Density, Viscosity, and Thermal Conductivity of Aqueous Benzoic Acid Mixtures between 375 K and 465 K

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The density, viscosity, and thermal conductivity of benzoic acid + water mixtures were measured at temperatures between 375 K and 465 K and concentrations ranging from 5 mass % benzoic acid to 100 mass % benzoic acid. Because the benzoic acid + water system exhibits a liquid−liquid immiscibility region at lower temperatures, care was exercised to ensure that the conditions chosen were in the single-phase region of the phase diagram. The data were correlated over the entire concentration range using the generalized corresponding states principle (GCSP).

Introduction

This work is part of our continuing work on the thermophysical properties of aqueous mixtures[1] and presents the density, viscosity, and thermal conductivity of solutions of benzoic acid and water over the entire concentration range. No thermophysical property data have been reported in the literature for this system, probably because the system forms a homogeneous liquid phase only at high temperatures (close to the melting point of benzoic acid at 396 K). In the present work, therefore, we have carefully chosen our experimental conditions in the single-phase region of the phase diagram and report data at temperatures between 375 K and 465 K. The data are correlated using the generalized corresponding states principle that has previously proved useful for interpolating and extrapolating thermophysical property data.

Experimental Section

Materials. Analytical reagent grade crystals of benzoic acid were purchased from the Mallinckrodt Company and used in the experiments without further purification. Benzoic acid + water mixtures were prepared gravimetrically using doubly distilled water.

Measurements. The densities and viscosities of the mixtures were measured using a pycnometer and a capillary viscometer. The pycnometer was calibrated using mercury, and the viscometer was calibrated by the manufacturer using viscosity standards. Both the pycnometer and viscometer were placed inside a high-pressure view cell for the visual observation of liquid levels. The view cell was pressurized to suppress boiling of the liquids and was placed in an air bath to stabilize the temperature. Temperature fluctuations in the view cell were less than ±0.1 K. The measurement reproducibility was ±0.1% for density and ±1% for viscosity, whereas the experimental uncertainty was estimated to be ±0.2% for density and ±2% for viscosity. Additional details regarding the apparatus and experimental procedure are given elsewhere.[2−4]

The thermal conductivity was measured using the relative transient hot-wire method in which a Pyrex capillary filled with mercury served as the insulated hot wire. We have previously used this apparatus to measure the thermal conductivity of electrically conducting liquids.[3−5] The hot-wire cell was placed inside a thermostated high-pressure vessel that kept the temperature in the cell constant to within ±0.1 K. The effective length of the wire was obtained by calibration using IUPAC suggested values of the thermal conductivity of water[6] and dimethylphthalate.[7] Each reported value of the measured thermal conductivity was obtained by averaging the results of five experiments. The values were reproducible within ±1% and were estimated to have an uncertainty of ±2%. Further details of the apparatus and technique are given elsewhere.[3−5]

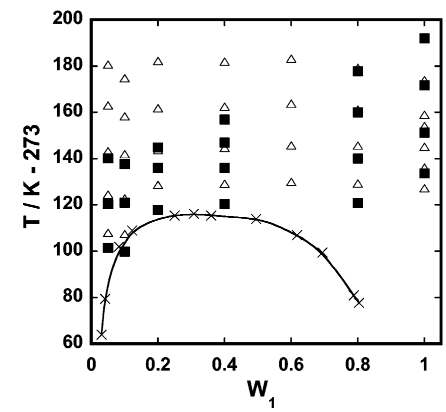

Figure 1. Liquid−liquid equilibrium region for benzoic acid (1) + water (2): ×, data of Sorensen and Arlt; △, temperatures and compositions of density and viscosity measurements in this work; ■, temperatures and pressures of thermal conductivity measurements. The solid line represents the best fit of the data.

Figure 1 shows the single- and two-phase regions of the phase diagram of benzoic acid + water.[9] Values of temperature and concentration chosen for density, viscosity, and thermal conductivity measurements are indicated by points on the phase diagram. All measurements were carried out in the single-phase (liquid) region of the phase diagram.

Results and Discussion

Table 1 lists the experimental densities, viscosities, and thermal conductivities of benzoic acid + water mixtures at mass fractions of benzoic acid given by w_1 = 0.05, 0.1,

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Table 1. Experimental Properties of Benzoic Acid (1) + Water (2) Mixtures

T/K	ρ/kg·m^{-3}	T/K	η/mPa·s	T/K	λ/W m^{-1} K^{-1}
		$w_1 = 0.05$			
379.6	963.7	381.1	0.288	374.6	0.671
394.6	951.9	397.6	0.256	393.6	0.675
413.4	935.5	416.4	0.219	413.3	0.676
433.1	915.2	436.1	0.194		
450.8	896.3	453.8	0.177		
		$w_1 = 0.10$			
379.1	974.1	380.6	0.319	373.0	0.658
392.9	961.0	395.9	0.272	394.2	0.662
412.1	945.4	415.1	0.236	410.9	0.670
428.4	929.6	431.4	0.211		
444.9	912.6	447.9	0.194		
		$w_1 = 0.20$			
400.3	963.5	401.8	0.329	391.0	0.648
413.8	950.8	416.8	0.274	409.2	0.650
431.9	933.7	434.9	0.234	418.0	0.651
452.4	912.0	455.4	0.206		
		$w_1 = 0.40$			
400.8	988.8	402.3	0.501	393.6	0.575
414.8	975.1	417.8	0.383	409.2	0.571
432.6	955.0	435.6	0.309	420.1	0.549
452.1	932.0	455.1	0.263	430.1	0.568
		$w_1 = 0.60$			
401.6	1013.8	403.1	0.708		
415.9	999.2	418.9	0.546		
433.9	981.1	436.9	0.399		
453.4	959.5	456.4	0.334		
		$w_1 = 0.80$			
400.9	1050.1	402.4	0.930	393.9	0.199
414.8	1035.0	418.8	0.690	413.2	0.197
431.3	1018.8	434.3	0.542	433.1	0.192
449.4	1000.5	452.4	0.438	451.0	0.188
		$w_1 = 1.00$			
401.3	1089.5	400.3	1.372	406.8	0.139
410.3	1080.2	409.3	1.238	424.4	0.137
419.3	1069.8	418.3	1.117	444.9	0.134
428.2	1060.2	427.2	1.026	465.1	0.132
432.1	1055.0	432.1	0.953		
447.1	1036.0	447.1	0.802		

0.2, 0.4, 0.6, and 0.8. The Table also lists the measured properties of pure benzoic acid ($w_1 = 1$). The temperature range of the measurements was 375 K to 465 K, and the pressures were about 20 MPa throughout the measurements in order to suppress boiling of the liquids. These pressures were not expected to affect the measurements to any appreciable extent.[6] The highest temperature for the measurement of thermal conductivity was the temperature for the onset of convection in the apparatus. Thus, the thermal conductivity of benzoic acid + water at low concentrations ($w_1 \leq 0.2$) could not be measured at $T \geq$ 430 K.

The density ρ, natural logarithm of viscosity ln η, and thermal conductivity λ of benzoic acid (1) + water (2) can be described by the following equations:

$$\rho = w_1\rho_1 + w_2\rho_2 + (\rho_1 - \rho_2)w_1w_2(A_3 + A_4 w_1 + A_5w_1^{2}) \quad (1a)$$

$$\ln \eta = w_1 \ln \eta_1 + w_2 \ln \eta_2 + (\ln \eta_1 - \ln \eta_2)w_1w_2(B_3 + B_4w_1 + B_5w_1^{2} + B_6 t + B_7tw_1) \quad (1b)$$

$$\lambda = w_1\lambda_1 + w_2\lambda_2 + (\lambda_1 - \lambda_2)w_1w_2(C_3 + C_4w_1 + C_5w_1^{2}) \quad (1c)$$

where $t = T/\mathrm{K} - 273.15$ and w_1 represents the mass fraction. In the case of pure benzoic acid and pure water, ρ_1, ln η_1, and λ_1 are given by

$$(\rho_1/\mathrm{kg{\cdot}m^{-3}}) = A_1 + A_2t \quad (2a)$$

$$\ln(\eta_1/\mathrm{mPa{\cdot}s}) = B_1 + B_2t \quad (2b)$$

$$(\lambda_1/\mathrm{W{\cdot}m^{-1}{\cdot}K^{-1}}) = C_1 + C_2t \quad (2c)$$

Also, ρ_2, ln η_2, and λ_2 were obtained by fitting literature data[6] between 293 K and 473 K and are given below:

$$(\rho_2/\mathrm{kg{\cdot}m^{-3}}) = 1002.17 - 0.116189t - 0.358024 \times 10^{-2}t^2 + 0.373667 \times 10^{-5}t^3 \quad (3a)$$

$$\ln(\eta_2/\mathrm{mPa{\cdot}s}) = -3.758023 + 590.9808/(t + 137.2645) \quad (3b)$$

$$(\lambda_2/\mathrm{W{\cdot}m^{-1}{\cdot}K^{-1}}) = 0.570990 + 0.167156 \times 10^{-2}t - 0.609054 \times 10^{-5}t^2 \quad (3c)$$

Equation 1c was originally proposed by Bohne et al.[9] for the thermal conductivity of aqueous ethylene glycol mixtures as a function of temperature and mass fraction. Analogous equations were therefore used to correlate the density ρ and the natural logarithm of viscosity ln η. Coefficients of eqs 1 and 2 (A_i, B_i, and C_i) obtained by fitting data are given in Table 2, which also lists average absolute deviations (AAD) and maximum absolute deviations (MAD) between experimental data and smoothed (correlated) values. The calculated AAD and MAD are about the experimental uncertainty for all three properties. The results for mixtures are given in Figures 2–4 where the experimental data and the correlations (eqs 1–3) are shown as a function of temperature for $w_1 = 0$ (pure water), 0.05, 0.1, 0.2, 0.4, 0.6, 0.8, and 1 (pure benzoic acid).

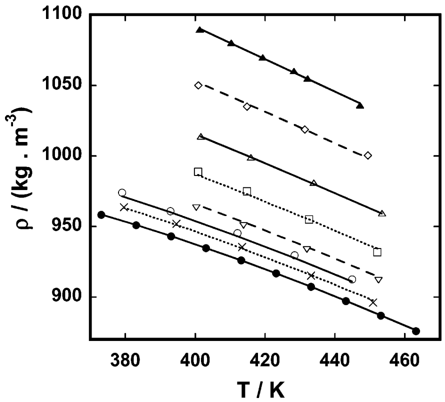

Figure 2. Density of benzoic acid (1) + water (2) mixtures as a function of temperature: ●, $w_1 = 0$; ×, $w_1 = 0.05$; ○, $w_1 = 0.10$; ▽, $w_1 = 0.20$; □, $w_1 = 0.40$; △, $w_1 = 0.60$; ◇, $w_1 = 0.80$; ▲, $w_1 = 1.0$. Solid lines represent best fits of the data.

Table 2. Coefficients A_i, B_i, and C_i of Equations 1 and 2

i	A_i	B_i	C_i
1	1238.1	1.774	0.1598
2	−1.1546	−0.01146	0.1479 × 10^{-3}
3	0.28825	−0.4716	−0.5480
4	−2.2878	4.354	−2.480
5	1.9102	−1.020	4.897
6		0.003999	
7		−0.02778	
AAD %	0.134	2.37	0.54
MAD %	0.275	7.12	2.93

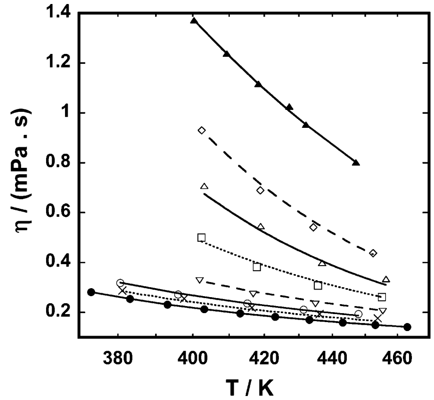

Figure 3. Viscosity of benzoic acid (1) + water (2) mixtures as a function of temperature. (Symbols and lines are the same as in Figure 2.)

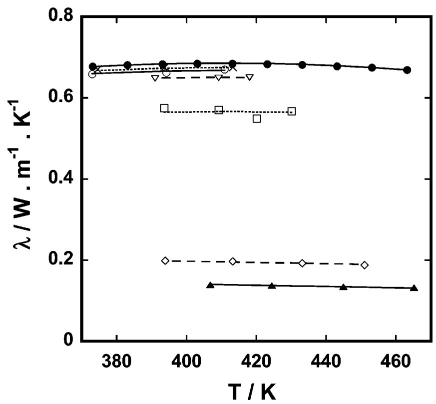

Figure 4. Thermal conductivity of benzoic acid (1) + water (2) mixtures as a function of temperature. (Symbols and lines are the same as in Figure 2.)

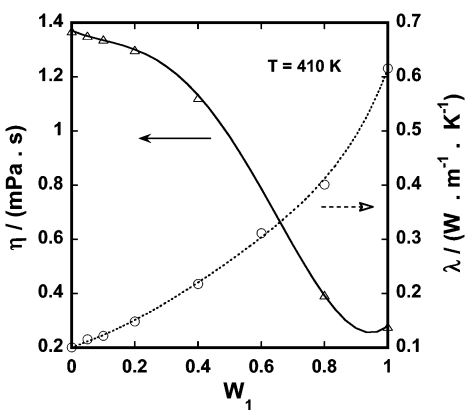

Figure 5. Viscosity (△) and thermal conductivity (○) of benzoic acid (1) + water (2) mixtures as a function of concentration at T = 410 K. Solid lines represent correlations (eqs 1 and 2).

It should be noted that eqs 1a−1c are empirical in nature and are useful only for interpolating experimental data. The minimum in the viscosity shown in Figure 5 should therefore be considered to be an artifact of the form of eq 1b.

Generalized Corresponding States Method

In previous work, the two-reference-fluid generalized corresponding states principle (GCSP) of Teja et al.[10−14] was used with some success to correlate and extrapolate thermophysical property data. The GCSP method relates the quantities $Z_C V_R$, ln $(\eta\xi)$, and $\lambda\phi$ of the mixture to the properties of two reference fluids $r1$ and $r2$ at the same reduced temperature T_R and reduced pressure P_R as follows:

Table 3. GCSP Correlations of the Density, Viscosity, and Thermal Conductivity of Benzoic Acid (1) + Water (2) Mixtures

	data	AAD %	MAD %	θ_{12}	ψ_{12}
[a]density	26	0.28	0.65	1.179	1.180
[a]viscosity	26	4.23	12.1	3.670	2.510
[b]thermal conductivity	17	5.35	9.49	0.619	−0.081

[a] Mole fraction-based mixing rules. [b] Mass fraction-based mixing rules.

$$Z_C V_R = x_1 (Z_C V_R)^{(r1)} + x_2 (Z_C V_R)^{(r2)} \tag{4a}$$

$$\ln(\eta\xi) = x_1 \ln(\eta\xi)^{(r1)} + x_2 \ln(\eta\xi)^{(r2)} \tag{4b}$$

$$\lambda\phi = x_1 (\lambda\,\phi)^{(r1)} + x_2 (\lambda\phi)^{(r2)} \tag{4c}$$

in which

$$\xi = V_C^{\,2/3} T_C^{\,-1/2} M^{-1/2} \tag{5a}$$

$$\phi = V_C^{\,2/3} T_C^{\,-1/2} M^{1/2} \tag{5b}$$

In the above equations, Z is the compressibility, and V is the volume. The subscript C denotes the critical point, and superscripts $r1$ and $r2$ denote the properties of two reference fluids. These equations can be extended to mixtures using

$$V_C = \Sigma\Sigma\, x_i x_j V_{Cij} \tag{6a}$$

$$T_C V_C = \Sigma\Sigma\, x_i x_j T_{Cij} V_{Cij} \tag{6b}$$

$$Z_C = \Sigma\, x_i Z_{Ci} \tag{6c}$$

where subscripts i and ii denote pure-component properties. When $(i \neq j)$,

$$V_{Cij} = \frac{1}{8}(V_{Ci}^{\,1/3} + V_{Cj}^{\,1/3})^3 \times \theta_{ij} \tag{7a}$$

$$T_{Cij} V_{Cij} = (T_{Cii} T_{Cjj} V_{Ci} V_{Cj})^{1/2} \times \psi_{ij} \tag{7b}$$

θ_{ij} and ψ_{ij} are binary interaction parameters that must be obtained by fitting experimental data. Critical properties (experimental or estimated values) of pure benzoic acid and water required in the calculations were obtained from the literature.[15] Other required properties were calculated from eqs 2 and 3. It was found that density and viscosity could be correlated better using mole fraction-based mixing rules, whereas thermal conductivity could be better correlated using mass fraction-based mixing rules. Binary interaction coefficients determined using the GCSP model are listed in Table 3 together with the corresponding AAD and MAD. The Table shows reasonable results using two adjustable parameters per binary system for each property.

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