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Densities and Viscosities of Binary and Ternary Mixtures and Aqueous Two-Phase System of Poly(ethylene glycol) 2000 + Diammonium Hydrogen Citrate + Water at Different Temperatures

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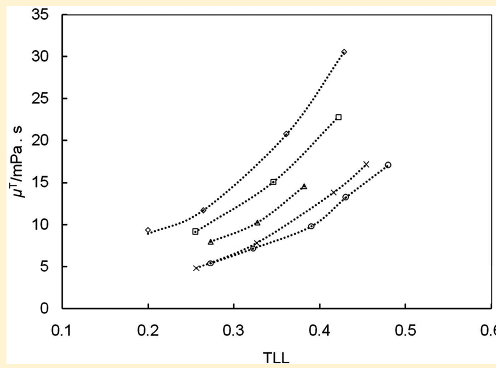
ABSTRACT: The densities and viscosities of aqueous solutions of poly(ethylene glycol) (PEG-2000) and diammonium hydrogen citrate were determined for mass fractions from 0.05 to 0.5 at different temperatures of (298.15, 303.15, 308.15, 313.15, and 318.15) K. The density data show a linear variation with mass fraction of the polymer and salt for all temperatures. The viscosity data of PEG 2000 and diammonium hydrogen citrate solutions were correlated as a function of mass fraction, using a nonlinear equation, for the five different temperatures covered in the present work. Densities and viscosities of PEG–diammonium hydrogen citrate two-phase systems have also been measured at (298.15, 303.15, 308.15, 313.15, and 318.15) K and are correlated with composition. The tie-line lengths (TLL) of the aqueous two-phase systems have also been estimated.



INTRODUCTION

Aqueous two-phase extraction has emerged as an efficient tool for the recovery and partial purification of the desired biomolecule from complex solutions such as fermentation broth, industrial effluent, and so forth. Aqueous two-phase systems can be formed by mixing appropriate amounts of polymer, salt/polymer, and water at a particular temperature and pH. It has several advantages over conventional liquid–liquid extraction and other downstream unit operations, such as the high (80 to 90%) water content in both phases provides a hydrophilic environment for the biomolecules, low interfacial tension (10^{-4} to 10^{-1} mN·m^{-1}),[1] easy scale-up, low energy, continuous operation,[2,3] integration of recovery and concentration in a single step, and high yield. A polymer–salt system is preferred over the polymer–polymer system due to high density difference, low viscosity, and low cost of salt compared to polymer.[4] Citrate and tartrate salts are more preferable due to its low impact on environment.[5] Data on the physicochemical properties of the system are necessary to design the extraction process[6] and are available for few PEG–salt systems in the literature.[6−9] Recently the authors published the binodal and liquid–liquid equilibrium data for the PEG 2000 + diammonium hydrogen citrate system.[10] In the present work, densities, viscosities, and refractive indices of the binary (PEG 2000 + water and diammonium hydrogen citrate +water), ternary (PEG 2000 + diammonium hydrogen citrate + water) solutions, and individual phases (top and bottom phases) of the aqueous two-phase system were estimated at different temperatures. The experimental results were analyzed and fitted to correlations used in the literature for various similar systems.[6−9]

MATERIALS AND METHODS

Materials. Polyethylene glycol [HO-$(CH_2CH_2O)_n$-CH_2OH] and poly(ethane-1,2-diol)-2000 (PEG-2000) (Catalog No. 8.21037.1000) with an average molar mass of 1800 g·mol^{-1} were purchased from Merck, and diammonium hydrogen citrate [$(NH_4)_2HC_6H_5O_7$] (CAS No. 3012-65-5) with a molar mass of 226.18 g·mol^{-1} and minimum mole fraction purity of 0.99 was purchased from Sigma-Aldrich and used without further purification. Double-distilled water was used for all of the experiments.

Apparatus and Procedure. Single phase binary systems (PEG 2000 + water and diammonium hydrogen citrate + water) were prepared by varying the PEG and salt concentration from 0 to 0.50 weight fraction and the ternary systems with the PEG 2000 and salt concentration in the range of 0.05 to 0.20 weight fraction. The solutions were prepared in a 50 cm^3 centrifuge tube by adding solutions of appropriate mass using an analytical balance (model AR2140, OHAUS-Essae-Teraoka Ltd., Japan) with an accuracy of ± 0.01 mg. The solutions were maintained at working temperature in thermostatic bath (model RW-0525G, Refrigerating Bath, JEIO Tech) with an uncertainty of ± 0.1 K.

The concentration of PEG 2000 and salt required to form the two-phase region was identified from the phase diagram.[10] The solutions were prepared in 50 cm^3 capped centrifuge tubes and were subjected to low speed centrifugation to hasten phase separation. The solutions were kept undisturbed for 12 h at appropriate temperature in a thermostatic bath to ensure proper

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Table 1. Coefficients of Equation 1[a]

T/K	a_0	a_1	a_2	AARD/%
298.15	1.334	0.1388	0.173	0.0484
303.15	1.333	0.1405	0.1772	0.0481
308.15	1.332	0.1415	0.1767	0.0499
313.15	1.3315	0.1409	0.1763	0.058
318.15	1.331	0.1396	0.1793	0.033

[a]Average arithmetic relative deviation (AARD) = $(\Sigma|(\text{exptl} - \text{cal})/(\text{exptl})|)/(N)\cdot 100$. Standard uncertainty u is $u(T) = \pm\ 0.1$ K.

Table 2. Densities of the PEG 2000 + Water and Diammonium Hydrogen Citrate + Water Systems at Various Temperatures[a]

	aqueous PEG 2000 solution density, $10^3\ \rho$/kg·m^{-3}				
W_P	298.15 K	303.15 K	308.15 K	313.15 K	318.15 K
0.0000	0.9970	0.9956	0.9940	0.9922	0.9902
0.0500	1.0053	1.0034	1.0023	0.9998	0.9983
0.1000	1.0132	1.0111	1.0103	1.0087	1.0068
0.1500	1.0223	1.0212	1.0193	1.0177	1.0156
0.2000	1.0305	1.0306	1.0282	1.0271	1.0257
0.2500	1.0386	1.0374	1.0358	1.0334	1.0320
0.3000	1.0481	1.0467	1.0451	1.0431	1.0418
0.3500	1.0580	1.0563	1.0541	1.0520	1.0505
0.4000	1.0686	1.0661	1.0636	1.0599	1.0576
0.5000	1.0863	1.0827	1.0801	1.0766	1.0742
	aqueous diammonium hydrogen citrate solution density, $10^3\ \rho$/kg·m^{-3}				
W_S	298.15 K	303.15 K	308.15 K	313.15 K	318.15 K
0.0000	0.9970	0.9956	0.9940	0.9922	0.9902
0.0500	1.0186	1.0175	1.0161	1.0150	1.0138
0.1000	1.0415	1.0401	1.0382	1.0364	1.0354
0.1500	1.0635	1.0622	1.0609	1.0593	1.0585
0.2000	1.0861	1.0843	1.0833	1.0817	1.0808
0.2500	1.1078	1.1067	1.1051	1.1035	1.1027
0.3000	1.1313	1.1306	1.1292	1.1282	1.1270
0.3500	1.1566	1.1547	1.1531	1.1511	1.1499
0.4000	1.1760	1.1754	1.1774	1.1751	1.1732

[a]W_P and W_S are the weight fractions of aqueous PEG2000 and diammonium hydrogen citrate solutions respectively. Standard uncertainties u are $u(T) = \pm\ 0.1$ K and $u(\rho) = \pm\ 0.1$ kg·m^{-3}.

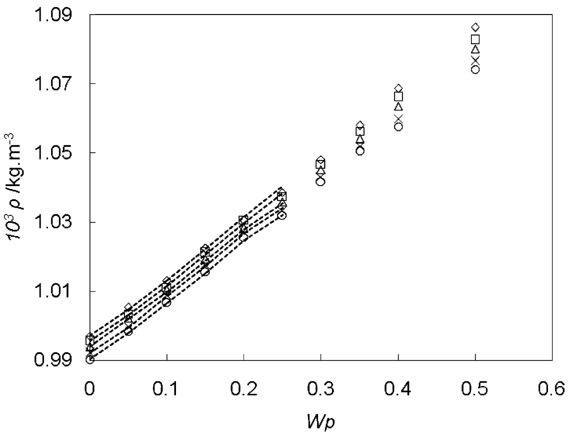

Figure 1. Aqueous PEG 2000 density at various temperatures: ◇, 298.15 K; □, 303.15 K; △, 308.15 K; ×, 313.15 K; ○, 318.15 K; ···, dotted lines corresponds to literature data.[9]

Table 3. Density of the PEG2000 + Diammonium Hydrogen Citrate + Water System at Various Temperatures[a]

		$10^3\ \rho$/kg·m^{-3}				
W_P	W_S	298.15 K	303.15 K	308.15 K	313.15 K	318.15 K
0.0500	0.0500	1.0248	1.0237	1.0226	1.0211	1.0197
0.1000	0.0500	1.0347	1.0328	1.0317	1.0300	1.0278
0.1500	0.0500	1.0447	1.0417	1.0397	1.0385	1.0368
0.2000	0.0500	1.0539	1.0457	1.0496	1.0478	1.0456
0.2500	0.0500	1.0642	1.0618	1.0595	1.0573	1.0551
0.0500	0.1000	1.0476	1.0462	1.0448	1.0433	1.0423
0.1000	0.1000	1.0562	1.0552	1.0527	1.0520	1.0512
0.1500	0.1000	1.0649	1.0641	1.0619	1.0605	1.0596
0.2000	0.1000	1.0736	1.0724	1.0710	1.0703	1.0689
0.0500	0.1500	1.0713	1.0705	1.0691	1.0664	1.0649
0.1000	0.1500	1.0800	1.0783	1.0772	1.0750	1.0737
0.1500	0.1500	1.0912	1.0878	1.0860	1.0843	1.0831
0.2000	0.1500	1.0995	1.0974	1.0945	1.0923	1.0908
0.0500	0.2000	1.0965	1.0922	1.0931	1.0911	1.0891
0.1000	0.2000	1.1083	1.1049	1.1033	1.0985	1.0974
0.1500	0.2000	1.1142	1.1132	1.1121	1.1110	1.1081
0.0500	0.2500	1.1186	1.1170	1.1147	1.1180	1.1126

[a]W_P and W_S are the weight fractions of PEG2000 and diammonium hydrogen citrate in ternary solution, respectively. Standard uncertainties u are $u(T)= \pm\ 0.1$ K and $u(\rho) = \pm\ 0.1$ kg·m^{-3}.

phase separation. The clear phases were separated using a pipet as described elsewhere.[11]

The densities of binary and ternary solutions and the separated phases were measured in automatic density meter (DDM 2911, Rudolph Research Analytical, USA). The uncertainty of density measurement was 0.1 kg·m^{-3}. The viscosity was measured using an Ostwald viscometer of different capillary sizes with an accuracy of ± 0.002 mPa·s, and temperature was maintained in thermostatic bath. Density and viscosity measurements were done in triplicate, and the average value was reported. Refractive index measurements of ternary and binary solutions and the separated phases were carried out in an automatic digital refractometer, Atago Co. Ltd. (RX-5000α), with an accuracy of ± 0.00004.

The PEG concentration in the ternary solutions was obtained from refractive index measurements. The refractive index of the solution depends on the concentration of all components (salt and PEG) present in the solution. To find the concentration of PEG in the solution, a correlation was developed in terms of PEG and salt weight fraction (eq 1). The linear relation between the polymer and salt concentration and measured refractive index value is given in eq 1. The coefficients of eq 1 were estimated by fitting the refractive index of the solution to the known weight fraction of PEG and salt present in the solutions.[12]

$$n_D = a_0 + a_1 W_p + a_2 W_S \tag{1}$$

where a_0 represents the refractive index of pure water at a particular temperature (data from Perry's Chemical Engineers' Handbook). Values of the constants a_1 and a_2 at different temperatures are presented in Table 1 and valid within weight fraction of polymer (W_P) = 0.05 to 0.2 and weight fraction of salt (W_S) = 0.05 to 0.2. The higher weight fraction samples were diluted accordingly, and the refractive index was measured.

The salt concentration in the top and bottom phase was determined by conductivity method, and eq 2 is used to relate the salt concentration and conductivity of the solution.

$$k = b_0 + b_1 W_S \tag{2}$$

Table 4. Coefficients of Equation 3[a]

	$10^3\ \rho_0$			AARD/%		
T/K	$kg \cdot m^{-3}$	A	B	PEG 2000 + water	diammonium hydrogen citrate + water	PEG 2000 + diammonium hydrogen citrate + water
298.15	0.997	0.1742	0.4486	0.1059	0.0756	0.1766
303.15	0.9956	0.1733	0.4492	0.0736	0.063	0.1716
308.15	0.994	0.1717	0.4508	0.0422	0.0888	0.1707
313.15	0.9922	0.1693	0.4533	0.0432	0.0724	0.2055
318.15	0.9902	0.1684	0.4561	0.0535	0.0412	0.1166

[a]Standard uncertainties u are $u(T) = \pm$ 0.1 K and $u(\rho) = \pm$ 0.1 $kg \cdot m^{-3}$.

Table 5. Viscosities of the PEG2000 + Water and Diammonium Hydrogen Citrate + Water Systems at Various Temperatures[a]

	aqueous PEG 2000 solution viscosity, μ/mPa·s				
W_P	298.15 K	303.15 K	308.15 K	313.15 K	318.15 K
0.0000	0.8900	0.8010	0.7230	0.6560	0.5990
0.0500	1.8680	1.5870	1.3169	1.0858	1.0077
0.1000	2.5395	2.0752	1.6276	1.2579	1.2646
0.1500	3.2558	2.5903	1.9385	1.3693	1.5572
0.2000	4.3746	3.4693	2.5274	1.5980	2.0545
0.2500	6.2905	5.0264	3.6725	2.1143	2.9578
0.3000	9.1688	7.5441	5.6740	3.1132	4.4512
0.3500	13.6595	11.4730	8.8067	4.7722	6.7453
0.4000	19.9184	16.8914	13.3645	7.2821	10.0100
0.5000	39.2851	34.1681	27.8650	15.5817	19.9000
	aqueous diammonium hydrogen citrate solution viscosity, μ/mPa·s				
W_S	298.15 K	303.15 K	308.15 K	313.15 K	318.15 K
0.0000	0.8900	0.8010	0.7230	0.6560	0.5990
0.0500	1.0257	0.9257	0.8354	0.7835	0.7146
0.1000	1.1460	1.0245	0.9344	0.8617	0.7807
0.1500	1.3031	1.1552	1.0572	0.9552	0.8355
0.2000	1.5359	1.3529	1.2249	1.0846	0.9267
0.2500	1.9065	1.6111	1.4918	1.2943	1.0913
0.3000	2.4475	2.1048	1.8786	1.6405	1.3827
0.3500	3.2145	2.7368	2.4301	2.1277	1.7881

[a]W_P and W_S are the weight fractions of aqueous PEG2000 and diammonium hydrogen citrate solutions, respectively. Standard uncertainties u are $u(T) = \pm$ 0.1 K, $u(\mu) = \pm$ 0.002 mPa·s.

where k is the conductivity ($\mu S \cdot cm^{-1}$); the values of b_0 and b_1 for diammonium hydrogen citrate solution are 5.744 and 502.6, respectively. The salt concentration was predicted by the equation with an accuracy of $\pm$ 0.0001 g.

RESULTS AND DISCUSSION

Experimentally measured densities of aqueous PEG 2000 and diammonium hydrogen citrate solutions at various temperatures are reported in Table 2. The densities are found to increase with an increase in PEG 2000 and diammonium hydrogen citrate concentrations and decrease with the increase in temperature.

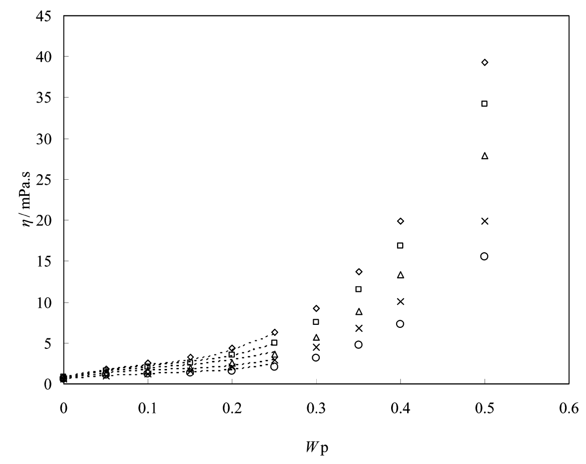

Figure 2. Experimental data on aqueous phase PEG2000 viscosity. ◇, 298.15 K; □, 303.15 K; △, 308.15 K; ×, 313.15 K; ○, 318.15 K; dotted line indicates the literature data.[9]

A similar trend was reported in the literature for PEG 6000–triammonium citrate,[13] PEG 4000–diammonium hydrogen phosphate,[7] PEG 2000–sodium citrate,[9] and PEG 200–water.[6] Figure 1 shows linearity between density and the concentration of aqueous PEG 2000 solution and the data from literature[9] as dotted lines. The density of the aqueous PEG 2000 was reported up to 0.25 weight fraction of PEG only by Murugesan and Perumalsamy.[9] In this present work, the density measurement was extended up to 0.5 PEG weight fractions. Aqueous single phase ternary systems (PEG2000 + diammonium hydrogen citrate + water) were prepared by mass and measured densities are reported in Table 3. Measured densities of the solutions could be correlated using eq 3.[7,9,13]

$$\rho/kg \cdot m^{-3} = AW_P + BW_S + \rho_o/kg \cdot m^{-3} \quad (3)$$

where ρ and ρ_0 are the densities of binary or ternary solutions and pure water at particular temperature and W_P and W_S are the mass fractions of PEG 2000 and diammonium hydrogen citrate, respectively. The experimental density values of the binary solutions were fitted in eq 3 with a maximum deviation of $\pm$ 0.3. Values of constants A and B and the pure water densities at

Table 6. Coefficients of Equation 4 with AARD/% Values at Different Temperatures

		PEG 2000 + water				diammonium hydrogen citrate + water			
T/K	μ_o/mPa·s	A	B	C	AARD/%	A	B	C	AARD/%
298.15	0.8900	24.9890	−132.1259	471.4524	0.1404	3.1458	−12.1990	63.3952	0.0642
303.15	0.8010	20.7926	−123.2330	430.2562	0.1542	3.0858	−13.6289	59.5424	0.4718
308.15	0.7230	16.7847	−114.7859	378.8997	0.0695	2.6730	−10.5354	47.7316	0.1683
313.15	0.6560	11.7133	−85.8108	244.1775	0.7443	3.2442	−16.6806	55.6645	0.2172
318.15	0.5990	11.0035	−67.8116	246.5625	0.2184	3.1946	−19.3014	57.7905	0.3184

Table 7. Viscosities of the PEG2000 + Diammonium Hydrogen Citrate + Water System at Various Temperatures[a]

		μ/mPa·s				
W_P	W_S	T = 298.15 K	T = 303.15 K	T = 308.15 K	T = 313.15 K	T = 318.15 K
0.0500	0.0500	2.2015	1.9647	1.5791	1.3027	1.1993
0.1000	0.0500	2.8406	2.5729	2.0018	1.6314	1.5003
0.1500	0.0500	3.4169	3.0500	2.3735	2.0273	1.8531
0.2000	0.0500	4.4030	3.7245	3.0823	2.6507	2.3179
0.2500	0.0500	6.0633	4.9310	4.1564	3.5777	3.1243
0.0500	0.1000	2.0488	1.8394	1.4927	1.2591	1.1463
0.1000	0.1000	2.7109	2.4062	1.9297	1.5803	1.4375
0.1500	0.1000	3.2924	2.9275	2.3248	1.9515	1.7544
0.2000	0.1000	4.3137	3.5688	2.8612	2.4989	2.1599
0.2500	0.1000	5.7282	4.6282	3.9574	3.2987	2.8666
0.0500	0.1500	2.0168	1.7792	1.5064	1.2671	1.1215
0.1000	0.1500	2.6913	2.3486	1.9040	1.5690	1.3948
0.1500	0.1500	3.1855	2.7711	2.2874	1.9093	1.6799
0.2000	0.1500	4.1330	3.4152	2.8038	2.4072	2.0611
0.0500	0.2000	2.1645	1.8771	1.6025	1.3448	1.1625
0.1000	0.2000	2.7684	2.3947	1.9579	1.6126	1.4072
0.1500	0.2000	3.3153	2.8544	2.3254	1.9249	1.6713
0.0500	0.2500	2.5362	2.0738	1.8204	1.5142	1.2954

[a] W_P and W_S are the weight fractions of PEG2000 and diammonium hydrogen citrate in ternary solution, respectively. Standard uncertainties u are $u(T) = \pm$ 0.1 K and $u(\mu) = \pm$ 0.002 mPa·s.

Table 8. Coefficients of Equation 5[a]

T/K	a	AARD/%
298.15	1.8787	0.5220
303.15	1.6284	0.3245
308.15	1.4494	0.3024
313.15	1.2542	0.1486
318.15	1.1954	0.2753

[a] Standard uncertainties u are $u(T) = \pm$ 0.1 K.

Table 9. Refractive Index of the PEG 2000 + Water and Diammonium Hydrogen Citrate + Water Systems at Various Temperatures[a]

	refractive index, n_D				
W_P	298.15 K	303.15 K	308.15 K	313.15 K	318.15 K
	PEG2000 + Water Solution				
0.0500	1.3390	1.3385	1.3375	1.3369	1.3360
0.1000	1.3475	1.3465	1.3455	1.3450	1.3435
0.1500	1.3540	1.3535	1.3525	1.3516	1.3505
0.2000	1.3615	1.3610	1.3600	1.3586	1.3580
0.2500	1.3685	1.3675	1.3666	1.3660	1.3645
0.3000	1.3770	1.3761	1.3750	1.3740	1.3725
0.3500	1.3840	1.3835	1.3826	1.3810	1.3800
0.4000	1.3925	1.3915	1.3900	1.3885	1.3870
0.5000	1.4075	1.4060	1.4050	1.4035	1.4015
W_S	298.15 K	303.15 K	308.15 K	313.15 K	318.15 K
	Diammonium Hydrogen Citrate + Water Solution				
0.0500	1.3435	1.3430	1.3415	1.3410	1.3400
0.1000	1.3515	1.3500	1.3495	1.3485	1.3480
0.1500	1.3610	1.3605	1.3595	1.3590	1.3585
0.2000	1.3695	1.3685	1.3675	1.3670	1.3665
0.2500	1.3790	1.3780	1.3775	1.3770	1.3765
0.3000	1.3870	1.3865	1.3860	1.3855	1.3850
0.3500	1.3975	1.3970	1.3965	1.3960	1.3955
0.4000	1.4090	1.4085	1.4080	1.4075	1.4068

[a] Standard uncertainties u are $u(T) = \pm$ 0.1 K and $u(n_D) = \pm$ 0.00004.

Table 10. Refractive Index of the PEG 2000 + Diammonium Hydrogen Citrate + Water System at Various Temperatures[a]

		refractive index, n_D				
W_P	W_S	298.15 K	303.15 K	308.15 K	313.15 K	318.15 K
0.0500	0.0500	1.3490	1.3485	1.3475	1.3470	1.3465
0.1000	0.0500	1.3550	1.3545	1.3540	1.3530	1.3525
0.1500	0.0500	1.3635	1.3630	1.3625	1.3620	1.3615
0.2000	0.0500	1.3700	1.3695	1.3690	1.3685	1.3680
0.2500	0.0500	1.3775	1.3770	1.3765	1.3760	1.3755
0.0500	0.1000	1.3575	1.3570	1.3560	1.3555	1.3550
0.1000	0.1000	1.3645	1.3640	1.3635	1.3630	1.3625
0.1500	0.1000	1.3710	1.3705	1.3700	1.3695	1.3690
0.2000	0.1000	1.3795	1.3790	1.3780	1.3775	1.3770
0.0500	0.1500	1.3665	1.3660	1.3655	1.3650	1.3645
0.1000	0.1500	1.3735	1.3730	1.3720	1.3715	1.3710
0.1500	0.1500	1.3800	1.3795	1.3790	1.3785	1.3780
0.2000	0.1500	1.3885	1.3880	1.3875	1.3870	1.3865
0.0500	0.2000	1.3766	1.3765	1.3760	1.3755	1.3750
0.1000	0.2000	1.3825	1.3820	1.3815	1.3810	1.3805
0.1500	0.2000	1.3910	1.3905	1.3900	1.3850	1.3845

[a] Standard uncertainties u are $u(T) = \pm$ 0.1 K, $u(n_D) = \pm$ 0.00004.

different temperatures with corresponding AARD% are given in Table 4. Further, the densities of ternary systems were predicted by using eq 3. The maximum error between experimental and predicted densities is ± 0.5 %.

The viscosity of the binary systems was found to decrease with an increase in temperature and is reported in Table 5. Viscosity data for the binary system were correlated by using the following polynomial equation[6,7,13]

$$\mu/\mathrm{mPa\cdot s} = AW^3 + BW^2 + CW + \mu_0/\mathrm{mPa\cdot s} \qquad (4)$$

where μ is the absolute viscosity of the solution and μ_0 is the viscosity of pure water at respective temperature. W is the mass fraction of either PEG 2000 or diammonium hydrogen citrate. Values of the coefficients (A, B, and C) are reported in Table 6 along with the AARD (%) values. Maximum deviation between calculated and predicted values for aqueous PEG 2000 and salt solution is ± 2.5. Viscosity data for the aqueous PEG 2000 system were compared with the available data from the literature[9] and plotted in Figure 2. Both experimental and literature data are found to be in good agreement with each other, and moreover, there is no linearity between polymer concentration and viscosity of the solution above the polymer concentration of 0.2 weight fraction.

The viscosity of the single phase ternary systems was found to decrease with increase in temperature and increase with the increase in salt and PEG2000 concentration. This behavior was observed for other ternary systems composed of PEG, salt, and water.[7−9,13−16] Viscosities of the ternary systems in Table 7 are fitted to the Grunberg-like equation,[7,8,13] and the values of constant a at different temperatures are provided in Table 8.

Table 11. Coefficients of Equation 6[a]

		PEG 2000 + water		diammonium hydrogen citrate + water	
T/K	a_0	A	AARD/%	A	AARD/%
298.15 K	1.334	0.1433	0.08262	0.1875	0.0952
303.15 K	1.333	0.1442	0.06599	0.0283	1.3883
308.15 K	1.332	0.1444	0.06224	0.0272	1.3978
313.15 K	1.3315	1.2256	0.0252	0.0259	1.4028
318.15 K	1.331	0.14	0.06978	0.0309	1.402

[a]Standard uncertainty u is $u(T) = \pm$ 0.1 K.

$$\ln(\mu_m/\mathrm{mPa{\cdot}s}) = c_1 \ln(\mu_p/\mathrm{mPa{\cdot}s}) + c_2 \ln(\mu_S/\mathrm{mPa{\cdot}s}) + c_1c_2a \quad (5)$$

where $c_1 = W_P/(W_P + W_S)$, $c_2 = W_S/(W_P + W_S)$, μ_m, μ_p, and μ_s represent the viscosity of the mixture, polymer, and salt, respectively. Relative errors between experimental viscosity and predicted values were calculated, and it was found that eq 5 predicts the viscosity of the single phase ternary solutions within the error limits of ± 0.2 %.

Refractive index measurements of the binary and ternary single phase region were carried out, and the values are presented in Tables 9 and 10, respectively. Binary solution refractive index values were correlated by using eq 6

$$n_D = a_o + AW \quad (6)$$

where a_o is the refractive index of pure water at particular temperature, W is the mass fraction of either PEG 2000 or diammonium hydrogen citrate, and the values of coefficient A and percentage of error are reported in Table 11.

Liquid−liquid equilibrium data and the top and bottom phase composition were analyzed and reported in Table 12 along with the phase volume ratio (top phase volume/bottom phase volume), tie line length, and density difference between the top and bottom phases. The tie-line length (TLL) was calculated using the following relationship, eq 7,

$$\mathrm{TLL} = [(W_P^T - W_P^B)^2 + (W_S^B - W_S^T)^2]^{1/2} \quad (7)$$

Phase volume ratio, tie line length, and density difference between the phases are found to increase with the increase in

Table 12. Density Difference between the Top Phase and the Bottom Phase, Phase Volume Ratio, and TLL for the PEG 2000 + Diammonium Hydrogen Citrate + Water Two-Phase System[a]

feed composition		top phase		bottom phase				
W_P	W_S	W_P^T	W_S^T	W_P^B	W_S^B	volume ratio	TLL	$\Delta\rho = (\rho^B - \rho^T)$
				T = 298.15 K				
0.2000	0.2200	0.3330	0.1226	0.1740	0.2437	1.4655	0.1999	0.0252
0.2200	0.2200	0.3630	0.1087	0.1560	0.2725	1.6176	0.2640	0.0389
0.2500	0.2200	0.4350	0.0675	0.1560	0.2968	1.7269	0.3611	0.0486
0.2800	0.2200	0.4870	0.0486	0.1560	0.3200	1.8307	0.4280	0.0595
				T = 303.15 K				
0.2000	0.2200	0.3560	0.1000	0.1550	0.2571	1.6159	0.2551	0.0452
0.2200	0.2200	0.4170	0.0680	0.1400	0.2854	1.7654	0.3460	0.0554
0.2500	0.2200	0.4690	0.0486	0.1380	0.3097	1.8452	0.4216	0.0662
				T = 308.15 K				
0.1800	0.2200	0.3550	0.0903	0.1380	0.2556	1.6981	0.2728	0.0388
0.2000	0.2200	0.3860	0.0769	0.1340	0.2734	1.6604	0.3270	0.0479
0.2200	0.2200	0.4290	0.0591	0.1280	0.2938	1.6667	0.3817	0.0649
				T = 313.15 K				
0.1600	0.2200	0.3380	0.0938	0.1412	0.2413	1.3014	0.2567	0.0375
0.1800	0.2200	0.3940	0.0690	0.1402	0.2601	1.3907	0.3264	0.0453
0.2000	0.2200	0.4600	0.0422	0.1377	0.2821	1.4558	0.4159	0.0555
0.2200	0.2200	0.4860	0.0333	0.1368	0.2909	1.5806	0.4539	0.0575
				T = 318.15 K				
0.1400	0.2200	0.3400	0.0809	0.1170	0.2387	0.8410	0.2732	0.0303
0.1600	0.2200	0.3740	0.0640	0.1150	0.2500	1.0365	0.3223	0.0386
0.1800	0.2200	0.4130	0.0481	0.0990	0.2804	1.1837	0.3906	0.0544
0.2000	0.2200	0.4510	0.0352	0.1030	0.2888	1.4966	0.4306	0.0554
0.2200	0.2200	0.4870	0.0288	0.1000	0.3032	1.3258	0.4800	0.0626

[a]W_P and W_S are the weight fractions of PEG 2000 and diammonium citrate in the ternary systems, and the superscripts T and B correspond to the top phase and bottom phase. Standard uncertainties u are $u(T) = \pm$ 0.1 K, $u(W) = \pm$ 0.0001, and $u(\rho) = \pm$ 0.1 kg·m^{-3}.

Table 13. Phase Composition and Physical Properties of the Two Phases Formed from PEG 2000 + Diammonium Hydrogen Citrate + Water System at Different Temperatures[a]

top phase								bottom phase							
		$10^3\rho^T$	$10^3\rho^T_{cal}$	μ^T	μ^T_{cal}					$10^3\rho^B$	$10^3\rho^B_{cal}$	μ^B	μ^B_{cal}		
W_P^T	W_S^T	$kg\cdot m^{-3}$	$kg\cdot m^{-3}$ (eq 3)	mPa·s	mPa·s (eq 5)	n_D^T	$n_{D,cal}^T$ (eq 1)	W_P^B	W_S^B	$kg\cdot m^{-3}$	$kg\cdot m^{-3}$ (eq 3)	mPa·s	mPa·s (eq 5)	n_D^B	$n_{D,cal}^B$ (eq 1)
T = 298.15 K															
0.3330	0.1226	1.1091	1.1100	9.3591	8.9015	1.4010	1.4015	0.1740	0.2437	1.1343	1.1366	3.9109	3.9073	1.4002	1.4003
0.3630	0.1087	1.1081	1.1090	11.6774	11.6862	1.4032	1.4032	0.1560	0.2725	1.1471	1.1464	3.8879	3.8791	1.4028	1.4028
0.4350	0.0675	1.1095	1.1031	20.7752	20.7583	1.4071	1.4061	0.1560	0.2968	1.1580	1.1573	4.1426	4.1278	1.4076	1.4070
0.4870	0.0486	1.1056	1.1036	30.5619	30.5616	1.4107	1.4100	0.1560	0.3200	1.1652	1.1677	4.4263	4.4162	1.4110	1.4110
T = 303.15 K															
0.3560	0.1000	1.0918	1.1022	9.1104	9.1119	1.4005	1.4008	0.1550	0.2571	1.1370	1.1380	3.1262	3.1264	1.4000	1.4004
0.4170	0.0680	1.0922	1.0984	15.0955	15.0947	1.4039	1.4037	0.1400	0.2854	1.1476	1.1481	3.1936	3.1967	1.4035	1.4033
0.4690	0.0486	1.0915	1.0987	22.8221	22.8377	1.4072	1.4075	0.1380	0.3097	1.1576	1.1586	3.4026	3.4085	1.4071	1.4073
T = 308.15 K															
0.3550	0.0903	1.0925	1.0957	7.9460	7.9451	1.4010	1.3982	0.1380	0.2556	1.1313	1.1329	2.5026	2.5026	1.3955	1.3967
0.3860	0.0769	1.0909	1.0949	10.2329	10.2328	1.4004	1.4002	0.1340	0.2734	1.1389	1.1403	2.5273	2.5272	1.3985	1.3993
0.4290	0.0591	1.0844	1.0943	14.5922	14.5587	1.4035	1.4032	0.1280	0.2938	1.1493	1.1484	2.6427	2.6429	1.4025	1.4020
T = 313.15 K															
0.3380	0.0938	1.0862	1.0919	4.7986	4.7989	1.3959	1.3957	0.1412	0.2413	1.1237	1.1255	1.4708	1.4708	1.3940	1.3940
0.3940	0.0690	1.0890	1.0902	7.8090	7.8097	1.3993	1.3992	0.1402	0.2601	1.1344	1.1338	1.5320	1.5313	1.3960	1.3971
0.4600	0.0422	1.0870	1.0892	13.8237	13.8239	1.4035	1.4038	0.1377	0.2821	1.1425	1.1434	1.6170	1.6177	1.3985	1.4007
0.4860	0.0333	1.0887	1.0896	17.1091	17.1089	1.4059	1.4059	0.1368	0.2909	1.1462	1.1472	1.6595	1.6593	1.4020	1.4021
T = 318.15 K															
0.3400	0.0809	1.0869	1.0844	5.4086	5.4094	1.3932	1.3930	0.1170	0.2387	1.1172	1.1188	1.5593	1.5593	1.3910	1.3901
0.3740	0.0640	1.0837	1.0824	7.1520	7.1512	1.3940	1.3947	0.1150	0.2500	1.1223	1.1236	1.5840	1.5833	1.3925	1.3919
0.4130	0.0481	1.0791	1.0817	9.8097	9.8069	1.3974	1.3973	0.0990	0.2804	1.1334	1.1348	1.6368	1.6364	1.3945	1.3951
0.4510	0.0352	1.0819	1.0822	13.2117	13.2115	1.4010	1.4003	0.1030	0.2888	1.1373	1.1393	1.6974	1.6976	1.3970	1.3972
0.4870	0.0288	1.0826	1.0853	17.0358	17.0358	1.4048	1.4042	0.1000	0.3032	1.1453	1.1453	1.7693	1.7699	1.3990	1.3993

[a]Standard uncertainties u are $u(T) = \pm 0.1$ K, $u(W) = \pm 0.0001$, $u(\rho) = \pm 0.1$ $kg\cdot m^{-3}$, and $u(\mu) = \pm 0.002$ mPa·s.

PEG concentration and increase with temperature for a particular PEG and salt concentration.[9,17,18] Experimentally measured and predicted density, viscosity, and refractive index of the top and bottom phases are in Table 13. Both experimentally estimated and predicted top phase viscosities were plotted against TLL in Figure 3. Predicted values were found to be in good agreement with the experimental values.

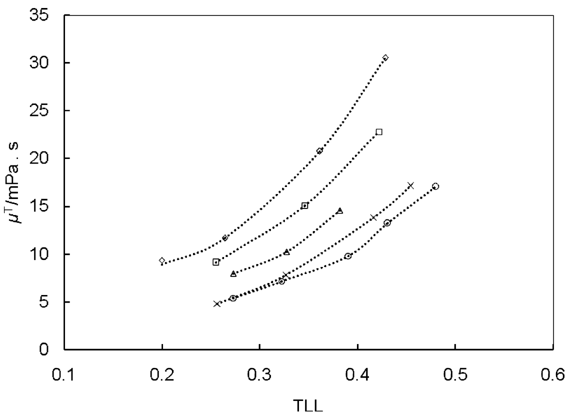

Figure 3. Effect of TLL on top phase viscosity: ◊, 298.15 K; □, 303.15 K; △, 308.15 K; ×, 313.15 K; ○, 318.15 K (dashed line, calculated using eq 5).

■ CONCLUSIONS

The densities, refractive index, and viscosities of the binary and ternary mixtures of the PEG 2000 + diammonium hydrogen citrate + water based aqueous two-phase system were measured and correlated for five different temperatures, (298.15, 303.15, 308.15, 313.15, and 318.15) K. Further, the TLL were calculated for the chosen aqueous two-phase system at the same temperature, and phase composition, density, viscosity, and the refractive index of the individual phases were measured and predicted using the developed correlations. All of the correlations were predicted, and their respective properties had low relative error. The top phase viscosity with respect to temperature and TLL was also analyzed and plotted.

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