

Short Articles

Densities and Viscosities of Binary Mixtures of Acetic Acid with Acetic Anhydride and Methenamine at Different Temperatures

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Densities and viscosities of the binary mixtures of acetic acid + acetic anhydride have been measured at temperatures from (293.15 to 338.15) K and atmospheric pressure over the whole concentration range of compositions. The excess molar volume (V^E) and viscosity deviation ($\Delta\eta$) were calculated from the experimental data and correlated by the Redlich–Kister equation. In addition, densities and viscosities of methenamine + acetic acid solutions were measured, and the results were represented by third-order and fourth-order (empirical) polynomials in terms of mole fraction of methenamine.

Introduction

Densities and viscosities are important fundamental data for the chemical design and the optimization of chemical process. They are also necessary for engineering calculation and research of mass transfer, heat transfer, and fluid flow. Acetic acid is a useful organic compound, and its mixture with acetic anhydride is required in many organic processes, such as the production of chloroacetic acid and dichloroacetic acid.^{1–4} So there is practical and theoretical value in determining the densities and viscosities of a binary mixture of acetic acid with acetic anhydride.

Densities and viscosities of the pure acetic acid and acetic anhydride have been reported in the literature, but densities and viscosities are few for a binary mixture of acetic acid with acetic anhydride. A survey of the literature shows that Pavol et al.¹³ measured the kinematic viscosities ν of the binary mixture of acid with acetic anhydride. In this work, we present density and viscosity data for the binary system of acetic acid + acetic anhydride from (293.15 to 338.15) K. The excess volume (V^E) and viscosity deviation ($\Delta\eta$) over the whole mole fraction range for this binary mixture have been fitted to the Redlich–Kister equation. Densities and viscosities of methenamine + acetic acid are also determined and represented by third-order and fourth-order (empirical) polynomials in terms of mole fraction of methenamine. The standard deviations (σ) and the absolute average deviation (AAD) between the experimental data and calculated values are also presented.

Experimental Section

Materials. All of the chemicals used in this study were obtained from Sinopharm Chemical Reagent Co., Ltd. The mass fraction purities, tested by gas chromatography, were as follows: acetic acid (0.995), acetic anhydride (0.985), and methenamine (0.995). All chemicals were used without further purification.

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Table 1. Comparison of Experimental and Literature Values of Densities ρ and viscosities η for Pure Compounds

T/K	$\rho/\text{g}\cdot\text{cm}^{-3}$		$\eta/\text{mPa}\cdot\text{s}$	
	exptl	lit.	exptl	lit.
Acetic Acid				
293.15	1.04942	1.04955 ⁵	1.204	1.2258 ⁷
		1.04928 ⁶		
		1.0493 ⁷		
298.15	1.04376	1.04392 ⁵	1.114	1.06 ⁸
		1.04378 ⁶		1.056 ⁹
		1.0436 ⁷		1.1150 ¹¹
		1.0440 ⁸		1.056 ¹⁵
		1.04392 ⁹		
303.15	1.03810	1.0365 ¹¹	1.037	0.98 ⁸
		1.03825 ⁵		1.024 ¹⁰
		1.0383 ⁸		1.042 ¹²
		1.0380 ¹²		1.04 ¹⁴
308.15	1.03244	1.0325 ⁷	0.964	0.9795 ⁷
		1.0325 ⁸		0.91 ⁸
		1.0323 ¹²		0.972 ¹²
323.15	1.01544	1.0155 ¹²	0.787	0.798 ¹²
				0.786 ¹⁵
328.15	1.00977	1.0102 ¹²	0.741	0.752 ¹²
333.15	1.00409	1.00400 ⁶ (333.26 K)	0.697	0.70 ¹⁴ (332.15 K)
338.15	0.99838	0.99646 ⁵ (340.15 K)	0.657	–
Acetic Anhydride				
293.15	1.08089	1.082 ¹⁶	0.888	0.907 ¹⁵
303.15	1.06871	–	0.778	0.783 ¹⁴
313.15	1.05650	–	0.688	0.699 ¹⁵

These liquids were dried over 4 Å molecular sieves and partially degassed by ultrasound prior to use. Their purities were further checked by measuring and comparing the densities and viscosities with their corresponding literature values as shown in Table 1.

Apparatus and Procedure. The density of the compounds and their binary mixtures was measured by an Anton Paar DMA 4500 oscillating U-tube densitometer with reproducibility of $\pm 1\cdot 10^{-5}$ g·cm⁻³. The temperature in the cell was regulated to ± 0.01 K with a solid-state thermostat. The apparatus was calibrated once a day with dry air and double-distilled freshly

Table 2. Densities ρ , Viscosities η , Excess Mole Volumes V^E , and Viscosity Deviations $\Delta\eta$ for the Binary Mixture of Acetic Acid (1) + Acetic Anhydride (2) at Different Temperatures

x_1	ρ g·cm ⁻³	η mPa·s	V^E cm ³ ·mol ⁻¹	$\Delta\eta$ mPa·s	x_1	ρ g·cm ⁻³	η mPa·s	V^E cm ³ ·mol ⁻¹	$\Delta\eta$ mPa·s
$T = 293.15$ K									
0.0000	1.08089	0.888	0.0000	0.000	0.4999	1.06956	0.975	-0.0383	-0.071
0.1000	1.07928	0.905	-0.0315	-0.015	0.5965	1.06668	1.004	-0.0446	-0.072
0.2000	1.07719	0.920	-0.0355	-0.032	0.6992	1.06310	1.041	-0.0394	-0.068
0.2999	1.07493	0.934	-0.0406	-0.049	0.8004	1.05919	1.084	-0.0363	-0.057
0.3996	1.07242	0.954	-0.0425	-0.061	0.8976	1.05494	1.145	-0.0309	-0.027
					1.0000	1.04942	1.204	0.0000	0.000
$T = 298.15$ K									
0.0000	1.07480	0.829	0.0000	0.000	0.4999	1.06366	0.908	-0.0406	-0.063
0.1000	1.07324	0.844	-0.0338	-0.014	0.5965	1.06080	0.933	-0.0455	-0.066
0.2000	1.07118	0.859	-0.0378	-0.027	0.6992	1.05727	0.966	-0.0403	-0.062
0.2999	1.06896	0.872	-0.0435	-0.043	0.8004	1.05341	1.008	-0.0369	-0.049
0.3996	1.06647	0.887	-0.0441	-0.055	0.8976	1.04921	1.057	-0.0310	-0.027
					1.0000	1.04376	1.114	0.0000	0.000
$T = 303.15$ K									
0.0000	1.06870	0.778	0.0000	0.000	0.4999	1.05775	0.849	-0.0427	-0.058
0.1000	1.06718	0.793	-0.0352	-0.011	0.5965	1.05493	0.874	-0.0474	-0.059
0.2000	1.06517	0.805	-0.0408	-0.025	0.6992	1.05145	0.903	-0.0421	-0.056
0.2999	1.06298	0.819	-0.0462	-0.037	0.8004	1.04764	0.936	-0.0383	-0.049
0.3996	1.06053	0.831	-0.0471	-0.051	0.8976	1.04348	0.985	-0.0313	-0.025
					1.0000	1.03810	1.037	0.0000	0.000
$T = 308.15$ K									
0.0000	1.06261	0.729	0.0000	0.000	0.4999	1.05183	0.793	-0.0436	-0.053
0.1000	1.06112	0.742	-0.0358	-0.010	0.5965	1.04905	0.814	-0.0483	-0.055
0.2000	1.05915	0.754	-0.0423	-0.022	0.6992	1.04562	0.842	-0.0431	-0.051
0.2999	1.05700	0.768	-0.0483	-0.032	0.8004	1.04185	0.873	-0.0384	-0.044
0.3996	1.05457	0.777	-0.0480	-0.046	0.8976	1.03775	0.919	-0.0315	-0.021
					1.0000	1.03244	0.964	0.0000	0.000
$T = 313.15$ K									
0.0000	1.05649	0.688	0.0000	0.000	0.4999	1.04590	0.748	-0.0455	-0.047
0.1000	1.05506	0.699	-0.0390	-0.011	0.5965	1.04316	0.766	-0.0499	-0.050
0.2000	1.05312	0.710	-0.0453	-0.021	0.6992	1.03978	0.791	-0.0446	-0.047
0.2999	1.05100	0.721	-0.0510	-0.031	0.8004	1.03606	0.820	-0.0394	-0.039
0.3996	1.04860	0.734	-0.0500	-0.040	0.8976	1.03201	0.860	-0.0318	-0.020
					1.0000	1.02677	0.902	0.0000	0.000
$T = 318.15$ K									
0.0000	1.05038	0.648	0.0000	0.000	0.4999	1.03996	0.703	-0.0459	-0.041
0.1000	1.04896	0.659	-0.0377	-0.008	0.5965	1.03726	0.721	-0.0494	-0.042
0.2000	1.04707	0.666	-0.0458	-0.020	0.6992	1.03393	0.743	-0.0447	-0.040
0.2999	1.04499	0.678	-0.0521	-0.028	0.8004	1.03027	0.770	-0.0398	-0.032
0.3996	1.04262	0.688	-0.0505	-0.037	0.8976	1.02628	0.800	-0.0322	-0.021
					1.0000	1.02111	0.841	0.0000	0.000
$T = 323.15$ K									
0.0000	1.04424	0.610	0.0000	0.000	0.4999	1.03401	0.661	-0.0472	-0.037
0.1000	1.04287	0.621	-0.0400	-0.007	0.5965	1.03134	0.676	-0.0504	-0.039
0.2000	1.04101	0.627	-0.0479	-0.018	0.6992	1.02806	0.699	-0.0448	-0.034
0.2999	1.03896	0.638	-0.0537	-0.025	0.8004	1.02446	0.723	-0.0400	-0.028
0.3996	1.03663	0.649	-0.0522	-0.032	0.8976	1.02054	0.751	-0.0328	-0.018
					1.0000	1.01544	0.787	0.0000	0.000
$T = 328.15$ K									
0.0000	1.03807	0.580	0.0000	0.000	0.4999	1.02804	0.625	-0.0485	-0.036
0.1000	1.03674	0.587	-0.0412	-0.009	0.5965	1.02539	0.639	-0.0497	-0.037
0.2000	1.03494	0.595	-0.0513	-0.018	0.6992	1.02218	0.660	-0.0450	-0.032
0.2999	1.03291	0.603	-0.0556	-0.025	0.8004	1.01864	0.680	-0.0401	-0.028
0.3996	1.03061	0.614	-0.0531	-0.031	0.8976	1.01479	0.708	-0.0330	-0.016
					1.0000	1.00977	0.741	0.0000	0.000
$T = 333.15$ K									
0.0000	1.03190	0.548	0.0000	0.000	0.4999	1.02205	0.590	-0.0486	-0.032
0.1000	1.03063	0.556	-0.0443	-0.007	0.5965	1.01944	0.605	-0.0493	-0.032
0.2000	1.02883	0.562	-0.0515	-0.016	0.6992	1.01630	0.622	-0.0456	-0.030
0.2999	1.02684	0.570	-0.0561	-0.023	0.8004	1.01282	0.640	-0.0406	-0.027
0.3996	1.02457	0.580	-0.0528	-0.027	0.8976	1.00903	0.665	-0.0332	-0.017
					1.0000	1.00409	0.697	0.0000	0.000
$T = 338.15$ K									
0.0000	1.02570	0.521	0.0000	0.000	0.4999	1.01604	0.558	-0.0494	-0.031
0.1000	1.02448	0.530	-0.0466	-0.005	0.5965	1.01348	0.575	-0.0503	-0.027
0.2000	1.02271	0.533	-0.0534	-0.015	0.6992	1.01039	0.590	-0.0463	-0.026
0.2999	1.02075	0.542	-0.0574	-0.020	0.8004	1.00697	0.605	-0.0412	-0.025
0.3996	1.01852	0.551	-0.0540	-0.025	0.8976	1.00324	0.629	-0.0334	-0.014
					1.0000	0.99838	0.657	0.0000	0.000

Table 3. Coefficients of the Redlich–Kister Equation and Standard Deviation for Excess Mole Volumes V^E and Viscosity Deviations $\Delta\eta$ of Binary Mixtures of Acetic Acid + Acetic Anhydride

T/K	property	A_0	A_1	A_2	σ
293.15	$V^E/\text{cm}^3 \cdot \text{mol}^{-1}$	-0.1603	0.0086	-0.2298	0.0030
	$\Delta\eta/\text{mPa} \cdot \text{s}$	-0.2848	-0.1113	0.0530	0.0022
298.15	$V^E/\text{cm}^3 \cdot \text{mol}^{-1}$	-0.1670	0.0109	-0.2386	0.0028
	$\Delta\eta/\text{mPa} \cdot \text{s}$	-0.2541	-0.1088	0.0438	0.0007
303.15	$V^E/\text{cm}^3 \cdot \text{mol}^{-1}$	-0.1767	0.0186	-0.2442	0.0026
	$\Delta\eta/\text{mPa} \cdot \text{s}$	-0.2307	-0.1113	0.0296	0.0017
308.15	$V^E/\text{cm}^3 \cdot \text{mol}^{-1}$	-0.1812	0.0240	-0.2472	0.0026
	$\Delta\eta/\text{mPa} \cdot \text{s}$	-0.2105	-0.1045	0.0402	0.0019
313.15	$V^E/\text{cm}^3 \cdot \text{mol}^{-1}$	-0.1883	0.0350	-0.2644	0.0027
	$\Delta\eta/\text{mPa} \cdot \text{s}$	-0.1878	-0.0886	0.0135	0.0012
318.15	$V^E/\text{cm}^3 \cdot \text{mol}^{-1}$	-0.1898	0.0354	-0.2624	0.0023
	$\Delta\eta/\text{mPa} \cdot \text{s}$	-0.1645	-0.0695	0.0071	0.0008
323.15	$V^E/\text{cm}^3 \cdot \text{mol}^{-1}$	-0.1940	0.0452	-0.2740	0.0025
	$\Delta\eta/\text{mPa} \cdot \text{s}$	-0.1474	-0.0581	0.0145	0.0009
328.15	$V^E/\text{cm}^3 \cdot \text{mol}^{-1}$	-0.1962	0.0579	-0.2898	0.0020
	$\Delta\eta/\text{mPa} \cdot \text{s}$	-0.1401	-0.0500	0.0018	0.0009
333.15	$V^E/\text{cm}^3 \cdot \text{mol}^{-1}$	-0.1977	0.0617	-0.3110	0.0025
	$\Delta\eta/\text{mPa} \cdot \text{s}$	-0.1245	-0.0552	-0.0155	0.0009
338.15	$V^E/\text{cm}^3 \cdot \text{mol}^{-1}$	-0.1981	0.0688	-0.3247	0.0027
	$\Delta\eta/\text{mPa} \cdot \text{s}$	-0.1136	-0.0496	-0.0026	0.0019

degassed water. The density of water was taken from Perry's Chemical Engineers' Handbook. The uncertainty in density measurements was $\pm 5 \cdot 10^{-5} \text{ g} \cdot \text{cm}^{-3}$. Density measurements were reproducible to $\pm 3 \cdot 10^{-5} \text{ g} \cdot \text{cm}^{-3}$.

Airtight stoppered bottles were used for the preparation of the mixtures. The mass of the dry bottle was first determined. The less volatile component of the mixture was introduced in the bottle, and the total mass was recorded. The other component was introduced, and the mass of the bottle along with the two components was determined. Each mixture was immediately used after it was well mixed by shaking. All the weightings were performed on an electronic balance (BS224S) accurate to $\pm 0.1 \text{ mg}$. The uncertainty in the mole fraction is estimated to be lower than $\pm 2 \cdot 10^{-4}$. The molar excess volumes were calculated from composition–density data with an uncertainty better than $\pm 0.002 \text{ cm}^3 \cdot \text{mol}^{-1}$. All mole quantities were based on the IUPAC relative atomic mass table.¹⁷

The viscosities of pure liquids and the mixtures were measured at atmospheric pressure and different temperatures using a commercial Ubbelohde capillary viscometer (type 1836-A, Shanghai Glass Instruments Factory, China) of 0.55 mm diameter. The viscometer was immersed in a thermostatic water bath (TV-4000, TAMSON) with temperature regulated within

$\pm 0.01 \text{ K}$. An electronic digital stopwatch with a readability of $\pm 0.01 \text{ s}$ was used for flow time measurement. Experiments were repeated a minimum of four times at each temperature for all mixtures, and the results were averaged. The viscosity η of the liquid was then calculated from the following relationship

$$\nu = \frac{\eta}{\rho} = k(t - \theta) \quad (1)$$

where t is the flow time; ν is the kinematic viscosity; and k and θ are the viscometer constant and the Hagenbach correction factor, respectively. The viscosity η was then calculated from the density ρ by the relation $\eta = \nu\rho$. The value k for the 0.55 mm diameter was provided by the manufacturer. The value θ , which is dependent on the flow time and the size of capillary, was taken from the tables supplied by the manufacturer.

The calibration of the viscometer was carried out with double distilled water and twice-distilled 1-octanol. During the heating, to minimize the evaporation losses, the viscometer's limbs are closed with Teflon caps. During the measurements of flow time, the caps of the limbs were removed. The overall uncertainty of the viscosity measurements is dependent on the temperature control of the viscometer, the time of the flow, and the mole fraction of the mixtures, which are of the order of $1 \cdot 10^{-2} \text{ K}$, $1 \cdot 10^{-2} \text{ s}$, and $3 \cdot 10^{-4}$, respectively. The uncertainty of viscosity measurements was within $\pm 0.005 \text{ mPa} \cdot \text{s}$.

Results and Discussion

1. Binary Mixtures of Acetic Acid + Acetic Anhydride. The experimental values of density and viscosity for the binary mixture at different temperatures and at atmospheric pressure are listed in Table 2. Excess molar volumes were calculated from our measurements according to the following equation

$$V^E = \frac{x_1 M_1 + x_2 M_2}{\rho} - \left(\frac{x_1 M_1}{\rho_1} + \frac{x_2 M_2}{\rho_2} \right) \quad (2)$$

where x_1 and x_2 are mole fractions; M_1 and M_2 are the molar masses; and ρ_1 and ρ_2 are the densities of pure components 1 and 2, respectively. Quantities without subscripts refer to the mixture.

The viscosity derivations were calculated from the following relation¹⁸

$$\Delta\eta = \eta - (x_1 \eta_1 + x_2 \eta_2) \quad (3)$$

where η is the viscosity of mixtures, and η_1 and η_2 are the

Table 4. Densities ρ and Viscosities η for the Methenamine (1) + Acetic Acid (2) Solutions at Different Temperatures

x_1	ρ	η	ρ	η	ρ	η	ρ	η	ρ	η
	$\text{g} \cdot \text{cm}^{-3}$	$\text{mPa} \cdot \text{s}$	$\text{g} \cdot \text{cm}^{-3}$	$\text{mPa} \cdot \text{s}$	$\text{g} \cdot \text{cm}^{-3}$	$\text{mPa} \cdot \text{s}$	$\text{g} \cdot \text{cm}^{-3}$	$\text{mPa} \cdot \text{s}$	$\text{g} \cdot \text{cm}^{-3}$	$\text{mPa} \cdot \text{s}$
	$T = 293.15 \text{ K}$		$T = 298.15 \text{ K}$		$T = 303.15 \text{ K}$		$T = 308.15 \text{ K}$		$T = 313.15 \text{ K}$	
0.0000	1.04942	1.024	1.04376	1.114	1.03810	1.037	1.03244	0.964	1.02677	0.902
0.0201	1.05860	1.497	1.05266	1.367	1.04665	1.248	1.0428	1.148	1.03620	1.059
0.0401	1.06670	1.865	1.06141	1.682	1.05587	1.523	1.05060	1.383	1.04566	1.268
0.0600	1.07567	2.363	1.07038	2.106	1.06517	1.893	1.05992	1.703	1.05502	1.549
0.0801	1.08577	3.021	1.08066	2.655	1.07544	2.355	1.06893	2.091	1.06352	1.879
0.1000	1.09187	3.841	1.08654	3.333	1.08161	2.919	1.07658	2.565	1.07168	2.296
0.1201	1.10076	4.951	1.09579	4.254	1.09080	3.657	1.08604	3.179	1.08127	2.806
0.1500	1.11119	7.154	1.10618	5.988	1.10114	5.085	1.09634	4.368	1.09163	3.821
	$T = 318.15 \text{ K}$		$T = 323.15 \text{ K}$		$T = 328.15 \text{ K}$		$T = 333.15 \text{ K}$			
0.0000	1.02111	0.841	1.01544	0.787	1.00977	0.741	1.00409	0.697		
0.0201	1.03010	0.992	1.02435	0.909	1.01923	0.845	1.01476	0.790		
0.0401	1.03961	1.179	1.03421	1.072	1.02898	0.988	1.02469	0.919		
0.0600	1.04952	1.435	1.04405	1.296	1.03922	1.185	1.03416	1.096		
0.0801	1.05774	1.719	1.05240	1.541	1.04733	1.395	1.04304	1.279		
0.1000	1.06560	2.073	1.06071	1.842	1.05572	1.657	1.05163	1.515		
0.1201	1.07649	2.512	1.06906	2.203	1.06400	1.970	1.05977	1.776		
0.1500	1.08600	3.352	1.08090	2.893	1.07588	2.545	1.07194	2.285		

viscosity of components 1 and 2, respectively. The data of excess molar volume and viscosity deviation are shown in Table 2.

The values of V^E and $\Delta\eta$ for each mixture were fitted to the Redlich–Kister equation

$$Y = x_1(1 - x_1) \sum_{i=0}^n A_i(2x_1 - 1)^i \quad (4)$$

where $Y = V^E$ or $\Delta\eta$; A_i are adjustable parameters; and x_1 is the fraction of component 1. In each case, the optimum number of coefficients (A_i) was determined from an examination of the variation of the standard derivation

$$\sigma(Y) = \left[\sum (Y_{\text{cal}} - Y_{\text{exp}})^2 / (n - m) \right]^{1/2} \quad (5)$$

where n is the total number of experimental values and m is the number of parameters. Table 3 lists the values of the parameters A_i together with the standard deviations.

The excess molar volume V^E versus the mole fraction of acetic acid x_1 is plotted in Figure 1. The excess thermodynamic properties, which depend on the composition and/or temperature, are of great importance in understanding the nature of molecular aggregation that exists in the binary mixtures. The values of excess molar volume were negative for acetic acid + acetic anhydride mixtures at all temperatures and over the whole concentration range of compositions. The excess molar volumes V^E decrease slightly with an increase in temperature from (293.15 to 338.15) K.

The dependence of the viscosity deviations $\Delta\eta$ on mole fraction of acetic acid x_1 was displayed in Figure 2. The values of viscosity deviations were also negative over the whole range of compositions, and the minimum existed at about $x_1 = 0.6$ within the whole region of experimental temperatures. The viscosity deviations increased slightly with an increase in temperature from (293.15 to 338.15) K.

2. Methenamine + Acetic acid Solutions. Densities and viscosities of the methenamine (1) + acetic acid (2) solutions were measured from $T = (293.15 \text{ to } 338.15) \text{ K}$ and in the mole fraction $x_1 = (0.0201 \text{ to } 0.15)$. The measured density values were listed in Table 4 and were regressed by the following equation¹⁹

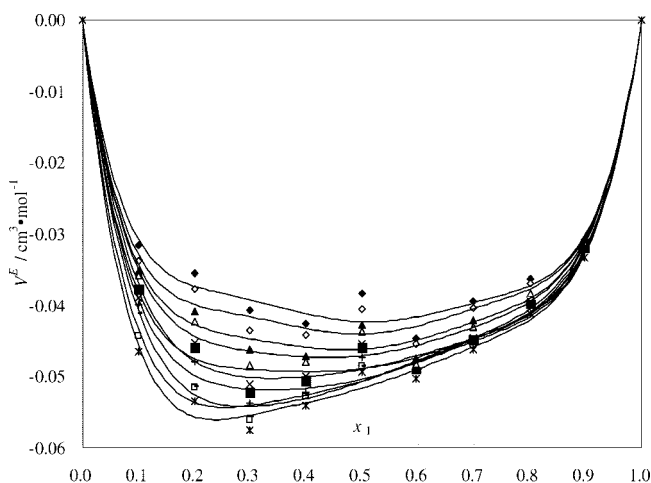


Figure 1. Excess molar volume V^E vs mole fraction of acetic acid x_1 for acetic acid (1) + acetic anhydride (2). \blacklozenge , 293.15 K; \diamond , 298.15 K; \blacktriangle , 303.15 K; \triangle , 308.15 K; \times , 313.15 K; \blacksquare , 318.15 K; $+$, 323.15 K; $-$, 328.15 K; \square , 333.15 K; $*$, 338.15 K. The symbols represent experimental values, and solid curves were correlated by the Redlich–Kister equation.

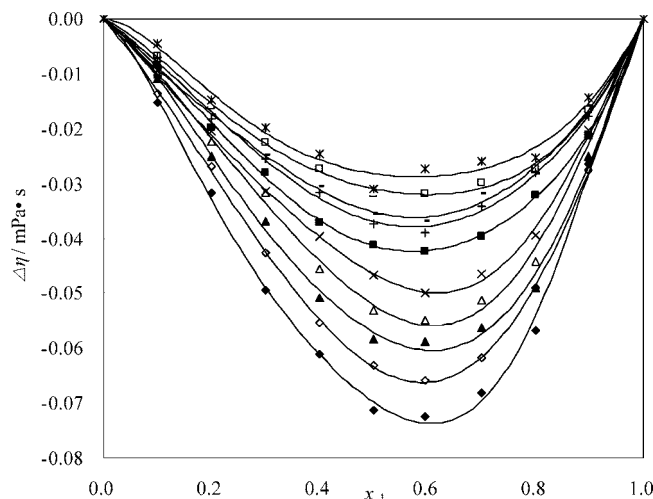


Figure 2. Viscosity deviation $\Delta\eta$ vs mole fraction of acetic acid x_1 for acetic acid (1) + acetic anhydride (2). \blacklozenge , 293.15 K; \diamond , 298.15 K; \blacktriangle , 303.15 K; \triangle , 308.15 K; \times , 313.15 K; \blacksquare , 318.15 K; $+$, 323.15 K; $-$, 328.15 K; \square , 333.15 K; $*$, 338.15 K. The symbols represent experimental values, and solid curves were correlated by the Redlich–Kister equation.

Table 5. Calculated Parameters (Obtained by Least-Squares Optimization) in the Expression for the Densities of Methenamine (1) + Acetic Acid (2) Solutions

T/K	$\alpha/g \cdot \text{cm}^{-3}$	$\beta/g \cdot \text{cm}^{-3}$	100 AAD ^a
293.15	0.4946	-0.2062	0.050
298.15	0.5011	-0.2110	0.058
303.15	0.5067	-0.2122	0.063
308.15	0.5029	-0.1871	0.042
313.15	0.5225	-0.2231	0.033
318.15	0.5113	-0.1878	0.061
323.15	0.5178	-0.2071	0.027
328.15	0.5416	-0.2590	0.025
333.15	0.5803	-0.3322	0.006

^a AAD = $(1/N) \sum_{i=1}^N |(\rho_i - \rho_i^{\text{calc}})| / \rho_i$; N = number of data points.

$$\rho = \rho_0 + \alpha x + \beta x^{32} \quad (6)$$

where α and β are the parameters; x is the mole fraction of methenamine; and ρ_0 is the density of solvent. The parameters obtained from a least-squares analysis for α and β are shown in Table 5. The equation gave a satisfactory description with the absolute average deviation (AAD).

The measured viscosity values were also listed in Table 4. Viscosity data were modeled using the following fourth-order polynomial expression¹⁹

$$\eta = \eta_0 + ax + bx^2 + cx^3 + dx^4 \quad (7)$$

where η and η_0 are the viscosities of the solution and the solvent, respectively; x is the mole fraction of methenamine; and a , b , c , and d are constants. Table 6 lists the values of the parameters a , b , c , and d together with the AAD.

Conclusion

Densities and viscosities of the binary mixture of acetic acid + acetic anhydride were measured at different temperatures and atmospheric pressure over the whole composition range. The excess molar volumes V^E and viscosity deviations $\Delta\eta$ were correlated using the Redlich–Kister polynomial equation. V^E values are negative for the binary mixtures and increase with temperature increase. The deviations of viscosity $\Delta\eta$ are negative for the binary mixtures over the entire composition range and become less negative with increasing temperature. Densities and viscosities of the methenamine + acetic acid

Table 6. Calculated Parameters (Obtained by Least-Squares Optimization) in the Expression for the Viscosities of Methenamine (1) + Acetic Acid (2) Solutions

<i>T</i> /K	<i>a</i> /mPa·s	<i>b</i> /mPa·s	<i>c</i> /mPa·s	<i>d</i> /mPa·s	100 AAD ^a
293.15	12.5980	81.2346	402.7790	1725.1	0.160
298.15	11.4531	43.7528	668.6045	-163.7404	0.184
303.15	8.6136	89.6907	-44.0099	1752.9	0.162
308.15	7.4051	82.3031	-133.2738	1761.1	0.174
313.15	6.0073	90.5897	-322.4563	2176.8	0.149
318.15	6.1003	68.5670	-214.8807	1539.1	0.219
323.15	4.4107	85.2896	-438.1814	1951.1	0.185
328.15	3.8942	69.0881	-288.8111	1266.8	0.220
333.15	15.4849	-189.4503	1791.7	-4632.3	0.862

^a AAD = $(1/N)\sum_{i=1}^N |(\eta_i - \eta_i^{\text{calc}})|/\eta_i$; *N* = number of data points.

system were measured, and the data for each property were correlated with the Masson equation and fourth-order polynomial, respectively. The goodness of the fitting eqs 6 and 7 was evaluated using AAD.

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