Subscripts

i component

Superscripts

s saturation

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Enthalpies of Formation, Densities, and Heat Capacities at 25 °C in the Liquid-Phase Region of the System $K_2O-P_2O_5-H_2O$

Basil B. Luff* and Robert B. Reed

Division of Chemical Development, National Fertilizer Development Center, Tennessee Valley Authority, Muscle Shoals, Alabama 35660

Measurements of the enthalpies of solution of monopotassium orthophosphate in various aqueous solutions of potassium hydroxide and phosphoric acid were made at 25 °C, and the apparent enthalpies of formation of the solutions were derived. Measurements of the densities and heat capacities of the solutions also were made.

The heat requirements in the production of fertilizer solutions may be determined by measurement of the enthalpies of formation of solutions of different K_2O:P_2O_5 ratios in the liquid-phase region of the system $K_2O-P_2O_5-H_2O$. This information also would be helpful in determining both the enthalpies of hydrolysis of potassium polyphosphate solutions and the enthalpies of formation of solutions containing additional components such as ammonia, urea, and chloride.

Reported here are the results of measurements of the enthalpies of solution of KH_2PO_4 in various aqueous solutions of KOH and H_3PO_4. The enthalpies of solution were combined with published values of enthalpies of formation to determine the enthalpies of formation of the solutions. The densities and the heat capacities of the solutions also are reported. Enthalpies of solution of H_3PO_4 (*1*), KH_2PO_4 (*2*), and K_2HPO_4 (*3*) have been reported. These data may be combined with published values of the enthalpies of formation of $H_3PO_4 \cdot 100H_2O$ (*4*), KH_2PO_4, and K_2HPO_4 (*5*) to derive the enthalpies of formation of orthophosphate solutions with mole ratios of K_2O:P_2O_5 of 0, 1, and 2.

Materials and Apparatus

Monopotassium orthophosphate was prepared by recrystallizing the reagent-grade salt from distilled water and drying at 105 °C. Chemical analyses showed this salt to contain 52.1% P_2O_5 and 34.6% K_2O (stoichiometric; 52.15% P_2O_5, 34.61% K_2O). The potassium hydroxide solutions were prepared from reagent-grade KOH and distilled water. Their concentrations, expressed in molality (m_1), were determined by acid titrations. The phosphoric acid solutions were prepared from reagent-grade H_3PO_4 and distilled water. Their concentrations, also expressed in molality (m_2), were determined by chemical analyses.

The solution calorimeter, the method of measurement, and the corrections applied have been described (*6*, *7*). The defined calorie was taken as 4.1840 absolute J. The average temperature for each of the solution periods is listed in the supplementary material (see paragraph at end of text regarding supplementary material). No corrections were applied to convert the enthalpies of solution to 25.00 °C.

Enthalpies of Solution of KH_2PO_4 in KOH Solutions

Monopotassium orthophosphate was added to each of the KOH solutions in successive increments to a final concentration near the saturation isotherm (*8*). The maximum temperature change during the solution period was arbitrarily set at about 1 °C, which limited the amount of solute to about 8 g at the lower concentrations of KH_2PO_4. The bulb volumes limited the amount of solute at the higher concentrations. The transfer of the final solution of one measurement from the calorimeter to a weighed fixed volume for the next measurement entailed some loss of the solution. Where larger amounts of solute were dissolved, there was still an excess of solution after the transfer and the excess could be removed before weighing the initial solution for the next measurement. Where smaller amounts of solute were dissolved, however, it was necessary to weigh the transferred solution and then add a weighed amount of the solvent (the KOH solution) to maintain the fixed volume. The concentration of the initial solution for the measurement thus could be determined. The concentration for each measurement, expressed as molality of KH_2PO_4 (m_2), is the average concentration of the initial and final solutions. The differential enthalpy of solution for each measurement was calculated from the equation

$$dT/dm_2 = 136.08934Q/1000w \quad (1)$$

where Q is the observed enthalpy change in calories, w is the

Table I. Coefficients of Eq 2 for KOH Solvents

		coeff				
m_1	m_2	A	B	C	D	SD, kcal (mol of KH_2PO_4)$^{-1}$
0.506	0.000-0.492		tabular integration			
0.506	0.492-1.570	3.935	-0.109			0.01
0.998	0.000-0.945		tabular integration			
0.998	0.945-2.684	4.317	-1.472	0.8957	-0.1760	0.01
1.495	0.000-0.500	-16.103				0.04
1.495	0.500-1.379		tabular integration			
1.495	1.379-3.032	0.432	3.814	-1.6306	0.2321	0.01
1.987	0.000-0.600	-16.141	-0.170	-0.3105		0.02
1.987	0.600-1.788		tabular integration			
1.987	1.788-3.406	3.056	0.082			0.02
3.029	0.000-1.060	-16.209	-0.247			0.05
3.029	1.060-1.700		tabular integration			
3.029	1.700-2.589	-1.263	0.139			0.00
3.029	2.589-4.217	0.907	1.147	-0.1385		0.02
4.121	0.000-1.400	-16.276	-0.216			0.05
4.121	1.400-2.000		tabular integration			
4.121	2.000-3.347	-2.020	0.371			0.02
4.121	3.347-5.138	-5.471	3.379	-0.4037		0.11
4.645	0.000-1.560	-16.273	-0.256			0.03
4.645	1.560-2.180		tabular integration			
4.645	2.180-3.685	-2.432	0.476			0.02
4.645	3.685-5.691	-7.695	4.345	-0.4235		0.15

Table II. Coefficients for Eq 4

	coeff						
	A	B	C	D	E	F	SD
$R < 1$	-5.996	1.997×10^{-1}	14.038	-4.716×10^{-3}	-8.832×10^{-1}	-2.393×10^{-2}	0.06
$1 < R < 2$	-3.087	4.317×10^{-1}	9.980	-12.483×10^{-3}	-4.546×10^{-1}	-8.958×10^{-2}	0.14
$R > 2$	15.572	1.060×10^{-1}	4.784×10^{-2}	-4.303×10^{-3}	-1.287×10^{-3}	8.238×10^{-3}	0.07

weight of KH_2PO_4 in grams dissolved during the measurement, and T is the total enthalpy change in kilocalories when m_2 mol of KH_2PO_4 is dissolved in 1000 g of the solvent. The gram formula weight of KH_2PO_4 is 136.08934. The measured values and the differential enthalpy of solution (dT/dm_2) for each measurement are listed in the supplementary material. The exothermic differential enthalpies of solution decrease rapidly in the concentration range equivalent to K_3PO_4 in water and change to endothermic at the concentration equivalent to K_2HPO_4 in water. Where it was convenient, the observed differential enthalpies of solution as a function of molality were fitted to equations of the form

$$dT/dm_2 = A + Bm_2 + Cm_2^2 + Dm_2^3 \quad (2)$$

for each solvent by the least-squares method. The coefficients of the equations for each of the solvents, along with their standard deviations and the concentration ranges in which they are effective, are listed in Table I. Integration of these equations with respect to m_2 plus the correct values for the integration constants and then division by m_2 gives the integral enthalpies of solution, ΔH, in kcal (mol of KH_2PO_4)$^{-1}$ as a function of molality. Where the differential enthalpies of solution change greatly with concentration, smooth curves were fitted to the observed values. Tabular integration and division by m_2 gave the integral enthalpies of solution at even values of m_2 in those concentration ranges. The ranges in which tabular integration was employed also are listed in Table I. The integral of eq 2 for each solvent and range of m_2 was solved for ΔH at the values of m_2 corresponding to integers of percent P_2O_5. In the ranges where tabular integration was employed, the values for ΔH were determined by straight-line interpolation between adjacent even values of m_2. Values for percent K_2O corresponding to the integers of percent P_2O_5 were calculated from straight-line equations through percent K_2O in the solvent and percent P_2O_5 and percent K_2O and KH_2PO_4. The equations for percent K_2O as a function of percent P_2O_5, along with values of m_2, ΔH, and percent K_2O corresponding to each integer of percent P_2O_5, are listed in the supplementary material.

As stated earlier, the differential enthalpies of solution and thus the slopes of the integral enthalpies of solution change markedly at concentrations where the mole ratio of KOH:KH_2PO_4 is 1 and 2, corresponding to K_2HPO_4 in water and K_3PO_4 in water, respectively. The mole ratio of KOH:KH_2PO_4, R, for each integer of percent P_2O_5 listed in the supplementary material was calculated from the equation

$$R = 1.50679(\%\ K_2O/\%\ P_2O_5) - 1 \quad (3)$$

where 1.50679 is the gram formula weight ratio P_2O_5:K_2O. These values for R also are listed in the supplementary material. Equations of the form

$$-\Delta H = A + BP + CR + DP^2 + ER^2 + FRP \quad (4)$$

where P is the percent P_2O_5, were fitted to the values of P, R, and ΔH by the least-squares method over three ranges of R ($R < 1$, $1 < R < 2$, and $R > 2$). The coefficients of the equations, the standard deviations, and the range of R for which each equation is effective are listed in Table II. Values for ΔH calculated from these equations also are listed in the supplementary material.

Enthalpy of Solution of KH_2PO_4 in H_3PO_4 Solutions

The procedure for determining the enthalpies of solution of KH_2PO_4 in H_3PO_4 solutions was similar to that described for KOH solutions, and eq 1 was used to determine the differential enthalpy of solution for each measurement (supplementary material).

Equation 2 was fitted to the observed differential enthalpies of solution as a function of solute molality for each solvent. The coefficients for eq 2 for each of the solvents, along with their standard deviations, are listed in Table III. Integration of these equations with respect to m_2 (the integration constant is zero in each case) and division by m_2 gives the integral en-

Table III. Coefficients of Eq 2 for H_3PO_4 Solvents

m_1	coeff A	B	C	D	SD, kcal (mol of KH_2PO_4)$^{-1}$
0.510	5.209	−2.108	1.383	−0.3463	0.05
1.019	5.151	−2.046	1.364	−0.3522	0.02
1.514	5.100	−1.849	1.068	−0.2383	0.02
1.988	5.031	−1.666	0.888	−0.1858	0.02
3.076	4.484	−1.317	0.582	−0.1048	0.01
4.106	4.658	−1.123	0.445	−0.0735	0.01
5.081	4.474	−0.967	0.368	−0.0566	0.01

thalpies of solution in kcal (mol of KH_2PO_4)$^{-1}$ as a function of molality. The integral of eq 2 for each solvent was solved for ΔH at the values of m_2 corresponding to integers of percent K_2O. Values for percent P_2O_5 corresponding to the integers of percent K_2O were calculated from straight-line equations through percent P_2O_5 in the solvent and percent P_2O_5 and percent K_2O in KH_2PO_4. The equations for percent P_2O_5 as a function of percent K_2O, along with values of m_2, ΔH, and percent P_2O_5 corresponding to each integer of percent K_2O, are listed in Table IV. The equation

$$\Delta H = 5.110 - 0.1619K + 0.003195P + 0.002053K^2 - 0.001183P^2 + 0.003722PK \quad (5)$$

where K is percent K_2O and P is percent P_2O_5, fits the values calculated from the integrals of eq 2, with a standard deviation of 0.02 kcal (mol of KH_2PO_4)$^{-1}$. Values for ΔH calculated from eq 5 also are listed in Table IV.

Enthalpy of Formation of K_2O–P_2O_5–H_2O Solutions

The solution of KH_2PO_4 in KOH solutions can be described by the equation

$$KH_2PO_4 + R(KOH{\cdot}xH_2O) = K_2HPO_4{\cdot}(R-1)KOH{\cdot}(Rx+1)H_2O \quad (6)$$

where $R > 1$ and by the equation

$$KH_2PO_4 + R(KOH{\cdot}xH_2O) = R(K_2HPO_4){\cdot}(Rx+R)H_2O{\cdot}(R-1)KH_2PO_4 \quad (7)$$

where $R < 1$. The enthalpies of formation of the resultant solutions, $\Delta H_f°$(soln), in kcal (mol of P_2O_5)$^{-1}$, can be determined from the equation

$$\Delta H_f°(\text{soln}) = 2[R\{\Delta H_f°(KOH{\cdot}xH_2O)\} + \Delta H_f°(KH_2PO_4) - \Delta H_f°(H_2O) + \Delta H_6] \quad (8)$$

where $R > 1$ and ΔH_6 is the integral enthalpy of solution for reaction 6 and from the equation

$$\Delta H_f°(\text{soln}) = 2[R\{\Delta H_f°(KOH{\cdot}xH_2O) - \Delta H_f°(H_2O)\} + \Delta H_f°(KH_2PO_4) + \Delta H_7] \quad (9)$$

where $R < 1$ and ΔH_7 is the integral enthalpy of solution for reaction 7. The standard enthalpy of formation of KH_2PO_4 is −376.1 kcal mol^{-1} and that of H_2O is −68.315 kcal mol^{-1} (9). The standard enthalpies of formation of the KOH solutions were calculated from an equation fitted to published values (10), with a standard deviation of 0.03 kcal (mol of KOH)$^{-1}$. The standard enthalpies of formation of K_2O–P_2O_5–H_2O solutions where the mole ratios of K_2O:P_2O_5 > 1 were calculated at integers of percent P_2O_5 and percent K_2O by using eq 3, 4, 8, and 9 and are listed in Table V.

Table IV. Integral Enthalpy of Solution of KH_2PO_4 in H_3PO_4 Solutions

% K_2O	% P_2O_5	m_2	ΔH, kcal mol^{-1}: integral of eq 2	eq 5
m_1 = 0.510, % P_2O_5 = 3.450 + 1.40710(% K_2O)				
1.0	4.857	0.2186	5.00	4.96
2.0	6.264	0.4507	4.82	4.85
3.0	7.671	0.6974	4.67	4.68
4.0	9.078	0.9602	4.55	4.56
5.0	10.486	1.2408	4.45	4.45
6.0	11.893	1.5410	4.36	4.35
7.0	13.300	1.8629	4.29	4.26
m_1 = 1.019, % P_2O_5 = 6.575 + 1.31681(% K_2O)				
1.0	7.892	0.2186	4.95	4.93
2.0	9.209	0.4507	4.77	4.79
3.0	10.525	0.6974	4.63	4.66
4.0	11.842	0.9602	4.51	4.54
5.0	13.159	1.2408	4.41	4.43
6.0	14.476	1.5410	4.33	4.33
7.0	15.793	1.8629	4.25	4.24
8.0	17.109	2.2091	4.16	4.16
m_1 = 1.514, % P_2O_5 = 9.355 + 1.23649(% K_2O)				
1.0	10.591	0.2186	4.91	4.89
2.0	11.828	0.4507	4.75	4.75
3.0	13.064	0.6974	4.61	4.63
4.0	14.301	0.9602	4.49	4.51
5.0	15.537	1.2408	4.39	4.41
6.0	16.774	1.5410	4.30	4.31
7.0	18.010	1.8629	4.23	4.22
8.0	19.247	2.2091	4.15	4.14
m_1 = 1.988, % P_2O_5 = 11.807 + 1.16564(% K_2O)				
1.0	12.973	0.2186	4.86	4.84
2.0	14.138	0.4507	4.71	4.71
3.0	15.304	0.6974	4.58	4.59
4.0	16.470	0.9602	4.46	4.47
5.0	17.635	1.2408	4.36	4.37
6.0	18.801	1.5410	4.28	4.27
7.0	19.966	1.8629	4.21	4.19
8.0	21.132	2.2091	4.13	4.11
m_1 = 3.076, % P_2O_5 = 16.773 + 1.02216(% K_2O)				
1.0	17.795	0.2186	4.70	4.70
2.0	18.817	0.4507	4.58	4.58
3.0	19.839	0.6974	4.46	4.46
4.0	20.862	0.9602	4.36	4.36
5.0	21.884	1.2408	4.27	4.26
6.0	22.906	1.5410	4.19	4.18
7.0	23.928	1.8629	4.11	4.10
8.0	24.950	2.2091	4.05	4.03
9.0	25.972	2.5822	3.98	3.97
m_1 = 4.106, % P_2O_5 = 20.780 + 0.90639(% K_2O)				
1.0	21.686	0.2186	4.54	4.54
2.0	22.593	0.4507	4.43	4.43
3.0	23.499	0.6974	4.33	4.33
4.0	24.406	0.9602	4.24	4.23
5.0	25.312	1.2408	4.15	4.15
6.0	26.218	1.5410	4.08	4.07
7.0	27.125	1.8629	4.01	4.00
8.0	28.031	2.2091	3.94	3.94
9.0	28.938	2.5822	3.88	3.89
10.0	29.844	2.9857	3.82	3.85
m_1 = 5.081, % P_2O_5 = 24.075 + 0.81119(% K_2O)				
1.0	24.886	0.2186	4.37	4.39
2.0	25.697	0.4507	4.28	4.29
3.0	26.509	0.6974	4.19	4.19
4.0	27.320	0.9602	4.11	4.11
5.0	28.131	1.2408	4.04	4.03
6.0	28.942	1.5410	3.97	3.96
7.0	29.753	1.8629	3.91	3.90
8.0	30.565	2.2091	3.85	3.85
9.0	31.376	2.5822	3.80	3.81
10.0	32.187	2.9857	3.75	3.77

Table V. Enthalpies of Formation of K_2O-P_2O_5-H_2O Solution, kcal (mol of P_2O_5)$^{-1}$

% P_2O_5	% K_2O												
	0	1	2	3	4	5	6	7	8	9	10	11	12
1	619.67	801.59	1109.75	1455.81	1801.69	2147.42	2493.04	2838.57	3184.01	3529.36	3874.60	4219.72	4564.70
2	619.55	712.06	801.92	923.77	1109.76	1282.69	1455.56	1628.38	1801.75	1973.88	2146.57	2319.20	2491.77
3	619.46	681.22	741.87	802.23	862.20	986.07	1109.79	1225.03	1340.24	1455.42	1570.58	1685.70	1800.78
4	619.38	665.75	712.26	757.38	802.52	847.10	924.59	1017.24	1109.84	1196.24	1282.63	1368.99	1455.32
5	619.31	656.44	693.69	731.02	766.75	802.80	838.47	887.83	961.99	1035.97	1109.88	1178.99	1248.07
6	619.24	650.21	681.28	712.44	742.81	773.07	803.05	832.78	863.43	925.24	986.92	1048.46	1109.92
7	619.18	645.75	672.41	699.14	725.92	751.76	777.62	803.29	828.77	854.06	899.05	951.92	1004.70
8	619.12	642.39	665.74	689.14	712.60	736.10	758.49	781.08	803.51	825.79	847.94	879.46	925.71
9	619.06	639.77	660.54	681.36	702.23	723.14	743.59	763.75	783.79	803.71	823.51	843.20	864.24
10	619.00	637.66	656.36	675.12	693.92	712.76	731.62	749.87	767.98	785.98	803.89	821.70	839.43
11	618.95	635.92	652.94	670.01	687.12	704.25	721.42	738.59	755.01	771.45	787.79	804.05	820.24
12	618.89	634.47	650.08	665.74	681.44	697.16	712.90	728.66			774.34	789.30	804.20
13	618.84	633.23	647.66	662.12	676.62	691.14	705.69	720.25				776.79	790.59
14	618.78	632.16	645.57	659.02	672.49	685.98	699.50	713.03					778.89
15	618.72	631.23	643.76	656.32	668.90	681.51	694.13	706.76					
16	618.66	630.40	642.16	653.95	665.76	677.58	689.42	701.28					
17	618.60	629.67	640.75	651.86	662.98	674.12	685.27	696.43	707.60				
18	618.54	629.00	639.48	649.99	660.50	671.03	681.57	692.12	702.68				
19	618.47	628.40	638.34	648.31	658.28	668.26	678.26	688.26	698.27				
20	618.40	627.85	637.31	646.79	656.27	665.77	675.27	684.78	694.29				
21	618.33	627.34	636.37	645.40	654.45	663.50	672.56	681.63	690.69				
22	618.26	626.88	635.50	644.14	652.79	661.44	670.10	678.76	687.42				
23	618.19	626.44	634.70	642.98	651.26	659.55	667.84	676.13	684.42				
24	618.11	626.03	633.96	641.91	649.86	657.81	665.76	673.72	681.67	689.62			
25	618.03	625.65	633.28	640.91	648.55	656.20	663.85	671.49	679.14	686.78			
26	617.95		632.63	639.99	647.35	654.71	662.07	669.43	676.79	684.14			
27	617.86				646.22	653.32	660.42	667.52	674.61	681.70			
28	617.77					652.02	658.88	665.73	672.58	679.43			
29	617.68						657.44	664.06	670.68	677.30			
30	617.59							662.50	668.91	675.31			
31	617.49									673.44	679.64		
32	617.40										677.70		

% P_2O_5	% K_2O												
	13	14	15	16	17	18	19	20	21	22	23	24	25
1	4909.49	5254.05	5598.33	5942.29	6285.87	6629.00							
2	2664.25	2836.63	3008.88	3180.98	3352.90	3524.61							
3	1915.81	2030.78	2145.67	2260.46	2375.14	2489.68							
4	1541.62	1627.88	1714.08	1800.22	1886.27	1972.22	2058.06						
5	1317.13	1386.16	1455.15	1524.09	1592.96	1661.76	1730.47						
6	1167.49	1225.03	1282.54	1340.01	1397.43	1454.80	1512.09						
7	1057.37	1109.94	1159.25	1208.53	1257.77	1306.96	1356.10	1405.16					
8	971.89	1017.99	1064.01	1109.92	1153.02	1196.09	1239.10	1282.06					
9	905.35	946.39	987.36	1028.26	1069.09	1109.84	1148.09	1186.30					
10	857.06	889.06	925.98	962.85	999.66	1036.39	1073.05	1109.68	1144.03				
11	836.35	852.39	875.73	909.28	942.78	976.22	1009.60	1042.91	1076.14				
12	819.03	833.80	848.50	864.61	895.35	926.04	956.67	987.24	1017.75				
13	804.33	818.01	831.64	845.21	858.72	883.52	911.83	940.08	968.27	996.40			
14	791.69	804.44	817.13	829.78	842.38	854.93	873.35	899.61	925.82	951.96			
15		792.64	804.52	816.37	828.17	839.92	851.63	864.49	888.97	913.40			
16			793.46	804.60	815.69	826.75	837.76	848.73	859.64	879.60	902.46		
17				794.18	804.65	815.08	825.48	835.84	846.15	856.40	871.26		
18					794.80	804.68	814.53	824.34	834.11	843.83	853.50		
19							804.69	814.01	823.30	832.54	841.74	850.88	
20								804.68	813.53	822.34	831.10	839.82	
21										813.07	821.44	829.77	
22											812.62	820.60	828.53
23													819.79

The solution of KH_2PO_4 in H_3PO_4 solutions can be described by the equation

$$KH_2PO_4 + (y/m_2)(H_3PO_4 \cdot xH_2O) = KH_2PO_4 \cdot (y/m_2)(H_3PO_4 \cdot xH_2O) \quad (10)$$

where y is the moles of phosphoric acid solution constituting 1000 g of the solvent. The enthalpies of formation of the resultant solutions in kcal (mol of P_2O_5)$^{-1}$ can be determined from the equation

$$\Delta H_f°(\text{soln}) = [2(m_2 + y)] \times [m_2\{\Delta H_f°(KH_2PO_4) + \Delta H_{10}\} + y\Delta H_f°(H_3PO_4 \cdot xH_2O)] \quad (11)$$

where ΔH_{10} is the integral enthalpy of solution for reaction 10.

The standard enthalpies of formation of the phosphoric acid solutions were calculated from the standard enthalpy of formation of $H_3PO_4 \cdot 100H_2O$ (−309.7 kcal mol^{-1}) and the enthalpies of solution of orthophosphoric acid. The standard enthalpies of formation of the K_2O–P_2O_5–H_2O solutions where the mole ratio K_2O:P_2O_5 < 1 were calculated at integers of percent P_2O_5 and percent K_2O by using eq 5 and 11 and are listed in Table V.

Densities and Heat Capacities of K_2O–P_2O_5–H_2O Solutions

The initial bulk charge of the liquid for each enthalpy of solution measurement was weighed at 25 °C in a modified volumetric flask that had been calibrated with water. From these

Table VI. Density (g mL^{-1}) of K_2O-P_2O_5-H_2O Solutions at 25 °C

% P_2O_5	% K_2O 0	1	2	3	4	5	6	7	8	9	10	11	12
0	1.001	1.010	1.020	1.030	1.041	1.051	1.062	1.073	1.084	1.096	1.107	1.119	1.131
1	1.008	1.017	1.027	1.037	1.048	1.058	1.069	1.080	1.091	1.103	1.115	1.127	1.139
2	1.015	1.024	1.034	1.044	1.055	1.065	1.076	1.087	1.099	1.110	1.122	1.134	1.147
3	1.022	1.031	1.041	1.052	1.062	1.073	1.084	1.095	1.106	1.118	1.130	1.142	1.154
4	1.029	1.039	1.049	1.059	1.069	1.080	1.091	1.102	1.114	1.126	1.138	1.150	1.162
5	1.036	1.046	1.056	1.066	1.077	1.088	1.099	1.110	1.122	1.134	1.146	1.158	1.170
6	1.043	1.053	1.064	1.074	1.085	1.095	1.107	1.118	1.130	1.141	1.154	1.166	1.178
7	1.051	1.061	1.071	1.082	1.092	1.103	1.114	1.126	1.138	1.150	1.162	1.174	1.187
8	1.059	1.069	1.079	1.089	1.100	1.111	1.122	1.134	1.146	1.158	1.170	1.182	1.195
9	1.066	1.076	1.087	1.097	1.108	1.119	1.131	1.142	1.154	1.166	1.178	1.191	1.204
10	1.074	1.084	1.095	1.105	1.116	1.127	1.139	1.150	1.162	1.174	1.187	1.199	1.212
11	1.082	1.092	1.103	1.113	1.124	1.136	1.147	1.159	1.171	1.183	1.195	1.208	1.221
12	1.090	1.100	1.111	1.122	1.133	1.144	1.156	1.167			1.204	1.217	1.230
13	1.098	1.109	1.119	1.130	1.141	1.152	1.164	1.176				1.225	1.239
14	1.107	1.117	1.128	1.139	1.150	1.161	1.173	1.185					1.248
15	1.115	1.125	1.136	1.147	1.158	1.170	1.181	1.193	1.206				
16	1.124	1.134	1.145	1.156	1.167	1.179	1.190	1.202	1.215				
17	1.132	1.143	1.154	1.165	1.176	1.188	1.199	1.211	1.224				
18	1.141	1.152	1.162	1.174	1.185	1.197	1.208	1.221	1.233				
19	1.150	1.160	1.171	1.183	1.194	1.206	1.218	1.230	1.242				
20	1.159	1.170	1.181	1.192	1.203	1.215	1.227	1.239	1.252				
21	1.168	1.179	1.190	1.201	1.213	1.224	1.237	1.249	1.261	1.274			
22	1.177	1.188	1.199	1.210	1.222	1.234	1.246	1.258	1.271	1.284			
23	1.186	1.197	1.208	1.220	1.232	1.244	1.256	1.268	1.281	1.294			
24	1.196	1.207	1.218	1.230	1.241	1.253	1.266	1.278	1.291	1.304			
25			1.228	1.239	1.251	1.263	1.275	1.288	1.301	1.314			
26				1.249	1.261	1.273	1.285	1.298	1.311	1.324			
27					1.271	1.283	1.296	1.308	1.321	1.334	1.348		
28						1.293	1.306	1.319	1.332	1.345	1.358		
29								1.329	1.342	1.355	1.369		
30									1.353	1.366	1.380		
31										1.377	1.390		
32											1.401		

% P_2O_5	% K_2O 13	14	15	16	17	18	19	20	21	22	23	24	25
0	1.144	1.157	1.170	1.183	1.196	1.210							
1	1.152	1.164	1.177	1.191	1.204	1.218							
2	1.159	1.172	1.185	1.198	1.212	1.226							
3	1.167	1.180	1.193	1.206	1.220	1.234							
4	1.175	1.188	1.201	1.215	1.228	1.242	1.256						
5	1.183	1.196	1.209	1.223	1.237	1.251	1.265						
6	1.191	1.204	1.218	1.231	1.245	1.259	1.273						
7	1.200	1.213	1.226	1.240	1.254	1.268	1.282	1.297					
8	1.208	1.221	1.235	1.248	1.262	1.276	1.291	1.305					
9	1.217	1.230	1.243	1.257	1.271	1.285	1.300	1.314					
10	1.225	1.238	1.252	1.266	1.280	1.294	1.309	1.323	1.338				
11	1.234	1.247	1.261	1.275	1.289	1.303	1.318	1.333	1.348				
12	1.243	1.256	1.270	1.284	1.298	1.312	1.327	1.342	1.357				
13	1.252	1.265	1.279	1.293	1.307	1.322	1.336	1.351	1.366	1.382			
14	1.261	1.274	1.288	1.302	1.317	1.331	1.346	1.361	1.376	1.392			
15	1.270	1.284	1.298	1.312	1.326	1.341	1.355	1.370	1.386	1.401			
16			1.307	1.321	1.336	1.350	1.365	1.380	1.396	1.411	1.427		
17				1.331	1.345	1.360	1.375	1.390	1.405	1.421	1.437		
18					1.355	1.370	1.385	1.400	1.416	1.431	1.447		
19							1.395	1.410	1.426	1.441	1.457	1.474	
20								1.420	1.436	1.452	1.468	1.484	
21									1.446	1.462	1.478	1.495	
22											1.489	1.505	1.522
23													1.533

weights the densities in g mL^{-1}, d, of the solutions were determined. The equation

$$d = 1.0008 + 0.006761P + 0.009439K + 0.0000567P^2 + 0.0001207K^2 + 0.0000613PK \quad (12)$$

fits the observed data, with a standard deviation of 0.004 g mL^{-1}. The concentrations of the solutions, the observed densities, and those calculated from eq 12 are listed in the supplementary material. Equation 12 was used to calculate the densities at integers of percent P_2O_5 and percent K_2O (Table VI).

The total weight of solution in the calorimeter, the temperature rise, and the electrical energy input during the second electrical calibration for each measurement made possible the determination of the heat capacity, s, in cal g^{-1} °C^{-1} for each solution at the average temperature of the calibration. The water equivalent of the calorimeter had been determined previously. The equation

$$s = 0.9847 - 0.008699P - 0.012670K - 0.0000287P^2 + 0.0000153K^2 + 0.0002159PK \quad (13)$$

Table VII. Heat Capacity (cal g^{-1} °C^{-1}) of K_2O-P_2O_5-H_2O Solutions at 25 °C

	% K_2O												
% P_2O_5	0	1	2	3	4	5	6	7	8	9	10	11	12
0	0.985	0.972	0.959	0.947	0.934	0.922	0.909	0.897	0.884	0.872	0.859	0.847	0.835
1	0.976	0.964	0.951	0.939	0.926	0.914	0.902	0.890	0.877	0.865	0.853	0.841	0.829
2	0.967	0.955	0.943	0.931	0.918	0.906	0.894	0.882	0.870	0.858	0.846	0.834	0.822
3	0.958	0.946	0.934	0.922	0.910	0.899	0.887	0.875	0.863	0.851	0.840	0.828	0.816
4	0.949	0.938	0.926	0.914	0.902	0.891	0.879	0.868	0.856	0.844	0.833	0.821	0.810
5	0.940	0.929	0.917	0.906	0.894	0.883	0.871	0.860	0.849	0.837	0.826	0.815	0.804
6	0.931	0.920	0.909	0.897	0.886	0.875	0.864	0.853	0.841	0.830	0.819	0.808	0.797
7	0.922	0.911	0.900	0.889	0.878	0.867	0.856	0.845	0.834	0.823	0.812	0.801	0.791
8	0.913	0.902	0.891	0.881	0.870	0.859	0.848	0.837	0.827	0.816	0.805	0.795	0.784
9	0.904	0.893	0.883	0.872	0.861	0.851	0.840	0.830	0.819	0.809	0.798	0.788	0.778
10	0.895	0.884	0.874	0.863	0.853	0.843	0.832	0.822	0.812	0.801	0.791	0.781	0.771
11	0.886	0.875	0.865	0.855	0.845	0.834	0.824	0.814	0.804	0.794	0.784	0.774	0.764
12	0.876	0.866	0.856	0.846	0.836	0.826	0.816	0.806			0.777	0.767	0.757
13	0.867	0.857	0.847	0.837	0.828	0.818	0.808	0.798				0.760	0.751
14	0.857	0.848	0.838	0.828	0.819	0.809	0.800	0.790					0.744
15	0.848	0.838	0.829	0.820	0.810	0.801	0.792	0.782	0.773				
16	0.838	0.829	0.820	0.811	0.802	0.792	0.783	0.774	0.765				
17	0.828	0.820	0.811	0.802	0.793	0.784	0.775	0.766	0.757				
18	0.819	0.810	0.801	0.793	0.784	0.775	0.767	0.758	0.749				
19	0.809	0.800	0.792	0.783	0.775	0.767	0.758	0.750	0.741				
20	0.799	0.791	0.783	0.774	0.766	0.758	0.750	0.741	0.733				
21	0.789	0.781	0.773	0.765	0.757	0.749	0.741	0.733	0.725	0.717			
22	0.779	0.771	0.764	0.756	0.748	0.740	0.732	0.725	0.717	0.709			
23	0.769	0.762	0.754	0.746	0.739	0.731	0.724	0.716	0.709	0.701			
24	0.759	0.752	0.744	0.737	0.730	0.722	0.715	0.708	0.700	0.693			
25			0.735	0.728	0.720	0.713	0.706	0.699	0.692	0.685			
26				0.718	0.711	0.704	0.697	0.690	0.684	0.677			
27					0.702	0.695	0.688	0.682	0.675	0.669	0.662		
28						0.686	0.679	0.673	0.667	0.660	0.654		
29								0.664	0.658	0.652	0.646		
30									0.649	0.643	0.637		
31										0.635	0.629		
32											0.621		

% P_2O_5	13	14	15	16	17	18	19	20	21	22	23	24	25
0	0.823	0.810	0.798	0.786	0.774	0.762							
1	0.817	0.805	0.793	0.781	0.769	0.757							
2	0.811	0.799	0.787	0.775	0.764	0.752							
3	0.805	0.793	0.781	0.770	0.758	[illegible]							
4	0.799	0.787	0.776	0.764	0.753	[illegible]	0.731						
5	0.792	0.781	0.770	0.759	0.748	0/37	0.726						
6	0.786	0.775	0.764	0.753	0.742	0.732	0.721						
7	0.780	0.769	0.758	0.748	0.737	0.726	0.716	0.705					
8	0.774	0.763	0.753	0.742	0.732	0.721	0.711	0.700					
9	0.767	0.757	0.747	0.736	0.726	0.716	0.706	0.696					
10	0.761	0.751	0.741	0.731	0.721	0.711	0.701	0.691	0.681				
11	0.754	0.744	0.735	0.725	0.715	0.705	0.695	0.686	0.676				
12	0.748	0.738	0.728	0.719	0.709	0.700	0.690	0.681	0.671				
13	0.741	0.732	0.722	0.713	0.703	0.694	0.685	0.676	0.666	0.657			
14	0.734	0.725	0.716	0.707	0.698	0.689	0.679	0.670	0.661	0.652			
15	0.728	0.719	0.710	0.701	0.692	0.683	0.674	0.665	0.656	0.648			
16			0.703	0.695	0.686	0.677	0.669	0.660	0.651	0.643	0.634		
17				0.688	0.680	0.671	0.663	0.655	0.646	0.638	0.630		
18					0.674	0.666	0.657	0.649	0.641	0.633	0.625		
19							0.652	0.644	0.636	0.628	0.620	0.612	
20								0.638	0.631	0.623	0.615	0.608	
21									0.625	0.618	0.610	0.603	
22											0.605	0.598	0.591
23													0.586

fits the observed data, with a standard deviation of 0.003 cal g^{-1} °C^{-1}. The concentrations of the solutions, the average temperature of each measurement, the observed heat capacities, and those calculated from eq 13 are listed in the supplementary material. Equation 13 was used to calculate the heat capacities at integers of percent P_2O_5 and percent K_2O (Table VII). The average temperature of all the observed heat capacities is 25.7 °C, with a standard deviation of 0.4 °C; but since the rate of change of heat capacity with temperature is small, no corrections were applied to convert the heat capacities to 25 °C.

Registry No. Potassium dihydrogen orthophosphate, 7778-77-0; potassium hydroxide, 1310-58-3; orthophosphoric acid, 7664-38-2.

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Supplementary Material Available: Tables of differential enthalpies, integral enthalpies, observed and calculated densities, and observed and calculated heat capacities (33 pages) are included in the supplementary material. Ordering information is given on any current masthead page.

Salting Effects of *p*-Aminophenol in Some Protic Solvents at 20 °C

Bharati Das*

Department of Chemistry, University of Roorkee, Roorkee, U.P., 247667, India

Ratna Ghosh

Department of Chemistry, Indian Institute of Technology, Kharagpur, W. Bengal, 721302, India

Saturation solubilities of *p*-aminophenol (PAP) in the presence of four salts, viz., NaCl, Na_2SO_4, $NaClO_4$, and KSCN, in three solvents, viz., water, ethyl acetate, and dioxane, have been determined at 20 °C. The effect of salts on the solubility of *p*-aminophenol and the salting coefficients, K_s, have been evaluated. The salting out decreases in the order Na_2SO_4 > NaCl > $NaClO_4$ > KSCN. Dioxane shows the highest salting order followed by ethyl acetate and water.

Introduction

The process of salting out is studied by shaking a solute between two immiscible solvent phases, one of them being the organic phase and the other the aqueous phase containing the salt called the salting-out agent, and then analyzing the solute concentration in one phase or both phases. However, if the information desired relates to miscible solvents, the ratio of solubilities in two separate solvents is measured and reported as the distribution coefficient. Furthermore, when protic solvents are used for salting studies, as in the present case, the ratio of the saturation solubility of the solute in pure solvent and in the presence of salt can be used to calculate the salting-out coefficient.

The solubility method has been used extensively to study the salting effect for various classes of organic compounds. Amino acids (*1*, *2*), phenols and cresols (*3*), toluene (*4*), benzoyltrifluoroacetone (*5*), hydrocarbons and substituted benzenes (*6*), monoalkylbenzene (*7*), etc., in the presence of salting agents have been studied by the solubility method. The solubility technique, however, requires relatively high concentrations of organic solutes to saturate many solvents.

We have determined the saturation solubilities of *p*-aminophenol (hereafter designated PAP) in the presence of four salts (both structure makers and structure breakers), viz., sodium chloride (NaCl), sodium sulfate (Na_2SO_4), sodium perchlorate ($NaClO_4$), and potassium thiocyanate (KSCN), in three protic solvents, viz., water, dioxane, and ethyl acetate, at 20 °C. The solubility technique was utilized here, due to the reason that PAP is almost insoluble in aprotic solvents (like benzene, toluene, etc.) and the extraction technique was not suitable for the present studies.

Experimental Section

E. Merck AnalaR-grade PAP was vacuum dried over anhydrous NaOH to remove any existing traces of water. All salts, viz., NaCl, Na_2SO_4, $NaClO_4$, and KSCN, were of AnalaR grade and were used without any further purification. Dioxane and ethyl acetate of BDH AnalaR grade and water were double distilled at temperatures much below their boiling points at a recovery rate of 1.0 mL min^{-1}.

Saturation solubilities of PAP in the absence and the presence of weighed amounts of salts in different solvents were calculated. Different amounts of salt required for different molarities (from 0.2 to 2 M) for a fixed volume of solvent were shaken along with excess PAP in stoppered Corning-glass boiling tubes for about 6 h to obtain saturation with respect to PAP. After being shaken, the solutions were set aside for several hours, or until the solutions became clear. A thermostatic shaker with an arrangement for holding as many as 18 boiling tubes was used for shaking. This maintained the temperature to ±0.2 °C.

A Carl Zeiss Specord UV–vis spectrophotometer with a thermostated cell compartment and 5.0- and 1.0-cm and 1.0-mm matched quartz cells were used for absorbance measurements.

The clear solution of PAP obtained after shaking was separated (diluted where required) and its absorbance noted in the UV region at 312 nm. The concentration was found from the known values, as the Beer–Lambert law was found to be valid. The precision in all cases was better than 1.0%. The reproducible values only have been recorded in Table I.

Results and Discussion

The salting coefficient, K_s, is most commonly determined from the solubility according to the empirical Setschenow equation (*8*)

$$\log f = \log (S^0/S) = K_s C_s \qquad (1)$$

where S^0 and S denote the solubility of PAP in pure solvent and in the presence of salt, respectively, C_s is the salt concentration, and f is the activity coefficient of PAP in the solvent when salt is added. The plot of log (S^0/S) against C_s gave straight