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The Low Temperature Removal of Small Quantities of Nitrogen or Methane from Hydrogen Gas by Physical Adsorption on a Synthetic Zeolite

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A flow system was used to measure the physical adsorption isotherms of two mixtures of nitrogen and hydrogen and two mixtures of methane and hydrogen on a synthetic zeolite. The measurements were made at liquid nitrogen temperature and at pressures of 4 to 85 atm. Static systems were used to measure the pure component isotherms of nitrogen, methane, and hydrogen at the same temperature and over the appropriate pressure ranges.

Although many different methods have been proposed for using pure component adsorption isotherms to predict the mixture isotherm, the only method giving quantitative agreement with the data of this study is the empirical "adsorption enhancement factor" (*4*).

In addition to the adsorption isotherms, the concentration-time or breakthrough curves of the mixtures were measured at flow rates ranging from 40 to 300 lb./(hr.)(sq.ft.). The method proposed by Eagleton and Bliss (*18*) was used to correlate these curves.

Since all materials, with the exception of helium, are solids at liquid hydrogen temperature, the concentration of impurities in the feed gas to a hydrogen liquefier must be reduced to levels equal to their solubilities in gaseous or liquid hydrogen. Otherwise solid deposition will occur, resulting in eventual plugging.

By using the experimental phase equilibrium data of Dokoupil (*1*), Baker and Paul (*2*) have established the desirable impurity levels of nitrogen and carbon monoxide in liquefaction grade hydrogen at 1 p.p.m. The data of Hiza and Herring (*3*) for the methane-hydrogen system indicate that the tolerable impurity level of methane will be considerably less than 1 p.p.m. Obviously, then, the final step in any hydrogen purification train must be a process capable of attaining a very high degree of purification. Although there are a number of possible processes for attaining the required impurity level, the only feasible one is physical adsorption at cryogenic temperatures.

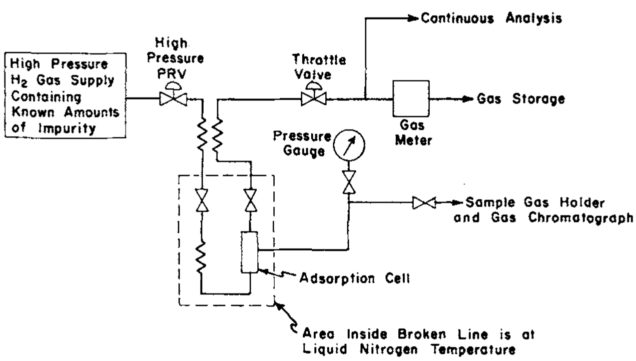

Fig. 1. Flow diagram for mixture adsorption.

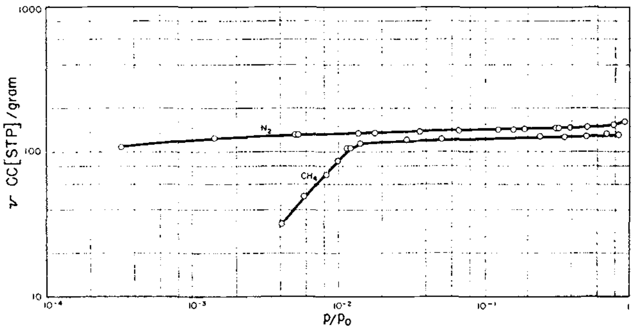

Fig. 2. Adsorption isotherms on a synthetic zeolite at 75.8°K.

The work reported here is part of a continuing experimental program (*4 to 7*)* designed to provide engineers with the equilibrium and kinetic data necessary for the proper design of cryogenic adsorbers.

EQUIPMENT AND PROCEDURE

The principal features of the equipment for measuring the mixture adsorption isotherms and the breakthrough curves are shown in Figure 1. Hydrogen gas containing a known concentration of impurity is introduced into the system at the desired operating pressure, cooled to liquid nitrogen temperature, and passed through a packed bed of adsorbent. After exchanging heat with the incoming stream, the purified gas is reduced in pressure through a throttling valve and goes to storage.

A small sample of the gas from the outlet of the adsorbent bed is passed through a thermal conductivity detector (for nitrogen) or a hydrogen flame ionization detector (for methane) to provide a continuous analysis of the effluent stream. When the concentrations at the inlet and outlet of the adsorbent bed are the same, the flow is stopped and the adsorption cell is isolated and then heated to desorb all gases. The desorbed gases are then flushed from the cell into the sample gas holder with ethane as the flush gas. The amount of desorbed gas is measured with a calibrated wet test meter, and the composition is determined with a gas chromatograph.

In addition to determining directly the adsorptive capacity of the zeolite for the trace component by analyzing the desorbed gases, an indirect measure of this capacity was obtained from a material balance on the adsorption cell. On the average, the capacities determined by material balance were within ± 4% of the values measured directly.

The temperature of the nitrogen bath was measured with a calibrated chromel-constantan thermocouple. A second thermocouple was used to measure the temperature difference between the liquid nitrogen bath and the center of the adsorbent bed to insure that the process was truly isothermal. There was no detectable temperature difference between the adsorbent and the refrigerant at any time during the experimental runs.

The adsorption cell was a brass cylinder with an I.D. of 0.75 in. and an overall length of 5.25 in. To reduce the possibility of radial concentration and velocity gradients in the gas entering the adsorbent bed, the first 1.5 in. of the cell were packed with small copper spheres about 0.6 in. in diameter. The pressure tap was a capillary tube (0.065 in. diameter), the end of which was placed in the center of the adsorbent bed, 0.25 in. in from the wall.

The dead-space volume of the adsorption cell and connected capillary tubing was determined by the standard helium expansion method. An adjustment was made for the change in volume of the cell between room temperature and liquid nitrogen temperature, but the correction for volume change due to pressure was negligible. At equilibrium, the amount of unadsorbed nitrogen or methane is very small, since the gas phase is almost pure hydrogen. The amount of hydrogen in the gas phase, however, is very large, and to properly correct for the unadsorbed hydrogen, the dead-space volume must be adjusted to account for the volume occupied by the adsorbed nitrogen or methane. The density of the adsorbed phase was assumed to be the same as that of the normal liquid or solid at the same temperature.

The pure component isotherms were determined with standard volumetric techniques. The equipment used for the nitrogen and methane isotherms is described elsewhere (*7*). To determine the hydrogen isotherm, carefully weighed samples of about 15 g. of adsorbent were placed in a high pressure cell, thoroughly reactivated, cooled to liquid nitrogen temperature, and then pressurized with pure hydrogen. The gas was then bled down through a calibrated wet test meter in small increments. When the pressure reached 1 atm., the refrigerant was removed and the cell heated to desorb the remaining gas. Since the temperature of the cell interior was measured with a thermocouple, the appropriate correction could be made for the gas remaining in the cell. A series of runs on different samples of adsorbent was made to insure reproducibility of the results. The isotherm shown in Figure 3 is a composite of three runs, all made on the same sample.

Materials

The adsorbent used in all of the experimental work was a synthetic zeolite.† Prior to each run, the adsorbent was reactivated for 12 to 18 hr. at 200°C. and 2 × 10^{-5} mm. Hg.

The nitrogen, hydrogen, and helium gases used in the pure component isotherm and free volume measurements all contained less than 100 p.p.m. total impurities. The methane, obtained commercially with a minimum guaranteed purity of 99.8%, was used without further purification. The gas mixtures were prepared in this laboratory and were analyzed with a mass spectrometer to determine the nitrogen or methane concentration and to insure that no other impurities were present.

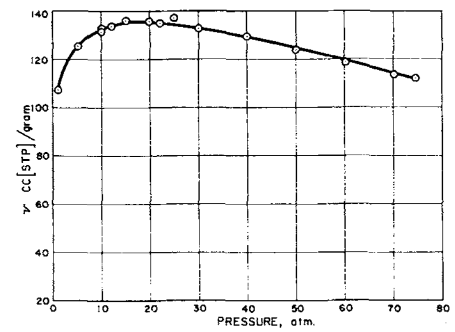

Fig. 3. Adsorption isotherm of hydrogen on a synthetic zeolite at 75.7°K.

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* Due to a computational error, the values reported in Table 4 of reference 6 are 4% high.

† Linde Molecular Sieves 5A, 1/16 in. pellets.

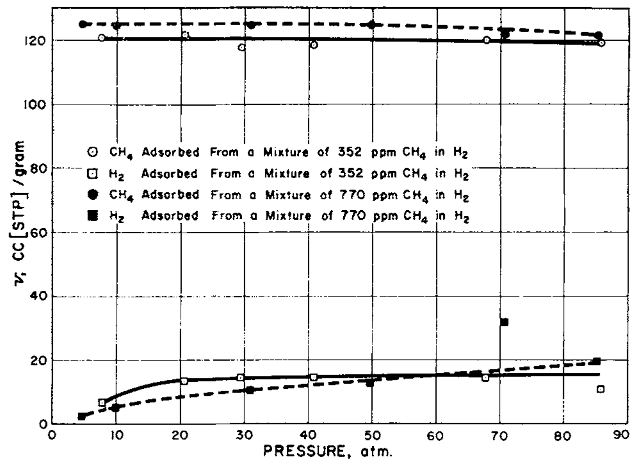

Fig. 4. Mixture adsorption isotherms on a synthetic zeolite at 75.9°K.

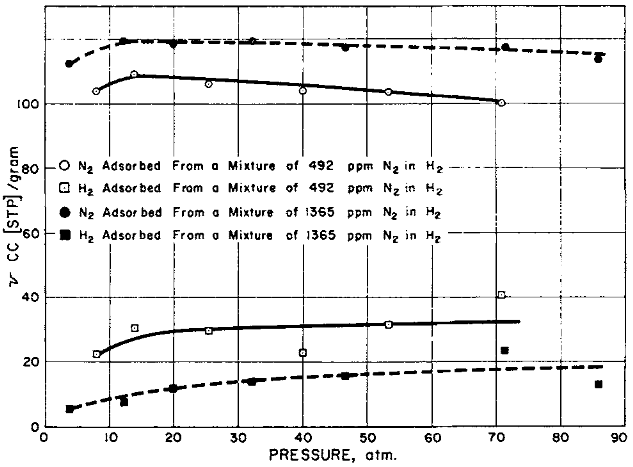

Fig. 5. Mixture adsorption isotherm on a synthetic zeolite at 75.8°K.

ADSORPTION ISOTHERMS

The pure component and mixture adsorption isotherms obtained in this study are presented in Figures 2, 3, 4, and 5.

The decrease in capacity that occurs at high pressures for the pure hydrogen isotherm is characteristic of high pressure isotherms in general and is a result of the way in which adsorption is defined (*8*).

Many methods have been suggested for predicting the adsorption properties of a mixture from the pure component isotherms. An excellent summary of most of these techniques is given by Young and Crowell (*9*). To find the most satisfactory method for predicting the equilibrium adsorption properties of cryogenic adsorbers, seven widely used methods were applied to the data. These methods were the mixed Langmuir isotherm (*9*); the empirical method of Koble and Corrigan (*10*); the equations of Lewis et al. (*11*) and Maslan et al. (*12*) based on the Polanyi adsorption potential; the semi-empirical method of Basmadjian and Cook (*13*); the empirical "adsorption enhancement factor" proposed by Hiza (*4*); and the recently proposed method of Myers and Prausnitz (*14*) based on the concept of an ideal adsorbed solution. All these methods gave qualitative agreement with the data, but the only method giving quantitative agreement was the adsorption enhancement factor.

The adsorption enhancement factor* is a dimensionless number defined by the equation

$$\phi_i = \frac{y_i P}{p_i} \tag{1}$$

The meaning of ϕ is best understood by considering the case of an ideal gas mixture ($A + B$) where component A is not adsorbed. In this case, the amount of B adsorbed from the gas mixture can be determined by calculating the partial pressure of B in the mixture and by using this value in conjunction with the pure component isotherm to determine the mixture isotherm. The enhancement factor for this situation is 1. This situation was realized by Loebenstein and Deitz in their work with nitrogen-helium mixtures (*15*). However, at high pressures, or if component A is appreciably adsorbed, gas phase nonidealities and competition of the adsorbates for the adsorbent surface will cause extremely large errors if this method is used. Thus, we define the adsorption enhancement factor as a correction factor to the partial pressure for both gas phase and adsorbate nonidealities.

It is, of course, possible to correct for nonideal gas phase behavior by redefining ϕ as

$$\phi_i = \frac{\bar{f}_i}{p_i} \tag{2}$$

However, ϕ still remains empirical and the correlation is not greatly improved, and so the simpler form is to be preferred.

Values of ϕ at 76°K. are presented in Figure 6. These curves were calculated from data obtained on silica gel with 915 p.p.m. nitrogen in hydrogen and 450 p.p.m. methane in hydrogen as the mixtures (*4*). When the adsorption enhancement factor curves obtained with silica gel are applied to the synthetic zeolite data of this report, the mixture isotherms of nitrogen and methane can be

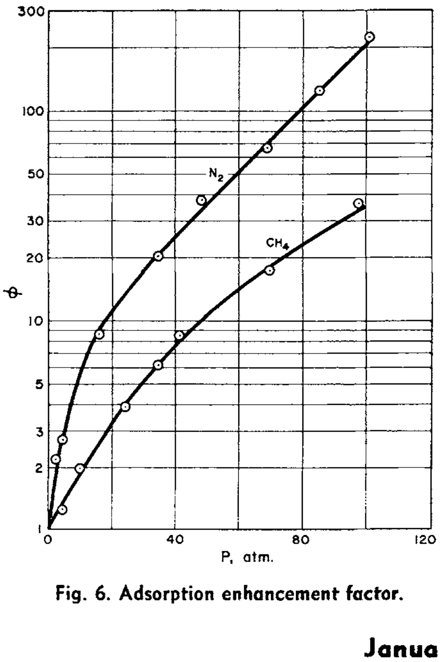

Fig. 6. Adsorption enhancement factor.

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* The term enhancement factor as used in solid-vapor phase equilibrium studies (*1*) is defined as $\frac{y_i P}{p_{o_i}}$, and represents the increase or enhancement of the observed partial pressure over the normal vapor pressure due to the increased pressure and the nonideal behavior of the gas phase. Since the term $\frac{y_i P}{p_i}$, used to relate pure component with mixture adsorption isotherms, is similar in form to the enhancement factor it is called the adsorption enchancement factor.

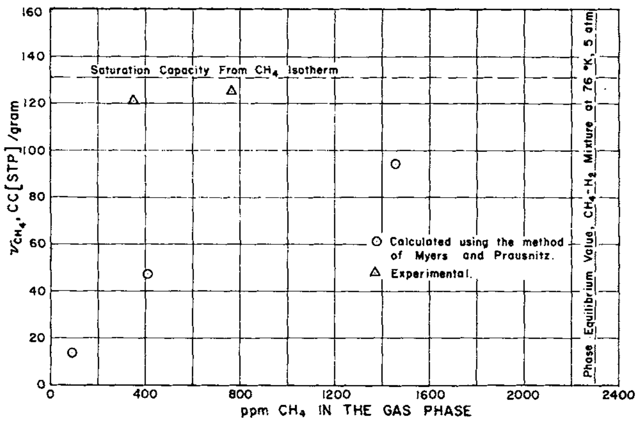

Fig. 7. Methane adsorbed from methane-hydrogen mixtures at 5 atm. and 75.9°K.

predicted with maximum errors in v of 14 and 5%, respectively. It is thus possible to use one set of empirical values of ϕ to calculate the mixture isotherms on both silica gel and synthetic zeolite, provided that the concentration of impurity in the gas phase is fairly low.

The curves of Figure 6 are applicable only to the trace component; they cannot be applied to the hydrogen adsorption data.

Although the method of Myers and Prausnitz failed to predict accurately the mixture isotherms, it is probably the most interesting technique, since it involves the least amount of empiricism. These authors define an activity coefficient for the adsorbed mixture in a manner analogous to the activity coefficient for a fluid. If this activity coefficient is then assumed to be 1, an equilibrium relationship for adsorption which is similar to Raoult's law for ideal solutions is obtained. This Raoult's law relation is used in conjunction with the pure component isotherms to predict the adsorption from a mixture.

In Figure 7 the adsorption isobar for methane at 5 atm. calculated by this technique is compared with the experimental values. There are a number of possible explanations for the lack of agreement, but the most likely one is that the activity coefficent of the adsorbed mixture is not 1.

BREAKTHROUGH CURVES

Adsorptive purifiers are fixed bed units in which the carrier gas containing the impurity to be adsorbed is passed through a packed bed of adsorbent. It is generally agreed that in this type of operation there are two distinct mass transfer processes: the diffusion of the impurity through the gas phase to the surface of the adsorbent, and diffusion into the particle. If both of these processes were extremely rapid equilibrium would exist at all points in the adsorbent bed, and a plot of the adsorber outlet concentration as a function of time would be a vertical line (Figure 9). Usually, however, one or both of the mass transfer processes are relatively slow, with the result that the concentration-time (breakthrough) curve assumes an S shape. The breakthrough curve has been the subject of extensive study, and excellent reviews have been presented by Vermeulen (*16*) and Klotz (*17*).

A general treatment of the problem is rendered virtually impossible by the complexity of the mathematics involved in the solution and by a lack of knowledge of the exact mechanisms involved in the mass transfer processes. Because of these difficulties, the usual approach is to make a series of simplifying assumptions to reduce the problem to a special case which can be solved analytically.

Of the many approaches that have been attempted, the one proposed by Eagleton and Bliss (*18*) appears to be the most consistent with this system. These authors make the following assumptions:

1. Constant inlet concentration and flow rate.
2. No radial concentration or pressure gradients.
3. Isothermal operation.
4. No axial diffusion.
5. The length of the mass transfer zone remains constant as it moves through the adsorbent bed.
6. Only the trace component (nitrogen or methane) is adsorbed. While this is not strictly true for the systems studied, the error due to this assumption should not be large.
7. The rate equations are

$$\left(\frac{\partial q}{\partial \theta}\right)_z = k_g S\,(C - C_{INT}) = k_s S\,(q_{INT} - q) \qquad (3)$$

8. The isotherm can be approximated by two straight lines:

$$C_{INT} = o, \text{ for } o < q_{INT} < \alpha$$
$$q_{INT} = \alpha + \left(\frac{a-\alpha}{C_o}\right) C_{INT},\; q_{INT} > \alpha \qquad (4)$$

With these assumptions the following equations are developed

for $C < C_d$

$$\ln \frac{C_d/C_o}{C/C_o} = \frac{-C_o k_g S W}{aV} + \frac{k_g S Z}{V} + 2 - \frac{C_o}{C_d} \qquad (5)$$

for $C > C_d$

$$\ln \frac{1 - C_d/C_o}{1 - C/C_o} = \left[\frac{C_d/C_o}{1 - C_d/C_o}\right]$$
$$\left[\frac{C_o k_g S W}{aV} - \frac{k_g S Z}{V} - 2 + \frac{C_o}{C_d}\right] \qquad (6)^*$$

where

$$C_d = \frac{\alpha}{a/C_o - r} \qquad (7)$$

and

$$r = \frac{-k_g S}{k_s S} \qquad (8)$$

The value for $k_g S$ is obtained from Equation (5) by plotting ln C/C_o vs. W and by determining the slope at low values of C/C_o. C_d is then obtained from Equation (6)

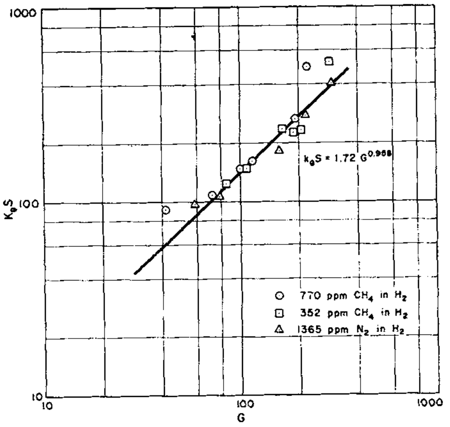

Fig. 8. Correlation of gas phase mass transfer coefficient.

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* There is a typographical error in this equation in the article of Eagleton and Bliss.

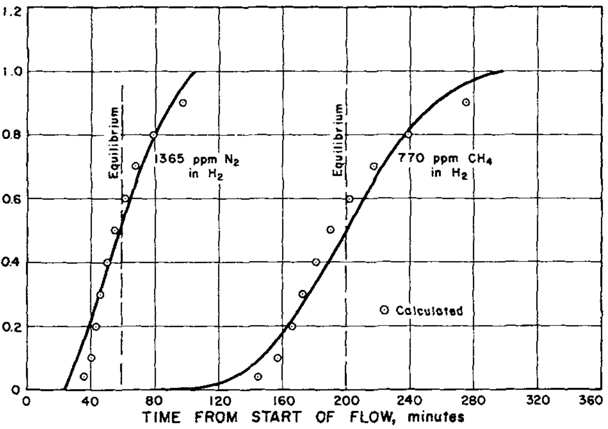

Fig. 9. Typical breakthrough curves.

by plotting ln $(1 - C/C_o)$ vs. W and by determining the slope at values of C/C_o greater than C_d/C_o. The values for r and k_sS can then be obtained from Equations (7) and (8). The relation of Glueckauf and Coates (*19*) can be used to calculate the particle phase diffusivity from the values of k_sS.

$$k_sS = \frac{60\, D_p}{d_p^2} \tag{9}$$

The experimental values obtained in this study for k_gS and k_sS showed considerable scatter, mainly due to the difficulty in obtaining accurate values for the slopes. The values for k_gS from seventeen runs are presented in Figure 8 as a function of the mass flow rate. Values of k_gS for runs made with 492 p.p.m. nitrogen in hydrogen are not shown, since lack of sensitivity in the thermal conductivity detector prevented an accurate determination of the breakthrough curves. The k_sS values are independent of flow.

The mass transfer coefficients are reasonably well correlated by the following relations:

$k_gS = 1.72\ G^{0.958}$ for all runs, $k_sS = 2.33$ for nitrogen, and $k_sS = 1.14$ for methane.

In Figure 9, breakthrough curves calculated with coefficients from these correlations are compared with some typical experimental curves.

The values of k_gS and G were used to calculate a mass transfer modulus $(\epsilon j_d/f)$ and a modified Reynolds number $(\sqrt{A_p}\ G/\mu)$ as proposed by Gupta and Thodos (*20*). At Reynolds numbers less than about 250, the data agree reasonably well with the generalized correlation. For higher Reynolds numbers, however, the agreement is poor, possibly due to imperfect radial distribution, longitudinal dispersion, or the short length of the bed in relation to the mass transfer zone.

Although the method of Eagleton and Bliss will not provide a perfect fit to the entire concentration-time curve, it can be used with some confidence to predict the breakthrough time (arbitrarily defined as the time when the outlet concentration is 0.1 C_o) for the systems studied.

DEGREE OF PURIFICATION

By maintaining a continuous analysis of the adsorber outlet with a hydrogen flame ionization detector, it was established that the methane content at the adsorber outlet before the appearance of the breakthrough curve was < 0.3 p.p.m. No such analysis could be made for the nitrogen runs, since the thermal conductivity detector lacked the necessary sensitivity. However, it is reasonable to assume that the same impurity levels were obtained, since Brilliantov and Fradkov (*21*) have shown that hydrogen can be purified to impurity concentrations below 2×10^{-4} p.p.m. with activated carbon at 80°K.

NOTATION

a = capacity of solid in equilibrium with gas of concentration C_o, lb./lb.
C = gas phase concentration of impurity, lb./lb. hydrogen
d_p = particle diameter, ft.
D_p = particle phase diffusivity, sq.ft./hr.
$\bar{f}_i$ = fugacity of component i in the gas mixture
G = mass flow rate based on overall bed cross section, lb./(hr.)(sq.ft.)
k_g = gas film mass transfer coefficient,

$$\frac{\text{lb. adsorbed}}{(\text{hr.})(\text{sq. ft.})\left(\dfrac{\text{lb. impurity}}{\text{lb. hydrogen}}\right)}$$

k_s = solid phase mass transfer coefficient,

$$\frac{\text{lb. adsorbed}}{(\text{hr.})(\text{sq. ft.})\left(\dfrac{\text{lb. impurity}}{\text{lb. hydrogen}}\right)}$$

m = amount of free space between particles, lb. hydrogen/lb. solid
p_i = equilibrium adsorption pressure from pure component isotherm
p_{o_i} = normal vapor pressure of component i
P = total system pressure, atm.
q = average concentration of adsorbate in the adsorbent, lb./lb. solid
S = surface area of the adsorbent for mass transfer, sq.ft./lb. solid
v = adsorbent capacity, cc. (S.T.P.)/g.
V = mass flow rate, lb./hr.
W = $V\theta - mZ$
y_i = mole fraction component i in the gas phase
Z = weight of the adsorbent, lb.
α = intercept value of q for the linear isotherm approximation
θ = time, hr.

Subscripts

INT = gas-solid interface
o = inlet conditions
d = point of discontinuity in the isotherm

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Laminar Converging Flow of Dilute Polymer Solutions in Conical Sections:

Part I. Viscosity Data, New Viscosity Model, Tube Flow Solution

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This investigation is reported in two parts. Necessary background information is introduced in Part I. The converging flow investigation proper is described in Part II (*18*).

In Part I, viscosity data are presented for polymer solutions used in the converging flow experiment. These data are fitted with a new three-parameter viscosity model which fits the data better than previous three-parameter models. (The viscosity model parameters are used in Part II to characterize rheological behavior of the polymer solutions in the converging flow experiment.) The corresponding relationship between flow rate and pressure drop for laminar flow in cylindrical tubes is derived. (In Part II this relationship is used in deriving an analogous relationship for slow non-Newtonian flow in conical sections.)

The primary purpose of Part I is to provide background information for Part II. However, the new viscosity model and the tube flow relationship are of some interest in themselves. The new viscosity model should prove useful for describing viscosity data of a variety of polymer solutions and polymer melts. A simple procedure for fitting the model to viscosity data is described. The tube flow relationship can be used for predicting pressure losses once the viscosity model parameters have been determined. Conversely, it can be used for determining the viscosity model parameters from tube flow data.

Polymer solutions and polymer melts exhibit several types of rheological phenomena. These include non-Newtonian viscosity, normal stresses in steady shear flow, and various time-dependent elastic effects. In some applications viscosity data alone give an adequate rheological description of such viscoelastic fluids. For example, viscosity data are sufficient for establishing the flow rate vs. pressure drop relationship for steady laminar flow in tubes—one of the simple viscometric flows having only one velocity component. In nonviscometric flows (for example, flow in conduits with varying cross section, flow in packed beds, turbulent flows), viscosity data may not be sufficient for establishing the flow rate vs. pressure drop relationship. The complexity of the fluid evidenced by normal stresses and time-dependent elastic effects may influence this relationship.

An a priori estimate of the magnitude of this effect cannot be made because little is known about nonviscometric flows. This investigation (*17*) provides information for one particular nonviscometric flow, namely, laminar converging flow in conical sections.

If one knew how to characterize completely the rheological behavior of viscoelastic fluids, the problem would be solved, at least in principle. In simple cases one might be able to derive the flow rate vs. pressure drop relationship. In more complex ones, consideration of the dimensionless form of the flow equations would indicate suitable dimensionless groups for correlating experimental data and would also indicate under what conditions order-of-magnitude simplifications could be made. Unfortunately, it is not yet known how to characterize completely the behavior of viscoelastic fluids. Many rheologists are currently occupied with this problem. A recent text by Lodge (*8*) provides an excellent introduction to this work.

The approach taken in this investigation was to assume that viscosity data were sufficient for establishing the flow rate vs. pressure drop relationship in the converging flow experiment. Good agreement between experiment and theory based on this hypothesis would verify the hypothesis, provided, of course, that the investigation were carefully done. A large discrepancy would refute the hypothesis, indicating need for additional rheological data. A more extensive investigation would then be required to determine what additional rheological data were needed and how they should be employed.

The investigation is reported in two parts. Necessary background information is introduced in Part I (this

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