ISSN 1070-3632, Russian Journal of General Chemistry, 2015, Vol. 85, No. 4, pp. 781–785. © Pleiades Publishing, Ltd., 2015.
Original Russian Text © S.S. Lysova, Yu.E. Zevatskii, E.V. Demidov, N.P. Novoselov, 2015, published in Zhurnal Obshchei Khimii, 2015, Vol. 85, No. 4, pp. 529–534.

Densimetric Study of Protolytic Equilibria in Aqueous Electrolyte Solutions

S. S. Lysova[a], Yu. E. Zevatskii[a–c], E. V. Demidov[a], and N. P. Novoselov[a]

[a] *St. Petersburg State University of Technology and Design, ul. Bol'shaya Morskaya 18, St. Petersburg, 191186 Russia*
e-mail: yuri@newchem.ru

[b] *Ul'yanov (Lenin) St. Petersburg State Electrotechnical University (LETI), ul. Professora Popova 5, St. Petersburg, 197376 Russia*

[c] *Novbytkhim Closed Joint-Stock Company, ul. Zheleznodorozhnaya 45, Gatchina, Leningrad oblast, 188350 Russia*

Received November 6, 2014

Abstract—A method was suggested for studying protolytic equilibria via analyzing the mechanical behavior of a substance. The method was verified by high-precision density measurements (accurate to within 5 mg/L) for aqueous solutions of a number of organic and inorganic acids and organic bases. The numerical values of the dissociation constants and the values of the observed molar volumes of solvated ionized and neutral molecules were calculated using the experimentally obtained concentration dependence of the density of the aqueous solutions at 25°C.

Keywords: densimetry, density of aqueous solutions, molar volume, dissociation (ionization) constant, weak and strong electrolytes

DOI: 10.1134/S1070363215040015

The density of substances in a condensed state has a significant influence on the physical mechanical properties of materials. In particular, the density of liquids strongly affects the transport process parameters, rheological and hydrodynamic properties, sound velocity, and the magnitude of the strictive effects caused by interaction with fields of different nature. For liquid solutions, measurement of density as dependent on the concentration (densimetry) is an effective method for studying solute–solvent interactions [1, 2].

The density and dynamic viscosity of aqueous solutions and organic suspensions are known to exhibit highly nonlinear pH dependences [3, 4]; in some cases, extremal dependences are observed [3] that has not yet been quantitatively understood. In practical terms, the adjustment of the acidity of medium appears as a tool for controlling processes where diffusion is the rate-limiting step.

We showed previously [5, 6] that, in the framework of the model of infinitely dilute binary solutions, the observed molar volume V of the solute can be calculated by Eq. (1):

$$V = M\left(\frac{1}{\rho\omega} - \frac{1}{\rho_S\omega} + \frac{1}{\rho_S}\right). \quad (1)$$

Here, ρ is the solution density, ρ_S, solvent density, ω, absolute weight fraction of the solute, and M, molar weight of the solute. For a solute dissociating in solution by the Brønsted–Lowry reaction AH ↔A^- + H^+, the observed molar volume can be expressed as a linear combination of the solvated volume of the undissociated molecules V_{AH} and the solvated volume of the dissociated molecules $V_{A^-H^+}$ [Eq. (2)]:

$$V = (1 - \alpha)V_{AH} + \alpha V_{A^-H^+}, \quad (2)$$

where α is the degree of dissociation of the compound in a binary solution. In solutions of weak electrolytes the degree of ionization can be calculated by Ostwald's dilution law [Eq. (3)] [7]:

$$K = \frac{\alpha^2 c}{1 - \alpha}. \quad (3)$$

Here, K is the dissociation constant of the compound, and c, solution molarity, which is related to the absolute weight fraction by expression (4):

$$c = \frac{\rho\omega}{M}. \quad (4)$$

Equations (1)–(4) give the concentration dependence of the electrolyte solution density [Eq. (5)]:

$$\rho^{calc} = \rho_S \left[1 - cV_{AH} - \frac{K}{2}\left(\sqrt{1 + \frac{4c}{K}} - 1\right)\Delta V\right] + Mc. \quad (5)$$

Here, ΔV is the change in the molar volume of the solvated molecules of the compound at dissociation in solution [Eq. (6)]:

$$\Delta V = V_{A^-H^+} - V_{AH}. \quad (6)$$

Hence, a theoretical model was proposed that links the concentration dependence of the density of a binary aqueous solution of a weak electrolyte with its dissociation constant and the observed molar volumes of prototropic forms of the electrolyte in solution.

Further development of this model could be helpful in describing the phenomena observed in [3, 4]. In this connection, we also developed here a technique for analyzing the acidity of medium based on the data of high-precision density measurements for aqueous solutions of electrolytes with different structures and strengths. The objects of our study were compounds with reliably known acid (pK_a –7–7 log units) and base (pK_b 3–9 log units) ionization constants.

The data of measurements of density (ρ_i) as dependent on the weight fraction in aqueous solutions, obtained for fifteen organic acids, two inorganic acids, and two organic bases, were processed by nonlinear regression analysis using the calculated dependence (5).

The application of nonlinear regression analysis to solving this problem yielded a system of Eqs. (7)–(9):

$$\sum_i^N \frac{(\rho_i^{calc} - \rho_i)c_i}{\sqrt{1 + \frac{4c_i}{K}}} = 0, \quad (7)$$

$$\sum_i^N (\rho_i^{calc} - \rho_i)c_i = 0, \quad (8)$$

$$\sum_i^N (\rho_i^{calc} - \rho_i)\left(\sqrt{1 + \frac{4c_i}{K}} - 1\right) = 0. \quad (9)$$

Here, N is the number of experimentally determined density values for solution of one of the compounds tested. The unknown parameters K, V_{AH}, and ΔV were determined by the numerical method described in [8].

For solving the system of Eqs. (7)–(9) we used the data from Table 1.

Table 2 lists the calculated against published (K^{publ}) values of the constant K, as well as the values of the observed molar volumes V_{AH} and ΔV. Also, Table 2 presents the variances calculated using the K, V_{AH}, and ΔV [Eq. (10)] data obtained and the sums of the absolute deviations of calculated from experimental densities $\Delta\rho$ [Eq. (11)].

$$\sigma = \sqrt{\frac{\sum_i^N (\rho_i - \rho_i^{calc})^2}{N - 1}}, \quad (10)$$

$$\Delta\rho = \frac{1}{N}\sum_i^N (\rho_i - \rho_i^{calc}). \quad (11)$$

As seen from Table 2, in 16 cases out of 19 the standard variances of the calculated from experimental densities of the solutions are smller than the instrumental error of the experimental measurements, which shows a good agreement between theory and experiment. For solutions of 2-nitropropane, picric acid, and hydrochloric acid the variances exceed, though insignificantly, the instrumental error of measurements (maximally 6.65 against 5 mg/L).

Obviously overestimated values of the constants calculated for 4-nitrophenol ($K^{publ} = 7 \times 10^{-8}$, $K_a = 7 \times 10^{-6}$), 2-nitropropane ($K^{publ} = 2 \times 10^{-8}$, $K_a = 6 \times 10^{-6}$), and aniline ($K^{publ} = 4 \times 10^{-10}$, $K_b = 3 \times 10^{-5}$) confirm our earlier conclusion [6] that densimetry is inapplicable to studying protolytic equilibria for very weak acids (bases) with $pK_a(pK_b) > 7$.

The acidity constant calculated for trimethylacetic acid is overestimated ($K^{publ} = 8.9 \times 10^{-6}$, $K_a = 5.9 \times 10^{-5}$) most probably due to the 0.1–0.3 M concentration of the solutions tested. The densities of more dilute trimethylacetic acid solutions insignificantly differed from that of distilled water, so these data could not be processed by the technique proposed.

It seems likely that the dissociation constants of electrolytes can be correctly determined by the densimetric technique via processing the densities at concentrations below 0.1 M that allow neglecting intermolecular interactions and association in aqueous solutions and, thereby, meeting the criterion of applicability of Ostwald's dilution law [7].

Table 1. Experimental densities of distilled water ρ_S and of the aqueous solutions of the compounds tested as a function of their concentrations at 25°C

Compound	ρ_S, g/L	Weight fraction/density of solution, g/L						
4-Nitrophenol	997.060	2.18×10^{-3}	1.46×10^{-3}	1.13×10^{-3}	8.04×10^{-4}	5.85×10^{-4}	4.16×10^{-4}	3.15×10^{-4}
		997.687	997.473	997.374	997.275	997.213	997.168	997.136
2-Nitropropane	997.042	5.81×10^{-3}	4.63×10^{-3}	3.72×10^{-3}	2.98×10^{-3}	2.28×10^{-3}	1.76×10^{-3}	1.29×10^{-3}
		997.474	997.369	997.06	997.258	997.202	997.166	997.133
Trimethylacetic acid	997.059	2.51×10^{-2}	2.23×10^{-2}	1.87×10^{-2}	1.62×10^{-2}	1.37×10^{-2}	1.10×10^{-2}	8.32×10^{-3}
		997.281	997.260	997.229	997.205	997.179	997.154	997.127
Benzoic acid	997.043	2.20×10^{-3}	1.87×10^{-3}	1.47×10^{-3}	1.12×10^{-3}	8.64×10^{-4}	6.07×10^{-4}	3.77×10^{-4}
		997.472	997.406	997.327	997.260	997.209	997.159	997.113
2-Acetylbenzoic acid	997.044	2.27×10^{-3}	1.90×10^{-3}	1.48×10^{-3}	1.12×10^{-3}	8.49×10^{-4}	5.93×10^{-4}	4.36×10^{-4}
		997.523	997.445	997.358	997.284	997.226	997.174	997.139
Propionic acid	997.045	6.89×10^{-3}	5.50×10^{-3}	4.01×10^{-3}	2.91×10^{-3}	2.16×10^{-3}	1.72×10^{-3}	1.28×10^{-3}
		997.616	997.515	997.389	997.290	997.234	997.195	997.160
Isobutyric acid	997.047	7.44×10^{-3}	6.03×10^{-3}	4.91×10^{-3}	4.09×10^{-3}	3.38×10^{-3}	2.76×10^{-3}	2.08×10^{-3}
		997.313	997.262	997.223	997.195	997.170	997.150	997.123
Cyclohexylacetic acid	997.044	4.79×10^{-3}	4.21×10^{-3}	3.43×10^{-3}	2.71×10^{-3}	2.11×10^{-3}	1.66×10^{-3}	1.28×10^{-3}
		997.288	997.278	997.263	997.246	997.228	997.211	997.194
Acetic acid	997.065	5.93×10^{-3}	4.79×10^{-3}	3.76×10^{-3}	2.91×10^{-3}	2.30×10^{-3}	1.77×10^{-3}	1.32×10^{-3}
		997.896	997.730	997.579	997.457	997.368	997.293	997.230
2-Methylbenzoic acid	997.029	1.05×10^{-3}	8.63×10^{-4}	7.23×10^{-4}	5.83×10^{-4}	4.43×10^{-4}	3.43×10^{-4}	2.47×10^{-4}
		997.214	997.187	997.164	997.141	997.119	997.102	997.085
4-Nitrobenzoic acid	997.041	2.32×10^{-4}	2.11×10^{-4}	1.86×10^{-4}	1.66×10^{-4}	1.49×10^{-4}	1.29×10^{-4}	1.12×10^{-4}
		997.127	997.119	997.108	997.100	997.094	997.086	997.079
Phenoxyacetic acid	997.036	1.47×10^{-3}	1.08×10^{-3}	8.02×10^{-4}	6.05×10^{-4}	4.41×10^{-4}	3.12×10^{-4}	2.35×10^{-4}
		997.381	997.294	997.227	997.185	997.149	997.116	997.096
Formic acid	997.048	1.17×10^{-2}	9.51×10^{-3}	5.68×10^{-3}	4.38×10^{-3}	3.24×10^{-3}	2.35×10^{-3}	1.69×10^{-3}
		999.600	999.082	998.290	998.018	997.769	997.575	997.430
Chloroacetic acid	997.038	2.30×10^{-3}	1.84×10^{-3}	1.42×10^{-3}	1.13×10^{-3}	8.79×10^{-4}	6.70×10^{-4}	4.57×10^{-4}
		997.901	997.732	997.582	997.477	997.379	997.303	997.221
Picric acid	997.045	5.12×10^{-3}	3.15×10^{-3}	2.21×10^{-3}	1.54×10^{-3}	1.17×10^{-3}	8.80×10^{-4}	5.63×10^{-4}
		999.544	998.585	998.119	997.815	997.619	997.476	997.319
Periodic acid	997.051	6.74×10^{-3}	4.76×10^{-3}	3.26×10^{-3}	2.12×10^{-3}	1.45×10^{-3}	6.82×10^{-4}	–
		1001.629	1000.253	999.220	998.436	997.991	997.481	–

Table 1. (Contd.)

Compound	ρ_S, g/L	Weight fraction/density of solution, g/L						
Hydrochloric acid	997.051	1.82×10^{-3}	1.48×10^{-3}	1.13×10^{-3}	9.23×10^{-4}	6.83×10^{-4}	5.13×10^{-4}	3.34×10^{-4}
		997.946	997.794	997.615	997.512	997.390	997.300	997.212
Aniline	997.061	8.26×10^{-3}	7.19×10^{-3}	6.19×10^{-3}	5.16×10^{-3}	4.22×10^{-3}	3.43×10^{-3}	2.68×10^{-3}
		997.423	997.372	997.330	997.284	997.247	997.211	997.169
Triethylamine	997.061	6.39×10^{-3}	5.21×10^{-3}	4.35×10^{-3}	3.51×10^{-3}	2.89×10^{-3}	2.33×10^{-3}	1.74×10^{-3}
		995.991	996.197	996.356	996.501	996.606	996.691	996.796

Table 2. Calculated K, V_{AH}, ΔV, σ, and Δρ parameters and published data K^{publ} for the series of the compounds tested

Compound	K^{publ}, M	K, M	V_{AH}, L/mol	ΔV, L/mol	σ, g/L	Δρ, g/L
4-Nitrophenol	7.08×10^{-8} [10]	6.50×10^{-6}	0.0953	0.1920	1.59×10^{-3}	4.08×10^{-5}
2-Nitropropane	2.11×10^{-8} [10]	6.08×10^{-6}	0.0822	0.0637	5.78×10^{-3}	1.02×10^{-3}
Trimethylacetic acid	8.90×10^{-6} [10]	5.90×10^{-5}	0.1014	0.0044	2.57×10^{-3}	6.31×10^{-5}
Benzoic acid	6.26×10^{-5} [10]	6.38×10^{-5}	0.0979	0.0104	5.34×10^{-4}	-1.61×10^{-5}
2-Acetylbenzoic acid	7.41×10^{-5} [10]	7.43×10^{-5}	0.1310	–0.0161	7.84×10^{-4}	6.68×10^{-5}
Propionic acid	1.34×10^{-5} [10]	1.33×10^{-5}	0.0684	–0.0254	4.47×10^{-3}	8.96×10^{-5}
Isobutyric acid	1.38×10^{-5} [10]	1.87×10^{-5}	0.0853	–0.0094	1.07×10^{-3}	6.14×10^{-6}
Cyclohexylacetic acid	3.09×10^{-5} [10]	2.96×10^{-5}	0.1458	–0.3568	2.59×10^{-4}	-6.80×10^{-7}
Acetic acid	1.75×10^{-5} [10]	1.73×10^{-5}	0.5091	0.0648	5.55×10^{-4}	1.43×10^{-4}
2-Methylbenzoic acid	1.26×10^{-4} [10]	1.25×10^{-4}	0.1197	–0.0615	5.96×10^{-4}	1.05×10^{-7}
4-Nitrobenzoic acid	3.62×10^{-4} [10]	5.20×10^{-4}	0.0863	0.0416	3.56×10^{-4}	2.07×10^{-8}
Phenoxyacetic acid	6.75×10^{-4} [10]	6.75×10^{-4}	0.1206	–0.0165	1.67×10^{-3}	8.26×10^{-8}
Formic acid	1.77×10^{-4} [10]	1.84×10^{-4}	0.0364	–0.0096	1.28×10^{-2}	5.80×10^{-6}
Chloroacetic acid	1.36×10^{-3} [9]	1.35×10^{-3}	0.0619	–0.0132	1.18×10^{-3}	-6.97×10^{-6}
Picric acid	1.95×10^{-1} 11]	1.92×10^{-1}	0.1289	–0.0125	5.55×10^{-3}	1.58×10^{-5}
Periodic acid	3.1×10^{-2} [11]	5.76×10^{-3}	0.0635	0.0283	8.71×10^{-4}	4.31×10^{-6}
Hydrochloric acid	10^{7} [11]	9.99×10^{6}	0.0091	0.0091	6.65×10^{-3}	-2.68×10^{-4}
Aniline[a]	3.98×10^{-10} [10]	2.79×10^{-5}	0.0891	0.0103	3.41×10^{-5}	3.39×10^{-7}
Triethylamine[a]	7.36×10^{-4} 10]	6.65×10^{-4}	0.1205	–0.0199	4.61×10^{-3}	-1.25×10^{-4}

[a] For bases dissociating by the $B + H^+ \leftrightarrow BH^+$ reaction, V_{AH} corresponds to V_B, $\Delta V = V_{BH^+} - V_{H^+} - V_B$, and K corresponds to the basicity constant K_B.

This method is apparently useful for studying protolytic equilibria in solutions of inorganic acids. Yet, when the constant calculated for hydrochloric acid was virtually identical to the corresponding published data, in contrast, that for periodic acid was about 5 times smaller. This fact can be explained by association of ions in the process of periodic acid dissociation in aqueous solutions at the concentrations tested.

It should be noted that densimetry does not provide acceptable results for solutions whose densities at concentrations up to 0.1 M are insignificantly different

from that of distilled water (like in the case of trimethylacetic acid).

The method we suggested employs the model interrelating the density of solutions and the acid-base properties of dissolved weak and strong electrolytes. Thus, an opportunity is provided to predict how changes in acidity of the medium would affect the density of solutions, emulsions, and suspensions formed by compounds containing prototropic and/or protophilic groups. This opportunity is of great practical significance since, by adjusting the acidity of these media, it is possible to control their viscosity.

An important advantage of this method over the methods conventionally used for studying protolytic equilibria in solutions is that during measurements the solution is not exposed to chemicals and electromagnetic or electrical fields. This may be essential for applications involving some technological, biological, and biochemical systems for which such exposures of the objects tested are undesirable.

EXPERIMENTAL

We used reagents with 98–99% weight fraction of the main component. The quality of the reagents was controlled by measuring the melting point for solids and the density for liquids. If necessary, the substances were purified by recrystallization or distillation.

Samples of the substances tested and the prepared solutions were weighed on an MV-210 A electronic analytical balance accurately to within 0.1 mg. A series of working solutions with different weight fractions of the compound tested were prepared by gravimetric dilution.The aqueous solutions were prepared by dissolving a required amount of the test compound in distilled water, and this was followed by dilution. First, the density of the high-concentration solution was measured, whereupon a certain amount of this solution was removed and replaced by equal amount of water after each measurement. The density of distilled water ρ_S was measured every time that a new measurement series was started, because its value changed by several units of the fifth decimal point.

The densities of the aqueous solutions of the substances tested were measured with an accuracy of 5×10^{-3} g/L using an Anton Paar DMA 5000 M digital density meter, whose working principle is based on the law of harmonic oscillation and in which a U-shaped tube is completely filled with the sample to be analyzed. Two built-in Pt 100 platinum thermometers together with Peltier elements allowed the density meter to measure the density of the sample at the desired temperature of 25°C (temperature accuracy 0.01°C).

REFERENCES

1. *Teoreticheskie i eksperimental'nye metody khimii rastvorov* (Theoretical and Experimental Methods of Solution Chemistry), Tsivadze, A.Yu., Ed., Moscow: Prospekt, 2011.
2. Sergeev, V.V., Dibrivnyi, V.N., and Van-Chin-Syan, Yu.Ya., *Russ. J. Gen. Chem*., 2012, vol. 82, no. 2, p. 202. DOI: 10.1134/S1070363212020065.
3. McWatters, K.H. and Holmes, M.R., *J. Food Sci*., 1979, vol. 44, p. 765. DOI: 10.1111/j.1365-2621.1979.tb08496.x.
4. Surh, J., Decker, E.A., and McClements, D.J., *Food Hydrocolloids*, 2006, vol. 20, p. 607. DOI: 10.1016/j.foodhyd.2005.07.004.
5. Zevatskii, Yu.E., Demidov, E.V., Novoselov, N.P., Lysova, S.S., Samoilov, D.V., and Vlasov, E.A., *Izv. S.-Peterb. Gos. Tekhnol. Inst. (Tekh. Univ.)*, 2011, vol. 11, no. 37, p. 20.
6. Zevatskii, Yu.E. and Lysova, S.S., *Dokl. Phys. Chem*., 2013, vol. 448 (2), p. 15. DOI: 10.1134/S0012501613020024.
7. Izmailov, N.A., *Elektrokhimiya rasrvorov* (Electrochemistry of Solutions), Kharkov: Kharkov. Gos. Univ., 1959.
8. Porshnev, S.V. and Belenkova, I.V., *Chislennye metody na baze Mathcad* (Numerical Methods Based on Mathcad), St. Petersburg: BKhV-Peterburg, 2005.
9. Apelblat, A., *J. Mol. Liq*., 2002, vol. 95, p. 99.
10. *Langes Handbook of Chemistry*, Dean, J.A., Ed., New York: McGraw-Hill, 1999, p. 24.
11. *Novyi spravochnik khimika i tekhnologa. Khimicheskoe ravnovesie. Svoistva rastvorov* (New Chemist's and Technologist's Handbook: Chemical Equilibria: Properties of Solutions), St. Petersburg: Professional, 2004.