The Viscosity of Mixed Salt Solutions.

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From the extensive work on the viscosity of binary liquid mixtures and of solutions of solids in liquids for these ten years⁽¹⁾, the author has come to the conclusion that his fundamental formula defines an ideal mixture law or a physical mixture law. The formula runs:

$$\eta=\frac{\eta_1}{1+K\dfrac{z_m}{1-z_m}}+\frac{\eta_2}{1+\dfrac{1}{K}\dfrac{1-z_m}{z_m}},$$

where η_1, η_2, and η are the viscosities of component 1, 2, and the mixture; z_m a formal molar fraction of component 2 in the mixture; and K the characteristic constant for the mixture or, precisely saying, the ratio of the characteristic constant of component 2 to that of component 1.

Since this formula represents the true viscosity on mixing two chemically indifferent liquids for the whole range of concentration, and that on dissolving a non-reactive solid in a liquid up to its saturation, one may easily arrive at the precognition that the same law will hold for the viscosity of mixed salt solutions, provided that the component solutions which do not react have a common solvent and the composition of the mixture has a constant total concentration throughout the admixture. If we take c_1 and c_2 the concentrations of two solutions in the mixture, e.g. in gram-mole per 1000 g. of solvent respectively in order to make this sum c, total concentration, to keep a constant by mixing appropriate weights of primary solutions of concentration c, $(1-z_m)$ and z_m in the above formula may be replaced by c_1/c and c_2/c respectively, since the quantity of solvent is unchanged before and after mixing. Naturally, K which means here the ratio of the characteristic constants of two solutions of a common solvent may take a value not so much differing from unity especially for dilute salt solutions.

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(1) This Bulletin, **4** (1929), 5, 25, 149, 288; **5** (1930), 47, 117; **8** (1933), 280, 293; **9** (1934), 155; **10** (1935), 153, 248; **11** (1936), 8, 64.

There have been a few measurements on the viscosity on mixing salt solutions under the above precaution. Stearn⁽²⁾ first measured the relative viscosities of the aqueous solution pairs of NaCl—KCl and NaI—KI; Ruby and Kawai⁽³⁾ made careful measurements, their precision being not less than one part in two thousand, on the relative viscosities of binary and ternary mixtures of HCl, KCl, and NaCl at the concentrations of 0.5, 1.0, 2.0, and 4.0 gram-mole per 1000 g. of water, and pointed out that the viscosities of binary mixtures of these electrolytes are consistently less than values computed by the rule of mixtures (additivity with respect to molar concentration), save in the cases of the most dilute mixtures; Tollert⁽⁴⁾ measured the viscosities of similar pairs of electrolyte solutions at only one composition and tested with fair success his own formula, $\eta = \sqrt{\eta_1\eta_2}(1+A'\sqrt{\gamma_1\gamma_2})$, in which γ_1 and γ_2 denote the concentrations of components in val/litre, and A' a specific constant of the mixture depending on temperature alone; and recently Banchetti⁽⁵⁾ examined, with the data of his own for the solution pairs of K_2SO_4—$ZnSO_4$ and urethane—urea and of those of others cited above, the formulas of Kendall, Bingham, and Tollert, and found that they all failed to represent the actual viscosities of mixtures at concentrated salt solutions. He referred the present author's paper on the viscosity of aqueous solutions of electrolytes⁽⁶⁾, but unfortunately he did not attempt to test the latter's fundamental formula given above. The present paper is, therefore, contributed to the study in this line as an appendix to the author's foregoing papers on the viscosity of binary mixtures.

The data employed in the following verification of the author's formula are adopted from the values observed by Banchetti and by Ruby and Kawai.

As seen from Tables 1, 2, 3, 4, and 5, in which z_m denotes a fractional concentration of the second salt solution in each pair of total concentration c in gram-mole per 1000 g. of water, the divergences of the calculated values from the observed values are all less than 2×10^{-3} and lie within the experimental error limit, so that the coincidence is said to be extremely satisfactory. For closer investigation of K in these pairs, however, we must have more accurate measurements.

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(2) A. E. Stearn, *J. Am. Chem. Soc.*, **44** (1922), 670.

(3) C. E. Ruby and J. Kawai, *J. Am. Chem. Soc.*, **48** (1926), 1120.

(4) H. Tollert, *Z. physik. Chem.*, A, **172** (1935), 129.

(5) A. Banchetti, *Gazz. chim. ital.*, **64** (1934), 229; **65** (1935), 159; **66** (1936), 446.

(6) This Bulletin, **10** (1935), 153.

Table 1. Urethane aq. (1)—Urea aq. (2), 25°C. (Banchetti).

z_m	$c = 0.5$			$c = 1.0$		
	$\eta_{obs.}$	$\eta_{calc.}$	Difference $\times 10^4$	$\eta_{obs.}$	$\eta_{calc.}$	Difference $\times 10^4$
0.00	1.0890	—		1.1755	—	
0.25	1.0713	1.0712	1	1.1416	1.1412	4
0.50	1.0536	1.0537	−1	1.1071	1.1071	0
0.75	1.0363	1.0363	0	1.0731	1.0731	0
1.00	1.0191	—		1.0393	—	
	$K = 1.021$			$K = 1.009$		

Table 2. $ZnSO_4$ aq. (1)—K_2SO_4 aq. (2), 25°C. (Banchetti).

z_m	$c = 0.1$			$c = 0.5$		
	$\eta_{obs.}$	$\eta_{calc.}$	Difference $\times 10^4$	$\eta_{obs.}$	$\eta_{calc.}$	Difference $\times 10^4$
0.00	1.0662	—		1.3656	—	
0.25	1.0548	1.0550	−2	1.2932	1.2930	2
0.50	1.0442	1.0441	1	1.2267	1.2269	−2
0.75	1.0337	1.0336	1	1.1662	1.1668	−6
1.00	1.0234	—		1.1115	—	
	$K = 1.067$			$K = 1.201$		

Table 3_1. HCl aq. (1)—KCl aq. (2), 25°C. (Ruby and Kawai).

z_m	$c = 0.5$			$c = 1.0$		
	$\eta_{obs.}$	$\eta_{calc.}$	Difference $\times 10^4$	$\eta_{obs.}$	$\eta_{calc.}$	Difference $\times 10^4$
0.0	1.0317	—		1.0617	—	
0.2	1.0250	1.0248	2	1.0483	1.0481	2
0.4	1.0182	1.0180	2	1.0351	1.0350	1
0.6	1.0112	1.0114	−2	1.0221	1.0224	−3
0.8	1.0048	1.0048	0	1.0102	1.0102	0
1.0	0.9983	—		0.9985	—	
	$K = 1.037$			$K = 1.096$		

Table 3_2. HCl aq. (1)—KCl aq. (2), 25°C. (Ruby and Kawai).

z_m	$c = 2.0$			$c = 4.0$		
	$\eta_{obs.}$	$\eta_{calc.}$	Difference $\times 10^4$	$\eta_{obs.}$	$\eta_{calc.}$	Difference $\times 10^4$
0.0	1.1210	—		1.2378	—	
0.2	1.0972	1.0968	4	1.2068	1.2052	16
0.4	1.0735	1.0734	1	1.1713	1.1709	4
0.6	1.0506	1.0508	−2	1.1341	1.1349	− 8
0.8	1.0285	1.0288	−3	1.0954	1.0970	−16
1.0	1.0076	—		1.0570	—	
	$K = 1.085$			$K = 0.881$		

Table 4_1. KCl aq. (1)—NaCl aq. (2), 25°C. (Ruby and Kawai).

z_m	$c = 0.5$			$c = 1.0$		
	$\eta_{obs.}$	$\eta_{calc.}$	Difference $\times 10^4$	$\eta_{obs.}$	$\eta_{calc.}$	Difference $\times 10^4$
0.0	0.9983	—		0.9985	—	
0.2	—			1.0166	1.0166	0
0.4	1.0169	1.0169	0	1.0352	1.0351	1
0.6	1.0264	1.0264	0	1.0537	1.0541	−4
0.8	—			1.0736	1.0736	0
1.0	1.0456	—		1.0936	—	
	$K = 0.974$			$K = 0.940$		

Table 4_2. KCl aq. (1)—NaCl aq. (2), 25°C. (Ruby and Kawai).

z_m	$c = 2.0$			$c = 4.0$		
	$\eta_{obs.}$	$\eta_{calc.}$	Difference $\times 10^4$	$\eta_{obs.}$	$\eta_{calc.}$	Difference $\times 10^4$
0.0	1.0076	—		1.0570	—	
0.2	1.0431	1.0435	−4	1.1309	1.1308	1
0.4	1.0811	1.0812	−1	1.2118	1.2121	−3
0.6	1.1209	1.1209	0	1.3022	1.3019	3
0.8	1.1632	1.1626	6	1.4030	1.4019	11
1.0	1.2065	—		1.5136	—	
	$K = 0.882$			$K = 0.771$		

Table 5_1. HCl aq. (1)—NaCl aq. (2), 25°C. (Ruby and Kawai).

z_m	$c = 0.5$ η obs.	η calc.	Difference $\times 10^4$	$c = 1.0$ η obs.	η calc.	Difference $\times 10^4$
0.0	1.0317	—		1.0936	—	
0.2	—			1.0862	1.0866	−4
0.4	1.0369	1.0370	−1	1.0797	1.0799	−2
0.6	1.0398	1.0397	1	1.0736	1.0736	0
0.8	—			1.0676	1.0675	1
1.0	1.0456	—		1.0617	—	
	$K = 0.914$			$K = 0.888$		

Table 5_2. HCl aq. (1)—NaCl aq. (2), 25°C. (Ruby and Kawai).

z_m	$c = 2.0$ η obs.	η calc.	Difference $\times 10^4$	$c = 4.0$ η obs.	η calc.	Difference $\times 10^4$
0.0	1.2065	—		1.5136	—	
0.2	1.1870	1.1865	5	1.4484	1.4474	10
0.4	1.1684	1.1681	3	1.3877	1.3875	2
0.6	1.1509	1.1512	−3	1.3329	1.3331	−2
0.8	1.1350	1.1355	−5	1.2834	1.2834	0
1.0	1.1210	—		1.2378	—	
	$K = 0.818$			$K = 0.792$		

The comparison among the results with other formulas which were given by Banchetti is reproduced here. In Tables 6 signify Δ_M, Δ_K, Δ_B, Δ_L, Δ_S, and Δ_I the average divergences of the observed and calculated viscosities by use of the formulas of viscosity linearity, Kendall's cube-root, Bingham, and Kendall's logarithmic, Banchetti, and Ishikawa.

Besides the formulas quoted above there have been proposed more than ten formulas. For the aid of further comparison, therefore, I will give severe tests for the validity of the hitherto existing formulas with two typical ideal mixtures in the classical meaning (mixtures in which there occurs no volume change on mixing), C_2H_5OH—i-C_3H_7OH(7) and $C_2H_4Br_2$—$C_2H_4Cl_2$(8).

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(7) G. S. Parks and K. K. Kelley, *J. Phys. Chem.*, **29** (1925), 727.

(8) W. MacFarlane and R. Wright, *J. Chem. Soc.*, **(1933)**, 114.

Table 6. The Validity of Various Formulas for Solution Pairs.

Pair	Deviations × 10^3					
	Δ_M	Δ_K	Δ_B	Δ_L	Δ_S	Δ_I
$c = 0.5$						
HCl — KCl	−0.5	−0.4	−0.2	−0.3	−1.6	0.1
KCl — NaCl	−0.3	−0.1	0.2	−0.1	0.6	0.0
HCl — NaCl	−0.3	−0.3	−0.3	−0.3	−1.2	0.0
$c = 1.0$						
HCl — KCl	−1.7	−1.4	−0.8	−1.2	−1.7	0.0
KCl — NaCl	−1.3	−0.6	0.7	−0.3	0.7	−0.1
HCl — NaCl	−0.7	−0.7	−0.6	−0.7	−0.5	−0.1
$c = 2.$						
HCl — KCl	−2.3	−1.3	0.5	−0.4	1.3	0.0
KCl — NaCl	−5.6	−3.0	2.2	−1.7	7.0	0.0
HCl — NaCl	−3.7	−3.3	−2.4	−3.0	2.9	0.0
$c = 4.0$						
HCl — KCl	4.0	6.3	10.0	7.2	19.7	−0.1
KCl — NaCl	−23.0	−12.2	8.0	−7.7	33.5	0.3
HCl — NaCl	−11.4	−8.2	−1.6	−6.5	22.6	0.2

(1) Bingham(9) (1906): $\varphi = \varphi_1(1-z_v)+\varphi_2 z_v$.

(2) Drucker and Kassel(10) (1911): $\varphi = \varphi_1(1-z)+\varphi_2 z$.

(3) Dolezalek(11) (1913): $\eta^{\frac{1}{2}} = \eta_1^{\frac{1}{2}}(1-z_v)+\eta_2^{\frac{1}{2}} z_v$.

(4) Kendall(12) (1913): $\log \eta = (1-z_m) \log \eta_1 + z_m \log \eta_2$.

(5) Ssachanov and Rjachowski(13) (1914):

$$\eta = \eta_1(1-z_m)^2+\eta_2 z_m^2+n\sqrt{\eta_1\eta_2}(1-z_m)z_m .$$

(6) Ssachanov and Rjachowski(14) (1915):

$$\eta = \eta_1(1-z_m)+\eta_2 z_m-k(1-z_m)z_m , \quad k = \eta_1+\eta_2-n\sqrt{\eta_1\eta_2} .$$

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(9) E. C. Bingham, *Am. Chem. J.*, **35** (1906), 195.

(10) K. Drucker and R. Kassel, *Z. physik. Chem.*, **76** (1911), 367.

(11) F. Dolezalek and A. Schulze, *Z. physik. Chem.*, **83** (1913), 45.

(12) J. Kendall, *Medd. Vetenskapzakad. Nobelinst.*, **2** (1913), No. 25, 1.

(13) A. Ssachanov and N. Rjachowski, *Z. physik. Chem.*, **86** (1914), 529.

(14) A. Ssachanov and N. Rjachowski, *J. Russ. Phys.-Chem. Soc.*, **47** (1915), 113.

(7) Kendall(15) (1917): $\eta^{\frac{1}{3}} = \eta_1^{\frac{1}{3}}(1-z_m)+\eta_2^{\frac{1}{3}}z_m\,.$

(8) Drucker(16) (1918): $\varphi d = \varphi_1 d_1(1-z_m)+\varphi_2 d_2 z_m\,.$

(9) Meyer and Mylius(17) (1920): $\varphi = \varphi_1\frac{b_1}{b}(1-z)+\varphi_2\frac{b_2}{b}z\,.$

(10) Macleod(18) (1924):

$$\eta = \eta_1\frac{x_1}{x}(1-z_m)+\eta_2\frac{x_2}{x}z_m\,,\ x = x_1(1-z_v)+x_2 z_v\,.$$

(11) Bateman and Baechler(19) (1926): $\eta^{(1-z_v)+kz_v} = \eta_1^{(1-z_v)}+\eta_2^{kz_v}\,.$

(12) Ishikawa(20) (1929): $\eta = \dfrac{\eta_1}{1+K\dfrac{z_m}{1-z_m}}+\dfrac{\eta_2}{1+\dfrac{1}{K}\,\dfrac{1-z_m}{z_m}}\,.$

(13) Bingham and Brown(21) (1932):

$$\varphi = \varphi_1(1-z_v)+\varphi_2 z_v-K(z-z_v)(v_1-v_2)\,.$$

(14) Cragoe(22) (1933): $\eta v = Ae^{\frac{B}{L'}}\,,\ L' = L_1'(1-z)+L_2'z\,.$

(15) Lautié(23) (1935): $\eta^{\frac{1}{2}} = \eta_1^{\frac{1}{2}}(1-z_m)+\eta_2^{\frac{1}{2}}z_m\,.$

In these formulas, η and φ and those with suffixes 1 and 2 are the viscosities and fluidities of the mixture and components 1 and 2 respectively; v and d and those with suffixes the specific volumes and densities of the mixture and the components respectively; and z, z_v, and z_m a weight, volume, and molar fraction of component 2 respectively. For an explanation of the other symbols used the reader is referred to the original papers.

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(15) J. Kendall and K.P. Monroe, *J. Am. Chem. Soc.*, **39** (1917), 1787.

(16) C. Drucker, *Z. physik. Chem.*, **92** (1918), 287.

(17) J. Meyer and B. Mylius, *Z. physik. Chem.*, **95** (1920), 349.

(18) D. B. Macleod, *Trans. Faraday Soc.*, **20** (1924), 348.

(19) E. Bateman and R. Baechler, *Proc. Am. Wood-Preserver's Assoc.*, (**1926**), 89.

(20) T. Ishikawa, this Bulletin, **4**, (1929), 5.

(21) E. C. Bingham and D. F. Brown, *J. Rheol.* **3** (1932), 95.

(22) C. S. Cragoe, *Proc. World Petroleum Congr.*, *London F*, (**1933**), 529.

(23) R. Lautié, *Bull. soc. chim.*, [5], **2** (1935), 2187.

Table 7. The Validity of Various Formulas for the Pair of C_2H_5OH (1)—*i*-C_3H_7OH (2), 25°C. (Parks and Kelley).

Formula	$z = 0.1639$ $z_v = 0.1646$ $z_m = 0.131$	$z = 0.3311$ $z_v = 0.3321$ $z_m = 0.275$	$z = 0.5013$ $z_v = 0.5025$ $z_m = 0.435$	$z = 0.6640$ $z_v = 0.6649$ $z_m = 0.607$	$z = 0.8277$ $z_v = 0.8285$ $z_m = 0.786$	Constants used
	Deviations × 10^5 (with respect to η)					
(1)	11	18	29	32	21	
(2)	11	19	29	33	22	
(3)	−37	−68	−83	−80	−62	
(4)	8	11	19	19	10	
(5)	2	1	3	−3	−4	$n = 1.942$
(6)	2	1	3	−3	−4	$k = 0.00241$
(7)	−2	−7	−5	−7	−10	
(8)	30	58	87	94	79	
(9)	−4	0	4	0	−23	$b_1/b = 0.989$ $b_2/b = 0.970$
(10)	—	—	—	—	—	
(11)	3	2	5	5	−1	$k = 0.807$
(12)	0	−1	3	−1	−1	$K = 0.777$
(13)	2	−2	−1	−1	−5	
(14)	−5	1	4	7	−6	$K = 1.65 \times 10^5$
(15)	−8	−16	−19	−24	−18	

Table 8. The Validity of Various formulas for the Pair of $C_2H_4Br_2$ (1)—$C_2H_4Cl_2$ (2), 25°C. (MacFarlane and Wright).

Formula	$z=0.1005$ $z_v=0.1636$ $z_m=0.1750$	$z=0.2404$ $z_v=0.3686$ $z_m=0.3875$	$z=0.3510$ $z_v=0.4860$ $z_m=0.5059$	$z=0.4997$ $z_v=0.6365$ $z_m=0.6550$	$z=0.6504$ $z_v=0.7659$ $z_m=0.7791$	$z=0.7492$ $z_v=0.8396$ $z_m=0.8501$	Constants used
	Deviations $\times 10^5$ (with respect to η)						
(1)	47	57	53	43	29	12	
(2)	−37	−66	−57	−47	−36	−32	
(3)	−36	−46	−53	−42	−31	−30	
(4)	1	−1	−1	3	1	−6	
(5)	−4	−6	0	5	4	−3	$n=1.867$
(6)	−4	−6	0	5	4	−3	$k=0.00299$
(7)	−15	−26	−25	−19	−13	−17	
(8)	−32	−54	−52	−45	−33	−32	
(9)	58	2	0	−3	0	−4	$b_1/b=1.08$ $b_2/b=1.02$
(10)	−1	−6	−7	−3	−3	−6	$x_1=0.0628$ $x_2=0.0911$
(11)	0	−2	−1	2	2	−6	$k=1.08$
(12)	2	−2	−1	1	−1	−7	$K=1.43$
(13)	−51	−86	−83	−70	−48	−46	
(14)	7	−1	2	1	−1	−10	$K=92.7$
(15)	−24	−39	−39	−29	−21	−22	

The superiority of the Ishikawa formula above the rest is readily accepted from the strict coincidences equably obtained in these examples as shown in Tables 6, 7, and 8.

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