J. Chem. Eng. Data 1990, 35, 420-423

Table IV. Constants of the Equation ϕ (cP^{-1}) = $A_\phi \times \exp(-B_\phi/T - T_{0,\phi})$ for the Fluidity–Temperature Data for the $Al(NO_3)_3 \cdot 10.03H_2O$ + $M(NO_3)_2 \cdot RH_2O$ Systems

$M(NO_3)_2 \cdot RH_2O$ mole fractn	temp range, K	$\ln A_\phi$	B_ϕ	$T_{0,\phi}$	10SE
$M(NO_3)_2 \cdot RH_2O = Ca(NO_3)_2 \cdot 3.99H_2O$					
0.3984	303–354	1.2367	619.81	204.41	0.036
0.5311	313–353	0.9180	534.95	213.35	0.057
0.6573	313–353	1.3113	633.42	205.30	0.054
0.7282	318–353	1.2745	627.84	207.31	0.038
0.8049	313–353	1.1909	636.50	210.26	0.033
0.8606	313–353	1.5122	716.16	203.20	0.032
0.9114	313–353	1.0874	598.98	212.40	0.016
0.9591	317–353	1.3640	676.42	203.54	0.060
1.0000	313–353	0.8023	573.72	210.27	0.081
$M(NO_3)_2 \cdot RH_2O = Cd(NO_3)_2 \cdot 4.12H_2O$					
0.1155	313–353	1.6417	716.93	193.79	0.041
0.2002	318–353	1.4926	666.61	197.41	0.024
0.3280	313–353	1.8981	782.02	183.73	0.060
0.4097	308–353	1.2535	580.02	204.16	0.027
0.5143	303–353	1.5299	647.54	197.42	0.032
0.7050	303–353	1.6107	656.11	195.09	0.049
0.7944	303–353	1.4541	614.11	198.24	0.025
0.8966	303–353	1.3197	586.36	201.69	0.020
1.0000	313–353	1.1714	545.22	204.91	0.014
$M(NO_3)_2 \cdot RH_2O = Mg(NO_3)_2 \cdot 6.02H_2O$					
0.2017	313–353	1.6320	735.39	187.12	0.062
0.3030	318–353	1.7565	778.33	181.99	0.035
0.3926	323–353	1.3616	657.32	193.57	0.027
0.4896	337–353	1.5352	700.44	187.00	0.029
$M(NO_3)_2 \cdot RH_2O = Zn(NO_3)_2 \cdot 6.10H_2O$					
0.1518	308–353	1.4815	648.01	197.14	0.048
0.2879	313–353	1.6399	669.17	193.41	0.043
0.4008	302–353	1.7117	666.96	194.56	0.047
0.4836	313–353	1.5123	602.69	202.41	0.022
0.5343	313–353	1.5767	629.76	199.34	0.023
0.7246	303–353	2.1521	728.97	183.59	0.036
0.8901	303–353	2.1560	704.04	179.35	0.027
0.9418	303–353	2.3937	772.86	172.91	0.038
1.0000	308–353	1.9450	652.45	182.54	0.058

its fluid behavior. The constants of eqs 3 and 4 were found by an iterative method (Tables III and IV).

Conductivity and viscosity composition isotherms for the binary mixtures of $Al(NO_3)_3 \cdot 10H_2O$ with (Ca, Cd, Mg, Zn)$(NO_3)_2 \cdot RH_2O$ are shown in Figures 1 and 2. Addition of $Ca(NO_3)_2 \cdot 4H_2O$ to the $Al(NO_3)_3 \cdot 10H_2O$ melt causes preferential orientation of the NO_3^- ion—the common anion—toward the $Al(H_2O)_n^{3+}$ ion due to its higher cationic potential (0.91) relative to that of the $Ca(H_2O)_n^{2+}$ ion (0.53) (*9*). Water released from the hydration sphere of the Al^{3+} ions occupies new sites in the hydration sphere of the Ca^{2+} ions, decreasing their mobility and consequently κ. The observed increase in κ beyond 83 mol % may be due to a saturation of these interactions. As expected, an opposite trend is observed in viscosity composition isotherms for this system.

Small variations in κ and η on addition of $Cd(NO_3)_2 \cdot 4H_2O$ and $Mg(NO_3)_2 \cdot 6H_2O$ to the $Al(NO_3)_3 \cdot 10H_2O$ melt are attributed to small changes in $Al(H_2O)_n^{3+}$–NO_3^- interactions. Cadmium and magnesium ions have been found to form contact ion pairs in concentrated solutions (*10*, *11*), because of which they would not alter the NO_3^- ion equilibrium in the mixture to a large extent. $Al(NO_3)_3 \cdot 10H_2O$ and $Zn(NO_3)_2 \cdot 6H_2O$ mixtures do not show much change in κ up to 53 mol % of the divalent salt. A decrease in κ due to $Al(H_2O)_n^{3+}$–NO_3^- interactions may be counterbalanced by an increase in κ due to water released from the hydration sphere of the Al^{3+} ions. A saturation effect of these interactions may be responsible for an increase in κ and a decrease in η on addition of zinc salt beyond this composition. Studies are in progress to provide further insight into these systems.

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Received for review August 25, 1989. Revised May 1, 1990. Accepted May 30, 1990.

Equilibrium Phase Behavior of the Poly(ethylene glycol)/Potassium Phosphate/Water Two-Phase System at 4 °C

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The two-phase liquid–liquid equilibria behavior of the system composed of poly(ethylene glycol), potassium phosphate, and water at 4 °C is presented. The effect of poly(ethylene glycol) molecular weight on phase separation at pH 7 was investigated by utilizing poly(ethylene glycol) of molecular weight 400, 600, 1000, 1500, 3400, 8000, and 20 000. By varying the ratio of monobasic to dibasic potassium phosphate and maintaining the poly(ethylene glycol) molecular weight at 3400, the effect of pH on phase equilibria was studied over the pH range 6–9.2.

Introduction

When poly(ethylene glycol) (PEG) is mixed with potassium phosphate and water at an appropriate pH and temperature, two phases are produced, the top phase being rich in PEG and the bottom phase containing primarily phosphate. As discovered by Albertsson (*1*, *2*), the phases of the system offer different physical and chemical environments and are delicate enough to be used for the purification of biological materials. However, in order to gain a fundamental understanding of phase separation and select an appropriate PEG/potassium phosphate/water system for purification purposes, phase equilibrium data are ultimately needed.

The main source of phase equilibrium data for the PEG/potassium phosphate/water system is that of Albertsson (*1*).

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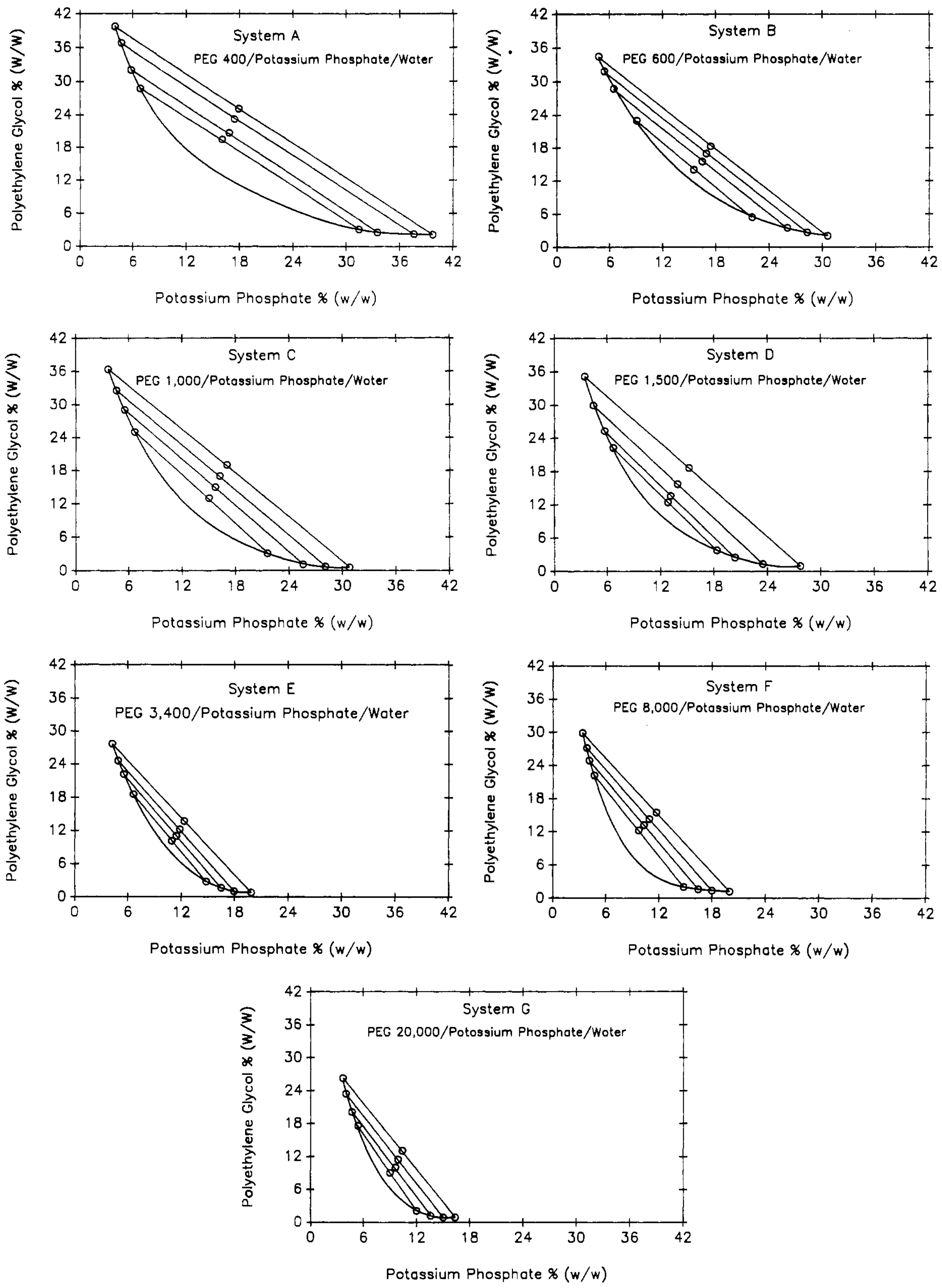

Figure 1. Phase diagrams for PEG/potassium phosphate/water at 4 °C, pH 7.

However, this data is not yet complete, particularly with regard to the systems at 4 °C, where biochemical research is frequently performed. In this paper, we present phase diagrams at 4 °C and pH 7 for the PEG/potassium phosphate/water system, using PEG of molecular weight 400, 600, 1000, 1500, 3400, 8000, and 20 000. The effect of pH on phase separation at 4 °C was also investigated for the PEG 3400/potassium phosphate/water system over the pH range of 6–9.2. It should be noted that the pH may be changed by varying the ratio of monobasic to dibasic potassium phosphate. This ratio is maintained the same throughout a phase diagram, which is at constant pH.

Experimental Methods

The experimental work was performed using the procedure outlined by Albertsson (*1*). The details of this procedure are as follows:

Table I. Phase Compositions for the PEG/Potassium Phosphate/Water System at 4 °C, pH 7

	concentration, % (w/w)								
	total system			bottom phase			top phase		
tie line no.	potassium phosphate	PEG	H_2O	potassium phosphate	PEG	H_2O	potassium phosphate	PEG	H_2O
	System A: PEG 400/Potassium Phosphate/Water								
1	16.00	19.40	64.60	31.45	3.05	65.50	6.85	28.75	64.40
2	16.80	20.60	62.60	33.51	2.54	63.95	5.78	32.02	62.20
3	17.40	23.20	59.40	37.61	2.24	60.15	4.69	36.79	58.52
4	17.90	25.10	57.00	39.73	2.12	58.15	3.95	39.73	56.32
	System B: PEG 600/Potassium Phosphate/Water								
1	15.50	14.00	70.50	22.06	5.41	72.53	9.04	23.01	67.95
2	16.43	15.51	68.06	26.05	3.47	70.48	6.43	28.73	64.84
3	16.90	17.00	66.10	28.29	2.66	69.05	5.38	31.88	62.74
4	17.40	18.30	64.30	30.59	2.00	67.41	4.78	34.48	60.74
	System C: PEG 1000/Potassium Phosphate/Water								
1	15.00	13.00	72.00	21.56	3.08	75.36	6.64	25.02	68.34
2	15.70	15.00	69.30	25.56	1.08	73.36	5.53	29.02	65.45
3	16.20	17.00	66.80	28.08	0.71	71.21	4.60	32.56	62.84
4	17.00	19.00	64.00	30.81	0.56	68.63	3.70	36.37	59.93
	System D: PEG 1500/Potassium Phosphate/Water								
1	12.83	12.40	74.77	18.33	3.79	77.88	6.64	22.22	71.14
2	13.12	13.66	73.22	20.37	2.50	77.13	5.69	25.30	69.01
3	13.90	15.74	70.36	23.48	1.34	75.18	4.44	29.95	65.61
4	15.17	18.64	66.19	27.71	0.98	71.31	3.46	35.13	61.41
	System E: PEG 3400/Potassium Phosphate/Water								
1	10.90	10.10	79.00	14.80	2.76	82.44	6.60	18.55	74.85
2	11.40	11.00	77.60	16.48	1.61	81.91	5.51	22.14	72.35
3	11.80	12.20	76.00	17.92	1.01	81.07	4.88	24.58	70.54
4	12.30	13.70	74.00	19.85	0.78	79.37	4.21	27.66	68.13
	System F: PEG 8000/Potassium Phosphate/Water								
1	9.70	12.20	78.10	14.77	2.00	83.23	4.68	22.19	73.13
2	10.30	13.20	76.50	16.43	1.60	81.97	4.13	24.85	71.02
3	10.90	14.30	74.80	17.98	1.35	80.67	3.84	27.14	69.02
4	11.70	15.50	72.80	19.96	1.19	78.85	3.34	29.82	66.84
	System G: PEG 20000/Potassium Phosphate/Water								
1	9.00	9.00	82.00	11.99	2.10	85.91	5.36	17.55	77.09
2	9.60	10.00	80.40	13.56	1.20	85.24	4.70	20.06	75.24
3	9.90	11.40	78.70	14.99	0.90	84.11	4.01	23.39	72.60
4	10.40	13.00	76.60	16.36	0.88	82.76	3.69	26.21	70.10

Table II. Phase Compositions for the PEG 3400/Potassium Phosphate/Water System over the pH Range 6–9.2 at 4 °C[a]

	concentration, % (w/w)								
	total system			bottom phase			top phase		
tie line no.	potassium phosphate	PEG	H_2O	potassium phosphate	PEG	H_2O	potassium phosphate	PEG	H_2O
	System H: PEG 3400/Potassium Phosphate/Water at pH 6								
1	12.50	10.50	77.00	17.50	2.49	80.01	8.04	18.11	73.85
2	13.00	11.00	76.00	18.68	1.88	79.44	7.10	20.81	72.09
3	14.00	12.00	74.00	20.79	1.00	78.21	6.15	24.54	69.31
4	15.00	13.00	72.00	23.27	0.60	76.13	5.65	27.14	67.21
	System I: PEG 3400/Potassium Phosphate/Water at pH 8								
1	9.20	13.80	77.00	14.75	2.04	83.21	4.59	23.11	72.30
2	10.30	14.80	74.90	17.47	0.78	81.75	3.74	27.33	68.93
3	11.00	16.00	73.00	19.04	0.64	80.32	3.30	30.03	66.67
4	12.00	17.00	71.00	21.18	0.52	78.30	2.93	32.89	64.18
	System J: PEG 1000/Potassium Phosphate/Water at pH 9.2								
1	9.20	13.80	77.00	14.63	2.26	83.11	4.40	23.95	71.65
2	10.30	14.80	74.90	17.53	0.73	81.74	3.75	27.91	68.34
3	11.00	16.00	73.00	19.49	0.39	80.12	3.22	30.82	65.96
4	12.00	17.00	71.00	21.48	0.21	78.31	2.79	33.91	63.30

[a] The data for the PEG 3400/potassium phosphate/water system at pH 7 is given in Table I.

Potassium phosphate stock solutions of 20% (w/w) at pH 6, 7, and 8 were prepared by using a dibasic to monobasic weight ratio of 0.5, 1.82, and 15., respectively. The stock solution at pH 9.2 was prepared with pure dibasic potassium phosphate. The biphasic systems constituting a phase diagram were then prepared by weighing appropriate quantities of PEG, potassium phosphate solution, and water into a 100-mL beaker. Typically, 40 g of a system were prepared. The solution was magnetically stirred for 45 min, after which it was poured into a 50-mL polypropylene centrifuge tube. The tube was tightly capped and then allowed to equilibrate for 48–72 h in a 4 °C refrigerator. The temperature in the refrigerator was controlled to ±0.1 °C.

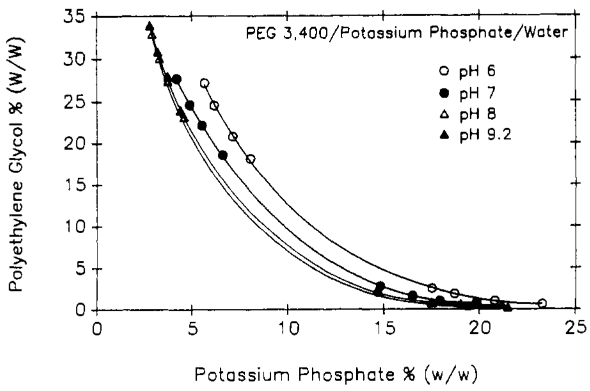

Figure 2. Binodial curves for PEG 3400/potassium phosphate/water over the pH range 6-9.2 at 4 °C.

A pasteur pipet was used to collect the top phase, while the lower phase was drained from the polypropylene tube by piercing a hole at its bottom.

Potassium phosphate concentration, which includes quantification of both potassium and phosphate, was determined to a precision of ±0.02% (w/v) by ion exchange chromatography and titration, as described in detail by Svehla (*3*). The column was filled with Dowex-50 cation exchange resin (8% cross-linked), while titration was performed with 0.1 N sodium hydroxide and bromocresol green as the indicator. The concentrations obtained on a weight per volume basis were converted to weight per weight by density measurements using pycnometry. The precision of the density was ±0.001 g/mL. In order to determine water content, samples of about 2-3 g from each phase were weighed into 20-mL polypropylene tubes, diluted with 5-7 mL of water, and freeze-dried for 24-72 h. In order to verify that no PEG was lost during the freeze-drying process, samples of PEG aqueous solutions were freeze-dried, and the weights before and after the drying were found to be the same. Therefore, no PEG was lost during the process. The precision of the water concentration was ±0.02% (w/w). Having determined the potassium phosphate and water concentrations, the PEG content was obtained by subtraction.

Materials

ACS reagent grade monobasic and dibasic potassium phosphate were obtained from Aldrich Chemical Co., Milwaukee, WI. Poly(ethylene glycol) of molecular weight 400, 600, 1000, 1500, 3400, 8000, and 20 000 was also obtained from Aldrich.

The Dowex 50-w cation exchange resin was purchased from Sigma Chemical Co., St. Louis, MO.

Results and Discussion

Phase diagrams have been obtained at 4 °C for PEG/potassium phosphate/water systems at pH 7 by utilizing PEG of molecular weight 400, 600, 1000, 1500, 3400, 8000, and 20 000. Phase equilibrium data have also been obtained for the PEG 3400/potassium phosphate/water system at pH 6, 7, 8, and 9.2. The phase compositions for the systems with varying PEG molecular weight and pH are presented in Tables I and II, respectively. Similarly, the phase diagrams for the two sets of systems are presented in Figures 1 and 2, respectively.

Analysis of binodial curves of systems A-G in Figure 1 reveals the effect of PEG molecular weight on phase separation. As the molecular weight is increased, the binodial curve shifts to lower PEG and phosphate concentrations. This trend is in agreement with the experimental results of Albertsson (*1*).

Examination of the binodial curves in Figure 2 demonstrates the effect of pH on phase separation at constant PEG molecular weight. As the system becomes more basic, the binodials shift to lower PEG and phosphate concentrations, as was observed for the molecular weight effect. The difference in position between the binodials begins to diminish at high pH, with the binodials for pH 8 and 9.2 being almost identical.

Acknowledgment

We give special thanks to Kanokrot Phalakornkul, a summer student from Princeton University, and Ge Zhang from the Beijing Specialty Gas Research Institute, China, for laboratory help with titration and freeze-drying.

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Received for review August 17, 1989. Accepted June 15, 1990. This work was supported by National Science Foundation Grant Nos. EET-8708839 and CBT-8702912.

Some Physicochemical Data on Tetrahydrate Sodium Perborate in Aqueous Solutions

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The solubility of tetrahydrate sodium perborate as a function of temperature in aqueous solutions has been determined. The results can be expressed by an Arrhenius-type equation. Experiments have also been carried out with solutions containing sodium metaborate. The solubility is greatly affected by the presence of metaborate. The density, viscosity, and diffusivity as a function of concentration have also been reported. Some equations are proposed to correlate the experimental results. Measured data are compared with some available data of the literature.

Introduction

Sodium perborate $NaBO_3 \cdot 4H_2O$ is a bleaching agent used in detergents and washing powders. It is produced by the reaction between aqueous solutions of sodium metaborate and hydrogen peroxide.

$$NaBO_2 + H_2O_2 + 3H_2O \rightarrow NaBO_3 \cdot 4H_2O$$

Some experimental physicochemical data relative to tetrahydrate sodium perborate in aqueous solutions are reported here.