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THE VISCOSITY AND FLUIDITY OF AQUEOUS POTASSIUM FERROCYANIDE SOLUTIONS¹

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The viscosity of aqueous electrolyte solutions is occupying considerable attention at the present time. The empirical equation put forward by Jones and Dole (1) relating the relative fluidity $\varphi = \varphi_c/\varphi_o$, to the square root of the concentration, c , (in mols per liter):

$$\varphi = 1 - A\sqrt{c} + B.c + \dots \quad (1)$$

has been theoretically derived from considerations of the Debye-Hückel theory (2) as:

$$\eta = \frac{\eta_c}{\eta_o} = 1 + A\sqrt{c} + \dots \quad (2)$$

and the Falkenhagen constant A for a dozen electrolytes has been evaluated experimentally through numerous recent measurements (3) and the interpretation of some earlier viscosity data (4).

Theoretically, the value of A must be positive for electrolytes, and zero for non-electrolytes. Experimental verification of the equation is given in Table I.

In the course of some investigations in progress in this laboratory, we found occasion to measure the viscosities of dilute aqueous solutions of potassium ferrocyanide with sufficient accuracy to warrant interpretation of our results in the light of the interionic attraction theory as a test of the Falkenhagen equation when applied to an electrolyte of the uni-tetravalent type.

¹Contribution from the Chemical Laboratory of Miami University, Oxford, Ohio.

EXPERIMENTAL

Apparatus.—The viscometer was of the Bingham variable-pressure type, constructed of Pyrex glass. Details of the apparatus are elsewhere described (3d, 7); it may be noted here that the pressures used ranged between 110 and 125 cm. of water, the pressures being estimated to the nearest 0.01 cm.;

TABLE I
COMPARISON OF THEORETICAL AND EXPERIMENTAL
VALUES OF A IN EQ. (1)

Solute	Temp.	A (Theory)	A (Found)	Reference
NH ₄ Cl	25°	0.0050	0.0057	3 f
LiCl*	25°	0.0237	0.0240	6
KCl	18°	0.0049	0.0052	3 a, b
KCl	25°	0.0050	0.0052	3 f, g
KCl	35°	0.0052	0.0051	3 b
KBr	25°	0.0049	0.0047	3 g
KClO ₃	18°	0.0051	0.0028	3 d
KClO ₃	18°	0.0051	0.0050	3 b
KClO ₃	25°	0.0054	0.0050	3 f
KClO ₃	35°	0.0058	0.0049	3 b
KBrO ₃	25°	0.0058	0.0058	3 f
LiIO ₃	18°	0.0094	0.0108	4 c
HNO ₃	18°	0.0021	0.0021	3 b
HNO ₃	35°	0.0025	0.0023	3 b
LiNO ₃	18°	0.0069	0.0082	4 a
KNO ₃	25°	0.0052	0.0050	3 f
RbNO ₃	18°	0.0049	0.0070	3 c
RbNO ₃	18°	0.0049	0.0050	3 b
RbNO ₃	25°	0.0051	0.0040	3 c
RbNO ₃	35°	0.0054	0.0056	3 b
CsNO ₃	18°	0.0048	0.0103	4 b
CsNO ₃	25°	0.0050	0.0043	3 f
BaCl ₂	18°	0.0145	0.0140	3 e
BaCl ₂	25°	0.0147	0.0201	1
Sucrose	25°	0	0	3 f
Urea	18°	0	0	5
Urea	25°	0	0	3 f, 5

*NOTE: In acetone.

the times of flow ranged between 1,325 and 1,925 seconds, the times being read to the nearest 0.1 second; while temperatures were read to 0.001° and the bath surrounding the instrument was controlled to $\pm 0.003^\circ$ C. with a Beckmann thermometer. The probable error of a determination of relative viscosity as the average of a pair of observations (from 5 determinations of the viscosity of water at 18° involving 13 observations)

obtained with the instrument by one of us, was computed by the method of least squares as 0.008 percent. Much practice is needful in attaining this precision, just as it is in other skills which depend upon exact co-ordination of hand and eye; and the mean error of the measurements carried out by the junior author and herein recorded amounts to 0.03 percent.

Materials.—Solvent: Ordinarily distilled water was redistilled from alkaline permanganate, and then distilled very slowly for a third time.

Solute: The potassium ferrocyanide was "Coleman and Bell's" C. P. quality, used as received.

Solutions were not optically clear, i. e., they showed some Tyndall effect when held in a strong light after vigorous shaking; but upon allowing the solutions to stand, and then drawing off samples for filling the viscometer from the upper level of liquid, stoppage of the capillary by dust particles was obviated.

Solutions.—Moderately concentrated solutions were made up by weight, and the concentrations in weight-percent were calculated to concentrations in mols per liter by means of tables of density. The more dilute solutions were made by measuring additional water into a measured volume of a more concentrated solution.

Densities.—Densities were interpolated from the International Critical Tables, (III, 92), as being of sufficient accuracy for the conversion of our moderately dilute solutions from a weight-percent basis to a mol-volume basis; and of more than sufficient accuracy for their use in viscosity measurement. Since our instrument is of the variable-pressure type, the density of the liquid enters only into a hydrostatic head correction (amounting to less than 0.1 percent of the total pressure) and into a kinetic energy correction (amounting to between 0.3 and 0.4 percent of the total pressure); an error in density of 3 percent will affect the precision of the viscosity measurements only 1 :10,000.

Data.—The experimental results are summarized in Table II. Three measurements of the viscosity of aqueous potassium ferrocyanide at 25° C. by Rankin and Taylor (8) are included for comparison.

TABLE II
SUMMARY OF EXPERIMENTAL DATA ON THE VISCOSITY AND FLUIDITY OF POTASSIUM FERROCYANIDE

No. of Runs	Conc. c	Density ρ	Viscosity η	$(\eta-1)/c$	\sqrt{c}	Fluidity ϕ	$(\phi-1)/\sqrt{c}$	ϕ Calc. by Eq.	Δ $\phi_{\text{obs.}} - \phi_{\text{calc.}}$	
18°										
2	0.2334	1.0536	1.09385	0.402	0.4831	0.9142	-0.1776	0.9136	0.0006	
4	0.1556	1.0350	1.0615	0.395	0.3945	0.9421	-0.1469	0.9406	0.0015	
3	0.0934	1.0203	1.0399	0.427	0.3056	0.9616	-0.12555	0.9627	-0.0011	
2	0.0424	1.0085	1.0197	0.465	0.2059	0.9807	-0.0938	0.9814	-0.0007	
2	0.0222	1.0038	1.0112	0.5045	0.1490	0.9889	-0.0744	0.9893	-0.0004	
2	0.0111	1.0012	1.0063	0.568	0.1054	0.9937	-0.0594	0.9939	-0.0002	
2	0.0028	0.9992	1.0019	0.679	0.0529	0.9981	-0.0358	0.9978	0.0003	
7	0	0.9986	1.0000	0	1.0000	1.0000	0	$\Sigma \Delta i = 0.0000$
										$\frac{\Sigma \Delta i }{N} = 0.0007$
25°										
	(0.5000)	(1.2575)	(0.515)	(0.7071)	(0.79525)	(-0.2896)	0.7967	(-0.0014)	
	(0.2500)	(1.1173)	(0.469)	(0.5000)	(0.8950)	(-0.2100)	0.8948	(0.0002)	
3	0.2327	1.0515	1.1079	0.464	0.4824	0.9026	-0.2019	0.9017	0.0009	
3	0.1551	1.0332	1.0714	0.460	0.3938	0.9334	-0.1692	0.9327	0.0007	
	(0.1250)	(1.9593)	(0.474)	(0.3536)	(0.9440)	(-0.1583)	0.9448	(-0.0008)	
3	0.0931	1.0187	1.0431	0.484	0.3051	0.95685	-0.1414	0.9579	-0.0010	
2	0.0423	1.0070	1.0232	0.5485	0.2057	0.9773	-0.1102	0.9792	-0.0019	
3	0.0222	1.0022	1.0120	0.5405	0.1490	0.9881	-0.0796	0.9881	0	
3	0.0111	0.9996	1.00635	0.572	0.1054	0.9937	-0.0599	0.9933	0.0004	
2	0.0055	0.9983	1.0033	0.600	0.0742	0.9967	-0.0444	0.9962	0.0005	
3	0.0028	0.9976	1.0018	0.642	0.0529	0.9982	-0.0340	0.9977	0.0005	
8	0	0.9970	1.0000	0	1.0000	1.0000	0	$\Sigma \Delta i = 0.0001$
										$\frac{\Sigma \Delta i }{N} = 0.0007$

NOTE: Bracketed values are taken from Rankin and Taylor for comparison.

INTERPRETATION OF RESULTS

When the values of $(\eta-1)/c$ were plotted as ordinates against the corresponding values of c as abscissas, (or preferably against the corresponding values of \sqrt{c} , since this effects a spreading of the points at low concentration) concave sagged curves were obtained which exhibited minima at about 0.18 mol per liter ($\sqrt{c} = 0.43$). While $(\eta-1)/c$ is strictly the slope of the chord connecting a point on the viscosity—concentration curve with the origin, it approximates the slope of the curve at that point; thus the initial downward slope of these curves corresponds to negative curvature in the $\eta-c$ curves, and the minimum to a point of inflection in the latter. These plots of the "Grüneisen function" emphasize that the negative curvature of the $\eta-c$ curve is more pronounced at the lower temperature; in accord with the expected behavior of electrolytes in aqueous solution (4a).

TABLE III
THE FLUIDITY AND VISCOSITY OF AQUEOUS
POTASSIUM FERROCYANIDE

Concentration mols per liter	18°		25°	
	ϕ	η	ϕ	η
0.001	0.9989	1.0011	0.9989	1.0011
0.0025	0.9980	1.0020	0.9978	1.0022
0.005	0.9967	1.0033	0.9964	1.0036
0.01	0.9944	1.0056	0.9938	1.0062
0.025	0.9882	1.0119	0.9868	1.0134
0.05	0.9786	1.0219	0.9759	1.0247
0.1	0.9604	1.0412	0.9550	1.0471
0.25	0.9081	1.1012	0.8948	1.1176

When the values of $(\phi - 1)/\sqrt{c}$ were plotted as ordinates against the corresponding values of \sqrt{c} as abscissas, the points lay approximately along straight lines which intersected the axis of $(\phi - 1)/\sqrt{c}$ at -0.0245 . The equations of these lines were established as:

$$(\phi - 1)/\sqrt{c} = -0.0245 - 0.3185 \sqrt{c} \text{ at } 18^\circ \text{ C.}$$

$$(\phi - 1)/\sqrt{c} = -0.0245 - 0.3720 \sqrt{c} \text{ at } 25^\circ \text{ C.}$$

whence:

$$\phi = 1 - 0.0245 \sqrt{c} - 0.3185 c \text{ at } 18^\circ \text{ C.} \quad (3)$$

$$\phi = 1 - 0.0245 \sqrt{c} - 0.3720 c \text{ at } 25^\circ \text{ C.} \quad (4)$$

The fluidities calculated by these equations, and the deviations from the observed fluidities, are given in Table II.

The relative viscosities and fluidities of aqueous potassium ferrocyanide at round concentrations, as calculated by means of Eqs. (3) and (4), are given in Table III.

SUMMARY AND CONCLUSION

Measurements have been made on the relative viscosity of aqueous solutions of potassium ferrocyanide at 18° and 25° C. over the range of 0.003 to 0.223 mol per liter. Our values at 25° C. accord well with some earlier values recorded in the literature.

The stiffening effect on the solution due to the electric forces of the ions in tending to maintain a space-lattice structure has been observed. While the data necessary for the computation of the constant A by means of the equation of Falkenhagen and Vernon (2e) are not available to us, and we have not found in the literature any computation of this constant for $K_4Fe(CN)_6$; the observed value : $A = 0.0245$, compares favorably in order of magnitude with the value to be expected.

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