Summary

1. Attention has been called to a non-electrolytic reaction between molten lithium salts and glass wherein sodium ions of the glass are displaced by lithium ions.

2. The reaction has value in analytical chemistry but, from the quantitative standpoint, its application is limited.

3. The nature of the phenomenon was studied in some detail.

LEXINGTON, KENTUCKY RECEIVED MARCH 1, 1935

NOTES

Comparison of Viscosity Data

BY FRANCIS T. MILES[1]

In a recent paper[2] Miss Mary D. Waller calculates for a number of compounds the ratios of the viscosities at the melting and boiling points and correlates the values of this ratio, η_f/η_b, with the molecular symmetry of the compounds. Molecules of high symmetry are found to have low values of η_f/η_b, and *vice versa*. In a preliminary paper[3] the same author states that the melting and boiling points can be used as comparison temperatures. It is well known, however, that the melting point of a compound is influenced by the symmetry of the molecule. Dietz and Andrews[4] have pointed out that in the series, benzene, dihydrobenzene, tetrahydrobenzene, cyclohexane, the melting points of the two symmetrical compounds, benzene and cyclohexane, are 100° higher than those of the unsymmetrical compounds, while the boiling points of all four compounds lie in a range of only 2°. These authors have proposed an explanation for this influence of molecular symmetry on the melting point. If a pair of compounds had the same boiling points and equal viscosities at equal temperatures, the less symmetrical of the two compounds, having the lower melting point, would have a higher viscosity at the melting point and therefore a higher ratio, η_f/η_b. It is interesting to calculate whether the changes of η_f/η_b in a series of similar compounds are due primarily to the variation of viscosity with temperature or merely to the lower melting points of the unsymmetrical compounds.

The variation of viscosity with temperature can be expressed approximately by an equation of the form

$$\log \eta = A + B/T_{\text{Abs.}}$$

and this relation was used by Miss Waller to extrapolate viscosity data to the melting and boiling points. It follows from this equation that

$$\log r = \log \eta_f - \log \eta_b = B(1/T_f - 1/T_b)$$

Thus it is possible to separate log r into two factors of which one, B, represents the variation of viscosity with temperature, and the other, $1/T_f - 1/T_b$, represents the extent of the liquid range and is independent of the viscosity of the liquid, except in so far as this may be a factor in determining the melting and boiling points. Miss Waller tabulates values of $T_b - T_f$ and states that changes in this do not explain the changes in r. In view of the above equation, however, it is interesting to compare log r and $1/T_f - 1/T_b$, and this is done in Tables I and II. The first four columns in each table are taken directly from Miss Waller's paper. In the fifth column are values of log r calculated from these data. Values of $1/T_f - 1/T_b$, calculated from the melting and boiling points, are given in column six, and in the last column values of B are calculated from the relation

$$\log r = B(1/T_f - 1/T_b)$$

TABLE I

	η_f	η_b	r	log r	$(1/T_f - 1/T_b) \times 10^3$	$B \times 10^{-2}$
Benzene	0.0082	0.0034	2.2	0.38	0.76	5.0
Toluene	.055	.0026	21	1.33	2.92	4.5
Ethylbenzene	.059	.0025	24	1.37	3.13	4.4
o-Xylene	.019	.0026	6.6	0.86	1.67	5.2
m-Xylene	.018	.0024	7.5	.88	2.14	4.1
p-Xylene	.00703	.0024	3	.47	1.04	4.6

TABLE II

	η_f	η_b	r	log r	$(1/T_f - 1/T_b) \times 10^3$	$B \times 10^{-2}$
Pentane	0.038	0.0021	18	1.26	3.83	3.3
Hexane	.0194	.0021	9	0.96	2.67	3.6
Heptane	.0279	.0021	13	1.12	2.77	4.05
Octane	.0189	.0021	9	0.96	2.11	4.55
Nonane	.025	.0021	12	1.08	2.14	5.05
Decane	.0232	.0021	11	1.04	1.90	5.5
Undecane	.0295	.0020	16	1.17	1.92	6.1

Table I gives the results for benzene and some of its homologs. Examination of the last two

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[2] Waller, *Phil. Mag.*, **18**, 579 (1934).

[3] Waller, *ibid.*, **18**, 505 (1934).

[4] Dietz and Andrews, *J. Chem. Phys.*, **1**, 62 (1933).

columns of this table shows that while B is approximately constant (within 30%) and shows no regular dependence on molecular symmetry, $1/T_f - 1/T_b$ varies over a four-fold range and shows a definite increase with decreasing symmetry. In other words the increase of r with decreasing molecular symmetry can be largely attributed to changes in $1/T_f - 1/T_b$. In the case of the paraffins (Table II) B increases regularly with the increase in the number of carbon atoms, as has been pointed out by Dunn,[5] while $1/T_f - 1/T_b$ decreases on changing from a hydrocarbon containing an odd number of carbon atoms to one containing an even number of carbon atoms and increases on proceeding to the next (odd) hydrocarbon. This is evident from Fig. 1 in which log r, B and $1/T_f - 1/T_b$ are plotted against the number of carbon atoms in the molecule. The alternation in r, pointed out by Miss Waller, can thus be traced to an alternation in $1/T_f - 1/T_b$ which is due to the well known alternation in the melting points.

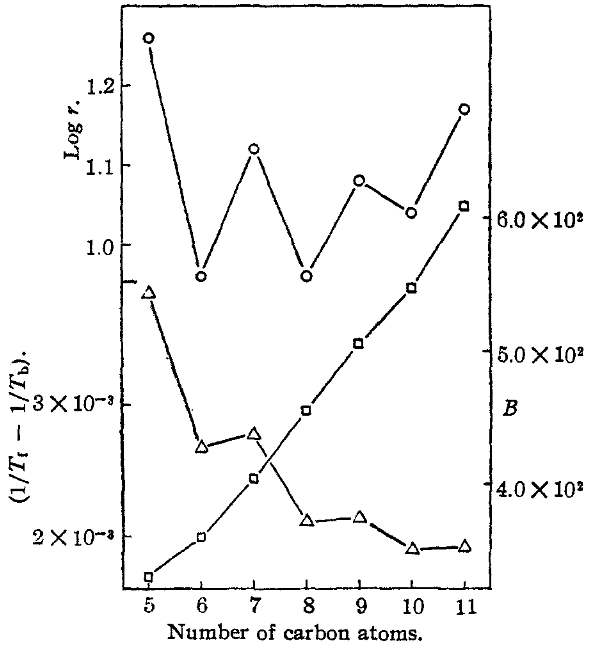

Fig. 1.—Log r, ⊙; $(1/T - 1/T)$, △; B, □.

From these calculations it appears that the correlation between values of r and molecular symmetry is due, in a large part at least, to the dependence of the melting point on molecular symmetry, which does not involve viscosity. It is doubtful, therefore, whether the melting point should be used as a standard temperature for the comparison of viscosities.

The writer is indebted to Professor Hans Erlenmeyer for advice and help on this note.

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BASEL, SWITZERLAND
RECEIVED JANUARY 9, 1935

An Explanation of Hysteresis in the Hydration and Dehydration of Gels

BY JAMES W. MCBAIN

It is well known that hysteresis in the hydration and dehydration of porous gels at moderately high relative humidities is connected with the filling and emptying of pores with liquid.[1]

Such hysteresis sometimes persists even after rigorous evacuation in the attempts to eliminate other impurities.[2] An explanation is usually sought in terms of "friction in the contact angle" or the familiar "Jamin effect."

It is the purpose of this note to present an alternative mechanism, suggested in discussion with the class on Sorption at Stanford University. Figure 1a gives in well-known fashion an illustration of the fact that capillary condensation occurs in wettable pores of sufficiently small radius and relatively high humidities in accordance with the formula of Lord Kelvin[3] as used by Anderson[1]

$$\ln p/p_s = -2\sigma v/rRT$$

where p is the pressure at concave surface, p_s is the pressure of saturated vapors of liquid in bulk at that temperature, σ is the surface tension, v is the volume of 1 gram mole of condensed liquid, r the radius of the capillary, R the gas constant, T the absolute temperature, and ln represents the natural logarithm to the base e.

The applicability of the formula depends upon the liquid and is generally restricted to pores of radius from about 20 Å. up to visible dimensions.

Figure 1b gives a diagram of a lecture experiment we have used to show two possible positions of true stable reversible equilibrium, where a stoppered bell jar has a narrow capillary passing through the stopper. Either the capillary is filled to the same height as in Fig. 1a, the bell jar

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(5) Dunn, *Trans. Faraday Soc.*, **22**, 401 (1926).

(1) McBain, "The Sorption of Gases and Vapours by Solids," George Routledge and Sons, Ltd., London, 1932; Zsigmondy, *Z. anorg. Chem.*, **71**, 356 (1911); "Kolloidchemie," O. Spamer, Leipzig, 5te Aufl., Bd. 11, p. 76, 1927; Zsigmondy, Bachmann and Stevenson, *Z anorg. Chem.* **75**, 189(1912); Anderson *Z. physik. Chem.*, **88**, 212 (1914).

(2) Lambert and Clark, *Proc. Roy. Soc.* (London), **A122**, 507 (1929); Foster, *ibid.*, **A147**, 128 (1934).

(3) Thomson, *Phil. Mag.*, [4] **42**, 448 (1871).