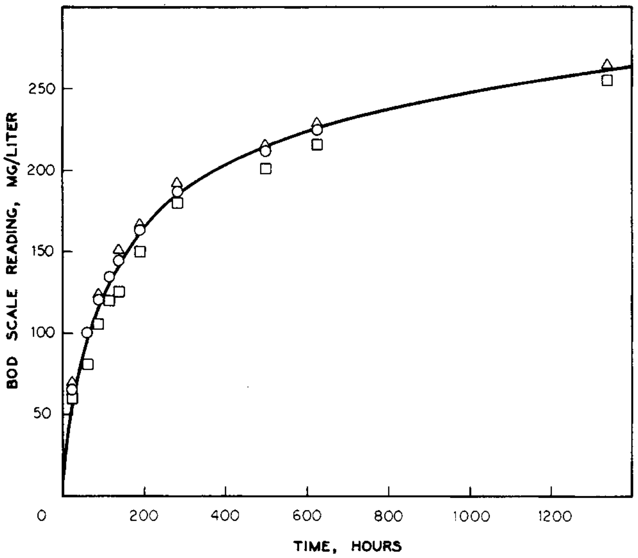

Fig. 5. Manometric oxygen sorption data for activated carbon in distilled water. Filtrasorb 300^R activated carbon, 8.2 g/l, 23°C.

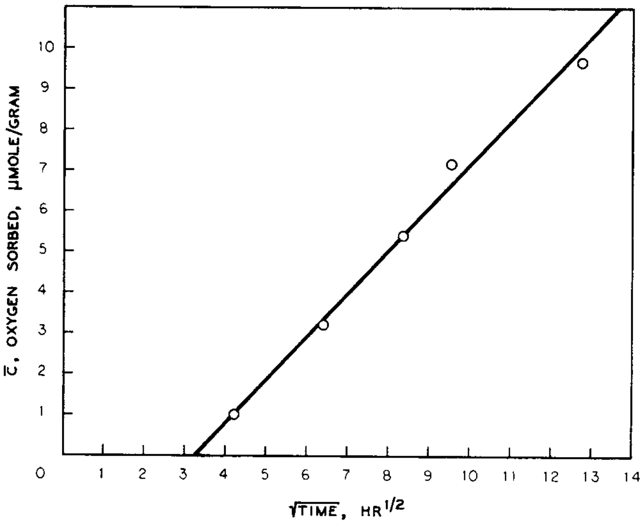

Fig. 6. Square-root time dependence of manometric oxygen sorption data. Filtrasorb 400^R, 8.2 g/l, 30°C.

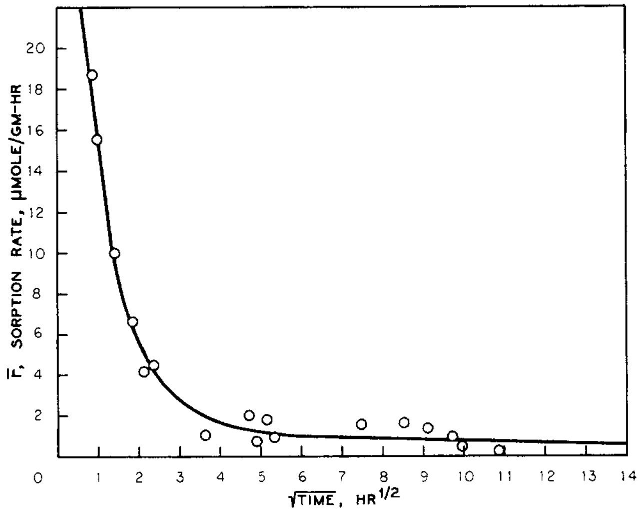

Fig. 7. Square-root time dependence of packed column oxygen sorption data. Filtrasorb 400^R, 2.5 cm diameter × 6 cm column; 2.1 l/hr., 23°C.

OXYGEN SORPTION

Interaction of activated carbon with dissolved oxygen was first noted as surprisingly large biological oxygen demand values with slurries of activated carbon in unfiltered secondary effluent, much greater than with the secondary effluent alone. Control runs eliminated biological action and nitrogen sorption, leaving sorption of dissolved oxygen on the activated carbon as the only plausible explanation. (See SUPPLEMENTARY MATERIAL.)

Column studies confirm that activated carbon does sorb dissolved oxygen. Typical data for a deep bed in Figure 3 show a classical breakthrough curve. Oxygen breakthrough occurs earlier with decreasing bed height; it takes place almost immediately with 6 to 10 cm beds. Figure 4 shows the displacement of sorbed oxygen by deoxygenated (nitrogen sparged) water. Oxygen eluted in such runs amounts to 6 to 10 μmole/g, some 2 to 5% of the oxygen sorbed prior to displacement.

Both manometric and column techniques were used to characterize the sorption of dissolved oxygen by activated carbon samples. Most runs were carried out with distilled water at 21° to 25°C, for dissolved oxygen concentrations near atmospheric saturation level, and typically lasted 1 to 2 wk. Additional runs were carried out at temperatures ranging from 6° to 40°C, in oxygen and nitrogen atmospheres, and in the presence of solutes such as sodium hydroxide or sodium carbonate. The activated carbons were used as received unless otherwise noted.

Figure 5 shows typical oxygen-uptake data from extended manometric runs. The reproducibility between replicate data points is within the expected ±6% limits See Supplementary material.)* A characteristic slowing down at long sorption times is seen after about 200 hr. Even in runs where the manometric bottles were opened briefly to replenish the oxygen supply, there was still a progressive slowing down. However, oxygen sorption proceeded at finite rates throughout all runs, even up to 1 700 hr.

Oxygen sorption as a function of time generally conforms to the diffusion limited sorption model of Weber and Morris (1963). The characteristic square-root-time dependency is evident in Figures 6 and 7, where the curves drawn represent, respectively, the regression equations

$$\bar{c} = A\, t^{1/2} + B \qquad (3a)$$

$$\bar{r} = 0.5\, A\, t^{-1/2} + B' \qquad (3b)$$

which were fitted to the experimental data by means of standard linear regression techniques (Deming, 1955). Rate factors (A) were calculated in this way for all manometric and shallow bed column runs. The values of B and B' were taken as error corrections to be subtracted from the experimental $\bar{c}$ or $\bar{r}$ data. The curve fitting for manometric runs was confined to data for oxygen partial pressures ≧ 105 mm Hg to minimize deviations owing to depletion of the oxygen supply.

Table 1 summarizes the results for sorption of dissolved oxygen with commercial activated carbons. The total sorptions listed are the largest values observed in any run with the given carbon; they are not equilibrium capacities. The range of 150 to 600 μmole/g would be narrower if all runs could have been extended to 1 700 hr. The rate factors, which range from 5 to 30 μmole/g-hr$^{1/2}$, are averages for the indicated conditions. Generally, A values were reproducible within ±15% for replicate runs. Temperature variations, the presence of solutes, and, in the case of manometric runs, dosage had only minor effects.

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* See paragraph on page 1204.

TABLE 1. SUMMARY OF OXYGEN SORPTION DATA
Values for 23°C, distilled water and aeration, except as indicated

Type	Rate factor (A), $\frac{\mu\text{mole}}{\text{g-hr.}^{1/2}}$	Maximum sorption $\bar{c}$ $\frac{\mu\text{mole}}{\text{g}}$	Maximum sorption run time hr.	Special conditions
Powdered activated carbon				
M(a)	25	540	545	Oxygen atmosphere
	9.0	320	1,694	—
S-51(b)	7.2	132	712	—
Granular activated carbon				
H-3000(c)	11.2	140	235	23°-40°C
H-4000(d)	8.0	145	235	29°-40°C
N(e)	8.0	195	712	—
F-400(f)	24	270	192	23°-30°C
F-300(g)	19	495	1,340	—
	20.5	230	120	0.1N Na_2CO_3
	29	295	120	0.1N NaOH
F-300 (Reactivated)	20	350	712	—
	29	105	12	6°C

a) Merck, pharmaceutical grade.
b) Darco S-51R, ICI America, Inc.
c) Hydrodarco 3000R, ICI America, Inc.
d) Hydrodarco 4000R, ICI America, Inc.
e) Nuchar WV-LR, Westvaco Corp.
f) Filtrasorb 400R Calgon Corp.
g) Filtrasorb 300R Calgon Corp.

A complete tabulation of results and conditions appears in the SUPPLEMENTARY MATERIAL.

It may be that sorption of dissolved oxygen is limited by very slow reactions rather than by intraparticle diffusion. Effective diffusivities inferred from our values of A and $\bar{c}$ (extrapolated to equilibrium) and manufacturers' specified particle sizes are on the order of 10^{-11} cm^2/s. However, none of the common reaction models could satisfactorily account for all of our rate data. The mechanism may involve several reactions occurring at different stages of the oxygen sorption, similar to the interaction of gaseous oxygen with activated carbon observed by Puri et al. (1971).

CHANGES IN SURFACE OXIDES

The acidic oxide groups were observed to increase as a result of oxygen sorption for samples of several commercial activated carbons which were prepared in 10 g batches in the manometric apparatus. The analysis for surface oxides was done by the multibase titration technique (Boehm et al., 1964). This consisted of batchwise equilibrations of 2 g activated carbon samples with a measured volume, about 150 ml, of 0.1 M sodium hydroxide, sodium carbonate, and sodium bicarbonate standard base solutions and determination of the resultant changes in alkalinity and sodium concentration. Details on the experimental methods, calculation of error bound estimates, and a complete tabulation of results are given in the Supplementary Material.*

Table 2 summarizes these studies. The effect is consistent for all activated carbons tested, that oxygen sorption enhances the capacities for base and for sodium ion by about 200 μeq/g. This is attributed to formation of additional carboxylic acid groups, which follows from the interpretation of multibase titrations that increases in base sorption from sodium bicarbonate to sodium carbonate to sodium hydroxide represent, respectively, stronger carboxylic acids, weaker carboxylic acids, and phenolic groups (Boehm et al., 1964).

In Table 2, comparison of the increases in acidic oxides with the measured oxygen sorption during preparation of the oxidized carbon samples shows yields of 0.45 to 1.8 μeq/mole of oxygen sorbed. The model stoichiometry

$$4\,R_2C = 0 + O_2 + 2\,H_2O \rightarrow 4\,R_2COOH \qquad (4)$$

would, thus, account for 10 to 50% of the measured oxygen sorption. This is the minimum for sorption attributed to oxidation, since other (less likely) reactions could be proposed with lower yields per mole of oxygen reacted. Physical adsorption can account for about 5% of the total sorption, based on the column results for oxygen elution. The balance of the oxygen sorption would have to be attributed to oxidation reactions that produce groups such as quinones or basic oxides which do not show up in our multibase titrations.

CLOSURE

Sorption of dissolved oxygen by activated carbon is seen to be a complicated phenomenon involving both adsorption and oxidation reactions which increase acidic oxide groups. The nature of these reactions is not yet resolved, but further work on oxygen sorption per se does not seem justified in view of the small oxygen demand which would be exerted by activated carbon at normal dosages for wastewater treatment. However, the interaction of activated carbon with dissolved oxygen in the presence of other species is a topic of considerable interest, as, for example, in catalytic oxidation of cyanide wastes. The data on oxygen sorption presented here provide a needed base line for such studies.

TABLE 2. EFFECT OF OXYGEN SORPTION ON ACIDIC OXIDE GROUPS

Activated carbon type	Multibase titration results, μeq/g(a): Enhanced base sorption from $NaHCO_3$	Enhanced base sorption from Na_2CO_3	Enhanced base sorption from NaOH	Enhanced Na sorption from NaOH	Increased oxides,(b) μeq/g	Oxygen sorbed, μmole/g	Oxide yield, μeq/μmole O_2 sorbed
S-51(c)	60	380	190	270	240	125	1.9
N(d)	40	270	170	270	195	195	1.0
F-300(e) reactivated	130	340	210	1,550	260	350	0.75
F-300(e)	60	180	220	400	210	470	0.45

a) Error bounds are about ±25 μeq/g for enhanced base sorption, ±150 μeq/g for enhanced Na sorption.
b) Weighted mean of multibase titration results for Na_2CO_3 and NaOH.
c) Darco S-51(R), ICI America, Inc.
d) Filtrasorb 300(R); Calgon Corp.
e) Nuchar WV-L(R); Westvaco Corp.

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* See paragraph on page 1204.

ACKNOWLEDGMENT

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NOMENCLATURE

A = rate factor, μmole/g-hr.$^{1/2}$
B = regression parameter in Equation (3*a*), μmole/g
B' = regression parameter in Equation (3*b*), μmole/g-hr.
c = dissolved oxygen concentration, μmole/l
c^* = dissolved oxygen saturation concentration, μmole/l
$\bar{c}$ = oxygen sorbed on activated carbon, μmole/g
Ka = sparger mass transfer coefficient, 1/hr.
Q = flow rate through column, l/hr.
$\bar{r}$ = rate of sorption, μmole/g-hr.
V = volume of solution circulated through column, l
W = weight of activated carbon in column, g

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Supplementary material has been deposited as Document No. 02692 with the National Auxiliary Publications Service (NAPS), c/o Microfiche Publications, 440 Park Ave. South, New York, N.Y. 10016 and may be obtained for $3.00 for microfiche or $5.00 for photocopies.

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R & D NOTES

Migration of Two Liquid Phases in Capillary Extrusion: An Energy Interpretation

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In the production of laminated plastic film and certain types of bicomponent fibers, two polymer melts are coextruded by being metered into a die in layered configuration (Figure 1*a*). Such a configuration, however, is known to be unstable; in circular capillary dies there is observed a tendency for mutual phase migration. Downstream, the low-viscosity phase tends to envelope the high-viscosity phase, as depicted in Figure 1*b*. Extensive experimental evidence presented by Lee and White (1974) and by Southern and Ballman (1973) indicates that the relative