If inactive domains (i.e., clusters) must exist, then entropy can best be maximized in their presence by subdividing the domains into the smallest possible sizes consistent with their continued existence. However, if the domains are to retain their integrity, they must be separated from one another by zones of activated molecules which are at least one molecule thick. Thus, one must conclude that the minimum thickness of the activated zones is one molecule.

On the other hand, if the activated zones should tend to grow thicker than this, it is obvious that they can do so only with the simultaneous coalescence of inactive domains into larger clusters, since at any given temperature the ratio of active to inactive molecules is fixed. Since the inactive domains represent a generally more ordered condition, such coalescence necessarily must lead to a reduction in the overall entropy of the system, inasmuch as enlargement of the activated zones cannot provide a compensating increase in entropy. Consequently, the demand for maximum entropy sets an upper limit of one molecule to the thickness of the activated zones. One is therefore forced to the conclusion that, on the average, the activated zones between inactive domains are exactly one molecule thick.

Summary

Viscosities are calculated from a two-parameter equation for both "non-associated" and "associated" liquids. The calculated values agree with the experimentally determined viscosities with mean errors of less than 3.5 per cent for normal paraffins up to twenty carbon atoms, and of less than five per cent for most associated liquids. The computations are expedited by a tabulation of the viscosity function, which is presented and which permits the determination of the entire viscosity-temperature profile of a liquid from an experimental knowledge of only two points on the curve.

Zusammenfassung

Mit Hilfe einer 2-Parameterformel werden Viskositäten für „assoziierte“ und „nichtassoziierte“ Flüssigkeiten berechnet. Die berechneten Werte zeigen durchschnittliche Abweichungen von weniger als 3,5% für normale Paraffine bis zu C20 und weniger als 5% für die meisten assoziierten Flüssigkeiten. Eine Tabelle dieser Viskositätsfunktion wird gegeben, mit deren Hilfe aus 2 Meßpunkten das Viskositätstemperaturverhalten vom Schmelzpunkt bis zum Siedepunkt vorhergesagt werden kann.

Schlüsselwörter

2) Data from F. D. Rossini et al., Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds (New York 1953).
3) Data from C. D. Hodgman et al., Handbook of Chemistry and Physics, 38th edn., pp. 2030-6 (New York 1956).
4) Andrade, E. N. da C., Phil. Magazine 17, 497, 698 (1934).

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Properties of the Liquid State

III: General Relationship Between Viscosity, Density and Temperature *)

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With 2 tables

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It has previously been shown (1) that the variation of liquid viscosities with temperature can be accurately expressed by the general relation,

$$\eta = \frac{q e^a}{V^{1/3a}}$$  \[1\]

where \( V \) is the molar (or, alternatively, the specific) volume of the liquid, \( q \) is a characteristic parameter of the liquid for the flow process and contains both a constant of integration and dimensional conversion factors, and \( a \) is the number of molecules on the edge of an (assumed cubic) domain of ordered inactive molecules which is separated from adjacent similar domains by a layer of activated molecules having energies in
excess of a characteristic threshold, $E_a$. The magnitude of $a$ at any temperature is expressed by the general function,

$$a = \frac{(1 - e^{-E_a/(RT)})^a}{1 - (1 - e^{-E_a/(RT)})^a}.$$  

The model used in deducing eqn. [1] assumed laminar flow in layers having a thickness of one unit cell in the generalized liquid model [i.e., $(a + 1)$ molecules], and the interlaminar resistance to flow was considered to be an function of this laminar thickness.

An alternative model for the flow process may also be conceived. Because of the undoubted fact that the unit cells of the liquid model must be randomly intermingled, one may visualize the lamina of flow as constituting networks of unit cells, intermeshed like two sheets of sandpaper with the rough sides pressed together. In this model, the spatial extent of the meshing process (i.e., the laminar thickness) must be an increasing function of the increasing sizes of the unit cells. The flow process which occurs at the boundaries of the laminae may then be regarded as involving, at least in the limit, a constant interlaminar resistance to flow. This may be expressed by

$$\eta_0 = \frac{dF_m}{d(\Delta u)},$$  

where $\eta_0$ is the constant interlaminar coefficient of resistance, while $\Delta u$ is the velocity difference between two adjacent laminae of thickness, $z$, the latter being now a function of the unit cell sizes but not that size itself. The quantity, $F_m$, is the applied force necessary to impart a constant velocity gradient to the bulk liquid which is flowing. However, in laminar flow, this gradient must be made up of steps, so that

$$\frac{du}{dx} = \frac{\Delta u}{z}.$$  

When the laminar thickness is regarded as an exponential function of the inactive domain size, eqn. [4] becomes

$$\Delta u = \frac{du}{dx} e^a,$$  

and, remembering that $du/dx$ is constant in the type of flow under consideration, differentiation of (5) yields

$$d(\Delta u) = \frac{du}{dx} e^a da.$$  


$$dF_m = \eta_0 \frac{du}{dx} e^a da,$$

and, since on the macro scale, flow under constant velocity gradient requires the condition that $dF_m = \frac{du}{dx} \cdot d\eta_m$, one may write

$$\eta_0 e^a da = d\eta_m.$$  

Integration of eqn. [8] between the limits, 0 to $a$ on the left and $\eta_0$ to $\eta_m$ on the right then yields

$$\eta_m = \eta_0 e^a$$

which upon conversion into the units of common dynamic viscosity, is seen to be identical to eqn. [1]. Thus, the same relationship between viscosity and temperature ensues regardless of the limiting model for the flow process used as the basis for the reasoning. In actual practice, it is probable that the real flow process lies somewhere between the two idealized extremes. However, the identity of the function resulting from both lines of reasoning suggests that this function may also be true for the intermediate, real situation. Moreover, the manner of deduction presented here shows more clearly than does the former one (1) that $q = \eta_0$ may now be regarded as a "quantum" of molar viscosity in accordance with eqn. [3].

The Density

Since eqn. [1] still contains a term involving the molar volume, if one is to complete the description of the temperature dependence of viscosity, it is necessary to deduce a function for the temperature-dependence of the molar volume. The consideration of this problem is most easily undertaken in terms of the linear dimension, and the flowing laminae discussed above provide a particularly convenient context in which to analyze the question, although it should be emphasized that this is a matter of convenience and not of necessity.

In terms of the limiting model just developed, the interlaminar regions may be regarded as "zones of disengagement" of constant width for any given liquid (consistent with the constant $\eta_0$), where the interlocking effects of randomly oriented unit cells undergo a brief hiatus. Such an interruption could occur either through a microscopic separation of the coherent lamina (accompanied by an increase in average intermolecular distance) after the fashion of a macroscopic tensile rupture, or by a small contraction of intralaminar distances which, in the aggregate, would permit an increasing interlaminar distance