Apparent Molar Compressibilities and Volumes of Some 1,1-Electrolytes in *N*,*N*-Dimethylacetamide and *N*,*N*-Dimethylformamide

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Densities of solutions of sodium tetraphenylborate, tetraphenylphosphonium bromide, sodium bromide, and sodium perchlorate solutions in *N*,*N*-dimethylacetamide and *N*,*N*-dimethylformamide have been measured over the concentration range of (0.015 to 0.40) mol·kg^{-1} at temperatures between $T = 283.15$ K and $T = 333.15$ K. From densities, apparent molar volumes and partial molar volumes of the salts at infinite dilution as well as the expansibilities have been evaluated. Moreover, the apparent molar isentropic compressibility of all electrolytes has been determined from sound velocity measurements at $T = 298.15$ K. The limiting apparent molar compressibilities have been discussed in terms of possible methods of splitting them into ionic contributions.

Introduction

Rational interpretation of thermodynamic properties of solutes requires splitting them into ionic components. Partial molar quantities of individual ions are, due to their additivity, of most interest. Unfortunately, thermodynamics does not give satisfactory clues how to extract ionic contributions. Some extrathermodynamic assumptions need to be accepted, which causes lots of controversies.

Hefter and Marcus in their paper discussed in detail all the methods available in the literature for obtaining partial molar volumes of different electrolytes in nonaqueous solvents.[1] They recalculated and adjusted some earlier results and proved that reported agreement in values of volumes obtained in different ways was accidental. However, the comparison of all splitting methods led them to the conclusion that the reference electrolyte method based on the observation that

$$V_\Phi^0(Ph_4P^+) - V_\Phi^0(Ph_4B^-) = 2 \pm 2\ cm^3 \cdot mol^{-1} \qquad (1)$$

and

$$V_\Phi^0(Ph_4As^+) - V_\Phi^0(Ph_4B^-) = 8 \pm 2\ cm^3 \cdot mol^{-1} \qquad (2)$$

where V_Φ^0(ion) indicates the partial molar volume of the reference electrolyte ions is the least objectionable split available at the present time.

As far as isentropic compressibilities ($K_{S,\Phi}^0$) are concerned, there is a little agreement on acceptable methods of dividing them into ionic components. Some approaches have been attempted. Laliberte and Conway used the extrapolation method for obtaining the ionic adiabatic compressibility of halide ions.[2] Debashis et al. could not use the same technique since the variation of the limiting apparent molar isentropic compressibilities of tetraalkylammonium bromides relative to the formula weight of cations in DMA was not linear.[3] They assumed that the limiting adiabatic compressibility of the bromide ion equals 0. The assumption of Davidson et al., on the other hand, was that the limiting adiabatic compressibility of the tetraphenylborate ion is 0.[4] However, their suggestion could be interpreted in terms of the equality of some properties of the Ph_4P^+ and Ph_4B^- ions. This method was also used by Lankford et al. to divide $K_{S,\Phi}^0$ into ionic components.[5] Singh et al. suggested a similar model based on Bu_4NBPh_4 as a reference electrolyte.[6]

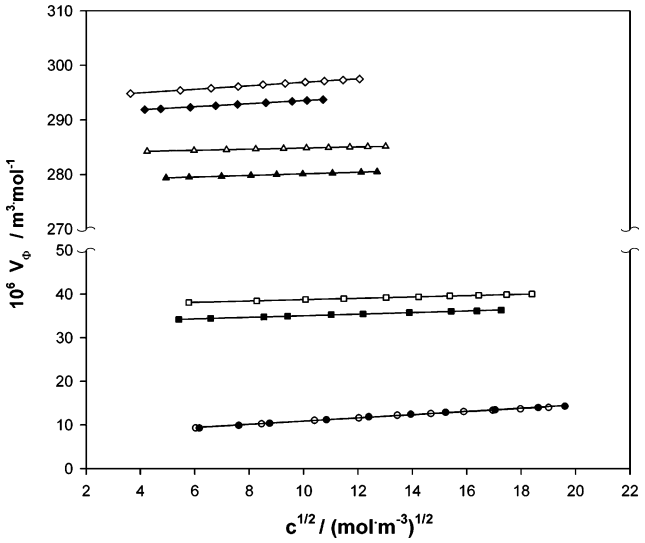

Figure 1. Apparent molar volumes V_Φ against the square root of molarity c of the Ph_4PBr, $NaBPh_4$, $NaClO_4$, and NaBr solutions in DMA and DMF for $T = 298.15$ K. Ph_4PBr: ◇, DMA; ◆, DMF. $NaBPh_4$: △, DMA; ▲, DMF. $NaClO_4$: □, DMA; ■, DMF. NaBr: ○, DMA; ●, DMF.

In this paper, experimental data at $T = 298.15$ K for sound velocity and at $T =$ (283.15, 293.15, 298.15, 303.15, 313.15, 323.15, and 333.15) K for density of sodium tetraphenylborate ($NaBPh_4$, NaTB), tetraphenylphosphonium bromide (Ph_4PBr, TPBr), sodium bromide (NaBr), and sodium perchlorate ($NaClO_4$) in *N*,*N*-dimethylacetamide (DMA) and *N*,*N*-dimethylformamide (DMF) solutions are reported. The apparent molar volume V_Φ, adiabatic compressibility κ_S, and apparent molar adiabatic compressibility $K_{S,\Phi}^0$ are calculated from the measured properties. Standard partial molar thermodynamic quantities of electrolytes are obtained from the extrapolation of their apparent molar values to infinite dilution and then divided into their ionic contributions with the method recommended by Hefter and Marcus.[1]

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Table 1. Densities ρ of $(C_6H_5)_4PBr$, $NaB(C_6H_5)_4$, NaBr, and $NaClO_4$ Solutions in DMA and DMF at Different Temperatures

m_s	ρ/kg·m^{-3}							m_s	ρ/kg·m^{-3}						
mol·kg^{-1}	283.15 K	293.15 K	298.15 K	303.15 K	313.15 K	323.15 K	333.15 K	mol·kg^{-1}	283.15 K	293.15 K	298.15 K	303.15 K	313.15 K	323.15 K	333.15 K
							$(C_6H_5)_4PBr$								
DMA	950.021	940.804	936.193	931.578	922.331	913.054	903.738	0.09165	962.188	953.060	948.496	943.929	934.784	925.616	916.412
0.01406	951.887	942.686	938.083	933.475	924.244	914.983	905.683	0.1064	964.157	955.046	950.489	945.934	936.799	927.645	918.458
0.03175	954.232	945.048	940.455	935.857	926.646	917.405	908.125	0.1215	966.173	957.073	952.528	947.974	938.858	929.724	920.552
0.04618	956.145	946.975	942.389	937.799	928.605	919.382	910.117	0.1374	968.299	959.215	954.677	950.132	941.033	931.915	922.764
0.06104	958.120	948.963	944.384	939.801	930.623	921.420	912.172	0.1520	970.261	961.195	956.660	952.125	943.041	933.934	924.796
0.07650	960.173	951.029	946.457	941.884	932.726	923.538	914.308								
DMF	958.058	948.546	943.780	939.002	929.420	919.790	910.103	0.06013	966.140	956.692	951.960	947.221	937.712	928.160	918.554
0.01828	960.516	951.023	946.268	941.503	931.944	922.340	912.676	0.07767	968.504	959.072	954.353	949.621	940.132	930.600	921.015
0.02382	961.259	951.772	947.021	942.259	932.707	923.110	913.454	0.09583	970.959	961.547	956.835	952.115	942.649	933.141	923.585
0.03591	962.883	953.408	948.665	943.911	934.373	924.792	915.151	0.1070	972.461	963.064	958.359	953.644	944.188	934.692	925.144
0.04822	964.538	955.077	950.339	945.592	936.071	926.505	916.880	0.1196	974.179	964.794	960.095	955.384	945.942	936.461	926.930
							$NaB(C_6H_5)_4$								
DMA	950.003	940.786	936.175	931.560	922.313	913.036	903.720	0.1083	957.502	948.430	943.894	939.357	930.271	921.166	912.028
0.01922	951.332	942.143	937.547	932.946	923.728	914.482	905.197	0.1260	958.738	949.691	945.166	940.642	931.582	922.501	913.392
0.03801	952.631	943.468	938.886	934.298	925.109	915.892	906.638	0.1446	960.032	951.009	946.494	941.986	932.953	923.903	914.825
0.05466	953.783	944.642	940.072	935.496	926.330	917.141	907.915	0.1611	961.184	952.181	947.677	943.181	934.171	925.144	916.098
0.07212	954.993	945.876	941.317	936.752	927.613	918.452	909.253	0.1786	962.402	953.419	948.929	944.443	935.454	926.456	917.435
0.09110	956.309	947.217	942.670	938.119	929.008	919.875	910.712								
DMF	958.066	948.546	943.781	939.014	929.430	919.797	910.117	0.08539	964.225	954.819	950.107	945.386	935.925	926.419	916.863
0.02586	959.931	950.451	945.702	940.946	931.402	921.807	912.162	0.1044	965.597	956.215	951.516	946.808	937.372	927.892	918.365
0.03546	960.623	951.156	946.413	941.661	932.132	922.551	912.920	0.1283	967.331	957.974	953.29	948.598	939.193	929.750	920.260
0.05140	961.772	952.327	947.594	942.851	933.344	923.786	914.179	0.1538	969.175	959.846	955.178	950.507	941.135	931.725	922.276
0.06859	963.012	953.588	948.866	944.134	934.650	925.118	915.536	0.1689	970.269	960.955	956.295	951.635	942.282	932.894	923.471
							NaBr								
DMA	950.075	940.857	936.243	931.629	922.382	913.105	903.788	0.2253	969.678	960.462	955.856	951.250	942.030	932.794	923.535
0.03868	953.482	944.270	939.665	935.054	925.818	916.557	907.255	0.2630	972.946	963.723	959.116	954.509	945.292	936.062	926.807
0.07570	956.712	947.505	942.900	938.292	929.062	919.805	910.522	0.2988	976.045	966.822	962.215	957.608	948.392	939.163	929.920
0.1142	960.054	950.844	946.239	941.632	932.405	923.157	913.876	0.3345	979.167	969.937	965.328	960.721	951.506	942.283	933.039
0.1524	963.367	954.156	949.551	944.945	935.721	926.476	917.208	0.3729	982.502	973.272	968.663	964.055	954.841	945.617	936.374
0.1896	966.587	957.368	952.763	948.155	938.935	929.697	920.430								
DMF	958.058	948.546	943.780	939.002	929.420	919.790	910.103	0.2020	975.812	966.267	961.486	956.699	947.102	937.468	927.787
0.04008	961.622	952.116	947.353	942.582	933.009	923.390	913.710	0.2400	979.129	969.568	964.782	959.988	950.382	940.736	931.044
0.06106	963.473	953.967	949.201	944.430	934.862	925.240	915.568	0.2991	984.336	974.747	969.946	965.140	955.516	945.860	936.163
0.08045	965.175	955.663	950.900	946.127	936.554	926.938	917.264	0.3558	989.324	979.703	974.892	970.076	960.427	950.752	941.044
0.1230	968.894	959.378	954.612	949.837	940.257	930.633	920.960	0.3930	992.603	982.961	978.139	973.315	963.652	953.964	944.250
0.1603	972.166	962.635	957.861	953.080	943.494	933.870	924.197								
							$NaClO_4$								
DMA	950.152	940.934	936.320	931.706	922.459	913.182	903.865	0.2122	967.335	958.199	953.635	949.069	939.930	930.776	921.596
0.03560	953.023	943.824	939.223	934.618	925.393	916.141	906.851	0.2471	970.186	961.065	956.505	951.946	942.820	933.678	924.524
0.07279	956.021	946.841	942.250	937.656	928.452	919.221	909.956	0.2817	973.030	963.911	959.357	954.804	945.692	936.568	927.423
0.1073	958.813	949.645	945.058	940.470	931.285	922.077	912.834	0.3171	975.941	966.835	962.288	957.739	948.639	939.529	930.406
0.1391	961.386	952.224	947.650	943.070	933.895	924.705	915.485	0.3508	978.735	969.635	965.091	960.546	951.458	942.362	933.248
0.1787	964.607	955.462	950.892	946.319	937.167	927.996	918.801								
DMF	958.066	948.546	943.781	939.026	929.444	919.808	910.117	0.1552	971.196	961.739	957.002	952.254	942.744	933.188	923.580
0.03096	960.681	951.181	946.423	941.664	932.101	922.487	912.820	0.2008	975.073	965.626	960.894	956.151	946.654	937.121	927.543
0.04574	961.930	952.437	947.681	942.921	933.366	923.762	914.104	0.2466	978.997	969.551	964.822	960.091	950.605	941.077	931.529
0.07671	964.547	955.067	950.315	945.560	936.018	926.430	916.790	0.2771	981.621	972.185	967.459	962.730	953.254	943.738	934.185
0.09316	965.935	956.464	951.715	946.958	937.426	927.846	918.216	0.3073	984.224	974.784	970.068	965.339	955.867	946.366	936.823
0.1271	968.807	959.339	954.597	949.847	940.327	930.760	921.149								

Experimental Section

Sodium tetraphenylborate, tetraphenylphosphonium bromide, sodium bromide (Fluka, puriss, electrochemical grade), and sodium perchlorate (Aldrich, puriss, analytical grade) were dried under reduced pressure at $T = 308$ K. DMA and DMF (Fluka, puriss, absolute, mass fraction $H_2O < 1{\cdot}10^{-4}$) were dried with 0.4 nm molecular sieves.

Solutions of all salts for density measurements were prepared by weighing diluted stock solutions of the corresponding salt. All preparations and manipulations involving anhydrous materials were performed in dry boxes.

The densities of the solutions were measured using an Anton Paar DMA 5000 densimeter with a precision of $1.0{\cdot}10^{-3}$ kg·m^{-3} and uncertainties of $5.0{\cdot}10^{-3}$ kg·m^{-3} for a single measurement. The instrument was equipped with the Peltier-type thermostating unit, and the temperature was kept constant at $T =$ (283.15, 293.15, 298.15, 303.15, 313.15, 323.15, and 333.15) K with the precision of 0.001 K according to the manufactureres declaration.

The sound velocities were measured using a sound analyzer OPTIME 1.0 from Optel (Poland) with an uncertainty of 0.05 m·s^{-1} by measuring the time it takes for a pulse of ultrasound to travel from one transducer to another (pitch−catch) or return to the same transducer (pulse−echo). The cell was thermostated at $T = (298.15 \pm 0.005)$ K and calibrated with double distilled water, and the sound velocity value of 1496.69 m·s^{-1} in pure water has been used.[7] The value for sound velocity in pure DMF is 1457.14 m·s^{-1} while the literature values vary from (1468.0 to 1448.55) m·s^{-1}.[8,9] The velocity of sound in DMA was found to be 1455.37 m·s^{-1}, while the literature values are in the range from (1456.48 to 1468) m·s^{-1}.[3,10−13]

Results and Discussion

Apparent Molar Volumes. The apparent molar volume V_Φ of a solute is defined as the difference between the volume of the solution and the volume of the pure solvent per mole of solute and is given by the equation:

$$V_\Phi = \frac{V - n_1 \cdot V_1^0}{n_2} \tag{3}$$

where V is the volume of the solution; n_1 and n_2 denote the

Table 2. Apparent Molar Volumes V_Φ of $(C_6H_5)_4PBr$, $NaB(C_6H_5)_4$, NaBr, and $NaClO_4$ Solutions in DMA and DMF at Different Temperatures

	m_s	$10^6 \cdot V_\Phi/m^3 \cdot mol^{-1}$							m_s	$10^6 \cdot V_\Phi/m^3 \cdot mol^{-1}$						
solvent	mol·kg^{-1}	283.15 K	293.15 K	298.15 K	303.15 K	313.15 K	323.15 K	333.15 K	mol·kg^{-1}	283.15 K	293.15 K	298.15 K	303.15 K	313.15 K	323.15 K	333.15 K
							$(C_6H_5)_4PBr$									
DMA	0.01406	294.61	294.77	294.83	294.95	295.01	295.01	294.96	0.09165	296.14	296.56	296.72	296.86	297.03	297.06	297.00
	0.03175	295.07	295.35	295.42	295.52	295.61	295.64	295.61	0.1064	296.36	296.76	296.93	297.03	297.29	297.37	297.34
	0.04618	295.39	295.71	295.82	295.92	296.01	296.01	296.04	0.1215	296.56	297.00	297.14	297.32	297.56	297.64	297.65
	0.06104	295.61	295.99	296.12	296.25	296.37	296.34	296.38	0.1374	296.72	297.17	297.33	297.50	297.75	297.87	297.88
	0.07650	295.89	296.31	296.47	296.58	296.68	296.72	296.76	0.1520	296.89	297.32	297.52	297.68	297.95	298.13	298.19
DMF	0.01828	291.55	291.85	291.89	291.80	291.75	291.45	291.28	0.07767	292.71	293.07	293.14	293.21	293.30	293.26	293.11
	0.02382	291.73	292.02	292.04	291.99	291.95	291.70	291.49	0.09583	292.94	293.30	293.42	293.48	293.57	293.54	293.34
	0.03591	292.01	292.33	292.34	292.30	292.32	292.11	291.94	0.1070	293.11	293.45	293.57	293.65	293.79	293.79	293.69
	0.04822	292.24	292.55	292.63	292.63	292.61	292.46	292.30	0.1196	293.24	293.60	293.74	293.86	294.02	294.04	293.94
	0.06013	292.46	292.77	292.87	292.87	292.92	292.82	292.61								
							$NaB(C_6H_5)_4$									
DMA	0.01922	283.75	284.13	284.25	284.42	284.66	284.74	284.77	0.1083	284.08	284.63	284.86	285.06	285.37	285.53	285.57
	0.03801	283.85	284.28	284.42	284.62	284.85	284.98	285.00	0.1260	284.15	284.69	284.94	285.14	285.46	285.66	285.72
	0.05466	283.91	284.38	284.55	284.74	285.03	285.13	285.15	0.1446	284.20	284.75	285.03	285.21	285.54	285.74	285.80
	0.07212	283.98	284.46	284.66	284.88	285.16	285.28	285.33	0.1611	284.25	284.83	285.11	285.29	285.65	285.87	285.91
	0.09110	284.04	284.55	284.77	284.98	285.28	285.44	285.43	0.1786	284.30	284.90	285.17	285.38	285.77	285.99	286.06
DMF	0.02586	278.78	279.07	279.37	279.88	280.11	280.38	280.75	0.1044	279.22	279.79	280.10	280.47	280.88	281.20	281.49
	0.03546	278.84	279.20	279.50	280.02	280.25	280.53	280.87	0.1283	279.31	279.95	280.26	280.62	281.07	281.38	281.66
	0.05140	278.95	279.36	279.66	280.13	280.43	280.73	281.04	0.1538	279.41	280.09	280.41	280.73	281.20	281.57	281.84
	0.06859	279.05	279.52	279.82	280.25	280.60	280.90	281.20	0.1689	279.46	280.17	280.50	280.81	281.30	281.67	281.93
	0.08539	279.12	279.68	279.99	280.39	280.77	281.06	281.35								
							NaBr									
DMA	0.03868	11.07	10.04	9.34	8.80	7.53	6.05	4.53	0.2253	13.87	13.08	12.64	12.19	11.20	10.10	8.85
	0.07570	11.84	10.85	10.29	9.76	8.58	7.31	5.75	0.2630	14.23	13.48	13.06	12.62	11.66	10.57	9.37
	0.1142	12.48	11.59	11.08	10.58	9.48	8.25	6.88	0.2988	14.56	13.82	13.40	12.97	12.03	10.98	9.77
	0.1524	12.98	12.12	11.64	11.16	10.11	8.94	7.58	0.3345	14.81	14.09	13.69	13.27	12.34	11.30	10.14
	0.1896	13.47	12.69	12.23	11.78	10.75	9.61	8.34	0.3729	15.13	14.43	14.03	13.62	12.71	11.70	10.58
DMF	0.04008	10.88	9.85	9.32	8.66	7.45	6.12	4.84	0.2020	13.40	12.78	12.45	12.07	11.29	10.39	9.40
	0.06106	11.33	10.36	9.92	9.34	8.14	6.99	5.65	0.2400	13.80	13.23	12.91	12.57	11.82	11.00	10.08
	0.08045	11.73	10.89	10.41	9.89	8.84	7.66	6.43	0.2991	14.24	13.74	13.47	13.16	12.47	11.69	10.80
	0.1230	12.45	11.66	11.23	10.77	9.84	8.84	7.70	0.3558	14.70	14.25	14.00	13.71	13.09	12.37	11.53
	0.1603	12.92	12.23	11.87	11.46	10.60	9.62	8.54	0.3930	14.96	14.55	14.31	14.04	13.45	12.76	11.95
							$NaClO_4$									
DMA	0.03560	39.80	38.72	38.04	37.48	36.19	34.73	33.13	0.2122	40.74	39.86	39.36	38.86	37.75	36.51	35.13
	0.07279	40.10	39.04	38.43	37.85	36.60	35.24	33.72	0.2471	40.92	40.05	39.57	39.08	38.00	36.81	35.43
	0.1073	40.27	39.27	38.74	38.20	36.99	35.63	34.16	0.2817	41.01	40.18	39.72	39.23	38.18	37.00	35.69
	0.1391	40.42	39.51	38.94	38.40	37.26	35.94	34.47	0.3171	41.16	40.34	39.88	39.41	38.39	37.24	35.94
	0.1787	40.62	39.71	39.19	38.68	37.54	36.27	34.83	0.3508	41.25	40.45	40.01	39.55	38.55	37.42	36.17
DMF	0.03096	36.02	34.74	34.18	34.01	32.66	31.12	29.43	0.1552	36.89	35.91	35.43	35.08	33.94	32.69	31.34
	0.04574	36.14	34.93	34.41	34.22	32.90	31.38	29.76	0.2008	37.12	36.20	35.74	35.39	34.31	33.07	31.71
	0.07671	36.38	35.25	34.77	34.46	33.23	31.82	30.28	0.2466	37.31	36.46	36.03	35.64	34.61	33.48	32.12
	0.09316	36.52	35.40	34.92	34.64	33.40	32.02	30.50	0.2771	37.40	36.56	36.14	35.75	34.74	33.62	32.36
	0.1271	36.74	35.75	35.26	34.92	33.75	32.45	30.98	0.3073	37.53	36.74	36.30	35.93	34.95	33.83	32.61

number of moles of the solvent and solute, respectively; and V_1^0 is the molar volume of the pure solvent. The limiting values of the apparent molar volumes are the primary source of the direct information concerning ion−solvent interaction.

In practice, values for the apparent molar volumes can be obtained through the density measurements using the equation

$$V_\Phi = \frac{M_2}{\rho_0} - \frac{\rho - \rho_0}{m_S \rho \rho_0} \tag{4}$$

where m_S denotes the number of moles of the solute per unit mass of solution (molonity); ρ and ρ_0 are densities of solution and solvent, respectively; and M_2 is the molar mass of the solute. Density data obtained for solutions of the tetraphenylphosphonium bromide, sodium tetraphenylborate, sodium bromide, and sodium perchlorate in DMA and DMF are given in Table 1. The resulting values of V_Φ are reported in Table 2. In Figure 1 the apparent molar volumes of NaTB, TPBr, NaBr, and $NaClO_4$ in DMA and DMF are plotted against the square root of molar concentration (c/mol·dm^{-3}) for $T = 298.15$ K.

For tetraphenylphosphonium bromide, sodium tetraphenylborate, and sodium perchlorate solutions the plots of V_Φ against $c^{1/2}$ are found to be linear over the concentration as well as temperature range studied. Therefore, Masson's equation

$$V_\Phi = V_\Phi^0 + S_V c^{1/2} \tag{5}$$

where V_Φ^0 and S_V are the apparent molar volume of solute at infinite dilution and the slope, respectively, can be used.[14] The coefficients of the Masson's equation and the respective values of the residual variance obtained for all the solutions and temperatures studied are listed in Table 3. For the sodium bromide solution, the apparent molar volume dependence on the square root of concentration can be described with the Redlich−Rosenfeld−Meyer (RRM)-type equation:

$$V_\Phi = V_\Phi^0 + A_V c^{1/2} + B_V c \tag{6}$$

where A_V and B_V are empirical coefficients. The respective coefficients of the polynomial described by eq 6 and values of the residual variance are given in Table 4.

There are data available for the theoretical slope estimation for DMA and DMF, but for $T = 298.15$ K only, while our data cover the temperature between $T = 283.15$ K and $T = 333.15$ K.[15]

The values of the limiting molar volumes of all salts investigated are a little higher in DMA than the respective values in DMF. The smallest differences were observed for sodium bromide. Those volume differences could be the result of different structure and volume of the two solvents studied. There is also a slight difference in solvation of salts by the two solvents.

Ionic Molar Volumes. Limiting apparent molar volumes of $NaBPh_4$, Ph_4PBr, NaBr, and $NaClO_4$ were split into ionic components using the reference electrolyte method recommended by Hefter and Marcus.[1] The respective values of

Table 3. Coefficients of Equation 5 for Apparent Molar Volume of the Solutions of $(C_6H_5)_4PBr$, $NaB(C_6H_5)_4$, and $NaClO_4$ in DMA and DMF at Temperatures between $T = 283.15$ K and $T = 333.15$ K

	solvent					
	DMA			DMF		
T	$10^6 \cdot V_\Phi^0$	$10^6 \cdot S_V$	$10^6 \cdot \sigma$	$10^6 \cdot V_\Phi^0$	$10^6 \cdot S_V$	$10^6 \cdot \sigma$
K	$m^3 \cdot mol^{-1}$	$(m^9 \cdot mol^{-3})^{1/2}$	$m^3 \cdot mol^{-1}$	$m^3 \cdot mol^{-1}$	$(m^9 \cdot mol^{-3})^{1/2}$	$m^3 \cdot mol^{-1}$
			$(C_6H_5)_4PBr$			
283.15	293.58 ± 0.070	0.27 ± 0.010	0.026	290.51 ± 0.038	0.254 ± 0.0049	0.013
293.15	293.68 ± 0.069	0.31 ± 0.013	0.027	290.76 ± 0.040	0.265 ± 0.0051	0.014
298.15	293.69 ± 0.083	0.32 ± 0.011	0.033	290.71 ± 0.042	0.283 ± 0.0049	0.013
303.15	293.76 ± 0.070	0.33 ± 0.009	0.027	290.50 ± 0.038	0.314 ± 0.0053	0.013
313.15	293.68 ± 0.079	0.36 ± 0.010	0.031	290.31 ± 0.061	0.347 ± 0.0080	0.021
323.15	293.59 ± 0.20	0.38 ± 0.016	0.048	289.83 ± 0.087	0.40 ± 0.014	0.031
333.15	293.54 ± 0.13	0.39 ± 0.016	0.044	289.58 ± 0.14	0.41 ± 0.018	0.048
			$NaB(C_6H_5)_4$			
283.15	283.47 ± 0.033	0.062 ± 0.0033	0.012	278.33 ± 0.016	0.088 ± 0.0014	0.004
293.15	283.76 ± 0.035	0.086 ± 0.0037	0.012	278.37 ± 0.035	0.142 ± 0.0038	0.011
298.15	283.79 ± 0.019	0.105 ± 0.0020	0.006	278.66 ± 0.034	0.145 ± 0.0039	0.012
303.15	283.98 ± 0.040	0.107 ± 0.0040	0.014	279.33 ± 0.047	0.117 ± 0.0050	0.015
313.15	284.14 ± 0.055	0.124 ± 0.0059	0.020	279.36 ± 0.039	0.154 ± 0.0044	0.013
323.15	284.14 ± 0.050	0.141 ± 0.0053	0.019	279.57 ± 0.023	0.167 ± 0.0027	0.007
333.15	284.13 ± 0.076	0.147 ± 0.0080	0.028	279.99 ± 0.031	0.154 ± 0.0035	0.011
			$NaClO_4$			
283.15	39.12 ± 0.058	0.115 ± 0.0045	0.022	35.30 ± 0.042	0.129 ± 0.0038	0.018
293.15	37.89 ± 0.039	0.139 ± 0.0027	0.014	33.82 ± 0.074	0.170 ± 0.0061	0.031
298.15	37.14 ± 0.038	0.157 ± 0.0031	0.014	33.24 ± 0.072	0.179 ± 0.0059	0.030
303.15	36.51 ± 0.049	0.166 ± 0.0038	0.018	33.13 ± 0.058	0.162 ± 0.0048	0.025
313.15	35.07 ± 0.054	0.191 ± 0.0041	0.020	31.60 ± 0.060	0.195 ± 0.0047	0.024
323.15	33.48 ± 0.046	0.217 ± 0.0035	0.016	29.87 ± 0.071	0.234 ± 0.0055	0.029
333.15	31.73 ± 0.042	0.244 ± 0.0035	0.017	28.01 ± 0.084	0.272 ± 0.0068	0.035

Table 4. Coefficients of Equation 6 for Apparent Molar Volume of the Solutions of NaBr in DMA and DMF at Temperatures between $T = 283.15$ K and $T = 333.15$ K

solvent	T / K	$10^6 \cdot V_\Phi^0$ / $m^3 \cdot mol^{-1}$	$10^6 \cdot A_V$ / $(m^9 \cdot mol^{-3})^{-1/2}$	$10^9 \cdot B_V$ / $(m^3 \cdot mol^{-1})^2$	$10^6 \cdot \sigma$ / $m^3 \cdot mol^{-1}$
DMA	283.15	8.59 ± 0.21	0.36 ± 0.039	−1.7 ± 1.4	0.027
	293.15	7.65 ± 0.13	0.41 ± 0.052	−2.6 ± 1.9	0.038
	298.15	6.62 ± 0.22	0.47 ± 0.040	−4.5 ± 1.5	0.028
	303.15	6.00 ± 0.27	0.49 ± 0.044	−4.6 ± 1.8	0.034
	313.15	4.43 ± 0.25	0.55 ± 0.045	−5.8 ± 1.7	0.032
	323.15	2.57 ± 0.18	0.63 ± 0.031	−7.8 ± 1.2	0.022
	333.15	0.78 ± 0.38	0.68 ± 0.067	−8.2 ± 2.6	0.049
DMF	283.15	8.51 ± 0.20	0.40 ± 0.034	−3.8 ± 1.3	0.027
	293.15	7.06 ± 0.23	0.48 ± 0.041	−4.9 ± 1.5	0.031
	298.15	6.37 ± 0.17	0.51 ± 0.028	−5.3 ± 1.1	0.023
	303.15	5.38 ± 0.17	0.58 ± 0.033	−6.8 ± 1.1	0.023
	313.15	3.63 ± 0.29	0.67 ± 0.050	−8.6 ± 1.9	0.040
	323.15	1.87 ± 0.21	0.76 ± 0.035	−10.2 ± 1.4	0.028
	333.15	0.24 ± 0.38	0.81 ± 0.069	−10.8 ± 2.6	0.053

Table 5. Values of the Limiting Partial Molar Volumes of the Tetraphenylphosphate, Tetraphenylborate, Sodium, Bromide, and Perchlorate Ions in DMA and DMF at Temperatures between $T = 283.15$ K and $T = 333.15$ K

T		$10^6 \cdot V_\Phi^0$ / $m^3 \cdot mol^{-1}$				
K	solvent	$(C_6H_5)_4P^+$	$(C_6H_5)_4B^-$	Na^+	Br^-	ClO_4^-
283.15	DMA	285.23	283.23	0.24	8.35	38.88
	DMF	281.17	279.17	−0.83	9.34	36.14
293.15	DMA	285.90	283.90	−0.14	7.79	38.03
	DMF	282.04	280.04	−1.67	8.73	35.49
298.15	DMA	286.43	284.43	−0.64	7.26	37.78
	DMF	282.50	280.50	−1.84	8.21	35.08
303.15	DMA	286.87	284.87	−0.89	6.89	37.40
	DMF	283.23	281.23	−1.89	7.27	35.03
313. 15	DMA	287.70	285.70	−1.56	5.99	36.63
	DMF	284.02	282.02	−2.66	6.29	34.26
323.15	DMA	288.58	286.58	−2.44	5.01	35.92
	DMF	284.77	282.77	−3.19	5.06	33.07
333.15	DMA	289.45	287.45	−3.32	4.10	35.05
	DMF	285.66	283.66	−3.67	3.91	31.69

V_Φ^0(ion) in DMA and DMF within the whole temperature range are listed in Table 5. Figure 2 shows the plots of the difference $V_{\Phi,T}^0$(ion) − $V_{\Phi,283.15}^0$(ion) against temperature for both solvents. As is seen, for the tetraphenylphosphonium and tetraphenylborate ions, the limiting apparent molar volume increases with temperature. This effect is caused by weak solvation as well as an increase in the intrinsic volumes of the ions. As for the sodium, bromide, and perchlorate ions, a decrease of partial molar volumes with temperature is observed. However, the influence of temperature appears to be higher for anions than the sodium cation, which considering better solvation for cations, seems to be incorrect. The reason for this is probably connected with the assumption $V_\Phi^0(Ph_4P^+) - V_\Phi^0(Ph_4B^-) = 2 \pm 2$ $cm^3 \cdot mol^{-1}$, which is used through the whole temperature range. Data analysis suggests, that in order to obtain correct $V_{\Phi,T}^0$(ion) − $V_{\Phi,283.15}^0$(ion) gradation, a gradual decrease in the values of the difference of volumes of tetraphenylphosphonium and tetraphenylborate ions with increasing temperature should be used. The changes of ionic volumes with temperature should be evaluated by using extrapolation techniques, which do not impose defined relations hips between cation and anion volumes.

Volume Expansibilities. The limiting values of the apparent molar volumes of sodium bromide and sodium perchlorate in both solvents depend on temperature, while for tetraphenylphosphonium bromide and sodium tetraphenylborate the volume change with increasing temperature is very slight and smaller than 1 cm^3.

The volume expansibilities for the limiting values of the apparent molar volumes are defined using the equation

$$\alpha_V^0 = \frac{1}{V_\Phi^0} \cdot \left(\frac{\partial V_\Phi^0}{\partial T} \right)_P \tag{7}$$

and calculated for $T = 298.15$ K. The derivative in eq 7 was calculated on the basis of the polynomial (eq 8) describing the limiting values of the apparent molar volumes dependence on temperature:

$$V_\Phi^0 = A_T + B_T \cdot (T/\mathrm{K} - 298.15) + C_T \cdot (T/\mathrm{K} - 298.15)^2 \tag{8}$$

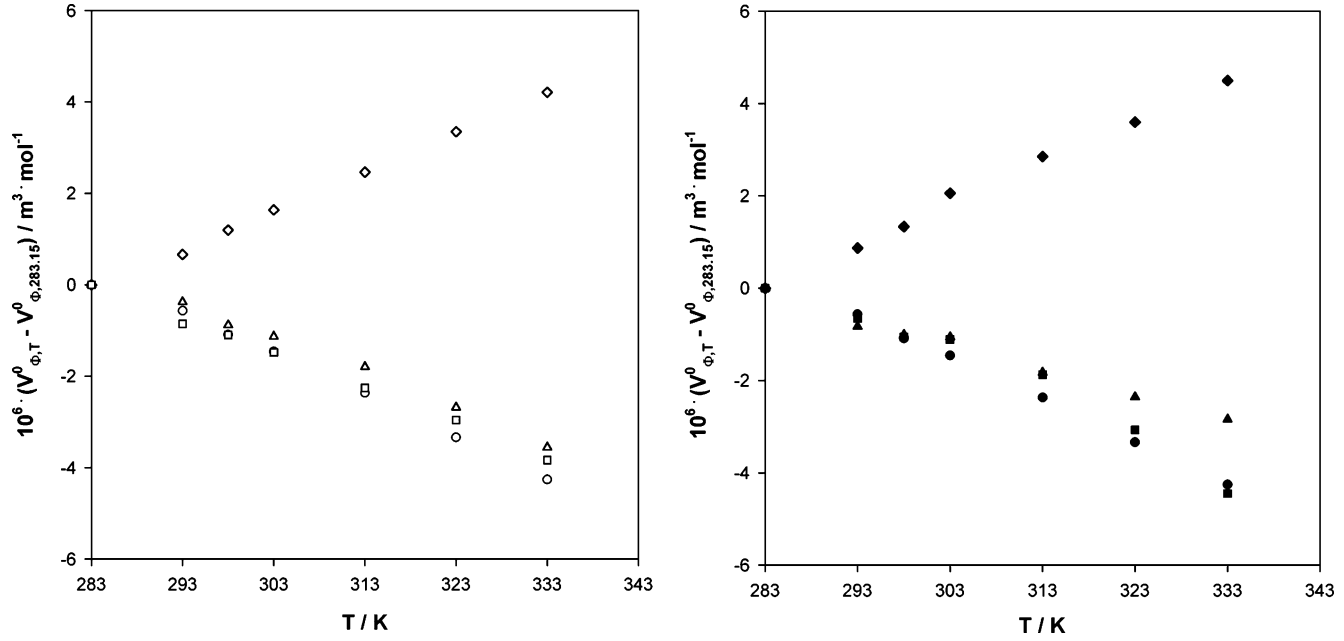

Figure 2. Plots of the difference $V^0_\Phi - V^0_{\Phi,283.15}$ for TP^+, TB^-, Na^+, Br^-, and ClO_4^- ions in DMA and DMF against temperature T. $TP^+ = TB^-$: ◇, DMA; ◆, DMF. Na^+: △, DMA; ▲, DMF. ClO_4^-: □, DMA; ■, DMF. Br^-: ○, DMA; ●, DMF.

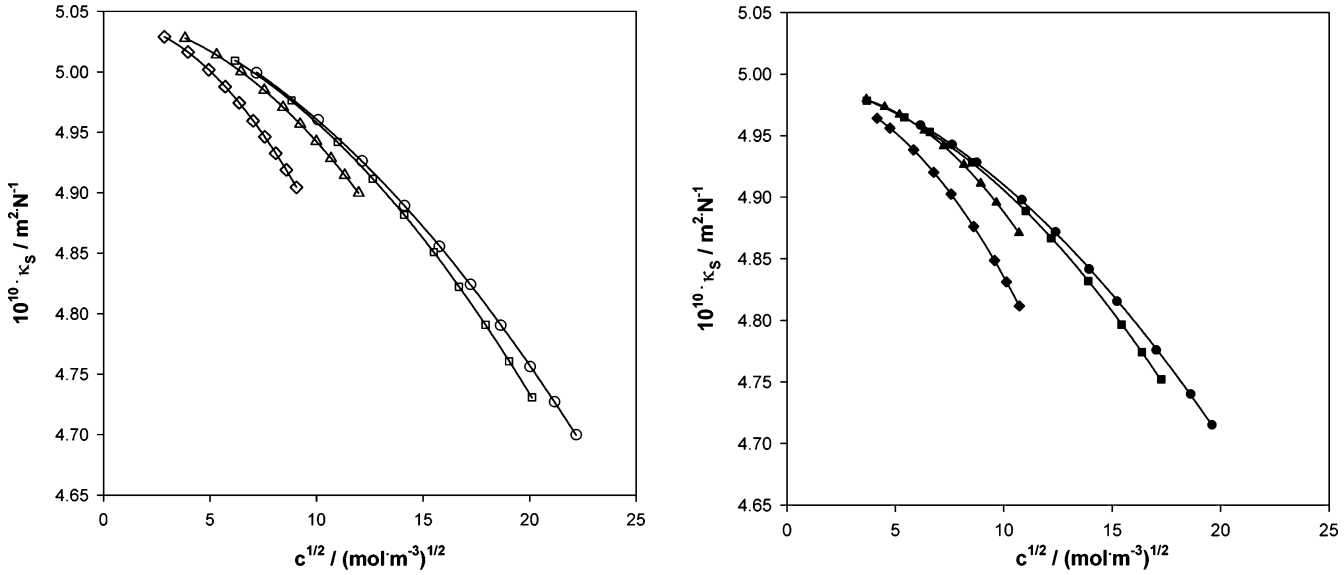

Figure 3. Plots of the adiabatic compressibilties κ_S of Ph_4PBr, $NaBPh_4$, $NaClO_4$, and NaBr solutions in DMA and DMF against the square root of molarity c for $T = 298.15$ K. Ph_4PBr: ◇, DMA; ◆, DMF. $NaBPh_4$: △, DMA; ▲, DMF. $NaClO_4$: □, DMA; ■, DMF. NaBr: ○, DMA; ●, DMF.

The values of volume expansibilities and the coefficients of eq 8 are listed in Table 6 along with the respective values of residual variance. As is seen, the values of the expansibility for sodium bromide and sodium perchlorate are in good agreement with each other in DMA and in DMF. The values of the expansibilities of tetraphenylphosphonium bromide and sodium tetraphenylborate are very small in the two solvents investigated. Thus we can assume that the limiting apparent molar volumes of Ph_4PBr and $NaBPh_4$ do not depend on temperature. However, in this case it does not mean that the limiting apparent molar volumes of ions do not change with temperature. For large tetraphenyl ions like the tetraphenylphosphonium cation or tetraphenylborate anion, the limiting apparent molar volume increases with temperature, whereas V^0_Φ of the small Na^+ and Br^- ions decreases with rising temperature. From this observation, we can assume that the two effects cancel each other out, which causes such small values for the volume expansibilities.

Apparent Molar Isentropic Compressibilities. The adiabatic compressibility is defined by the thermodynamic relation

$$\kappa_S = -\frac{1}{V}\cdot\left(\frac{\partial V}{\partial P}\right)_S \tag{9}$$

where V is volume, P is pressure, and S is entropy. It is related to density ρ and sound velocity u by the Laplace equation:

$$\kappa_S = \frac{1}{u^2\rho} \tag{10}$$

Apparent molar isentropic compressibility is defined by the equation

$$K_{S,\Phi} = \frac{V\cdot\kappa_S - n_1\cdot V_1^0\cdot\kappa_S^0}{n_2} \tag{11}$$

where V is the volume of the solution; n_1 and n_2 denote the

Table 6. Parameters of Equation $V_\Phi^0 = A_T + B_T\cdot(T/K - 298.15) + C_T\cdot(T/K - 298.15)^2$ and Volume Expansibility α_V^0 for $(C_6H_5)_4PBr$, $NaB(C_6H_5)_4$, NaBr, and $NaClO_4$ Solutions in DMA and DMF[a]

solvent	A_T / cm³·mol⁻¹	B_T / cm³·mol⁻¹	10^3C_T / cm³·mol⁻¹	σ / cm³·mol⁻¹	$10^3\alpha_V^0$ / K⁻¹
			$(C_6H_5)_4PBr$		
DMA	293.69 ± 0.083	0.0034 ± 0.0035	−0.2 ± 0.15	0.033	0.0114 ± 0.0116
DMF	290.71 ± 0.042	−0.0079 ± 0.015	−8.1 ± 5.2	0.143	−0.0272 ± 0.0503
			$NaB(C_6H_5)_4$		
DMA	283.79 ± 0.019	0.020 ± 0.0084	−0.27 ± 0.28	0.078	0.0714 ± 0.0280
DMF	278.66 ± 0.034	0.035 ± 0.026	0.11 ± 0.88	0.249	0.13 ± 0.095
			NaBr		
DMA	6.62 ± 0.22	−0.14 ± 0.020	−0.66 ± 0.59	0.166	−22 ± 2.2
DMF	6.37 ± 0.17	−0.16 ± 0.018	−0.54 ± 0.61	0.174	−25 ± 2.3
			$NaClO_4$		
DMA	37.14 ± 0.038	−0.14 ± 0.011	−0.47 ± 0.25	0.069	−3.7 ± 0.22
DMF	33.24 ± 0.072	−0.13 ± 0.039	−0.53 ± 1.16	0.331	−3.8 ± 1.1

[a] Coefficient A_T is equal to $V^0_{\Phi,298.15}$.

Table 7. Sound Velocities u, Adiabatic Compressibilities κ_S, and Apparent Molar Compressibilities $K_{S,\Phi}$ of $(C_6H_5)_4PBr$, $NaB(C_6H_5)_4$, NaBr, and $NaClO_4$ Solutions in DMA and DMF at the Temperature 298.15 K

m_s / mol·kg⁻¹	u / m·s⁻¹	$10^{10}\cdot\kappa_S$ / m²·N⁻¹	$10^{14}\cdot K_{S,\Phi}$ / m⁵·mol⁻¹·N⁻¹	m_s / mol·kg⁻¹	u / m·s⁻¹	$10^{10}\cdot\kappa_S$ / m²·N⁻¹	$10^{14}\cdot K_{S,\Phi}$ / m⁵·mol⁻¹·N⁻¹
			$(C_6H_5)_4PBr$				
DMA	1455.37	5.043					
0.008695	1456.48	5.029	−2.01	DMF	1457.13	4.990	
0.01672	1457.48	5.016	−1.98	0.01828	1459.04	4.964	−5.47
0.02591	1458.65	5.002	−2.00	0.02382	1459.65	4.956	−6.05
0.03470	1459.78	4.988	−1.99	0.03591	1460.99	4.938	−6.46
0.04309	1460.86	4.974	−1.97	0.04822	1462.41	4.920	−7.08
0.05227	1462.09	4.960	−2.00	0.06013	1463.80	4.903	−7.35
0.06073	1463.16	4.946	−1.93	0.07767	1465.92	4.876	−7.92
0.06911	1464.32	4.933	−1.96	0.09583	1468.17	4.849	−8.27
0.07773	1465.46	4.919	−1.92	0.1069	1469.60	4.831	−8.60
0.08651	1466.70	4.904	−1.95	0.1196	1471.24	4.812	−8.82
			$NaB(C_6H_5)_4$				
DMA	1455.37	5.043					
0.01559	1456.71	5.028	3.94	DMF	1457.13	4.990	
0.02993	1457.91	5.014	4.03	0.01418	1457.88	4.980	5.59
0.04447	1459.12	5.000	4.10	0.02142	1458.39	4.973	5.34
0.06051	1460.47	4.985	4.13	0.02852	1458.90	4.967	5.20
0.07546	1461.71	4.971	4.19	0.04246	1460.02	4.954	4.87
0.09038	1462.96	4.957	4.22	0.05507	1461.15	4.942	4.58
0.1056	1464.23	4.942	4.26	0.07020	1462.55	4.926	4.33
0.1206	1465.49	4.928	4.30	0.08415	1464.03	4.911	4.03
0.1355	1466.73	4.914	4.34	0.09795	1465.56	4.896	3.78
0.1515	1468.04	4.900	4.39	0.12015	1467.98	4.871	3.54
			NaBr				
DMA	1455.37	5.043		DMF	1457.13	4.990	
0.05475	1457.93	4.999	−7.96	0.04008	1459.05	4.958	−7.93
0.1073	1460.10	4.960	−7.56	0.06106	1459.96	4.943	−7.74
0.1551	1461.96	4.926	−7.32	0.08045	1460.77	4.928	−7.59
0.2092	1463.87	4.889	−7.07	0.1229	1462.45	4.898	−7.32
0.2592	1465.61	4.856	−6.88	0.1603	1463.87	4.872	−7.13
0.3081	1467.09	4.824	−6.68	0.2020	1465.66	4.842	−7.04
0.3593	1468.88	4.791	−6.55	0.2400	1467.09	4.816	−6.90
0.4124	1470.68	4.756	−6.42	0.2991	1469.24	4.776	−6.72
0.4591	1472.12	4.727	−6.29	0.3558	1471.04	4.740	−6.51
0.5024	1473.56	4.700	−6.20	0.3930	1472.48	4.715	−6.44
			$NaClO_4$				
DMA	1455.37	5.043		DMF	1457.13	4.990	
0.04049	1457.63	5.009	−6.72	0.01435	1457.94	4.978	−7.18
0.08250	1459.76	4.976	−6.53	0.03096	1458.84	4.965	−7.02
0.1276	1461.96	4.942	−6.35	0.04574	1459.61	4.953	−6.91
0.1682	1463.93	4.911	−6.23	0.07671	1461.23	4.928	−6.78
0.2089	1465.82	4.882	−6.09	0.12708	1463.82	4.889	−6.61
0.2511	1467.81	4.851	−5.98	0.15522	1465.30	4.867	−6.56
0.2898	1469.70	4.822	−5.90	0.20077	1467.55	4.832	−6.42
0.3335	1471.76	4.791	−5.80	0.24660	1469.96	4.797	−6.34
0.3749	1473.83	4.761	−5.73	0.27706	1471.40	4.774	−6.26
0.4170	1475.84	4.731	−5.65	0.30730	1472.84	4.752	−6.18

number of moles of the solvent and solute, respectively; V_1^0 is the molar volume of the pure solvent; κ_S and κ_S^0 are the adiabatic compressibilities of solution and solvent.

The apparent molar isentropic compressibilities for all salts investigated were calculated on the basis of the equation

$$K_{S,\Phi} = \frac{M_2\cdot\kappa_S^0}{\rho_0} - \frac{\kappa_S^0 d - \kappa_S\rho_0}{m_S\rho\rho_0} \qquad (12)$$

where M_2 is the molecular mass of the salt; m_S denotes a number

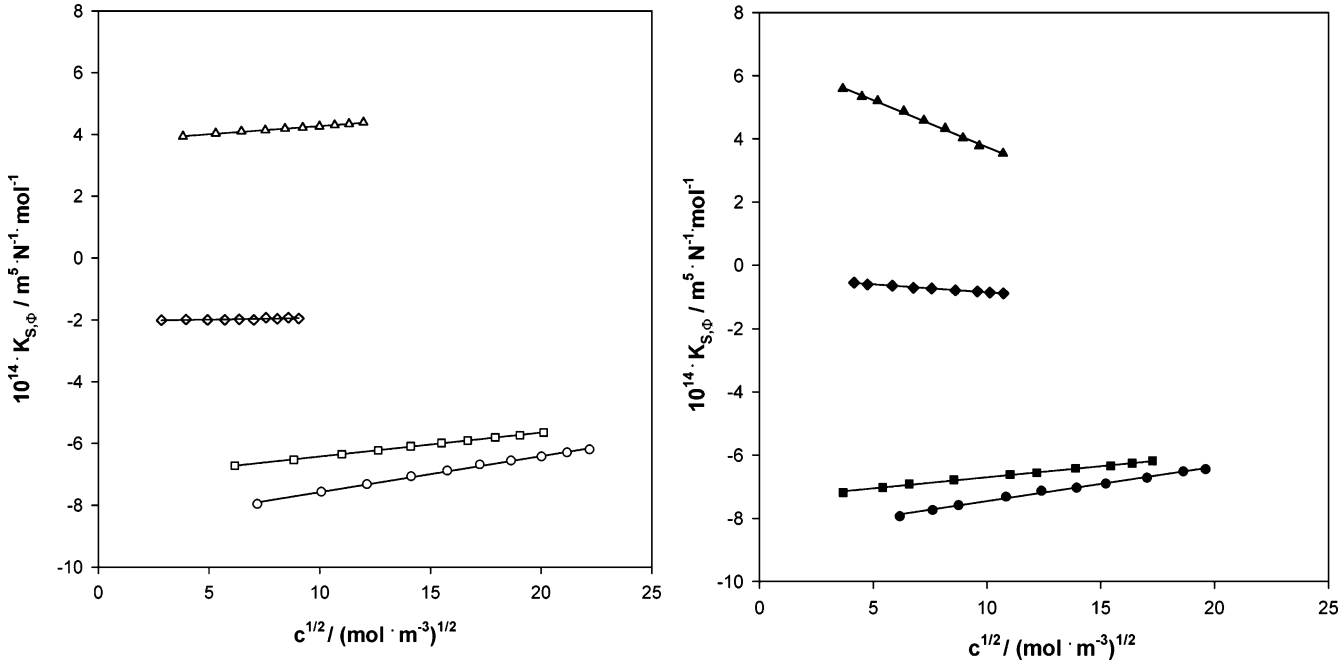

Figure 4. Plots of the apparent molar adiabatic compressibilties $K_{S,\Phi}$ of Ph_4PBr, $NaBPh_4$, $NaClO_4$, and NaBr solutions in DMA and DMF against the square root of molarity c for $T = 298.15$ K. Ph_4PBr: ◇, DMA; ◆, DMF. $NaBPh_4$: △, DMA; ▲, DMF. $NaClO_4$: □, DMA; ■, DMF. NaBr: ○, DMA; ●, DMF.

Table 8. Coefficients of Equation $\kappa_S = \kappa_S^0 + A_1c^{1/2} + A_2c$ for Adiabatic Compressibilities of the Solutions of $(C_6H_5)_4PBr$, $NaB(C_6H_5)_4$, $NaClO_4$, and NaBr in DMA and DMF at the Temperature 298.15 K, Where $\kappa_S^0 = 5.043 \cdot 10^{-10}$ m^2·N^{-1} for DMA and $\kappa_S^0 = 4.990 \cdot 10^{-10}$ m^2·N^{-1} for DMF

	$(C_6H_5)_4PBr$	$NaB(C_6H_5)_4$	$NaClO_4$	NaBr
		DMA		
$10^{14} \cdot A_1$/(m^7·N^{-2}·mol^{-1})$^{1/2}$	−0.4 ± 0.7	−3 ± 1.5	−15 ± 3.1	−24 ± 5.0
$10^{14} \cdot A_2$/m^5·N^{-1}·mol^{-1}	−16.84 ± 0.085	−9.7 ± 0.14	−7.0 ± 0.19	−5.9 ± 0.30
$10^{10} \cdot \sigma$/m^2·N^{-1}	0.0001	0.0003	0.0011	0.0021
		DMF		
$10^{14} \cdot A_1$/(m^7·N^{-2}·mol^{-1})$^{1/2}$	4.7 ± 0.72	19 ± 4.9	−7 ± 3.5	−15 ± 4.9
$10^{14} \cdot A_2$/m^5·N^{-1}·mol^{-1}	−15.93 ± 0.078	−12.1 ± 0.55	−7.6 ± 0.23	−6.4 ± 0.29
$10^{14} \cdot \sigma$/m^2·N^{-1}	0.0001	0.0010	0.0011	0.0019

Table 9. Coefficients of Equation 14 for Apparent Molar Adiabatic Compressibilities of the Solutions of $(C_6H_5)_4PBr$, $NaB(C_6H_5)_4$, $NaClO_4$, and NaBr in DMA and DMF at the Temperature 298.15 K

	$(C_6H_5)_4PBr$	$NaB(C_6H_5)_4$	$NaClO_4$	NaBr
		DMA		
$10^{14} \cdot K_{S,\Phi}^0$/m^5·mol^{-1}·N^{-1}	−2.05 ± 0.025	3.74 ± 0.025	−7.20 ± 0.011	−8.74 ± 0.042
$10^{16} \cdot S_K$/(m^{13}·mol^{-3}·N^{-2})$^{1/2}$	1.2 ± 0.83	5.3 ± 0.27	7.8 ± 0.21	11.7 ± 0.57
$10^{14} \cdot \sigma$/m^5·mol^{-1}·N^{-1}	0.021	0.009	0.010	0.034
		DMF		
$10^{14} \cdot K_{S,\Phi}^0$/m^5·mol^{-1}·N^{-1}	−0.36 ± 0.031	6.7 ± 0.12	−7.40 ± 0.048	−8.55 ± 0.098
$10^{16} \cdot S_K$/(m^{13}·mol^{-3}·N^{-2})$^{1/2}$	−4.9 ± 0.42	−30 ± 1.8	7.0 ± 0.42	10.9 ± 0.70
$10^{14} \cdot \sigma$/m^5·mol^{-1}·N^{-1}	0.011	0.041	0.023	0.040

of moles of the solute per kilogram of solution (molonity); and ρ and ρ_0 are the densities of solution and solvent, respectively. The symbols κ_S and κ_S^0 are explained above. Values of sound velocities, adiabatic compressibilities, and apparent molar isentropic compressibilities along with the corresponding molonity of each solution are listed in Table 7. It has been found that for all of the solutions investigated the plots of adiabatic compressibility κ_S against concentration are not linear and the best description is obtained using the equation:

$$\kappa_S = \kappa_S^0 + A_1c^{1/2} + A_2c \tag{13}$$

where κ_S^0 in Pa^{-1} is the adiabatic compressibility of the pure solvent at $T = 298.15$ K. Coefficients A_1 and A_2 as well as the respective values of residual deviations are given in Table 8. The concentration dependencies of the adiabatic compressibility coefficients for solutions of NaTB, TPBr, $NaClO_4$, and NaBr in DMA and DMF at 298.15 K are presented in Figure 3. In both solvents investigated the tendency of the changes observed is similar. Among the salts studied the highest impact on solution compressibility is from tetraphenylphosphonium bromide and sodium tetraphenylborate. Because of the complex structure of TP^+ and TB^- ions consisting of four stiff phenyl rings, the influence of the corresponding salts on solution compressibilities is quite significant, even though their interactions with the solvent are weak.

In Figure 4 the values of the apparent molar compressibilities of Ph_4PBr, $NaBPh_4$, $NaClO_4$, and NaBr are presented as a function of the square root of concentration. As can be seen, all the plots are linear indicating, that the equation

$$K_{S,\Phi} = K_{S,\Phi}^0 + S_Kc^{1/2} \tag{14}$$

where $K^0_{S,\Phi}$ represents the limiting apparent molar adiabatic compressibility and S_K is the experimental slope, may be used for extrapolation. Equation 14, which has the form analogous to the Masson's equation, was first introduced and applied by Gucker.[16] The coefficients of eq 14, their uncertainties as well as the respective values of the residual deviations σ are collected in Table 9. All salts investigated have little influence on solvent compressibility. Positive values of apparent molar compressibility of $NaBPh_4$ indicate that its presence in solution breaks the solvent structure. This effect is attributed to the TB^- ion since it has been established from NMR[17] as well as DRS[18] measurements that Na^+ is a structure-making ion. This statement is also confirmed by negative values of limiting apparent molar volumes of the sodium ion in DMA and DMF. In the case of TPBr, the values of the apparent molar adiabatic compressibilities are negative, which suggests that the tetraphenylphosphonium ion is better solvated in comparison to the tetraphenylborate anion. Therefore it is evident that assuming equality of compressibilities of the reference electrolyte ions in order to evaluate ionic contributions is an oversimplification. It also seems to be obvious that in the case of other reference electrolytes like Bu_4NBPh_4 this assumption is particularly inadequate.

Conclusions

Assuming the equality of $K^0_{S,\Phi}(TP^+)$ and $K^0_{S,\Phi}(TB^-)$, the negative values of $K^0_{S,\Phi}(Br^-)$ ($-10.22 \cdot 10^{-14}$ $m^5 \cdot mol^{-1} \cdot N^{-1}$ for DMA and $-7.81 \cdot 10^{-14}$ $m^5 \cdot mol^{-1} \cdot N^{-1}$ for DMF) and $K^0_{S,\Phi}(ClO_4^-)$ ($-5.73 \cdot 10^{-14}$ $m^5 \cdot mol^{-1} \cdot N^{-1}$ for DMA and $-6.66 \cdot 10^{-14}$ $m^5 \cdot mol^{-1} \cdot N^{-1}$ for DMF) were obtained. These results suggest that the latter two anions decrease the compressibility of the solvent much stronger than does the sodium cation. This is in contradiction with the results of other studies confirming better solvation of cations in both solvents investigated. However, the reference electrolyte method is still the best way for obtaining ionic volumes of many electrolytes. Marcus and Hefter estimated that the intrinsic volume of the TP^+ and TB^- ions reaches 95 % of the whole ion volume.[1] This means that the differences in solvation of the TP^+ and TB^- ions have the slightest impact on values of ionic volumes. On the other hand, the intrinsic compressibility of the ions is very small, and that is why the reference electrolyte method is not suitable for dividing the limiting apparent molar adiabatic compressibilities into ionic contributions.

Literature Cited

(1) Hefter, G.; Marcus Y. A. Critical review of methods for obtaining ionic volumes in solution. *J. Solution Chem*. **1997**, *26*, 249−266.

(2) Laliberte, L. H.; Conway, B. E. Solute and solvent structure effects in volumes and compressibilities of organic ions in solution. *J. Phys. Chem.* **1970**, *74* (23), 4116−4125.

(3) Debashis, D.; Bijan, D.; Hazra, D. K. Ultrasonic velocities and isentropic compressibilities of some symmetrical tetraalkylammonium salts in *N*,*N*-dimethylacetamide at 298.15 K. *J. Mol. Liq.* **2004**, *111*, 15−18.

(4) Davidson, I.; Perron, G.; Desnoyers, J. E. Isentropic compressibilities of electrolytes in acetonitrile at 25 °C. *Can. J. Chem*. **1981**, *59*, 2212−2217.

(5) Lankford, J. I.; Holladay, W. T.; Criss, C. M. Isentropic compressibilities of univalent electrolytes in methanol at 25 °C. *J. Solution Chem.* **1984**, *13* (10), 699−720.

(6) Singh, J.; Kaur, T.; Ali, V.; Gill, D. S. Ultrasonic velocities and isentropic compressibilities of some tetraalkylammonium and copper-(I) salts in acetonitrile and benzonitrile. *J. Chem. Soc. Faraday Trans.* **1994**, *90* (4), 579−582.

(7) Del Gross, V. A.; Mader, C. W. Speed of sound in pure water. *J. Acoust. Soc. Am*. **1972**, *52*, 144−1446.

(8) Ali, A.; Nain, A. K.; Kamil, M. Physico-chemical studies of non-aqueous binary liquid mixtures at various temperatures. *Thermochim. Acta* **1996**, *274*, 209−221.

(9) Gill, D. S.; Anand, H.; Puri, J. K. Isentropic compressibilities of some copper(I), sodium(I) and tetraalkylammonium salts evaluated from ultrasonic velocity measurements in acetonitrile + *N*,*N*-dimethylformamide mixtures at 298.15 K. *J. Mol. Liq.* **2003**, *108* (1−3), 265−282.

(10) Aminabhavi, T. M.; Gopalakrishna, B. Density, viscosity, refractive index, and speed of sound in aqueous mixtures of *N*,*N*-dimethylformamide, dimethyl sulfoxide, *N*,*N*-dimethylacetamide, acetonitrile, ethylene glycol, diethylene glycol, 1,4-dioxane, tetrahydrofuran, 2-methoxyethanol, and 2-ethoxyethanol at 298.15 K. *J. Chem. Eng. Data* **1995**, *40*, 856−861.

(11) Aralaguppi, M. I.; Jadar, C. V.; Ortego, J. D.; Mehrotra, S. C. Density, refractive index, and speed of sound in binary mixtures of 2-ethoxyethanol with dimethyl sulfoxide, *N*,*N*-dimethylformamide, and *N*,*N*-dimethylacetamide at different temperatures *J. Chem. Eng. Data* **1997**, *42*, 301−303.

(12) Ali, A.; Nain, A. K. Ultrasonic study of molecular interactions in *N*,*N*-dimethylacetamide + ethanol binary mixtures at various temperatures. *Acoust. Lett.* **1996**, *19*, 181.

(13) Aminabhavi, T. M.; Patil, V. B. Density, viscosity, refractive index, and speed of sound in binary mixtures of ethenylbenzene with *N*,*N*-dimethylacetamide, tetrahydrofuran, *N*,*N*-dimethylformamide, 1,4-dioxane, dimethyl sulfoxide, chloroform, bromoform, and 1-chloronaphthalene in the temperature interval (298.15−308.15) K. *J. Chem. Eng. Data* **1998**, *43*, 497−503.

(14) Masson, D. O. Solute molecular volumes in relation to solvation and ionization. *Philos. Mag.* **1929**, *8*, 218−235.

(15) Marcus, Y. *The Properties of Solvents*; John Wiley & Sons: London, 1998.

(16) Gucker, F. T. The compressibility of solutions. I. The apparent molal compressibility of strong electrolytes. *J. Am. Soc. Chem.* **1933**, *55* (7), 2709−2718.

(17) Rao, Ch. P.; Balaram, P.; Rao, N. R. ^{13}C nuclear magnetic resonance studies of the binding of alkali and alkaline earth metal salts to amides *J. Chem. Soc. Faraday Trans. 1* **1980**, *76*, 1008-1013

(18) Wurm, B.; Munsterer, M.; Richardi, J.; Buchner, R.; Barthel, J. Ion association and solvation of perchlorate salts in *N*,*N*-dimethylformamide and *N*,*N*-dimethylacetamide. A dielectric relaxation study. *J. Mol. Liq.* **2005**, *119*, 97−106.

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