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Viscosities of Aqueous *tert*-Butyl Alcohol Solutions

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The kinematic viscosities of dilute aqueous solutions of *tert*-butyl alcohol, for concentrations of 0–2.5 kmol/m^3 and temperatures from 303.15 to 333.15 K, have been measured. Use is made of the Eyring equation to correlate kinematic viscosities with the alcohol mole fraction and temperature. Enthalpies and entropies of activation for viscous flow, needed in the Eyring equation, are also provided. These correlate linearly with composition.

Introduction

tert-Butyl alcohol (TBA) is an important oxygenated octane enhancer that can be produced by direct hydration of isobutene on a solid catalyst (*1*), either in a slurry or in a trickle-bed reactor (*2*, *3*). Generally, interphase mass-transfer data, as well as intraparticle diffusion rate data, are necessary for reactor design. Both mass-transfer coefficients and effective diffusivities are strongly affected by changes in viscosity of the liquid phase. For the above process, this consists of an aqueous TBA solution with small amounts of dissolved butene. For the range of operating conditions in a trickle-bed process (*2*), TBA may accumulate to concentrations up to 3 kmol/m^3, whereas the butene is present in small amounts (0.01 kmol/m^3). Therefore, only the viscosity of the binary mixture, water–TBA, is of interest.

The most significant thermodynamic properties of the system TBA–water are well documented in the literature by Kenttämaa et al. (*4*). These include, among other properties, the viscosity as a function of composition. However this is given only at 298.15 K.

The purpose of this work was to measure and correlate the viscosities of water–TBA mixtures for the ranges of temperatures and compositions to be found in multiphase catalytic reactors.

Experimental Methods

Chemicals. Certified, analytical-grade TBA, from Panreac (Barcelona, Spain), with a stated minimum purity of 99% was used without further treatment, since the main impurity was water (0.3%). Deionized plus distilled water (conductivity 0.1 μS/cm), from laboratory facilities (MilliQ water purification system, Millipore Co.), was used.

Viscometry. Viscosity measurements were performed in an Ubbelohde, suspended-level, glass-capillary viscometer supplied by Schott-Geräte (Hofheim A.T.S., West Germany) in accordance with ASTM D 2515, Model 52510/I (0.4-mm-i.d. capillary). TBA solutions were prepared by weighing the alcohol ($\pm 10^{-4}$ g) into 1-L volumetric flasks, making up to the final volume with water. In order to remove suspended matter, the solutions were filtered over Millipore membranes (100 μm), prior to use. The viscometer was previously cleaned with filtered acetone and dried at room temperature by application of vacuum. The apparatus was vertically suspended in a large thermostated bath in which temperature was held constant to within ±0.1 K. About 15 mL of solution was used in each run. Prior to reading of the flow time, samples were equilibrated for 15 min. Flow times were measured with a precision of 0.2 s. Typical flow times ranged from 60 to 200 s (see Table I). At least six readings for each sample were made.

Table I. Experimental Viscosities of Aqueous TBA Mixtures

X_A	T,[a] K	t, s	$10^6\nu$, m^2/s	ρ,[b] kg/m^3	$10^3\eta$,[c] Pa s
0.0000	303	92.25	0.796	995.7	0.793
	313	77.00	0.651	992.2	0.646
	323	67.50	0.559	988.1	0.553
	333	57.10	0.456	983.2	0.449
0.0088	303	108.90	0.952	988.8	0.941
	313	90.17	0.776	985.3	0.765
	323	75.70	0.639	981.2	0.627
	333	63.00	0.515	977.2	0.503
0.0179	303	128.05	1.129	984.2	1.111
	313	103.83	0.904	980.5	0.887
	323	85.75	0.735	976.1	0.717
	333	70.00	0.584	971.8	0.567
0.0429	303	190.50	1.701	971.4	1.652
	313	145.90	1.293	966.1	1.250
	323	111.35	0.975	960.2	0.936
	333	90.10	0.776	954.3	0.740
0.0532	303	216.00	1.933	965.7	1.867
	313	171.33	1.526	959.6	1.465
	323	122.00	1.073	953.2	1.023
	333	97.85	0.849	946.9	0.804

[a] Actual temperatures were 303.15, 313.15, 323.15, and 333.15 K, with a precision of ±0.1 K. [b] Data from Kenttämaa et al. (*4*). [c] Calculated from measured kinematic viscosities and densities from Kenttämaa (*4*).

Viscometer Calibration. For the streamline flow of a Newtonian liquid at steady state, with no slip at the wall, the absolute viscosity is related to the flow rate by means of the Poiseuille equation. Allowance for conversion of some of the total pressure head into kinetic energy gives the following expression for the kinematic viscosity (*5*):

$$\nu = \frac{\eta}{\rho} = \frac{\pi r^4 \Delta P}{8\rho Q L} - \frac{mQ}{8\pi L} \tag{1}$$

Since flow rates are inversely proportional to flow times, eq 1 can be written in terms of t as

$$\nu = At - \frac{B}{t} \tag{2}$$

With ΔP written in terms of the total liquid height as

$$\Delta P = \rho g \Delta z \tag{3}$$

the final expressions for A and B become

$$A = \frac{\pi r^4 \Delta P}{8 V \rho L} = \frac{\pi r^4 g \Delta z}{8 V L} \tag{4}$$

$$B = \frac{mV}{8\pi L} \tag{5}$$

which depend only on the geometry of the viscometer, the flowing volume, and m, which is constant (*5*). In practice, A and B are best found from calibration runs (*5*).

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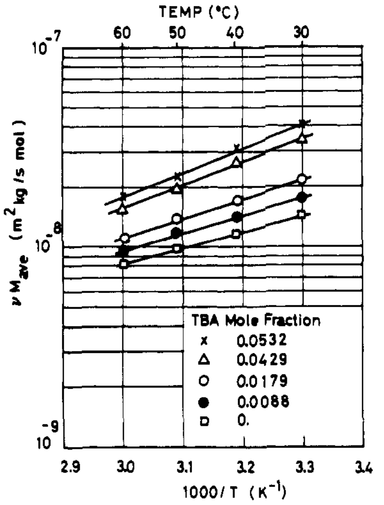

Figure 1. Temperature dependence of kinematic viscosities as a function of alcohol mole fraction.

Table II. Measured Enthalpies and Entropies of Activation for Viscous Flow (T = 303.15 – 333.15 K)

X_A	ΔH, J/mol	ΔS, J/(mol K)	X_A	ΔH, J/mol	ΔS, J/(mol K)
0.0000	15 260	20.57	0.0429	22 150	35.96
0.0088	17 070	24.77	0.0532	23 670	39.50
0.0179	18 340	27.32			

A and B were determined by measuring the flow times of pure water at four temperatures (303.15, 313.15, 323.15, and 333.15 K) at which kinematic viscosities are known (*6*). Linear regression analysis of a plot of νt against t^2 for pure water at the four temperatures provides estimates of $A = 9.022 \times 10^{-9}$ m^2/s^2 and $B = 3.351 \times 10^{-6}$ m^2, as slope and intercept of the plot, with a correlation coefficient of 0.9996. Knowledge of A and B allows determination of viscosities from the flow times for water–TBA mixtures using eq 2.

Results

The results are given in Table I for the ranges of temperature and TBA mole fraction of this study. Kinematic viscosities increase as alcohol concentration increases at constant temperature. Also, the increase in viscosity with TBA concentration is less at higher temperature than at lower temperature. In order to correlate the kinematic viscosity data with a single expression, the Eyring equation (*7*) is assumed to apply. This is

$$\nu = \left(\frac{hN}{M_{av}}\right) \exp\left(\frac{\Delta H}{RT} - \frac{\Delta S}{R}\right) \tag{6}$$

where

$$M_{av} = \sum_i X_i M_i \tag{7}$$

is the average molecular weight of the mixture. In eq 6, ΔH and ΔS respectively represent the enthalpy and entropy of activation for the viscous flow according to the theory of Eyring (*7*). The form of eq 6 suggests a method to evaluate these quantities. Thus, a semilog plot of νM_{av} against $1/T$, at constant composition, will provide ΔH from the slope and ΔS from the intercept.

Table III. Comparison of Predicted and Experimental Kinematic Viscosities (X_A = 0–0.053, T = 303.15–333.15 K)

X_A	T, K	ΔH,[a] J/mol	ΔS,[a] J/(mol K)	$10^6\nu$,[b] m^2/s	$10^6\nu$(exptl), m^2/s	error, %
0.0000	303	15 490	21.09	0.820	0.796	3.0
	313			0.673	0.651	3.4
	323			0.560	0.559	0.2
	333			0.471	0.456	3.2
0.0088	303	16 850	24.15	0.949	0.952	–0.2
	313			0.767	0.776	–1.2
	323			0.627	0.639	–1.7
	333			0.519	0.515	0.8
0.0179	303	18 260	27.31	1.105	1.129	–2.1
	313			0.877	0.904	–3.0
	323			0.705	0.735	–3.9
	333			0.757	0.584	–1.4
0.0429	303	22 140	36.00	1.686	1.701	–0.9
	313			1.273	1.293	–1.5
	323			0.978	0.975	0.4
	333			0.764	0.776	–1.5
0.0532	303	23 730	39.58	2.009	1.933	3.9
	313			1.486	1.526	–2.6
	323			1.121	1.073	4.4
	333			0.857	0.849	1.3

[a] Calculated from correlated ΔH, eq 8, and ΔS, eq 9. [b] Calculated from the Eyring equation (6).

The results are given in Figure 1. For each composition the enthalpy of activation is constant with temperature but increases with an increasing content of TBA. A similar trend is observed for the entropy of activation. The variations of ΔH and ΔS as a function of the mole fraction of TBA can be obtained by linear regression of the data points of Figure 1. The results are given in Table II. In turn, regression analysis of ΔH and ΔS as a function of the mole fraction, X_A, shows that they vary linearly with composition and can be expressed empirically with the following equations:

$$\Delta H = 15490 + 155.0 \times 10^3 X_A \tag{8}$$

$$\Delta S = 21.09 + 347.5 X_A \tag{9}$$

with correlation coefficients better than 0.9986.

Conclusions

The viscosities of aqueous TBA mixtures for alcohol concentrations between 0 and 2.5 kmol/m^3 and temperatures ranging from 303.15 to 333.15 K have been measured. Kinematic viscosities can be empirically predicted by taking the theoretical Eyring equation, eq 6, with an average molecular weight given by eq 7 and with enthalpies and entropies of activation for viscous flow calculated from eqs 8 and 9. Predicted and experimental kinematic viscosities are shown in Table III, for all the TBA mole fractions and temperatures of this study. The last column of Table III shows that the agreement is satisfactory.

Glossary

A	constant of eq 3, m^2/s^2
B	constant of eq 3, m^2
g	local acceleration of gravity, m/s^2
ΔH	enthalpy of activation for viscous flow, J/mol
h	Planck constant, $=6.6242 \times 10^{-34}$ J s
L	effective capillary length, m
m	empirical coefficient of eq 1
M_{av}	average molecular weight, kg/mol
N	Avogadro number, $=6.02283 \times 10^{23}$ mol^{-1}
ΔP	total pressure head, Pa
Q	liquid flow rate, m^3/s
r	capillary radius, m
R	perfect gas law constant, =8.314 J/(mol K)

ΔS	entropy of activation for viscous flow, J/(mol K)
t	flow time, s
T	temperature, K
V	flowing volume, m^3
X_A	alcohol mole fraction
Δz	total liquid height, m
η	absolute viscosity, Pa s
ν	kinematic viscosity, m^2/s
ρ	density, kg/m^3

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Vapor–Liquid Equilibria for Three Binary Systems Made of Methyl Ethyl Ketone with Acetone, Methyl Acetate, or *N*-Amyl Alcohol

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Vapor–liquid equilibria were measured for the three binary systems made of methyl ethyl ketone with acetone, methyl acetate, or *n*-amyl alcohol at 100 kPa of pressure by the dew-point–bubble-point temperature method. The dew-point–bubble-point temperature apparatus previously proposed by the authors was modified in the present study. Combining the experimental dew-point and bubble-point temperature curves, vapor–liquid equilibria were obtained without using any analytical instrument. The experimental vapor–liquid equilibrium data were correlated with the Wilson equation and further with the pseudocubic equation of state previously proposed by the authors.

Introduction

Vapor–liquid equilibrium relations are required for practical use, such as in the design and operation of distillation equipment. The dew-point–bubble-point temperature method (*1*, *2*) is one way for measuring vapor–liquid equilibria (VLE). The dew-point–bubble-point temperature apparatus previously proposed by the authors (*1*, *3*) was modified in the present study. The VLE were obtained for the three binary systems of methyl ethyl ketone with acetone, methyl acetate, or *n*-amyl alcohol at 100 kPa of pressure by the dew-point–bubble-point temperature method.

Experimental Section

The dew-point–bubble-point temperature apparatus previously proposed by the authors (*1*, *4*, *5*) was modified as shown in Figure 1. In the present modification, the liquid volume in the dew- and bubble-point stills was changed from 15 to 33 cm^3 to improve the accuracy of temperature measurements. The constructions of the feeder and condenser were further modified to prevent the contamination with water from the air. The experimental procedures are the same as in the previous papers (*1*, *3*). Temperature was measured by means of a Hewlett-Packard 2804A quartz thermometer with an accuracy of 0.01 K. The solutions of desired composition were prepared with an accuracy of 0.001 in mole fraction by use of an automatic balance.

Special-grade reagents were supplied by the Wako Pure Chemical Industries, Ltd. All reagents were purified by fractional distillation in a 30-plate Oldershaw column. The physical properties of the materials used are listed in Table I.

Results

The experimental dew- and bubble-point data are given in Tables II–IV and shown in Figures 2–4. After the experimental dew-point temperature curve and the bubble-point one were combined, smoothed VLE data were obtained, as given in Tables V–VII and shown in Figures 5–7. For the acetone + methyl ethyl ketone system, the present experimental data lie between the data of Othmer et al. (*6*) and Babich et al. (*7*), as shown in Figures 2 and 5. For the methyl acetate + methyl ethyl ketone system, substantial differences are seen when the liquid-phase results of this study are compared with the data of Babich et al. (*7*), as shown in Figure 3. For the methyl ethyl ketone + *n*-amyl alcohol system, large differences are observed between the present experimental data and the data of Miller et al. (*8*), as shown in Figures 4 and 7. On the vapor–liquid equilibrium measurements, Miller et al. (*8*) and Othmer et al. (*6*) determined the equilibrium composition with the refractive index measurements. Babich et al. (*7*) analyzed chromatographically. The present experimental data were obtained without using any analytical instrument. Figures 8–10 give the calculation results of the conventional area test on consistency. The VLE data reported in the present study seem most reliable when compared with the previous data (*6*–*8*), as shown in Figures 8–10.

The VLE data were correlated with the Wilson (*9*) equation. The vapor-phase correction was made with that given by Hayden and O'Connell (*10*–*12*), with use of the parameters shown in Table VIII. The association parameters of unlike molecules were evaluated as the arithmetic mean of the constituent pure components. Wilson parameters Λ_{12} and Λ_{21} were determined to minimize the sum of squares of the deviations in bubble-point temperatures, all points weighted equally.