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The Pressure Coefficient of Viscosity

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May 26, 1947

THE writer showed in a recent paper¹ that the pressure coefficient of viscosity, if expressed in the form proposed by Eyring and co-workers,² can be used as a measure of the displacement of a molecule from its equilibrium position during the flow process. The pressure coefficient largely determines, therefore, the magnitude of the energy of activation for hole formation.¹ In order to calculate the latter from first principles, it was found that only ΔV_{\ddagger}^3 remained to be calculable from physical constants not derived from viscosity measurement.

The concept of ΔV_{\ddagger} as the size of the hole required for a molecule to move into suggests that the amount of available volume in the liquid should influence the numerical value of ΔV_{\ddagger} . One could expect that in a liquid of loose packing the hole-size requirement be smaller than in a closely packed liquid, and *vice versa*. A good measure of the tightness of packing seems to be the expansion at the melting point ΔV_f and the structural type of the lattice system. The latter is today quite generally believed to be carried over from the solid into the liquid state, at least in the neighborhood of the melting point.

A rough indication of the correctness of this picture would be constancy of the volume fraction represented by the sum of ΔV_{\ddagger} and ΔV_f , e.g.,

$$\Delta V_{\ddagger} + \Delta V_f = V/n, \quad (1)$$

where n = universal constant, possibly dependent upon the lattice type.

Table I shows that this is indeed the case. For the few liquids, of which viscosity-pressure and melting-point expansion⁴ data are available, n appears to have the values 3 and 5, at least for the ΔV_{\ddagger} determination closest to the melting point. All of the substances for which $n=3$ show rhombic or monoclinic crystal structure in the solid state, whereas cubic or hexagonal arrangement seems to be

TABLE I. Relationship between viscosity-pressure coefficient ΔV_{\ddagger} and the melting-point expansion ΔV_f .

Substance	ΔV_{\ddagger} cm ³	$(\Delta V_{\ddagger} + \Delta V_f)/V$	t °C	
Benzene	16.6	.32	30	$n \sim 3$
<i>p</i> -xylene		.32	75	
Aniline	21.3	.32	30	
Cyclohexane	26.6	.30	75	
Methanol†	7.9	.26/8	30	
Carbon tetrachloride	18.4	.21	30	$n \sim 5$
Chlorobenzene	13.2	.20	30	
Bromobenzene	13.5	.19	30	
Acetone†	11.7	.20	30	
Ethyl ether†	10.1	.15	30	
Ethyl bromide†	10.7	.20	30	$n \sim 3$
Ethyl iodide†	10.5	.17	30	
<i>n</i> -pentane	15.3	.31††	30	
Neopentane	34.4	.32††	30	
<i>n</i> -hexane	17.3	.30††	30	$n \sim 3$
Eugenol	34.2	.30††	30	

† These compounds have melting points which are >100°C below the temperature of viscosity measurement. The ΔV_{\ddagger} data may, therefore, not be comparable with those of the other compounds.

†† ΔV_f values were estimated from rather approximate dT_m/dp data.

preferred when $n=5$. This sequence is in accord with the well-known difference in restraint imposed on free rotation of molecules in the respective solid lattices.

The temperature and pressure coefficient of ΔV_f does not explain the very complicated temperature and pressure dependence of ΔV_{\ddagger} .

These data indicate quite clearly, however, that ΔV_{\ddagger} is a function of both the structure of the liquid and the spatial configuration of the individual molecule, as had been pointed out previously.

The writer takes this opportunity to thank Professor F. London for directing his attention to an error made in the numerical calculation of Fig. 1 in reference 1. The lowest point at $\theta=90^\circ$ is at $b=4$ and not at $b=2$. A revised drawing will be presented in a forthcoming paper.

¹ A. Bondi, J. Chem. Phys. **14**, 592 (1946).

² A. E. Stearn and H. Eyring, Chem. Rev. **29**, 509 (1941).

³ ΔV_{\ddagger} is defined by $(\partial \Delta F_{\ddagger} / \partial p) T = \Delta V_{\ddagger}$, where $\Delta F_{\ddagger} = RT \ln(V\eta/Nh)$ is the free energy of activation for viscous flow.

⁴ D. Rozental, Bull. Soc. Chim. Belg. **15**, 585 (1936).

Method for Extending Study of Metal Ion-Cation Exchanger Isotope Fractionation

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June 2, 1947

FEW experiments dealing with isotope fractionation in cation-cation exchanger equilibria have been reported since the pioneer work of Taylor and Urey.¹ The purpose of this communication is to indicate procedures by which isotope separation data can be obtained for additional elements using equipment available in a relatively large number of laboratories.

Small quantities (about 5 to 50 microcuries, depending on the specific experiment) of radio-isotopes are added to the element in normal abundance and the solutions used in cation-exchange column studies. Detection of small volume "leading samples" is effected by suitably installing one or more Geiger-counter tubes near the exit end of the column. The concentration of the radio-isotope is proportional to the measured sample activity per unit weight of the element when the measurements are made under comparable conditions.

Of special interest from the standpoint of small atomic mass and convenience of measurement are the systems Be⁷-Be⁹ and Be⁹-Be¹⁰. The systems Na²²-Na²³ and Na²³-Na²⁴ can be used for sodium studies. The fractionation of K³⁹-K⁴¹ was explored by Taylor and Urey.¹ Radio-isotope K⁴² can be used in column experiments. It is less convenient to study the fractionation of the naturally radioactive K⁴⁰, since a relatively large potassium sample is required. In the case of calcium, Ca⁴¹ and Ca⁴⁵ may be used. The mass difference between the latter and the most abundant natural isotope Ca⁴⁰ is an advantage in this work.

Experiments of this kind should afford a more thorough understanding of the mass effect and the isotope separating properties of the various types of cation exchangers. Several exploratory experiments have been started in our laboratory.

¹ T. I. Taylor and H. C. Urey, J. Chem. Phys. **6**, 429 (1938).