J. Chem. Eng. Data 1994, 39, 453-456

Densities and Molar Volumes of Na_2SO_4 and $MgSO_4$ in Ethanol + Water Mixtures at 15, 25, and 35 °C

Manuela M. Sánchez, Bernardo Domínguez, Raquel R. Raposo, and Andrés Vivo*

Department of Physical Chemistry, University of La Laguna, Tenerife, Spain

---

The densities of Na_2SO_4 and $MgSO_4$ have been determined at 15, 25, and 35 °C in EtOH + H_2O. The results have been analyzed using the Redlich equation for the density as a function of the concentration. The apparent molar volumes at infinite dilution have been calculated from the coefficients of the Redlich equation and from the theoretical slopes S_v of these mixtures at 25 °C, and results compared and interpreted in terms of the different interactions.

Introduction

There are few measurements of molar volumes of electrolytes in water + organic solvents where the electrolytes show association. Sodium and magnesium sulfates are associated in these mixtures, and the changes of volume due to the formation of ion pairs would be expected to be positive. From a knowledge of the association constants (*1*) we can determine if the deviations from the limit law behavior are principally due to association.

Experimental Section

Densities of the mixed solvents, water, and the electrolyte solutions were determined using an Anton Paar Model DMA-60 oscillating-tube densimeter and a measuring cell (DMA-602). The accuracy was estimated as $\pm 5 \times 10^{-6}$ g·cm^{-3}. The density measurements were made at 15.00, 25.00, and 35.00 °C in a water ultrathermostat which was maintained within ±0.005 °C and measured by means of a Beckmann differential thermometer calibrated against a calorimeter thermometer 1 °C scale in 1/200 divisions, with the tested point at 25 ± 0.001 °C (NBS). Temperature was controlled in the measuring cell with a DT-100 (Anton Paar) digital precision thermometer. Merck Suprapur Na_2SO_4 was recrystallized in conductivity water and dried at 150 °C under vacuum for two days. Merck $MgSO_4\cdot 7H_2O$, analytical reagent grade, was melted at 700 °C and then dried for several days at 200 °C. Merck (pa quality) absolute ethanol was analyzed for its water content (less than 0.2% by mass), the necessary corrections to the solvent composition of the mixtures being carried out. Masses of the salts were accurate to $\pm 5 \times 10^{-6}$ g and those of the solvents to ±0.01 g, and all sample weights were corrected to vacuum. The conductivity water used was of Milli-Q4 quality and showed an average specific conductance below 5×10^{-7} S·cm^{-1} at 25 °C. Fourteen different concentrations of each salt were used, within the dilute range $0.001 < c \leq 0.2$ mol·dm^{-3} of the aqueous solutions and four mixtures in the water-rich region: 10, 20, 25, and 30 mass % EtOH.

Results and Discussion

In the solvent mixtures the density d of the electrolyte solution of concentration c was represented by the Redlich equation

$$d/(\mathrm{g\cdot cm^{-3}}) = d^\circ + A[c/(\mathrm{mol\cdot dm^{-3}})] + B[c/(\mathrm{mol\cdot dm^{-3}})]^{3/2} + D[c/(\mathrm{mol\cdot dm^{-3}})]^2 \quad (1)$$

which is based on the theoretical concentration dependence on the ϕ_v and is preferred to Root's equation (*2*).

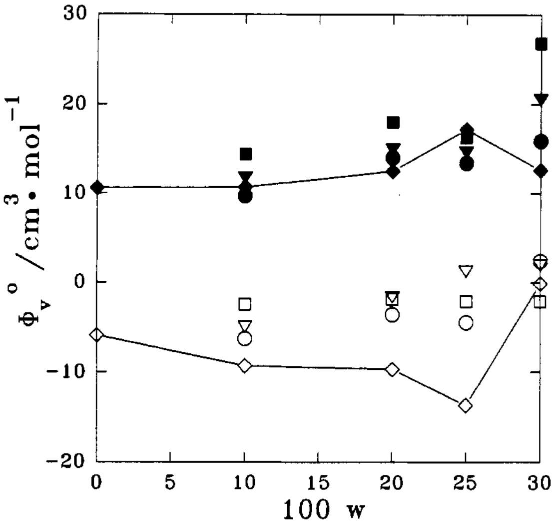

Figure 1. ϕ_v° against w in w EtOH + $(1 - w)$ H_2O: filled symbols, Na_2SO_4; open symbols, $MgSO_4$; ◇, 25 °C (Table 5); ○, 15 °C; □, 25 °C; ▽, 35 °C (ϕ_v°'s evaluated from eq 3).

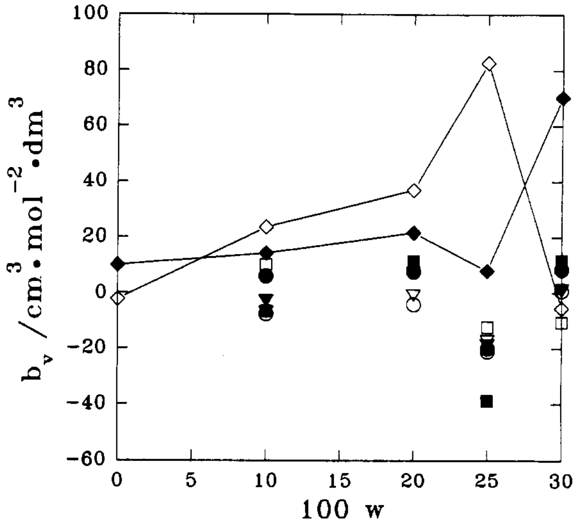

Figure 2. b_v against w in w EtOH + $(1 - w)$ H_2O: filled symbols, Na_2SO_4; open symbols, $MgSO_4$; ◇, 25 °C (Table 5); ○, 15 °C; □, 25 °C; ▽, 35 °C (b_v°'s evaluated from eq 3).

In general, the apparent molar volumes ϕ_v are extrapolated to zero concentration to yield partial molar volumes at infinite

---

* To whom correspondence should be addressed.

0021-9568/94/1739-0453$04.50/0

Table 1. Relative Densities *d* of Na_2SO_4 Solutions in *w* EtOH + (1 − *w*) H_2O at 15, 25, and 35 °C, Where *w* is Mass Fraction

$t = 15$ °C		$t = 25$ °C		$t = 35$ °C		$t = 15$ °C		$t = 25$ °C		$t = 35$ °C	
$10^3c^a/$ (mol·dm^{-3})	$d^b/$ (g·cm^{-3})	$10^3c^a/$ (mol·dm^{-3})	$d^b/$ (g·cm^{-3})	$10^3c^a/$ (mol·dm^{-3})	$d^b/$ (g·cm^{-3})	$10^3c^a/$ (mol·dm^{-3})	$d^b/$ (g·cm^{-3})	$10^3c^a/$ (mol·dm^{-3})	$d^b/$ (g·cm^{-3})	$10^3c^a/$ (mol·dm^{-3})	$d^b/$ (g·cm^{-3})
$w = 0$											
0	0.999 101	0	0.997 047	0	0.994 035	79.884	1.009 472	71.541	1.007 167	79.560	1.004 036
1.1679	0.999 259	0.99644	0.997 178	1.2145	0.994 202	99.681	1.012 010	98.364	1.009 528	99.141	1.006 461
5.3839	0.999 818	4.9779	0.997 693	4.0681	0.994 587	122.02	1.014 837	121.25	1.012 373	121.28	1.009 178
10.468	1.000 489	9.9597	0.998 339	7.7544	0.995 071	139.46	1.017 057	138.71	1.014 546	138.86	1.011 331
19.956	1.001 733	19.939	0.999 621	12.689	0.995 692	159.71	1.019 594	159.48	1.017 127	158.52	1.013 749
39.707	1.004 308	39.371	1.002 142	40.231	0.999 129	179.36	1.022 054	178.81	1.019 505	178.51	1.016 179
49.773	1.005 606	49.759	1.003 414	53.229	1.000 795	201.39	1.204 809	201.79	1.022 320	200.48	1.018 847
62.327	1.007 225	61.997	1.004 956	62.172	1.001 871						
$w = 0.10$											
0	0.983 061	0	0.980 437	0	0.976 887	59.182	0.990 723	119.64	0.995 470	117.98	0.991 568
1.4746	0.983 250	1.4464	0.980 619	1.2714	0.977 126	78.280	0.993 153	136.67	0.997 556	136.34	0.993 797
4.9049	0.983 707	4.8956	0.981 065	3.1511	0.977 342	97.497	0.995 584	156.47	1.000 005	155.63	0.996 153
9.8113	0.984 350	10.026	0.981 722	6.3443	0.977 765	120.59	0.998 497	176.20	1.002 425	196.99	1.001 150
19.664	0.985 646	19.577	0.982 945	10.596	0.978 300	137.94	1.000 642	197.60	1005 008		
38.612	0.988 080	49.125	0.986 695	44.767	0.982 579	157.67	1.003 107				
49.256	0.989 439	97.677	0.992 742	77.810	0.986 620						
$w = 0.20$											
0	0.970 728	0	0.966 418	0	0.961 363	77.810	0.980 460	103.41	0.979 135	76.210	0.970 765
1.1437	0.970 854	1.4476	0.966 582	4.3334	0.961 992	118.88	0.985 455	117.70	0.980 829	95.998	0.973 133
4.8491	0.971 333	5.2944	0.967 066	7.9927	0.962 419	135.89	0.987 513	134.11	0.982 797	117.48	0.975 702
9.6536	0.971 970	11.566	0.967 843	11.033	0.962 803	154.93	0.989 832	153.97	0.985 154	34.24	0.977 650
19.392	0.973 171	19.432	0.968 832	23.969	0.964 380	137.79	0.992 070	174.03	0.987 530	153.38	0.979 929
38.870	0.975 619	38.590	0.971 220	38.481	0.966 176			194.23	0.989 910	173.65	0.982 309
48.499	0.976 798	48.115	0.972 381	46.676	0.967 165					193.13	0.984 598
60.634	0.978 331	60.207	0.973 878	60.092	0.968 797						
$w = 0.25$											
0	0.964 269	0	0.958 983	0	0.953 058	65.443	0.972 055	76.341	0.968 204	94.983	0.964 555
1.4431	0.964 461	1.1489	0.959 099	1.5144	0.953 548	72.202	0.972 827	96.038	0.970 524	116.80	0.967 083
4.8312	0.964 888	4.7788	0.959 560	2.9056	0.953 702	98.102	0.975 752	116.97	0.972 983	132.84	0.968 960
9.5256	0.965 461	11.467	0.960 384	7.4623	0.954 295	125.14	0.978 757	133.105	0.974 840	151.83	0.971 124
19.456	0.966 683	19.146	0.961 335	9.4993	0.954 538	150.81	0.981 571	152.76	0.977 131	170.82	0.973 319
40.556	0.970 233	38.222	0.963 650	48.835	0.959 348	159.84	0.982 554	172.27	0.979 452	191.91	0.975 686
48.265	0.970 073	47.832	0.964 802	59.321	0.960 334	198.97	0.986 771	192.25	0.981 697		
56.813	0.971 063	59.709	0.966 222	75.832	0.962 296						
$w = 0.30$											
0	0.956 895	0	0.950 679	0	0.944 059	75.987	0.966 475	76.666	0.959 704	75.209	0.952 945
1.1763	0.957 026	1.2134	0.950 831	2.7887	0.944 591	100.58	0.969 576	94.750	0.961 795	95.053	0.955 249
4.7798	0.957 470	4.9623	0.951 277	6.5229	0.945 042	109.58	0.970 711	115.91	0.964 200	114.40	0.957 448
10.886	0.958 168	11.686	0.952 087	10.200	0.945 541	120.18	0.972 049	131.95	0.966 039	131.59	0.959 368
18.980	0.959 174	18.961	0.952 950	21.229	0.946 607	128.55	0.973 106	151.46	0.968 223	150.62	0.961 524
39.812	0.961 917	38.003	0.955 200	38.616	0.948 684	180.37	0.979 661	169.51	0.970 245	169.41	0.963 665
47.795	0.962 558	47.485	0.956 327	48.402	0.950 001	199.21	0.982 048	190.89	0.972 645	190.77	0.965 987
63.511	0.964 903	59.520	0.957 733	59.192	0.951 109						

[a] Accuracy in *c*, ±5 × 10^{-7} mol·dm^{-3}. [b] Accuracy in *d*, ±5 × 10^{-6} g·cm^{-3}.

Table 2. Relative Densities *d* of $MgSO_4$ Solutions in *w* EtOH + (1 − *w*) H_2O at 15, 25, and 35 °C, Where *w* is Mass Fraction

$t = 15$ °C		$t = 25$ °C		$t = 35$ °C		$t = 15$ °C		$t = 25$ °C		$t = 35$ °C	
$10^3c^a/$ (mol·dm^{-3})	$d^b/$ (g·cm^{-3})	$10^3c^a/$ (mol·dm^{-3})	$d^b/$ (g·cm^{-3})	$10^3c^a/$ (mol·dm^{-3})	$d^b/$ (g·cm^{-3})	$10^3c^a/$ (mol·dm^{-3})	$d^b/$ (g·cm^{-3})	$10^3c^a/$ (mol·dm^{-3})	$d^b/$ (g·cm^{-3})	$10^3c^a/$ (mol·dm^{-3})	$d^b/$ (g·cm^{-3})
$w = 0$											
1.3995	0.999 278	1.4389	0.997 228	0.99202	0.994 159	79.688	1.008 934	79.323	1.006 724	79.323	1.003 673
4.9744	0.999 732	4.9453	0.997 667	2.9625	0.994 405	99.901	1.011 373	99.120	1.009 092	98.763	1.005 992
9.9568	1.000 355	9.9250	0.998 284	6.9260	0.994 895	122.25	1.014 066	121.42	1.011 766	121.07	1.008 639
19.784	1.001 580	19.748	0.999 502	9.8916	0.995 257	139.82	1.016 188	138.81	1.013 827	138.44	1.010 699
39.915	1.004 074	39.667	1.001 928	39.953	0.998 936	159.89	1.018 575	158.67	1.016 192	158.98	1.013 104
49.612	1.005 270	49.150	1.003 071	49.300	1.000 059	179.60	1.020 917	179.18	1.018 602	178.28	1.015 380
62.299	1.006 811	61.973	1.004 632	61.899	1.001 588	202.27	1.023 603	201.74	1.021 276	199.55	1.017 853
$w = 0.10$											
1.2896	0.983 218	1.1485	0.980 585	0.97348	0.977 002	77.960	0.992 574	77.994	0.989 884	118.08	0.991 026
4.7999	0.983 665	4.8870	0.981 036	4.8506	0.977 485	97.756	0.994 964	97.596	0.992 222	135.83	0.993 120
9.7301	0.984 278	9.7368	0.981 639	9.7636	0.978 088	109.56	0.996 377	119.70	0.994 838	156.29	0.995 504
19.532	0.985 495	19.489	0.982 837	19.399	0.979 243	137.02	0.999 650	136.65	0.996 821	175.41	0.997 721
39.070	0.987 873	39.178	0.985 214	48.491	0.982 761	156.63	1.001 966	156.03	0.999 133	197.65	1.000 302
48.763	0.989 080	48.455	0.986 356	77.529	0.986 232	177.00	1.004 383	176.36	1.001 515		
61.385	0.990 587	61.129	0.987 859	97.033	0.988 558	196.96	1.006 720	198.01	1.004 038		
$w = 0.20$											
1.3455	0.970 892	1.3587	0.966 577	1.2462	0.961 533	76.986	0.979 926	96.273	0.977 803	133.58	0.977 072
4.7843	0.971 319	4.8083	0.967 006	5.0729	0.961 968	96.499	0.982 180	117.97	0.980 317	153.03	0.979 275
9.6129	0.971 897	10.523	0.967 685	9.5691	0.962 514	118.07	0.984 750	134.87	0.982 270	171.86	0.981 403

Table 2. (Continued)

t = 15 °C		t = 25 °C		t = 35 °C		t = 15 °C		t = 25 °C		t = 35 °C	
10^3c^a/(mol·dm^{-3})	d^b/(g·cm^{-3})	10^3c^a/(mol·dm^{-3})	d^b/(g·cm^{-3})	10^3c^a/(mol·dm^{-3})	d^b/(g·cm^{-3})	10^3c^a/(mol·dm^{-3})	d^b/(g·cm^{-3})	10^3c^a/(mol·dm^{-3})	d^b/(g·cm^{-3})	10^3c^a/(mol·dm^{-3})	d^b/(g·cm^{-3})
					w = 0.20						
20.258	0.973 202	21.498	0.969 003	19.053	0.963 664	135.32	0.986 724	154.12	0.984 506	193.54	0.983 902
38.789	0.975 382	48.016	0.972 148	48.382	0.967 146	154.78	0.988 958	174.64	0.986 857		
48.219	0.976 575	60.227	0.973 575	95.539	0.972 694	194.79	0.993 550	197.02	0.989 410		
60.623	0.977 987	76.936	0.975 548	117.02	0.975 176						
					w = 0.25						
1.1296	0.964 417	1.1015	0.959 115	1.4227	0.953 223	117.25	0.977 919	76.546	0.967 919	75.790	0.961 981
4.6560	0.964 837	4.7223	0.959 562	4.7265	0.953 635	134.26	0.979 834	95.804	0.970 117	94.718	0.964 152
9.4886	0.965 426	9.5630	0.960 101	9.4866	0.954 204	153.72	0.982 038	116.73	0.972 506	116.02	0.966 570
19.202	0.966 579	20.460	0.961 381	18.893	0.955 339	172.39	0.984 162	133.70	0.974 430	132.98	0.968 532
48.044	0.969 983	38.273	0.963 481	37.771	0.957 570	193.83	0.986 539	153.77	0.976 658	151.38	0.970 583
76.740	0.973 315	47.534	0.964 565	47.339	0.958 642			172.21	0.978 779	170.89	0.972 768
95.990	0.975 493	59.892	0.965 999	59.220	0.960 073			194.84	0.981 270	190.84	0.975 001
					w = 0.30						
1.0864	0.957 022	1.2605	0.950 823	1.2598	0.944 220	76.043	0.965 587	94.685	0.961 492	93.994	0.954 825
4.6498	0.957 454	4.7369	0.951 233	4.6109	0.944 634	95.268	0.967 770	115.36	0.963 765	114.90	0.957 184
9.4832	0.957 989	9.5883	0.951 811	9.3396	0.945 166	116.45	0.970 126	132.81	0.965 720	130.98	0.958 917
21.687	0.959 402	18.970	0.952 894	18.786	0.946 229	132.75	0.971 910	151.78	0.967 804		
38.230	0.961 326	46.947	0.956 080	47.015	0.949 659	152.08	0.974 081	171.96	0.970 016		
47.174	0.962 335	59.338	0.957 504	58.610	0.950 831	171.02	0.976 178				
59.412	0.963 730	75.920	0.959 382	75.017	0.952 675	193.05	0.978 561				

[a] Accuracy in c, ±5 × 10^{-7} mol·dm^{-3}. [b] Accuracy in d, ±5 × 10^{-6} g·cm^{-3}.

Table 3. Coefficients *A*, *B*, and *D* of Eq 1

	t = 15 °C			t = 25 °C			t = 35 °C		
w	A^a	10^3B^b	10^3D^c	A^a	10^3B^b	10^3D^c	A^a	10^3B^b	10^3D^c
				Na_2SO_4					
0.10	0.1325	-11.21	-5.967	0.1304	-14.61	2.314	0.1280	-14.56	6.438
0.20	0.1285	-10.10	-7.397	0.1274	-11.21	-7.461	0.1247	-6.201	-10.96
0.25	0.1291	-44.55	19.38	0.1278	-29.06	17.45	0.1265	-39.08	36.98
0.30	0.1268	-4.794	-8.181	0.1224	-16.35	-1.331	0.1167	-1.765	-11.05
				$MgSO_4$					
0.10	0.1266	-18.09	7.609	0.1251	-16.08	6.383	0.1228	-5.529	-9.867
0.20	0.1239	-17.08	4.087	0.1218	-11.60	0.2899	0.1222	-9.614	-8.547
0.25	0.1247	-31.24	20.44	0.1190	-5.418	16.10	0.1224	-17.63	11.72
0.30	0.1181	-12.92	-0.7942	0.1184	-13.88	-1.683	0.1224	-28.13	10.01

[a] Standard deviation $\sigma(A) = 2 \times 10^{-4}$ kg·mol^{-1}. [b] Standard deviation $\sigma(B) = 7 \times 10^{-4}$ kg·mol$^{-3/2}$·dm$^{3/2}$. [c] Standard Deviation $\sigma(D) = 9 \times 10^{-4}$ kg·mol^{-2}·dm^3.

dilution $\phi_v°$, using the Redlich–Meyer equation (*3*)

$$\phi_v - S_v c^{1/2} = \phi_v° + b_v c \qquad (2)$$

where S_v is the Debye–Hückel limiting slope and b_v is an empirical parameter depending on the nature of the electrolyte. With aqueous solutions, $\phi_v°$ values are usually obtained by a direct extrapolation to zero concentration of the plots according to eq 2. This procedure cannot be used for the ethanol + water systems because all the solvent properties involved in a calculation of S_v are not known. For this reason, alternative methods must be used to obtain the $\phi_v°$, S_v*, and b_v values for both Na_2SO_4 and $MgSO_4$ in the different mass percent EtOH mixtures.

By combining the definition of the apparent molar volume [$\phi_v = [-10^3(d - d°) + M_2c]/d°c$] with eq 2, the density of an electrolyte solution can be determined, eq 1, by using the additivity principle, $\phi_v°$'s and S_v's are additive, and b_v's can be additive for this kind of system (*4*), with

$$\phi_v° = (M_2 - 10^3A)/d°; \quad S_v{}^* = -10^3B/d°; \quad b_v = -10^3D/d° \qquad (3)$$

Tables 1 and 2 give the concentrations and the experimental densities for the two salts in the various ethanol + water mixtures. Table 3 gives the coefficients of eq 1 (A, B, and D were obtained by a curve-fitting procedure), but the parameters from eq 3 evaluated by this method have uncertainties in $\phi_v°$ of ±2 cm^3·mol^{-1}, in S_v* of ±8 cm^3·mol$^{-3/2}$·dm$^{3/2}$, and in b_v of ±10 cm^3·mol^{-2}·dm^3. Besides this method assumes S_v* to be independent of the nature of the electrolyte, which is not strictly true. For these reasons $\phi_v°$ values obtained are not as accurate as those which could be obtained by a direct extrapolation to zero concentration of the plots according to eq 2. Although a large amount of data are available in aqueous solution, only little is known on ethanol + water systems. These studies (*5*) measured the density of several salts in these mixtures, but they used Masson's equation to obtain $\phi_v°$ values. Extrapolations to infinite dilution using this equation are unreliable (*6*).

Table 4. Dielectric Constant ε and Isothermal Compressibility β of *w* EtOH + (1 − *w*) H_2O Mixtures

t/°C	w	ε	$10^{12}\beta$/Pa
15	0	82.04[a]	4.17[c]
25	0	78.36[a]	4.561[c]
25	0.10	72.89[b]	4.251[d]
25	0.20	67.05[b]	4.138[d]
25	0.25	64.11[b]	4.198[d]
25	0.30	61.15[b]	4.353[d]
35	0	74.85[a]	4.442[c]

[a] Reference 12. [b] Interpolated data, ref 13. Standard deviation $\sigma(D) = 0.07$. [c] Reference 14 instead of the usual data reported from refs 3 and 15. [d] Interpolated data, ref 7. Standard deviation $\sigma(\beta) = 1.7 \times 10^{-13}$ Pa^{-1}.

Table 5. $\phi_v°$, S_v (Theoretical Slope), and b_v of Na_2SO_4 and $MgSO_4$ in w EtOH + (1 − w) H_2O Mixtures, Calculated by a Direct Extrapolation to Zero Concentration of the Plots According to Eq 2

		Na_2SO_4			$MgSO_4$		
t/°C	w	$\phi_v°$[a]/ (cm^3·mol^{-1})	S_v[b]/ (cm^3·mol$^{-3/2}$·dm$^{3/2}$)	b_v[a]/ (cm^3·mol^{-2}·dm^3)	$\phi_v°$[a]/ (cm^3·mol^{-1})	S_v[b]/ (cm^3·mol^{-2}·dm^3)	b_v[a]/ (cm^3·mol^{-2}·dm^3)
15	0	8.3	8.871	13.1	−7.0	13.52	0.74
25	0	10.6	9.670	10.0	−5.9	14.89	−2.3
25	0.10	10.7	11.2	14.2	−9.3	17.1	23.6
25	0.20	12.5	12.8	21.6	−9.7	19.6	36.9
25	0.25	17.2	13.6	7.9	−13.7	20.9	82.6
25	0.30	12.6	14.3	70.2	−0.11	22.1	−5.6
35	0	8.7	10.63	35.0	−5.2	16.37	−6.0

[a] Fit standard error 0.5 [b] Theoretical limiting slopes $S_v = kw^{3/2}$. $k = N^2e^2(8\pi/1000\epsilon^3RT)^{1/2}[(\delta \ln\epsilon/\delta P)_T - \beta/3]$ and $w = 1/2\sum\nu_iz_i^2$, where ν_i = number of ions, z_i = valency, $e = 1.60217733 \times 10^{-19}C$, N = Avogadro's constant = 6.0221367×10^{23} mol^{-1}, R = 8.314 510 J·mol^{-1}·K^{-1}, ϵ = dielectric constant, $(\delta \ln\epsilon/\delta P)_T$ is from ref 14, and β = isothermal compressibility, ref 14.

The method that one must use to evaluate the parameters is to calculate the approximate theoretical slopes S_v for these mixtures. Since we do not know the pressure dependence of the dielectric constants, we can assume that they are the same as those of water; the isothermal compressibility coefficients of the mixtures at 25 °C are known (*7*) (Table 4). There are differences between values of $\phi_v°$ (Figure 1) and b_v values (Figure 2) obtained by both methods, because even considering the uncertainties, we cannot apply the additivity principle when ionic association exists (*6*). The values of $\phi_v°$ and b_v evaluated from eq 3 are not as accurate as those of Table 5, even considering the approximate values, $(\delta \ln \epsilon/\delta P)_T$, used in this last one.

The apparent molar volumes at infinite dilution of both 1–2 and 2–2 electrolytes increase with temperature and with ethanol concentration in the mixed solvent, and the b_v values show positive deviations from the limit law of Redlich.

The properties of an ethanol + water mixture containing ~25 mass % EtOH are clearly complicated, as revealed by conductivities of salt solutions (*8*), diffusion coefficients (*9*), and permittivities (*10*). These complexities are also revealed in the properties reported here. There is a type of interaction to consider that can possibly cause the deviations from the limiting law. The thermodynamic association constants are in the range from 12 to 25 and from 210 to 1300 for Na_2SO_4 and $MgSO_4$ solutions at 25 °C, respectively, from aqueous solutions to a 30 mass % EtOH mixture (*1*), and they affect the b_v values. On the other hand, the temperature dependence on $\phi_v°$'s can be looked at in terms of ionic solvation (*11*), raising the temperature, decreasing the ionic solvation, and increasing the ion pairing the greater the $\phi_v°$'s. In short, the $\phi_v°$'s seem to represent the true volumes of the electrolytes, and the b_v's for these electrolytes take into account the ion pairs, principally in the $MgSO_4$ solutions.

Literature Cited

(1) Quintana, C.; Llorente, M. L.; Sanchez, M. M.; Vivo, A. *J. Chem. Soc., Faraday Trans 1* **1986**, *82*, 3307.
(2) Root, V. C. *J. Am. Chem. Soc.* **1933**, *55*, 850.
(3) Redlich, O.; Meyer, D. M. *Chem. Rev.* **1964**, *64*, 221.
(4) Millero, F. J. In *Structure and Transport Processes in Water and Aqueous Solutions*; Horne, R. A., Ed.; Wiley-Interscience: New York, 1971; Chapter 13, p 519.
(5) Padova, J. *J. Phys. Chem.* **1963**, *39*, 2599. Bateman, R. L. *J. Am. Chem. Soc.* **1949**, *71*, 2291.
(6) Millero, F. J. *Chem. Rev.* **1971**, *71*, 147.
(7) Kiyohara, O.; Benson, G. C. *J. Solution Chem.* **1981**, *4*, 281.
(8) Vivo, A.; Esteso, M. A.; Llorente, M. L.; Dominquez, B. *An. Quim.* **1981**, *77*, 204.
(9) Arevalo, A.; Tejera, E.; Vivo, A. *An. Quim.* **1974**, *70*, 7.
(10) Barthel, J. *I Colloquium on Solution Chemistry*, April, 1992; University of La Laguna: Tenerife, Spain, 1992.
(11) Pogue, R.; Atkinson, G. *J. Chem. Eng. Data* **1988**, *33*, 370.
(12) Owen, B. B.; Miller, R. C.; Milner, C. E.; Cogan, H. L. *J. Phys. Chem.* **1961**, *65*, 2065.
(13) Akerlöf, G. *J. Am. Chem. Soc.* **1932**, *54*, 4125.
(14) Diaz Peña, M.; McGlashan, M. L. *Trans. Faraday Soc.* **1959**, *55*, 2018.
(15) Smith, L. B.; Keyes, F. G. *Proc. Am. Acad. Arts Sci.* **1934**, *69*, 285.

Received for review August 10, 1993. Revised January 4, 1994. Accepted February 14, 1994.[⊗]

[⊗] Abstract published in *Advance ACS Abstracts*, April 1, 1994.