USE OF MOLECULAR CHARACTERISTICS TO CALCULATE VISCOSITY OF MINERAL SOLUTIONS

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The possibility of using molecular characteristics in the determination of the thermophysical parameters of fluids is shown. Approximate equations for the calculation of the dynamic viscosity of aqueous solutions of mineral salts are obtained through the use of similarity theory and molecular data.

At the present time, the theory of fluids allows one to obtain mainly qualitative relationships [1]. Therefore it is impossible to determine with its use the complete physical properties of one-component fluids. In the transition to salt solutions, the problem of calculating the physical constants becomes tremendously complicated and there is no analytical solution for this problem. There is experimental data on the properties of solutions only for a narrow range of temperatures and pressures and then not for the entire group of fluids mentioned. The consequences of such a situation are extremely undesirable because lack of knowledge of the thermophysical characteristics of solutions retards the development of reasonable designs for evaporative equipment. There is no data for the properties of the complex salt solutions [2] which are used in salt rectification.

All macroscopic properties of matter can be determined by solving the Schrodinger equation [3]. Unfortunately, using existing computers and methods of calculation, it can be solved for complex atoms only in ten billion years [4], i.e., it is insoluble in practice. Under these conditions, the introduction of molecular characteristics for the determination of thermophysical constants is most promising, in our opinion, since the properties of matter are determined by its structure (number and location of identical elementary particles). Knowledge of the linear dimensions of molecules and ions makes it possible to calculate certain properties [1, 3-6] such as density, molar volume, surface energy, modulus of elasticity, and other characteristics of matter in liquid and solid phases. In addition, there is great interest in the use of other molecular data. For the calculation of intermolecular interaction parameters, Altenburg [7] used the sum of the outer electrons of a molecule. This method made it possible to proceed to the calculation of the coefficients of viscosity, thermal conductivity, and diffusion [6]. The next molecular characteristic, the sum of nuclear charges, can be used for the determination of the fusion temperature of elements [4], the enthalpy of oxide formation [8], the atomic radius [4], etc. The molecular mass is widely used as a characteristic for the determination of physical constants of fluids: viscosity [9], thermal conductivity, heats of fusion and vaporization, diffusion coefficient, and other quantities [6, 10]. The important role of the linear dimension of an atom, from which one can determine the radius of the external electron shell [11], makes feasible the use of still another molecular characteristic — sum of electron layers, ΣC. The value of the molecular diameter d is also proportional to the sum of the nuclear charges [4]. At the same time, d is inversely proportional to the sum of the external electrons [12] and to the molecular mass [13]. Thus

$$d \equiv \frac{(\Sigma C)(\Sigma z)}{M(\Sigma E)}. \tag{1}$$

Previously we used in place of (1) [14, 15] the quantity l, which is derived from d, in the following form:

$$l = \left[\frac{(\Sigma C)(\Sigma z)}{M(\Sigma E)}\right]^{1/3}. \tag{2}$$

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The properties of aqueous solutions of mineral salts* can also be evaluated from molecular characteristics. For example, the dehydrating power of salts with identically charged cations and uniform structure of electron shells varies in proportion to ΣE and ΣZ, and is inversely proportional to the ion radius [16, 17]. The work of Debye and McCall [2] is the basis for this conclusion. This circumstance in conjunction with that noted above makes it possible to use the molecular characteristics of solutions in the form of a characteristic dimension l_s [18]. This is a complex quantity which is an additive function of the molecular data for the solute and solvent:

$$l_s = \left[\frac{(\Sigma C)_s (\Sigma Z)_s}{(\Sigma E)_s M_s} \right]^{1/3}. \qquad (3)$$

The quantity (3) is proportional to the mean diameter of the hydrated ion. Formulas for the calculation of the molecular characteristics in (3) are given in [18].

Of the thermophysical characteristics of fluids, viscosity occupies a special position with respect to range of variation and to complexity of determination by theoretical means [19], which leads to a considerable deviation between theoretical and experimental [19, 14] values of μ (up to ±30% and sometimes ±200% and more).

We use similarity theory and molecular characteristics for the approximate determination of solution viscosities. Similarity in the temperature dependence of both water and solution viscosities [18, 20] leads to the relation

$$\mu_s = \mu_w N_\mu, \qquad (4)$$

where N_μ is a conversion factor [21]. N_μ can be represented by [18]

$$N_\mu = C \left(\frac{k_T + k_H}{k_H} \right)^{n_1} \left(\frac{l_s}{l_w} \right)^{n_2}. \qquad (5)$$

To shorten the intermediate calculations in this paper, we use a single basic current solution temperature of 107°C (for the determination of k_T and k_H). It corresponds approximately to the average temperature depression for solution which boil at atmospheric pressure. Using Eq. (5), we obtain

$$\frac{\mu_s}{\mu_w} = CK^{n_1}L^{n_2}. \qquad (6)$$

from Eq. (4) after the introduction of new notation. The ratio μ_s/μ_w is a quantity which depends on the dimensionless concentration and on molecular characteristics. As shown by analysis of experimental data [22], Eq. (6) is valid within a certain range of the quantity ϑ which takes into account the relation between absolute salt content and the degree of saturation of the solution:

$$\vartheta = K - (b + 1). \qquad (7)$$

Small values of ϑ show how far from saturation are solutions having a high mass concentration.

Analysis of the experimental data shows that all solutions considered can be divided into three groups.

First Group. Solutions for which

$$L > 1 \ (L = 1.004 - 1.1), \ K = 1.03 - 1.36, \ \vartheta < 0, \ |\vartheta| = |0.03 - 0.17|,$$

and also solutions with the characteristics:

$$L < 1 \ (L \leqslant 0.971), \ K = 1.23 - 1.53, \ \vartheta > 0, \ |\vartheta| = |0.13 - 0.326|.$$

By analysis of the experimental data [22], the following empirical equation was obtained for these solutions:

$$\frac{\mu_s}{\mu_w} = K^{3+|\vartheta|}L^6. \qquad (8)$$

Second Group. Solutions characterized by the quantities

$$L > 1, \ \vartheta > 0, \ K = 1.04 - 1.51,$$

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*Here we have in mind solutions which are formed by a metal cation and an inorganic-acid anion.

TABLE 1. Comparative Data for Viscosity of Electrolyte Solutions at p = 1 bar and t = 20°C

Solution concentration B, %	K	L	ϑ	$u_{ex} \cdot 10^5$ msec/m^2	$u_{calc} \cdot 10^5$ msec/m^2	Relative error, %
$CaCl_2$						
8,3	1,058	1,02	—0,025	120	137	+12,4
12	1,086	1,035	—0,034	137	157	+12,75
21,3	1,175	1,06	—0,038	210	232	+ 8,7
35	1,334	1,099	—0,016	510	424	—20,3
$MgSO_4$						
10	1,233	0,9709	+0,133	186	171	—8,75
15	1,421	0,963	+0,271	283	311	+9,0
20	1,526	0,956	+0,326	410	407	—0,735
KNO_3						
10	1,041	0,988	—0,059	97	97,5	+0,513
20	1,09	0,984	—0,11	97	97,5	+0,513
KBr						
10	1,104	1,0046	+0,004	96	97,5	+1,54
20	1,234	1,0199	+0,033	95	97,5	+2,56
37	1,503	1,0536	+0 133	104	97,5	—6,67
KCl						
10	1,192	1,008	+0,092	99	97,5	—1,54
16	1,3	1,017	+0,14	101	97,5	—3,59
20	1,433	1,028	+0,233	102	97,5	—4,63
NaCl						
10	1,275	0,9783	+0,1755	119	113,5	—4,86
15	1,498	0,9817	+0,278	133	135	+1,49
25	1,8255	0,977	+0,575	181	162	—11,8

and also solutions in which

$$L < 1 \quad (L \leqslant 0.988), \ \vartheta < 0, \ K = 1.04 - 1.25.$$

The viscosity of solutions in the second group differs little from the viscosity of water. As a result of a comparison of the experimental data [22], we assume for them

$$\mu_s \cong 0.98\mu_w. \tag{9}$$

Third Group. In this group are solutions with the parameters

$$1 > L \geqslant 0.976, \ K = 1.27 - 1.83, \ \vartheta > 0, \ |\vartheta| = |0.17 - 0.575|.$$

The computational equation for these solutions obtained from an analysis of the experimental data takes the form

$$\frac{\mu_s}{\mu_w} = KL^5. \tag{10}$$

In Eqs. (8)-(10), the viscosities μ_s and μ_w are compared at an identical temperature. Comparative data for solution viscosity is presented in Table 1. The proposed method of calculation is characterized by relative complexity and is approximate. A positive aspect of this method is the possibility of predicting certain properties of solutions without performing laborious experiments. Considering the theoretical difficulties in the determination of viscosity, the deviation of calculated values from experimental values is acceptable.

The use of the proposed method makes is possible to obtain equations for the calculation of other physical constants. For example, an equation for the calculation of surface tension in solutions has been given [18]. In addition, the use of molecular characteristics for the determination of the thermophysical constants of solutions in implicit form offers an opportunity to calculate the intensity of heat transfer during boiling of these fluids [23], which is of great value in the design of evaporative devices.

NOTATION

ΣE, ΣZ, ΣC	are the sums in all atoms of one molecule: of external electrons, positive charges and electron layer, respectively by [14, 18];
M	is the molecular mass;
l	is the characteristic dimension proportional to molecule diameter;
K	is the current relative concentration, $K = k_T + k_H/\bar{k}_H$;

k_T	is the current concentration, g salt/100 g water;
k_H	is the concentration of saturated solution corresponding to characteristic temperature;
B	is the mass concentration, %;
b	is the mass concentration in fractions of unity, $b = B/100$;
ϑ	is the excess dimensionless concentration;
μ	is the dynamic viscosity, $N/sec \cdot m^2$, $\vartheta = K-(b + 1)$;
s	is the index characterizing solution;
w	is the subscript referring to water.

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