COMMUNICATIONS TO THE EDITOR

Hazards with Ammonia and Mercury

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In the January, 1963, issue of the *A.I.Ch.E. Journal*, an article entitled "The Viscosity of Ammonia: Experimental Measurements for the Dense Gaseous Phase and a Reduced State Correlation for the Gaseous and Liquid Regions," by Hiroshi Shimotake and George Thodos, appeared in which viscosity values were obtained in a transient capillary type of viscometer. The experimental procedure required that ammonia be compressed over mercury. When this study was initiated in 1958, there was concern about the possible explosive effects of this system of ammonia in contact with mercury. A cursory literature search was conducted to obtain information on this subject, but nothing was mentioned and the investigation was started in which pressures up to 5,000 lb./sq.in. and temperatures as high as 200°C. were attained. It was not until after this study had been completed that the possible hazard was learned. This information is contained on page 71 of the text, "High Pressure Technology" [McGraw-Hill, New York (1956)] by E. W. Comings in which the following is mentioned:

> Under pressure mercury forms a compound with ammonia consisting of several molecules of ammonia per atom of mercury. This compound apparently is not explosive; however, as the pressure is lowered the ratio of ammonia to mercury decreases and a compound similar to fulminate is formed. This has been known to detonate and is a serious hazard. The hazard is greatest when a system containing mercury and ammonia is being depressurized or the ammonia removed.

Kenneth E. Walker of the du Pont Company has communicated to the author that they have found in their research work that there is a serious hazard in having ammonia in contact with mercury. Specifically he pointed out that "under certain conditions, which are not well understood, a compound is formed which is shock sensitive and explodes with considerable violence." This hazard has also been reported by others. For instance, the Matheson Gas Data Book, published by the Matheson Company, Incorporated, in 1961, states: "Ammonia can combine with mercury to form explosive compounds, therefore, instruments containing mercury that will be exposed to ammonia should not be used."

A. M. J. F. Michels, E. M. L. Dumoulin, and J. H. Gerver [*Rec. trav. chim.*, **76**, 5-12 (1957)] have reported the results of an experimental study entitled "The Reaction of Ammonia on Mercury in the Presence of Traces of Water." These investigators concluded that an explosive compound results at high pressures only in the presence of small quantities of water. This compound has been identified to be an aminomercury oxide and is explosive. Their study corroborates the results of R. G. Roberts [*Science*, **94**, 591 (1941)] who found that pure ammonia does not react with well-purified mercury, even at high pressures and temperatures, and perhaps explains why no explosion was encountered in the study of Shimotake and Thodos in which the ammonia used was most likely completely dry.

This information is brought to the attention of *Journal* readers so that no one in the future attempts to duplicate the procedure described by Shimotake and Thodos without extreme caution. In experimental studies involving the contact of ammonia with mercury, the ammonia should be completely dried by contact with sodium wire. This situation is documentary evidence of the need to exercise extreme caution in experimental studies where complete experimental background is not available.

Hysteresis in Liquid Mixing Systems

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Experiments with a conventional liquid mixing system, consisting of a cylindrical tank equipped with four vertical baffles and a six blade-flat blade turbine impeller, have demonstrated the existence of a hysteresis effect when the rotating impeller is slowly raised from near the bottom of the tank. Under these conditions a metastable axial flow pattern characteristic of propeller agitation exists over a range of impeller heights. This was visually demonstrated with a suspension of small solid particles in the liquid. This axial flow pattern reverts to the normal radial flow pattern again when the impeller is raised above a certain height.

When the rotating impeller is lowered below the standard height of one third the diameter of the tank, the normal radial flow pattern and power output persists over part of the range where the axial, propeller type of flow

TABLE 1. PHYSICAL PROPERTIES OF THE LIQUIDS USED

Liquid	Temperature, T, °F.	Density, e, lb./cu. ft.	Viscosity, μ, cm./sec.
Cylinder oil	73	55.2	2,750
Gulf Paragon no. 84 oil	75	57.2	955
Castor oil	70	59.4	840
Mobil Society of Automotive Engineers No. 50/50 lubricating oil	77	54.9	480
Mobil Society of Automotive Engineers No. 20/20 lubricating oil	82	54.5	103

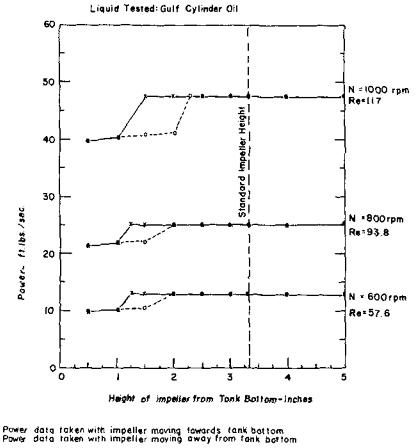

Fig. 1. Experimental hysteresis loop for 10 in. diam. tank.

existed during the upward movement of the impeller. When the impeller is brought sufficiently close to the bottom of the tank, the flow pattern will shift to that of a propeller and the power output will drop. Figure 1 is a typical plot of power output vs. impeller height. The existence of hysteresis, a range of impeller heights in which two power outputs exist, is clearly shown.

If the impeller is stopped and then started, the upper curve in Figure 1 is followed irrespective of the direction in which the impeller is moved. Hysteresis exists only during continuous impeller operation. This effect has been observed at mixing Reynolds numbers of from 20 to 1,000 with the Newtonian materials listed in Table 1. The mixing-power number at the low impeller height is 15% to 20% below the power number for the standard height.

This effect of hysteresis has little practical significance, since the height of an impeller in a tank is rarely, if ever, changed during a process. However, the impeller in a tank is often located near the bottom. The design engineer must take into account the reduced power and altered flow pattern when the impeller is low, so that the equipment is designed to do a satisfactory mixing job. A reduced power output means reduced mixing, and the speed of the impeller should accordingly be increased to compensate.

The Viscosity of Polar Substances in the Dense Gaseous and Liquid Regions

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Jossi, Stiel, and Thodos (*11*) have presented a relationship for the prediction of the viscosity of nonpolar substances. The residual viscosity, $\mu - \mu^*$, was assumed to be a function of the density, molecular weight, and critical constants of the substance, and through a dimensional analysis treatment the correct dependencies were established by the use of experimental data. The resulting relationship, in which the group $(\mu - \mu^*)\xi$ is related to the reduced density, was found to reproduce the reported viscosities for ten substances with a high degree of accuracy. Relationships between $\mu^*\xi$ and T_R, which have also been presented for nonpolar gases (*24*), may be used to calculate the viscosities of these substances at normal pressures (0.2-5 atm.).

Through a dimensional analysis treatment of experimental viscosity data for polar gases, Stiel and Thodos (*25*) have developed the following relationship for polar substances which do not exhibit hydrogen bonding:

$$(\mu^*\xi) z_c^{2/3} = [1.90\, T_R - 0.29]^{4/5} \times 10^{-4} \qquad (1)$$

Similarly, they found that for polar gases which exhibit hydrogen bonding

$$(\mu^*\xi) z_c^{5/4} = [7.55\, T_R - 0.55] \times 10^{-5} \qquad (2)$$

Values calculated from Equations (1) and (2) were found to compare favorably with the corresponding experimental values.

An approach similar to that used by Jossi et al. (*11*) has been employed to develop a relationship which may be used in conjunction with Equations (1) and (2) for the prediction of the viscosity for polar substances in the dense gaseous and liquid regions. If, as in the previous treatment for the viscosity of polar substances at moderate pressures, the critical compressibility factor, z_c, is considered to be an appropriate variable representing the electrostatic nature of the molecules, the application of dimensional analysis to the residual relationship for viscosity is identical to the previous development for nonpolar substances by Jossi, Stiel, and Thodos (*11*), in which the following expression resulted:

$$(\mu - \mu^*)\xi = \frac{\alpha}{R^{1/6}} z_c^m \rho_R^n \qquad (3)$$

TREATMENT OF EXPERIMENTAL VISCOSITY DATA

Experimental high pressure viscosities for the gaseous and liquid phases available in the literature for fourteen polar substances, including five Freons, three alcohols, methyl chloride, chloroform, sulfur dioxide, ethyl ether, ammonia, and hydrazine, were used in conjunction with experimental P-V-T data to establish the constant α and the exponents m and n of Equation (3). The substances are listed in Table 1 along with their critical constants, calculated ξ-values, and the sources of the experimental viscosities and densities utilized.

For each substance values of the quantity $(\mu - \mu^*)\xi$ were calculated from the experimental viscosities and the corresponding values for atmospheric pressure and were plotted against reduced density. Sufficient viscosity data over a complete range of reduced density were available only for methyl alcohol, ethyl alcohol, isopropyl alcohol, ammonia, and ethyl ether. The viscosity data of Golubev and Petrov (*9*), which had not been previously available in this country, were very valuable in establishing the behavior of these substances over a complete range. With the exception of sulfur dioxide only liquid viscosities, many of them for saturated conditions, were available for the other substances.

High pressure density values are not readily available for polar substances, and for several of the substances only viscosity values for saturated conditions could be used because of the lack of density data for other conditions of temperature and pressure. Densities of isopropyl alcohol had to be obtained from the generalized correlation of Lydersen, Greenkorn, and Hougen (*13*) and from the values reported for *n*-propyl alcohol by Ramsay and Young (*18*). The critical density of hydrazine was estimated from the reported saturated liquid densities for the substance (*1*, *29*) by the use of the rectilinear diameter rule proposed by Cailletet and Mathias (*6*).

RESULTS AND CONCLUSIONS

Plots of $(\mu - \mu^*)\xi$ against ρ_R were found to be essentially the same for all

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