VISCOSITY OF DILUTED AQUEOUS $K_2CO_3/KHCO_3$ SOLUTIONS

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The applicability of the equation derived for calculating the dynamic viscosity of ternary non-electrolyte mixtures, to the correlation of viscosity data of the H_2O–$K_2CO_3/KHCO_3$ system is verified in this work. It was found out that the values of dynamic viscosity obtained experimentally are in good agreement with the viscosity values calculated from this equation. The equation constants – interaction coefficients – were determined from the measurements of dynamic viscosity on mixing the basic solutions of K_2CO_3 and $KHCO_3$ of known concentration. The correlation equation makes it possible to calculate viscosity of the $K_2CO_3/KHCO_3$ solutions in the K_2CO_3 and $KHCO_3$ concentration range from 0 to about 2.0 kmol m^{-3}.

When measuring the interfacial area and mass transfer coefficient in liquid, such gas–liquid systems are utilized to advantage in which solute reacts chemically with a component of absorbent. Owing to the chemical reaction, the composition of absorption solution, and thus its physical properties are changed. To the basic properties which it is necessary to investigate, belong viscosity and density. The experimental determination of these quantities is possible but not always advantageous for it mostly extends the time-consuming measurements. The tabular data (e.g. refs[1,2]) refer mostly to aqueous solutions with one component, the dependence of viscosity and density on concentration and temperature being reported.

The aim of this work is to present a suitable calculating method which would make it possible to calculate the viscosity of aqueous $K_2CO_3/KHCO_3$ solutions with sufficient accuracy.

THEORETICAL

A number of equations has been proposed for the viscosity of liquid binary non-electrolyte mixtures. Of these relations, the most accurate is considered the equation derived by McAllister[3]. This equation was generalized to hold also for ternary mixtures[4]. In this case, it is already rather complicated – the number of terms on the right-hand side of the equation is twenty one – and contains six binary and one ternary interaction coefficients. Škubla[5] succeded in decreasing the number of terms on keeping the high reliability of the equation with the same number of coefficients. For ternary systems he derived the equation

$$\mu = x_1^2\varphi_1\mu_1 + x_2^2\varphi_2\mu_2 + x_3^2\varphi_3\mu_3 + 3\mu_{12}x_1(x_1x_2^2\varphi_1^2\varphi_2)^{1/3} + \\ + 3\mu_{21}x_2(x_1^2x_2\varphi_1\varphi_2^2)^{1/3} + 3\mu_{13}x_1(x_1x_3^2\varphi_1^2\varphi_3)^{1/3} + 3\mu_{31}x_3(x_1^2x_3\varphi_1\varphi_3^2)^{1/3} + \\ + 3\mu_{23}x_2(x_2x_3^2\varphi_2^2\varphi_3)^{1/3} + 3\mu_{32}x_3(x_2^2x_3\varphi_2\varphi_3^2)^{1/3} + 6\mu_{123}(x_1^2x_2^2x_3^2\varphi_1\varphi_2\varphi_3)^{1/3} \qquad (1)$$

which contains six binary and one ternary interaction parameters which do not depend on composition but are a function of temperature. To apply Eq. (*1*), it is necessary to know the dynamic viscosity of pure components as well.

Direct use of Eq. (*1*) for a mixture of electrolytes is not possible for it is not possible to define the viscosity of pure components. For this reason, so-called basic electrolyte solutions were introduced in papers[6,7] (for the H_2O–$NaOH/Na_2CO_3$ system) and in paper[8] (for the H_2O–$Na_2CO_3/NaHCO_3$ system). They are referred to as solutions which have precisely defined and measurable properties. Thus, the solutions of a certain concentration of electrolytes can be obtained by mixing water (subscript 1) and two basic solutions (subscripts 2, 3). This solution can then be classified as the ternary mixture. The mixing can be well illustrated in a ternary diagram – see Fig. 1. Mole fractions in Eq. (*1*) are to be obtained from a mass balance of mixing. On the assumption that the solutions of the electrolytes considered can be considered as diluted, it is possible to determine volume fractions of components from the volume additivity.

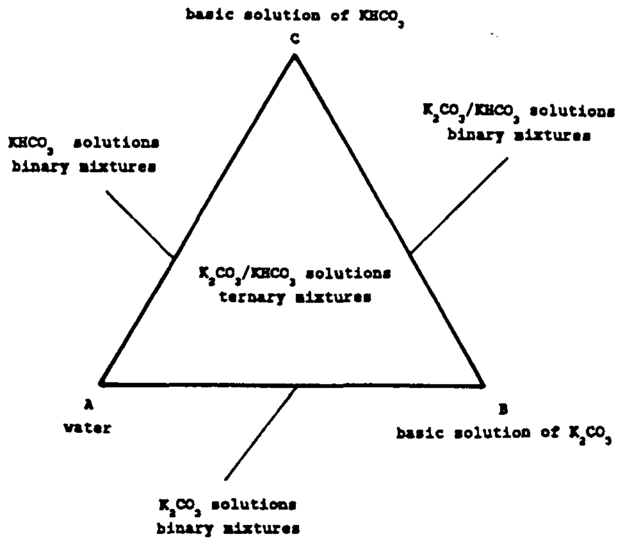

Fig. 1

Ternary diagram of the water–K_2CO_3 solution–$KHCO_3$ solution system

EXPERIMENTAL

The basic solutions were prepared by weighing the solid substances. Further, the diluted aqueous solutions of K_2CO_3 and $KHCO_3$ were prepared (by weighing or diluting the basic solutions) and the $K_2CO_3/KHCO_3$ solutions represented by points inside the ternary diagram (by weighing or mixing the basic solutions and water). The (binary) $K_2CO_3/KHCO_3$ solutions were obtained by mixing the basic solutions. Besides, the solutions were prepared satisfying the conditions which are specified below. For the necessary analysis of solutions (potentiometric titration), the universal titrator OH 407 (Radelkis) was used. The properties of basic solutions are given in Table I.

The viscosity of basic and other solutions was measured with the Ubbelohde viscosimeter tempered to a constant temperature with the accuracy of 0.1 K. Each measurement was repeated at least five times, and the arithmetic mean of outflow times was used for calculating the kinematic viscosity. The density of solutions was determined pycnometrically. From these measurements, the binary and ternary interaction coefficients were determined at the temperature of 20, 25, and 30 °C.

When applying Eq. (*1*), it is necessary to convert the concentration of K_2CO_3 and $KHCO_3$ in the given solution to mole fractions of previously defined components. In harmony with the diagram in Fig. 1, the symbols c_{ji}, V_j, ρ_j (j = A, B, C; i = 1, 2, 3) for initial solutions and c_i, ρ (subscript j = mix is omitted) for the mixture formed, are used. When calculating mole fractions, first it is necessary to determine the ratios of volumes of basic solutions and water, p, q ($p = V_B/V_A$; $q = V_C/V_A$) which are necessary when mixing to attain the K_2CO_3 and $KHCO_3$ concentrations in the given solution. From the mass balance of mixing, it follows

$$c_2 = p\,c_{B2}\,\rho/(\rho_A + p\,\rho_B + q\,\rho_C)\,, \tag{2}$$

$$c_3 = q\,c_{C3}\,\rho/(\rho_A + p\,\rho_B + q\,\rho_C)\,. \tag{3}$$

By rearranging Eqs (*2*) and (*3*), it is possible to obtain the relations for calculating quantities p and q

$$p = c_2\,c_{C3}\,\rho_A/(c_{B2}\,c_{C3}\,\rho - c_{B2}\,c_3\,\rho_C - c_2\,c_{C3}\,\rho_B)\,, \tag{4}$$

$$q = c_{B2}\,c_3\,\rho_A/(c_{B2}\,c_{C3}\,\rho - c_{B2}\,c_3\,\rho_C - c_2\,c_{C3}\,\rho_B)\,. \tag{5}$$

On using ratios p and q, it is possible to express mole and volume fractions

$$x_1 = c_{A1}/z\,, \tag{6}$$

$$x_2 = p\left\{[(\rho_B - c_{B2}\,M_{K_2CO_3})/M_{H_2O}] + c_{B2}\right\}/z\,, \tag{7}$$

$$x_3 = q\left\{[(\rho_C - c_{C3}\,M_{KHCO_3})/M_{H_2O}] + c_{C3}\right\}/z\,, \tag{8}$$

where

$$z = c_{A1} + p\left\{[(\rho_B - c_{B2}\,M_{K_2CO_3})/M_{H_2O}] + c_{B2}\right\} + \\ + q\left\{[(\rho_C - c_{C3}\,M_{KHCO_3})/M_{H_2O}] + c_{C3}\right\}. \tag{9}$$

Volume fractions can be determined from the equations

$$\varphi_1 = 1/(1 + p + q)\,, \tag{10}$$

$$\varphi_2 = p/(1+p+q)\,, \tag{11}$$

$$\varphi_3 = q/(1+p+q)\,. \tag{12}$$

RESULTS AND DISCUSSION

Use of Eq. (*1*) for correlating the dynamic viscosity of the K_2CO_3/$KHCO_3$ solutions represented by points inside the ternary diagram does not fulfil the aim of correlating the viscosity data within the K_2CO_3 and $KHCO_3$ concentrations from 0 to about 2.0 kmol m^{-3}. For this purpose it was necessary to define further basic solution with the same K_2CO_3 and $KHCO_3$ concentration equal 2.0 kmol m^{-3}, to prepare new binary and ternary mixtures by mixing the new basic solution with the original basic solutions and then to apply Eq. (*1*) to this region in the same way. However, the considered ternary mixtures can be prepared also by mixing the basic solutions 1,2 on simultaneous evaporating water ($V_A < 0$). Then it is necessary to consider fictional negative mole and volume fractions of water (p, $q < 0$). This approach was used in papers[7,8]. In this way, the studied problem is divided into two parts: determination of interaction coefficients for diluted solutions (region I) and for solutions with a higher concentration (region II).

The interaction coefficients of Eq. (*1*) were found out by the multiple linear regression, the values of dynamic viscosity of water and basic solutions being considered known. In case of concentrated solutions, Eq. (*1*) was rearranged first in terms of the rules for the root extraction and in the original set, the measurements concerning to the K_2CO_3/$KHCO_3$ solutions (ternary mixtures) were replaced by the data for the K_2CO_3/$KHCO_3$ solutions satisfying the conditions

$$c_{B2}\frac{c_{C3}\,\rho - c_3\,\rho_C}{c_{C3}\,\rho_B} < c_2 < c_{B2}\,, \tag{13}$$

$$c_{C3}\frac{c_{B2}\,\rho - c_2\,\rho_B}{c_{B2}\,\rho_C} < c_3 < c_{C3}\,, \tag{14}$$

which were derived from the limiting value of denominator in Eqs (*4*) and (*5*).

TABLE I
Physical properties of basic solutions – experimental values for c_{B2} = 1.956 kmol m^{-3} and c_{C3} = 1.973 kmol m^{-3}

t, °C	μ_B, mPa s	μ_C, mPa s	ρ_B, kg m^{-3}	ρ_C, kg m^{-3}
20.0	1.881	1.302	1210.1	1119.7
25.0	1.677	1.171	1208.1	1117.2
30.0	1.522	1.055	1205.7	1114.4

The values of the binary and ternary interaction coefficients μ_{ik} and μ_{123} at the temperatures of 20, 25, and 30 °C are given in Table II. The data in the upper part of the respective column refer to the diluted solutions, in the lower part there are the interaction coefficients for the concentrated solutions.

Equation (*1*) proposed for correlating the viscosity data makes it possible not only to calculate the dynamic viscosity of the aqueous $K_2CO_3/KHCO_3$ solutions but also the K_2CO_3 or $KHCO_3$ solutions. In the latter case, the terms with x_3, φ_3 or x_2, φ_2 will not

TABLE II
Binary and ternary interaction coefficients in mPa s, Eq. (*1*)

t, °C	μ_{12}	$s \cdot 10^2$	μ_{21}	$s \cdot 10^2$	μ_{13}	$s \cdot 10^2$
20.0	1.211	1.56	1.418	1.61	1.071	1.68
	1.226	1.80	1.413	2.08	1.117	1.79
25.0	1.119	1.29	1.328	1.33	1.034	1.38
	1.130	1.28	1.244	1.30	1.022	1.47
30.0	1.000	0.86	1.170	0.92	0.914	0.92
	1.009	0.98	1.121	0.99	0.936	1.12

t, °C	μ_{31}	$s \cdot 10^2$	μ_{23}	$s \cdot 10^2$	μ_{32}	$s \cdot 10^2$
20.0	1.181	1.52	1.668	1.73	1.475	1.87
	1.138	1.79	1.655	1.51	1.476	1.53
25.0	1.043	1.25	1.531	1.43	1.384	1.55
	1.000	1.26	1.487	1.07	1.329	1.09
30.0	0.955	0.84	1.380	0.96	1.210	1.04
	0.905	0.96	1.346	0.81	1.199	0.83

t, °C	μ_{123}	$s \cdot 10^2$
20.0	1.231	2.10
	1.389	2.79
25.0	0.875	1.73
	1.298	1.98
30.0	0.901	1.15
	1.173	1.51

apply in Eq. (*1*). The comparison of the measured and calculated values of dynamic viscosity for the aqueous K_2CO_3 and $KHCO_3$ solutions is given in Table III. It is apparent from this table that between the measured and calculated values of dynamic viscosity of the K_2CO_3 and $KHCO_3$ solutions there exists a good agreement – the maximum relative error does not exceed 3.0%. The values of dynamic viscosity of the aqueous K_2CO_3/$KHCO_3$ solutions calculated from Eq. (*1*) are compared with the measured

TABLE III
Comparison of measured and calculated values of dynamic viscosity of aqueous K_2CO_3 and $KHCO_3$ solutions

c_2, kmol m^{-3}	c_3, kmol m^{-3}	t, °C	μ_{exp}, mPa s	μ_{cal}, mPa s	δ, %
0.494	0	20.0	1.160	1.163	-0.26
0.985	0	20.0	1.355	1.347	0.59
1.207	0	20.0	1.436	1.445	-0.63
1.566	0	20.0	1.610	1.631	-1.30
1.874	0	20.0	1.825	1.824	0.05
0.494	0	25.0	1.041	1.061	-1.92
0.985	0	25.0	1.212	1.239	-2.28
1.207	0	25.0	1.296	1.326	-2.31
1.566	0	25.0	1.439	1.482	-2.99
1.874	0	25.0	1.648	1.634	0.85
1.207	0	30.0	1.164	1.183	-1.63
1.566	0	30.0	1.307	1.330	0.54
1.874	0	30.0	1.481	1.478	0.20
0	0.460	20.0	1.055	1.056	-0.09
0	0.999	20.0	1.138	1.133	0.44
0	1.150	20.0	1.150	1.157	-0.61
0	1.496	20.0	1.217	1.216	0.08
0	1.734	20.0	1.263	1.258	0.40
0	0.999	22.0	1.086	1.096	-0.92
0	0.460	25.0	0.947	0.971	-2.53
0	1.150	25.0	1.036	1.054	-1.74
0	1.496	25.0	1.092	1.095	-0.27
0	1.734	25.0	1.136	1.129	0.62
0	0.999	27.5	0.967	0.986	-1.96
0	0.460	30.0	0.854	0.868	-1.64
0	1.150	30.0	0.940	0.950	-1.06
0	1.496	30.0	0.990	0.990	0
0	1.734	30.0	1.028	1.021	0.68

values of μ in Table IV. The tabular presentation of results shows that even in this case, Eq. (*1*) is sufficiently reliable.

On the basis of interaction coefficients calculated from experimental data at different temperatures t_0, t_1, t_2 ($t_0 < t_1 < t_2$), the interaction coefficients at arbitrary temperature $t \in < t_0, t_2 >$ may be obtained by interpolation, and these use in Eq. (*1*) for calculating the dynamic viscosity of aqueous $K_2CO_3/KHCO_3$ solutions at the temperature t. Analo-

TABLE IV

Comparison of measured and calculated values of dynamic viscosity of aqueous $K_2CO_3/KHCO_3$ solutions

c_2, kmol m^{-3}	c_3, kmol m^{-3}	t, °C	μ_{exp}, mPa s	μ_{cal}, mPa s	δ, %
1.329	0.408	20.0	1.596	1.610	-0.88
0.522	0.507	20.0	1.244	1.240	0.32
1.306	0.499	20.0	1.625	1.625	0.00
1.175	0.381	22.0	1.436	1.444	-0.56
0.392	0.761	22.0	1.185	1.167	1.52
1.017	0.200	22.0	1.360	1.335	1.84
1.253	0.183	25.0	1.343	1.355	-0.89
0.626	0.304	25.0	1.124	1.112	1.07
0.328	1.409	25.0	1.191	1.199	-0.67
1.175	0.381	28.0	1.266	1.271	-0.39
1.044	0.507	28.0	1.239	1.234	0.40
0.783	0.761	28.0	1.183	1.169	1.18
0.582	1.125	30.0	1.124	1.127	-0.27
1.566	0.299	30.0	1.403	1.404	-0.07
1.904[a]	1.264	20.0	2.320	2.284	1.55
1.431[a]	1.107	20.0	1.852	1.867	-0.81
1.009[a]	1.001	20.0	1.583	1.592	-0.57
1.431[a]	1.107	23.0	1.748	1.745	0.17
0.999[a]	1.431	23.0	1.577	1.584	-0.44
1.514[a]	0.751	25.0	1.634	1.631	0.18
1.513[a]	1.259	25.0	1.781	1.763	1.01
1.904[a]	1.264	25.0	2.092	2.055	1.77
1.431[a]	1.107	25.0	1.668	1.671	-0.18
1.493[a]	0.802	30.0	1.458	1.474	-1.10
1.513[a]	0.991	30.0	1.530	1.527	0.20
1.007[a]	1.678	30.0	1.439	1.433	0.42
1.009[a]	1.001	30.0	1.285	1.292	-0.54
1.680[a]	1.012	30.0	1.623	1.630	-0.43

[a] Solutions with higher concentration (region II).

gously one can also proceed on calculating the dynamic viscosity of aqueous K_2CO_3 or $KHCO_3$ solutions. For the interpolation, it is possible to use, e.g., the Lagrange polynomial in the form

$$\mu_{ik}(t) = \frac{(t-t_1)(t-t_2)}{(t_0-t_1)(t_0-t_2)}\mu_{ik}(t_0) + \frac{(t-t_0)(t-t_2)}{(t_1-t_0)(t_1-t_2)}\mu_{ik}(t_1) + \\ + \frac{(t-t_0)(t-t_1)}{(t_2-t_0)(t_2-t_1)}\mu_{ik}(t_2)\,, \tag{15}$$

where t_0, t_1, and t_2 are temperatures of 20, 25, and 30 °C. As it follows from Table IV, this method yields good results.

Only part of the total number of 375 measurements is given in Tables III and IV. The total set of measurements was evaluated on the basis of mean square relative error – this error is 1.1%.

SYMBOLS

c	molar concentration, kmol m^{-3}
M	molar mass, kg $kmol^{-1}$
p, q	volume ratio
s	standard deviation, mPa s
t	temperature, °C
V	volume, m^3
x	mole fraction
z	group of physical quantities defined by Eq. (9), kmol m^{-3}
δ	relative error, %
μ	dynamic viscosity, mPa s
μ_{ik}	binary interaction coefficients, mPa s
μ_{123}	ternary interaction coefficient, mPa s
ρ	density, kg m^{-3}
φ	volume fraction

Subscripts

A	referring to stream A
B	referring to stream B
C	referring to stream C
cal	calculated value
exp	experimental value
1	referring to component 1
2	referring to component 2
3	referring to component 3

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