KINEMATIC VISCOSITIES OF ACETONE, VINYL ACETATE, CROTONALDEHYDE, ACETIC ACID, ACETIC ANHYDRIDE AND THEIR BINARY AND TERNARY MIXTURES

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Kinematic viscosities of acetone, vinyl acetate, crotonaldehyde, acetic acid, acetic anhydride, their binary mixtures and two ternary mixtures (acetone–vinyl acetate–acetic acid and vinyl acetate–acetic acid–acetic anhydride) were measured. The values of coefficients of the Linke, McAllister, and Chandramouli–Laddha equations were calculated. The temperature dependence of the coefficients of last two equations can be expressed in terms of a function in exponential form, coefficients of which are tabulated.

Acetone, crotonaldehyde, and acetic anhydride are formed as by-products during the vapour-phase synthesis of vinyl acetate from acetylene and acetic acid. For calculations concerning the separation part of this technology it is necessary to know viscosities of the mixtures consisting of these substances. For this reason the temperature dependences of kinematic viscosities of acetone, vinyl acetate, crotonaldehyde, acetic acid, and acetic anhydride, the temperature and concentration dependences of their two- and two three-component mixtures (acetone–vinyl acetate–acetic acid and vinyl acetate–acetic acid–acetic anhydride) were measured.

The dependence of kinematic viscosity of pure liquid on temperature can be expressed in terms of the equation proposed by Linke[1]

$$v = A \exp\left(B/T\right). \tag{1}$$

Kinematic viscosities of binary mixtures are correlated best by the equation which was derived by McAllister[2] on the basis of Eyring's theory of absolute reaction rates:

$$\ln v_m = x_i^3 \ln v_i + 3x_i^2 x_j \ln v_{ij} + 3x_i x_j^2 \ln v_{ji} + x_j^3 \ln v_j - $$
$$- \ln\left(x_i + x_j M_j/M_i\right) + 3x_i^2 x_j \ln\left[(2 + M_j/M_i)/3\right] + $$
$$+ 3x_i x_j^2 \ln\left[(1 + 2M_j/M_i)/3\right] + x_j^3 \ln\left(M_j/M_i\right). \tag{2}$$

In a similar way, Chandramouli and Laddha[3] derived the equation for ternary mixtures

$$\ln v_m = x_i^3 \ln v_i + x_j^3 \ln v_j + x_k^3 \ln v_k + 3x_i^2 x_j \ln v_{ij} + 3x_i x_j^2 \ln v_{ji} + 3x_i^2 x_k \ln v_{ik} + $$
$$+ 3x_i x_k^2 \ln v_{ki} + 3x_j^2 x_k \ln v_{jk} + 3x_j x_k^2 \ln v_{kj} + 6x_i x_j x_k \ln v_{ijk} - $$

$$
\begin{aligned}
&- \ln\left(x_i M_i + x_j M_j + x_k M_k\right) + x_i^3 \ln M_i + x_j^3 \ln M_j + x_k^3 \ln M_k + \\
&+ 3x_i^2 x_j \ln\left[(2M_i + M_j)/3\right] + 3x_i^2 x_k \ln\left[(2M_i + M_k)/3\right] + \\
&+ 3x_j^2 x_i \ln\left[(2M_j + M_i)/3\right] + 3x_j^2 x_k \ln\left[(2M_j + M_k)/3\right] + \\
&+ 3x_k^2 x_i \ln\left[(2M_k + M_i)/3\right] + 3x_k^2 x_j \ln\left[(2M_k + M_j)/3\right] + \\
&+ 6x_i x_j x_k \ln\left[(M_i + M_j + M_x)/3\right].
\end{aligned}
\tag{3}
$$

In the equations given above, A, B are the pure-component constants which, in a certain range of temperatures, are independent of temperature T, x_i, x_j, x_k, v_i, v_j, v_k, M_i, M_j, M_k denote the mole fractions, kinematic viscosities, and molecular masses of pure substances, respectively. The viscosity coefficients v_{ij}, v_{ji}, v_{ik}, v_{ki}, v_{jk}, v_{kj}, and v_{ijk} do not depend on composition but only on temperature, and like the pure component constants A, B must be determined from experimental data on viscosities. The results of this evaluation are given in this work.

EXPERIMENTAL

The substances used for the measurements were purified and stabilized in advance by standard procedures described in the literature. Acetone, acetic acid, and acetic anhydride (all of A.R. purity) by the methods according to the literature[4,5], vinyl acetate and crotonaldehyde (Duslo, Šaľa) by the literature[6,7]. All the substances were rectified before the stabilization itself on a forty-plate packed column (in case of crotonaldehyde under vacuum) at a reflux ratio 60 : 1. The purity of substances obtained in this way was checked chromatographically.

The experimental determinations were carried out using the Ubbelohde viscosimeter, the temperature of the sample measured being determined with the accuracy of $\pm 0.025°\text{C}$. Kinematic viscosity was calculated from the relation

$$
v = 0.01\tau - 2.808/\tau,
\tag{4}
$$

where τ is the time of the passage of a liquid sample through a certain length of capillary. Each measurement was repeated 8—10 times, and then only average values were evaluated. The measurements of kinematic viscosities of pure substances served simultaneously to verify the justifiability of employing Eq. (4) for calculating kinematic viscosities from the data measured. This verification was carried out for 17 kinematic viscosities of acetone, vinyl acetate, acetic acid, and acetic anhydride at different temperatures. The data on kinematic viscosities calculated from the values of dynamic viscosities and densities published in the literature[8-24] were used for comparison. The mean value of absolute values of relative deviations of our viscosities and those calculated in this way is 0.52%, the maximum deviations are −1.35% and +1.04%. The dependence of the crotonaldehyde viscosity on temperature was not found in literature.

All the data on kinematic viscosities v, viscosity coefficients v_{ij}, v_{ji}, v_{ik}, v_{ki}, v_{jk}, v_{kj}, and v_{ijk} are given in units mm^2/s.

RESULTS

The experimentally found values of kinematic viscosities of pure substances were evaluated in terms of Eq. (1), the best values of the constants A and B having been

sought. The method of least squares was used, the computation being performed in two alternatives: by using the linear (L) and nonlinear (N) regression analysis. For the nonlinear regression analysis, the procedure by Box[25] was chosen. In Table I we give the calculated values of constants A, B, along with the temperature interval in which the measurements were carried out, the number of experimental points (n), with the results of statistical evaluation, and with the designation of the way of regression analysis which has led to lower values of deviations.

The mean relative deviation $\bar{\varepsilon}$ was calculated as

$$\bar{\varepsilon} = \sum_{1}^{n}(|\varepsilon_1|)/n \tag{5}$$

and the root mean square deviation σ as

$$\sigma = \left(\sum_{1}^{n}\varepsilon_1^2/(n-2)\right)^{1/2}, \tag{6}$$

where the relative deviation ε_1 equals

$$\varepsilon_1 = 100(v_{1,exp} - v_{1,calc})/v_{1,exp}. \tag{7}$$

The experimental values of kinematic viscosities of binary mixtures were correlated by Eq. (2). The coefficients v_{ij}, v_{ji} were calculated by the same alternative procedures as in the foregoing case. They are given in Table II along with the results of statistical evaluation. The viscosities of pure components at temperatures above their boiling points, needed for inserting into Eq. (2), were extrapolated in terms of Eq. (1).

TABLE I

Coefficients of Eq. (1)

Substance	t, C	n	A	B	$\bar{\varepsilon}$, %	σ, %	ε_{max}	Method
Acetone	10—50	5	0·04211	665·1	0·273	0·364	0·373	L
Vinyl acetate	20—68	7	0·02243	877·4	0·088	0·125	0·180	L, N
Crotonaldehyde	20—90	14	0·03469	825·0	0·262	0·353	0·660	L, N
Acetic acid	20—85	8	0·01725	1 239·2	1·20	1·69	2·87	L
Acetic anhydride	20—85	8	0·02341	1 045·0	0·645	0·910	1·18	L

TABLE II

Coefficients of Eq. (2) for binary systems

t, °C	n	v_{ij}	v_{ji}	$\bar{\varepsilon}$, %	σ, %	ε_{max}, %	Method
			Acetone(i)–vinyl acetate(j)				
20	16	0·4216	0·4402	0·139	0·184	0·331	L, N
30	16	0·3845	0·4005	0·216	0·284	0·447	N
40	16	0·3531	0·3697	0·204	0·329	0·802	N
50	16	0·3323	0·3417	0·158	0·238	0·587	N
			Acetone(i)–crotonaldehyde(j)				
20	11	0·4594	0·5453	0·181	0·280	0·534	L, N
30	11	0·4222	0·4952	0·226	0·326	0·654	L
40	11	0·3911	0·4592	0·275	0·392	0·668	L
50	11	0·3711	0·4172	0·242	0·367	0·639	L
60	9	0·3462	0·3836	0·228	0·320	0·416	L
68	6	0·3311	0·3599	0·136	0·232	0·324	L
			Acetone(i)–acetic acid(j)				
20	12	0·6038	0·8656	0·356	0·538	1·21	L
30	12	0·5430	0·7781	0·355	0·455	0·705	L
40	12	0·5019	0·6860	0·310	0·449	0·683	L
50	12	0·4544	0·6279	0·461	0·609	0·808	L
60	8	0·4431	0·5545	0·224	0·338	0·539	L
68	7	0·4381	0·5087	0·460	0·713	1·07	L
			Acetone(i)–acetic anhydride(j)				
20	11	0·5464	0·6979	0·518	0·819	1·78	L
30	11	0·4872	0·6319	0·516	0·660	0·988	L
40	11	0·4459	0·5706	0·376	0·588	1·18	L
50	11	0·4152	0·5199	0·506	0·676	1·02	L
60	9	0·3937	0·4715	0·366	0·648	1·31	N
68	8	0·3634	0·4409	0·148	0·256	0·494	N
80	5	0·3475	0·3937	0·039	0·068	0·091	L, N
			Vinyl acetate(i)–crotonaldehyde(j)				
20	11	0·4935	0·5326	0·130	0·204	0·475	L
30	11	0·4446	0·4851	0·329	0·477	0·904	L
40	11	0·4092	0·4433	0·290	0·440	0·845	L
50	11	0·3685	0·4134	0·384	0·555	1·08	L
60	11	0·3437	0·3793	0·365	0·544	0·985	L
68	11	0·3250	0·3558	0·279	0·384	0·590	L, N
80	8	0·3056	0·3311	0·299	0·456	0·710	L, N

TABLE II

(*Continued*)

t, °C	n	ν_{ij}	ν_{ji}	$\bar{\varepsilon}$, %	σ, %	ε_{max}, %	Method
			Vinyl acetate(i)–acetic acid(j)				
20	11	0·5428	0·6136	0·551	0·838	1·47	L
30	11	0·4886	0·5444	0·487	0·706	1·27	L
40	11	0·4408	0·5000	0·439	0·624	0·960	N
50	11	0·4081	0·4443	0·283	0·514	0·996	N
60	11	0·3750	0·4068	0·631	0·917	1·46	N
68	11	0·3404	0·3990	0·390	0·632	1·28	L
80	10	0·3292	0·3451	0·406	0·607	0·942	L
			Vinyl acetate(i)–acetic anhydride(j)				
20	11	0·5696	0·6895	0·329	0·508	0·947	L
30	11	0·5077	0·6184	0·355	0·506	1·09	L
40	11	0·4618	0·5529	0·253	0·387	0·741	L
50	11	0·4219	0·5029	0·138	0·205	0·411	L
60	11	0·3901	0·4611	0·117	0·188	0·410	L
68	11	0·3684	0·4277	0·275	0·450	0·934	L
80	9	0·3332	0·3909	0·407	0·630	1·12	N
			Crotonaldehyde(i)–acetic acid(j)				
20	11	0·7910	0·9414	0·202	0·305	0·615	L, N
30	11	0·7056	0·8401	0·152	0·242	0·476	L
40	11	0·6397	0·7645	0·230	0·352	0·816	N
50	11	0·5769	0·6681	0·250	0·367	0·739	N
60	11	0·5269	0·6132	0·200	0·312	0·617	L, N
68	11	0·4967	0·5722	0·290	0·436	0·734	L
80	11	0·4522	0·5078	0·284	0·449	1·03	L
			Crotonaldehyde(i)–acetic anhydride(j)				
20	13	0·6764	0·7654	0·106	0·178	0·310	N
30	13	0·6097	0·6708	0·229	0·332	0·763	L
40	13	0·5518	0·6106	0·241	0·325	0·574	L, N
50	13	0·5070	0·5476	0·253	0·337	0·552	L
60	13	0·4618	0·5162	0·339	0·461	0·860	L
68	13	0·4294	0·4709	0·230	0·333	0·804	N
80	13	0·3965	0·4263	0·140	0·195	0·422	L, N

TABLE II
(*Continued*)

t, °C	n	v_{ij}	v_{ji}	$\bar{\varepsilon}$, %	σ, %	ε_{max}, %	Method
			Acetic acid(i)–acetic anhydride(j)				
20	11	1·0227	0·9236	0·247	0·379	0·765	L
30	11	0·8945	0·8100	0·239	0·379	0·825	N
40	11	0·8002	0·7093	0·214	0·328	0·555	L
50	11	0·7144	0·6371	0·294	0·451	0·947	N
60	11	0·6361	0·5790	0·204	0·303	0·589	L
68	11	0·5837	0·5350	0·165	0·230	0·335	L
80	11	0·5328	0·4722	0·063	0·011	0·164	L, N

The temperature dependence of the coefficients v_{ij} and v_{ji} obtained from experimental data for individual binary systems was expressed in terms of Eq. (8)

$$v_{ij(ji)} = a_{ij(ji)} \exp\left(b_{ij(ji)}/T\right). \tag{8}$$

The values of the coefficients $a_{ij(ji)}$ and $b_{ij(ji)}$ calculated only by the linear procedure along with the results of statistical evaluation are in Table III.

$\bar{\varepsilon}$ and σ have been calculated in terms of Eqs (5) and (6), ε_1 being here equal

$$\varepsilon_1 = 100(K_{1,exp} - K_{1,calc})/K_{1,exp}, \tag{9}$$

where K is an arbitrary coefficient of Eq. (8).

The experimental values of kinematic viscosities for the ternary mixtures acetone––vinyl acetate–acetic acid and vinyl acetate–acetic acid–acetic anhydride have been evaluated by means of Eq. (3). The values of ternary coefficients v_{ijk} together with the statistical evaluation are given in Table IV. When calculating the ternary coefficients v_{ijk} at temperatures 35 and 45°C, the values of viscosities of pure substances and the values of binary coefficients calculated from Eqs (1) and (8) have been used.

The calculated ternary coefficients v_{ijk} have been correlated as a function of temperature in terms of Eq. (10)

$$v_{ijk} = a_{ijk} \exp\left(b_{ijk}/T\right). \tag{10}$$

The values of coefficients a_{ijk} and b_{ijk} for both the ternary systems (calculated only by a linear procedure) along with the statistical evaluation are given in Table V.

TABLE III
Values of coefficients of Eq. (8)

| Component | | a_{ij} | b_{ij} | $\bar\varepsilon, \%$ | $\varepsilon_{max}, \%$ | a_{ji} | b_{ji} | $\bar\varepsilon, \%$ | $\varepsilon_{max}, \%$ |
i	j								
Acetone–vinyl acetate		0.03157	758.6	0.520	0.79	0.02907	796.1	0.160	0.32
Acetone–crotonaldehyde		0.04569	675.1	0.428	0.87	0.02860	865.5	0.452	1.22
Acetone–acetic acid		0.05560	692.2	1.96	4.22	0.02006	1 106.7	0.870	1.86
Acetone–acetic anhydride		0.03774	777.9	1.33	1.90	0.02454	984.0	0.583	1.12
Vinyl acetate–crotonaldehyde		0.02767	842.1	0.877	1.73	0.03185	825.7	0.338	0.82
Vinyl acetate–acetic acid		0.02553	894.3	1.11	3.17	0.02224	971.6	1.07	2.39
Vinyl acetate–acetic anhydride		0.02547	908.7	0.477	0.79	0.02288	995.1	1.306	2.02
Crotonaldehyde–acetic acid		0.02913	966.7	0.389	0.65	0.02502	1 065.3	0.727	1.73
Crotonaldehyde–acetic anhydride		0.02830	930.5	0.320	0.84	0.02610	987.5	0.856	2.01
Acetic acid–acetic anhydride		0.02089	1 140.1	0.616	1.18	0.01860	1 143.5	0.547	1.06

DISCUSSION

All 10 binary systems exhibit a relatively simple viscosity behaviour: The viscosity curves show either negative deviations from the quasiideal (linear) course or are linear. In this way one may explain relatively good fit of the measured and calculated viscosity data when Eq.(2) describes 89·2% systems from the total number of 65 isothermal systems studied with lower mean deviation than 0·5% and 64·5% systems with lower mean deviation than 0·3%. The majority of isothermal systems have lower deviations between the measured and calculated values of viscosities when the coefficients of Eq. (2) have been calculated by the linear method of least squares than when using the nonlinear procedure. The differences in relative deviations,

TABLE IV

Values of the coefficient v_{ijk} in Eq. (3) for two ternary systems

t	n	v_{ijk}	$\bar{e}$, %	σ, %	ε_{max}, %	Method
		Acetone(i)–vinyl acetate(j)–acetic acid(k)				
30	27	0·6346	0·499	0·673	1·28	N
35	27	0·6051	0·471	0·591	1·24	N
40	27	0·5813	0·654	0·809	1·54	L
45	27	0·5569	0·546	0·690	1·66	N
50	27	0·5374	0·616	0·700	1·47	N
		Vinyl acetate(i)–acetic acid(j)–acetic anhydride(k)				
30	36	0·7168	0·489	0·599	1·35	N
35	36	0·6595	0·342	0·434	0·976	L
40	36	0·6221	0·559	0·677	1·38	L
45	36	0·5958	0·496	0·599	1·49	N
50	36	0·5788	0·432	0·555	1·41	L

TABLE V

Values of coefficients of Eq. (10)

Component			a_{ijk}	b_{ijk}	$\bar{e}$, %	ε_{max}, %
i	j	k				
Acetone–vinyl acetate–acetic acid			0·04312	814·6	0·16	0·20
Vinyl acetate–acetic acid–acetic anhydride			0·02277	1 040·6	1·29	1·67

however, have been very small, and differ mostly in the third and seldom in the second decimal place. These findings are in harmony with the conclusions by Musulin[26] who reports that the nonlinear method of least squares gives better results when the deviations between the measured and calculated values are larger, which may occur *e.g.* in the case when the measured system does not satisfy assumptions under which the functional relation was derived, and, on the other hand, with small values of deviations, the differences between the results obtained by the linear and nonlinear methods are very small, next to negligible.

REFERENCES

1. Linke R.: Z. Phys. Chem. (Wiesbaden) *187*, 227 (1940).
2. McAllister R. A.: AIChE J. *6*, 427 (1960).
3. Chandramouli V. V., Laddha G. S.: Indian J. Technol. *1*, 199 (1963).
4. Weissberger A., Proskauer E. S., Riddick J. A., Toops E. E.: *Organic Solvents, Physical Properties and Methods of Purification*, p. 379. J. Wiley, New York 1955.
5. Ibid, p. 390.
6. Ibid, p. 378.
7. Janda J.: *Vinylové monoméry*, p. 167, 182. SVTL, Bratislava 1958.
8. Miller C. C.: Proc. Roy. Soc. Ser. A *106*, 724 (1924).
9. Gallant R. W.: Hydrocarbon Process. *47*, 6, 139 (1968).
10. Timmermans M. J., Hennant-Roland M.: J. Chim. Phys. Physicochim. Biol. *27*, 401 (1930).
11. Bingham E. C., White G. F., Caldwell J. L.: Z. Phys. Chem. (Wiesbaden) *83*, 641 (1913).
12. Sastri S. R. S., Rao M. V. R.: Chem. Age India *21*, 7, 675 (1970).
13. Costello J. M., Bowden S. T.: Rec. Trav. Chim. Pay-Bas *77*, 803 (1958).
14. Ritter H. L., Simons J. H.: J. Amer. Chem. Soc. *67*, 757 (1945).
15. Price T. W.: J. Chem. Soc. *115*, 1116 (1919).
16. Gallant R. W.: *Hydrocarbon Process*. 47, 8, 127 (1968).
17. Kaye G. W. C., Laby T. H.: *Tables of Physical and Chemical Constants*, p. 37. Longmans, London 1968.
18. Hála E., Reiser A.: *Fysikální chemie* 1, p. 160. Academia, Prague 1971.
19. Union Carbide Corp., *Chemicals and Plastics, Vinyl Acetate Monomer*, No 108-05-4. Product Information, New York 1967.
20. White D. O., Cuthbertson A. C.: Can. J. Res. B *15*, 7 (1937).
21. Green C., Marsden J., Cuthbertson A. C.: Can. J. Res. B *9*, 396 (1933).
22. Rudoi-Kolker V. M., Grigoryan Kh. A.: Zh. Prikl. Khim. *37*, 7, 1622 (1964).
23. Wright F. J.: J. Chem. Eng. Data *6*, 454 (1961).
24. Lewis D. T.: J. Chem. Soc. *1940*, 32.
25. Box G. E. P.: Bull. Inst. Int. Statistique *36*, 215 (1958).
26. Musulin B.: J. Chem. Educ. *50*, 1, 79 (1973).

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