

Viscosity and density of isomeric butanol/water mixtures as functions of composition and temperature

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Viscosity and density of 27 binary mixtures of *sec*-, *iso*-, and *tert*-butanol with water were measured at $273 \leq T/K \leq 353$ and the results summarized using polynomials. At fixed T the density depended strongly but monotonically on mole fraction. The excess volume V^E was large and negative. In $H_2O/tert$ -butanol as T increased V^E increased, while in H_2O/sec - or *iso*-butanol V^E decreased with increasing T . The excess viscosity was large and positive in all cases.

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Opérant à des températures allant de 273 à 353 K, on a mesuré les viscosités et les densités de 27 mélanges binaires d'eau avec les *sec*-, *iso*- et *tert*-butanols et on a résumé les résultats en utilisant des polynômes. A température constante, la densité dépend beaucoup de la fraction molaire, mais d'une façon monotone. La valeur du volume en excès V^E est importante et négative. Dans le mélange $H_2O/tert$ -butanol, la valeur de V^E augmente avec une augmentation de la température; par ailleurs, dans les mélanges H_2O/sec - ou *iso*-butanol, les valeurs de V^E diminuent avec une augmentation de la température. Dans tous les cas, la valeur de la viscosité en excès est importante et positive.

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Introduction

Studies of the reactivity of solvated electrons in hydroxylic solvents utilize values of the dynamic viscosity η in examining diffusion behavior (1–3). Values of η are sometimes not available and must be measured (3). During studies in mixtures of butanols and water (4) viscosity and density values were measured for 27 binary mixtures of water with *sec*-, *iso*-, or *tert*-butanol. The results are reported here.

Experimental

A. Materials

The butanols were obtained from BDH Chemicals: *sec*- (AnalaR, >99 mol%), *iso*- (OmniSolv, >99.0 mol%), and *tert*- (BDH Assured). They were further purified by (a) drying for 3 weeks on Davison 3A Molecular Sieves; (b) treated for one day at 323 K under argon (Liquid Carbonic Canada Ultra High Purity, >99.999 mol%) with sodium borohydride (~ 1 g/L); (c) fractionally distilled from the borohydride under argon through an 80 cm long by 2.3 cm diameter glass column packed with 3 mm glass helices, discarding the first 15% and last 35%; and (d) holding the collected 50% in an argon-pressured syphon system until use. The residual water content was determined by Karl Fischer titration to be 0.05 mol% in *sec*- and *iso*-butanol and 0.03 mol% in *tert*-butanol.

n-Butanol (Aldrich Gold Label, >99 mol%) was bubbled with Linde UHP argon and had 0.05 mol% water by Karl Fischer titration.

Ordinary distilled water was further purified in a SYBRON/Barnstead NANOpure II system.

Aldrich HPLC *n*-heptane (99.9 mol%) and Phillips Petroleum Research Grade *n*-pentane (99.93 mol%), *n*-hexane (99.99 mol%), methylcyclohexane (99.86 mol%) and *n*-octane (99.88 mol%) were (a) stirred with concentrated sulphuric acid for 1 day to remove olefins; (b) decanted and swirled for 10 min with Davison 5A Molecular Sieves; and (c) bubbled with Linde UHP argon.

B. Viscosity measurements

1. Calibration with water

The kinematic viscosity ν (m^2/s) was calculated from the efflux time t measured in Ubbelohde suspended level viscometers O_c (Schott Geräte #24501-03) and I (Schott Geräte #24501-01). An optical meniscus detection system determined t in units of 0.01 s with a precision of $\pm 0.009\%$ (5).

Viscometer O_c was calibrated by measuring t for water at $283.00 \leq T/K \leq 342.42$ and comparison with literature ν values using

$$[1] \quad \nu = At - B/t$$

where A and B are the viscometer constants. Each t was the average of ~ 6 determinations. Values of ν were obtained from

$$[2] \quad \nu = \eta/\rho$$

where the dynamic viscosities η ($kg/m\ s = Pa\ s$) were taken from a critical review (6), and ρ were from ref. 7a. Values of ν (m^2/s) calculated using $A = 2.8550 \times 10^{-9} m^2/s^2$ and $B = 2.2823 \times 10^{-6} m^2$ agreed with those in ref. 6 within an average deviation of 0.08%. Equation [1] is the usual calibration relation in the literature. However, the manufacturer's table of Hagenbach corrections to t (8) showed that it used

$$[3] \quad \nu = Kt - K_E/t^2$$

where K and K_E are the constants instead of A and B . Equation [3] was also used in another work (9). Fitting our t values for water to literature values of ν (m^2/s) yielded $K = 2.8458 \times 10^{-9} m^2/s^2$ and $K_E = 3.4223 \times 10^{-4} m^2\ s$; however, the average deviation between ν calculated from eq. [3] and the literature values increased to 0.10%. Hence we calculated ν from measured t using eq. [1].

2. Calibration with organic liquids

To calibrate viscometer I water could not be used, because its ν values have too small a range. Organic liquids were used. Although suspended level viscometers were designed to minimize the surface tension effect (10), ref. 11 suggested that calibrating with water, which at 293 K has a surface tension $\sigma = 73 \times 10^{-3} N/m$ (7b), would give calibrating constants 1.2% lower than if hydrocarbons or alcohols were used ($\sigma \sim 20$ to $30 \times 10^{-3} N/m$ (7b)). Such an effect was absent in ref. 9 where constants obtained by water calibration gave viscosities of toluene ($\sigma = 29 \times 10^{-3} N/m$ at 293 K (7b)) at $298 \leq T/K \leq 368$ agreeing within an average deviation of 0.15% of other values in the literature.

A surface tension effect would affect studies in alcohol-water mixtures as σ changes with composition (7b). The possibility of a surface tension effect in the viscometers was investigated by determining flow times t (each being the average of at least three measurements) of *n*-heptane, *n*-octane, and *n*-butanol in the water-calibrated viscometer O_c . Densities ρ used to calculate the present η are the average of values cited in the viscosity literature sources (12–14). The η values (Table 1) are in general agreement with the rather scattered earlier works and do not support consideration of a surface tension effect in the present work.

At the same time that the organic solvent measurements were done in viscometer O_c , viscometer I was filled with that solvent and stabilized in the same bath. To calibrate viscometer I, values were correlated by eq. [1]; the resulting $A = 1.0303 \times 10^{-8} m^2/s^2$ and $B = 2.3128 \times$

TABLE 1. Comparison of viscosity values

Liquid	T K	ν^a $10^{-6} \text{ m}^2/\text{s}$	ρ kg/m^3	η^b			
				This work	Ref. 7c	Ref. 12	Other
<i>n</i> -C ₇ H ₁₆	298.17	0.569	683.8 ^c	0.389	0.386	0.392	0.396 ^d
<i>n</i> -C ₈ H ₁₈	298.24	0.726	698.4 ^c	0.507	0.511	0.514	0.514 ^d
<i>n</i> -BuOH	307.84	2.538	798.5 ^e	2.027	2.034	2.026	1.993 ^f
	318.23	2.005	790.7 ^e	1.585	1.579	1.580	1.549 ^f

^aMeasured in viscometer 0₂ calibrated with water at $283.15 \leq T/K \leq 342.42$, $10^{-4} \text{ m}^2/\text{s} = \text{Stoke}$.

^bDynamic viscosity in $10^{-3} \text{ Pa s} = 10^{-2} \text{ P}$, see eq. [2].

^cAverage of refs. 12 and 13.

^dReference 13.

^eAverage of refs. 12 and 14.

^fReference 14.

TABLE 2. Comparison of densities at 298.15 K

Liquid	ρ (kg/m^3)			Δ (%) ^a
	This work	Ref. 12	Other	
<i>n</i> -C ₅ H ₁₂	626.8	626.2	626.3 ^b	0.09
<i>n</i> -C ₆ H ₁₄	658.7	659.4	—	-0.11
<i>c</i> -C ₆ H ₁₁ -CH ₃	769.2	—	769.4 ^c	-0.03
<i>n</i> -BuOH	809.5	809.6	809.4 ^d	0.00

^aAverage of percent differences from eq. [4].

^bReference 13.

^cReference 7d.

^dReference 14.

10^{-6} m^2 gave calculated ν values that agree with measured values, with an average deviation of 0.06%.

C. Density measurements

The liquid densities were determined from volume changes of a known mass of sample (15). Six Pyrex dilatometers, each consisting of two 1.000 mL pipettes sealed to a 10, 20, or 25 cm³ bulb, were used. The two pipettes connected in parallel made the cell easier to clean and fill. The samples were sealed in the dilatometer using ground-glass-jointed caps and springs. The mass of sample was the difference between the filled and unfilled dilatometer, weighed at $294 \pm 1 \text{ K}$ on a Stanton Instruments Ltd. (model C.L.I.) analytical balance. Sample masses of ~ 9 to $\sim 20 \text{ g}$ were measured to 0.1 mg with a precision of $\pm 0.1 \text{ mg}$ as determined by repeated weighings of a given mass. The pipette scales were readable to 0.001 mL with a precision of $\pm 0.001 \text{ mL}$. Each dilatometer was calibrated with water with the meniscus at positions covering the entire length of the pipette portion, and at $274.16 \leq T/K \leq 347.93$.

To estimate the reliability of the measurements, densities were measured in four liquids at 293.15 K and compared with values in the literature (Table 2). The percent deviation Δ

$$[4] \quad \Delta = 100 \left(1 - \frac{\text{lit.}}{\text{present}} \right)$$

varied from 0.09% to -0.11%. The reliability of the present densities is indicated by the average percent deviation,

$$[5] \quad \Delta_{\text{av}} = \frac{100}{n} \sum_i |\Delta_i|$$

(n is the number of samples and subscript i denotes the i th sample) which for the liquids in Table 2 was 0.06%.

D. Temperature control

The viscometer or dilatometer was mounted in 4 L bath of light paraffin oil (Fisher Scientific) or of water. The bath was stirred using a

propellor that was belt-driven by a Bodine Electric Company induction motor (model NSI-12) at about 1000 rpm. The temperature of the bath was regulated using a platinum resistance detector (Omega Engineering Inc. model TFD) in conjunction with a General Resistance Instruments temperature detector simulator (model RTD-100) in a Wheatstone bridge configuration with a Princeton Applied Research precision lock-in amplifier (model HR-8) as null detector. The lock-in amplifier in turn drove a power amplifier that controlled the heating rate of a Cenco 250 W knife heater. To get more rapid change in temperature, a 1000 W heater plugged into a standard Electrical Products voltage adjuster was used to raise the bath temperature towards the desired value, and then the lock-in amplifier controlled knife heater continued the approach toward constant temperature. At $273 \leq T/K \leq 300$ a Tecumseh (model AE 1343 AA) refrigeration unit pumped Freon-12 through a 5 cm \times 10 cm expansion chamber outfitted with aluminum heat dissipation fins which was immersed in the bath, and supplied an $\sim 45 \text{ W}$ heat loss to the bath; the knife heater was used to balance this cooling and determined the final temperature.

The stability of the bath temperature was measured, using a second Omega FTD platinum resistance detector, to be $\pm 0.002 \text{ K}$ for $> 2 \text{ h}$. The bath temperature during viscosity or density measurements was recorded to 0.01 K with a Fluke 2189A platinum resistance thermometry system. The system consisted of a factory-matched Fluke 2180A digital thermometer and a Fluke Y2039 resistance temperature probe. Prior to use the system was adjusted at the ice point to 273.15 K; the accuracy at the ice point was $\pm 0.01 \text{ K}$ (16b). After all measurements were finished, the ice point check was repeated; the drift over the measurement period was less than 0.01 K. The uncertainty in temperature at $\sim 353 \text{ K}$ was about twice that at 273.15 K (16a). Hence, while the bath stability was $\pm 0.002 \text{ K}$, the accuracy of temperature measurement was $\pm 0.01 \text{ K}$ near 273 K and $\pm 0.02 \text{ K}$ near 353 K.

E. Mixture composition

As in earlier work (1-3) the alcohol-water mixtures were prepared by volume measurement using pipettes cleaned by (a) washing with hot nitric acid; (b) many flushes with purified water; (c) *n*-hexane; (d) drying in an oven reserved for clean glassware. The pipette volumes were calibrated by weighing the delivered mass of water. Mole fractions were determined to ± 0.0005 .

Results

The density and viscosity of a mixture were measured at fixed mole fraction x as functions of temperature. More generally useful in thermodynamics are ρ and η at fixed T as functions of x . To convert the results the densities and viscosities were fitted with polynomials in temperature, and the fitting parameters were used to interpolate, typically less than 1 degree, to the desired temperatures used in Section D.

A. Temperature dependence of density

The experimental values of the densities ρ (kg/m^3) at the

TABLE 3. Temperature dependence of density^a

x_w^b	T/K^c range	n^d	a_0	a_1	$10^3 a_2$	$\Delta_{av} (\%)^e$	$\Delta_{max} (\%)^f$
H ₂ O in <i>sec</i> -BuOH							
0.000	283–343	5	1069.1	–0.894		0.08	0.12
0.100	275–353	7	1076.3	–0.902		0.10	0.18
0.200	283–343	5	1084.2	–0.906		0.06	0.08
0.300	275–353	7	1085.3	–0.887		0.08	0.10
0.400	275–353	7	1097.4	–0.896		0.09	0.15
0.500	275–353	7	1105.1	–0.880		0.07	0.12
0.600	284–353	6	1117.7	–0.875		0.08	0.14
0.680	275–353	7	1122.4	–0.842		0.07	0.13
0.970	275–353	7	779.3	1.716	–3.489	0.03	0.05
0.980	275–353	7	717.4	2.086	–3.982	0.02	0.03
0.990	275–353	7	708.3	2.147	–4.027	0.03	0.03
1.000 ^g	278–363 ^h	20	753.6	1.887	–3.594	0.02	0.05
H ₂ O in <i>iso</i> -BuOH							
0.000	275–353	7	1037.0	–0.805		0.07	0.11
0.100	275–354	7	1051.1	–0.831		0.06	0.11
0.200	275–349	8	1056.0	–0.828		0.04	0.05
0.300	275–353	7	1067.9	–0.843		0.07	0.12
0.400	275–346	7	1075.9	–0.839		0.05	0.07
0.450	283–346	7	1089.2	–0.863		0.05	0.12
0.990	275–353	7	713.2	2.117	–3.985	0.04	0.06
H ₂ O in <i>tert</i> -BuOH							
0.000	302–353	4	1121.5	–1.144		0.05	0.07
0.100	293–353	6	1101.0	–1.053		0.10	0.15
0.300	283–348	6	1094.3	–0.980		0.04	0.07
0.500	275–343	6	1105.6	–0.933		0.08	0.13
0.600	284–354	6	1115.8	–0.911		0.04	0.06
0.650	283–348	6	1127.2	–0.913		0.06	0.10
0.750	283–334	6	1136.2	–0.857		0.03	0.04
0.910	283–353	6	1170.3	–0.745		0.03	0.05
0.950	283–353	6	915.8	0.892	–2.374	0.02	0.03

^aEquation [6], a_i in $\text{kg/m}^3 \text{K}^i$.
^bMole fraction of water in alcohol.
^cMeasured in 0.01 K.
^dNumber of experimental values.
^eAverage percent deviation of the calculated from the experimental densities.
^fLargest magnitude of Δ_i .
^gReference 7a.

conditions listed in Table 3 were fitted to

$$[6] \quad \rho = a_0 + a_1 T + a_2 T^2$$

yielding the parameters values a_i ($\text{kg/m}^3 \text{K}^i$) in Table 3. Substituting the calculated ρ for lit. in eq. [4], the average percent deviation (eq. [5]) and largest value of Δ for each mixture fitting were obtained. Except for $x_w \geq 0.95$, a fit with $\Delta_{av} < 0.1\%$ was obtained using $a_2 = 0$. The quadratic term at $x_w \geq 0.95$ reflects the curvature of water density towards a maximum at 277.13 K (7a, 17).

Earlier composition studies often concentrate on the water-rich region (18a, 18b). To compare our results with literature values, densities were generated from eq. [6] and Table 3 at the temperature of the earlier study, for H₂O/*tert*-BuOH at 293.15 and 298.15 K, and for *sec*-BuOH/H₂O at 293.15 and 328.15 K, and then fitted to:

$$[7] \quad \rho (\text{kg/m}^3) = \sum_{j=0}^7 c_j x^j$$

Tables of c_j are available from the Depository of Unpublished

Data.¹ Our values were fitted by eq. [7] to $\Delta_{av} \approx 0.02\%$. The same calculated lines fitted literature values to typically $< 0.1\%$ (11, 17, 19, 20), although one study at $x_w > 0.861$ (18b) differed from our and other (11, 19) data by $\sim 0.4\%$.

B. Temperature dependence of viscosity

Viscosities of liquids (21) and gases (22) are often fitted to polynomials in $\ln T$ and powers of T . The present results are represented by:

$$[8] \quad \ln \eta = b_0 + b_1/T + b_2/T^2 + b_3/T^3$$

to $\sim 0.1\%$. The fitting parameters b_i in K^{-i} were those in Table 4, giving η in 10^{-3}Pa s ($= 10^{-2}$ Poise).

Discussion

The composition dependence of thermophysical properties of binary mixtures are often described in terms of properties that

¹Complete set of data may be purchased from the Depository of Unpublished Data, CISTI, National Research Council of Canada, Ottawa, Ont., Canada K1A 0S2.

TABLE 4. Parameters^a of temperature dependence of viscosity

x_w^b	T/K^c range	n^d	b_0	$10^{-2} b_1$	$10^{-5} b_2$	$10^{-8} b_3$	$\Delta_{av} (\%)^e$	$\Delta_{max} (\%)^f$
H ₂ O in <i>sec</i> -BuOH								
0.000	295–343	7	14.1616	-175.968	60.1405	-5.74516	0.01	0.03
0.100	296–363	7	8.50318	-121.966	43.5450	-4.12279	0.03	0.08
0.200	305–353	6	-2.98089	-7.35163	5.74238		0.03	0.07
0.300	297–353	7	-2.39655	-10.6417	6.22064		0.04	0.06
0.400	297–343	6	-2.13835	-12.3782	6.55305		0.02	0.04
0.500	297–343	6	-1.97165	-13.4180	6.76191		0.02	0.04
0.600	297–354	7	-1.50166	-16.3220	7.25580		0.06	0.09
0.680	296–353	8	-1.14159	-18.4122	7.58934		0.03	0.06
0.970	304–353	6	-16.7055	142.879	-47.9283	6.11713	0.03	0.07
0.980	303–354	6	-11.8145	91.3406	-29.8474	3.97164	0.00	0.01
0.990	303–354	6	-14.2332	113.215	-36.26011	4.53677	0.01	0.02
1.000	283–363 ^g	9 ^g	-9.24096	62.65074	-19.0815	2.53846	0.04	0.09
H ₂ O in <i>iso</i> -BuOH								
0.000	297–363	8	4.73580	-91.9084	36.8499	-3.74467	0.03	0.07
0.100	299–363	8	-13.7037	89.3958	-22.3706	2.66483	0.07	0.16
0.200	298–354	7	-4.24979	2.84959	3.94311		0.05	0.11
0.300	300–363	8	-2.88761	-5.87670	5.33538		0.07	0.13
0.400	298–363	7	-3.13074	-4.57166	5.17796		0.03	0.05
0.450	299–354	7	-2.68923	-7.55512	5.69054		0.06	0.13
0.990	303–353	6	-1.41213	-13.1455	5.21390		0.08	0.14
H ₂ O in <i>tert</i> -BuOH								
0.000	305–353	7	-23.0081	218.356	-80.4042	11.0575	0.02	0.04
0.100	305–353	6	3.71664	-58.1758	15.3161		0.05	0.09
0.300	303–343	5	2.32528	-47.1763	13.3169		0.02	0.04
0.500	303–343	5	1.02506	-37.7354	11.7378		0.10	0.19
0.650	303–343	5	1.88409	-41.9617	12.2517		0.04	0.08
0.750	304–353	6	2.31467	-43.6517	12.3264		0.04	0.07
0.910	303–344	5	-34.5271	323.929	-109.382	13.2601	0.00	0.01
0.950	303–344	5	-27.3695	254.761	-87.2164	10.8101	0.01	0.02

^a b_i in K^{-i} ; η in 10^{-3} Pa s.

^bMole fraction of water in alcohol.

^cMeasured to 0.01 K.

^dNumber of experimental values.

^eAverage absolute percent deviation; eq. [5] using calculated values as literature.

^fLargest absolute Δ , eq. [4].

^gReference 6.

for ideal mixtures have values Y_{ID} that are additive in mole fraction (18, 21, 23–26):

$$[9] \quad Y_{ID} = x_1 Y_1 + x_2 Y_2$$

where $x_1 + x_2 = 1$ and Y_i is the value for pure component i . The measured Y_{EXPTL} is then related to an excess Y^E where

$$[10] \quad Y^E = Y_{EXPTL} - Y_{ID}$$

A. Excess volume

For density the additive property is molar volume $V = M/\rho$, where M the molar mass for the mixture is $M_M = \sum_i x_i M_i$.

The ideal mixture volume V_{ID} is $[(x_w M_w/\rho_w) + (x_A M_A/\rho_A)]$ in our work (subscript w refers to water and A to alcohol).

Example excess volumes V^E calculated by

$$[11] \quad V^E = \frac{M_M}{\rho_{EXPTL}} - V_{ID}$$

from densities obtained from [6] and parameters in Table 3 are compared to literature values (18c, 20) in Fig. 1. At 298.15 K the present and ref. 18c results in H₂O/*tert*-BuOH were in good agreement (Fig. 1a). Reference 18c results were expressed as

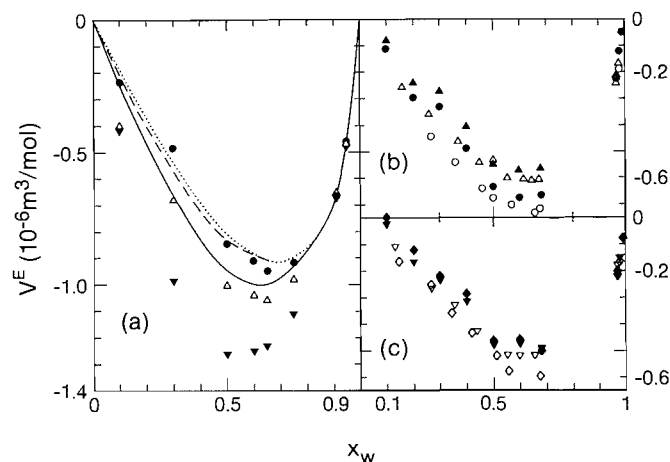


FIG. 1. Excess volume against mole fraction of water in (a) *tert*-BuOH at 298.15 K (●, ····), 313.15 K (△, ---) and 353.15 K (▼, —); (●, △, ▼) are present results and lines are from ref. 18c. (b) and (c) *sec*-BuOH at 278.15 K (○, ●), 298.15 K (△, ▲), 328.15 K (▽, ▼), and 353.15 K (◇, ◆); solid symbols are present values and open symbols are from ref. 20.

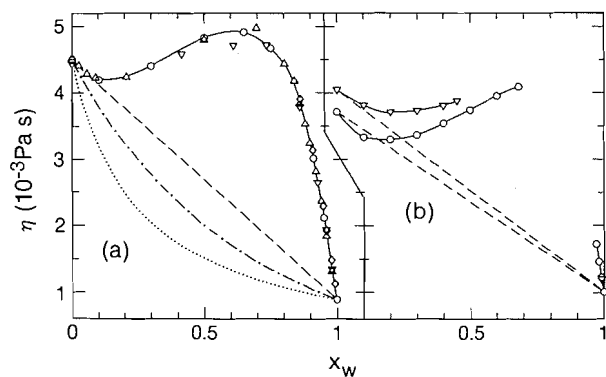


FIG. 2. Dynamic viscosity against mole fraction of water in (a) *tert*-BuOH at 298.15 K. η_{EXPTL} are \circ (present work), Δ (ref. 11), ∇ (ref. 33), and \diamond (ref. 34). — is empirical; other lines are eq. [12] (---) and eq. [9] with $Y_i = \eta_i$ (----) or ϕ_i (.....). (b) *sec*-BuOH (\circ) or *iso*-BuOH (∇) at 293.15 K. — is empirical and ---- are eq. [9] with $Y_i = \eta_i$.

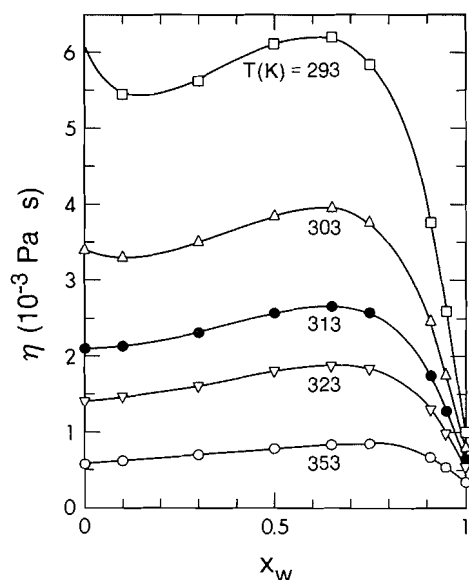


FIG. 3. Effect of temperature on composition dependence of viscosity of *tert*-butanol/water mixtures. The value of η of pure supercooled *tert*-butanol at 293 K was obtained by extrapolation from higher temperatures.

line graphs and that same notation is used in Fig. 1a. The minimum in our V^E plot deepened with increasing temperature to a greater extent than indicated by ref. 18c, and the position of the minimum moved toward $x_w = 0.5$.

Figure 1b and 1c contain the comparison of $\text{H}_2\text{O}/\text{sec}$ -BuOH results at 0.1 MPa (20). The V^E values decreased in magnitude as T increased from 278 to 328 K, but on further heating to 353 K remained approximately constant. In $\text{H}_2\text{O}/\text{iso}$ -BuOH and $\text{H}_2\text{O}/\text{sec}$ -BuOH V^E decreased with increasing T , which indicated that increasing thermal agitation of the molecules made these solutions less nonideal. Tables of V^E illustrating this point along with $\text{H}_2\text{O}/\text{tert}$ -BuOH V^E are available from the Depository of Unpublished Data.¹

B. Viscosity

The main problem in calculating an excess viscosity η^E is the lack of agreement about the form of the ideal mixture viscosity η_{ID} . The problem was examined in detail early in this century

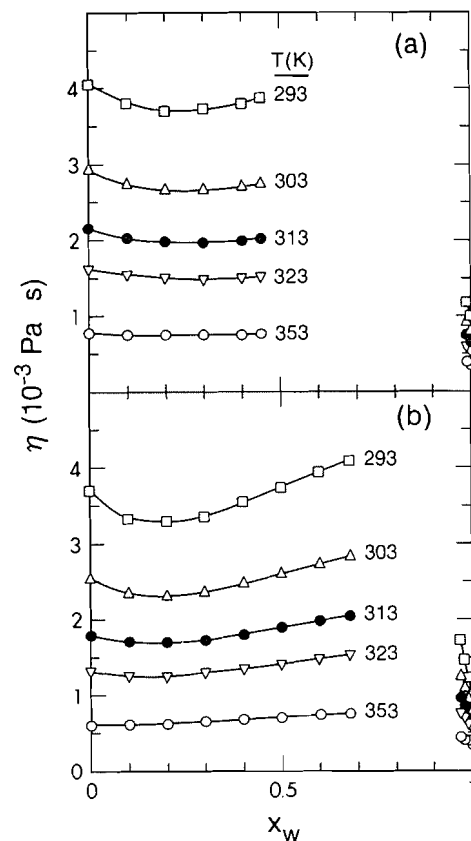


FIG. 4. Effect of temperature on composition dependence of viscosity of (a) *iso*-butanol/water; (b) *sec*-butanol/water.

(28) but is still apparent in the current literature (21, 23, 24, 27). While eqs. [9] and [10] could be used to define η^E (23, 29) the only mixture in which η could be described by eq. [9] appears to be $\text{H}_2\text{O}/\text{HDO}/\text{D}_2\text{O}$ (30), in which the components are quite similar. The most widely used relation appears to be that of Arrhenius (31) as modified by Kendall and Monroe from volume fraction to mole fraction (28), η_{AR} , that is eq. [9] with $Y_i = \ln \eta_i$,

$$[12] \quad \ln \eta_{\text{AR}} = x_1 \ln \eta_1 + x_2 \ln \eta_2$$

There is also disagreement about whether $[\ln \eta_{\text{EXPL}} - \ln \eta_{\text{AR}}]$ (21, 24, 30, 32) or $[\eta_{\text{EXPTL}} - \eta_{\text{AR}}]$ (27) is the more meaningful. Other models are power-root (28, 29) and fluidity $\phi \equiv 1/\eta$ equations (28, 33).

Example curves of η_{EXPTL} obtained from the measurements summarized by the parameters of Table 4 are shown in Fig. 2. For $\text{H}_2\text{O}/\text{tert}$ -BuOH and $\text{H}_2\text{O}/\text{sec}$ -BuOH the values of η_{EXPTL} in the mixtures near $x_w = 0.6$ were larger than in the pure components. The present values of η_{EXPTL} in $\text{H}_2\text{O}/\text{tert}$ -BuOH are in good agreement with earlier values (11, 33, 34), except near $x_w = 0.65$ where refs. 11 and 33 differed by $\sim 3\%$ (Fig. 2). The relative viscosities in ref. 34 were multiplied by $\eta_w = 8.906 \times 10^{-4} \text{ Pa s}$ for plotting in Fig. 2.

We tested eqs. [12] and eq. [9] with $Y_i = \eta_i$, and ϕ_i . In each case the calculated values were far from η_{EXPTL} (Fig. 2).

We also tested

$$[13] \quad \eta^P = x_1 \eta_1^P + x_2 \eta_2^P$$

with $P = 1/3$ (28), $1/2$ (35), or $1/2.5$ (36). The curves were intermediate to eq. [12] or [9] with $Y_i = \eta_i$ but all decrease monotonically with increasing x_w . The only clear conclusion

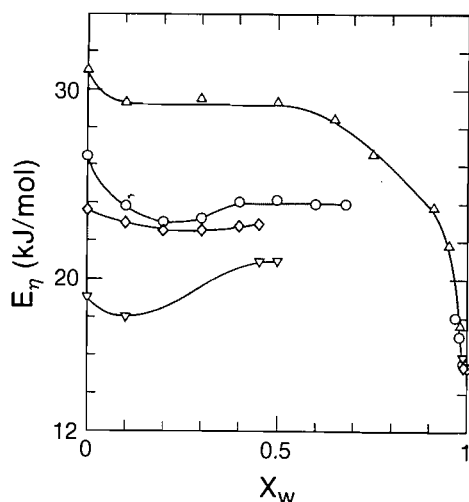


Fig. 5. Variation of energy of activation for viscous flow E_η with composition, over the range $298 < T/K < 353$. Δ , *tert*-butanol; \circ , *sec*-butanol; \diamond , *iso*-butanol; ∇ , *n*-butanol (ref. 37).

from Fig. 2 is that regardless of the form for η_{ID} the present work indicates a large positive excess viscosity, consistent with stronger hydrogen bonding in the mixture than in the pure components, and consistent with the observed negative excess volume (Fig. 1).

Upon increasing the temperature the viscosities of the pure alcohols and the aqueous mixtures decreased more rapidly than did that of water. The S-shapes of the η against x_w curves decreased with increasing temperature (Figs. 3 and 4).

An average Arrhenius temperature coefficient of viscous flow, E_η , was obtained by fitting the measured viscosities over the temperature range $293 < T/K < 353$ to eq. [8] with $b_2 = b_3 = 0$. In this case $E_\eta = b_1 R$, where R is the gas constant. Values of E_η for binary mixtures of the four isomeric butanols with water are plotted in Fig. 5. The viscosity data for 1-butanol (37) have a lower precision ($\sim 1\%$) than those for the other isomers ($\sim 0.1\%$).

Addition of a small amount of water to a butanol disrupts the alcohol liquid structure and decreases the resistance to flow (Fig. 5). Addition of a small amount of a butanol to water stiffens the liquid structure and increases the resistance to flow. In the central composition region the viscosity and its temperature coefficient change relatively little, which probably indicates a relatively random fluid structure.

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