recently cooled liquid. The observed differences, depending on rate of freezing, can similarly be explained as arising from differences in heat conductivity within the sample, which depends on the size of crystals among other factors.

The results of the present investigation neither support nor definitely disprove these effects reported by Railing. They do, however, offer strong evidence against the slow *cis–trans* isomerization suggested by him in explanation. The presence of *cis* and *trans* isomers would be expected to produce variations in the melting point and other peculiar effects which were definitely not observed. Also, according to Railing's suggestions, absorption of heat and apparent cooling would be expected after melting the material. No such cooling effect was observed in the heat of fusion experiments.

## Summary

The thermal behavior of ethylene dichloride and ethylene dibromide was investigated from 15°K. to room temperature, for which range values of the heat capacities are given. The following melting points (0°C. = 273.10°K.) and heats of fusion were determined: $C_2H_4Cl_2$, 237.2 ± 0.1°K., 2112.0 ± 2 cal./mole; $C_2H_4Br_2$, 283.0 ± 0.2°K., 2615.8 ± 5.0. The following temperature and heat of transition values were determined: $C_2H_4Br_2$, 249.54 ± 0.10°K., 463.8 ± 2.0 cal./mole. From these data, the following values of entropy at 298.1°K. were calculated: $C_2H_4Cl_2$(l), 49.84 ± 0.15 cal./deg. mole; $C_2H_4Br_2$(l), 53.37 ± 0.20 cal./deg. mole.

Ethylene dichloride shows no sharp transition but has a peak in the heat capacity curve near 177°K. which may correspond partially to the transition in ethylene dibromide. A possible explanation of the transitions is offered.

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[CONTRIBUTION FROM THE MALLINCKRODT CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

# The Viscosity of Solutions of Electrolytes as a Function of the Concentration. VI. Potassium Bromide and Lanthanum Chloride

BY GRINNELL JONES AND ROBERT ELIOT STAUFFER

The general objective of this paper and of the others of this series is a study of the viscosity of solutions of electrolytes as a function of the concentration, temperature and nature of the salt. The earlier papers[1] should be consulted for a more detailed theoretical discussion and for a description of the experimental technique.

The potassium bromide used in this work was prepared by S. Baeckström.[2]

The lanthanum chloride was originally purified from other rare earths by the late Professor Charles James and had been used in previous investigations in this Laboratory[3] and recovered by precipitation as the oxalate. The oxalate was ignited to the oxide, dissolved in a solution of hydrochloric acid in ethyl alcohol, filtered through a sintered glass filter, chilled with ice and hydrogen chloride gas passed into the solution until the lanthanum chloride was precipitated. The salt was dried by centrifugal drainage and reprecipitated from alcohol in the same manner. The use of ethyl alcohol instead of water gives better yields. A suitable quantity for each solution was placed in a platinum boat inside of a quartz tube and heated to 600° for four hours in a stream of hydrogen chloride gas without fusion. The salt was cooled in an atmosphere of hydrogen chloride gas and then the acid gas replaced by dried air and the boat put into a weighing bottle by the use of a Richards bottling apparatus. The solutions were then made up by weight.

The solutions prepared from the salt dried in this manner had a *p*H of about 6.0 when tested with brom thymol blue, which agrees with the earlier work of Kolthoff and Elmquist,[4] and of Jacques[5] and of Jones and Bickford.[6] No corrections were applied for this slight hydrolysis. Erratic results were obtained at first and the cause was traced to a slight deposit of lanthanum hydroxide in the capillary tube of the viscometer. However, it was found that the deposit was formed during the rinsing of the viscometer with hot water after a series of measurements, which in-

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[1] Grinnell Jones and M. Dole, THIS JOURNAL, **51**, 2950 (1929); Grinnell Jones and S. K. Talley, *ibid.*, **55**, 624, 4124 (1933); *Physics*, **4**, 215 (1933); Grinnell Jones and H. J. Fornwalt, THIS JOURNAL, **57**, 2041 (1935); **58**, 619 (1936); **60**, 1683 (1938); Grinnell Jones and R. E. Stauffer, *ibid.*, **58**, 2558 (1936); **59**, 1630 (1937); Grinnell Jones and S. M. Christian, *ibid.*, **59**, 484 (1937); Grinnell Jones and E. Ferrell, *J. Chem. Soc.*, 325 (1939).

[2] Grinnell Jones and S. Baeckström, THIS JOURNAL, **56**, 1519 (1934).

[3] Grinnell Jones and C. F. Bickford, *ibid.*, **56**, 602 (1934); Grinnell Jones and L. T. Prendergast, *ibid.*, **58**, 1376 (1936).

[4] I. M. Kolthoff and R. Elmquist, THIS JOURNAL, **50**, 959 (1928).

[5] A. G. Jacques, Dissertation, Harvard University, 1931, p. 344.

[6] Grinnell Jones and C. F. Bickford, THIS JOURNAL, **56**, 605 (1934).

fluenced subsequent measurements with water or other solutions. By rinsing at first with hydrochloric acid instead of with water the tubes were kept clean and more consistent and reliable measurements obtained.

In some cases a correction not exceeding a few hundredths of one per cent. was applied by interpolation to bring the results to the round concentration given, but if the correction required was substantial the actual data are given and the interpolated values at the round concentration are shown in parentheses. The lanthanum chloride solutions were measured at both 25 and 0° but measurements were made at 0° only on the potassium bromide solutions because measurements on this salt at 25° already had been made in this Laboratory.

The kinetic energy correction has been applied to the data, but no correction[7] has been applied for surface tension effects because the surface tension data are not available.

TABLE I

DENSITY AND RELATIVE VISCOSITY OF POTASSIUM BROMIDE SOLUTIONS AT 0°

| | | | | Jones and Dole equation | |
|---|---|---|---|---|---|
| $c$ | $d^0_4$ | $\eta$ | $(\eta - 1)/c$ | Simple $\Delta\eta \times 10^5$ | Extended $\Delta\eta \times 10^5$ |
| 0.00025 | (0.99989) | 1.00007 | +0.28 | + 4 | +4 |
| .0005 | .99994 | 1.00005 | + .10 | + 3 | +3 |
| .001 | .99995 | 0.99992 | − .08 | − 7 | −7 |
| .002 | 1.00004 | .99985 | − .07 | − 4 | −4 |
| .005 | 1.00032 | .99950 | − .10 | − 5 | −5 |
| .01 | 1.00077 | .99896 | − .10 | + 5 | +5 |
| .02 | 1.00165 | .99760 | − .12 | + 4 | +4 |
| .05 | 1.00435 | .99330 | − .134 | − 2 | −8 |
| .1 | 1.00869 | .98635 | − .136 | | −4 |
| .2 | 1.01747 | .97284 | − .136 | | +5 |
| .5 | 1.04353 | .93649 | − .127 | | −1 |
| 1 | 1.08629 | .88866 | − .111 | | |
| 2 | 1.17007 | .82882 | − .0856 | | |
| 2.98978 | 1.25120 | .80363 | − .0657 | | |
| (3) | (1.25203) | ( .80341) | | | |
| 3.750 | 1.31269 | .80234 | − .05271 | | |

| | Range of validity, $M$ | Av. deviation, % |
|---|---|---|
| Root equation | | |
| $d^0_4 = 0.999871 + 0.089603c - 0.003196c^{3/2}$ | 3.75 | 0.002 |
| Jones and Dole equation | | |
| $\eta = 1 + 0.00450\sqrt{c} - 0.15377c$ | 0.05 | .004 |
| $\eta = 1 + 0.00450\sqrt{c} - 0.15459c + 0.04244c^2$ | .5 | .005 |

TABLE II

DENSITY AND RELATIVE VISCOSITY OF LANTHANUM CHLORIDE SOLUTIONS AT 25°

| | | | | Jones and Dole equation | |
|---|---|---|---|---|---|
| $c$ | $d^{25}_4$ | $\eta$ | $(\eta - 1)/c$ | Simple $\Delta\eta \times 10^5$ | Extended $\Delta\eta \times 10^5$ |
| 0.00025 | (0.99713) | 1.00067 | +2.68 | +5 | + 5 |
| .0005 | ( .99718) | 1.00091 | +1.82 | −5 | − 5 |
| .001 | .99729 | 1.00152 | +1.52 | −1 | 0 |
| .0025 | .99763 | 1.00291 | +1.16 | −3 | 0 |
| .005 | .99820 | 1.00499 | +1.00 | +1 | + 6 |
| .01 | .99933 | 1.00879 | +0.879 | +8 | +19 |
| .025 | 1.00275 | 1.01891 | + .756 | −8 | +20 |
| .05 | 1.00839 | 1.03517 | + .703 | +1 | +25 |
| .1 | 1.01965 | 1.06632 | + .6632 | −1 | −26 |
| .25 | 1.05299 | 1.16314 | + .6525 | | + 3 |
| ( .5) | (1.10755) | (1.34913) | | | |
| .502687 | 1.10812 | 1.35132 | + .6988 | | |
| .990638 | 1.21256 | 1.83815 | + .84607 | | |
| (1) | (1.21454) | (1.84945) | | | |

| | Range of validity, $M$ | Av. deviation, % |
|---|---|---|
| Root equation | | |
| $d^{25}_4 = 0.997074 + 0.229324c - 0.01184c^{3/2}$ | 1.0 | 0.002 |
| Jones and Dole equation | | |
| $\eta = 1 + 0.0304\sqrt{c} + 0.5672c$ | 0.1 | .004 |
| $\eta = 1 + 0.0304\sqrt{c} + 0.5551c + 0.14629c^2$ | .25 | .011 |

TABLE III

DENSITY AND RELATIVE VISCOSITY OF LANTHANUM CHLORIDE SOLUTIONS AT 0°

| | | | | Jones and Dole equation | |
|---|---|---|---|---|---|
| $c$ | $d^0_4$ | $\eta$ | $(\eta - 1)/c$ | Simple $\Delta\eta \times 10^5$ | Extended $\Delta\eta \times 10^5$ |
| 0.00025 | | 1.00051 | +2.0 | − 5 | − 5 |
| .0005 | | 1.00072 | +1.44 | −14 | −13 |
| .001 | 1.00011 | 1.00129 | +1.29 | − 6 | − 5 |
| .0025 | 1.00047 | 1.00266 | +1.06 | + 8 | +11 |
| .005 | 1.00107 | 1.00444 | +0.888 | +10 | +16 |
| .01 | 1.00221 | 1.00751 | + .751 | − 1 | + 9 |
| .025 | 1.00570 | 1.01614 | + .646 | −12 | + 9 |
| .05 | 1.01150 | 1.03003 | + .6006 | + 9 | +32 |
| .1 | 1.02302 | 1.05621 | + .5621 | − 2 | −28 |
| ( .25) | (1.05708) | (1.13849) | | | + 3 |
| .250395 | 1.05717 | 1.13872 | + .5540 | | |
| .250462 | | 1.13876 | | | |
| ( .5) | (1.11267) | (1.30258) | | | |
| .505272 | 1.11443 | 1.30640 | + .6064 | | |
| .997033 | 1.22039 | 1.76661 | + .7689 | | |
| (1) | (1.22102) | (1.77023) | | | |

| | Range of validity, $M$ | Av. deviation, % |
|---|---|---|
| Root equation | | |
| $d^0_4 = 0.999871 + 0.23665c - 0.01521c^{3/2}$ | 1.0 | 0.001 |
| Jones and Dole equation | | |
| $\eta = 1 + 0.02780\sqrt{c} + 0.47440c$ | 0.1 | .007 |
| Jones and Dole | | |
| $\eta = 1 + 0.02780\sqrt{c} + 0.46276c + 0.14190c^2$ | .25 | .013 |

**Interpretation of the Data.**—The densities of these solutions can be expressed over the entire range of concentration studied by equations of the form suggested by Root[8] with an average deviation of only 0.002%. These equations are

for KBr at 0°; $d^0_4 = 0.999871 + 0.089603c - 0.003196c^{3/2}$
for $LaCl_3$ at 25°; $d^{25}_4 = 0.997074 + 0.229324c - 0.01184c^{3/2}$
at 0°; $d^0_4 = 0.999871 + 0.23665c - 0.01521c^{3/2}$

These salts give the Grüneisen effect as usual.

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(7) The correction factor for this instrument should be computed by the equation

$$f = 1 + 0.0076 \frac{\sigma_0/\rho_0 - \sigma_c/\rho_c}{\sigma_0/\rho_0}$$

see Jones and Fornwalt, THIS JOURNAL, **60**, 1691 (1938).

(8) W. C. Root, THIS JOURNAL, **55**, 850 (1933).

The solutions of potassium bromide at 0° give another example of a salt which causes a diminution in viscosity at moderate concentration but nevertheless gives an increase in viscosity at extreme dilution.

The viscosity of these solutions relative to that of pure water can be expressed by the Jones and Dole equation; $\eta = 1 + A\sqrt{c} \pm Bc$ as follows

for KBr at 0°; $\eta = 1 + 0.0045\sqrt{c} - 0.15377c$; valid up to 0.05 $N$

for LaCl$_3$ at 25°; $\eta = 1 + 0.0304\sqrt{c} + 0.5672c$; valid up to 0.1 $M$

for LaCl$_3$ at 0°; $\eta = 1 + 0.0278\sqrt{c} + 0.4744c$; valid up to 0.1 $M$

Table IV gives a comparison of the values of the coefficient of the square root term ($A$) determined experimentally and that computed by the Falkenhagen and Vernon equation.

TABLE IV

COMPARISON OF THE THEORETICAL AND EXPERIMENTAL VALUES OF THE COEFFICIENT OF THE SQUARE ROOT TERM

| | Equiv. cond. used in calcg. cation | anion | $A$ computed | $A$ exper. |
|---|---|---|---|---|
| KBr at 0° | 40.6 | 43.1 | 0.0044 | 0.0045 |
| LaCl$_3$ at 25° | 71 | 76.34 | .0280 | .0304 |
| | 68 | 76.34 | .0288 | |
| LaCl$_3$ at 0° | 35.5 | 41.3 | .0270 | .0278 |
| | 35 | 41.3 | .0272 | |

These results furnish additional evidence in support of that given in the earlier papers of this series that the Falkenhagen and Vernon equation is essentially correct both as to the influence of valence type and temperature.

Cox and Wolfenden[9] have made a series of measurements on dilute solutions of lanthanum chloride at 18° from which they find an experimental value of $A$ of 0.037 ± 0.002. They compute a theoretical value of 0.0318 but do not state the value of the equivalent conductivities and other parameters which they used in these calculations. They say "Aqueous solutions of magnesium sulfate and lanthanum chloride do not give results in accordance with the Falkenhagen equation and these electrolytes are the first cases to be investigated which have shown an unmistakable divergence. Such a divergence is not unexpected as it is characteristic of the behavior of electrolytes of higher valence-type in respect to other properties such as those of heats of dilution, etc. The discrepancy is presumably associated with the higher terms of the ionic atmosphere theory."

Our data do not confirm this conclusion as to lanthanum chloride. Our experimental data are consistently lower than theirs and agree much better with computed values of $A$.

The only other measurements on potassium bromide at 0° which we have found in the literature are by Taylor and Ranken[10] on 1, 2 and 3 $N$ KBr. These results are appreciably higher than ours and since data on dilute solutions are lacking they are not significant in determining the experimental value of $A$.

## Summary

1. The absolute densities and relative viscosities of many solutions of potassium bromide have been determined at 0° and of solutions of lanthanum chloride at 25 and 0°.
2. These results confirm the Root equation for densities, the Jones and Dole equation for viscosities and the Falkenhagen and Vernon equation for the influence of the interionic attraction on the viscosity.

CAMBRIDGE, MASS. RECEIVED NOVEMBER 25, 1939

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[9] W. M. Cox and J. H. Wolfenden, *Proc. Roy. Soc.* (London), **145A**, 475 (1934). L. W. Öholm, *Soc. Sci., Fennica., Commentationes Phys.-Math.*, **9**, No. 2, 1937, gives measurements on lanthanum chloride solutions at 20°.

[10] W. W. Taylor and C. Ranken, *Proc. Roy. Soc. Edinburgh*, **25**, 231 (1904).