Surface Tension–Viscosity Relationship for Liquids

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An extended equation is proposed, $\gamma = \gamma_N e^{-B/(\eta_l - \eta_v)}$ relating absolute viscosity (η) to surface tension γ. This relationship is shown to be valid for a variety of liquids, over the entire liquid range extending from the critical temperature (T_c) to the temperature at which the viscosity becomes infinite (T_N).

RECENTLY, Pelofsky (*11*) proposed the following relationship between surface tension and the absolute viscosity which is, apparently, valid for a large variety of liquids

$$\gamma = A\, e^{\frac{-B}{\eta_l}} \qquad (1)$$

In the above form, Equation 1 can apply only to a restricted temperature range and will necessarily fail at the critical temperature as viscosity is finite while $\gamma = 0$.

Although there is no apparent theoretical justification at the present time for Equation 1, the purpose of this note is to extend the above empirical treatment by introducing the concept of the vapor viscosity (η_v) in equilibrium with the liquid. The author proposes that Equation 1 be written as

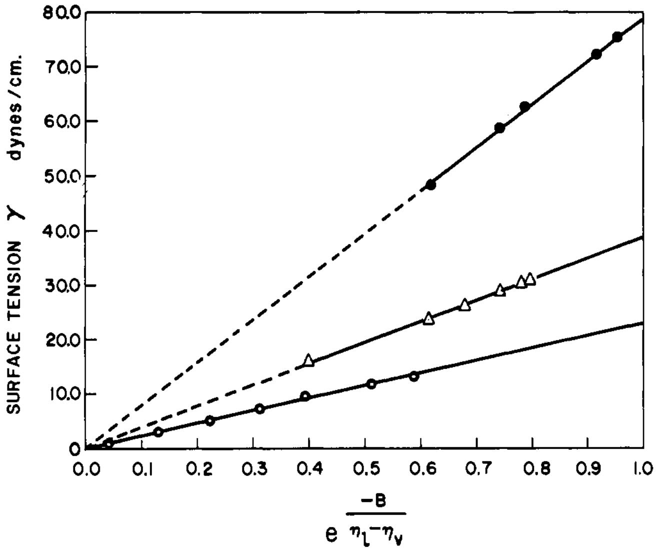

Figure 1. Surface tension for several liquids plotted as a function of $e^{-B/(\eta_l - \eta_v)}$ over entire liquid range

● Water
△ Benzene
○ Argon

$$\gamma = A\, e^{\frac{-B}{(\eta_l - \eta_v)}} \qquad (2)$$

where, $A = \gamma_N$.

At T_c Equation 2 satisfies the boundary condition that as $\gamma_{LV} \rightarrow 0$, exp. $[-B/(\eta_l - \eta_v)] \rightarrow 0$. When $\eta_l \gg \eta_v$, which is at $T \ll T_c$, Equation 1 is obtained. In the vicinity of the critical temperature, when η_v makes a sizable contribution, considerable deviations from linearity are observed when Equation 1 is employed.

The author selected several liquids where data are available over an appreciable temperature interval to demonstrate the validity of Equation 2. These data are plotted in Figure 1. Apparently, argon is the only liquid for which there are extensive and reliable data near the critical region. Here, the agreement is excellent. The discrepancy between the literature values of η_l for water in the critical temperature region makes the extension of the plot to the region doubtful (*3*). For all the liquids quoted by Pelofsky, as well as those shown in Figure 1, the plots pass through the origin.

As has been indicated by Pelofsky, the slope may be an indication of the surface tension of the substance at the temperature where $\eta = \infty$. Table I attempts a correlation between the temperature where $\eta \rightarrow \infty$ and the temperature of homogeneous nucleation. Homogeneous nucleation as opposed to heterogeneous nucleation results from a spontaneous phase change without the assistance of impurities. The principal component of the energy barrier in homogeneous nucleation is the thermal energy that keeps two particles from clustering together. A special feature of nucleation phenomena is that in forming particles of a new phase, energy is required to form the new surface. Opposing these forces are the intermolecular attractive forces. When the

Table I. Correlation between T_N and T^* for a Variety of Liquids

Liquid	γ_N Dynes/Cm.	γ_M, Dynes/Cm.	$\partial\gamma/\partial T$, Dynes/Cm.-°K.	T_M, °K.	T^*, °K.	T_N, °K.	References	
							Surface tension	Viscosity
Sodium	212.8	200.2 ± 0.6	−0.11	371.0	...	256.5	(*8*)	(*4*)
Potassium	120.7	110.3 ± 1.0	−0.06	337.2	...	164.2	(*8*)	(*4*)
n-Decane	30.48	29.3	−0.110	243.5	233[c]	233	(*1*)	(*1*)
Argon	22.9	13.43	−0.25	83.78	...	45.9	(*14*)	(*4*)
Benzene	38.87	30.95	−0.13	278.4	208.2 ± 2[a]	217.5	(*10*)	(*6*)
Water	79.10	75.63	−0.14	273.2	232.7 ± 1[a]	248.2	(*10*)	(*4*)
CCl_4	36.14	31.67	−0.121	250.2	200.2 ± 2[a]	213	(*10*)	(*6*)
KBr	105.4	88.6	−0.073	1013	845[a]	783	(*5*)	(*6*)
NaBr	108.2	98.9	−0.056	1023	857[a]	857	(*5*)	(*6*)
NaCl	132.1	116.3	−0.093	1074	905[a]	904	(*5*)	(*6*)
Polyethylene	31.6	27.0	−0.06	418	358[b]	352	(*13*)	(*12*)

[a] Ref. (*7*). [b] Ref. (*1*). [c] Critical temperature.

intermolecular attractive forces exceed the thermal and surface forces, which tend to prevent clustering, irreversible formation of a new phase occurs. If this approach is valid, it would permit an estimation of the T_N without performing the usual droplet experiment of Turnbull and Cormia (*15*). The temperature corresponding to an infinite viscosity, T_N, is obtained from an analysis of the liquid surface tension data. The surface tension data for the liquids in Table I were plotted as a function of temperature and extrapolated to lower temperatures by assuming $(\partial\gamma/\partial T)$ to be constant. In general, the plots of γ *vs.* T were sufficiently linear to warrant such an approximation. The temperature at which $\gamma = \gamma_N$, is defined as T_N. The values of T_N for a variety of liquids are listed in Table I.

Several interesting correlations are immediately apparent from the foregoing analysis. Apparently, T_N represents a temperature below which there is no liquid phase but only a crystalline or glassy state.

The intercept for argon suggests that a considerably greater lowering of the temperature of the liquid could be effected before homogeneous nucleation occurs, but, apparently heterogeneous nucleation cannot be avoided (*2*, *9*). It is possible that heterogeneous nucleation has not been avoided in the case of KBr where $T_N < T^*$. Equation 1, as well as Equation 2, indicates a functional relationship of $\eta_l - \eta_v$ which is different from that in the usually accepted Williams, Landel, Ferry (*16*) equation.

ACKNOWLEDGMENT

The author expresses his appreciation to Harry L. Frisch for helpful discussions and for his aid in preparing the manuscript.

NOMENCLATURE

A = γ_N
B = constant, gram/cm.-sec. (poise)
T = temperature, ° K.
T^* = temperature of homogeneous nucleation, ° K.
T_c = critical temperature, ° K.
T_M = melting temperature, ° K.
T_N = temperature where $\eta_l = \infty$, ° K.
γ = surface tension, dynes/cm.
γ_N = surface tension at T_N, dynes/cm.
η_l = absolute liquid viscosity, gram/cm.-sec. (poise)
η_v = absolute vapor viscosity, gram/cm.-sec. (poise)
η_c = absolute critical viscosity, gram/cm.-sec. (poise)

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Received for review April 5, 1967. Accepted July 27, 1967.

Densities of Potassium Hydroxide Solutions

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Densities of aqueous solutions of potassium hydroxide are reported for the temperature range 60° to 161° C. and the concentration range 0 to 77.1% by weight.

A KNOWLEDGE of the properties of aqueous potassium hydroxide solutions at relatively high temperatures and concentrations is of value in the design and operation of fuel cells and batteries. Density data for potassium hydroxide solutions for the temperature range 0° to 70° C. and a concentration range of 0 to 50 wt.% have been reported by Akerlof and Bender (*1*), and Kelly, Borza, and Harriger (*3*) have reported densities at lower temperatures (−54° to 0° C.) for the same concentration range.

EXPERIMENTAL

Solutions were prepared from reagent grade KOH containing less than 1% carbonate. Solutions were analyzed for both total alkalinity and carbonate content to check against buildup of potassium carbonate. Concentrations in Table I are total alkalinity reported as weight per cent KOH. Aqueous solutions of concentrations below the saturation value at room temperature were stored in polyethylene bottles. More concentrated solutions were stored in Teflon bottles and kept in an oven at temperatures varying from 80° to 140° C., the temperature used depending on the concentration.

The method used to determine densities was the hydrostatic weighing method of Kohlrausch, and the usual precautions were taken (*2*). A silver plummet was used, and was electroplated with pure silver to reduce corrosion. The plummet was calibrated at temperatures up to 100° C. using water and following the procedure described by Bauer and Lewin (*2*); plummet volumes at higher temperatures were