

Figure 6. Temperature dependence of solubility of isobutene in various mixtures of acid and *tert*-butanol

(c_t in g-mol/l.; c_a in wt %; H in torr cm³/g-mol). The regression coefficients obtained and their individual confidence intervals to a 95% confidence coefficient are:

$$\begin{aligned} b_0 &= 2.514 \pm 0.841 \\ b_1 &= 0.276 \pm 0.057 \\ b_2 &= -0.338 \pm 0.034 \\ b_3 &= -0.0027 \pm 0.00065 \end{aligned} \quad (11)$$

The residual variation concerning the logarithmic values of H is $s = 0.105$. By applying the F-test for "lack of fit", it was

proved that the selected model satisfactorily represents the experimental data.

Temperature Dependence

For several mixtures of acid, *tert*-butanol, and water, the solubility was measured temperature dependent. Some examples are given in Figure 6. No uniform behavior was observed. At a concentration of approximately 40 wt % sulfuric acid and 3–3.5 g-mol/l. *tert*-butanol, the solubility appears to be only weakly dependent on the temperature.

Acknowledgment

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Densities and Viscosities of Binary Systems Toluene–Acetone and 4-Methyl-2-Pentanone–Acetic Acid at 20, 25, 35, and 45 °C

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Densities and viscosities of the binary miscible liquid systems toluene–acetone and 4-methyl-2-pentanone–acetic acid are measured at 20, 25, 35, and 45 °C. The results compare well with the theories proposed by Hildebrand and Kosanovich.

The evaluation and prediction of the transport properties of binary miscible liquid systems as functions of composition and temperature are of theoretical and practical importance, but very little data are available.

A general statistical mechanical theory has been proposed by Bearman and Kirkwood (3) and Bearman (4) to predict the transport properties. Based on the thermodynamics of irre-

versible processes, Albright (1) also proposed an equation to relate the intradiffusion of components of a solution to the viscosity of the solution. These and other statistical and thermodynamic approaches have not yet been successfully reduced to numerical results. Hildebrand (6) and Hildebrand and Lamoreaux (7) proposed general equations for the viscosity and diffusivity of pure liquids, and Cullilan and Kosanovich (5) extended the equations for viscosity to mixtures and showed it to be valid for reduced temperatures ≥ 0.46 . Hildebrand's equation for the single components is:

$$\phi = B \left(\frac{V - V_0}{V_0} \right) \quad (1)$$

where ϕ is the fluidity ($1/\eta$), V is the molecular volume (M/ρ), V_0 is the ultimate molecular volume when viscous flow ceas-

es, and B is a measure of the capacity of the molecules to absorb externally imposed momentum (5).

The present data are compared with Equation 1 for the single components and for the binary systems as suggested by Cullilan and Kosanovich (5).

Experimental

The density and viscosity data for the two binary miscible systems, toluene-acetone and 4-methyl-2-pentanone-acetic acid are measured at 20, 25, 35, and 45 °C.

Fluka analytical grade toluene, acetone, 4-methyl-2-pentanone, and acetic acid were used. The mixtures were prepared by volume in duplicates using automatic microburets accurate to ± 0.02 ml; the mole fractions are thus estimated to be accurate to ± 0.001 .

The density was measured with a precision Lauda DMA 50 densitometer based on the principle of the measurement of the period of oscillation of a small U-shaped Duran 50 glass cell filled with the liquid whose density is to be evaluated rel-

ative to the period of oscillation of the calibrating fluids, usually air and water (8). It has an accuracy of $\pm 2 \times 10^{-5}$ ms in the measurement of the period of oscillation corresponding to a relative error in the density of $\pm 3 \times 10^{-5}$ g/ml. Temperature control using a calibrated thermometer was better than ± 0.05 °C.

The viscosity was measured with a Viscomatic viscometer equipped with a digital timer accurate to ± 0.001 s. The viscometer is essentially an Ubbelohde-type viscometer based on the principle of capillary flow and was calibrated with triple distilled water at 20, 25, 35, and 45 °C and with toluene at 25 °C. Correction for air buoyancy, changes in the effective head due to difference between the calibrating and operating temperatures, and changes in the mean effective head with surface tension were all evaluated according to Swindells et al. (9). The relative accuracy of the apparatus is ± 0.001 cP. Temperature control was better than ± 0.01 °C.

Duplicate mixtures showed reproducibility to within ± 0.00028 g/ml for the density measurements and ± 0.0015 cP for the viscosity measurements.

Table I. Molecular Volume and Fluidity of Single Liquid Components

Component	Temp, °C	Molecular vol V , cm ³ /g-mol	Fluidity ϕ , cP ⁻¹
$B = 18.4085, V_0 = 97.2852$			
Toluene	20	106.287	1.7068
	25	106.867	1.8099
	35	108.020	2.0292
	45	109.210	2.2583
$B = 19.6791, V_0 = 63.3961$			
Acetone	20	73.510	3.1446
	25	74.044	3.3014
	35	75.136	3.6390
	45	76.290	4.0064
$B = 18.2226, V_0 = 114.3674$			
4-Methyl-2-pentanone	20	125.122	1.7010
	25	125.845	1.8305
	35	127.220	2.0530
	45	128.740	2.2867
$B = 12.1354, V_0 = 53.6306$			
Acetic acid	20	57.229	0.8158
	25	57.541	0.8848
	35	58.160	1.0209
	45	58.798	1.1715

Table II. Comparison of Density and Viscosity of Single Components with Published Data

Component	Temp, °C	Source of data			
		Present study	API	TRC	Ref 11
Density ρ , g/ml					
Toluene	20	0.8668	0.8669	...	
	25	0.8621	0.8623	...	
Acetone	20	0.7901	0.7905	0.78998	
	25	0.7844	0.78498	0.78440	
4-Methyl-2-pentanone	20	0.8005	0.8008	0.80080	
	25	0.7959	0.7961	0.79610	
Acetic acid	20	1.0493	1.04926	1.04926	
	25	1.0436	1.04364	1.04366	
Viscosity η , cP					
Toluene	20	0.5859	0.5848	...	
	25	0.5525	0.5500	...	
	35	0.4928	0.4898
	45	0.4428	0.4398
Acetone	25	0.3029	0.3040
4-Methyl-2-pentanone	25	0.5463	0.5420

Table III. Density and Viscosity of System Toluene-Acetone

Mole fraction x of toluene	Density ρ , g/ml	Viscosity η , cP
20 °C		
1.000	0.8668	0.5859
0.862	0.8599	0.5472
0.735	0.8527	0.5095
0.617	0.8453	0.4775
0.509	0.8378	0.4506
0.409	0.8303	0.4200
0.317	0.8224	0.3966
0.229	0.8144	0.3740
0.148	0.8070	0.3525
0.072	0.8002	0.3349
0.000	0.7901	0.3180
25 °C		
1.000	0.8621	0.5525
0.862	0.8551	0.5138
0.735	0.8478	0.4807
0.618	0.8403	0.4521
0.509	0.8327	0.4236
0.410	0.8251	0.3994
0.317	0.8170	0.3764
0.229	0.8090	0.3530
0.148	0.8015	0.3344
0.073	0.7937	0.3172
0.000	0.7844	0.3029
35 °C		
1.000	0.8529	0.4928
0.862	0.8456	0.4630
0.736	0.8381	0.4335
0.619	0.8304	0.4072
0.510	0.8225	0.3829
0.411	0.8146	0.3615
0.318	0.8065	0.3407
0.230	0.7982	0.3204
0.149	0.7900	0.3036
0.073	0.7826	0.2891
0.000	0.7730	0.2738
45 °C		
1.000	0.8436	0.4428
0.863	0.8361	0.4162
0.737	0.8283	0.3916
0.610	0.8203	0.3670
0.511	0.8125	0.3470
0.412	0.8041	0.3264
0.319	0.7957	0.3081
0.230	0.7873	0.2923
0.149	0.7788	0.2767
0.073	0.7704	0.2628
0.000	0.7613	0.2496

Results and Discussion

Single components. The molecular volume and fluidity of the four single components toluene, acetone, 4-methyl-2-pentanone, and acetic acid at 20, 25, 35, and 45 °C are given in Table I. The viscosities follow the Hildebrand equation and the values of B and V_0 in Equation 1 are also given in Table I for the four liquids.

Table II compares the experimental densities and viscosities with the data of the American Petroleum Institute Project 44 (2) and the Thermodynamic Research Center Project (10) as well as those of Weissberger and Proskauer (11). The density data agree to within $\pm 0.05\%$, whereas the viscosity of toluene is systematically larger than the values reported in the API project (2) by a maximum of $+0.7\%$. Viscosity data for the other components (not available in the API or TRC projects) are compared with those reported by Weissberger and Proskauer (11) showing a maximum deviation of 0.7% for acetone and 4-methyl-2-pentanone.

Table IV. Density and Viscosity of System 4-Methyl-2-pentanone–Acetic Acid

Mole fraction x of 4-methyl-2-pentanone	Density ρ , g/ml	Viscosity η , cP
	20 °C	
1.000	0.8005	0.5848
0.806	0.8273	0.6691
0.647	0.8523	0.7427
0.514	0.8772	0.8105
0.406	0.9023	0.8773
0.314	0.9264	0.9417
0.234	0.9508	1.0043
0.164	0.9755	1.0648
0.103	0.9996	1.1219
0.048	1.0242	1.1789
0.000	1.0493	1.2258
	25 °C	
1.000	0.7959	0.5463
0.805	0.8226	0.6272
0.647	0.8476	0.6880
0.514	0.8730	0.7520
0.406	0.8973	0.8108
0.314	0.9213	0.8743
0.234	0.9457	0.9325
0.164	0.9701	0.9866
0.103	0.9942	1.0371
0.048	1.0187	1.0852
0.000	1.0436	1.1302
	35 °C	
1.000	0.7873	0.4871
0.805	0.8134	0.5546
0.647	0.8382	0.6078
0.514	0.8634	0.6636
0.406	0.8873	0.7072
0.314	0.9121	0.7592
0.234	0.9358	0.8030
0.164	0.9597	0.8505
0.103	0.9835	0.8955
0.048	1.0078	0.9387
0.000	1.0325	0.9795
	45 °C	
1.000	0.7780	0.4373
0.805	0.8040	0.4944
0.646	0.8286	0.5401
0.514	0.8546	0.5844
0.405	0.8773	0.6271
0.313	0.9010	0.6696
0.233	0.9249	0.7080
0.164	0.9488	0.7456
0.102	0.9735	0.7844
0.048	0.9967	0.8200
0.000	1.0213	0.8536

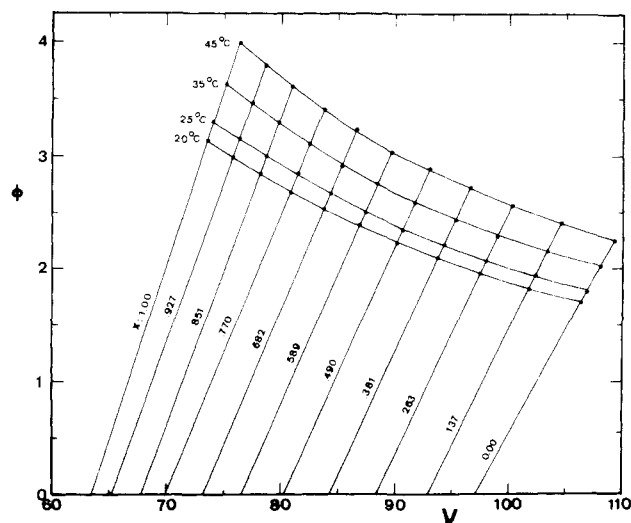


Figure 1. Variation in fluidity ϕ (cP^{-1}) of system toluene–acetone with molecular volume V ($\text{cm}^3/\text{g-mol}$) for different mole fractions of acetone x (—) at 20, 25, 35, and 45 °C

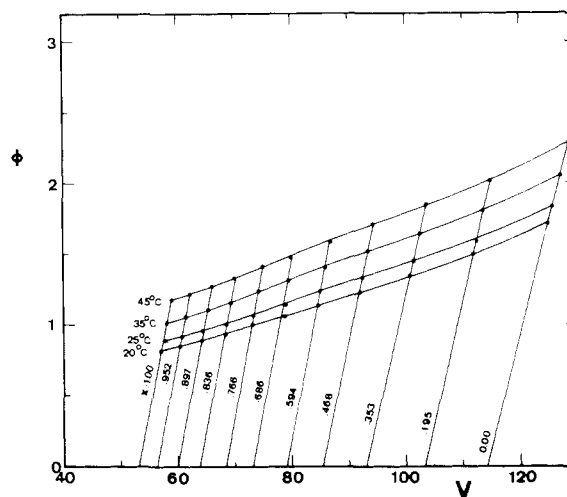


Figure 2. Variation in fluidity ϕ (cP^{-1}) of system 4-methyl-2-pentanone–acetic acid with molecular volume V ($\text{cm}^3/\text{g-mol}$) for different mole fractions of acetic acid x (—) at 20, 25, 35, and 45 °C

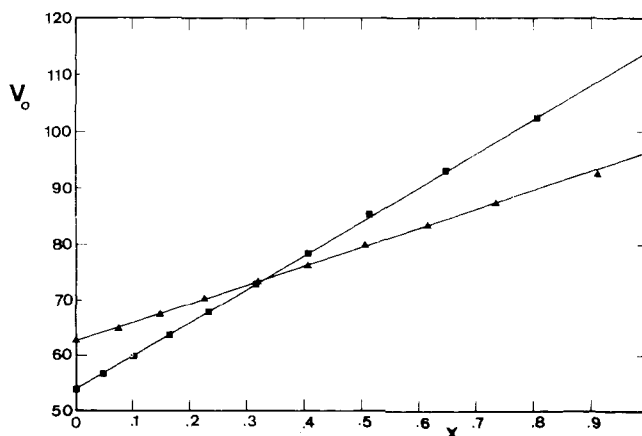


Figure 3. Variation in V_0 ($\text{cm}^3/\text{g-mol}$) with mole fraction of acetone or acetic acid x for systems toluene–acetone \blacktriangle and 4-methyl-2-pentanone–acetic acid \blacksquare

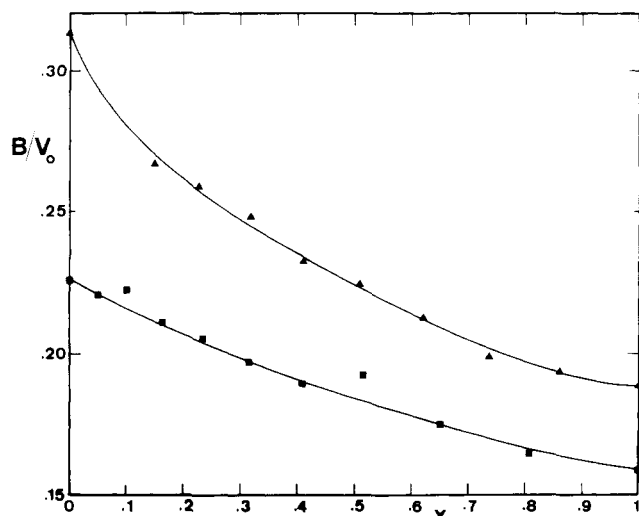


Figure 4. Variation in B/V_0 (g-mol/cm³ cP) with mole fraction of acetone or acetic acid x for systems toluene-acetone ▲ and 4-methyl-2-pentanone-acetic acid ■

Binary systems. Unsmoothed density and viscosity data for the two systems at the four temperatures are listed in Tables III and IV. Cullilan and Kosanovich (5) have suggested that Equation 1 can be used for any mixture so that V in Equation 1 be the molecular volume of the solution and ϕ be the fluidity of the mixture, respectively. Plots of ϕ against V for the two systems are shown in Figures 1 and 2. Unlike the data reported by Cullilan and Kosanovich (5) for the system acetone-carbon tetrachloride, the present data show a regular increase in the value of B/V_0 and an almost linear de-

crease in the value of V_0 as the mole fraction of acetone in the first system and acetic acid in the second system increase, as shown in Figures 3 and 4.

Nomenclature

B = constant in Equation 1, cP⁻¹
 M = molecular weight
 V = molecular volume, cm³/g-mol
 V_0 = ultimate molecular volume, cm³/g-mol
 x = mole fraction

Greek Letters

ρ = density, g/ml
 η = viscosity, cP
 ϕ = fluidity, cP⁻¹

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Binary Vapor-Liquid Equilibria of Some Amyl Alcohols

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Vapor-liquid equilibrium data were determined at 760 mm Hg for the binary systems *tert*-amyl-isoamyl alcohol, isoamyl-*n*-amyl alcohol, and *tert*-amyl-*n*-amyl alcohol with a Dvorak-Boublik recirculation still. The three binaries presented small negative deviations from ideal solution behavior. Liquid activity coefficients were correlated with the Redlich-Kister and Wilson equations. Boiling points were predicted by a two-constant empirical correlation.

The amyl isomer systems reported here represent an example of vapor-liquid equilibria where the chemical species differ only in the geometrical position of the alcohol function. Amyl alcohols are a by-product of the fermentation of grain (fusel oil), and their main use is in the manufacture of solvents.

Ocon et al. (6, 7) measured the vapor-liquid equilibrium at 760 mm Hg of mixtures of active amyl alcohol (1-rotatory 2-methyl-1-butanol) and isoamyl alcohol (3-methyl-1-butanol)

without determining the activity coefficients, and claimed that their data were more reliable than those of Hafslund and Lovell (3). Ivanov et al. (5) determined the vapor-liquid equilibrium of the same system at various constant compositions of isoamyl alcohol and calculated the relative volatility and the coefficients of the Van Laar equations at 100, 300, 500, and 760 mm Hg. Their results showed that the binary was symmetric and presented small negative deviations from ideal solutions. Brusset et al. (2) determined the degree of association of the different pentanols at 25 °C and found that the tertiary form presented the highest degree of association and that the association decreased substantially when adding spherical solvents like carbon tetrachloride.

Experimental

Purity of materials. Analytical grade reagents purchased from Merck and Fluka were used without further purification after gas chromatography analysis failed to show any significant impurities, particularly water. Physical properties of the pure components appear in Table I.