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Partial Molar Volume of Some Monovalent Salts and Polar Molecules in Organic Solvents

Paul G. Giugia, Jae H. Byon, and Charles A. Eckert*

Department of Chemical Engineering, University of Illinois, Urbana, Illinois 61801

The partial molar volumes of a number of monovalent salts and polar species were measured in a series of organic solvents. The solvents included ethanol, methanol, *N*-methylformamide (NMF), propylene carbonate, sulfolane, acetonitrile, acetone, and 4-methyl-2-pentanone. The polar species were *n*-propyl bromide, *n*-propyl iodide, and *n*-propyl chloride. The monovalent salts that were examined included LiBr, LiI, $LiNO_3$, NaI, KI, RbI, CsBr, tetrabutylammonium iodide, tetrabutylammonium bromide, and tetrabutylammonium perchlorate. The major observation was that the solvent effect on the partial molar volumes was most pronounced for monovalent salts. The solvent effect on the partial molar volume of the neutral solute was very small. The largest solvent effects are seen for the small monovalent salts when comparing aprotic and protic solvents. The conclusion was that the nonionic solutes do not grossly change the structure of the solvent, but the ionic solutes change the structure of the solvent significantly.

Introduction

The partial molar volumes of a number of neutral and ionic species were measured in a series of aprotic and protic solvents. The expectation was that the nature of the solvent structure could be determined by using neutral and ionic solutes as probes. If the solvent effect of a particular solute is relatively small, the structure of that group of solvents is relatively unaffected by that solute. Such solutes are considered ineffective probes. If the solvent effect is large, the nature of the structure of that group of solvents can be ranked. This information is invaluable in developing a mental picture of the structure of organic liquids even though the method does not yield direct structural information.

These data were gathered in conjunction with a kinetic study which yields similar information about the nature of an ionic transition-state species (*1*).

The partial molar volume is the derivative of the volume with respect to the number of solute molecules (*2*).

$$\bar{v}_2 = (\partial V/\partial n_2)_{T,P,n_1} \tag{1}$$

where V = volume and, n_2 = number of solute molecules. The total volume (V) is simply related to the partial molar volumes.

$$V = \bar{v}_1 n_1 + \bar{v}_2 n_2 \tag{2}$$

However, the quantity that is experimentally accessible is the apparent molar volume (ϕ):

$$V = n_1 v_1 + n_2 \phi \tag{3}$$

where v_1 is the molar volume of the pure solvent. Applying eq 1 to eq 3 relates the partial molar volume to the apparent molar volume.

$$\bar{v}_2 = (\partial V/\partial n_2)_{T,P,n_1} = \phi + n_2(\partial \phi/\partial n_2)_{T,P,n_1} \tag{4}$$

There are a number of methods that can be used to measure the apparent molar volume. Most of them are involved with measuring densities (*3–5*). Density measurements are accurate but very tedious. A second approach to the problem is to measure the volume change on mixing. This technique is called dilatometry. Grieger et al. (*6*) developed a fast, accurate dilatometric technique using micrometer syringes. The two techniques that were developed and used in this effort are modifications of Grieger's original work. The first uses micrometer syringes as Grieger did. The second uses a mercury flow scheme to make injections.

The apparent molar volume of a solution is related to the volume change on mixing as follows. Before mixing the total volume of two different solutions is

$$V^a + V^b = n_1^a v_1 + n_2^a \phi^a + n_1^b v_1 + n_2^b \phi^b \tag{5}$$

And, of course, after mixing

$$V = n_1 v_1 + n_2 \phi \qquad n_1 = n_1^a + n_1^b \qquad n_2 = n_2^a + n_2^b \tag{6}$$

Defining the volume change on mixing (ΔV)

$$\Delta V = V - V^a - V^b = n_2 \phi - n_2^a \phi^2 - n_2^b \phi^b \tag{7}$$

Rearranging eq 7 yields the experimentally important relationship for the apparent molar volume.

$$\phi = \frac{\Delta V + n_2^a \phi^a + n_2^b \phi^b}{n_2^a + n_2^b} \tag{8}$$

Therefore, if the apparent molar volumes of the two starting solutions are known from previous measurements and the volume change on mixing is known, the apparent molar volume of the resulting solution can be determined.

The data of ϕ vs. concentration for nonelectrolytes are nearly linear (*6*, *7*). As a result eq 4 is simple to apply to these systems. The apparent molar volumes of electrolytes are very different from those of nonelectrolytes in that they are a strong function of concentration. An empirical method discovered by Masson (*8*) was used to correlate ϕ vs. concentration (C) for electrolytes.

$$\phi = \phi_0 + S_v C^{1/2} \tag{9}$$

This relationship has been applied with a great deal of success by Millero (*9*, *10*) and was found to apply to the systems explored in this study.

Electrolytes in acetone and 4-methyl-2-pentanone are partially associated. In this study only the partial molar volumes of the dissociated salts were of interest. Since the dissociation constants for the salts in question are available in the literature (*11*), the apparent molar volumes of electrolytes in these two solvents have been corrected for ionic association making the assumption that the apparent molar volume of the associated salt is a constant. In general this is a small correction since very dilute solutions were used in most situations.

To measure the partial molar volume of a solid solute, we injected a concentrated solution. The densities of such solutions were determined by standard pycnometric techniques. Details of the method were discussed previously (*6*).

Experimental Section

Materials. All of the preparations of materials were purification procedures. The recommendations of Perrin et al. (*12*)

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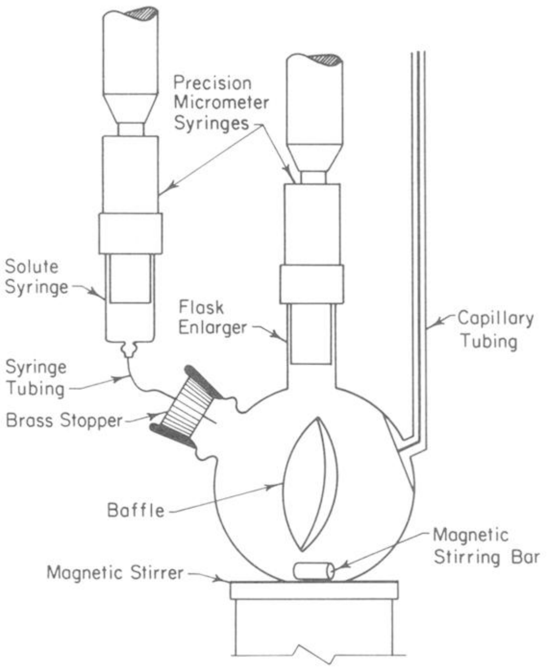

Figure 1. High volume injection dilatometer.

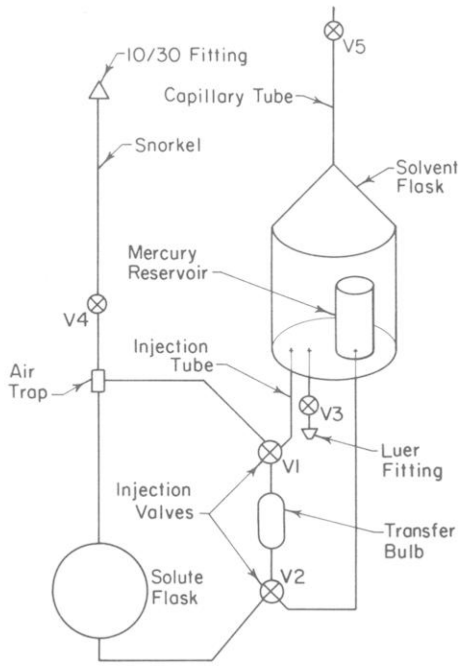

Figure 2. Schematic of high volume flow dilatometer.

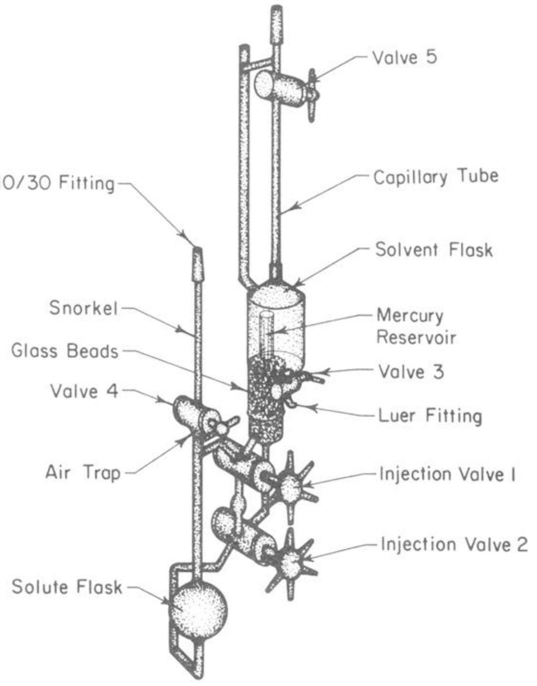

Figure 3. Details of high volume flow dilatometer.

were followed for solvent purification. When a distillation was required, it was carried out in a 1.5-m column packed with nichrome helices. This column is equivalent to 50 theoretical plates. The reflex ratio was greater than 4:1, and the first 15% and the last 20% of the batch distillate were discarded if the temperature of the condensate did not indicate other action. When a desiccant was required for direct contact to a solvent, Linde 4A molecular sieves were used. The sieves were prepared by drying them for more than 24 h under a moderate vacuum at 200 °C. The purity of the solvents was checked by gas chromatography and by measuring the solvent index of refraction. Samples with impurities greater than 0.1% by either method were rejected.

The electrolytes used in this study were prepared by vacuum drying under modest heat (i.e., <200 °C). It was assumed that all of the electrolytes had minor contaminants. As a result all of the electrolyte solutions were analyzed by titration. The titration process was standardized against KCl and NaCl solutions.

High Volume Injection Dilatometer. The equipment is depicted on Figure 1. The technique was developed to minimize the time and effort required for partial molar volume determination. It consists of a central flash and solute syringe. The central flask (~300 mL) is equipped with a precision micrometer syringe so that its volume can be adjusted accurately. The precision micrometer syringes were obtained from Gilmont Instrument Co. They could measure changes in volume to ±0.003 mL.

The dilatometer is operated as follows. Solutions with known composition and apparent molar volume are loaded in the central flask and in the solute syringe. Much care was taken to avoid including gas bubbles. Solvents were boiled, and electrolytes were placed under vacuum before each use. Once loaded the flask and solute syringe was placed in a temperature bath that was controlled to ±0.002 °C. Before an injection the level in the capillary tube was noted accurately (±0.05 mm). An injection was made by first enlarging the flask with the flask enlarger syringe. The fluid level in the capillary recedes. The flask is then filled to the mark on the capillary by injecting solute from the solute syringe. Care was taken to move the syringes in only one direction. The change in volume on mixing is the difference between the volume enlargement of the central flask and the volume injected. The apparent molar volume is then determined by application of eq 8.

This apparatus was used to measure the partial molar volumes of all of the nonionic solutes and the ionic solutes in the protic solvents. The error in partial molar volume is no greater than ±0.2 mL/mol for these systems.

High Volume Flow Dilatometer. This piece of equipment is represented schematically in Figure 2 and is shown with some physical details in Figure 3. This dilatometer was developed to optimize the accuracy of the measurement.

Measuring the partial molar volume of electrolytes in aprotic solvents requires much more precision than does making the same measurement on organic liquids because typical salts are solids and cannot be injected in their pure state. A solution of the salt in question must be used. Since electrolytes are not very soluble in aprotic organic liquids, a typical injection does not involve many ions and the resulting volume change is small.

Table I. Partial Molar Volumes (cm^3/mol) at Infinite Dilution at 25 °C

solvent	ε	solvent type	solute (molar vol, cm^3/mol)														
			i-PrCl (88.0)	*i*-PrBr (90.8)	*i*-PrI (94.8)	LiCl (20.4)	LiBr (25.1)	LiI (38.3)	$LiNO_3$ (28.9)	NaCl (27.0)	NaI (40.9)	KI (53.0)	RbI (59.8)	CsBr (53.4)	$(Bu)_4NBr$ (300)	$(Bu)_4NI$ (320)	$(Bu)_4NClO_4$ (330)
propylene carbonate	65	aprotic		92.2	100.4							86.7	88.8		310	323	
sulfolane[a]	43	aprotic		90.2	99.4							38.7	44.7		302	335	
acetonitrile	37	aprotic		92.4	100.0		−10	1.0			4.0						
acetone	21	aprotic	89.6	92.7	100.0		−37	−31	−35		−19						
4-methyl-2-pentanone	13	aprotic		93.9	100.8									−34	226	240	314
ethanol	24	protic	88.7	91.8	98.8	−13.0	−6.2	3.6	−2.4		15.9						
methanol	33	protic		92.5	99.8	−5.1	0.8	10.7		−3.3[b]	11.8[b]	21.9[b]					
N-methylformamide	182	protic		90.7	98.5	16.9	19.8	32.5			37.5	46.2					

[a] Data at 40 °C. [b] Reference *9*.

Table II. Partial Molar Volumes at Infinite Dilution at Temperatures Other than 25 °C

solvent	solute	$\bar{V}_2$, cm^3/mol	temp, °C
methanol	LiBr	4.0	15
methanol	LiBr	−2.5	35
methanol	LiBr	−9.1	50
methanol	LiI	7.7	35
methanol	LiI	1.0	50
ethanol	LiBr	−19.0	50
ethanol	LiI	−9.0	50
NMF	LiBr	21.7	50
NMF	LiI	32.8	50
sulfolane	KI	38.7	40
sulfolane	RbI	44.7	40
sulfolane	CsI	54.0	40
sulfolane	Bu_4NBr	302	40
sulfolane	Bu_4NI	335	40

The apparatus developed for this experiment is capable of measuring volume changes as small as 0.0002 mL while making consecutive injections. This is 1 order of magnitude better than the high volume injection dilatometer. This level of accuracy is absolutely required for making the reported measurements.

This dilatometer relies on a mercury flow system to make injections. The solvent section of this dilatometer consists of a 700-mL flask, a mercury reservoir, and a precision-bore capillary tube. The mercury is used for injections, and the capillary tube is used to determine the volume change on mixing. The solute section of the dilatometer consists of a 50-mL solute flask, a 2-mL transfer bulb, and the injection valves. The transfer bulb contains enough solute for a typical injection. An injection is made by turning the valves so that the mercury in the solvent section pushes the solute from the transfer bulb into the solvent flask. The volume change on mixing is seen by a change in position of the meniscus in the capillary tube. The position of the meniscus is measured with a cathetometer. The transfer bulb can be refilled by turning the injection valves to a position where the mercury falls out of the transfer bulk into the solute flask. In this operation the mercury in the transfer bulb is replaced by solute, and the injection process can be repeated.

This method has three major advantages over the injection dilatometer. First, the volume change on mixing is read directly off the capillary. Second, the meniscus moves only as far as is required by the volume change on mixing. Third, the solute is always separated from the solvent by a slug of mercury.

The accuracy of this dilatometer depends on the reproducibility of the injection valves and on the degree of temperature control. The temperature bath used with this apparatus controlled temperature fluctuation to within 0.001 °C. The performance of the valves was tested by injecting water to water. The volume change was always less than 0.0001 mL and frequently less than 0.000 05 mL. The partial molar volumes measured in aprotic solvents with this apparatus are accurate to better than ±2%.

Results and Discussion

Table I is a compilation of infinite dilution partial molar volumes at 25 °C. Figure 4 is a plot of a series of typical data sets for nonionic solutes showing the apparent molar volume vs. concentration. In Figure 5, typical results are shown for ionic solutes. A few measurements were made at temperature other than 25 °C. The results of these measurements are listed in Table II. All of the apparent molar volume data as a function of concentration can be found in Table III. The apparent molar volumes for nonionic solutes have been excluded from this table because the observed concentration dependence was small.

Table III. Apparent Molar Volume Data of Electrolytes

m^a	ϕ	m^a	ϕ
LiCl in Methanol at 25 °C			
0.006 90	−4.0	0.043 10	−2.5
0.013 78	−3.7	0.054 3	−2.2
0.020 66	−3.4	2.882	6.7
0.031 89	−2.9		
LiBr in Methanol at 15 °C			
0.004 442	4.5	0.102 1	6.7
0.008 852	4.8	0.136 0	7.0
0.013 24	4.9	0.169 8	7.2
0.017 65	5.2	0.203 6	7.4
0.034 31	5.5	4.495	15.2
0.068 35	6.1		
LiBr in Methanol at 25 °C			
0.004 23	1.5	0.065 44	3.4
0.008 46	1.8	0.098 01	4.0
0.012 67	2.1	0.130 5	4.4
0.016 89	2.3	0.163 0	4.8
0.032 83	2.8	4.275	13.8
LiBr in Methanol at 35 °C			
0.004 50	−1.7	0.069 31	0.7
0.008 99	−1.4	0.103 7	1.5
0.013 47	−1.2	0.138 0	2.0
0.017 95	−0.9	0.172 4	2.4
0.022 43	−0.7	4.495	12.3
0.034 84	−0.2		
LiBr in Methanol at 50 °C			
0.002 37	−8.4	0.039 00	−4.9
0.004 73	−7.6	0.050 58	−4.3
0.009 00	−7.2	0.062 23	−3.9
0.013 27	−6.8	0.073 83	−3.5
0.020 29	−6.2	2.779	+9.2
0.027 28	−5.6		
LiI in Methanol at 25 °C			
0.002 06	11.2	0.022 61	12.4
0.004 12	11.4	0.028 7	12.6
0.007 84	11.8	0.034 8	12.8
0.011 54	12.1	0.044 8	13.1
0.015 23	12.2	0.054 9	13.4
0.018 91	12.3	2.508 9	22.4
LiI in Methanol at 35 °C			
0.003 51	8.6	0.035 08	10.2
0.007 62	8.9	0.052 59	10.8
0.010 53	9.1	1.971 7	20.1
0.017 56	9.4		
LiI in Methanol at 50 °C			
0.002 08	2.0	0.027 51	4.6
0.004 19	2.4	0.033 67	5.0
0.006 28	2.8	0.039 83	5.3
0.010 07	3.0	0.050 04	5.7
0.013 84	3.4	0.060 27	6.0
0.017 60	3.8	0.070 48	6.3
0.021 36	4.1	2.508 9	18.3
LiCl in Ethanol at 25 °C			
0.001 96	−11.3	0.016 52	−7.9
0.003 92	−10.5	0.022 03	−7.5
0.007 48	−9.3	0.031 03	−6.6
0.011 00	−8.6	2.299 8	6.7
LiBr in Ethanol at 25 °C			
0.002 85	−4.7	0.065 52	0.4
0.005 68	−4.2	0.087 3	1.1
0.008 51	−3.8	0.109	1.7
0.011 36	−3.4	0.130 6	2.2
0.021 90	−2.1	2.828 7	12.7
0.043 77	−0.7		
LiBr in Ethanol at 50 °C			
0.001 67	−16.8	0.013 54	−12.4
0.003 34	−15.5	0.017 10	−11.8
0.005 01	−14.8	0.020 65	−11.3
0.006 66	−14.3	0.025 54	−10.7
0.008 33	−13.7	0.030 44	−10.2
0.009 99	−13.3	1.946 3	7.9
LiI in Ethanol at 25 °C			
0.002 74	4.7	0.041 86	8.5
0.005 48	5.5	0.062 63	9.3
0.008 21	5.8	0.083 40	9.9
0.010 94	6.2	0.104 22	10.3
0.013 67	6.5	2.774	22.1
0.020 91	7.3		
LiI in Ethanol at 50 °C			
0.001 597	−6.6	0.020 00	−1.4
0.003 189	−5.2	0.024 68	−0.9
0.004 78	−4.7	0.029 35	−0.3
0.006 37	−4.1	0.034 01	0.2
0.009 789	−2.9	0.038 67	0.6
0.013 19	−2.3	1.889 1	17.3
0.016 60	−1.8		
NaI in Ethanol at 25 °C			
0.003 23	17.0	0.014 95	18.3
0.006 46	17.4	0.020 22	18.6
0.009 68	18.0	1.386 8	29.0
$LiNO_3$ in Ethanol at 25 °C			
0.002 01	0.1	0.016 89	4.4
0.004 00	1.1	0.022 52	5.1
0.007 63	2.5	0.028 15	5.6
0.011 24	3.4	2.408 5	20.8
LiCl in NMF at 25 °C			
0.024 0	17.0	0.072 0	17.3
0.048 0	17.2	1.827 7	18.5
LiBr in NMF at 25 °C			
0.015 0	20.2	0.045 0	20.5
0.030 0	20.4	1.126 3	23.7
LiBr in NMF at 50 °C			
0.010 6	22.0	0.031 8	22.0
0.021 2	22.0	1.370 0	22.7
LiI in NMF at 25 °C			
0.010 78	32.6	0.032 34	32.9
0.021 56	32.8	0.813 9	34.3
LiI in NMF at 50 °C			
0.009 82	32.8	0.049 1	32.9
0.019 62	32.8	1.276 9	33.8
0.029 4	32.8		
NaI in NMF at 25 °C			
0.010 5	37.5	0.031 5	37.5
0.021 0	37.5	0.793 3	37.5
KI in NMF at 25 °C			
0.009 5	46.2	0.028 5	46.2
0.019 0	46.2	0.722 7	46.2
KI in Sulfolane at 40 °C			
0.000 290	38.5	0.000 713	38.7
0.000 433	38.9	0.000 851	38.7
0.000 574	38.8	0.000 987	38.6
RbI in Sulfolane at 40 °C			
0.000 046	43.9	0.000 225	41.7
0.000 92	42.7	0.000 269	41.7
0.000 137	42.1	0.000 312	41.6
0.000 181	41.9	0.000 355	41.5
CsI in Sulfolane at 40 °C			
0.000 077	53.4	0.000 379	51.1
0.000 154	52.0	0.000 452	51.0
0.000 230	51.5	0.000 525	50.9
0.000 305	51.2		
Bu_4NBr in Sulfolane at 40 °C			
0.000 117	303.1	0.000 574	301.3
0.000 233	302.3	0.000 685	301.3
0.000 348	301.7	0.000 795	301.2
0.000 461	301.4	0.000 904	301.2
Bu_4NI in Sulfolane at 40 °C			
0.000 089	335.2	0.000 174	326.3
0.000 115	333.0	0.000 201	323.7
0.000 146	329.9		

Table III (*Continued*)

KI in Propylene Carbonate at 25 °C			
0.000 049	89.2	0.000 339	87.9
0.000 098	88.3	0.000 387	88.0
0.000 147	87.9	0.000 434	87.9
0.000 196	88.0	0.000 527	87.9
0.000 244	88.1	0.000 619	87.8
0.000 292	88.1		
RbI in Propylene Carbonate at 25 °C			
0.000 045	85.5	0.000 313	79.8
0.000 091	83.5	0.000 357	79.6
0.000 136	81.9	0.000 400	79.4
0.000 181	81.0	0.000 444	79.4
0.000 225	80.5	0.000 487	79.4
0.000 269	80.0		

Bu_4NBr in Propylene Carbonate at 25 °C			
0.000 068	310.7	0.000 470	311.1
0.000 136	310.5	0.000 536	311.1
0.000 204	310.9	0.000 601	311.1
0.000 271	311.0	0.000 666	311.1
0.000 337	311.0	0.000 731	311.2
0.000 404	311.0		
Bu_4NI in Propylene Carbonate at 25 °C			
0.000 028	324.0	0.000 223	321.0
0.000 057	322.1	0.000 250	321.0
0.000 085	321.5	0.000 277	320.9
0.000 113	321.0	0.000 304	320.9
0.000 141	321.0	0.000 331	321.0
0.000 168	321.0	0.000 357	321.0
0.000 196	320.9		

m^a	c^c	ϕ^d	ϕ^d
LiI in Acetone at 25 °C			
0.003 161	0.002 481	0.861	−23.8
0.006 298	0.004 944	0.803	−20.2
0.009 431	0.007 404	0.766	−18.4
0.014 54	0.011 41	0.726	−16.4
0.019 64	0.015 42	0.698	−15.1
0.028 14	0.022 09	0.664	−13.7
0.044 40	0.034 88	0.623	−11.9
0.060 73	0.047 67	0.596	−11.0
1.302 4	1.022 4		0.2
$LiNO_3$ in Acetone at 25 °C			
0.002 38	0.001 868	0.150	1.3
0.004 75	0.003 729	0.112	2.3
0.008 70	0.006 83	0.0868	3.7
0.012 64	0.009 92	0.0740	4.5
0.016 59	0.013 02	0.0660	4.8
0.029 18	0.022 91	(0.0520)	5.8
0.612 8	0.481 0		13.7
LiBr in Acetone at 25 °C			
0.002 829	0.002 221	0.402	−15.9
0.003 434	0.002 696	0.378	−15.5
0.005 645	0.004 431	0.321	−13.6
0.006 857	0.005 383	0.301	−13.6
0.008 448	0.006 632	0.281	−12.0
0.011 25	0.008 831	0.256	−11.1
0.012 55	0.009 851	0.247	−11.4
0.014 08	0.011 05	0.238	−10.6
0.018 24	0.014 31	0.218	−10.2
0.023 92	0.018 78	0.200	−9.5
0.028 11	0.022 07	0.190	−9.2
0.042 08	0.033 03	0.168	−8.2
0.042 13	0.033 07	0.168	−8.4
0.056 03	0.043 99	0.154	−7.4
0.060 26	0.047 3	0.151	−7.9
0.845 3	0.663 6		−1.1
1.117 9	0.877 6		−0.5
NaI in Acetonitrile at 25 °C			
0.002 48	0.001 925	0.963	4.3
0.004 95	0.003 842	0.937	4.7
0.007 43	0.005 767	0.916	4.8
0.011 48	0.008 911	0.888	4.9

m^a	c^c	ϕ^d	ϕ^d
0.015 22	0.011 81	0.867	5.2
0.022 27	0.017 29	0.835	5.4
0.035 22	0.027 34	0.792	5.8
0.048 16	0.037 38	0.760	6.1
1.048			17.0
NaI in Acetone at 25 °C			
0.002 09	0.001 64	0.902	−15.1
0.002 872	0.002 254	0.881	−14.0
0.004 17	0.003 27	0.854	−13.4
0.005 687	0.004 465	0.829	−11.6
0.006 25	0.004 91	0.821	−11.7
0.008 499	0.006 672	0.795	−10.4
0.010 42	0.008 18	0.777	−10.4
0.013 09	0.010 28	0.758	−9.1
0.017 68	0.013 88	0.729	−8.0
0.020 79	0.016 32	0.714	−8.1
0.025 31	0.019 87	0.696	−6.6
0.031 14	0.024 44	0.678	−6.5
0.032 93	0.025 85	0.672	−5.6
1.177 1	0.924 0		13.1
1.356 8	1.065 1		13.9
LiI in Acetonitrile at 25 °C			
0.003 95	0.003 066	0.954	1.7
0.007 90	0.006 13	0.924	2.4
0.014 45	0.011 22	0.888	2.8
0.021 0	0.016 3	0.860	3.2
0.0276	0.021 42	0.837	3.6
0.034 1	0.026 47	0.818	4.0
0.040 6	0.031 5	0.801	4.2
0.046 8	0.036 3	0.788	4.4
1.016 3			11.9
LiBr in Acetonitrile at 25 °C			
0.004 96	0.003 85	0.754	−7.7
0.009 90	0.007 68	0.661	−7.0
0.014 85	0.011 53	0.606	−6.5
0.019 80	0.015 37	0.566	−6.1
0.024 7	0.019 17	0.536	−5.8
0.029 6	0.022 98	0.512	−5.6
0.034 5	0.026 78	0.493	−5.4
0.039 4	0.030 58	0.476	−5.2
0.044 3	0.034 39	0.462	−5.0
0.758 2			2.7

[a] m = molarity, mol/kg. [b] ϕ = apparent molar volume, cm^3/mol. [c] c = molarity, mol/L. [d] θ = degree of ionization.

The solvent 4-methyl-2-pentanone is a special case. Salts are only sparingly soluble in this solvent. Therefore, the concentration dependence of the apparent molar volume was not accessible. The reported volumes are calculated from density measurements only. The listed volumes are apparent molar volumes at 0.001 M.

The data in Table I demonstrate that the solvent effect on the partial molar volume of a nonionic solute is small. In contrast, the solvent effect on the partial molar volume of an ionic solute is substantial. Furthermore, the partial molar volumes for the nonionic solutes are very near their molar volumes. This is true for only a couple of solvents with ionic solutes.

It seems reasonable that, if a solute does not disrupt the structure (i.e., packing geometry) of a solvent, its partial molar volume will be very similar to its intrinsic molar volume. Conversely, if a solute does change the solvent structure, it is likely that its partial molar volume will be different from its intrinsic molar volume. Of course, exceptions to both rules do exist and can easily be rationalized; however, the gross trends are irre-

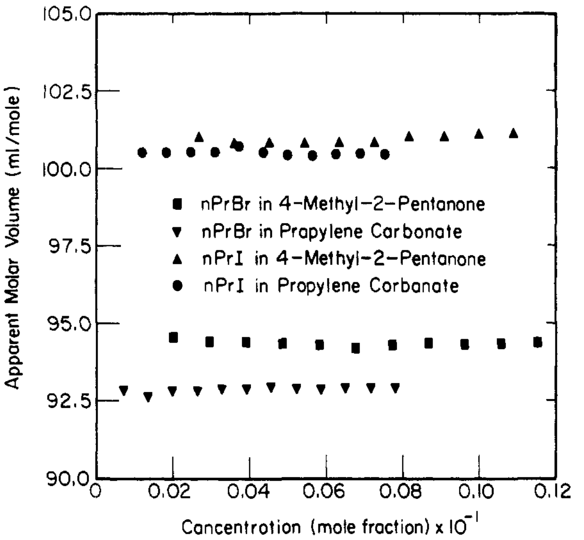

Figure 4. Apparent molar volume of nonionic solutes as a function of concentration at 25 °C.

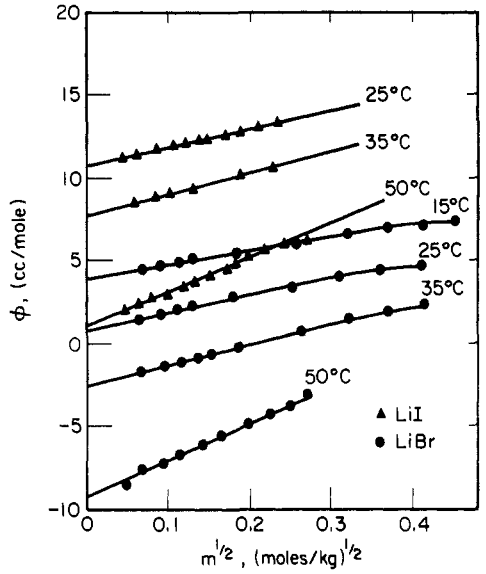

Figure 5. Apparent molar volume of some ionic solutes as a function of concentration.

futable. The nonionic solutes used in the study do not grossly change the structure of the solvents and the ionic solute can.

Substantial contractions (i.e., volumes smaller than ideal) are seen for ionic solutes in the low dielectric constant solvents. Generally contractions on mixing in dilute solutions are associated with an increase in solvent structure due to interactions with the solute (*13*, *14*). For the low dielectric constant solvents and ionic solutes, the solute-solvent interaction is much more energetic and much more long-ranged than the solvent-solvent interactions. Ionic solutes cause striking contractions of these solvents. For many salts negative partial molar volumes are observed; that is, the volume after mixing is smaller than the volume of the solvent alone before mixing. The solvent structure is grossly altered with the addition of ions.

The structure of the more polar solvents are much less affected by the addition of ions. This does not necessarily mean that the solute-solvent interactions are less energetic than in less polar solvents. In fact, one would expect that the energetics of these interactions would be larger for the more polar solvents (*15*). The solute-solvent and solvent-solvent interactions must be similar for the more polar solvents. Therefore, the structure of the more polar solvents is much more highly developed than it is for the less polar solvents.

Partial molar volumes in dilute solutions offer a unique opportunity to probe the solvent structure with macroscopic observations. The volume of a solution is related to the solvent packing geometry and the solvent polarity. This type of information is crucial in forming a mental picture of the structure of ionic solutions in nonaqueous media. The value of this information is magnified when one realizes that the solvent effect on ionic partial molar volumes is paralleled by a solvent effect on ionic activities. The ability to adjust ionic activities by choosing a solvent has ramifications in the rates and equilibrium properties of many industrial processes and reactions. Therefore, understanding and controlling these factors is very desirable.

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Density of 2-Butoxyethanol from 20 to 60 °C

Ian A. McLure,* Francisco Guzman-Figueroa, and Ian L. Pegg
Department of Chemistry, The University of Sheffield, Sheffield, S3 7HF, U.K.

The density of purified samples of 2-butoxyethanol has been measured from 20 to 60 °C by densimetry and pycnometry. The results are well described by $d/(\mathrm{g\ cm^{-3}}) = 0.91694 - (8.149 \times 10^{-4})(t/°\mathrm{C}) - (5.1 \times 10^{-7})(t/°\mathrm{C})^2$ with a standard deviation of 3×10^{-5} g cm^{-3}.

During an investigation of the physical properties of its aqueous mixtures (*1*) we have measured the density of 2-butoxyethanol at 11 temperatures from 20 to 60 °C. The starting material was supplied by Cambrian Chemicals Ltd. with a quoted purity of 99 mol %. It was further purified by four fractionations in a stream of nitrogen in a 70-cm glass column

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