# Note on Surface Viscosimetry

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## Additional information on J. Chem. Phys.

## Note on Surface Viscosimetry

Dervichian and Joly[1] have recently corrected an equation of Bresler and Talmud,[2] which describes the viscous flow of a monolayer through a canal above a fluid substrate. While pointing out its qualitative agreement with their experimental results, they express pessimism as to the possibility of an adequate theoretical treatment of the problem. At the same time they dismiss an equation developed by us[3] as inapplicable to surface viscosimeters of current design. This leads us to make several comments on the theoretical and practical aspects of the problem.

The relation between our theory and that of Bresler and Talmud is most easily clarified by a statement of the physical assumptions made in each case. Bresler and Talmud assume complete slip between the substrate and film, introducing a resistance term into the hydrodynamical equation for the film, proportional to its velocity relative to the stationary substrate. We, on the other hand, assume no slip between film and substrate and introduce a resistance term proportional to the normal velocity gradient at the film-substrate boundary. In view of the fact that the substrate is a viscous fluid, our assumption appears to be in better accord with ordinary hydrodynamical ideas. Moreover, since our resistance term depends upon the viscosity coefficient of the substrate, we are not forced to introduce an arbitrary frictional constant as are Bresler and Talmud.

Dervichian and Joly state that our equation applies only to deep canals, but this is not the case. It is only necessary that the bottom of the canal be closed. From the practical standpoint, however, a deep canal needs no bottom. Our equation for the area flux, $A$, may be written to an adequate approximation as follows,

$$A = \frac{\alpha a^3}{12\eta}\left[1 + \frac{a\eta_0}{\pi\eta}\coth\left(\frac{\pi h}{a}\right)\right]^{-1}, \qquad (1)$$

where $\alpha$ is the film pressure gradient, $a$ and $h$ the width and depth of the canal, $\eta_0$ and $\eta$ the respective viscosity coefficients of substrate and film. We remark that Eq. (1) predicts the same type of limiting dependence on the canal width, $a$, as the corrected Bresler-Talmud formula. If both $a/h$ and $a\eta_0/\eta$ are small relative to unity, Eq. (1) reduces effectively to the surface analog of Poiseuille's formula,

$$A = \alpha a^3/12\eta. \qquad (2)$$

On the other hand, if the canal is broad and shallow with $a/h$ and $a\eta_0/\eta$ large relative to unity, the limiting form is,

$$A = (\alpha\pi^2 h/12\eta_0)a, \qquad (3)$$

in which the flux is proportional to the first power of the canal width and is independent of the film viscosity. These are exactly the features which led Dervichian and Joly to favor the Bresler-Talmud equation.

It does not seem a valid criticism of our equation that it is inapplicable to surface viscosimeters of current design. Rather, the possibility of developing an accurate theory for a special type of canal would seem to be a recommendation for the redesign of the instrument and the abandonment of models for which the integration of

the hydrodynamical equations is prohibitively difficult. However, we are in agreement with Dervichian and Joly that there are many practical difficulties to be overcome before the canal viscosimeter can be regarded as an accurate instrument. Turbulence effects, difficult of correction, may be a source of trouble. One might expect them to be particularly dangerous with wide short slits of the type sometimes used by Dervichian. It may also be difficult to prevent some slip of the film at the edges of the canal due to imperfect contact. Compressibility of the film and variation of its viscosity with pressure, by no means negligible factors in many cases, greatly complicate the hydrodynamical equations. Their effect could be minimized by regulating the exit pressure in the canal so that the total pressure drop is small relative to the entrance pressure. Unfortunately, this procedure entails considerable difficulty in the design and operation of the viscosimeter.

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[1] Dervichian and Joly, J. Chem. Phys. 6, 226 (1938).
[2] Bresler and Talmud, Physik. Zeits. Sowjetunion 4, 864 (1933).
[3] Harkins and Kirkwood, J. Chem. Phys. 6, 53 (1938).

## A Temperature Effect in the Infra-Red Spectrum of Phenol

As part of a research program on various organic compounds,* the infra-red spectrum of phenol, from $1\mu$ to $15\mu$, was determined at temperatures of 25°C, 42°C, and 101°C. The spectrometer[1] used was a Wadsworth mounting of a rocksalt prism. The absorption cells were made from partially cleaved rocksalt plates and gave a sample thickness of about 0.01 mm.

The transmission curves in Fig. 1 show that the principal effect of a temperature change is a shift in the positions of the three absorption bands found at about $3\mu$, $7.4\mu$, and $8.2\mu$. The band found at $3.1\mu$ in the spectrum of phenol at 25°C (solid phenol) shifts to $2.96\mu$ when the phenol is melted (42°C) and shifts slightly further ($2.92\mu$) when the liquid phenol is heated to 101°C. The position of the $\nu(O-H)$ absorption, $2.96\mu$, in liquid phenol agrees well with the position of this band as found by Gordy and Nielsen[2] in the spectra of concentrated solutions of phenol in various solvents. The small shift of this band when the temperature was raised to 101°C indicates that the degree of association has not been appreciably changed. The shift of this band to $3.1\mu$ in the spectrum of solid phenol may be due to further association of the "hydrogen bond" type mentioned by Gordy and Nielsen or to forces involved in the crystal structure.

The bands, found at $7.33\mu$ and $8.16\mu$ in solid phenol, shift to longer wave-lengths as the temperature is increased. These shifts are approximately continuous with temperature as contrasted with the shift in the $3\mu$ band. In addition to the wave-length shift, the $8.16\mu$ band increases markedly in intensity and breadth when the sample is melted. The changes in the $8.16\mu$ band mentioned above
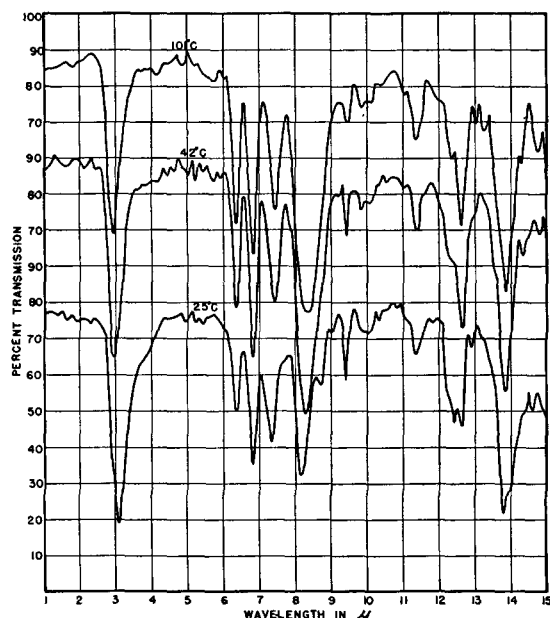
FIG. 1. The transmission spectra of phenol at various temperatures. Cell thickness approximately 0.01 mm.

and the fact that bands at approximately this wave-length are found in the spectra of a large number of compounds containing OH constitute evidence that this band is connected with the hydroxyl group.

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[1] R. B. Barnes, R. R. Brattain and F. Seitz, Phys. Rev. **48**, 582 (1935).
[2] W. Gordy and A. H. Nielsen, J. Chem. Phys. **6**, 12 (1938).

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## Effect of Deuterium Substitution on Color*

Although it is well known that substitution of a deuterium for a hydrogen atom in a compound modifies the physical properties of the compound, still there is no case recorded in the literature where such a substitution changes the color of the compound. Such a color change has been observed by us with nitroethane under special conditions.

When an equivalent quantity of $Ba(OD)_2$ is added to about $0.02N$ proto-nitroethane in heavy water, a proton is removed from the nitroethane to yield the ion $CH_3CH = NO_2^-$ according to the equation:

$$2CH_3CH_2NO_2 + Ba^{++} + 2OD^- = 2CH_3CH = NO_2^- + Ba^{++} + 2HOD. \quad (1)$$
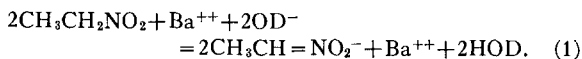
If to this solution be added now an equivalent quantity of $D_2SO_4$, a deuteron is reintroduced into the nitroethane to yield:

$$2CH_3CH = NO_2^- + Ba^{++} + D_2SO_4 = 2CH_3CHDNO_2 + BaSO_4 \downarrow . \quad (2)$$
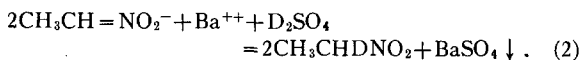
Throughout these operations the solution remains perfectly colorless.

However, if an equivalent quantity of $Ba(OD)_2$ be again added, the solution turns *light yellow* very rapidly. In this case the reaction involved is:[1]

$$2CH_3CHDNO_2 + Ba^{++} + 2OD^- = 2CH_3CD = NO_2^- + Ba^{++} + 2HOD. \quad (3)$$
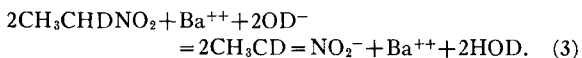
The color can be discharged and brought back by repeated alternate additions of $D_2SO_4$ and $Ba(OD)_2$.

These same operations with $CH_3CH_2NO_2$ in light water and with $Ba(OH)_2$ and $H_2SO_4$ yield no colored solutions.

It will be observed that the only difference between the products in Eq. (1), where there is no color, and Eq. (3), where the yellow color appears, is in the nitroethane ion. In the former the ion is $CH_3CH = NO_2^-$, while in the latter it is $CH_3CD = NO_2^-$, the difference being in the substitution of a deuterium for a hydrogen atom on the carbon $\alpha$ to the nitro group.

From these observations in both $H_2O$ and $D_2O$ it can be concluded that $CH_3CH_2NO_2$, $CH_3CHDNO_2$, $CH_3CD_2NO_2$ and $CH_3CH = NO_2^-$ are colorless, while the ion $CH_3CD = NO_2^-$ is colored a light yellow in solutions about $0.02N$ with respect to nitroethane. Preliminary absorption measurements indicate that absorption starts at 5000–5200A and continues into the ultraviolet.

Because of the possible connection between the development of color and ease of proton and deuteron transfer in conjunction with acid-base catalysis and acid strength ultraviolet and visible absorption spectra are being investigated.

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[1] Wynne-Jones, J. Chem. Phys. **2**, 381 (1934).