1896 © *1983 The Chemical Society of Japan* *Bull. Chem. Soc. Jpn.*, ***56***, *1896—1902 (1983)* [Vol. 56, No. 7

The Cation-Cation Interactions in Aqueous Mixed Electrolyte Solutions of Quaternary Phosphonium Chlorides

Katsuko Takaizumi* and Toshiki Wakabayashi
The College of General Education, Tohoku University, Kawauchi, Sendai 980

(Received September 20, 1982)

Density measurements were carried out at six temperatures between 1 and 55 °C for three series of aqueous mixed electrolyte solutions, each of which contained $(n\text{-Bu})_4\text{PCl}$ and Ph_4PCl with the mole ratios, 3:1, 1:1, and 1:3, respectively. The mixed solutions are assumed to be the model solutions of the phosphonium chlorides, $(n\text{-Bu})_{4-n}\text{Ph}_n\text{PCl}(n=1,2,\text{ and }3)$, with respect to the pair-wise interactions between the cations, for which a model has been proposed in a previous paper.[1] The volume B-coefficients(B_V) determined for the model salts are in good agreement with those for the corresponding pure salts and those reproduced by the equation derived from the model. The results indicate that the phenyl groups affect weakly the butyl cospheres in both the intermolecular processes and intramolecular processes and that among the ion-ion interactions the cation-cation interactions are the main factor for determining the B_V's. These can be decomposed into three parts, arising from the butyl-butyl, phenyl-phenyl, and butyl-phenyl interactions.

In a previous paper[1], we reported the volume behavior of the quaternary phosphonium salts, $(n\text{-Bu})_{4-n}\text{Ph}_n\text{PCl}(n=1\text{—}4)$ and Bu_4PBr, in aqueous solutions in the temperature range 1—55 °C. The volume B-coefficients(B_V), which would reflect the effects arising from the pair-wise interactions between ions through the ionic cospheres,[2] were determined. It was possible to reproduce the numerical values for B_V of the salts with n from 1 to 3 from those of the salts with n of 0 and 4 by the equation derived from these assumptions: (a) the B_V's are determined mainly by the effects resulting from the cation-cation interactions; (b) when any two cations approach each other, the interaction takes place between a cosphere of one of the hydrocarbon groups on a cation and that on another cation, and we have three types of the interactions, butyl-butyl, phenyl-phenyl, and butyl-phenyl; (c) each interaction takes place on a purely chance basis, that is, in proportion to the 'concentration' of the group. If these assumptions are adequate, we may anticipate that, in the aqueous mixed electrolyte solutions containing $(n\text{-Bu})_4\text{PCl}$ and Ph_4PCl with the mole ratio, $(4\text{-}n):n$, the B_V's found for the mixed salts(model salts) should be the same as those found for the pure salts.

In this paper, we report the volumetric properties of three kinds of model salts corresponding to the pure salts with $n=1$, 2, and 3, respectively, and $(n\text{-Bu})_4\text{PCl}$ in aqueous solutions at the temperatures 1, 5, 10, 25, 40, and 55 °C.

Experimental

The $(n\text{-Bu})_4\text{PCl}$ was obtained from Alfa Division Ventron and was purified as follows. The salt was dissolved in water, washed repeatedly with a small amount of CH_2Cl_2 to remove colored substances, extracted in the presence of NaCl(*ca.* 2 mol kg^{-1}) into CHCl_3 phase, which was then washed with a small amount of deionized water, and finally extracted into conductivity-grade water. The aqueous solution was degassed to remove CHCl_3 at about 40 °C under reduced pressure and then filtered through a Millipore filter. The clathrate-like hydrate, obtained by cooling the aqueous solution, was collected. The aqueous solution was analyzed gravimetrically for the anion content using AgNO_3. The methods for purifying the Ph_4PCl and for preparing the stock solution were the same as previously reported.[1,3]

Three kinds of mixed stock solutions were prepared by mixing both the stock solutions on a weight basis to give the mole ratios of Bu_4PCl to Ph_4PCl, 3:1, 1:1, and 1:3. The solutions for density measurement were obtained by dilution from the mixed stock solutions on a weight basis.

General procedures and reproducibility for the density measurements were essentially the same as those reported previously.[1,3] The measurements were carried out over the concentration range from about 0.04 to 1.5 mol dm^{-3} for each series of the mixed solutions and at the temperatures, 1, 5, 10, 25, 40, and 55 °C. The temperatures of the water bath, in which the pycnometers were immersed, were controlled to 0.01 °C for the measurements at 1, 5, and 55 °C, 0.005 for 25 °C, and 0.007 for 10 and 40 °C.

Results and Discussion

The apparent molar volumes, ϕ_V, for the model salts corresponding to Bu_3PhPCl, $\text{Bu}_2\text{Ph}_2\text{PCl}$ and BuPh_3PCl, at six temperatures are listed in Table 1. The ϕ_V's for Bu_4PCl, which had not been determined in the previous work,[1] are also listed.

The ϕ_V's were obtained from the density data by the usual equation:

$$\phi_\text{V} = \frac{1}{m}\left(\frac{1000+mM}{d_\text{soln}} - \frac{1000}{d_\text{o}}\right), \tag{1}$$

where m and M are the molality and molecular weight of the model salt which equals that of $(n\text{-Bu})_{4-n}\text{Ph}_n\text{PCl}$.

The ϕ_V's are assumed to follow the equation;

$$\phi_\text{V} = \phi_\text{V}^\circ + A_\text{V}c^{1/2} + B_\text{V}c + C_\text{V}c^2 + D_\text{V}c^3, \tag{2}$$

where ϕ_V° is the standard partial molar volume of the model salt, A_V the Debye-Hückel limiting slope, and the other coefficients are empirical parameters. The values for A_V at various temperatures were taken from the table compiled by Redlich and Meyer.[4] The other coefficients were determined by the least-squares method to fit the ϕ_V's to the equation.

The numerical values for these coefficients are presented in Table 2, together with the uncertainties (σ_i) of the coefficients and the standard deviations(σ) between the observed and reproduced ϕ_V's. The corresponding coefficients for the pure salts are also listed, for comparison. The differences between ϕ_V's for Bu_4PCl in this work and those in the previous work[1], which were obtained from ϕ_v's for $\mathrm{Bu_4PBr}$ by subtracting the differences in the anionic partial molar volume, $\phi^\circ_{\mathrm{v},-}(\mathrm{Br}^-)-\phi^\circ_{\mathrm{v},-}(\mathrm{Cl}^-)$[3], are within 0.08% except for the difference at 1 °C, about 0.15% (Table 2).

Figure 1 shows the ϕ_v's of the mixed salts as a function of the square root of concentration (mol dm^{-3}), together with those of the pure salts. The ϕ_v curves of the three mixed salts are very similar to those for the corresponding pure salts in the low concentration range, while at higher concentrations the similarity in the ϕ_v behavior is not found. This aspect is re-

Table 1. Densities and apparent molar volumes at 1, 5, 10, 25, 40, and 55 °C

	1 °C		5 °C		10 °C		25 °C		40 °C		55 °C	
m	d	ϕ_v	d	ϕ_v	d	ϕ_v	d	ϕ_v	d	ϕ_v	d	ϕ_v
mol kg^{-1}	g cm^{-3}	cm^3 mol^{-1}	g cm^{-3}	cm^3 mol^{-1}	g cm^{-3}	cm^3 mol^{-1}	g cm^{-3}	cm^3 mol^{-1}	g cm^{-3}	cm^3 mol^{-1}	g cm^{-3}	cm^3 mol^{-1}
						$\mathrm{Bu_4PCl}$						
0.07122	0.999516	300.41	0.999490	301.70	0.999109	303.46	0.996270	306.98	0.991254	311.27		
0.08141	0.999499	299.95	0.999459	301.25	0.999056	300.09			0.991121	311.24		
0.10424	0.999408	299.77	0.999364	300.84	0.998940	302.50						
0.11138	0.999407	299.48			0.998914	302.27	0.995856	306.89	0.990770	310.87	0.983977	315.60
0.13630	0.999324	299.31	0.999250	300.35	0.998758	302.18	0.995661	306.42	0.990467	310.81	0.983613	315.56
0.13681	0.999292	299.53	0.999196	300.74	0.998729	302.37	0.995649	306.47	0.990492	310.56	0.983646	315.24
0.18530	0.999201	298.89	0.999050	300.11	0.998517	301.72	0.995253	306.05	0.989940	310.41	0.982972	315.17
0.24685	0.999203	297.94	0.998962	299.26	0.998238	301.34	0.994837	305.45	0.989322	310.03	0.982186	314.92
0.33982	0.999377	296.61	0.998991	298.05	0.998207	299.82	0.994324	304.65	0.988488	309.52	0.981103	314.54
0.44143	0.999663	295.52	0.999131	297.03	0.998180	298.88	0.993879	303.95	0.987633	309.18	0.979988	314.29
0.56538	1.00023	294.23	0.99950	295.86	0.99831	297.85	0.99340	303.36	0.98676	308.69	0.978635	314.16
0.69649	1.00095	293.09	0.99999	294.84	0.99856	296.94	0.99299	302.85	0.98587	308.43	0.97746	313.95
0.87027	1.00020	291.86	1.00074	293.78	0.99897	296.02	0.99250	302.39	0.98469	308.32	0.97584	313.95
1.1033	1.00337	290.76	1.00164	292.88	0.99936	295.38	0.99180	302.13	0.98330	308.18	0.97386	313.97
1.3962	1.00441	290.37	1.00223	292.61	0.99944	295.23	0.99075	302.21	0.98151	308.32	0.97159	314.06
1.7214	1.00463	290.79	1.00206	293.06	0.99887	295.70	0.98935	302.59	0.97959	308.57	0.96933	314.16
1.9738	1.00413	291.54	1.00141	293.74	0.99805	296.29	0.98812	303.02	0.97811	308.85	0.96768	314.36
1.9977	1.00408	291.60	1.00134	293.80	0.99798	296.35	0.98802	303.05	0.97787	308.96	0.96731	314.50
2.7220	1.00133	293.97	0.99850	295.86	0.99495	298.14	0.98449	304.23	0.97391	309.75	0.96301	314.99
3.5674	0.99763	296.22	0.99477	297.90	0.99117	299.92	0.98058	305.44	0.96986	310.57	0.95881	315.53
4.9556	0.99198	298.88	0.98917	300.32	0.98561	302.08	0.97509	306.97	0.96436	311.66	0.95342	316.22
6.8699	0.98587	301.18	0.98311	302.45	0.97968	303.98	0.96930	308.40	0.95879	312.68	0.94798	316.94
						$\mathrm{Bu_4PCl : Ph_4PCl = 3 : 1}$						
0.02319									0.992332	312.37		
0.04200	1.000481	300.85	1.000494	302.10								
0.06409	1.000810	300.40	1.000800	301.60	1.000427	303.41	0.997525	308.17	0.992537	312.21		
0.07557	1.000993	300.10	1.000957	301.45	1.000591	302.91	0.997653	307.57	0.992581	312.37	0.985890	316.74
0.09173	1.001227	300.03	1.001172	301.36	1.000743	303.28			0.992664	312.28		
0.11519	1.001634	299.32	1.001541	300.72	1.001079	302.57	0.997983	307.37	0.992793	312.10	0.986001	316.63
0.12982	1.001791	299.76	1.001684	301.12	1.001196	302.99			0.992865	312.08	0.986013	316.83
0.16125	1.002341	299.03	1.002187	300.44	1.001655	302.25	0.998372	307.14	0.993048	311.86	0.986137	316.49
0.17171	1.002484	299.08	1.002304	300.55	1.001774	302.26	0.998460	307.10			0.986139	316.65
0.20487	1.003050	298.58	1.002797	300.21			0.998777	306.78	0.993310	311.59	0.986277	316.34
0.22660	1.003422	298.30	1.003136	299.94	1.002483	301.84	0.998962	306.72	0.993452	311.43	0.986333	316.35
0.29929	1.004552	297.97	1.004201	299.46	1.003451	301.30	0.999657	306.24			0.986588	316.09
0.38903	1.00608	297.17	1.00560	298.71	1.00469	300.63	1.00055	305.69	0.99447	310.77	0.98692	315.81
0.42806	1.00670	297.00	1.00617	298.53	1.00522	300.41	1.00086	305.68	0.99470	310.67	0.98703	315.82
0.64842	1.01041	295.58	1.00955	297.25	1.00821	299.29	1.00296	304.83	0.99609	310.06	0.98786	315.32
0.83176	1.01343	294.65	1.01229	296.41	1.01063	298.55	1.00461	304.35	0.99718	309.73	0.98853	315.03
1.0399	1.01662	293.91	1.01515	295.79	1.01314	298.03	1.00635	303.98	0.99833	309.47	0.98927	314.77
1.3040	1.02021	293.37	1.01840	295.30							0.99011	314.55
1.5986	1.02344	293.27	1.02133	295.22	1.01857	297.54	1.01005	303.66	1.00087	309.15	0.99096	314.38
1.9856	1.02676	293.50	1.02437	295.39	1.02129	297.67	1.01190	303.76	1.00213	309.19	0.99175	314.38
2.3424	1.02902	293.91	1.02663	295.62								
2.6466	1.03028	294.48	1.02766	296.22	1.02420	298.40	1.01413	304.10	1.00373	309.34	0.99294	314.32

TABLE 1. (Continued)

	1 °C		5 °C		10 °C		25 °C		40 °C		55 °C	
m	d	ϕ_V	d	ϕ_V	d	ϕ_V	d	ϕ_V	d	ϕ_V	d	ϕ_V
mol kg^{-1}	g cm^{-3}	cm^3 mol^{-1}	g cm^{-3}	cm^3 mol^{-1}	g cm^{-3}	cm^3 mol^{-1}	g cm^{-3}	cm^3 mol^{-1}	g cm^{-3}	cm^3 mol^{-1}	g cm^{-3}	cm^3 mol^{-1}
Bu_4PCl : Ph_4PCl=1 : 1												
0.02982	1.000923	300.23	1.000940	301.83	1.000632	303.41	0.997847	308.63				
0.04716									0.993331	313.19		
0.07444	1.002433	300.10	1.002380	301.58	1.002002	303.33	0.999030	308.46	0.993966	313.11		
0.11010	1.003627	299.92					0.999965	308.30	0.994790	312.97		
0.15604	1.005179	299.48	1.004994	301.13	1.004441	303.13			0.995839	312.79		
0.19901					1.005735	302.80	1.002257	307.92	0.996801	312.67		
0.26090	1.008590	298.99	1.008286	300.48	1.007553	302.48	1.003837	307.59	0.998190	312.37		
0.31829	1.010436	298.64	1.010037	300.21	1.009219	302.17						
0.39960	1.01296	298.31	1.01247	299.82	1.01152	301.80	1.00725	307.04	1.001210	311.81		
0.48275	1.01553	297.87	1.01491	299.44	1.01382	301.44	1.00922	306.75	1.00294	311.57		
0.57470	1.01828	297.45	1.01754	299.04	1.01630	301.06	1.01137	306.38	1.00481	311.29		
0.68911	1.02157	297.01	1.02059	298.78	1.01922	300.75	1.01386	306.15	1.00701	311.06		
0.81612	1.02503	296.64	1.02395	298.33	1.02237	300.36	1.01654	305.85	1.00934	310.82		
0.96052	1.02869	296.39	1.02743	298.10	1.02566	300.13	1.01944	305.55	1.01194	310.47		
1.1356	1.03294	296.01	1.03148	297.74	1.02951	299.77	1.02268	305.30	1.01474	310.30		
1.2951	1.03659	295.72	1.03493	297.48	1.03281	299.47	1.02552	305.04	1.01727	310.02		
Bu_4PCl : Ph_4PCl=1 : 3												
0.04255												
0.04262			1.002220	301.06	1.001874	303.28	0.999025	308.62				
0.06785									0.995110	313.45	0.988354	318.82
0.07530					1.003513	303.14	1.000510	308.60				
0.09839	1.005204	299.37							0.996360	313.58	0.989533	318.63
0.13221	1.007008	298.99	1.005110	300.95			1.003020	308.59	0.997801	313.00		
0.13782	1.007289	299.05			1.006564	303.05			0.997937	313.70	0.991004	318.65
0.17833	1.009342	299.10	1.007080	301.05	1.008474	303.08	1.005065	308.20			0.992535	318.33
0.18433	1.009686	298.86	1.009121	300.76	1.008809	302.76	1.005288	308.39	0.999835	313.27	0.992757	318.30
0.23004	1.011970	298.80	1.009462	300.83	1.010931	302.71	1.007241	308.18				
0.23634			1.011664	300.47	1.011238	302.62	1.007523	308.09	1.001903	312.97	0.994712	317.84
0.28033	1.014379	298.90			1.013178	302.78	1.009354	307.95				
0.29739	1.01524	298.71	1.014023	300.48	1.01403	302.42	1.01011	307.71	1.00429	312.60	0.99694	317.47
0.35497	1.01792	298.73			1.01654	302.41						
0.36488	1.01843	298.57	1.01744	300.38	1.01701	302.25	1.01284	307.49	1.00686	312.29	0.99925	317.41
0.44308	1.02206	298.25	1.01793	300.23	1.02040	301.96	1.01591	307.28	1.00970	312.08	1.00197	316.97
0.53283	1.02597	298.18	1.02140	300.05	1.02411	301.77	1.01928	307.09	1.01282	311.89	1.00495	316.63
0.62536	1.02997	297.85	1.02524	299.84	1.02785	301.43	1.02268	306.79	1.01597	311.60	1.00787	316.40
0.73763	1.03450	297.68	1.02913	299.49	1.03208	301.28	1.02656	306.59	1.01959	311.37	1.01130	316.07
0.85839	1.03921	297.40	1.03348	299.39	1.03652	300.96	1.03063	306.24	1.02342	310.94	1.01486	315.71
1.00515	1.04444	297.32	1.03808	299.06					1.02764	310.75		

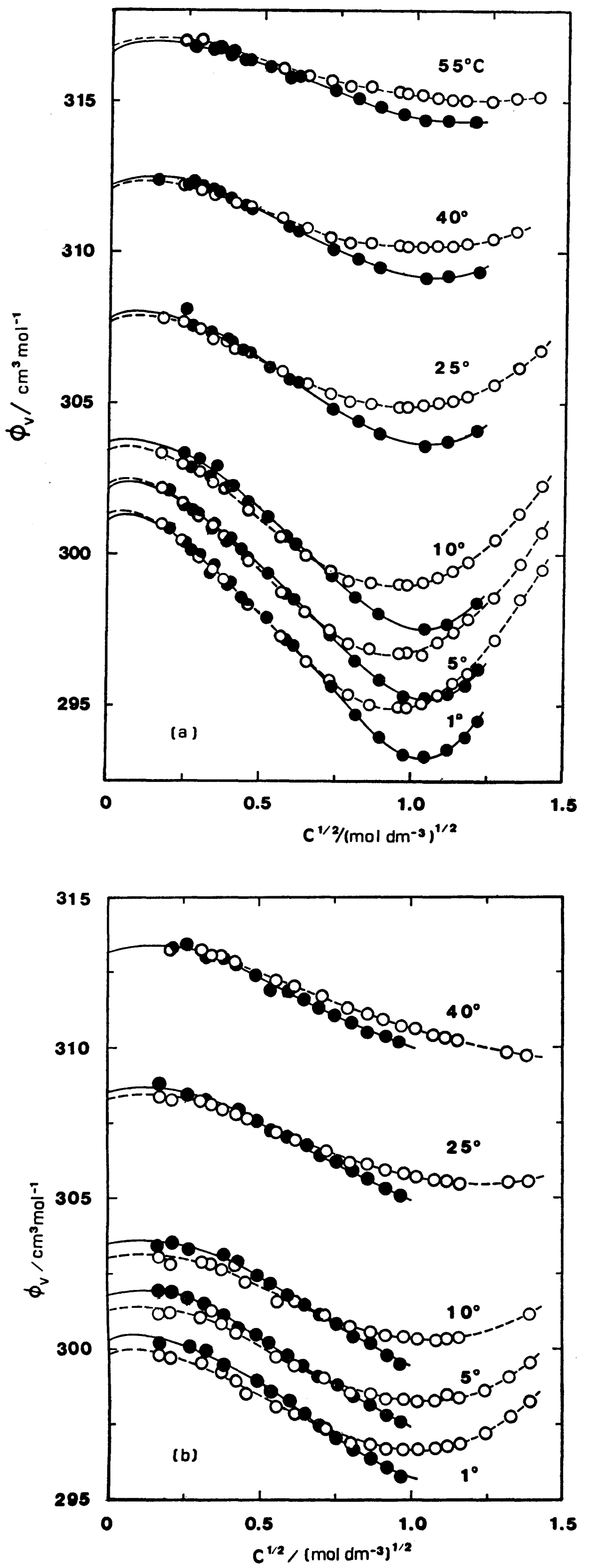
flected in the agreement of the B_V value for the mixed salts with that for the pure salts (Fig. 2 and Table 2). This may be an important clue for interpreting the physical meaning of the B_V's obtained as empirical parameters. Before discussing the subject, we note that the B_V value is very close to half of B_{2V} which is the coefficient of the linear term of c in the equation for the partial molar volume.[15] Some discussion about B_V will follow.

For dilute solutions, we may reasonably expect that, besides the long-range interactions among ions due to the coulombic force, there may be pairwise interactions between ions at short distances originating from various kinds of potentials. (The potentials other than the coulombic one used by Friedman and co-workers[7,8] are the following; the core repulsion potential, the potential of the ion-cavity interaction between two ions, and the Gurney potential representing the effect of the overlap of the cospheres when the ions come close together. The B_V coefficient would contain the contributions derived from all these potentials.) The agreement in B_V, therefore, suggests strongly that in any given mixed system at low concentrations the ion-ion interactions would take place in a way similar

TABLE 2. STANDARD PARTIAL MOLAR VOLUMES AND COEFFICIENTS FOR Eq. 2

t / °C	ϕ°_V / cm³ mol⁻¹	σ_ϕ	B_V / cm³ mol⁻² dm³	σ_B	C_V / cm³ mol⁻³ dm⁶	σ_C	D_V / cm³ mol⁻⁴ dm⁹	σ_D	σ
$\mathrm{Bu_4PCl}$ a)									
1	302.10	0.27	−26.89	1.43	16.78	1.62	−2.36	0.48	0.48
	(309.13)	0.18	−25.48	0.79	17.60	0.86	−3.01	0.24	0.31)
	(302.54) b)								
5	303.13	0.24	−25.25	1.18	16.22	1.33	−2.43	0.40	0.38
	(310.00	0.15	−23.72	0.63	16.90	0.67	−3.00	0.19	0.27)
	(303.34) b)								
10	304.59	0.18	−23.85	0.93	15.87	1.05	−2.57	0.32	0.30
	(311.14	0.14	−21.21	0.56	15.24	0.58	−2.74	0.16	0.22)
	(304.40) b)								
25	307.59	0.14	−16.71	0.72	11.64	0.82	−2.02	0.25	0.23
	(314.81	0.06	−15.44	0.24	11.55	0.26	−2.20	0.07	0.10)
	(307.83) b)								
40	311.48	0.05	−12.85	0.23	9.34	0.27	−1.78	0.08	0.07
	(318.80	0.10	−11.43	0.39	8.64	0.41	−1.71	0.11	0.15)
	(311.59) b)								
55	315.61	0.08	−9.45	0.37	6.77	0.42	−1.34	0.13	0.10
	(323.12	0.06	−8.19	0.24	5.82	0.26	−1.15	0.07	0.09)
	(315.69) b)								
$\mathrm{Bu_4PCl : Ph_4PCl} = 3 : 1$ c)									
1	300.92	0.08	−15.89	0.34	6.92	0.23			0.18
	(301.32	0.09	−19.28	0.53	14.20	0.67	−2.80	0.22	0.16)
5	302.13	0.06	−14.68	0.26	6.32	0.18			0.14
	(302.34	0.06	−17.45	0.34	12.79	0.43	−2.53	0.14	0.10)
10	303.72	0.08	−13.62	0.34	5.88	0.23			0.15
	(303.45	0.06	−14.61	0.36	10.54	0.45	−2.08	0.15	0.10)
25	307.84	0.04	−10.44	0.17	4.37	0.12			0.07
	(307.77	0.05	−10.52	0.28	7.08	0.35	−1.38	0.12	0.09)
40	312.29	0.05	−8.90	0.24	3.56	0.15			0.10
	(312.08	0.05	−8.22	0.26	5.19	0.32	−1.06	0.11	0.07)
55	316.60	0.05	−7.00	0.19	2.38	0.14			0.08
	(316.81	0.07	−7.57	0.38	4.51	0.46	−1.01	0.15	0.10)
$\mathrm{Bu_4PCl : Ph_4PCl} = 1 : 1$ d)									
1	300.34	0.04	−9.50	0.22	3.28	0.22			0.06
	(299.84	0.04	−9.82	0.23	6.23	0.30	−1.10	0.10	0.07)
5	301.84	0.07	−9.49	0.28	3.51	0.26			0.05
	(301.30	0.10	−9.23	0.60	5.67	0.77	−1.01	0.26	0.14)
10	303.52	0.06	−8.43	0.31	2.60	0.32			0.08
	(303.04	0.09	−8.08	0.52	4.43	0.35	−0.70	0.23	0.14)
25	308.55	0.07	−8.42	0.28	2.95	0.25			0.04
	(308.26	0.04	−7.87	0.26	4.35	0.35	−0.88	0.10	0.07)
40	313.10	0.03	−8.08	0.16	2.79	0.17			0.04
	(313.14	0.08	−7.66	0.48	3.88	0.63	−0.85	0.22	0.12)
$\mathrm{Bu_4PCl : Ph_4PCl} = 1 : 3$ e)									
1	299.24	0.11	−5.00	0.64	0.97	0.75			0.11
	(299.51	0.07	−5.44	0.31	2.05	0.26			0.11)
5	301.00	0.08	−5.20	0.50	0.91	0.71			0.09
	(301.17	0.08	−5.53	0.36	1.94	0.30			0.13)
10	303.12	0.06	−5.25	0.16					0.11
	(303.04	0.07	−5.17	0.30	1.52	0.25			0.11)
25	308.48	0.06	−5.74	0.16					0.11
	(308.48	0.06	−5.81	0.25	1.45	0.21			0.09)
40	313.48	0.11	−6.43	0.28					0.22
	(313.73	0.05	−7.08	0.23	1.78	0.19			0.08)
55	318.53	0.09	−7.53	0.26					0.17
	(318.86	0.06	−8.58	0.29	2.26	0.25			0.10)

a) The bracketed values are for $\mathrm{Bu_4PBr}$, taken from Ref. 1. b) The values converted into $\phi^\circ_V(\mathrm{Bu_4PCl})$ from $\phi^\circ_V(\mathrm{Bu_4PBr})$ by subtracting $(\bar{V}^\circ_-(\mathrm{Br}^-)-\bar{V}^\circ_-(\mathrm{Cl}^-))$; *cf.* Ref. 3. c) The bracketed values are for $\mathrm{Bu_3PhPCl}$, taken from Ref. 1. d) The bracketed values are for $\mathrm{Bu_2Ph_2PCl}$, taken from Ref. 1. e) The bracketed values are for $\mathrm{BuPh_3PCl}$, taken from Ref. 1.



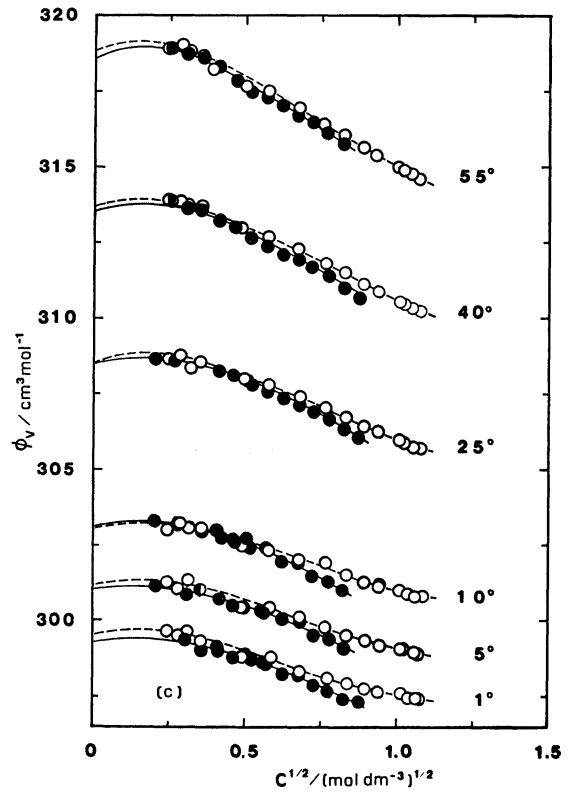


Fig. 1. Comparison of ϕ_v's for the model salts with those for the pure ralts.
Model salt; —●—. Pure salt; --○--. (a) 3:1 model salt and Bu_3PhPCl, (b) 1:1 model salts and Bu_2Ph_2PCl, (c) 1:3 model salt and $BuPh_3PCl$.

to those in the corresponding pure system. Since the actual species in the mixed systems are quite different from those in the pure systems, we should obtain B_v values for the mixed systems different from those for the pure systems, if the B_v's determined from experimental data reflect significantly the effects from short-range interactions among more than two ions, and if the states of cosphere water around a group, say, butyl (or phenyl) group on the cations with n from 1 to 3 differ considerably from those around the butyl(or phenyl) groups on the Bu_4P^+(or Ph_4P^+) ion. Thus we may conclude that the present B_v's reflect mainly pairwise interactions between ions: $++$, $+-$, and $--$, and that the cosphere around a group on the cations(n=1—3) is affected weakly by the unlike groups, as concluded in previous papers.[1,18]

There are indications that the cation-cation interactions are the dominant contribution to the excess volumes of some salts containing large-sized organic cations. As may be seen from Table 2, the concentration dependence of ϕ_v of Bu_4PCl at all temperatures examined is very similar to that of Bu_4PBr; the differences between their B_v's are only around 10% and the higher coefficients, C_v and D_v, are in agreement within the experimental uncertainties. If the cation-anion interactions contribute largely to the excess volume, different results would have been obtained because the two anions are known to affect the water structures differently. The situation is similar for the cations containing phenyl groups: the B_v values at 25 °C of Bu_3PhPCl and Bu_3PhPBr are $-10.5(\pm.28)$ and $-11(\pm.4)$, and those of Bu_2Ph_2PCl and Bu_2Ph_2PBr, $-7.87(\pm.26)$ and $-7(\pm.5)$ cm^3 mol^{-2} dm^3, respectively.[1,3] Volume behavior peculiar to the hydrophobic salts such as n-Bu_4NX[5,6] and (n-Bu)$_3$N(CH$_2$)$_8$N(n-Bu)$_3$Br$_2$[16] in aqueous solutions has been interpreted in terms of the clathrate-like model of hydration, in which the cation-cation pairing through water sheath were assumed to be the dominant effect in determining their volume behavior. The results of a model calculation for tetraalkylammonium halides (R_4NX) by Streng and Wen[9,10] shows that, of the three excess volume parameters, V_{++}, V_{+-}, and V_{--}, V_{++} is negative and several times larger in magnitude than V_{+-} for higher three cations(from R=ethyl to *n*-butyl) but is comparable with tetramethylammonium halides, in the calculation V_{--} was assumed to be zero and the anions were the Cl^- and Br^- ions. One reason for these observations is suggested by the cosphere overlap model: the contribution to the excess volume from cosphere overlapping depends on the volume(V_{mu}) of the cosphere-overlap region, from which the cosphere material(water) relaxes to the bulk water. This process results in volume changes of the system caused by the change of the state of water, both in the cosphere region shared by the two ions and in the relaxing part. The V_{mu} is reasonably expected to become increasingly larger as the size of the participant ions increases.

From the above, we assume that the B_v obtained here reflect all the effects resulting from the pairwise interactions between cations. This is of course an oversimplified interpretation for B_v, but is a first step in approaching the volumetric properties of the salts which contain large-sized ions. For a nonelectrolyte solute, the B_v coefficient may have a more distinct meaning,[2] that is, it may be correlated with the pressure derivative of the pair interaction coefficient in the virial-type expression for the chemical potential of the solute.

Based on this assumption, a further analysis for B_v is possible. In a given mixed system, there happen three types of cation-cation interactions: Bu_4P^+–Bu_4P^+, Ph_4P^+–Ph_4P^+, and Bu_4P^+–Ph_4P^+. Since the present cations have nearly the same molar volume and are roughly spherical in shape, we assume approximately that a given cation i would encounter another cation j at a short distance, where the cosphere overlap takes place(cation pairing), with a relative probability proportional only to the number density of species j.[17] Thus, for the mixed system containing Bu_4PCl and Ph_4PCl with the mole ratio, $(4-n):n$, we can express a conditional probability $P_{ij}(n)$, with which we find the cations i and j in a cation pair, by the equation:

$$P_{BB}(n) = \left(\frac{4-n}{4}\right)^2, \quad P_{PP}(n) = \left(\frac{n}{4}\right)^2,$$
$$P_{BP}(n) = 2\left(\frac{4-n}{4}\right)\left(\frac{n}{4}\right), \tag{3}$$

where the subscripts B and P stand for the cations Bu_4P^+ and Ph_4P^+, respectively. The $B_v(n)$, the B_v coefficient expected for the mixed system, therefore, can be given by

$$B_v(n) = B_v(0)P_{BB}(n) + B_v(4)P_{PP}(n) + bP_{BP}(n), \tag{4}$$

where $B_v(0)$ and $B_v(4)$ are the observed B_v's for Bu_4PCl and Ph_4PCl in each pure solution, respectively. Here, *b* is the volume contribution from pairwise interactions between the unlike cations. The *b* value is unknown and three limiting cases are examined.

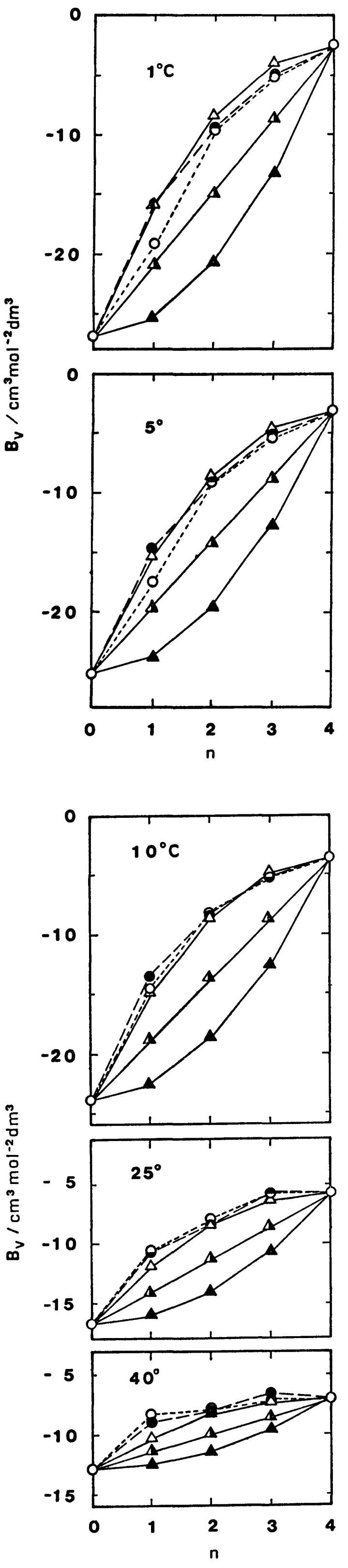


Fig. 2. Comparison of the B_v-coefficients.
Observed B_v; model salt: ——●——, pure salt: --○--. Calculated B_v; Case 1; —◭—, Case 2; —△—, Case 3; —▲—.

1) $b=[B_\mathrm{V}(0)+B_\mathrm{V}(4)]/2$, 2) $b=B_\mathrm{V}(4)$, and 3) $b=B_\mathrm{V}(0)$. In Fig. 2, the limiting cases are compared together with the observed B_V's.14) Clearly, case 2 is most suitable throughout these n values and temperatures. In terms of the cosphere overlap model, case 2 means that when unlike two cations interact at a short distance, a part of the cosphere water around a phenyl group relaxes to the bulk water in a way similar to the case of the Ph_4P^+–Ph_4P^+ interaction, while the butyl cosphere is maintained.

Equation 4 is quite the same as that for the pure systems, if we read the subscripts B and P as the butyl and phenyl group and $P_{ij}(n)$ as the conditional probability with which we find group i and j in a cation pair(two like cations containing n phenyl groups). This is the reason for examining the present systems as the model systems for the aqueous solutions of the $Bu_{4-n}Ph_nPCl$ salts.

In essence, Eq. 4 is derived by neglecting the effects arising from the coulombic interactions, except for the limiting long-range coulombic interaction, which is partially taken into account through the second term in Eq. 2. It is expected, therefore, that the present approach would be more reasonable for nonelectrolyte solutes. Wood and coworkers11,12) have developed a method to assign pairwise group-group interaction parameters for enthalpies and chemical potentials of nonelectrolytes in aqueous solutions. The basic assumptions in our previous work1) (the assumptions b and c in this introduction) are essentially the same as theirs. Whether or not the approach presented here is reasonable would depend on the relative magnitudes of two contributions: from short-range pairwise interactions and from the coulombic interactions. It seems that the short-range interactions become relatively more important as ion size increases. In this respect, the result obtained by Visser *et al.*13) should be noted; they applied Savage and Wood's concept to several tetraalkylammonium bromides in aqueous solutions and found that values of the functional group interaction parameters(enthalpy) for both nonelectrolytes and electrolytes are in reasonable agreement.

We believe that the present results support the simple assumptions made in the previous work for interpreting the B_V coefficients found experimentally for the phosphonium halides in aqueous solutions, and that the present approach can be an empirical way to test the validity of the simple additivity rule assumed for splitting the pairwise interaction parameters for enthalpy and free energy as well as volume into contributions from group-group interactions.

References

1) T. Wakabayashi and K. Takaizumi, *J. Solution Chem.*, **11**, 565 (1982).

2) H. L. Friedman and C. V. Krishnan, "Thermodynamics of Ion Hydration," in "Water: A Comprehensive Treatise," ed by F. Franks, Plenum Press, New York (1973), Vol. 3, Chap. 1, pp. 1—118.

3) K. Takaizumi and T. Wakabayashi, *J. Solution Chem.*, **9**, 809 (1980).

4) O. Redlich and D. M. Meyer, *Chem. Rev.*, **64**, 221 (1964).

5) W. Y. Wen and S. Saito, *J. Phys. Chem.*, **68**, 2639 (1964); **69**, 3569 (1965).

6) W. Y. Wen and K. Nara, *J. Phys. Chem.*, **71**, 3907 (1967).

7) H. L. Friedman and P. S. Ramanathan, *J. Phys. Chem.*, **74**, 3756 (1970); P. S. Ramanathan and H. L. Friedman, *J. Chem. Phys.*, **54**, 1086 (1971).

8) P. S. Ramanathan, C. V. Krishnan, and H. L. Friedman, *J. Solution Chem.*, **1**, 237 (1972).

9) W. Y. Wen, *J. Solution Chem.*, **2**, 253 (1973).

10) W. H. Streng and W. Y. Wen, *J. Solution Chem.*, **3**, 865 (1974).

11) J. J. Savage and R. H. Wood, *J. Solution Chem.*, **5**, 733 (1976).

12) T. R. Tasker and R. H. Wood, *J. Phys. Chem.*, **86**, 4040 (1982); and references cited therein.

13) C. de Visser, W. J. Heuvelsland, and G. Somsen, *J. Solution Chem.*, **7**, 193 (1978).

14) The B_V values for Ph_4PCl were taken from Ref. 1: -2.48, -3.05, -3.54, -5.77, and -6.98 cm^3 mol^{-2} dm^3 at 1, 5, 10, 25, and 40 °C, respectively.

15) The partial molar volume of 1:1 salt can be expressed as

$$\overline{V}_2 = \phi_\mathrm{V}^\circ + \frac{3}{2}A_\mathrm{V}c^{1/2} + B_{2\mathrm{V}}c + B_{3\mathrm{V}}c^2 + B_{4\mathrm{V}}c^3 + \cdots. \qquad \text{(A)}$$

Converting the ϕ_V to $\overline{V}_2$ by the usual way, we can determine the coefficients $B_{2\mathrm{V}}$, $B_{3\mathrm{V}}$, *etc.* For all the present salts, the $B_{2\mathrm{V}}$ values agreed well with the B_V values times 2 within about 0.3%. The agreement is what is expected. Using the coefficients for ϕ_V (Eq. 2), we obtain the expression for $\overline{V}_2$ as a polynomial in $c^{1/2}$:

$$\overline{V}_2 = \phi_\mathrm{V}^\circ + \frac{3}{2}A_\mathrm{V}c^{1/2} + 2B_\mathrm{V}c + [-A_\mathrm{V}\phi_\mathrm{V}^\circ/2000]c^{3/2} + [\quad]c^2 + \cdots.$$

The $c^{3/2}$ term is negligible, *i.e.*, *ca.* 0.3 cm^3 mol^{-1} even at 1 mol dm^{-3}. Hence $B_{2\mathrm{V}}$ in Eq. A is very close to $2B_\mathrm{V}$.

16) T. L. Broadwater and D. F. Evans, *J. Phys. Chem.*, **73**, 164 (1969).

17) The pair correlation function g_{ij} is determined by the free energy of pairwise interaction between i and j. The Gurney potential for, say, butyl-butyl overlapping may differ considerably from those for other overlappings, and hence the relative probability to find a cation pair is not proportional to the concentration product(c_ic_j) only, even if other potentials are assumed to be the same. However, the same assumption as used in this work has usually been made in empirical approaches,11-13) and may be a permissible one in view of the present stage of theory.

18) T. Wakabayashi and K. Takaizumi, *Bull. Chem. Soc. Jpn.*, **56**, 1749 (1983).