[Contribution from the Department of Chemistry, University of Kentucky]

Densities and Viscosities of Solutions of the Zinc Halides in Methanol from −50 to 20°[1]

By L. R. Dawson, H. K. Zimmerman, Jr., Wm. E. Sweeney and G. P. Dinga

Density and viscosity data are reported for solutions of the chloride, bromide and iodide of zinc in methanol at concentrations from 0.1 to 4 or 5 molal over the temperature range, −50° to 20°. The results in their entirety do not seem to be amenable to a simple interpretation in terms of present theories of viscosity, but it is found that for concentrations up to 1.5 to 2 molar the data satisfy roughly the empirical relation, $\eta_{sp.} = C^a \cdot F(T)$, which is very similar in form to the function used to obtain "intrinsic" viscosities for high polymers. Parameters for the logarithmic form of this relation are given for the solutions of each zinc halide.

Conductance data for solutions of the zinc halides in methanol below room temperature display certain peculiarities not shown by uni-univalent electrolytes in that solvent.[2] Because of the intimate relationship between viscosity and conductivity, it is of interest to determine how viscosity varies in the same solutions and at the same temperatures in order to discover whether irregularities in viscosity also occur under similar conditions. Consequently, such viscosity data have been determined and are reported here.

Experimental

The methanol used in this study was prepared from the C.P. absolute grade by drying over copper sulfate and distilling through an efficient fractionating column. Analysis by the Karl Fischer method showed about 0.03% water in this solvent. The zinc chloride was originally of reagent grade purity and was dried by prolonged heating, just below the melting point, in a stream of dry hydrogen chloride. Zinc bromide was prepared directly in methanol by placing finely divided zinc in the solvent and passing dry hydrogen bromide gas through the stirred mixture at room temperature. Analysis showed 0.07% water or less in the resulting stock solution. Zinc iodide, reagent grade, was dried by prolonged desiccation (approximately four weeks) over anhydrone at reduced pressure, the vacuum being renewed by pumping at frequent intervals. Stock solutions of the chloride and the iodide (the bromide preparation served as stock for this salt) were prepared and assayed for solute content by the Mohr method for the halide. Solutions for investigation were then prepared from these stocks by dilution with methanol on a weight basis. In order to prevent absorption of water, all transfers were performed in a dry-box.

Densities were determined by use of a pycnometer which was a modified form of that described by Wright and Tartar.[3] It consisted of a bulb to which was attached a calibrated large-bore capillary. The capacity of the apparatus was about 20 ml. The pycnometer was calibrated above 0° by use of double-distilled water; at lower temperatures, methanol was used as a standard.[4]

For the viscosities an Ostwald–Fenske type viscometer was employed. Calibrations were based upon the viscosities of anhydrous methanol[5] and anhydrous *n*-butanol[6] used as standards.

Temperatures were controlled to ±0.5° by a manually operated bath of Dry Ice and acetone contained in a gallon dewar flask which was surrounded by an insulated box.

Results[7]

In order to permit the calculation of the viscosities sought, the densities of the same solutions were determined over the entire range of temperatures. The viscosity data were obtained from the densities and the flow times and converted into centipoises through the standard data.[5,6] The densities are considered to be precise to within better than 0.2% (volume readings available to ±0.01 ml. in approximately 18 ml., and weights to 0.1 mg.), while the precision of the viscosities is about equal to that of the standard data, *i.e.*, 1 to 2%.

Discussion

Attempts to interpret the present results in terms of the Arrhenius type of relation for viscosity as a function of temperature

$$\eta = B \exp (E_{\text{vis.}}/RT) \qquad (1)$$

for which a theoretical basis has been laid by Ewell and Eyring,[8] indicate that for constant solute concentrations the function in the present cases is not linear except for the solvent and for the very lowest solute concentrations employed. This effect is to be expected in systems of this type, in which relatively powerful chemical[9] and electrostatic forces are present. Further attempts to determine the extent of the interaction due to these forces by means of a theory for viscosity in terms of solute concentration[10] have led to results the meaning of which is not completely understood. Interaction parameters calculated from Vand's theory turn out to be very peculiar functions of temperature. "Shape" factors calculated from the same theory behave in a much more regular manner as functions of temperature, the values obtained tending to converge at some temperature above the range studied. Assignment of physical meanings to the results so calculated is not practicable however, even on a qualitative basis, since Vand assumes (1) only one solute species, (2) negligible Brownian motion, and (3) absence of coulombic forces, conditions which these systems do not satisfy. We are forced to conclude that in view of these restrictions, application of his theory to the present data will not be feasible until the theory is generalized further.

Additional efforts to determine a linear relation between solution viscosities and densities ("free space")[11,12] failed also, the broad range of temperatures and concentrations in question leading to non-linear relationships for all cases examined. However, it was found that isothermal plots of the

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(1) Based on research performed under contract No. W36-039-sc-38184 for the U. S. Army Signal Corps.

(2) L. R. Dawson, A. Tockman, H. K. Zimmerman and G. R. Leader, This Journal, **73**, 4327 (1951).

(3) K. A. Wright and H. V. Tartar, *ibid.*, **61**, 544 (1939).

(4) "Landolt-Börnstein-Roth Tabellen," 5th ed., Vol. I, p. 452.

(5) S. Mitsukuri and T. Tonomura, *Proc. Imp. Acad. (Japan)*, **3**, 155 (1927).

(6) T. Tonomura and K. Uehara, *Bull. Chem. Soc. Japan*, **6**, 118 (1931).

(7) For tables summarizing the data on densities and viscosities for the solutions studied order Document No. 3257 from American Documentation Institute, 1719 N Street, N. W., Washington 6, D. C., remitting $1.00 for microfilm (images 1 inch high on standard 35 mm. motion picture film) or $1.00 for photocopies (6 × 8 inches) readable without optical aid.

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logarithm of specific viscosity against the logarithm of the molar concentration for the individual zinc halide solutions were very nearly linear up to concentrations of 1.5 to 2.0 molar. Above that limit, the curves become quite sharply concave upward. Within the region of linearity, a series of rough empirical relations can be obtained, the slopes being approximately constant for a given solute, and the intercepts being a function of temperature. Study of the variation of the intercepts with temperature permits introduction of temperature into the expression for the specific viscosity. By means of this kind of stepwise treatment, an empirical equation has been developed for each of the three solution systems, having the form

$$\log \eta_{sp} = a \log C + b - \frac{1}{T}(d + eT^2 - T^3)f \qquad (2)$$

where

η_{sp} = specific viscosity = $\eta_{relative} - 1$
C = molar concentration
T = absolute temperature
d = $E_{vis.}/2.303R$ for the solvent alone
$E_{vis.}$ = activation energy for viscous flow of the solvent

The parameters, a, b, e and f, for each salt are presented in Table I.

From Eq. (2), it follows that the specific viscosity may be written as

$$\eta_{sp.} = C^a F(T) \qquad (3)$$

which is very similar in form to the function which is graphed to obtain the "intrinsic" viscosities of high polymers.[13] While it is known in the polymer field that the non-concentration term $F(T)$ is in fact a function of temperature, no adequate theoretical explanation of the functional relationship seems to be available. It is also known that the same function is dependent upon solute particle size.[14] The variations of the parameters, b, e and f, with solute species in the present study reflect this dependency but, again, a quantitative interpretation must await the development of a more comprehensive theory.

TABLE I

PARAMETERS IN THE EMPIRICAL RELATION FOR SPECIFIC VISCOSITY AS A FUNCTION OF CONCENTRATION AND TEMPERATURE[a]

Salt	a	b	e	f
$ZnCl_2$	1.39	5.46	0.013	~0
$ZnBr_2$	1.40	5.78	.014	~0
ZnI_2	1.26	8.70	.053	−0.000077

[a] d = 542.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF KENTUCKY]

The Conductivities of Solutions of the Zinc Halides in Methanol from −50 to 20°[1]

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Data are reported for the conductance of solutions of zinc chloride, bromide and iodide in methanol from about 0.1 to 4 or 5 molal over the temperature range between −50° and 20°. It is shown that in the greater part of the temperature and concentration range studied, conductance is not strictly a function of viscosity, but probably depends, in addition, upon the kinds and amounts of zinc halide complexes formed.

For a considerable time, it has been known that the conductance of zinc chloride displays a maximum as a function of concentration in non-aqueous medium.[2] Moreover, Getman and Gibbons[3] have shown that, for two temperatures at least, the conductance of zinc chloride in methanol has a negative temperature coefficient. In addition, Mead and Fuoss[4] have found a maximum in the conductance of aqueous zinc chloride solutions, as a function of concentration, using technical grade materials. Apparently, however, no attempt has been made to carry out a systematic study of the conductances of all three of the zinc halides in the same solvent over a wide range of temperatures and concentrations. As a consequence, the study reported here was undertaken in order to extend the existing data and thereby to obtain a fairly comprehensive picture of the conducting behavior of concentrated solutions of the halides in methanol.

Materials and Apparatus

The materials used in this work were prepared as described in a previous communication.[5] In order that the results might be strictly comparable, the solutions used were exactly the same as those previously employed.

Conductivities were measured by means of a Wheatstone bridge circuit consisting of the following components: a variable resistance consisting of two resistance boxes, a Leeds and Northrup 10,000 ohm coil-type decade resistance box inductance compensated and graduated in 0.1 ohm intervals, and a Shallcross No. 935 megohm decade box with a resistance of 1,100,000 ohms graduated in steps of 10,000 ohms; a Leeds and Northrup Kohlrausch-type slide-wire of 10 ohms resistance, drum-wound in a helix of ten turns; a compensating capacitor consisting of tandem type air condenser; Western Electric Model 509 headphones; and wiring consisting of shielded cable. The source of current was a 1000 cycle Cenco A. F. vacuum tube oscillator with taps of 50, 500 and 5000 ohms impedance; the 500 ohm tap was employed. The detector circuit also made use of a Masco Model MA-25 three-stage audio amplifier set in a Signal Corps FT-250-A mounting to protect the amplifier from (extraneous) vibration.

Results and Discussion

The results of the conductivity measurements are presented in Figs. 1, 2 and 3 for the chloride, bromide and iodide, respectively. Because of the virtual certainty that a significant amount of complex

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(1) Based on research performed under contract No. W36-039-sc-38184 for the U. S. Army Signal Corps.

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