Viscosities of Binary Mixtures of *n*-Butyl Acetate–Methyl Ethyl Ketone or Isoamyl Alcohol at 35° C

RAMASWAMI THAYUMANASUNDARAM and PALURI BHIMESWARA RAO[1]
Department of Chemical Engineering, Indian Institute of Technology, Madras, India

Measurements of viscosity as a function of composition at 35° C for the binary mixtures of *n*-butyl acetate–methyl ethyl ketone or isoamyl alcohol are reported. The experimental values for the viscosity agree with those calculated from the equations suggested by McAllister, Katti, and Chaudhri, and from the equation using the Redlich and Kister equation for the Gibbs excess free energy, within about 8% error.

In the previous investigation (*5*), the viscosities of the binary mixtures of 1-butanol–methyl ethyl ketone, 1-butanol–isoamyl alcohol, and isoamyl alcohol–methyl ethyl ketone were studied at 35° C as functions of composition. In a continuation of this work, the authors determined the viscosities of the binary mixtures of *n*-butyl acetate–methyl ethyl ketone or isoamyl alcohol as functions of composition at 35° C to study the validity of the equations proposed by the previous workers (*2*-*4*) for these systems.

EXPERIMENTAL

Laboratory reagent grade *n*-butyl acetate, isoamyl alcohol, and methyl ethyl ketone from British Drug House Co., India, were distilled twice over sodium at atmospheric pressure in a laboratory pyrex glass Vigreux fractionating column having an effective length of 36 cm. The fractions were collected within about 0.5° C of their boiling points. The observed boiling points were corrected to 760 mm pressure using Craft's rule (*1*) to get the experimental normal boiling points.

Table I. Physical Properties of Materials (*6*)

	Normal bp, ° C		Density at 35° C, g/ml		Refractive index at 35° C		Viscosity at 35° C, cP[a]	
	Exptl	Lit	Exptl	Lit	Exptl	Lit	Exptl	Lit
Isoamyl alcohol	132	132	0.8001	0.7990[b]	1.4011	1.4011[b]	2.8153	2.3550[b]
Methyl ethyl ketone	79.5	79.6	0.7891	0.7890[b]	1.3711	1.3713[b]	0.3657	0.3460[b]
n-Butyl acetate	126.1	126.5	0.8665	0.8668[b]	1.3874	1.3873[b]	0.6042	0.6084[b]

[a] cP = centipoises. [b] Obtained by using temperature correction.

Table II. Viscosities at 35° C

		$\nu \times 10^2$						
Run	Mole fraction of *n*-butyl acetate	Exptl	Calcd (*2*)	Deviation, %	Calcd (*3*)	Deviation, %	Calcd (*4*)	Deviation, %
					n-Butyl acetate (*A*)–methyl ethyl ketone (*B*)			
1	0.9004	0.669	0.667	+0.3	0.669	+0.00	0.667	+0.3
2	0.7997	0.642	0.637	+0.7	0.641	+0.3	0.641	+0.2
3	0.7000	0.606	0.609	−0.6	0.618	−1.0	0.615	−1.6
4	0.5997	0.584	0.583	+0.1	. . .	. . .	0.608	−4.1
5	0.4997	0.569	0.559[a]	+1.5	0.558	+2.0	0.562	+1.2
6	0.4000	0.533	0.537	−0.6	. . .	. . .	0.535	−0.3
7	0.3000	0.520	0.516	+0.6	0.511	+1.7	0.509	+2.1
8	0.2002	0.484	0.497	−2.6	0.492	−1.7	0.486	+4.1
9	0.0999	0.468	0.479	−2.4	0.487	−4.1	0.470	+4.3
					n-Butyl acetate (*A*)–isoamyl alcohol (*B*)			
1	0.0998	2.631	2.643	−0.5	2.572	+2.2	2.668	−1.4
2	0.2003	2.091	2.054	+1.8	2.007	+4.0	2.132	−1.9
3	0.3001	1.715	1.660	+3.3	1.654	+3.6	1.782	−3.9
4	0.3999	1.418	1.392	+1.8	. . .	. . .	1.521	−7.3
5	0.4998	1.221	1.212[a]	+0.6	1.257	−2.9	1.251	−2.4
6	0.5999	1.019	1.095	−7.4	. . .	. . .	1.012	+0.7
7	0.6997	0.917	1.026	−11.9	1.025	−11.7	0.834	+9.1
8	0.8002	0.811	1.000	−23.3	0.922	−13.7	0.742	+8.6
9	0.9002	0.734	1.011	−37.7	0.814	−10.9	0.775	−5.6

[a] Smoothed experimental data at $X = 0.5$.

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[1] To whom correspondence should be addressed.

Table III. Physical Constants Used in Calculation of ν (2–4)

Equation no.	*n*-Butyl acetate (*A*)–methyl ethyl ketone (*B*)	*n*-Butyl acetate (*A*)–isoamyl alcohol (*B*)
1	W_{visc} = 11.8 cal. per gram mole	W_{visc} = –487.4 cal per gram mole
2	$\nu_{AB} = 0.6183$ $\nu_{BA} = 0.5089$	$\nu_{AB} = 1.245$ $\nu_{BA} = 1.100$
3	$B = 0.0282$; $C = -0.0600$; $D = -0.0860$	$B = -0.7420$; $C = -0.7605$; $D = -1.1392$

Table IV. Error Analysis

System	Equation	Standard error[a]	Standard % error[b]
n-Butyl acetate-methyl ethyl ketone	1	±0.007	±1.3
	2	±0.010	±2.0
	3	±0.010	±2.6
n-Butyl acetate-isoamyl alcohol	1	±0.123	±15.6
	2	±0.074	±8.3
	3	±0.060	±5.5

[a] Standard error = $\left[\dfrac{\sum(\nu_{\text{exptl}} - \nu_{\text{calcd}})^2}{\text{no. of observations}}\right]^{1/2}$.

[b] Standard %, error = $\left[\dfrac{\sum\{[(\nu_{\text{exptl}} - \nu_{\text{calcd}})/\nu_{\text{exptl}}]100\}^2}{(\text{no. of observations})}\right]^{1/2}$.

The refractive index was measured for sodium light with a Carl Zeiss Abbe Refractometer. The fourth decimal place could be readily estimated by visual observation. The adjustment of the refractometer was tested with double distilled water. The refractive index of this water sample agreed with the literature value within about ±0.0002. The density was determined by using a 10-ml pycnometer. The physical properties of the three purified samples were compared with the literature values in Table I.

The Ubbelohde viscometer used in this investigation was calibrated using double distilled water, and the viscosities were determined using a stopwatch with an accuracy of 0.1 sec. The measurements of the viscosity, refractive index, and density were done at 35° ± 0.01°C using an ultra-thermostat.

RESULTS AND DISCUSSION

The experimental observed values of viscosity for the different compositions of the two binary systems given in column 2 of Table II were the average values of at least two determinations. The replicate determinations differed by not more than ±0.001 cP. The flow times were sufficiently great to make the kinetic energy correction unnecessary.

In column 3 of Table II, the viscosity values calculated from the equation suggested by Katti and Chaudhri (*2*) (Equation 1) were given. The raw experimental data were smoothed over the total concentration range and the term W_{visc}/RT was calculated from the smoothed viscosity value at $x = 0.5$.

$$\log \nu M = X_A \log \nu_A M_A + X_B \log \nu_B M_B + X_A X_B (W_{\text{visc}}/RT) \quad (1)$$

The viscosity values calculated using McAllister equation (*3*) (Equation 2) were given in column 5 of Table II. The terms ν_{AB} and ν_{BA} in Equation 2 were calculated by using experimental viscosity values for the runs 4 and 6:

$$\log \nu = X_A^3 \log \nu_A + 3\,X_A^2 X_B \log \nu_{AB} + 3\,X_A X_B^2 \log \nu_{BA} +$$
$$X_B^3 \log \nu_B + X_B^3 \log (M_B/M_A) + 3\,X_A^2 X_B \log [(2\,M_A + M_B)/3\,M_A] +$$
$$3\,X_A X_B^2 \log [(2\,M_B + M_A)/3\,M_A] - \log [(X_A M_A + X_B M_B)/M_A] \quad (2)$$

The viscosity values given in column 7 of Table II were calculated from Equations 3 and 4. The constants *B*, *C*, and *D* were all obtained simultaneously using all the raw data by the method of least squares:

$$\log \nu M = X_A \log \nu_A M_A + X_B \log \nu_B M_B + G^E_{AB}/RT \quad (3)$$

where G^E_{AB}/RT is given by Redlich and Kister (*4*) as

$$G^E_{AB}/RT = X_A X_B [B + C(X_A - X_B) + D(X_A - X_B)^2] \quad (4)$$

The constants *B*, *C*, *D*, ν_{AB}, ν_{BA}, and W_{visc} for these two systems at 35°C were given in Table III.

Table IV shows the error analysis for ν_{calcd} by using Equations 1–4 for both the systems. The viscosity values for the *n*-butyl acetate–isoamyl alcohol system calculated by Equation 1 have standard percent error of more than 15% because of the omission of the constants *C* and *D* in Equation 1, which are high compared to the same constants for the other system. Except for this large error, the experimental values agree with the calculated values within about 8%.

NOMENCLATURE

X = mole fraction
ν = kinematic viscosity, cm^2/sec
W_{visc} = interaction energy for the activation of flow, cal/g mol
ν_{AB}, ν_{BA} = McAllister binary constants
B, C, D = constants in the Redlich and Kister equation for Gibbs excess free energy
G^E = Gibbs excess free energy

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