However, this might be explained by variations in the sorption coefficient λ and the intraparticle diffusivity of sucrose as the resin composition changes. In fact, O'Connell (*2*) has reported that D_s for completely acidified resin is 1.15 times larger than for sodium form resin, while λ is 1.30 times higher in acid form resin. In the absence of intermediate data, one may assume that λ and D_s then vary linearly with $\overline{C}_{Ha}$ between these limits. If such a variation is arbitrarily forced into a form such that $\lambda(D_s)^{1/2}$ is proportional to $\overline{C}_{Ha}$ raised to an arbitrary power, it may be shown that a good fit results when this power is 0.17. When this is then put back into the large h asymptote of Equation (15), one sees that K should vary with $\overline{C}_{Ha}$ to the 0.67 power. This is now in excellent agreement with the experimental results of Figure 3.

Finally, one may question the use of different arguments for the Na^+ and K^+ cases. Support for this approach may be found in the higher free water content of K^+ loaded resins. As pointed out by Helfferich (*7*), diffusion of nonelectrolytes is higher in the K^+ form than in the Na^+ form, although the total water contents of both forms are comparable. Similar behavior with respect to the sorption coefficient is likely. Therefore, the differences in the results are not altogether surprising. In fact, recent data obtained by Handel (*8*) with Ca^{++} poisoned resin show good linearity on a plot similar to Figure 3 but a dependence on $\overline{C}_{Ha}$ to the 0.83 power. Since the free water content of Ca^{++} resin is still lower than Na^+ form resin, the larger power is perhaps not unexpected.

The net result of this work has been the demonstration that the inversion of sucrose by acidified ion exchange resin catalyst remains of apparent first order as catalyst activity falls. The change in activity has been shown to be directly related to the apparent acid capacity of the resin catalyst. Analysis of the process has shown that the dependence may be predicted quantitatively in terms of the usual Wheeler-Thiele formulation for reaction coupled with intraparticle diffusion but with due regard for the effects of catalyst composition on the diffusivity and sorption coefficient of sucrose in the resin. It is clear that the analysis shown here is qualitatively correct and can be made quantitative if sufficient supporting data are available for the deactivating ions in question.

NOTATION

C_s = concentration of sucrose in solution, moles/liter
$\overline{C}_H$ = concentration of hydrogen ions in resin, meq./ml.
D_s = diffusivity of sucrose within resin, sq.cm./sec.
E = effectiveness factor
f = ratio of resin volume to completely acidified volume
h = Thiele modulus, see Equation (5)
k = first-order rate constant, sec.$^{-1}$
k_0 = second-order rate constant for sucrose inversion, ml./(sec.)(meq.)
Q = volumetric flow rate, liters/min.
R = resin particle radius, cm.
R_s = rate of inversion per unit resin volume, moles/(cc.)(sec.)
V = resin volume, cc.
x = fractional conversion of sucrose

ϵ = void fraction in packed bed reactor
λ = sorption coefficient for sucrose
τ = reactor space time, min.

Subscript

a = apparent, based on resin in the completely acidified form

LITERATURE CITED

1. Reed, E. W., and J. S. Dranoff, *Ind. Eng. Chem. Fundamentals*, **3**, 304 (1964).
2. O'Connell, J. E., D.Sc. dissertation, Mass. Inst. Technol., Cambridge (1964).
3. Lifshutz, Norman, and J. S. Dranoff, *Ind. Eng. Chem. Process Design Develop.*, **7**, 266 (1968).
4. Lifshutz, Norman, M.S. thesis, Northwestern Univ., Evanston, Ill. (1966).
5. McGovern, T. J., M.S. thesis, Northwestern Univ., Evanston, Ill. (1968).
6. Helfferich, F., "Ion Exchange," p. 306, McGraw-Hill, New York (1962).
7. *Ibid.*, p. 533.
8. Handel, G. M., Senior Project Report, Northwestern Univ., Evanston, Ill. (1968).

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Motion of Liquid Drops in Non-Newtonian Systems

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Predictive equations for terminal velocities of liquid drops in Newtonian and non-Newtonian systems are reviewed. The wave theory analogy is extended to include liquid-liquid systems. Experimental data obtained with seven different systems are presented. The agreement with predictive equations is satisfactory. Interface rigidity was observed in all the systems investigated.

While the motion of gas bubbles through non-Newtonian liquids has been studied both theoretically and experimentally (*1* to *3*, *11*), much less is known about the analogous problem for liquid drops (*4*, *11*); as far as we know, no information at all is available concerning the motion

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of drops of non-Newtonian liquids. This paper presents the results of an experimental investigation of this problem, together with a survey of available equations for predicting terminal velocities of liquid drops in non-Newtonian systems.

PREDICTIVE EQUATIONS FOR THE TERMINAL VELOCITY

Spherical Drops at Low Reynolds Number

The motion at low Reynolds number of spherical drops through Newtonian liquids is governed by the following equation:

$$U = \frac{Y}{18}\,\frac{g\Delta\rho}{\mu_o}\,d^2 \tag{1}$$

The dimensionless factor Y depends on the viscosity ratio (*5, 12*):

$$Y = \frac{3\mu_o + 3\mu_i}{2\mu_o + 3\mu_i} \tag{2}$$

When $\mu_i >> \mu_o$, $Y = 1$, and Equation (1) reduces to the form originally obtained by Stokes (*13*). The largest value of Y is 3/2 and corresponds to a negligible viscosity of the drop liquid, that is, to the case of gas bubbles.

Very often, when the viscosity of the drop liquid is very low, Stokes' law applies. This is due to rigidity of the surface produced by the action of unavoidable impurities in the liquid which concentrate at the interface.

In the case of non-Newtonian liquids, generalizations of Equation (1) have been published for power law fluids. These have been obtained by means of variational principles and are in the form of upper and lower bounds for the (unknown) true solution.

The equations which have been obtained can always be cast as

$$U = \left[\frac{g\,\Delta\rho}{18\,m\,Y}\right]^{\frac{1}{n}} d^{\frac{1+n}{n}} \tag{3}$$

which can be obtained directly from simple dimensional considerations (*2*).

The dimensionless factor Y depends both on a properly defined viscosity ratio and on the flow behavior index:

$$Y = Y(X, n) \tag{4}$$

where

$$X = \mu_i\ U^{1-n}/m\ d^{1-n} \tag{5}$$

The apparent viscosity ratio X has been introduced by Nakano and Tien (*11*).

When $X >> 1$, that is, for the case of a rigid sphere, both the upper and lower bounds for Y have been calculated by Wasserman and Slattery (*15*). The dependency of Y on both X and n has been studied by Nakano and Tien (*11*), but only the upper bound has been calculated.

While in the case of Newtonian liquids the ratio among the largest and smallest values of Y is 3/2, much larger values are obtained for non-Newtonian liquids if $n < 1$; this was first indicated on the basis of a qualitative argument by Astarita and Apuzzo (*2*) and then confirmed by explicit calculations of Nakano and Tien (*11*).

Spherical Drops at Large Reynolds Numbers

Motion of drops at large Reynolds numbers has been studied extensively only for the case $X << 1$, (say, motion of gas bubbles). For Newtonian field liquids, Equation (1) can again be used, with $Y = ½$ (*7, 10*). For non-Newtonian field liquids, Equation (3) can be used, with Y a function of n which has been calculated by Astarita and Marrucci (*3*):

$$Y = \frac{2^{n-1}\,3^n}{1+4n}\int_0^1 (1+2x^2)^{\frac{n+1}{2}}\,dx \tag{6}$$

Inclusion of the effect of elasticity of the field liquid has been discussed qualitatively by Astarita (*1*).

When the viscosity of the drop liquid is not negligible, the solution is available only for Newtonian liquids, as recently calculated by Harper and Moore (*6*):

$$Y = \frac{\mu_o}{2\mu_o + 3\mu_i} \tag{7}$$

Large Drops

The motion of large spherical-cap gas bubbles has been investigated recently by Mendelson (*9*), who has been very successful in applying an analogy with wave theory. This analogy also correctly takes into account the effect of wall proximity (*8*), and it seems a logical next step to apply the same analogy to the case of liquid drops, that is, to the case where the density of the drop fluid is not negligible.

Direct application of two-fluid wave theory, as discussed by Vehausen and Laitone (*14*), would yield the following equation for the drop velocity:

$$(\rho_i + \rho_o)\ U^2 = \frac{gd}{2}\Delta\rho + \frac{2\sigma}{d} \tag{8}$$

Equation (8) is basically a balance among inertia (left-hand side), gravity, and surface tension (right-hand side). When extended to the analysis of motion of liquid drops, it should be considered that the drop liquid is in steady motion, and therefore it does not contribute any inertia force, in contrast with the classical wave problem. The density of the drop fluid should therefore be dropped, and a more correct form is expected to be

$$\rho_o U^2 = \frac{gd}{2}\Delta\rho + \frac{2\sigma}{d} \tag{9}$$

Inasmuch as wave theory is based on the assumption that viscous forces are negligible, the rheological behavior of both fluids is immaterial, and Equation (9) is expected to hold for both Newtonian and non-Newtonian systems.

Drops of Non-Newtonian Liquids

No information is available for the case where the drop liquid is non-Newtonian. A logical extension of the concepts discussed above for low Reynolds number problems is to define a generalized apparent viscosity ratio X' as

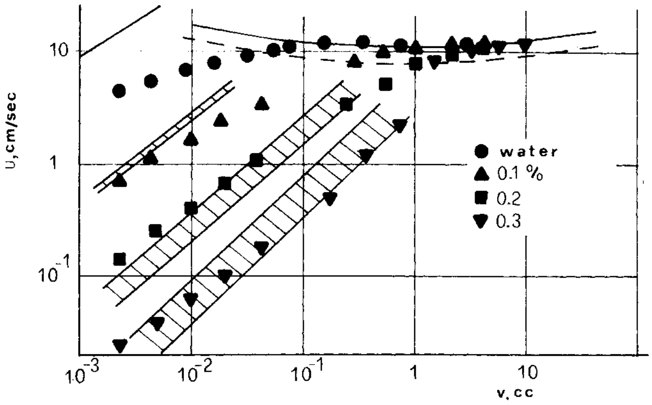

Fig. 1. Terminal velocities of chlorobenzene drops in non-Newtonian field liquids. Straight lines are extension of Stokes' law; shaded area is the range of uncertainty between calculated upper and lower bound.

TABLE 1. SYSTEMS INVESTIGATED

(Physical Properties at 20°C.)

No.	Drop fluid	Field fluid	Interfacial tension, dyne/cm.
1	Chlorobenzene density: 1.107 g./cc. Newtonian, =0.8 centipoise	Water	35.5
2	Chlorobenzene density: 1.107 g./cc. Newtonian, =0.8 centipoise	0.1% ET-597 density: 0.998 g./cc. $m = 0.235$; $n. = 0.745$	34.5
3	Chlorobenzene density: 1.107 g./cc. Newtonian, =0.8 centipoise	0.2% ET-597 density: 0.998 g./cc. $m=1.36$; $n.=0.590$	34.5
4	Chlorobenzene density: 1.107 g./cc. Newtonian, =0.8 centipoise	0.3% ET-597 density: 0.998 g./cc. $m=3.10$; $n.=0.530$	34.5
5	Water	Vaseline oil density: 0.875 g./cc. Newtonian, =225 centipoise	
6	0.1% ET-597	Vaseline oil	
7	0.3% ET1597	Vaseline oil	

$$X' = \frac{m_i}{m_o}\left(\frac{U}{d}\right)^{n_i-n_o} \qquad (10)$$

If $X' >> 1$, no circulation is expected to occur within the drop, and the equations discussed previously (that is, generalizations of Stokes' law) are thus expected to hold. If $X' << 1$, friction due to circulation within the drop is negligible, and again the equations discussed previously (in the form valid when $X << 1$) can be used. Analytical solutions of the equations of motion for the case where $X' \sim 1$ are presumably very difficult to obtain.

EXPERIMENTAL

Experiments have been carried out in two different containers, both having a square cross section and transparent Lucite walls. The first container has a cross section of 8.0 × 8.0 cm. and a height of 140 cm.; it was used for equivalent drop diameter up to 1 cm. The second container has a cross section of 30 × 30 cm. and a height of 80 cm.; it was used only for equivalent drop diameters above 0.5 cm. No corrections for wall proximity effects were thus made on the data because the tank-to-drop diameter ratio was in excess of 16 for all experiments.

The systems investigated are reported in Table 1. The non-Newtonian liquids were aqueous solutions of ET-597, a drag-reducing additive.

For each system, photographs were taken of drops of different volumes and were used to calculate geometrical details of the shape of the drop. Only the ratio of the horizontal dimension d_o to the vertical dimension dv is reported in this work.

Physical properties of the solutions used are reported in Table 1. Rheological properties (that is, values of m and n) were obtained in the shear rate range from 20 to 200 sec.$^{-1}$.

RESULTS AND DISCUSSION

Non-Newtonian Field Liquid

Terminal velocities for systems 1, 2, 3, and 4 are reported in Figure 1. The straight lines are calculated from Equation (3); the upper and lower bounds for Y have been calculated from Wasserman and Slattery's correlation (*15*). Thus, the shaded areas represent the range of values predicted for rigid spheres, that is, when $X >> 1$.

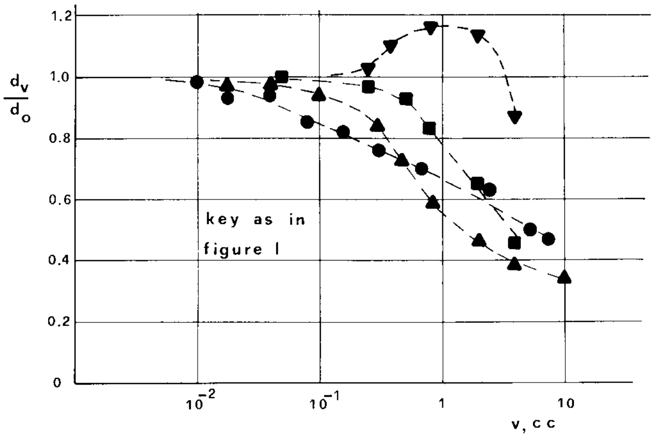

Fig. 2. Aspect ratio for chlorobenzene drops in non-Newtonian field liquids.

In fact, values of X for the data points are always very low, so that the Y value relative to $X = 0$ would be expected to hold. Only the upper bound of the same is known from Nakano and Tien's work (*11*), corresponding to a lower bound for the velocity. With the exception of the data relative to the smallest drops in the 0.2% solution, the values calculated for $X = 0$ are always larger than the experimental value. This indicates that although the drop liquid is much less viscous than the field liquid, the drops in fact behave like rigid spheres. This is not surprising behavior; in fact, even the motion of gas bubbles is often governed by Stokes' law and not by Hadamard-Rybczynsky's law, unless the field liquid is entirely free of any trace of surface active material. Interface rigidity is commonly observed in the motion of small drops and bubbles. This effect could presumably be avoided by using high purity water (*16*), but it was unavoidable with the non-Newtonian liquids, which are polymer solutions. Comparison was thought to be more significant if ordinary tap water was used.

The two curves on the top of Figure 1 are plots of Equations (9) (solid line) and (8) (dashed line). Although the difference between the two lines is not very large, the data clearly indicate that Equation (9) is preferable. Data reported by Winnikow and Chao (*16*) show

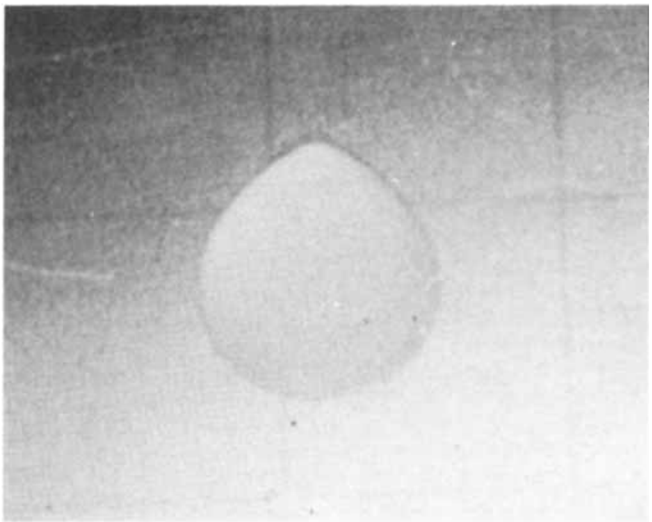

Fig. 3. A drop of chlorobenzene, v = 1.6 cc., falling through 0.3% ET-597 solution.

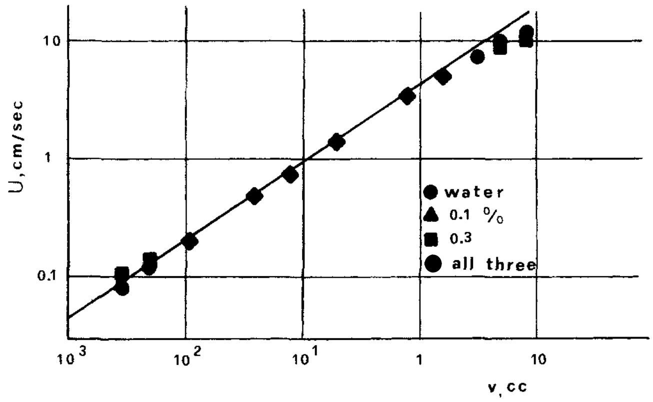

Fig. 4. Terminal velocities of drops in vaseline oil.

that in high purity water, Equation (9) may underestimate the terminal velocity; this may be due to dynamic surface tension effects.

The principal contribution of the present work is the extension of Mendelson's analogy to both Newtonian and non-Newtonian liquid-liquid systems.

The results of the photographic investigation of drop shapes are reported in Figure 2. In non-Newtonian liquids, the shape departs from spherical at larger volumes, but very large drops are even flatter than in Newtonian liquids. For the more concentrated solution (0.3%), the prolate form (that is, the vertical dimension larger than the horizontal one) was observed at drop volumes of the order of 1 cc. This shape, typical of non-Newtonian field liquids, had already been observed for liquid drops (*4*) and for gas bubbles (*2*). Figure 3 is a photograph showing the characteristic tail of prolate drops.

Non-Newtonian Drops Liquid

Terminal velocities for systems 5, 6, and 7 are reported in Figure 4.

For the conditions of the experiments, the drop liquid was, in general, less viscous than the field liquid; in fact, values of X' for the three systems considered range from 0.0045 (system 4) to 1.88 (smallest drop for system 7). Nonetheless, the data show that the properties of the drop liquid are entirely irrelevant; Stokes' law, that is, the equation obtained for $X' \to \infty$, correlates equally well all the data. Again, the phenomenon of interface rigidity is important enough so that the behavior of rigid spheres is approached, even when the drop liquid is much less viscous than the field liquid.

The viscosity of the field liquid is high enough so that for the largest possible volumes the Stokes regime is also approximately attained. The wave theory regime cannot be reached.

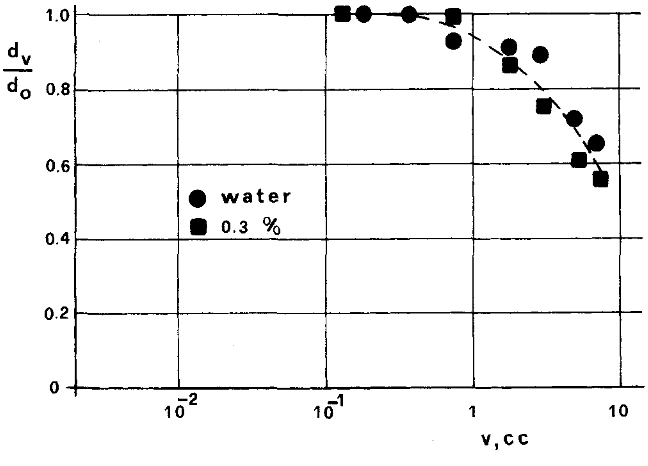

Fig. 5. Aspect ratio for systems 5 and 7.

The irrelevancy of the physical properties of the drop liquid is shown also by the geometric data reported in Figure 5.

CONCLUSIONS

Available predictive equations for terminal velocities can be used satisfactorily for liquid drops in non-Newtonian systems. Interface rigidity is generally so important that extensions of Stokes' law to non-Newtonian systems are preferable to equations obtained by taking into account the relative viscosities of drop and field liquids.

The motion of large liquid drops, in both Newtonian and non-Newtonian systems, is adequately described by an extension of the wave theory analogy, originally proposed for gas bubbles by Mendelson (*9*).

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Luigi Nicodemo has been of great help in carrying out the present work.

NOTATION

d = equivalent drop diameter, cm.
g = gravity acceleration, cm./sec.^{2}
m = consistency, g./cm., sec.$^{2-n}$
n = flow behavior index, dimensionless
U = terminal velocity, cm./sec.
v = drop volume, cc.
x = dummy variable
X = see Equation (5), dimensionless
X' = see Equation (10), dimensionless
$\Delta\rho$ = density difference, g./cc.
μ = viscosity, g./cm., sec.
ρ = density, g./cc.
σ = surface tension, g./sec.^{2}

Subscripts

i = drop liquid
o = field liquid

LITERATURE CITED

1. Astarita, Gianni, *Ind. Eng. Chem. Fundamentals*, **5**, 548 (1966).
2. ————, and Gennaro Apuzzo, *AIChE J.*, **11**, 815 (1965).
3. ————, and Giuseppe Marrucci, *Rend. Accad. Naz. Lincei*, **8-36**, 836 (1964).
4. Fararoui, A., and R. C. Kintner, *Trans. Soc. Rheol.*, **5**, 369 (1961).
5. Hadamard, J., *Compt. Rend.*, **152**, 1735 (1911).
6. Harper, J. F., D. W. Moore, *J. Fluid Mech.*, **32**, 367 (1968).
7. Levich, V. G., *Zh. Eksperim. i Teor. Fiz.*, **19**, 18 (1949).
8. Maneri, C. C., and H. D. Mendelson, *AIChE J.*, **14**, 295 (1968).
9. Mendelson, H. D., *ibid.*, **13**, 250 (1967).
10. Moore, D. W., *J. Fluid Mech.*, **16**, 161 (1963).
11. Nakano, Y., and Chi Tien, *AIChE J.*, **14**, 145 (1968).
12. Rybczynsky, W., *Bull. Ac. Sci. Cracovia*, **A-40** (1911).
13. Stokes, G. G., "Mathematical and Physical Papers," Cambridge Univ. Press, England (1880).
14. Vehausen, J. H., and E. V. Laitone, in "Encyclopaedia of Physics," Band IX, Vol. XI, p. 634, Springer-Verlag, Germany (1960).
15. Wasserman, M. L., and J. C. Slattery, *AIChE J.*, **10**, 383 (1964).
16. Winnikow, S., and B. T. Chao, *Phys. Fluids*, **9**, 50 (1966).

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