interactions with complex formation (*12*). The four curves are not regularly spaced and a marked gap is observed in excess viscosities from mixture II to III.

In the systems studied, excess volumes are positive throughout the whole range of mole fractions and lead to maxima showing little variation with temperature. Figure 2 shows the results obtained for the four mixtures at 20 °C; with increasing chain length the maximum increases and is located near $X_1 \simeq 0.5$; positive V^E values have been explained in terms of complex formation (*13*). However, Palmer and Smith (*14*), based on their investigation on 1-propanol + dichloromethane mixtures at 25 °C, attributed positive V^E to a breaking of hydrogen bridges, caused by dichloromethane. The formation of high-volume complexes would justify the high values obtained for excess volumes.

According to Reed (*15*) and Meyer (16), excess free energy of activation may be considered a reliable measure to detect the presence of interactions between molecules; positive values of ΔG^{*E} can be seen in binary mixtures where specific interactions between molecules take place; negative ΔG^{*E} indicate a characteristic behavior of mixtures in which dispersion forces are dominant (*17*). In this investigation high negative values of ΔG^{*E} were obtained for mixtures I-IV; in some cases positive ΔG^{*E} values appeared in the proximity of pure components. These results are shown in Figure 3, with a minimum located at $X_1 \simeq 0.66$.

Glossary

μ	dipole moment, D
η	viscosity, cP
ν	kinematic viscosity, m^2 s^{-1}
ρ	density, g cm^{-3}
η^E	excess viscosity, cP
V^E	excess volume, cm^3 mol^{-1}
ΔG^{*E}	excess free energy, kJ mol^{-1}
X_1	ester mole fraction
X_2	acetonitrile mole fraction
Y^E	thermodynamic excess property
a_i	polynomial coefficients
n_{exptl}	number of data points
n	number of adjustable parameters
T	temperature, K
V	molar volume, cm^3 mol^{-1}
R	gas constant
M	molecular weight

Registry No. Acetonitrile, 75-05-8; methyl benzoate, 93-58-3; ethyl benzoate, 93-89-0; propyl benzoate, 2315-68-6; butyl benzoate, 136-60-7.

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Partial Molar Volumes and Compressibilities of 1-1 Type Chlorides, Bromides, $[Ph_4P]Cl$, and $Na[Ph_4B]$ in Water-Acetone Mixtures

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The densities and adiabatic compressibilities have been measured at 298.15 K for solutions of NaCl, KCl, CsCl, NaBr, KBr, $[Ph_4P]Cl$, and $Na[Ph_4B]$ dissolved in water-acetone mixtures up to acetone content 50 wt %. The partial molar volume V_2^0 and partial molar adiabatic compressibilities K_s^0 have been calculated. Variation with composition of the solvent system was more remarkable for K_s^0 than for V_2^0. In solvents containing more than 10 wt % of acetone, K_s^0 of $[Ph_4P]Cl$ and $Na[Ph_4B]$ were positive, while all the other 1-1 type salts always had negative K_s^0 values. Ionic division of K_s^0 of an electrolyte based on the assumption $K_s^0([Ph_4P]^+) = K_s^0([Ph_4B]^-)$ seems unacceptable in this mixed solvent.

Introduction

It is well-known that the partial molar volume and partial molar adiabatic compressibility are very helpful parameters for elucidation of various aspects of solute-solvent interactions. Information deduced from the respective parameters is complementary to each other. Behavior of electrolytes in mixed solvents, especially in those containing water as one of the components, is currently arousing considerable interest because of its importance as fundamental data in solution chemistry and potentiality in industrial purposes. However, in addition to the paucity of physical constants of binary mixed solvents in general, the thermodynamic behavior of an electrolyte dissolved in such mixed solvents often shows highly complex solvent composition dependence. Therefore, for discussion of the solute-

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solvent interaction in ternary system, one should place reliance on well-defined parameters such as V_2^0 and K_s^0.

To be free from disturbance due to ionic association occurring in low dielectric media, simple 1-1 type chloride and bromide were used as sample electrolytes, while water-acetone mixture was adopted as the solvent, for which we previously (*1*) reported some results on tetramethylammonium chloride and bromide along with those of some of the bolaform elec trolytes (*1*).

The division of thermodynamic quantities of electrolytes into those of the component ionic species has been done with the help of various theoretical and semiempirical foundations. One of the methods of division frequently used is based on an extrathermodynamic assumption that ions of large dimension and similar chemical structure should have the same thermodynamic character. A number of investigators have used such salts as $[Ph_4P]Cl$, $[Ph_4As]Cl$, and $Na[Ph_4B]$ as samples of the ionic division. This is especially the case for thermodynamic data of electrolytes in nonaqueous media, for this method of ionic division can circumvent difficulty due to lack of the physical property data of the nonaqueous media concerned. For this reason we also carried out measurements for $[Ph_4P]Cl$ and $Na[Ph_4B]$ and the solvent composition dependence of V_2 and K_s^0 will be compared with those of other simple 1-1 type salts.

Experimental Section

Reagents. Guaranteed grade NaCl, KCl, CsCl, NaBr, and KBr were purchased from Nakarai Chemicals Co., Ltd. They were used without further purification. The sample $[Ph_4P]Cl$ was purified by the method of recrystallization from the solution dissolved in mixture of acetone and 2-propanol (9:1 in volume ratio), while no purification was carried out for $Na[Ph_4B]$. All reagents were dried in an electric vacuum oven and kept in a desiccator over P_2O_5 under reduced pressure. Guaranteed grade acetone and distilled deionized water were used for preparation of the mixed solvents. All solutions were prepared by weight.

Procedure of Measurements. In our previous reports (*2-4*) the ultrasonic velocities were measured for a series of complex compounds by using a laboratory constructed sing-around apparatus. The sing-around method is suitable to detect the small variation of ultrasonic velocity of the sample solution from that of certain reference liquid. The mixed solvent water-acetone concerned in this work shows large variation of ultrasonic velocity with the solvent composition, which at maximum amounts to about 80 m s^{-1}. In addition, ultrasonic absorption expressed in the form of α/f^2 also varies significantly from 22.5 to more than 100 × 10^{-17} Np s^2 cm^{-1} with the composition. In this situation, we were forced to adopt interferometry for ultrasonic velocity measurements, which leads to the velocity data apparently worse than those given by the sing-around method but can give values much more self-consistent throughout the entire solvent composition. The accuracy of ultrasonic velocity measurements seems to be within 0.2 m s^{-1}. Densities were measured with a digital vibrating densimeter Anton Paar DMA-02C. All measurements were done at 298.15 K.

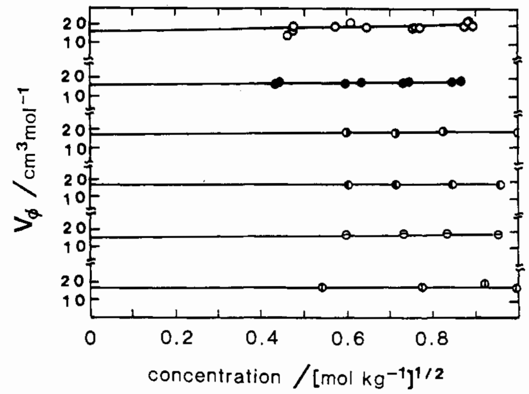

Figure 1. Variation of V_ϕ of NaCl with $m^{1/2}$ in water-acetone system at 298.15 K: (O) 50 wt %; (●) 40 wt %; (◑)30 wt %; (◐) 20 wt %; (⊖) 10 wt %; (⦶) 0 wt %.

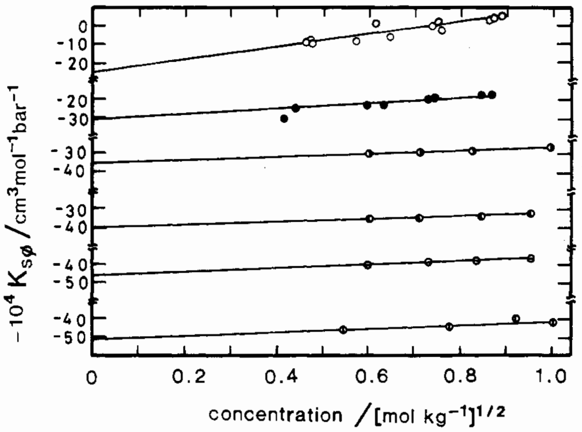

Figure 2. Variation of $K_{s\phi}$ of NaCl with $m^{1/2}$ in water-acetone system at 298.15 K: (O) 50 wt %; (●) 40 wt %; (◑) 30 wt %; (◐) 20 wt %; (⊖) 10 wt %; (⦶) 0 wt %.

Results

The experimental results are given in Tables I-III. Although the density measurements are reproducible to 5 × 10^{-6} g cm^3 for pure aqueous media, the situation becomes markedly worse for the water-acetone system. The density of this mixed solvent varied from time to time, perhaps due to the vaprization of highly volatile component, acetone.

The apparent molar volumes were calculated as usual by using the equation

$$V_\phi = \frac{1000}{mdd_1}(d_1 - d) + \frac{M_2}{d} \qquad (1)$$

The Debye-Hückel theory serves as the basis for extrapolation of V_ϕ to infinite dilution:

$$V_\phi = V_2^0 + S_v m^{1/2} + B_v m \qquad (2)$$

However, the coefficient S_v has not been available for the water-acetone system except for the case of pure water. Within experimental error, we could express the concentration dependence of V_ϕ by an empirical equation

$$V_\phi = V_2^0 + S_v' m^{1/2} \qquad (3)$$

where S_v' is a fitting parameter.

Table I. Density and Ultrasonic Velocity of NaCl, KCl, and CSl in Water–Acetone at 298.15 K

	m/mol kg^{-1} solvent	d/g cm^{-3}	u/m s^{-1}	V_ϕ/cm^3 mol^{-1}	$10^4K_{s\phi}$/cm^3 mol^{-1} bar^{-1}
		NaCl			
acetone, 0 wt %		0.997 049	1497.0		
	0.295 378	1.009 00	1515.5	17.69	−46.7
	0.603 676	1.021 09	1534.1	18.12	−44.6
	0.847 734	1.028 44	1545.4	20.71	−39.4
	1.000 761	1.036 18	1557.0	18.56	−42.2
acetone, 10 wt %		0.983 278	1551.8		
	0.355 977	0.997 48	1571.8	17.92	−40.0
	0.535 388	1.004 35	1581.2	18.33	−38.5
	0.698 012	1.010 67	1589.8	18.33	−37.8
	0.904 472	1.018 52	1600.7	18.47	−36.9
acetone, 20 wt %		0.969 414	1577.6		
	0.360 482	0.983 84	1594.7	17.43	−35.3
	0.504 896	0.989 38	1601.8	17.85	−34.9
	0.709 707	0.997 22	1610.6	18.07	−33.6
	0.904 211	1.004 33	1619.3	18.53	−32.6
acetone, 30 wt %		0.953 734	1572.3		
	0.363 379	0.967 95	1584.7	18.01	−29.3
	0.513 286	0.973 63	1590.5	18.28	−29.5
	0.681 262	0.979 95	1595.1	18.47	−28.1
	0.995 443	0.991 48	1603.6	18.84	−26.2
acetone, 40 wt %		0.935 907	1540.4		
run 1	0.189 323	0.943 55	1546.5	16.23	−33.3
	0.359 178	0.949 88	1547.2	17.77	−23.5
	0.556 847	0.957 17	1547.7	18.44	−19.1
	0.718 253	0.963 52	1549.0	18.02	−18.6
acetone, 40 wt %		0.935 995	1541.0		
run 2	0.194 867	0.943 65	1545.0	17.43	−25.0
	0.405 484	0.951 77	1548.3	17.72	−22.9
	0.534 728	0.956 50	1548.1	18.26	−19.4
	0.754 286	0.964 50	1549.3	18.73	−17.3
acetone, 50 wt %		0.915 811	1490.8		
run 1	0.217 534	0.924 31	1489.3	17.07	−9.5
	0.424 314	0.931 59	1487.3	19.14	−6.4
	0.579 951	0.937 18	1482.5	19.43	−1.5
	0.761 359	0.942 89	1475.2	20.79	4.5
acetone, 50 wt %		0.915 956	1494.4		
run 2	0.225 792	0.924 85	1491.8	16.66	−6.4
	0.376 403	0.929 80	1488.4	19.68	−0.3
	0.565 494	0.937 22	1482.2	18.54	2.8
	0.793 062	0.943 95	1477.0	21.08	5.7
acetone, 50 wt %		0.915 938	1491.0		
run 3	0.226 390	0.924 30	1490.5	19.60	−10.2
	0.331 096	0.928 18	1489.8	19.49	−9.2
	0.549 788	0.936 24	1482.6	19.35	−0.9
	0.745 119	0.942 83	1476.3	20.20	3.3
		KCl			
acetone, 0 wt %		0.997 049	1497.0		
	0.130 943	1.003 16	1504.6	27.68	−43.2
	0.261 057	1.009 10	1511.0	27.98	−39.8
	0.402 273	1.015 48	1518.5	28.16	−39.0
	0.476 622	1.018 77	1522.2	28.32	−38.3
acetone, 10 wt %		0.983 056	1551.1		
run 1	0.128 867	0.989 17	1557.4	26.58	−36.3
	0.266 535	0.995 58	1563.8	26.89	−35.0
	0.403 857	1.001 51	1569.9	28.03	−33.2
	0.568 199	1.009 03	1577.5	27.79	−32.9
acetone, 10 wt %		0.983 190	1550.1		
run 2	0.134 022	0.989 49	1557.7	27.02	−40.4
	0.275 687	0.996 15	1564.4	26.84	−37.3
	0.423 720	1.002 65	1570.7	27.78	−34.5
	0.573 798	1.009 33	1577.5	27.96	−33.5
acetone, 20 wt %		0.969 209	1577.5		
	0.054 293	0.971 80	1580.0	26.08	−34.7
	0.107 309	0.974 25	1582.3	26.74	−33.7
	0.162 511	0.976 85	1584.4	26.67	−32.6
	0.217 384	0.979 32	1586.7	27.11	−32.0
	0.275 357	0.981 96	1588.9	27.28	−31.2
	0.333 324	0.984 61	1590.9	27.31	−30.4
acetone, 30 wt %		0.954 007	1572.1		
run 1	0.131 753	0.960 01	1577.1	27.91	−30.5
	0.282 991	0.966 90	1581.7	27.71	−28.3
	0.429 241	0.973 43	1585.9	27.85	−26.9
	0.604 625	0.980 88	1590.1	28.51	−24.7

Table I (Continued)

	m/mol kg^{-1} solvent	d/g cm^{-3}	u/m s^{-1}	V_ϕ/cm^3 mol^{-1}	$10^4K_{s\phi}$/cm^3 mol^{-1} bar^{-1}
acetone, 30 wt %		0.953 769	1572.9		
run 2	0.150 836	0.960 91	1577.6	25.93	−28.2
	0.294 928	0.967 50	1581.8	26.60	−26.9
	0.435 351	0.973 51	1585.6	27.75	−25.3
	0.566 517	0.979 47	1588.4	27.56	−24.3
acetone, 40 wt %		0.936 031	1540.3		
	0.112 996	0.941 05	1542.5	28.81	−22.1
	0.169 443	0.943 56	1543.4	28.70	−21.5
	0.224 124	0.946 02	1544.6	28.49	−21.7
	0.290 885	0.948 97	1544.6	28.49	−19.2
	0.342 818	0.951 20	1545.3	28.68	−18.7
acetone, 50 wt %		0.915 603	1490.3		
run 1	0.055 186	0.918 22	1490.3	24.78	−15.8
	0.110 017	0.920 63	1489.5	26.76	−8.3
	0.171 038	0.923 20	1489.4	28.22	−8.5
	0.230 837	0.925 76	1487.7	28.64	−3.6
	0.293 284	0.928 47	1487.6	28.71	−4.8
	0.352 668	0.931 05	1486.0	28.69	−2.7
acetone, 50 wt %		0.916 113	1493.2		
run 2	0.139 224	0.922 12	1491.2	29.75	−0.4
	0.437 975	0.935 27	1486.0	28.67	0.4
	0.588 336	0.940 85	1483.8	30.45	2.0
		CsCl			
acetone, 0 wt %		0.997 049	1497.0		
	0.054 969	1.004 05	1496.5	40.54	−33.7
	0.118 333	1.012 15	1496.2	39.93	−34.9
	0.181 157	1.020 05	1495.4	40.22	−33.0
	0.237 340	1.027 08	1494.8	40.35	−32.4
acetone, 10 wt %		0.983 172	1550.9		
	0.074 185	0.992 77	1550.3	37.05	−35.6
	0.127 018	0.999 31	1549.4	39.14	−31.8
	0.173 143	1.005 08	1548.7	39.44	−30.8
	0.260 798	1.015 93	1547.1	39.96	−28.7
acetone, 20 wt %		0.969 479	1577.5		
	0.062 692	0.977 36	1576.3	39.56	−28.5
	0.108 535	0.983 03	1575.2	40.29	−26.5
	0.182 777	0.992 40	1573.4	39.29	−26.2
	0.255 243	1.000 31	1572.4	43.75	−23.5
acetone, 30 wt %		0.953 861	1572.4		
	0.051 559	0.960 43	1571.1	36.27	−29.2
	0.128 857	0.970 04	1568.7	37.89	−25.6
	0.192 407	0.977 96	1566.3	37.91	−23.5
	0.254 980	0.984 27	1563.9	44.00	−17.3
acetone, 40 wt %		0.936 194	1542.7		
run 1	0.062 198	0.944 18	1540.1	33.03	−24.8
	0.130 853	0.952 32	1535.7	38.57	−12.0
	0.182 600	0.958 75	1533.2	37.97	−13.0
	0.259 047	0.968 01	1530.6	38.38	−15.5
acetone, 40 wt %		0.936 233	1541.2		
run 2	0.038 530	0.940 93	1539.4	40.54	−14.7
	0.069 701	0.944 79	1538.8	39.44	−23.2
	0.078 761	0.946 33	1537.6	33.23	−21.8
	0.127 609	0.951 83	1535.7	39.76	−17.1
	0.207 530	0.961 68	1531.9	38.89	−16.3
	0.275 475	0.969 81	1529.5	39.35	−17.0
acetone, 50 wt %		0.916 259	1492.1		
	0.061 361	0.923 77	1488.4	37.66	−9.3
	0.129 337	0.931 68	1484.4	41.07	−5.8
	0.191 660	0.939 24	1479.2	39.92	−1.1
	0.251 620	0.946 21	1476.7	40.62	−4.4

The apparent molar adiabatic compressibilities were calculated by using the equation

$$K_{s\phi} = \frac{1000}{mdd_1}(\beta_s d_1 - \beta_{s,1} d) + \frac{M_2}{d}\beta_s \qquad (4)$$

Similarly as for V_ϕ, we describe the concentration dependence of $K_{s\phi}$ as

$$K_{s\phi} = K_s^0 + S_{Ks}' m^{1/2} \qquad (5)$$

The V_ϕ and $K_{s\phi}$ values calculated at each measured concentration are included in Tables I–III. Figures 1 and 2 show respectively the variation of V_ϕ and $K_{s\phi}$ of NaCl with concentration in various solvent systems. As illustrated in Figure 1, the coefficient S_V' in eq 1 was generally small and similar concentration dependences of V_ϕ were observed for the other salts in the concentrations investigated.

All the V_2^0 and K_s^0 values evaluated are summarized in Table IV and the results for NaCl, $[Ph_4P]Cl$, and $Na[Ph_4B]$ are also illustrated in Figures 3 and 4. As typically seen for the case of NaCl, the simple 1–1 type chloride and bromide show very small solvent composition dependence of V_2^0. The

Table II. Density and Ultrasonic Velocity of NaBr and KBr in Water–Acetone at 298.15 K

	m/mol kg^{-1} solvent	d/g cm^{-3}	u/m s^{-1}	V_ϕ/cm^3 mol^{-1}	$10^4K_{s\phi}$/cm^3 mol^{-1} bar^{-1}
		NaBr			
acetone, 0 wt %		0.997 049	1497.0		
	0.094 927	1.004 53	1499.4	23.70	−39.9
	0.200 209	1.012 61	1502.3	24.61	−39.3
	0.302 873	1.020 51	1505.1	24.70	−38.9
	0.409 903	1.028 66	1508.5	24.82	−39.1
acetone, 10 wt %		0.983 174	1550.9		
	0.100 804	0.990 96	1553.0	24.53	−34.3
	0.207 083	0.999 11	1554.5	24.65	−32.4
	0.293 074	1.005 74	1557.4	24.43	−34.7
	0.427 396	1.015 80	1559.4	24.86	−32.8
acetone, 20 wt %		0.969 474	1577.5		
	0.089 387	0.976 26	1577.6	25.18	−23.6
	0.196 838	0.984 41	1579.8	25.02	−29.2
	0.295 959	0.992 48	1581.4	22.88	−31.3
	0.430 912	1.002 10	1582.9	24.75	−29.0
acetone, 30 wt %		0.953 860	1572.4		
	0.106 322	0.961 87	1572.9	24.89	−27.3
	0.206 237	0.969 42	1573.6	24.54	−27.5
	0.314 541	0.977 73	1574.0	23.85	−27.4
	0.433 998	0.986 49	1574.3	24.41	−26.3
acetone, 40 wt %		0.936 247	1541.9		
	0.111 103	0.944 53	1541.4	24.44	−24.6
	0.204 046	0.951 68	1540.9	23.13	−25.0
	0.314 123	0.959 93	1540.5	23.25	−24.9
	0.422 584	0.967 52	1539.9	24.61	−23.1
acetone, 50 wt %		0.916 260	1492.1		
run 1	0.098 553	0.923 32	1490.3	26.75	−15.1
	0.209 518	0.931 59	1490.3	24.75	−23.8
	0.322 899	0.939 64	1486.2	25.39	−16.2
	0.435 300	0.947 42	1483.5	26.15	−14.0
acetone, 50 wt %		0.916 692	1491.8		
run 2	0.099 415	0.924 23	1489.2	21.85	−14.1
	0.215 516	0.931 65	1487.9	29.15	−13.0
	0.332 421	0.940 68	1486.0	25.71	−16.3
	0.433 900	0.947 36	1484.5	27.22	−15.0
		KBr			
acetone, 0 wt %		0.997 049	1497.0		
	0.083 778	1.004 11	1498.9	34.38	−35.9
	0.176 231	1.011 80	1500.9	34.62	−34.8
	0.272 533	1.019 74	1502.5	34.83	−33.3
	0.353 250	1.026 34	1503.5	34.91	−31.9
acetone, 10 wt %		0.983 240	1550.1		
	0.081 823	0.990 07	1551.8	34.43	−33.4
	0.171 546	0.997 58	1553.2	34.09	−31.7
	0.256 143	1.004 56	1553.8	34.20	−29.5
	0.348 278	1.012 05	1555.3	34.44	−29.1
acetone, 20 wt %		0.969 196	1577.5		
run 1	0.033 965	0.972 12	1577.7	31.12	−28.6
	0.068 288	0.974 96	1577.9	32.68	−26.4
	0.102 549	0.977 81	1578.4	33.05	−28.0
	0.137 181	0.980 66	1578.3	33.40	−25.7
	0.175 437	0.983 77	1578.4	33.83	−25.0
acetone, 20 wt %		0.969 201	1577.5		
run 2	0.067 282	0.974 92	1578.0	32.16	−28.6
	0.101 471	0.977 74	1578.2	32.95	−27.3
	0.135 650	0.980 55	1578.4	33.33	−26.7
	0.176 235	0.983 89	1578.7	33.56	−26.2
	0.198 252	0.985 69	1579.0	33.69	−26.5
acetone, 30 wt %		0.954 007	1572.1		
run 1	0.082 647	0.960 80	1573.3	34.22	−31.6
	0.192 421	0.969 71	1573.5	34.50	−27.1
	0.272 455	0.976 37	1573.3	33.78	−25.9
	0.360 859	0.983 45	1572.9	34.04	−24.0
acetone, 30 wt %		0.953 769	1573.0		
run 2	0.091 993	0.961 44	1573.0	32.79	−24.8
	0.193 121	0.969 49	1573.1	34.70	−23.1
	0.270 786	0.976 12	1573.4	33.24	−24.6
	0.358 268	0.982 93	1573.1	34.26	−22.8
acetone, 40 wt %		0.936 062	1540.2		
run 1	0.070 528	0.941 69	1540.3	35.88	−26.3
	0.107 522	0.944 72	1540.2	34.91	−25.4
	0.142 843	0.947 59	1540.5	34.62	−26.9
	0.178 436	0.950 43	1540.5	34.67	−26.5

Table II (Continued)

	m/mol kg^{-1} solvent	d/g cm^{-3}	u/m s^{-1}	V_ϕ/cm^3 mol^{-1}	$10^4K_{s\phi}$/cm^3 mol^{-1} bar^{-1}
acetone, 40 wt %		0.936 231	1541.9		
run 2	0.086 906	0.943 31	1541.6	33.96	−24.2
	0.181 489	0.951 22	1540.2	32.37	−21.6
	0.268 290	0.958 00	1540.1	33.76	−21.6
	0.364 642	0.966 07	1539.1	32.70	−21.8
acetone, 50 wt %		0.915 707	1489.6		
run 1	0.036 238	0.918 72	1489.1	30.58	−24.2
	0.072 212	0.921 63	1488.8	31.90	−23.8
	0.109 811	0.924 61	1488.3	32.99	−22.4
	0.146 394	0.927 52	1487.4	33.26	−19.6
	0.185 020	0.930 59	1486.5	33.47	−18.3
	0.208 031	0.932 49	1486.6	33.15	−20.2
acetone, 50 wt %		0.916 113	1493.16		
run 2	0.103 455	0.924 47		33.38	
	0.168 745	0.929 70	1489.5	33.48	−14.5
	0.281 964	0.938 49	1487.0	34.48	−13.3
	0.366 981	0.945 43	1484.5	33.93	−12.2

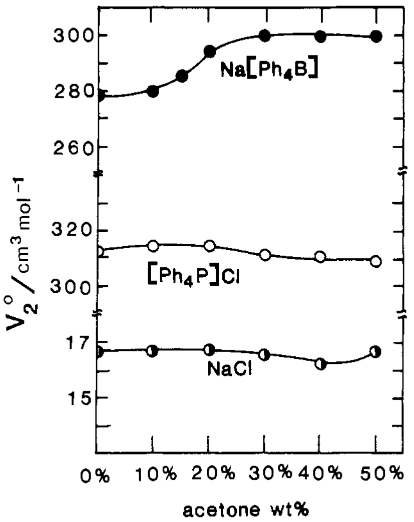

Figure 3. Variation of V_2^0 of Na[Ph$_4$B], [Ph$_4$P]Cl, and NaCl in the water–acetone system at 298.15 K: (●) Na[Ph$_4$B]; (○) [Ph$_4$P]Cl; (◑) NaCl.

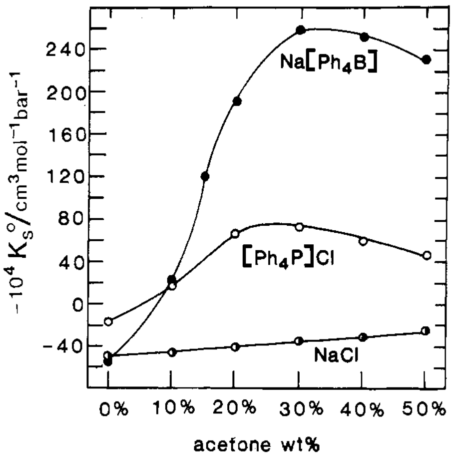

Figure 4. Variation of K_s^0 of Na[Ph$_4$B], [Ph$_4$P]Cl, and NaCl in the water–acetone system at 298.15 K: (●) Na[Ph$_4$B]; (○) [Ph$_4$P]Cl; (◑) NaCl.

maximum acetone content concerned in this work is 50 wt %, which corresponds to 23.7 mol %. For comparison of the variation of V_2^0 with solvent composition, our previous results deserve mention: In the water–methanol system (*5*) no appreciable variation was found for the V_2^0 of CsCl and KCl up to 30 mol% of methanol but the V_2^0 of these salts diminished apparently in the solvents containing more than 70 mol % of methanol. Also in the water–ethanol system (*6*) the V_2^0 of CaCl$_2$ varied from 16.95 in water to 16.5 cm^3 mol^{-1} in 10 mol %, 13.6 cm^3 mol^{-1} in 30 mol %, and finally −40.6 cm^3 mol^{-1} in pure ethanol. Very recently it has been reported (*7*) that in water–acetamide mixture, the V_2^0 values increase regularly with acetamide content up to 50 wt % (23.35 mol %), which is the maximum acetamide content investigated. In this mixed solvent of water–acetamide the variation is not so marked (for NaCl the change amounts to 2.1 cm^3 mol^{-1}). Attention may be called for the rather large increase of V_2^0 of Na[Ph$_4$B] in the solvent composition 10–30 mol % of acetone, while solvent dependence is very small for V_2^0 of [Ph$_4$P]Cl. Values of V_2^0 are far more larger for the two salts [Ph$_4$P]Cl and Na[Ph$_4$B] than those of the ordinary salts MX. Consequently, ionic division of the V_2^0(MX) based on the data on [Ph$_4$P]Cl and Na[Ph$_4$B] may contain uncertainties relatively high for the discussion of the values V_2^0(M$^+$) or V_2^0(X$^-$).

In contrast to the case of V_2^0, gradual increase of K_s^0 with increasing acetone content in the solvent is observed for the ordinary salts. But the two phenyl complexes having a very large ionic part, [Ph$_4$P]Cl and Na[Ph$_4$B], show behavior highly specific in the following points: Values of K_s^0 increase to become positive in solvents containing no more than several weight percent of acetone. They increase with acetone content up to 30 mol %; then they begin to decrease with further increase of acetone content in the solvent. For these two complex salts the electrostrictive effects of ions are weak even in water and the effects disappear completely as a result of decreasing dielectric constant with increasing acetone content in the mixed solvent. On comparison with the result for NaCl, the positive values of K_s^0 and the appearance of its maximum for both the complexes indicate the specific character in solute–solvent interactions of these bulky and strong hydrophobic ions [Ph$_4$P]$^+$ and [Ph$_4$B]$^-$ in water–acetone mixture. Figure 4 also suggests that the simple extrathermodynamic assumption

$$K_s^0([\mathrm{Ph_4P}]^+) = K_s^0([\mathrm{Ph_4B}]^-)$$

is not acceptable in this mixed solvent.

Table III. Density and Ultrasonic Velocity of Na[Ph_4B] and [Ph_4P]Cl in Water-Acetone at 298.15 K

	m/mol kg^{-1} solvent	V_ϕ/m s^{-1}	V_ϕ/m s^{-1}	V_ϕ/m s^{-1}	$10^4K_{s\phi}$/cm^3 mol^{-1} bar^{-1}
		Na[Ph_4B]			
acetone, 0 wt %		0.997 049	1497.0		
	0.026 019	0.998 75	1503.2	277.10	−48.1
	0.056 121	1.000 69	1510.1	276.98	−45.4
	0.088 417	1.002 74	1517.6	276.86	−45.1
acetone, 10 wt %		0.983 170	1550.7		
run 1	0.030 051	0.985 21	1553.2	277.21	41.4
	0.059 913	0.987 21	1554.8	277.25	49.1
	0.086 076	0.988 68	1555.9	280.28	55.8
	0.121 969	0.990 79	1556.8	281.27	62.6
acetone, 10 wt %		0.983 161	1550.2		
run 2	0.035 879	0.985 65	1553.2	275.67	39.9
	0.059 069	0.987 06	1554.6	278.72	47.3
	0.092 532	0.989 11	1555.5	279.88	57.6
	0.116 645	0.990 56	1557.0	280.35	57.0
acetone, 15 wt %		0.976 332	1568.0		
	0.031 751	0.978 30	1566.0	284.81	115.0
	0.067 232	0.980 42	1564.2	285.59	123.4
	0.088 963	0.981 90	1563.7	283.21	117.2
	0.121 757	0.983 51	1562.7	286.57	117.5
acetone, 20 wt %		0.969 426	1577.6		
	0.031 834	0.971 36	1572.7	287.76	176.5
	0.055 837	0.972 33	1569.8	296.83	177.4
	0.092 869	0.974 41	1565.1	294.37	173.0
	0.113 734	0.975 47	1564.0	294.59	165.6
acetone, 30 wt %		0.953 861	1571.9		
	0.030 873	0.955 45	1564.9	301.55	234.9
	0.062 678	0.957 28	1558.8	297.77	222.4
	0.093 772	0.959 77	1553.9	287.72	204.7
	0.124 229	0.960 25	1550.5	300.21	205.1
acetone, 40 wt %		0.936 007	1540.8		
	0.034 430	0.938 00	1534.3	298.78	223.3
	0.061 698	0.939 43	1528.7	301.21	232.3
	0.097 846	0.941 47	1523.3	300.08	221.7
	0.124 839	0.943 29	1520.6	296.72	208.6
acetone, 50 wt %		0.915 888	1490.6		
run 1	0.032 996	0.918 30	1488.0	293.12	163.3
	0.063 794	0.919 70	1482.9	301.09	202.0
	0.097 250	0.921 99	1479.8	296.88	191.1
	0.130 582	0.923 95	1477.7	297.45	183.4
acetone, 50 wt %		0.916 260	1491.8		
run 2	0.029 019	0.917 77	1488.6	310.92	202.3
	0.067 898	0.920 11	1483.7	304.74	203.5
	0.088 849	0.921 32	1480.8	304.03	207.3
	0.132 800	0.924 26	1478.0	299.10	188.2
		[Ph_4P]Cl			
acetone, 0 wt %		0.997 049	1497.0		
	0.022 421	0.998 49	1501.6	311.00	−13.5
	0.054 427	1.000 51	1507.2	311.0	−2.4
	0.079 125	1.002 06	1512.1	310.71	−4.8
	0.109 675	1.003 95	1517.2	310.49	−1.0
acetone, 10 wt %		0.983 281	1550.1		
	0.028 261	0.985 07	1554.4	315.15	20.9
	0.053 411	0.986 84	1556.6	311.12	34.2
	0.085 363	0.988 85	1560.6	312.02	33.8
	0.104 673	0.990 31	1563.2	309.61	30.5
acetone, 20 wt %		0.969 372	1577.2		
	0.026 029	0.971 16	1578.9	313.02	64.5
	0.056 054	0.973 34	1581.2	310.08	57.6
	0.082 697	0.974 90	1582.7	313.80	63.2
	0.110 193	0.976 93	1585.0	311.28	58.7
acetone, 30 wt %		0.953 808	1572.2		
	0.038 178	0.956 62	1574.1	311.19	68.6
	0.055 346	0.958 01	1575.3	308.21	63.0
	0.092 832	0.960 58	1577.3	310.66	65.5
	0.111 640	0.961 95	1578.9	310.20	62.2
acetone, 40 wt %		0.936 004	1541.2		
	0.027 365	0.938 18	1543.4	309.03	49.0
	0.061 560	0.940 76	1545.3	310.75	58.3
	0.089 276	0.942 94	1546.8	309.57	59.6
	0.119 625	0.945 65	1549.4	305.33	52.0
acetone, 50 wt %		0.916 125	1491.8		
	0.035 080	0.918 97	1494.9	311.75	41.4
	0.062 930	0.921 39	1497.1	307.82	40.9
	0.091 252	0.923 50	1499.5	310.41	42.9
	0.124 521	0.926 59	1501.5	305.55	43.0

Table IV. V_2^0 and K_s^0 of 1-1 Type Electrolytes Dissolved in Water-Acetone System at 298.15 K

	V_2^0/cm^3 mol^{-1}							K_s^0/cm^3 mol^{-1} bar^{-1}						
	0[a]	10[a]	15[a]	20[a]	30[a]	40[a]	50[d]	0[a]	10[a]	15[a]	20[a]	30[a]	40[a]	50[a]
NaCl	16.7	16.7		16.8	16.6	16.3	16.7	-50.9	-45.8		-41.1	-35.0	-31.5	-25.0
KCl	26.5	26.1		26.0	26.5	27.5	27.0	-44.9	-40.5		-36.8	-32.5	-27.8	-23.2
CsCl	38.1	37.5		37.5	37.8	38.0	37.8	-37.1	-34.1		-31.0	-27.7	-23.9	-20.1
NaBr	23.4	23.1		23.8	23.7	23.5	23.8	-42.1	-37.8		-33.5	-30.0	-27.3	-24.5
KBr	33.5	33.0		32.5	33.1	33.7	32.5	-36.9	-32.9		-29.1	-25.7	-25.1	-23.1
$[Ph_4P]Cl$	312.2	314.3		314.7	311.2	310.0	309.2	-18.0	19.0		66.5	72.0	60.0	47.0
$Na[Ph_4B]$	277.2	279.3	285.0	294.6	300.1	299.9	300.1	-55.0	24.0	120.0	191.0	257.5	252.0	230.0

[a] Weight percent of acetone.

Glossary

d	density of solution g cm^{-3}
d_1	density of solvent, g cm^{-3}
m	molality, mol kg^{-1} solvent
u	ultrasonic velocity, m s^{-1}
$K_{s\phi}$	apparent molar adiabatic compressibility of solute, cm^3 (mol·bar)$^{-1}$
K_s^0	partial molar adiabatic compressibility of solute at infinite dilution, cm^3 (mol·bar)$^{-1}$
M_2	molar mass of solute, g mol^{-1}
V_ϕ	apparent molar volume of solute, cm^3 mol^{-1}
V_2^0	partial molar volume of solute at infinite dilution, cm^3 mol^{-1}
β_s	adiabatic compressibility of solution, given as 100/(u^2d), bar^{-1}
$\beta_{s,1}$	adiabatic compressibility of solvent, given as 100/(u_1^2d), bar^{-1}

Registry No. NaCl, 7647-14-5; KCl, 7447-40-7; CsCl, 7647-17-8; NaBr, 7647-15-6; KBr, 7758-02-3; $[Ph_4P]Cl$, 2001-45-8; $Na[Ph_4B]$, 143-66-8; acetone, 67-64-1.

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Liquid-Liquid Equilibria for the Quaternary System Water-Phosphoric Acid-1-Hexanol-Cyclohexanone at 25 °C

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Mutual solubility and tie-line data at 25 °C and atmospheric pressure were obtained for the quaternary system water-phosphoric acid-1-hexanol-cyclohexanone, using an analytical method. In the liquid-liquid extraction of wet process phosphoric acid, no advantage is observed in the use of the mixed solvent, 1-hexanol and cyclohexanone, as an extractant solvent instead of the pure solvents.

Introduction

Solvent extraction of phosphoric acid from aqueous solutions has been widely studies in recent years, mainly with alcohols, ethers, ketones, and amines, and a very complete review was done by Blumberg (*1*). Other solvents used were trialkyl phosphates (*2*) and trialkylphosphine oxides (*3*).

The present work reports experimental equilibrium data for the system water-phosphoric acid-1-hexanol-cyclohexanone at 25 °C and atmospheric pressure. The system contains two pairs of partly miscible compounds, water-1-hexanol and water-cyclohexanone; two type 1 systems in the Treybal's classification (*4*), water-phosphoric acid-1-hexanol and water-phosphoric acid-cyclohexanone; one type 2 ternary system in the same classification, 1-hexanol-water-cyclohexanone; and one ternary system with complete miscibility, 1-hexanol-phosphoric acid-cyclohexanone.

Experimental Section

Chemicals. All chemicals were supplied by Merck. Organic solvents (Analytical Reagent Grade) contained less than 0.5% of volatile impurities, confirmed by chromatographic analysis, and the phosphoric acid (CP Grade) content was 85 wt % and less than 0.1% of impurities. Deionized water was used with subsequent treatment in Millipore filters to remove organic residuals and to reduce conductivity. Chromatographic analysis of water did not show any presence of detectable impurities.

Ternary Equilibrium Data Determination. Binodal curves and tie-line data were obtained simultaneously by means of an analytical method (*5*) in ternary systems. Heterogeneous mixtures of known overall composition were stirred for 12 h in a thermostated bath at 25 ± 0.1 °C, and they settled for at least 12 h before proceeding to the analysis of each component in each of the equilibrium phases.

Water and organic solvents were determined by chromatographic analysis, using a Hewlett-Packard 5840-A chromatograph equipped with electronic integrator. A good separation

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