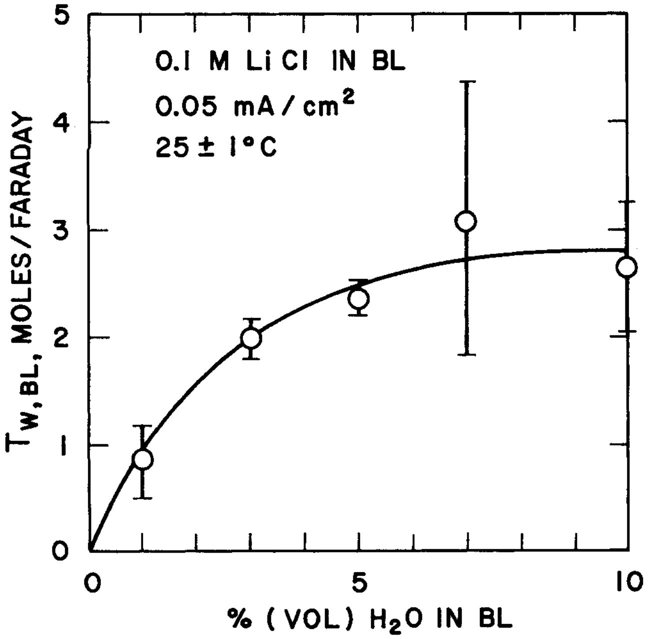

Fig. 2. The transference of water in a 0.1m lithium chloride solution in butyrolactone.

showed that the electro-osmotic exudate contained 64% (mole) water which may be compared with 32% (mole) water in the initial solution, that is a molar enrichment factor of two was obtained.

The separation process appeared to depend on the state of hydration of the membrane in a manner similar to that observed for the electro-osmotic transport of water through ion exchange membranes in aqueous solutions (*4*). Although more detailed studies are required to characterize the process adequately, it also appeared to be based on a selective solvation reaction such as:

$$Li^+ \ (BL)_m + n\,H_2O \rightleftharpoons Li^+ \ (H_2O)_n + m\mathrm{BL}$$

and the subsequent selective transference of the cationic species through an ion-specific membrane. If indeed this is the basis for the separation phenomenon, the electro-osmotic fractionation technique should be applicable to a variety of systems involving solvents or solutes which exhibit differential solvation or complexation with ions which can be extracted selectively through a membrane. An immediate application is the removal of water from γ-butyrolactone which is of interest in the field of organic electrolyte battery technology.

LITERATURE CITED

1. Dey, A. N., *J. Electrochem. Soc.*, **114**, 823 (1967).
2. *Ibid.*, **115**, 160 (1968).
3. Gray, D. H. and J. K. Mitchell, *Proc. Am. Soc. Civ. Eng.*, 93, SM6, 209 (1967).
4. Carr, C. W., R. McClintock, and K. Sollner, *J. Electrochem. Soc.*, **109**, 251 (1962).
5. Kedem, O., *Ber. Bunsenges Phys. Chem.*, 71, 775 (1967).
6. Dey, A. N., and M. L. B. Rao, paper Sixth Intern. Power Source Symposium, Brighton, England (Sept., 1968).

Heat Transfer to Drag-Reducing Polymer Solutions

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The drag-reducing property of dilute polymer solutions under certain turbulent flow conditions was first recognized and investigated by Toms (*1*). Among the more recent work in this area is that of Metzner and Park (*2*), Hershey and Zakin (*3*), and Virk, et al. (*4*). The usual speculative explanation for this phenomenon is an interaction of viscoelasticity with turbulence. In general, the friction factors for this phenomenon are found to be a function of Reynolds number and of the polymer species, polymer concentration, and pipe diameter. In contrast to these general dependencies, Virk, et al. (*4*), working with a homologous series of polyethylene oxides, have found that the maximum possible drag reduction is limited by a unique asymptote which is independent of molecular weight, concentration, and pipe diameter. Thus the gross flow behavior is bounded by the solvent line and by the maximum drag reduction asymptote. In power law form, these are respectively:

$$f/2 = 0.023\, N_{Re}^{-0.20} \qquad (1)$$

$$f/2 = 0.21\, N_{Re}^{-0.55} \qquad (2)$$

Although considerable gross flow data exists for momentum transfer, there is little heat transfer data. A heat transfer reduction is anticipated, but no theoretical basis exists for predicting the quantitative relationship between the drag reduction and the heat transfer reduction. For this reason, experiments (*5*) of a preliminary nature were undertaken to examine heat transfer. Data on wall heat transfer were obtained for a pipe flow ranging from 500 to 25,000 in Reynolds number. The solutions used were Newtonian and were of polyethylene oxide and distilled water, as listed in Table 1.

EXPERIMENTAL METHOD

The wall heat transfer rate was measured electrically. A thin coating (3×10^{-5} in.) of platinum on the inside walls of a 0.117 in. I.D. quartz tube, through which the solution flowed, served both as a resistance thermometer and as a wall heat source. The thermal developing section was 15.2 diam. and the test section, 2.8 diam. The hydraulic developing length to the heat transfer section was 230 diam.

By passing both a large and a small current through the platinum film and measuring the resistance with a Kelvin bridge, one obtained both the wall and upstream temperatures. The large (heating) current was measured by a standard resistor-potentiometer technique from which the heat flux at the wall (I^2R) was determined. Finally, the average bulk temperature at the test section was calculated by an energy balance based on the wall heat flux and the upstream temperature.

The wall, bulk, and upstream temperatures ranged between 37 to 39, 25.5 to 26.5, and 24.8 to 25.2°C. respectively. Corrections for variable fluid properties were made only for the

Table 1. Polymer Properties

Polymer designation	Molecular weight	Intrinsic viscosity (dl/g.)	Concentrations (PPM)	Relative viscosity
Polyox* W301	6.1×10^6	20.1 (25.1°C.) 18.4 (37.4°C.)	10	1.02
Polyox* N3000	0.76×10^6	3.84 (25.1°C.) 3.52 (37.4°C.)	10, 100, 1000	1.00, 1.04, 1.44

*** A product of Union Carbide Chemicals Co.**

laminar flow data and then via the Sieder-Tate factor, $(\mu_b/\mu_w)^{0.14}$. The heat transfer data reported are the average for the test section and are for constant heat flux. The results of Hartnett (*6*) and Sparrow, et al. (*7*) indicate that, for normal Newtonian fluids in turbulent flow and with the present 15 diam. developing section, the heat transfer coefficient should be within 1% of its fully developed value. It is assumed here that the coefficients for the polymer solution in turbulent flow are also fully developed values. This assumption is supported by the heat transfer data of Gupta, et al. (*8*) for drag-reducing solutions of ET-597 in water. The entrance lengths for water and 500 ppm. solution were not significantly different and were 10 to 25 and 10 to 35 diam. respectively. The data of the 4,500 ppm. solution, which had entrance lengths greater than 48 diam., cannot be considered as representative of the drag-reducing phenomenon since it was limited to the early stages of transition. The critical Reynolds number was about 6,000 and at the maximum Reynolds number of 10,300 the data were still within 25% of the values calculated for laminar flow. Since the water and polymer solution entrance lengths appear not to be conspicuously different, a rough estimate of the possible error in the present data can be made by using the results of Harnett and of Sparrow, et al. Even for an entrance length (based on a 1% deviation) as large as 50 diam., the present data would be in error by only 5%.

RESULTS

The experimental results on heat transfer are given in Figures 1 and 2 for the laminar and turbulent regimes respectively. For laminar flow, the polymer solutions obey the normal Newtonian fluid correlations. The data has a maximum deviation of 5% from the theoretical results of Sellars, Tribus, and Klein (*9*). With the present experimental technique, laminar regime data were most susceptible to error; the ± 5% agreement in this region therefore provides a critical test of data precision.

For water in turbulent flow, the heat transfer data are in excellent agreement with the Dittus-Boelter (*10*) correlation:

$$(N_{St})(N_{Pr})_b^{0.6} = 0.0234\,(N_{Re})_b^{-0.20};\ N_{Re} > 6{,}000 \quad (3)$$

The maximum heat transfer reduction obtained by the polymer solutions was limited by the following best-fit asymptote (data of polylox N3000 at 1,000 ppm and of polylox W301 at 10 ppm),

$$(N_{St})(N_{Pr})_b^{0.6} = 0.184\,(N_{Re})_b^{-0.54} \quad (4)$$

The right-hand sides of Equations (2) and (4) differ by less than 4% which is within the limits of experimental error. Equating the two, one concludes that both the solvent line and the maximum reduction asymptote obey a Chilton-Colburn type analogy,

$$(N_{St})(N_{Pr})_b^{0.6} = (f/2) \quad (5)$$

Equation (5) also appears to specify, within 10%, the behavior of those data points not on the asymptote (5); but for these points, the use of the pressure drop data of Virk, et al. (*4*) is subject to greater uncertainty and thus the applicability of the analogy to the polymer-dependent region remains somewhat conjectural.

COMPARISON WITH OTHER DATA

Before evaluating other data in light of the percent results, a brief comment is warranted on the difficulties of making any comparison between heat transfer and friction data. When the two measurements are made at substantially different conditions (for example, different bulk temperatures, large radial variation of properties, etc.), the basis for comparison becomes ambiguous. These difficulties in normalizing the conditions, which are further compounded by solutions which have shear thinning characteristics, may be the cause of the contradictory results reported by the several investigators (*8, 11* to *13*). The present heat transfer data and the friction data of Virk, et al. were obtained in the same flow apparatus

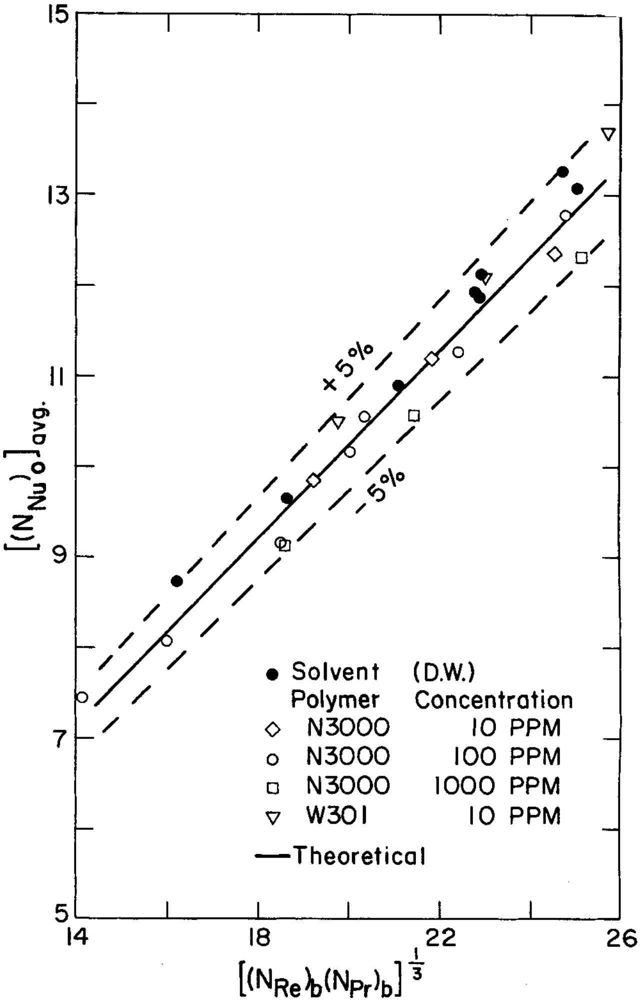

Fig. 1. Laminar regime.

TABLE 2. COMPARISON OF 500 PPM ET-597 DATA (8) WITH PREDICTED VALUES

Flow rate (lb./min.)	$(f/2)_{\text{exp}} \times 10^3$ [Figures 5 and 6, (8)]	$(N_{St})_{\text{exp}} \times 10^3$	$(N_{St})_{\text{calc}} \times 10^3$ [Equation (5)]	$(T_w - T_b)_{\text{approx}}$ (°C.)	% ERROR $\left[\frac{(N_{St})_{\text{calc}} - (N_{St})_{\text{exp}}}{(N_{St})_{\text{calc}}}\right] \times 100$
50	3.20	0.600	0.755	33	+21
100	2.12	0.412	0.500	24	+18
150	1.56	0.337	0.368	19	+ 8
200	1.29	0.293	0.304	17	+ 4
250	1.09	0.257	0.257	15	0
300	0.955	0.223	0.225	15	+ 1

and at bulk temperatures which differed by 1°C. The polymer solutions, as characterized by the intrinsic viscosity, were identical.

McNally (*11*) has recently obtained heat transfer and friction data for solutions of 2, 10, and 20 ppm W301 Polyox in water. The measurements were for 0.78 in. I.D. pipe flow ranging from 25,000 to 167,000 in N_{Re}. The heat transfer bulk and wall temperatures were 38 to 46°C. and 88 to 93°C. respectively; the temperature levels in the pressure drop section were 20 to 25°C. With the data represented as $j = (N_{St})(N_{Pr})_f^{2/3}$ vs. $(N_{Re})_f$, the heat transfer onset Reynolds number (beyond which the reduction begins) was threefold larger than the corresponding one for friction.

To normalize the heat transfer data, McNally made the reasonable assumption that under ideal isothermal conditions the heat transfer and friction onset points should be nearly the same. A correction, of the following form, was used to make the onset points coincide and yet not alter the correlation of the pre-onset data: $j_{\text{corr.}} = j(C)^{0.2}$ and $(N_{Re})_{\text{corr.}} = (N_{Re})_f/C$. With $C = 2.76$, all 23 data points are correlated by $j_{\text{corr.}} = (f/2)$ with a mean absolute deviation of 5%. Since the W301 theta temperature (88°C.) is lower than the wall temperatures employed, the resulting correlation is surprisingly good in this particular case.

Gupta, Metzner, and Hartnett (*8*) have presented heat transfer and friction data for 0.745 in. I.D. pipe flow. The solutions employed were of ET-597 in water at concentrations of 100, 500, and 4,500 ppm. Only the 500 ppm data will be evaluated here, since the lower and higher concentration data either exhibited virtually no drag reduction or were limited to the early stages of transition. The Prandtl numbers, evaluated at the bulk temperature and at the wall shear stress, ranged from 10.87 to 11.38 for the 500 ppm solution. The values calculated from Equation (5), using a N_{Pr} of 11.1, are compared in Table 2 to Gupta's smoothed data. Included in the table are approximate values of $(T_w - T_b)$ which have been calculated from the fact that the heat input was nearly constant throughout the runs. The agreement is excellent at the higher flow rates; the error at lower flow rates appears to be directly associated with larger values of $(T_w - T_b)$.

Gupta, et al. have implied, quite erroneously, that the heat transfer reduction is conspicuously more than the drag reduction. They define the reduction by comparing, at the same velocity, the data of 500 ppm ET-597 (which has a relative viscosity of approximately 2) with that of the solvent, but fail to consider the difference in viscosity. To separate the purely viscous effects from the drag-reducing phenomenon, the reduction should be defined with respect to a hypothetical nondrag reducing fluid of the same viscosity as the polymer solution. From table 2 of reference 8, the ratio of (h_p/h_s) to (τ_{wp}/τ_{ws}) is 0.68 at a flow of 200 lb./min. Making a correction for the purely viscous effects, the ratio becomes 1.03 thereby showing that the drag-reducing phenomenon is not the cause of the discrepancy.

Astarita and Marrucci (*12*) have reported 0.47 in. I.D. pipe flow data for ET-597 at concentrations of 600 and 1,000 ppm. The data is given in terms of Colburn j-factor and $(f/2)$ vs. N_{Re}. The 1,000 ppm data is mostly in the transition region and is therefore difficult to analyze. Beyond the transition region and for a N_{Re} range of 20,000 to 50,000, the 600 ppm data is represented well by $j = 19\ (N_{Re})^{-0.95}$ and $(f/2) = 32\ (N_{Re})^{-0.95}$. Eliminating N_{Re} results in $j = 0.6\ (f/2)$ which, it should be noted, conflicts with the results obtained from Gupta's data for nearly the same solution. The discrepancy might be associated with the method used to evaluate the fluid properties and normalize the data. To make the heat transfer onset point (obtained by extrapolating the data) coincide with the friction one, a McNally correction factor of $C = 0.50$ can be applied and would result in $j_{\text{corr.}} = (f/2)$.

Pruitt, Whitsitt, and Crawford (*13*) have given data for solutions of Separan AP-30 in water at concentrations of 10, 100, and 1,000 ppm. The two higher concentrations were highly shear-thinning and, therefore, will not be analyzed here. The Prandtl numbers were evaluated at the wall temperature and at the wall shear stress. For $N_{Re} > 10{,}000$ Equation (5) predicts the behavior of 10 ppm data with a mean absolute deviation of 12%. Use of Prandtl numbers evaluated at the more customary bulk temperature and at the wall shear stress would reduce the error of the predicted values considerably.

In a recent article Wells (*14*) has derived an equation for predicting heat transfer rates to drag-reducing solutions. An implicit assumption in the derivation is that the heat transfer and friction onset points are the same. Thus, Wells' equation could not predict the data of

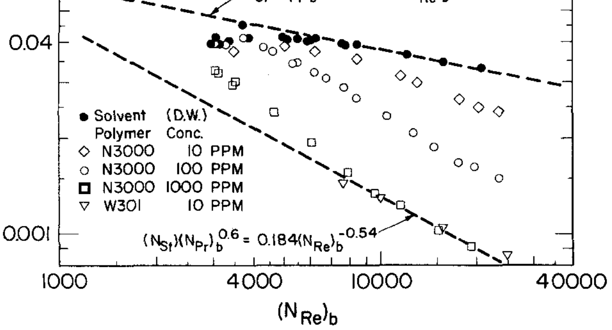

Fig. 2. Turbulent regime.

TABLE 3. COMPARISON OF PRESENT DATA [5] WITH PREDICTED VALUES

	EXPERIMENTAL				CALCULATED			PERCENT ERROR $\left[\frac{(N_{St})_{\text{calc}} - (N_{St})\text{exp}}{(N_{St})_{\text{calc}}}\right] \times 100$	
Fluid	$(N_{Pr})_b$	$(N_{Re})_b \times 10^{-3}$	$(N_{St}) \times 10^3$	$(f/2) \times 10^3$	$(N_{St}) \times 10^3$ Equation (5)	u_L^+	$(N_{St}) \times 10^3$ Equation (6)	Equation (5)	Equation (6)
N3000	6.14	6.31	1.25	3.89	1.31	13.0	1.11	+5	−13
10 ppm	6.16	11.70	1.05	3.03	1.02	14.1	0.882	−3	−19
	6.18	17.82	0.885	2.54	0.852	15.1	0.748	−4	−18
	6.19	23.73	0.809	2.26	0.756	15.9	0.668	−7	−21
N3000	8.95	6.11	0.520	1.86	0.499	22.5	0.372	−4	−40
1000 ppm	8.98	9.68	0.359	1.30	0.349	26.7	0.262	−3	−37
	9.00	15.38	0.274	0.973	0.260	30.7	0.197	−5	−39
	9.01	19.33	0.244	0.858	0.230	32.5	0.174	−6	−42
W301	6.34	7.68	0.475	1.54	0.510	24.6	0.381	+7	−25
10 ppm	6.34	10.07	0.428	1.32	0.435	26.5	0.327	+2	−31
	6.35	15.62	0.345	1.02	0.336	29.8	0.254	−3	−36
	6.36	24.96	0.282	0.773	0.255	33.9	0.194	−11	−45

McNally and of Astarita unless a McNally correction factor were applied. But, it has just been shown that, with such a correction, Equation (5) predicts all the heat transfer data quite well. In contradistinction, Wells' equation does not correctly predict the present data (5).

The equations given by Wells can be simplified to the following:

$$(N_{St}) = \frac{(f/2)}{1.02\, u_L^+\ (f/2)^{1/2}(N_{Pr} - 1)(N_{Pr})^{-1/3} + 1.2} \tag{6}$$

$$u_L^+ = 5.77 \log(u_L^+) + 5.5 + \alpha \log(u^*/u^*_{\text{onset}}) \tag{7}$$

$$(f)^{-1/2} = 4 \log[(N_{Re})(f)^{1/2}] - 0.394 + \frac{\alpha}{(2)^{1/2}} \log(u^*/u^*_{\text{onset}}) \tag{8}$$

The N_{Re} and N_{Pr} are evaluated at the wall shear stress. The constants α and u^*_{onset} are needed only if a prediction of friction factors is to be made. The evaluation of these constants is somewhat arbitrary when the friction data does not correlate by a straight line on a log-log plot of $(f)^{1/2}$ vs. $N_{Re}(f)^{1/2}$. For predicting heat transfer from a known friction factor, the two constants need not be evaluated as they can be eliminated by combining Equations (7) and (8).

The values predicted by both Equations (5) and (6) are compared to the present data in Table 3. The predicted values using Wells' equation (6) are in significant error even at low drag reductions.

CONCLUSION

The reduction phenomenon is bounded by the solvent line and by a unique maximum reduction asymptote. Both of these limits obey the same empirical Chilton-Colburn type analogy. This analogy also appears to be applicable to the polymer-dependent region if the wall-bulk temperature difference is small and if the solution is not highly shear-thinning.

ACKNOWLEDGMENT

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NOTATION

C = McNally correction factor
f = Fanning's friction factor
h = heat transfer coefficient
j = $[(N_{St})(N_{Pr})_f^{2/3}]$ or $[(N_{St})(N_{Pr})_b^{2/3}(\mu_w/\mu_b)^{0.14}]$
N_{Nu} = Nusselt number
N_{Pr} = Prandtl number
N_{Re} = Reynolds number
N_{St} = Stanton number $[(N_{Nu})/(N_{Pr})_b(N_{Re})_b]$
T = temperature, °C.
u^* = friction velocity $[\tau_w/\rho]^{1/2}$
u_L = velocity at edge of sublayer
u_L^+ = $[u_L/u^*]$
u^*_{onset} = friction velocity beyond which reduction begins
α = parameter in Equations (7) and (8)
μ = viscosity, centipoises
τ = shear stress, dynes/sq.cm.

Subscripts

b = evaluated at bulk temperature
f = evaluated at $T = 0.5\ (T_w + T_b)$
o = corrected for variable fluid property
p = polymer solution
s = solvent
w = evaluated at the wall

LITERATURE CITED

1. Toms, B. A., *Proc. Intn. Congr. Rheol.*, **2,** 135 (1948).
2. Metzner, A. B., and M. G. Park, *J. Fluid Mech.*, **20,** 291 (1964).
3. Hershey, H. C., and J. L. Zakin, *Ind. Eng. Chem. Fundamentals*, **6,** 381, (1967).
4. Virk, P. S., E. W. Merrill, H. S. Mickley, K. A. Smith, and E. L. Mollo-Christensen, *J. Fluid Mech.*, **30,** 305 (1967).
5. Keuroughlian, G. H., thesis, Mass. Inst. Tech., Cambridge (1967).
6. Hartnett, J. P., *Trans. Am. Soc. Mech. Eng.*, **77,** 1211 (1955).
7. Sparrow, E. M., T. M. Hallman, and R. Siegel, *Appl. Sci. Res., Sect. A*, **7,** 37 (1957).
8. Gupta, M. K., A. B. Metzner, and J. P. Hartnett, *Int. J. Heat Mass Transfer*, **10,** 1211 (1967).
9. Sellars, J. R., M. Tribus, and J. S. Klein, *Trans. Am. Soc. Mech. Eng.*, **78,** 441 (1956).
10. Dittus, F. W., and L. M. K. Boelter, Univ. Calif., *Publ. Eng.*, **2,** 443 (1930).
11. McNally, W. A., Ph.D. thesis, Univ. Rhode Island (1968).
12. Marrucci, G., and G. Astarita, *Ind. Eng. Chem. Fundamentals*, **6,** 471 (1967).
13. G. T. Pruitt, N. F. Whitsitt, and H. R. Crawford, Nat. Aeronaut. Space Admin. Contract No. NAS 7-369, The Western Co. Res. Div., Dallas, Texas (1966).
14. Wells, S. C., *AIChE J.*, **14,** 406 (1968).