- (6) Briggs, D. K. H., Ind. Eng. Chem. 49, 418 (1957).
- (7) Bromley, L. A., University of California Radiation Lab., Berkeley, Calif., Rept. UCRC-1852 (June 12, 1952).
- (8) Bromley, L. A., Wilke, C. R., Ind. Eng. Chem. 43, 1641 (1951).
- (9) Burns, W. G., Morris, B., Wilkinson, R. W., J. Sci. Instr. 35, 291 (1958).
- (10) Cecil, O. B., Koerner, W. E., Munch, R. H., J. CHEM. ENG. DATA 2, 54 (1957).
- (11) Ellard, J. A., King, C. D., Hedley, W. H., Moodie, W. J., Woo, C., Yanko, W. H., "Organic Coolant Essential Data," Sixth Quarterly Report, 1 July to 30 September 1962, Monsanto Research Corp., Rept. IDO-11,003 (1962).
- (12) Ellard, J. A., King, C. D., Milnes, M. V., Hedley, W. H., Moodie, W. J., Yanko, W. H., "Organic Coolant Essential Data," Annual Report, Monsanto Research Corp., Rept. IDO-11,004 (1962).
- (13) Ellard, J. A., King, C. D., Milnes, M. V., Moodie,
  W. J., Yanko, W. H., "Organic Coolant Essential Data," Annual Report, Monsanto Research Corp., Rept. IDO-11,000 (Jan. 23, 1962).
- (14) Gercke, R. H. J., Keen, R. T., Atomics International, Quarterly Progress Report NAA-SR-6777 (September 1961).
- (15) Grunberg, L., Nissan, A. H., Ind. Eng. Chem. 42, 885 (1950).

- (16) Hedley, W. H., Milnes, M. V., Yanko, W. H., "Viscosity and Thermal Conductivity of Polyphenyls in the Liquid and Vapor States," Monsanto Research Corp., Rept. IDO-11,007 (1963).
- Horrocks, J. K., McLaughlin, E., Proc. Roy. Soc. London A273, 259 (1963).
   Mandel, H., Ewbank, N., "Critical Constants of Di-
- Mandel, H., Ewbank, N., "Critical Constants of Diphenyl and the Terphenyls," Atomics International, Rept. NAA-SR-5129 (December 1960).
   McCready, D. W., "Thermal Conductivity of Lubri-
- (19) McCready, D. W., "Thermal Conductivity of Lubricating Oils and Hydraulic Fluids," WADC TH58-405 (December 1958).
- (20) McEwen, M., "Organic Coolant Databook," Monsanto Co., Tech. Pub. AT-1 (July 1958).
- (21) McLaughlin, E., Ubbelohde, A. R., Trans. Faraday Soc. 54, 1804 (1958).
- (22) Mason, H. L., Trans. ASME 76, 817 (1954).
- (23) Riedel, L., Chem. Ing. Tech. 23, 321 (1951).
- (24) Stone, J. P., Ewing, C. T., Blachly, C. H., Walker, B. E., Miller, R. R., Ind. Eng. Chem. 50, 895 (1958).
- (25) Stone, J. P., Ewing, C. T., Miller, R. R., J. CHEM. ENG. DATA 7, 519 (1962).
- (26) Zieband, H., Burton, J. T. A., Ibid., 6, 579 (1961).

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# Viscosity of Solutions of Some Electrolytes in Heavy Water

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The viscosities of solutions of nine electrolytes—KCl, Kl, KBr, KMnO<sub>4</sub>, LiCl, Li<sub>2</sub>SO<sub>4</sub>, Na<sub>2</sub>CO<sub>3</sub>, NaF, and MnSO<sub>4</sub>—in heavy water have been determined at  $25^{\circ}$ ,  $35^{\circ}$ ,  $45^{\circ}$ ,  $60^{\circ}$ ,  $75^{\circ}$ , and  $90^{\circ}$  C. at various concentrations up to near saturation.

**L**NVESTIGATIONS of viscosity of electrolyte solutions can give some information about their structure (1, 4). There are also relationships between viscosity and heat of evaporation (2) or activity coefficients of solution components (3). This paper investigates the differences that may be caused in viscosity and solution structure by replacing ordinary water with heavy water.

### EXPERIMENTAL

The viscosities of solutions were measured with an Ostwald viscosimeter (Figure 1). The time of flow was four minutes for ordinary water at  $25^{\circ}$  C. Because of the viscosimeter design, the solutions did not come into contact with the atmosphere, thus protecting the heavy water from dilution by air moisture.

Viscosity was calculated according to the formula

$$\eta = \eta_0 \frac{\rho t}{\rho_0 t_0} \tag{1}$$

where  $\eta = \text{viscosity}, \rho = \text{density}, t = \text{time of flow, and 0 refers}$  to pure heavy water, which was used as a reference standard.

The ratio  $\rho/\rho_0$  was measured in two manometers (Figure 2). One of the manometers was filled with the solution under investigation and the second one with pure heavy

water, which was also used for preparing the solution. The ratio  $\rho/\rho_0 = \Delta h_0/\Delta h$ , where  $\Delta h$  is the difference of liquid levels in the arms of the manometer. The level of liquid was measured with a cathetometer.

Measurements were made in each case, and the ratio  $\rho/\rho_0$  was determined for each solution. The viscosimeter and manometers were thermostated with an accuracy of  $\pm 0.05^{\circ}$  C.

#### MATERIALS

The heavy water used in these experiments was produced in the USSR. Its concentration was determined by the picnometric method. For measurements 1 to 27, the concentration of heavy water was 99.8 mole % D<sub>2</sub>O; for 28 to 35, 98.8 mole % D<sub>2</sub>O; and for 36 to 43, 98.5 mole %D<sub>2</sub>O. Before preparation of the solutions, the heavy water was distilled twice.

The salts used were of analytical purity and were dried but not purified before use.

#### RESULTS

Measurements were made for the solutions of nine salts— KCl, KI, KBr, KMnO<sub>4</sub>, LiCl, Li<sub>2</sub>SO<sub>4</sub>, Na<sub>2</sub>CO<sub>3</sub>, NaF, and MnSO<sub>4</sub>—at 25°, 35°, 45°, 60°, 75°, and 90° C.

Table I. Viscosity of Solutions of Some Electrolytes in Heavy Water (Centipoises)										
No.	Concn., Mole %	25	35	1'emp 45	60	75	90			
1	0.0	1.103	0.864	0.713	0.551	0.445	0.366			
				201						
2	0.5	1.095	0.868	0.714	0.552	0.448	0.368			
3	1.0	1.080	0.859	0.709	0.554	0.451	0.373			
4	2.2	1.076	0.871	0.732	0.582	0.477	0.398			
5	4.0	1.089	0.889	0.755	0.603	0.501	0.423			
6	6.4	1.101	0.912	0.784	0.632	0.529	0.451			
				KI						
7	1.1	1.036	0.829	0.692	0.542	0.442	0.369			
8	2.1	0.970	0.794	0.667	0.541	0.453	0.374			
9	3.6	0.942	0.776	0.662	0.536	0.457	0.381			
10	5.3	0.936	0.783	0.680	0.556					
11 12	7.6 12.1	$0.972 \\ 1.098$	$0.823 \\ 0.942$	$0.715 \\ 0.827$	0.597 0.695	$0.508 \\ 0.601$	$0.440 \\ 0.521$			
			1	KBr						
13	1.2	1.086	0.854	0.715	0.557	0.462	0.380			
14	3.75	1.046	0.856	0.725	0.581	0.483	0.414			
10	5.6 6.7	1.024	0.803	0.732	0.600	0.519				
17	7.3	1.018	0.868	0.754	0.617	0.512	0.437			
18	8.1	1.047	0.884	0.767	0.635	0.541	0.463			
			K	M-0						
10	0.01	1 101	A 050		0.550	0.150	0.054			
19	0.21	1.101	0.873	0.717	0.553	0.452	0.371			
20	0.34	1.092	0.801	0.709	0.001	0.450	0.368			
22	0.62	1.075	0.850	0.704	0.547	0.440	0.366			
			_							
	2.4		]	LiCl						
23	2.4	1.335	1.039	0.854	0.653	0.526	0.431			
24 25	,7.0 14 1	3 692	1.001	1.112	0.000	1 453	0.009			
26	19.7	6.900	5.334	4.216	3,123	2.410	1.851			
27	21.5	8.914	6.744	5.422	3.879	2.924	2.270			
			T.							
28	0.5	1 243	0.975	0.802	0.613	0 494	0.403			
29	1.6	1.740	1.355	1.102	0.833	0.650	0.533			
30	3.2	2.887	2.216	1.770	1.315	1.021	0.808			
31	5.2	5.343	3.964	3.084	2.232	1.694	1.307			
			N	a.CO.						
32	0.9	1.400	1 094	0.895	0.691	0.550	0 444			
33	1.8	1.847	1.443	1.167	0.884	0.701	0.564			
34	3.1	2.881	2.174	1.725	1.262	0.969	0.764			
35	4.1	4.233	3.115	2.435	1.713	1.280	0.990			
			,	NaF						
36	0.54	1.159	0.913	0.747	0.576	0.463	0.380			
37 38	1.22	1.246	0.980	0.800	0.615	0.493	0.404			
00	1.03	1.320	1.043	0.007	0.000	0.020	0.420			
			М	nSO₄						
39 40	0.5	1.297	1.00	0.827	0.620	0.503	0.411			
40 41	1.2	1.590	1.247	1.008	0.765	0.609	0.489			
42	2.0 2.9	2.100	2 404	1.371	1.040	1.087	0.040			
43	3.7	4.452	3.327	2.575	1.878	1.432	1.167			
-					2.0.0		2.207			

	Concn	Temp., ° C.						
No.	Mole %	25	35	45	60	75	90	
1	0.0	1.000	1.000	1.000	1.000	1.000	1.000	
			I	KCl				
2	0.5	1.012	1.012	1.012	1.012	1.012	1.012	
3	1.0	1.028	1.029	1.027	1.031	1.026	1.022	
4	2.2	1.040	1.046	1.041	1.042	1.039	1.041	
5 6	4.0 6.4	1.094	1.087	1.082	1.120	1.120	1.120	
				KI				
7	1.1	1.067	1.068	1.069	1.059	1.062	1.055	
8	2.1	1.095	1.094	1.097	1.097	1.096	1.096	
9 10	3.6 5.3	1.170	1.170	1.170	1.170	1.170	1.170	
10	7.6	1.370	1.366	1.369	1.373	1.370	1.363	
12	12.1	1.560	1.558	1.555	1.548	1.547	1.557	
			ł	KBr				
13 14	$\frac{1.2}{3.7}$	1.075	1.075	1.076	1.065	1.057	1.073	
14	5.6	1.219	1.219	1.215	1.215	1.109	1.109	
16	6.7	1.248	1.247	1.249	1.252	1.249	1.253	
17	7.3	1.276	1.269	1.273	1.269	1.265	1.261	
18	8.1	1.285	1.289	1.287	1.287	1.287	1.287	
			KI	MnO₄				
19	0.21	1.009	1.024	1.010	1.030	1.008	1.012	
20	0.34	1.016	1.017	1.015	1.016	1.010	1.014	
$\frac{21}{22}$	0.62	1.024	1.034 1.024	1.035	1.030	1.025	1.027	
			Т	- CI				
23	2.4	1.042	1.040	1.040	1.039	1.037	1.039	
24	7.6	1.088	1.040	1.040	1.085	1.085	1.079	
25	14,1	1.176	1.173	1.174	1.175	1.178	1.181	
$\frac{26}{27}$	$\begin{array}{c} 19.7 \\ 21.5 \end{array}$	$\begin{array}{c} 1.219 \\ 1.232 \end{array}$	$1.220 \\ 1.233$	$\begin{array}{c} 1.220 \\ 1.233 \end{array}$	$\begin{array}{c} 1.221 \\ 1.232 \end{array}$	$\begin{array}{c} 1.220 \\ 1.229 \end{array}$	$1.219 \\ 1.239$	
			Ŧ	: 80				
28	0.5	1.028	1.028	1.024	1.026	1.027	1.025	
29	1.6	1.073	1.077	1.079	1.083	1.084	1.080	
30 31	3.2 5.2	$\begin{array}{c} 1.146 \\ 1.212 \end{array}$	$1.140 \\ 1.209$	$\begin{array}{c} 1.147 \\ 1.210 \end{array}$	$1.156 \\ 1.208$	$1.157 \\ 1.213$	$1.165 \\ 1.213$	
<i><b>J</b></i> 0	0.0	1.055	1 055	a <sub>2</sub> CO <sub>3</sub>	1 050	1.059	1 055	
33	1.8	1.109	1.000	1.000	1.053	1.052	1.057	
34	3.1	1.166	1.173	1.177	1.176	1.166	1.169	
35	4.1	1.210	1.220	1.215	1.223	1.225	1.211	
			]	NaF				
36	0.54	1.017	1.018	1.021	1.018	1.019	1.019	
37 38	$\begin{array}{c} 1.22 \\ 1.63 \end{array}$	$\begin{array}{c} 1.028 \\ 1.038 \end{array}$	$1.020 \\ 1.038$	$1.018 \\ 1.040$	$1.018 \\ 1.040$	$1.028 \\ 1.043$	$1.024 \\ 1.042$	
30	0.5	1 039	1 020	1 029	1 000	1 045	1.040	
40	1.2	1.071	1.039	1.082	1.038	1.045	1.042	
41	2.0	1.168	1.165	1.160	1.164	1.161	1.156	
42	2.9	1.211	1.210	1.205	1.200	1.196	1.198	
43	3.7	1.284	1.286	1.280	1.275	1.281	1.281	

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Figure 1. An Ostwald viscosimeter

The viscosity values and the values of  $\rho/\rho_0$  are listed (Tables I and II). The estimated precision is  $\pm 0.8\%$ . The greater part of the error comes from values of  $\rho/\rho_0$ , which were determined with an estimated accuracy of  $\pm 0.5\%$ .

#### DISCUSSION

The viscosities of heavy water solutions are greater than the viscosities of ordinary water solutions at the same temperature and salt concentration. However, the character of the curves is similar. For instance, both heavy water



Figure 2. U-tubes for determination of density of solutions

and ordinary water solutions of KCl, KI, KBr, and KMnO<sub>4</sub> exhibit a minimum of viscosity, which disappears with temperature increase. For the other salts, viscosities increase with concentrations for both ordinary and heavy water.

A discussion of structure of electrolyte solutions on the basis of above data would be premature. Such an analysis will be made separately, after more relevant data are available.

# LITERATURE CITED

- (1) Good, W., Electrochim. Acta 9, 203 (1964); Ibid., 10, 1 (1965).
- Panchenkov, G.M., Zh. Fiz. Khim. 20, 811 (1946); Ibid., 20, 1011 (1946); Ibid., 21, 187 (1947); Ibid., 24, 1390 (1950).
- (3) Reik, H.G., Z. Electrochem. 59, 35 (1955); Ibid., 59, 126 (1955).
- (4) Stokes, R.H., Mills, R., "Viscosity of Electrolyte Solutions and Related Properties," Pergamon, London, 1960.

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# Solubilities and Refractive Indices of Some Inorganic Salts in Heavy Water

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Solubilities and refractive indices were measured for concentrated solutions in heavy water of 14 salts—LiCl, NaF, NaCl, NaBr, Nal, Na<sub>2</sub>CO<sub>3</sub>, NaClO<sub>4</sub>, KCl, KSCN, KMnO<sub>4</sub>, K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>, K<sub>4</sub>Fe(CN)<sub>6</sub>, CsCl, and Li<sub>2</sub>SO<sub>4</sub>—at 25°, 35°, 45°, 60°, 75.5°, and 91°C.

**D**URING an investigation, it was necessary to determine the differences of solubilities of some salts in heavy and light water. Some of the relevant data were available in the literature (2, 4, 5, 6, 7, 9, 10), but they were not sufficient. In this work, measurements of solubility were made for 14 salts—LiCl, NaF, NaCl, NaBr, NaI, NaClO<sub>4</sub>,

 $\label{eq:2.1} \begin{array}{l} Na_2CO_3,\,KCl,\,KSCN,\,KMnO_4,\,K_2Cr_2O_7,\,K_4Fe(CN)_6,\,CsCl,\\ and\,Li_2SO_4\mbox{--}at\,25^\circ,\,35^\circ,\,45^\circ,\,60^\circ,\,75.5^\circ\,and\,91^\circ\,C. \end{array}$ 

## SOLUBILITY DETERMINATION METHOD

A curve of refractive indices of salt solutions against concentration at a constant temperature was plotted. At