the fuming sulfuric acid region as a mole ratio of SO_3 to H_2SO_4 (Y), as shown in Figure 2. Some of the data of Miles and Carson were recalculated by using this concentration and are shown in Figure 2.

The solubility at 101.3 kPa pressure as a function of temperature is shown in Figure 3. Although some of the data, such as those of Milbauer, are shown directly, some of the lines are simply interpolations of the available data as obtained from Figure 2. If we compare Figure 2 with Figure 3, it may be observed that the SO_2 solubility values of Milbauer in 62.0% acid may be too low when compared with data of other workers. More particularly, the recently published results of Domka et al. (*8*) appear not to conform in magnitude or in slope to those of other workers, and for these reasons appear to be in significant error. A further comparison of additional data by Domka et al. for various SO_2 partial pressures again indicates serious discrepancies when compared with our work and that of Miles and Carson. Figure 3 shows a consistent pattern for SO_2 solubilities in various concentrations of acid, and in water, as a function of temperature.

Glossary

h	Henry's law constant, kPa/mole fraction
H	log h
p	partial pressure of gas, kPa
P	log p
T	absolute temperature, K
x	mole fraction dissolved gas at a gas partial pressure of 101.3 kPa: moles of SO_2/(moles of H_2SO_4 + moles of SO_2 + moles of water)
x_p	mole fraction dissolved gas at a gas partial pressure $p \neq 101.3$ kPa
X	log x_p
y	mole fraction H_2SO_4 in solvent solution
Y	concentration of dissolved SO_3 in fuming sulfuric acid; mole ratio, moles of SO_3/mole of H_2SO_4

Registry No. SO_2, 7446-09-5; H_2SO_4, 7664-93-9.

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Viscosities and Densities of Some Binary Liquid Mixtures of Esters at 303.15 and 313.15 K

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Viscosities and densities have been measured as a function of mole fraction at 303.15 and 313.15 K for binary liquid systems of benzene + *n*-propyl acetate and benzene + ethyl butyrate and carbon tetrachloride + *n*-propyl acetate, + *n*-butyl acetate, and + ethyl butyrate. The mixture viscosities were fitted to an empirical equation proposed by Katti and Chaudhri. It was found that the equation predicts the mixture viscosities reasonably well at both the temperatures and the agreement between the experimental and calculated viscosities is satisfactory.

Introduction

This investigation is a part of the authors research program (*1-5*) on the thermodynamic and transport properties of binary liquid mixtures of esters. Continued interest in the thermodynamic and transport properties of binary liquid mixtures containing esters (*6-9*) makes it desirable to study systematically the influence of esters and the chemical structure of the other component upon the viscosities. In addition, the present study of viscosities was undertaken to test further the validity of the Katti and Chaudhri equation at higher temperatures. As a contribution toward a more comprehensive description along these lines, we report in this paper the measurements of viscosities and densities for binary liquid mixtures of benzene + *n*-propyl acetate and benzene + ethyl butyrate and carbon tetrachloride + *n*-propyl acetate, + *n*-butyl acetate, and + ethyl butyrate at 303.15 and 315.15 K.

Experimental Section

Materials. The solvents benzene, carbon tetrachloride, and *n*-butyl acetate, all analytical grade (BDH), were purified as per the standard procedure given by Riddick and Bunger (*10*). *n*-Propyl acetate (Fluka AG) and ethyl butyrate (Fluka AG) with a reported purity of >99% were used without further treatment. *n*-Butyl acetate (AR, BDH) was dried and fractionally distilled. All the chemicals were distilled before use. Further the purities were checked by measuring their refractive indexes at 303.15 K (Table I).

Measurements. Densities were measured with a pycnometer having a bulb volume of about 20 cm^3 and internal diameter of the capillary of about 1 mm. The pycnometer was calibrated at 303.15 and 313.15 K with doubly distilled water and benzene. The temperature of the thermostat was maintained constant to within ±0.005 K at the desired value and

Table I. Physical Properties of Pure Components in the Present Work and in the Literature

liquid	temp, K	density d, kg m^{-3} exptl	density d, kg m^{-3} lit.	viscosity η, mPa s exptl	viscosity η, mPa s lit.	refractive index n_D exptl	refractive index n_D lit.[c]
benzene	303.15	868.4	868.4[b]	0.560	0.562[b]	1.4947	1.4947
	315.15	857.4		0.491			
carbon tetrachloride	303.15	1574.8	1574.8[b]	0.845	0.845[b]	1.4547	1.4547
	315.15	1555.3		0.744			
n-propyl acetate	303.15	877.0	877.2[a]	0.518	0.517[b]	1.3793	1.3796
	315.15	864.8		0.449			
n-butyl acetate	303.15	871.5	871.3[a]	0.628	0.628[a]	1.3827	1.3827
	315.15	860.9		0.557			
ethyl butyrate	303.15	868.6	868.7[a]	0.595	0.595[a]	1.3881	1.3881
	313.15	857.6		0.559			

[a] Reference *10*. [b] Reference *11*. [c] Extrapolated values from ref *10*.

Table II. Density (d), Absolute Viscosity (η), Excess Viscosity (η^E), and Interaction Energy (W_{visc}) for Various Binary Mixtures

x_1	d, kg m^{-3}	η, mPa s	η(eq 3), mPa s	η^E, mPa s	W_{visc}, J mol^{-1}	x_1	d, kg m^{-3}	η, mPa s	η(eq 3), mPa s	η^E, mPa s	W_{visc}, J mol^{-1}
Benzene (1) + *n*-Propyl Acetate (2) at 303.15 K											
0.0633	876.3	0.514	0.515	−0.007		0.6141	870.9	0.517	0.519	−0.026	
0.1259	875.8	0.515	0.513	−0.008		0.7078	870.4	0.524	0.525	−0.022	
0.1865	875.3	0.513	0.511	−0.012		0.7972	869.8	0.529	0.533	−0.021	
0.3006	874.2	0.512	0.510	−0.018		0.8812	869.1	0.539	0.542	−0.014	
0.4062	872.7	0.513	0.511	−0.021		0.9631	868.5	0.551	0.553	−0.006	
0.5133	871.8	0.514	0.514	−0.025	−368.4						
Benzene (1) + *n*-Propyl Acetate (2) at 313.15 K											
0.1951	864.5	0.448	0.447	−0.009		0.6029	860.2	0.455	0.457	−0.019	
0.4024	862.4	0.449	0.450	−0.017	−288.5	0.8029	858.6	0.466	0.471	−0.017	
0.5082	861.2	0.453	0.453	−0.017							
Benzene (1) + Ethyl Butyrate (2) at 303.15 K											
0.0662	868.5	0.591	0.589	−0.002		0.6452	868.1	0.554	0.556	−0.017	
0.2048	868.5	0.581	0.578	−0.006		0.7372	868.1	0.551	0.555	−0.017	
0.3293	868.5	0.571	0.569	−0.012		0.8161	868.1	0.551	0.555	−0.014	
0.4394	868.4	0.563	0.564	−0.016		0.8938	868.2	0.554	0.556	−0.008	
0.5452	868.3	0.559	0.559	−0.016	−72.7	0.9658	868.2	0.555	0.557	−0.004	
0.5996	868.2	0.555	0.558	−0.018							
Benzene (1) + Ethyl Butyrate (2) at 313.15 K											
0.2126	858.2	0.539	0.537	−0.006		0.6031	858.2	0.506	0.507	−0.012	
0.4055	858.3	0.521	0.520	−0.010	−14.0	0.8066	857.5	0.496	0.497	−0.008	
0.5070	858.3	0.513	0.513	−0.012							
Carbon Tetrachloride (1) + *n*-Propyl Acetate (2) at 303.15 K											
0.0422	901.3	0.526	0.527	−0.006		0.5271	1214.6	0.657	0.657	−0.033	
0.1298	954.2	0.547	0.547	−0.013		0.6005	1266.7	0.676	0.682	−0.038	
0.2541	1031.9	0.576	0.578	−0.025		0.7049	1343.1	0.716	0.719	−0.043	−173.3
0.3335	1083.3	0.598	0.599	−0.029		0.8748	1473.5	0.784	0.788	−0.030	
0.4880	1187.7	0.639	0.645	−0.039		0.9403	1525.9	0.815	0.817	−0.010	
Carbon Tetrachloride (1) + *n*-Propyl Acetate (2) at 313.15 K											
0.2073	989.8	0.494	0.492	−0.016		0.6010	1251.1	0.593	0.596	−0.033	
0.4055	1117.0	0.541	0.540	−0.028	−188.8	0.8020	1398.9	0.661	0.664	−0.025	
0.5078	1186.1	0.568	0.568	−0.031							
Carbon Tetrachloride (1) + *n*-Butyl Acetate (2) at 303.15 K											
0.1942	977.0	0.664	0.658	−0.006		0.7049	1322.0	0.759	0.765	−0.022	−60.2
0.3145	1048.4	0.685	0.679	−0.011		0.7537	1361.3	0.774	0.777	−0.018	
0.4207	1116.1	0.702	0.700	−0.017		0.8196	1415.9	0.788	0.794	−0.018	
0.5252	1187.4	0.720	0.720	−0.022		0.8765	1464.8	0.803	0.810	−0.015	
0.5754	1223.4	0.732	0.732	−0.021		0.9415	1522.1	0.823	0.828	−0.009	
Carbon Tetrachloride (1) + *n*-Butyl Acetate (2) at 313.15 K											
0.2041	971.3	0.587	0.584	−0.008		0.6040	1229.0	0.651	0.653	−0.019	
0.4028	1091.4	0.619	0.616	−0.013		0.8058	1387.2	0.695	0.697	−0.013	
0.5068	1160.4	0.634	0.634	−0.018	−63.6						
Carbon Tetrachloride (1) + Ethyl Butyrate (2) at 303.15 K											
0.0610	900.5	0.606	0.605	−0.004		0.6324	1263.4	0.726	0.727	−0.027	
0.1443	946.2	0.621	0.619	−0.010		0.7331	1341.4	0.748	0.756	−0.026	
0.2812	1026.3	0.648	0.645	−0.017		0.8278	1419.2	0.778	0.785	−0.024	
0.3929	1096.4	0.672	0.669	−0.021		0.8866	1470.2	0.798	0.804	−0.018	
0.5226	1183.9	0.699	0.699	−0.027		0.9455	1523.4	0.819	0.825	−0.012	
0.5625	1212.1	0.708	0.709	−0.028	−114.3						
Carbon Tetrachloride (1) + Ethyl Butyrate (2) at 313.15 K											
0.2056	969.0	0.586	0.584	−0.011		0.6059	1228.3	0.647	0.650	−0.024	
0.4083	1093.1	0.615	0.614	−0.020		0.7990	1377.6	0.690	0.691	−0.017	
0.5058	1157.9	0.631	0.631	−0.022	−129.2						

Table III. Values of Parameters for Eq 2 and the Standard Deviation of Various Binary Mixtures

system	temp, K	A_0	A_1	A_2	$\sigma(\eta^E)$
benzene + *n*-propyl acetate	303.15	−0.0931	−0.0208	−0.0444	0.002
	313.15	−0.0714	−0.0393	−0.0306	0.001
benzene + ethyl butyrate	303.15	−0.0728	0.0226	−0.0062	0.005
	313.15	−0.0506	0.0153	0.0348	0.002
carbon tetrachloride + *n*-propyl acetate	303.15	−0.1570	−0.0710	−0.0432	0.005
	313.15	−0.1252	−0.0508	−0.0051	0.000
carbon tetrachloride + *n*-butyl acetate	303.15	−0.0752	−0.0731	−0.0138	0.002
	313.15	−0.0686	−0.0318	0.0081	0.002
carbon tetrachloride + ethyl butyrate	303.15	−0.1010	−0.0766	−0.0572	0.001
	313.15	−0.0901	−0.0338	0.0099	0.001

checked by means of a calibrated platinum resistance thermometer. The values of densities thus estimated here are accurate to ±0.2 kg m^{-3}. Viscosities of pure liquids and of the mixtures were determined at 303.15 and 313.15 K by using an Ubbelohde viscometer. The method and calibration of the viscometer has already been reported elsewhere (*5*). Kinetic energy corrections were applied to viscosity data. The estimated error was ±0.003 mPa s. In making determinations, both the pycnometer and the viscometer were maintained in the bath until at least two consecutive measurements of the liquid height in the capillaries or the flow time indicated that the sample had reached the temperature of the bath. The refractive indexes for the sodium D line of the pure components at 303.15 K were determined with a Abbe refractometer with an estimated error of ±0.0002. Binary mixtures were prepared by mixing weighed amounts of the pure liquids. All weighings were made on a Mettler balance and corrected to vacuum. Caution was taken to prevent evaporation, and the possible error in the mole fractions is estimated to be less than 10^{-4}.

Results and Discussion

The experimental results for the pure liquids at 303.15 and 313.15 K are reported in Table I along with the literature values at 303.15 K for comparison. In general the agreement with the literature (*10*, *11*) data is satisfactory. Table II shows the experimental values of densities and viscosities for the various binary mixtures studied at 303.15 and 313.15 K over the entire range of composition. The excess viscosities η^E calculated from the relation

$$\eta^E = \eta_{12} - x_1\eta_1 - x_2\eta_2 \tag{1}$$

were fitted to the following empirical equation

$$\eta^E = x_1x_2[A_0 + A_1(x_1 - x_2) + A_2(x_1 - x_2)^2] \tag{2}$$

where 1 and 2 represent the pure components, 12 represents their mixture, and A_0, A_1, and A_2 are constants. The method of least squares was used to determine the values of the constants. The values of these constants together with their standard deviation $\sigma(\eta^E)$ are summarized in Table III. The mixture viscosities have been recalculated by using the Katti and Chaudhri equation

$$\ln \eta_{12}V_{12} = x_1 \ln \eta_1V_1 + x_2 \ln \eta_2V_2 + x_1x_2(W_{\text{visc}}/RT) \tag{3}$$

where V is the molar volume and W_{visc} is the interaction energy. The molar volume of the mixture is defined by the equation

$$V = (x_1M_1 + x_2M_2)/d \tag{4}$$

where d is the density of the mixture. W_{visc} at equimolar concentration ($x_1 = x_2 = 0.5$) for each binary system was calculated by using the following equation

$$W_{\text{visc}} = \Delta G^{*E}/x_1x_2 \tag{5}$$

where ΔG^{*E} is the excess free energy of activation of flow (*4*) calculated at equimolar concentration. The calculated values of the mixture viscosities and W_{visc} for each binary system are included in Table II.

From this analysis it is evident that the Katti and Chaudhri equation is very effective in fitting the present binary data at various temperatures. The agreement of the computed and the experimental data was found to be within about 1%, and the difference does not change much from system to system. To the best of our knowledge no data on viscosities for the same binary systems at these temperatures as those reported here have been studied so that a direct comparison is not possible.

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Registry No. Benzene, 71-43-2; *n*-propyl acetate, 109-60-4; ethyl butyrate, 105-54-4; carbon tetrachloride, 56-23-5; *n*-butyl acetate, 123-86-4.

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