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Viscosities, Refractive Indexes, and Conductivities of Phosphoric Acid in *N,N*-Dimethylformamide + Water Mixtures

Lyubov P. Safonova,* Alexander A. Pryahin, Julia A. Fadeeva, and Ludmila E. Shmukler

Institute of Solution Chemistry of Russian Academy of Sciences, Akademicheskaya Str., 1, 153045 Ivanovo, Russia

The viscosities at $T = (298.15 \text{ to } 338.15 \text{ K})$, refractive indexes, and specific conductivities of phosphoric acid in *N,N*-dimethylformamide + water mixtures at $T = 298.15$ K have been measured over the whole concentration range of components. The excess properties of the system as functions of component ratio have been calculated and fitted to the Redlich−Kister equation. Dependence of these properties on composition has been discussed.

Introduction

Earlier, with different methods of physical−chemical analysis (viscosimetry, conductometry, IR-spectroscopy, etc.), the binary phosphoric acid + *N,N*-dimethylformamide (DMF) system was studied.[1–3] It was shown that phosphoric acid in DMF solutions is very weakly dissociated. The conclusions on prevalence of strong intermolecular interactions in the system resulting in H-bonded complex formation were formulated. The dissociation degree of phosphoric acid most probably changes significantly with addition of water to nonaqueous solvent (DMF) influencing the character of interactions in aqueous−organic H_3PO_4 solution.

However, only properties of corresponding binary systems have been reported in the literature. In numerous works, the viscosity,[4–9] refractive index,[7,8,10] and volumetric properties[4,5,11,12] of binary H_2O + DMF and $H_3PO_4 + H_2O$ mixtures have been studied. Also, conductivity of H_3PO_4 solutions in water is available in the literature.[13–15] On the other hand, there are no studies of the H_3PO_4 + DMF system except for our earlier works.[1–3]

The aim of this work was to study interactions in the H_3PO_4 + DMF + H_2O system by physical−chemical methods.

Experimental

100 % phosphoric acid was prepared by dissolving an excess of P_2O_5 (ASC reagent, ≥ 98.0 %, Aldrich) in aqueous phosphoric acid (≥ 85 wt. % in H_2O 99.999 %, Aldrich). The excess related to 100 % H_3PO_4 was determined by titration with a solution of NaOH (OP-300, Radelkis). Extra water was added to bring down the concentration to as close to 100 % H_3PO_4 as possible. The H_3PO_4 concentration obtained this way differs by less than 1 % from 100 %.

N,N-Dimethylformamide (Biotech grade solvent, 99.9+ %, Aldrich) was doubly fractionally distilled in a vacuum (P = 133 Pa) at $T = 310.15$ K, and only the intermediate fraction was used. The distilled solvent was dried using molecular sieves with a pore diameter of 0.4 nm for 72 h and repeatedly fractionally distilled, collecting the intermediate fraction. The water content in DMF, determined by Karl Fischer titration, was less than 0.03 %.

Double-distilled water with specific conductance of $1 \cdot 10^{-6}$ $S \cdot cm^{-1}$ was used. All solutions were prepared by mass using a high-resolution balance (ME215S, Sartorius) with an uncertainty of $\pm 1 \cdot 10^{-5}$ g. Ternary mixtures were prepared by mixing a mixed solvent (H_2O + DMF at known composition) with pure H_3PO_4. Ternary systems were composed of series of these pseudobinary mixtures H_3PO_4 + S, where S is mixed solvent H_2O + DMF. The uncertainty in the mole fraction is less than $\pm 1 \cdot 10^{-4}$.

Refraction index (n_D) for the sodium D-line was measured using a refractometer (IRF-454B, KOMZ, Russia) thermostatted to within ± 0.02 K. The uncertainty in the measurements was ± 0.001 units.

Specific conductivities (κ) were determined with an LCR-meter (LCR817, GW Instek, Taiwan) at a frequency of 1000 Hz using the three-electrode measuring cell. The cell contained three parallel platinum discs, each with a 10 mm diameter. The cell constant was obtained from measurements at 298 K with 0.1 $mol \cdot L^{-1}$ aqueous KCl solution (specific conductivity 12.88 $mS \cdot cm^{-1}$ at 298.15 K) A thermostatically controlled bath (± 0.01 K) was used for all measurements. Relative uncertainty was calculated to be ± 0.2 % for specific conductivity.

For viscosity measurement in the viscosity range (0.5 to 2.5) $mPa \cdot s$, the Ubbelhode viscometer had an automatic measurement outflow time (the accuracy of the outflow time measurement is ± 0.01 s). A thermostatically controlled bath (± 0.01 K) was used for all measurements. The viscometer was calibrated with water, acetone, and 1-propanol. The uncertainty in the measurements was ± 0.001 $mPa \cdot s$. For viscosity measurement in the viscosity range higher than 2.5 $mPa \cdot s$, the BROOKFIELD DV-II+Pro rotational viscometer was used. The accuracy of the oven control was ± 0.01 K. Relative uncertainty in the measurements was ± 1 %.

For recalculation of kinematic viscosity ν measured with an Ubbelhode viscometer to dynamic ones η and calculation of molecular refraction, the density of solutions was measured by a vibrating glass tube densimeter (VIP-2M, TERMEX, Russia). The accuracy of the oven control was ± 0.01 K. Uncertainty in the density measurement was ± 0.0003 $g \cdot cm^{-3}$.

Because the phosphoric acid freezing point is $T = 315.35$ K, all experimental points for pure phosphoric acid at $T = 298.15$

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* To whom correspondence should be addressed: E-mail: lps@isc-ras.ru. Tel.: +7 4932 351679. Fax: +7 4932 336237.

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Table 1. Specific Conductivities, κ, for Different Concentration Solutions of H_3PO_4 ($x_{H_3}PO_4$) in DMF and Mixed Solvent H_2O + DMF with Various Values of Mole Fractions of DMF at T = 298.15 K

DMF		0.07 DMF		0.3 DMF	
xH_3PO_4	10^4 κ/S·cm^{-1}	xH_3PO_4	10^4 κ/S·cm^{-1}	xH_3PO_4	10^4 κ/S·cm^{-1}
0.1033	2.391	0.0465	456.8	0.0501	40.37
0.1181	2.504	0.0935	845.6	0.1000	79.78
0.1422	2.403	0.1886	1052	0.1996	142.0
0.1793	2.221	0.2839	867.1	0.2995	151.1
0.1860	2.011	0.3824	679.4	0.3996	140.4
0.2652	1.504	0.4811	562.3	0.5001	137.4
0.3591	1.612	0.5832	4835	0.5495	141.0
0.6001	7.703	0.6847	457.3	0.5997	153.8
0.9143	178.0	0.7869	437.0	0.6490	169.6
1	385.0[a]	0.8902	421.2	0.7001	195.0
				0.7351	200.6
				0.7827	242.3
				0.8989	324.7

[a] The value was obtained by extrapolation of experimental dependences for solutions to pure H_3PO_4.

Table 2. Refraction Indexes, n_D, for Different Concentration Solutions of H_3PO_4, xH_3PO_4, in H_2O, DMF, and Mixed Solvent H_2O + DMF with Various Values of Mole Fraction of DMF at T = 298.15 K

	n_D						
xH_3PO_4	H_2O	0.1 DMF	0.2 DMF	0.4 DMF	0.6 DMF	0.8 DMF	DMF
0	1.354	1.371	1.386	1.412	1.426	1.428	1.424
0.1	1.376	1.390	1.403	1.423	1.435	1.438	1.436
0.2	1.396	1.407	1.4177	1.433	1.443	1.446	1.445
0.3	1.413	1.421	1.429	1.442	1.450	1.453	1.453
0.4	1.427	1.433	1.439	1.449	1.455	1.459	1.459
0.5	1.438	1.443	1.448	1.455	1.460	1.462	1.464
0.6	1.448	1.451	1.454	1.459	1.462	1.465	1.466
0.7	1.454	1.456	1.458	1.461	1.464	1.465	1.467
0.8	1.458	1.459	1.460	1.462	1.463	1.464	1.465
0.9	1.459	1.459	1.460	1.460	1.461	1.462	1.462
1	1.457[a]						

[a] The value was obtained by extrapolation of experimental dependences for solutions to pure H_3PO_4.

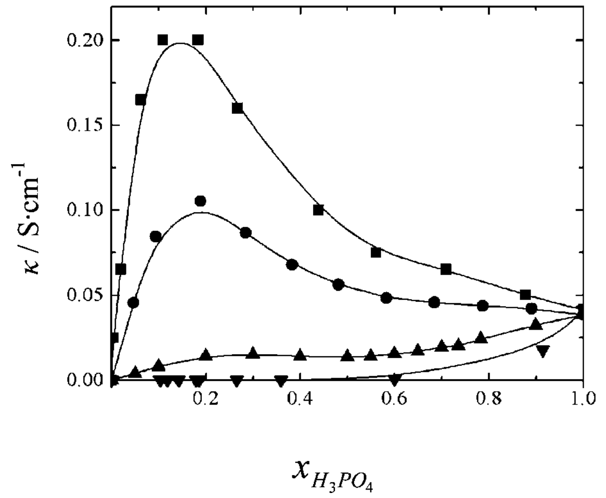

Figure 1. Specific conductivities of H_3PO_4 solutions in mixed solvent H_2O + DMF as functions of acid concentration at T = 298.15 K. Concentration of DMF in mixed solvent H_2O + DMF is: ■, 0 (the data from ref 15); ●, 0.07; ▲, 0.3; ▼, 1.

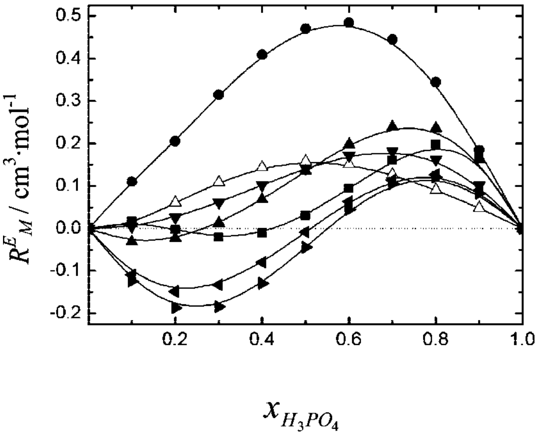

Figure 2. Excess molecular indexes of H_3PO_4 solutions in mixed solvent H_2O + DMF as functions of acid concentration at T = 298.15 K. Concentration of DMF in mixed solvent H_2O + DMF is: solid triangle pointing right, 0; solid triangle pointing left, 0.1; ▲, 0.2; ▼, 0.4; ■, 0.6; Δ, 0.8; ●, 1.

Table 3. Coefficients of the Redlich−Kister Equation for R^E_M of H_3PO_4 + S (H_2O + DMF) for Various Values of Mole Fraction of DMF in Mixed Solvent S at T = 298.15 K

composition of H_2O + DMF	A_0	A_1	A_2	δ
H_2O	−0.1742	1.6246	−0.0826	0.0078
0.1 DMF	−0.0295	1.4380	−0.1084	0.0024
0.2 DMF	0.5444	1.3501	0.3119	0.0009
0.4 DMF	0.5706	0.7029	0.0421	0.0014
0.6 DMF	0.11598	1.0601	1.3884	0.0016
0.8 DMF	0.6328	0.1579	−0.4539	0.0040
DMF	−1.87507	0.6988	−0.4022	0.0067

K and T = 308.15 K were obtained by extrapolation of experimental dependences for solutions to pure H_3PO_4.

Results and Discussion

The results obtained for the ternary system phosphoric acid + *N,N*-dimethylformamide + water have been discussed as a binary solution of H_3PO_4 in mixed solvent (H_2O + DMF). On the basis of experimental data, some excess properties were calculated.

Conductivity. Specific conductivities κ of H_3PO_4 solution in mixed solvent H_2O + DMF at T = 298.15 K are listed in Table 1, and dependences of ones as acid concentrations are presented in Figure 1. As one knows, the dissociation constants of phosphoric acid in water are the following:[16,17] $pK_1 = 2.148$; $pK_2 = 7.199$; $pK_3 = 12.35 \pm 0.02$. As one can see, the second and third dissociation constants are rather small. Therefore, in aqueous solution, phosphoric acid can be regarded as a 1:1 electrolyte. With acid concentration rising, the number of ions per volume unit increases. On the other hand, the dissociation degree decreases, and viscosity of a solution increases lowering the ion mobility. All these effects lead to the extreme on the conductivity concentration dependence for aqueous H_3PO_4 solution (Figure 1). The same behavior is observed for most electrolyte aqueous solutions.[18] As can be seen (Figure 1), the increase of DMF content in mixed solvent diminishes dramatically the specific conductivity of solutions. This decrease in the κ values may be attributed to the decrease of acid dissociation degree (because the value of the dielectric constant of mixed solvent H_2O + DMF reduces). Also, a decrease in the κ values may be attributed to the increase in the viscosity of mixed solvent. At DMF concentration in mixed solvent H_2O + DMF higher than 0.3 mol fraction (m.f.), the maximum for the dependence of specific conductivity on acid concentrations is not observed.

Molecular Refraction. Refractive indexes n_D of H_3PO_4 solution in mixed solvent H_2O + DMF at T = 298.15 K are

Table 4. Viscosities, η, for Different Concentration Solutions of H_3PO_4, xH_3PO_4, in H_2O and Mixed Solvent H_2O + DMF with Various Values of Mole Fractions of DMF[a] from T = (298.15 to 328.15) K[b]

	η/mPa·s				
$x\mathrm{H_3PO_4}$	T/K = 298.15	T/K = 308.15	T/K = 318.15	T/K = 328.15	T/K = 338.15
H_2O					
0	0.890	0.730	0.610	0.52	0.450
0.1004	3.23	2.58	2.14	1.78	1.54
0.1992	7.47	5.85	4.65	3.90	3.24
0.3002	14.50	10.9	8.55	6.84	5.67
0.4001	25.5	19.0	13.8	10.7	8.58
0.4980	39.0	27.4	19.3	14.6	11.3
0.6003	58.5	37.8	27.0	19.7	15.4
0.6982	77.7	51.6	35.7	25.8	19.3
0.8051	116	75.6	51.6	36.0	26.5
0.8966	1465	94.2	63.3	44.0	32.5
1	189.6	120	79.2	55.5	40.5
0.1 DMF					
0	1.74	1.33	1.06	0.870	0.730
0.0953	5.06	3.97	3.24	2.44	2.45
0.1919	11.7	8.78	6.77	5.37	4.43
0.2883	22.3	16.1	12.0	9.40	7.51
0.3874	38.8	27.5	19.9	15.1	11.7
0.4864	60.3	40.6	28.3	20.8	15.9
0.5884	84.5	56.1	37.8	27.5	20.5
0.6893	110	71.8	47.6	34.1	25.2
0.7904	129	84.0	56.4	39.8	29.5
0.8922	160	100	68.0	47.3	34.8
0.2 DMF					
0	2.35	1.76	1.37	1.09	0.89
0.1001	7.80	5.83	4.5	3.57	3.00
0.2012	20.9	15.3	11.5	9.12	7.41
0.2993	43.8	30.6	21.4	15.8	12.2
0.3963	78.3	51.4	35.3	25.3	19.0
0.4996	119	76.5	50.8	35.5	26.0
0.5345	132	82.2	54.6	38.4	28.1
0.6007	151	92.8	63.3	42.6	31.6
0.6947	169	105	69.3	47.3	34.2
0.7814	179	112	72.6	49.6	35.8
0.901	186	117	76.8	52.6	38.3
0.3 DMF					
0	2.48	1.86	1.44	1.15	0.95
0.1006	9.15	6.66	5.07	4.02	3.24
0.1866	27.7	19.4	14.1	10.8	8.46
0.3125	71.4	47.4	32.9	23.5	17.9
0.4031	128	80.7	52.6	36.6	26.4
0.4996	209	119	76.5	52.2	36.9
0.5473	228	136	86.1	58.2	40.6
0.5942	240	143	91.8	62.7	42.9
0.6256	249	149	93.6	63.6	43.7
0.7033	241	144	90.6	62.8	43.5
0.7601	234	138	89.4	62.1	43.2
0.7948	227	137	88.2	60.9	42.4
0.8978	203	124	82.2	56.7	40.6
0.4 DMF					
0	2.22	1.71	1.35	1.09	0.950
0.1041	9.67	7.08	5.31	4.13	3.46
0.1999	32.6	22.2	15.8	11.9	9.18
0.3003	89.5	55.5	37.2	26.8	20.0
0.4013	151.5	91.2	58.8	40.5	28.7
0.4999	322	180	113	73.2	49.6
0.5343	350	197	120	78.7	53.6
0.5811	384	218	131	85.0	58.2
0.6503	385	218	133	87.6	60.9
0.7001	361	202	125	82.5	56.5
0.7988	275	164	104	70.8	48.9
0.8978	208	127	84.6	58.8	41.2

	η/mPa·s				
$x\mathrm{H_3}PO_4$	T/K = 298.15	T/K = 308.15	T/K = 318.15	T/K = 328.15	T/K = 338.15
0.5 DMF					
0	1.83	1.45	1.3	0.97	0.82
0.1001	7.92	5.83	1.18	3.54	2.96
0.2001	33.4	23.0	16.4	12.3	9.57
0.2994	115	68.9	46.6	32.8	25.0
0.4002	242	143	88.8	59.1	41.7
0.4972	454	251	149	93.6	63.3
0.5496	559	312	178	110	74.4
0.5963	609	334	188	118	78.3
0.6345	604	329	190.2	119	78.6
0.6849	557.9	305	181	115	77.4
0.7499	431.9	247	149	98.4	67.2
0.8002	361.1	207	130	87.0	59.4
0.9014	235.7	145	95.4	65.1	45.6
0.6 DMF					
0	1.51	1.23	1.03	0.87	0.75
0.1035	6.42	4.94	3.86	3.1	2.54
0.1991	30.2	21.2	14.9	11.2	8.68
0.2997	115	72.0	47.2	33.1	24.5
0.3994	307	172	106	70.2	48.6
0.4983	651	343	197	120	79.5
0.5535	812	413	231	141	90.7
0.5818	885	456	256	157	97.2
0.6474	9170	466	259	158	103
0.7040	7010	390	215	137	87.3
0.7493	606	334	198	126	82.8
0.7999	474	266	164	104	71.4
0.8998	268	162	104	70.5	50.1
0.7 DMF					
0	1.24	1.04	0.890	0.770	0.66
0.0997	4.69	3.73	2.99	2.47	2.14
0.2004	24.6	17.5	12.6	9.72	7.8
0.2835	91.2	58.3	38.8	27.7	20.8
0.4008	337	193	117	75.9	51.1
0.4999	753	387	221	134	85.5
0.5475	952	488	269	161	102
0.5974	1125	563	310	181	115
0.6492	1170	588	330	192	127
0.7004	1110	585	316	184	119
0.7294	992	511	288	172	111
0.7997	543	312	181	116	78.9
0.8978	319	185	118	79.5	55.2
0.8 DMF					
0	1.030	0.890	0.780	0.68	0.61
0.1044	3.78	3.10	2.61	2.22	1.87
0.2022	19.3	14.2	10.5	8.18	6.57
0.3010	107	67.2	44.2	31.0	22.3
0.4003	287	167	102	67.5	45.9
0.4974	918	449	253	151	96.5
0.5487	1272	633	337	195	120
0.5972	1578	751	397	227	144
0.6505	1638	815	415	239	147
0.7004	1461	720	384	222	138
0.7480	1093	567	318	188	121
0.8014	715	396	234	144	94.5
0.9006	320	188	119	81.0	56.1
0.9 DMF					
0	0.89	0.78	0.7	0.62	0.56
0.1004	2.49	2.11	1.83	1.58	1.4
0.1994	12.7	9.84	7.56	6.11	5.03
0.2999	90.9	58.7	39.7	28.1	20.8
0.4009	413.3	235	140	87.6	58.6
0.5007	1123	562	303	175	115
0.5487	1620	762	397	227	137
0.5979	2016	936	501	270	166
0.6498	2465	1038	535	303	176
0.6996	2274	1059	522	286	172
0.7783	1509	735	400	227	141
0.7988	1353	595	346	197	123
0.9119	371	215	134	88.8	62.2

[a] Viscosities of H_3PO_4 solutions in DMF at T = (298.15 to 328.15 K) are presented in ref 1. [b] The values in italic type were obtained by extrapolation of experimental dependences for solutions to pure H_3PO_4.

listed in Table 2. Using that experimental data, the Lorentz−Lorenz molecular refraction (R_M) was calculated:

$$R_M = \frac{n_D^2 - 1}{n_D^2 + 2} \cdot \frac{M}{\rho} \tag{1}$$

where M and ρ are average molecular mass and density of a solution.

The excess molecular refractions R_M^E for binary H_3PO_4 + S were calculated from the equation

$$R_M^E = R_M^{\text{exptl}} - (x_{H_3PO_4} R_M(H_2O) + x_s R_M(S)) \tag{2}$$

where S denotes mixed solvent H_2O + DMF.

The dependence of excess molecular refractions at $T = 298.15$ K as acid concentrations is presented in Figure 2.

As one can see, the values of R_M^E are positive for H_3PO_4 solutions in DMF and mixed solvent H_2O + DMF with high DMF concentrations at all H_3PO_4 concentrations. For H_3PO_4 solutions in water and mixed solvent H_2O + DMF with low DMF concentrations, values of R_M^E are positive only at high H_3PO_4 concentrations.

Values of R_M^E were fitted with the Redlich−Kister equation

$$R_M^E = x_{H_3PO_4} x_S \sum_{i=0}^{m} A_i (x_{H_3PO_4} - x_S)^i \tag{3}$$

The root-mean-square deviation from the fitted curve was defined by the following equation

$$\delta = \left[\sum_{i=1}^{n} (R_M^E(\text{exptl}) - R_M^E(\text{calcd}))^2 / n \right]^{1/2} \tag{4}$$

The coefficients of A_i and δ values are presented in Table 3.

Viscosity. The experimental viscosities (η) as acid concentrations in mixed solvent H_2O + DMF at $T = (298.15$ to 338.15 K) are given in Table 4. The viscosity of aqueous H_3PO_4 solutions increases steadily with growing acid concentration (Table 4). For solutions of phosphoric acid in DMF and mixed solvent (when $x_{DMF} > 0.3$ m.f.), the acid concentration dependence of viscosity has a maximum at about 0.6 m.f. H_3PO_4, the height of which decreases with increasing temperature.

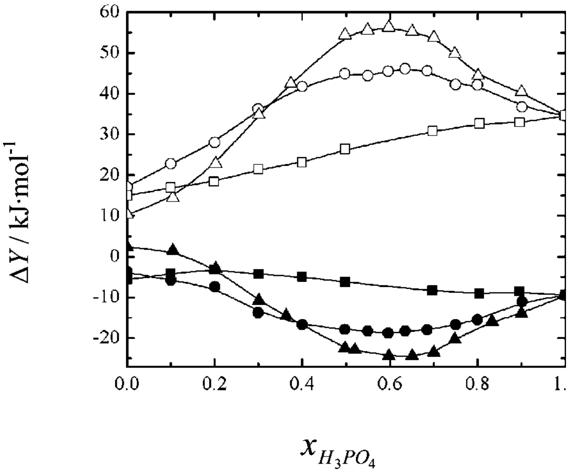

Figure 3. Values of $\Delta H_\eta^{\mp}$ (unclosed symbols) and ($-T\Delta S_\eta^{\mp}$) (closed symbols) of H_3PO_4 solutions in mixed solvent H_2O + DMF as a function of acid concentration. Concentration of DMF in mixed solvent H_2O + DMF is: ■, □, 0; ●, ○, 0.5; ▲, △, 0.8.

The thermodynamic functions of activation of viscous flow have been calculated using experimental viscosities at various temperatures.

$$\Delta G_\eta^{\#} = RT\left(\ln(\eta) - \ln\left(\frac{hN_A}{V}\right)\right) \tag{5}$$

where h and N_A are the Planck constant and Avogadro constant.

$$\Delta S_\eta^{\#} = -\frac{\partial \Delta G_\eta^{\#}}{\partial T} \tag{6}$$

$$\Delta H_\eta^{\#} = \Delta G_\eta^{\#} + T\Delta S_\eta^{\#} \tag{7}$$

In Figure 3, dependences of $\Delta H_\eta^{\#}$ and $\Delta S_\eta^{\#}$ calculated for H_3PO_4 solutions in H_2O and mixed solvent H_2O + DMF as acid concentrations at $T = 298.15$ K are shown as examples. As one can see, the main contribution to the activation free energy $\Delta G_\eta^{\#}$ comes from the enthalpy term at all acid concentrations and all mixed solvent compositions.

The viscous flow activation free energy of the binary mixture is additive on a mole fraction basis

$$\Delta G_{\text{mix}}^{\#} = x_{H_3PO_4} \Delta G_{H_3PO_4}^{\#} + x_S \Delta G_S^{\#} \tag{8}$$

Using this equation and eq 5, the excess viscosities for pseudobinary H_3PO_4 + S mixtures were calculated (S denotes mixed solvent H_2O + DMF)

$$\eta^E = \eta_{\text{mix}}^{\text{exptl}} - \exp(x_{H_3PO_4} \ln(\eta_{H_3PO_4} V_{H_3PO_4}) + x_S \ln(\eta_S V_S) - \ln(V_{\text{mix}})) \tag{9}$$

Values of η^E were fitted with the Redlich−Kister equation, and the coefficients of that and the root-mean-square deviation from fitted curve δ are presented in Table 5.

In Figure 4, the dependence of the excess viscosity on acid concentrations at $T = 298.15$ K is shown. At DMF concentration higher than 0.3 m.f. in mixed solvent, the dependence gets extreme character. The extreme intensity increases with increasing DMF concentration in mixed solvent H_2O + DMF. It has been suggested in our earlier study[1] of H_3PO_4 + DMF mixtures that this extreme is caused by formation of complexes with presumable composition of H_3PO_4:DMF = 2:1. Then, addition of water in DMF should be varied of maximum position on the dependence of the excess viscosity on acid concentrations toward lower acid concentration, but this does not take place. The independence of maximum position of η^E on acid concentrations (at 0.6 m.f. acid) from composition of mixed solvent H_2O + DMF possibly results from association processes in phosphoric acid itself. It is well known that there is equilibrium in 100 % of H_3PO_4 in the liquid state

$$2H_3PO_4 \leftrightarrow H_4P_2O_7 + H_2O \tag{10}$$

and about 15 % of P atoms are in the pyrophosphoric acid.[19] Probably, addition solvents to 100 % H_3PO_4 lead to equilibrium mixing to the left. It should be noticed that the similar behavior of viscosity concentration dependence is observed for phosphoric acid mixtures with the other organic solvents.[20]

Conclusions

In summary, there are several processes in the studied solution, namely, ionic dissociation, molecular association, and destruction/formation of H-bonds. Each of them dominates in a certain region of concentration of phosphoric acid and mixed solvent.

Table 5. Coefficients of the Redlich−Kister Equation for η^E of H_3PO_4 + S (H_2O + DMF) for Various Values of Mole Fraction of DMF in Mixed Solvent S from T = (298.15 to 328.15) K

T/K	A_0/Pa·s	A_1/Pa·s	A_2/Pa·s	A_3/Pa·s	A_4/Pa·s	A_5/Pa·s	δ/Pa·s
			$H_2$0				
298.15	−0.420	0.0554	−0.0411				0.0015
308.15	−0.256	0.0396	−0.0226				0.0011
318.15	−0.163	0.0312	−0.0096				0.0008
328.15	−0.112	0.0192	−0.0077				0.0004
338.15	−0.0780	0.0142	−0.0022				0.0003
			0.1 DMF				
298.15	−0.292	0.1213	−0.0451				0.0016
308.15	−0.174	0.0747	−0.0428				0.0010
318.15	−0.110	0.0492	−0.0193				0.0004
328.15	−0.071	0.0307	−0.0203				0.0002
338.15	−0.049	0.0228	−0.0108				0.0001
			0.2 DMF				
298.15	−0.0279	0.292	−0.1596				0.0034
308.15	−0.0188	0.164	−0.0977				0.0016
318.15	−0.0084	0.102	−0.0723				0.0011
328.15	−0.0070	0.0528	−0.0576				0.0007
338.15	−0.0028	0.0370	−0.0407				0.0005
			0.3 DMF				
298.15	0.329	0.518	−0.581				0.0117
308.15	0.182	0.270	−0.339				0.0061
318.15	0.109	0.157	−0.198				0.0033
328.15	0.0711	0.101	−0.126				0.0020
338.15	0.0457	0.0590	−0.086				0.0011
			0.4 DMF				
298.15	0.777	1.677	−1.25	−2.39			0.0161
308.15	0.411	0.873	−0.667	−1.23			0.0082
318.15	0.242	0.484	−0.381	−0.646			0.0050
328.15	0.151	0.293	−0.228	−0.256			0.0028
338.15	0.0985	0.189	−0.154				0.0018
			0.5 DMF				
298.15	1.501	2.84	−3.35	−4.14	2.19		0.0240
308.15	0.800	1.45	−1.81	−2.06	1.23		0.0119
318.15	0.443	0.764	−0.906	−1.006	0.561		0.0054
328.15	0.265	0.443	−0.476	−0.557	0.236		0.0026
338.15	0.173	0.268	−0.294	−0.334	0.111		0.0016
			0.6 DMF				
298.15	2.37	4.70	−5.72	−7.14	4.38		0.0454
308.15	1.18	2.31	−2.53	−3.38	1.70		0.0183
318.15	0.644	1.19	−1.33	−1.64	0.906		0.0089
328.15	0.384	0.684	−0.729	−0.915	0.436		0.0047
338.15	0.241	0.393	−0.433	−0.486	0.254		0.0025
			0.7 DMF				
298.15	2.73	9.29	−2.74	−27.8	−1.227	23.3	0.0347
308.15	1.36	4.31	−1.12	−11.8	−0.949	9.32	0.0170
318.15	0.748	2.23	−0.672	−5.98	−0.382	4.72	0.0088
328.15	0.437	1.17	−0.419	−2.92	−0.139	2.22	0.0043
338.15	0.270	0.712	−0.206	−1.73	−0.170	1.30	0.0030
			0.8 DMF				
298.15	3.58	14.6	−2.91	−48.5	−3.26	43.4	0.0446
308.15	1.72	6.68	−1.05	−20.9	−1.99	18.1	0.0204
318.15	0.912	3.19	−0.580	−9.11	−0.875	7.45	0.0071
328.15	0.522	1.70	−0.354	−4.66	−0.411	3.77	0.0037
338.15	0.321	0.989	−0.225	−2.61	−0.231	2.06	0.0023
			0.9 DMF				
298.15	4.52	20.1	4.94	−53.5	−16.6	39.5	0.0851
308.15	2.14	8.36	1.20	−20.9	−5.86	14.7	0.0310
318.15	1.13	3.98	0.408	−8.96	−2.50	5.79	0.0100
328.15	0.629	2.06	0.0875	−4.49	−1.134	2.88	0.0055
338.15	0.385	1.12	−0.0696	−2.22	−0.462	1.30	0.0025
DMF[a]							
298.15	6.22	34.9	11.2	−104.7	−32.0	85.0	0.2021
308.15	2.96	15.5	5.92	−42.2	−15.6	31.6	0.0778
318.15	1.57	7.58	2.12	−20.5	−6.34	15.7	0.0339
328.15	0.837	3.57	1.005	−8.49	−2.98	5.79	0.0129
338.15	0.481	1.93	0.566	−4.25	−1.63	2.73	0.0074

[a] Calculated from ref 1.

Conductivity data showed that ionic dissociation of phosphoric acid decreases with DMF content and increases in mixed solvent H_2O + DMF. At DMF concentrations in mixed solvent H_2O + DMF more than 0.3 m.f., ionic dissociation of H_3PO_4 becomes small. The dependence of some properties (η, n_D) of H_3PO_4 solutions in mixed solvent H_2O + DMF (when $x_{DMF} > 0.3$ m.f.) as acid concentrations has a maximum with position at about 0.6 acid mole fraction

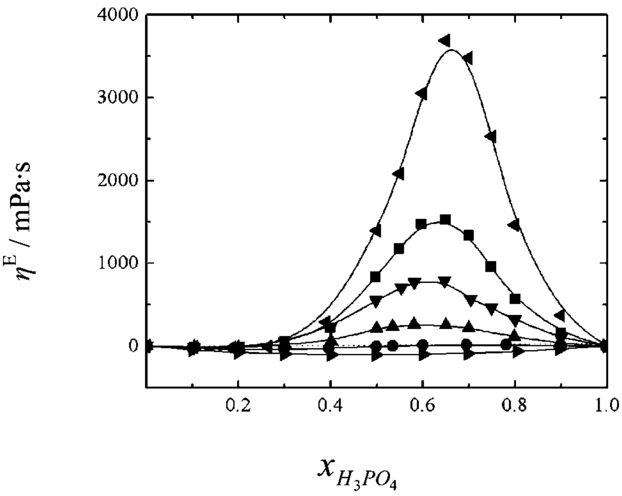

Figure 4. Excess viscosities of H_3PO_4 solutions in mixed solvent H_2O + DMF as functions of acid concentration at 298.15 K. Concentration of DMF in mixed solvent H_2O + DMF is: solid arrow pointing right, 0; ●, 0.2; ▲, 0.4; ▼, 0.6; ■, 0.8; solid arrow pointing left, 1.

independently of H_2O + DMF composition. This is evidently caused by the molecular association processes in the acid itself.

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