

Viscosity of the Ternary Solutions Containing Water, Organic Solvent, and Hydrochloric Acid

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The determination of the coefficients of kinematic viscosity for the ternary systems containing water, hydrochloric acid, and organic solvent (methyl alcohol, ethyl alcohol, and acetone) is described. This investigation concerns diffusion processes involving the ion exchange of chlorocomplexes of corrosion and fission products on anion exchangers. The values of viscosity coefficients have been determined and the validity of the relationship between the viscosity and composition of ternary systems has been tested. It has been found that the viscosity isotherms have convex shape with maxima at low concentrations of hydrochloric acid (up to 1 M) for all three investigated organic solvents. At higher concentrations of hydrochloric acid in the ternary system, its viscosity increases with decreasing dielectric constant.

At present, there are only few experimental data available on the viscosity values of the ternary systems containing water, organic solvent, and mineral acid. Recently, these systems have been applied in increasing degree to analytical separations in ion exchange reactions. The separation process in dynamic arrangement may be affected by the ion exchange rate to a great extent. The rate of the ion exchange process controlled by the coefficient of internal or film diffusion is influenced considerably by the diffusion coefficient of the corresponding substance which is proportional to the temperature and viscosity of solution.

Many experimental data indicate that the viscosity isotherms of binary liquid solutions consisting of components with slight interactions have a monotonous and convex course with respect to the axis of composition and they do not possess any relative extreme [1]. If the individual components interact in a binary system, the isotherms show a maximum. The position of this maximum on the composition axis corresponds to the composition of the substance arising in the system [2] and it gives information on the ratios of particular components in the region of extreme stability.

In general, the dependence of the viscosity of such solutions on the composition of system may be expressed in terms of the polynomial

$$\eta = \sum_{i=0}^n a_i W^i \quad (1)$$

where a_i and W denote the coefficients of polynomial and weight percentage of individual components in the mixture, respectively.

Using this equation, *Mikhail* and *Kimel* [3] studied the relationship between the viscosity and composition of the binary mixtures containing methyl alcohol and water. The calculated values of viscosity coefficient were in good agreement with those found by measurement.

Grüneisen [4] revealed that viscosity of dilute solutions of electrolytes is a non-linear function of concentration. Deviations from linearity increase with decreasing concentration.

Jones and *Dole* [5] found a linear dependence of viscosity η of binary solutions of electrolytes on the square root of concentration c within the interval from infinite dilution to the concentration $c = 0.1$ M

$$\eta = 1 + A \sqrt{c} + Bc. \quad (2)$$

Onsager and *Fuoss* [6] have expressed the relationship between the viscosity of solutions and the concentration of electrolytes more accurately by introducing another term into the equation (2)

$$\eta = 1 + A \sqrt{c} + Bc + Dc \log c, \quad (3)$$

where A , B , and D are constants.

The behaviour of electrolytes in non-aqueous solvents is analogous, but the validity region of above equations is limited to more dilute solutions [7].

Gorenbein and *Rusin* [8] studied relation between the dielectric constant of solvent and the viscosity of electrolyte solutions. They found that viscosity of electrolyte solutions increases with decreasing dielectric constant of medium. This phenomenon may be influenced by increasing association of electrolytes.

This paper treats measurement of viscosity of the binary solutions containing an organic solvent (methyl alcohol, ethyl alcohol or acetone) and water as well as of the ternary solutions containing hydrochloric acid in addition to above components.

Experimental

Viscosity measurements were carried out using Höppler viscosimeter kept at the temperature of $20 \pm 0.1^\circ\text{C}$. The density of solutions was determined pycnometrically. The individual solutions were prepared by mixing the calculated volumes of individual components. Measurement of the falling time of the viscosimeter ball was repeated ten times for each sample. Viscosity of solution was calculated from the average falling time and density of solution using the viscosimeter constants. After each measurement, the viscosimeter was rinsed once with distilled water and subsequently twice with a portion of the solution under measurement.

Results and Discussion

The viscosity of solutions containing 0, 20, 40, 55, 65, 75, 85, 95, and 100 volume % of organic solvent (methyl alcohol, ethyl alcohol, acetone), as well as hydrochloric acid at concentration 0–3 M was measured. The results of these measurements showing the dependence of viscosity on the content of organic solvent at varying concentrations of hydrochloric acid are presented in Figs. 1–3.

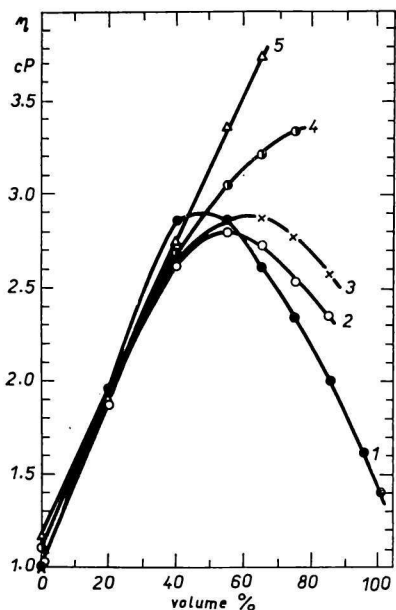


Fig. 1. Viscosity of the solutions water—ethyl alcohol—hydrochloric acid. Axis of abscissas: volume % of ethyl alcohol; axis of ordinates: η [cP].
 1. 0 M-HCl; 2. 0.5 M-HCl; 3. 1.0 M-HCl;
 4. 2.0 M-HCl; 5. 3.0 M-HCl.

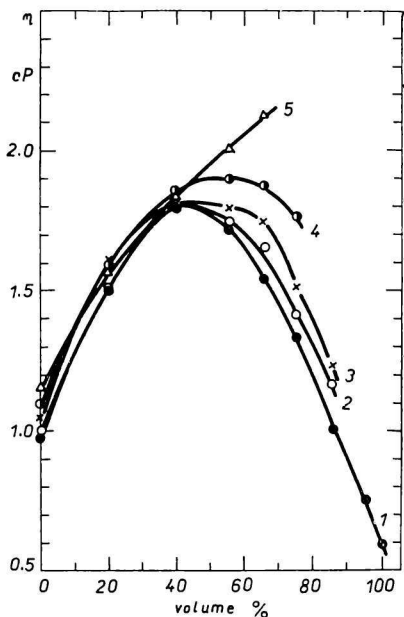


Fig. 2. Viscosity of the solutions water—methyl alcohol—hydrochloric acid. Axis of abscissas: volume % of methyl alcohol; axis of ordinates: η [cP].
 1. 0 M-HCl; 2. 0.5 M-HCl; 3. 1.0 M-HCl;
 4. 2.0 M-HCl; 5. 3.0 M-HCl.

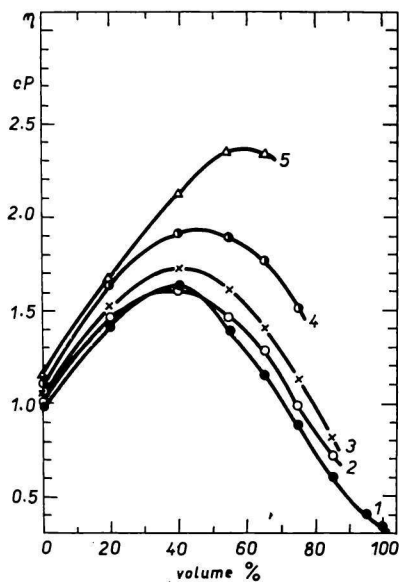


Fig. 3. Viscosity of the solutions water—acetone—hydrochloric acid. Axis of abscissas: volume % of acetone; axis of ordinates: η [cP].
 1. 0 M-HCl; 2. 0.5 M-HCl; 3. 1.0 M-HCl;
 4. 2.0 M-HCl; 5. 3.0 M-HCl.

The systems studied possess the viscosity isotherms of convex type with a maximum. These results allow us to suppose an interaction among individual components of solution. The assumption that the individual components interact in the mixture of ethyl alcohol and water was confirmed by the study of the heats of mixing. It has been demonstrated that the heat of mixing exhibits maximum value in the region of 16 mole % of ethyl alcohol (40 weight %) [9] where the maximum of the viscosity isotherm occurs.

Table 1

The values of the slope k of the dependence of $(\eta \eta_0^{-1} - 1) (\sqrt{c})^{-1}$ on \sqrt{c} for hydrochloric acid and dielectric constants ϵ [14] for solvent systems

Volume % of organic solvent	Ethyl alcohol		Methyl alcohol		Acetone	
	ϵ	k	ϵ	k	ϵ	k
0	80.37	0.069	80.37	0.069	80.37	0.069
20	68.66	0.049	71.05	0.032	68.58	0.084
40	56.49	0.094	61.24	0.036	56.00	0.152
55	47.52	0.111	54.03	0.048	46.22	0.204
65	41.90	0.114	48.99	0.133	39.72	0.238
75	36.51	0.208	43.96	0.148	33.42	0.318
85	31.46	0.261	39.13	0.200	27.47	0.380
95	27.01	0.452	34.57	0.296	22.08	0.500

Table 2

Viscosity of ternary system in dependence on temperature

Volume % of organic solvent	Composition of solution (20°C)	Methyl alcohol η [cP]			Ethyl alcohol η [cP]			Acetone η [cP]		
		c_{HCl} [M]	20°C	40°C	60°C	20°C	40°C	60°C	20°C	40°C
40	6	2.43	1.73	—	3.45	2.44	—	3.30	2.24	—
40	1.5	1.83	1.17	0.79	2.63	1.56	0.98	1.81	1.13	0.79
40	1.0	1.81	1.13	0.76	2.62	1.47	0.93	1.72	1.06	0.72
40	0.5	1.80	1.09	0.71	2.62	1.40	0.88	1.62	0.99	0.68
85	1.5	1.40	0.99	0.72	2.99	1.82	1.24	0.93	0.68	—
85	1.0	1.27	0.90	0.66	2.59	1.57	1.07	0.82	0.60	—
85	0.5	1.16	0.81	0.59	2.36	1.39	0.91	0.71	0.52	—

Similarly, the volume contraction of solutions containing organic solvent and water as well as the corresponding relative decrease in molar volumes of individual components show the same course as the viscosity of solution and reach a maximum at about 45 volume % of organic solvent [10].

From the results shown in Figs. 1–3, it is to be seen that the viscosity isotherm at 20°C has a maximum in the concentration region of about 45 volume % of organic

solvent (methyl alcohol, ethyl alcohol, acetone). This fact is most conspicuous in the case of binary mixtures consisting of organic solvent and water. The authors of the papers [11, 12] came to equal conclusion that the viscosity isotherm for ethyl alcohol—water mixtures possesses a maximum. Likewise, the viscosity isotherms of other water-miscible organic solvents, *e.g.* alcohols, acetone, expressing the dependence on composition of the binary system [2, 13] represent a type of convex isotherm with a maximum. Similar course of viscosity isotherm can be observed in the case of ternary system containing hydrochloric acid as the third component.

The variation of relative viscosity of the electrolyte solution with its concentration can be expressed by the approximative equation

$$\frac{\eta}{\eta_0} = 1 + A \sqrt{c} + Bc, \quad (4)$$

where η_0 and η denote viscosities of the solvent and the ternary solution, respectively.

The values of $(\eta \eta_0^{-1} - 1) (\sqrt{c})^{-1}$ were plotted against the square root of electrolyte concentration. For low concentrations, linear relationships were obtained. It appeared that the slope of these relationships increases with the content of organic solvent in solution.

The results obtained have confirmed that the viscosity of electrolyte solution rises with decreasing dielectric constant in ternary solutions with increasing content of hydrochloric acid. Table 1 contains the dielectric constants ϵ [14] of corresponding solution of organic solvent and the slope k of the dependence of $(\eta \eta_0^{-1} - 1) (\sqrt{c})^{-1}$ on \sqrt{c} for the solutions of hydrochlorid acid in various solvents.

The character of viscosity-temperature change for ternary solutions is presented in Table 2. The results of viscosity measurements in ternary solutions performed at 20, 40 and 60°C indicate that the logarithm of viscosity seems to be a linear function of the reciprocal value of temperature so as it is in binary systems or in simple liquids. The value of variation coefficient of the obtained viscosity data fluctuated over the range from 0.9 to 4.4 on dependence from temperature.

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