Table IV. Smoothed Values of Excess Enthalpies of Mixing of Tri-*n*-dodecylamine with Hydrocarbons at 303.15K (Φ_2 Volume Fraction of Hydrocarbon H^E J/ml)

Φ_2	*n*-Octane, $H^{E a}$	Benzene, $H^{E b}$	Chlorobenzene, $H^{E c}$
0.1	0.124	2.564	1.543
0.2	0.190	4.552	2.809
0.3	0.235	6.022	3.651
0.4	0.273	6.967	4.025
0.5	0.303	7.347	3.965
0.6	0.314	7.110	3.553
0.7	0.292	6.218	2.888
0.8	0.228	4.675	2.057
0.9	0.124	2.549	1.103

[a] $H^E = \Phi_1\Phi_2[1.214 + 0.455(\Phi_1 - \Phi_2) + 0.257(\Phi_1 - \Phi_2)^2 - 0.714(\Phi_1 - \Phi_2)^3]$. $\sigma_d = 0.003$ J ml^{-1}. $\sigma_m = 0.007$ J ml^{-1}. [b] $H^E = \Phi_1\Phi_2[29.39 - 1.598(\Phi_1 - \Phi_2) - 1.537(\Phi_1 - \Phi_2)^2 + 2.665(\Phi_1 - \Phi_2)^3]$. $\sigma_d = 0.162$ J ml^{-1}. $\sigma_m = 0.39$ J ml^{-1}. [c] $H^E = \Phi_1\Phi_2[15.86 + 5.036(\Phi_1 - \Phi_2) - 1.817(\Phi_1 - \Phi_2)^2 - 0.310(\Phi_1 - \Phi_2)^3]$. $\sigma_d = 0.08$ J ml^{-1}. $\sigma_m = 0.115$ J ml^{-1}.

cal interactions (*3*). These reactions are usually endothermic, as are the heats of mixing in the systems under consideration.

The tridodecylamine-octane mixtures are the most ideal, the endothermic heats of mixing being of a comparable magnitude to those of two hydrocarbons, if one of them is slightly polar. The dipole moment of the amine is of the order of 0.3 debyes (*7*). The substantial difference in the H^E values between this system and those with the two aromatic hydrocarbons may be taken as fair evidence that the contribution of n–π interactions between the lone-pair electrons of the nitrogen atom and the π-electrons of the aromatic ring to the observed heats of mixing is small. That the H^E values are more endothermic than in the corresponding amine–octane system can best be explained by assuming that the energy needed for breaking the ring–ring bonds is not compensated by the energy of the interaction between the nitrogen of the amine and the π-electrons of the aromatic ring. Chlorobenzene is apparently a less associated liquid than benzene.

We are reporting (*5*) evidence to show that the strength of n–π interactions is strongly dependent on the length of the hydrocarbon chain in the tertiary amine molecule. Long aliphatic chains screen the nitrogen effectively and thus diminish its availability for interactions with π-electrons.

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Apparent Molal Volumes of Aqueous NaF, Na_2SO_4, KCl, K_2SO_4, $MgCl_2$, and $MgSO_4$ Solutions at 0° and 50°C

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The apparent molal volumes, Φ_V's, of dilute (0.002–1*m*) aqueous solutions of NaF, Na_2SO_4, KCl, K_2SO_4, $MgCl_2$, and $MgSO_4$ are determined at 0° and 50°C from precision density measurements made with a magnetic float densitometer. The infinite dilution apparent molal volumes, Φ_V°'s, are determined by using the Redlich equation, $\Phi_V = \Phi_V^\circ + S_V c^{1/2} + b_V c$, where S_V is the Debye-Hückel limiting law slope, and b_V is a deviation constant. At 0°C the deviations are positive for all the salts except $MgCl_2$. The temperature dependence of the b_V for all the salts is similar to other common electrolytes ($\partial b_V/\partial T$ is negative). The effect of temperature on the Φ_V°'s of all the electrolytes is similar in that $\partial^2\Phi_V^\circ/\partial T^2$ is negative. The ion–ion and ion–water interactions responsible for the observed behavior of the Φ_V's are briefly discussed.

Although there are reliable density and apparent molal volume data for many aqueous electrolyte solutions at 25°C (*8*), little reliable data are available at other temperatures (*14*). Recently (*11, 13*) we had need for reliable apparent molal volume data for some sea salts (NaCl, $MgCl_2$, Na_2SO_4, $MgSO_4$, NaF, KCl, K_2SO_4) at temperatures between 0° and 40°C. The present paper contains results of the densities and apparent molal volumes of some of these sea salts at 0° and 50°C from 0.002 to 1 molal.

Experimental

All the solutions were made by weight with reagent-grade (Baker Analyzed) chemicals (without further purification) and ion-exchanged water (Millipore Super Q). The concentrations of the KCl, K_2SO_4, Na_2SO_4, and $MgSO_4$ stock solutions were analyzed by heating to dryness, whereas the concentrations of the $MgCl_2$ stock solution were analyzed for Cl^- by titration with $AgNO_3$.

The magnetic float densitometer used to make the density measurements and a review of the development of the magnetic float method were described in detail elsewhere (*12*). The densitometer consists of a 110-cm^3 solution container which fits into a brass support containing a solenoid. The float (32 cm^3) is made of borosilicate glass and contains a magnet. The densitometer was calibrated with ion-exchanged water by using the densities (g/ml) tabulated by Kell (*7*). The density measurements

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Table I. Densities and Apparent Molal Volumes of Aqueous KCl, NaF, Na_2SO_4, K_2SO_4, $MgCl_2$, and $MgSO_4$ Solutions at 0° and 50°C[a]

m	1000 Δd	Φ_V
NaF, 0°C		
0.009715	0.4700	−6.400
0.029258	1.4109	−6.235
0.090096	4.3064	−5.792
0.153786	7.2963	−5.424
0.243098	11.4628	−5.113
0.268629	12.6310	−4.976
0.360703	16.8610	−4.684
0.360255	16.8286	−4.653
0.497018	23.0247	−4.246
Na_2SO_4, 0°C		
0.003567	0.4971	2.648
0.008254	1.1471	3.037
0.008351	1.1611	2.977
0.011673	1.6213	3.120
0.013831	1.9194	3.237
0.014836	2.0598	3.181
0.015569	2.1597	3.301
0.017031	2.3627	3.283
0.017661	2.4497	3.309
0.017808	2.4695	3.343
0.019987	2.7706	3.392
0.020799	2.8816	3.469
0.024185	3.3478	3.584
0.024998	3.4572	3.709
0.024998	3.4581	3.673
0.026919	3.7232	3.699
0.030351	4.1948	3.797
0.034785	4.8005	4.000
0.040737	5.6091	4.309
0.049147	6.7567	4.511
0.054676	7.4985	4.841
0.061606	8.4390	4.998
0.070549	9.6379	5.359
0.082529	11.2352	5.822
0.099410	13.4818	6.320
0.105998	14.3357	6.682
0.126706	17.0637	7.228
0.147918	19.8493	7.680
0.177700	23.7353	8.258
0.259374	34.2313	9.715
0.347180	45.2643	11.143
0.469650	60.3261	12.803
0.557229	70.8333	13.922
0.705014	88.2276	15.514
0.921454	112.8616	17.562
$MgCl_2$, 0°C		
0.008785	0.7386	11.125
0.010774	0.9056	11.123
0.015048	1.2617	11.355
0.018179	1.5231	11.410
0.025081	2.0935	11.717
0.026659	2.2248	11.732
0.031383	2.6133	11.910
0.043333	3.5927	12.258
0.056311	4.6538	12.508
0.07966	6.5606	12.778
0.09649	7.9352	12.876
0.13720	11.2162	13.315
0.17359	14.1197	13.678
0.25072	20.2238	14.262
0.34124	27.2805	14.861
0.42814	33.9473	15.399
0.50904	40.1183	15.767
0.62437	48.7665	16.311
0.70544	54.7187	16.729
0.82932	63.8230	17.159
1.01833	77.4084	17.818
1.01840	77.4134	17.818
KCl, 50°C		
0.028720	1.3309	27.496
0.059958	2.7644	28.146
0.16026	7.3134	28.497
0.33955	15.2979	28.857
0.57774_5	25.6514	29.215
0.76650	33.6785	29.442
1.00327	43.4879	29.743
$MgCl_2$, 50°C		
0.003191	0.2568	13.918
0.007843	0.6290	14.203
0.010834	0.8671	14.369
0.016475	1.7590	14.449
0.022025	1.7590	14.531
0.026501	2.1108	14.742
0.035536	2.8435	14.357
0.046302	3.6677	15.166
0.055539	4.3914	15.303
0.089625	7.0445	15.738
0.096011	7.5486	15.708
0.12308	9.6294	16.068
0.17339	13.4882	16.453
0.24965	19.2903	16.885
0.37062	28.2719	17.716
0.47693	36.1026	18.160
0.64665	48.3318	18.879
0.82633	60.9902	19.552
0.99421	72.5900	20.097
$MgSO_4$, 50°C		
0.002439	0.3039	−5.816
0.006453	0.7968	−4.674
0.013103	1.6036	−3.538
0.018164	2.2115	−2.892
0.026523	3.2115	−2.201
0.040100	4.8309	−1.576
0.064372	7.7068	−0.810
0.10706	12.7219	0.102
0.17204	20.2727	1.092
0.24497	28.6377	2.014
0.35275	40.8393	3.101
0.44699_6	51.3353	3.974
0.58829	66.8730	5.040
0.72061	81.2010	5.909
0.88872	99.1366	6.867
NaF, 50°C		
0.010102	0.4338	−1.484
0.019600	0.8406	−1.432
0.039394	1.6840	−1.290
0.079954	3.4070	−1.149
0.143533	6.0842	−0.918
0.243280	10.2267	−0.557
0.337712	14.1444	−0.400
0.430678	17.9545	−0.203
0.571046	23.6743	0.029
0.803873	32.9935	0.440
K_2SO_4, 0°C		
0.003007	0.4511	24.227
0.004334	0.6501	24.231
0.005597	0.8387	24.370
0.007897	1.1835	24.430
0.010278	1.5363	24.738
0.014920	2.2738	25.237
0.014715	2.1919	25.150
0.019454	2.8944	25.398
0.027948	4.1439	25.872
0.034366	5.0833	26.204
0.036851	5.4457	26.337
0.048361	7.1219	26.800
0.054081	7.9512	27.014
0.069961	10.2435	27.555
0.099044	14.4057	28.399
0.13033	18.8196	28.980
0.15934	22.9357	29.631
0.21831	31.1124	30.794
0.28097	39.6358	31.121
0.36472	50.8675	33.103
$MgSO_4$, 0°C		
0.005170	0.6822	−11.583
0.007469	0.9800	−10.853
0.014391	1.8805	−10.306
0.019090	2.4784	−9.456
0.027767	3.5784	−8.498
0.032379	4.1641	−8.228
0.036607	4.6909	−7.761
0.044662	5.7127	−7.521
0.053878	6.8711	−7.136
0.063246	8.0435	−6.778
0.069471	8.8634	−6.686
0.089133	11.2628	−5.947
0.100205	12.6247	−5.573
0.11478	14.4291	−5.291
0.14239	17.8252	−4.755
0.18277	22.7279	−3.915
0.24491	30.2141	−2.936
0.36328	44.2783	−1.474
0.49772	59.9735	−0.140
0.71312	84.5670	1.623
0.89006	104.2264	2.941
0.89033	104.2576	2.941
Na_2SO_4, 50°C		
0.002226	0.2804	14.745
0.006220	0.7824	14.905
0.006274	0.7878	15.129
0.012695	1.5905	15.401
0.014306	1.7918	15.432
0.026513	3.3076	15.912
0.044254	5.4907	16.572
0.085346	10.4949	17.608
0.15125	18.3991	18.803
0.22660	27.2975	19.811
0.28814	34.4945	20.415
0.41164	48.6398	21.654
0.53857	62.9239	22.637
0.69983	80.6510	23.768
0.79824	91.2671	24.386
1.00476	113.0439	25.583
1.00476	113.0488	25.578
K_2SO_4, 50°C		
0.001994	0.2761	24.556
0.003113	0.4304	34.743
0.004975	0.6861	35.089
0.007964	1.0954	35.438
0.012674	1.7388	35.786
0.018302	2.5036	36.171
0.027868	3.7863	37.067
0.035209	4.7737	37.317
0.048770	6.5807	37.910
0.067813	9.1260	38.176
0.096542	12.9375	38.604
0.10892	14.5455	39.014
0.13386	17.8327	39.210
0.16999	22.5195	39.777
0.20329	26.8477	40.013
0.22523	29.6710	40.228
0.25632	33.6047	40.702
0.31119	40.5636	41.166
0.36270	46.9749	41.730
0.36880	47.7854	41.642
0.52848	67.2859	43.030
0.70706	88.5197	44.181

[a] Densities are in units of g/ml, and Φ_V is in units of ml/mol.

were made by the weight dilution technique (*9*) and on single stock solutions (*12*). Duplicate density measurements on the same solution agreed to within ±2 ppm. The reproducibility of ±0.2 in the apparent molal volumes in the most dilute solutions (0.002) indicates that the density precision within a given experimental run was ±0.3 ppm.

The temperature of the bath containing the densitometer was set to ±0.001°C with a platinum resistance thermometer (calibrated by NBS) and a G-2 Mueller bridge. The bath was regulated to better than ±0.001°C with a Tronac thermal regulator. This temperature variation corresponds to a density uncertainty of ±0.3 ppm or ±0.2 in the apparent molal volume in the most dilute solutions. During an experimental run, the bath was monitored with a Hewlett-Packard quartz crystal thermometer and recorder.

Results and Discussion

The densities of dilute aqueous solutions of NaF, Na_2SO_4, K_2SO_4, $MgCl_2$, and $MgSO_4$ were determined at 0° and 50°C with the magnetic float densitometer. Measurements on KCl solutions were made only at 50°C. The results of the difference ($\Delta d = d - d^\circ$) between the density of solutions (d) and the density of water (d°) at various molal concentrations (m) are given in Table I. The apparent molal volumes (Φ_V's) of these solutions were calculated from

$$\Phi_V = \frac{1000(d - d^\circ)}{dd^\circ m} + \frac{M}{d} \qquad (1)$$

where m is the molality, and M is the molecular weight of electrolytes (using the 1969 atomic weights). The Φ_V's of these solutions are given in Table I and are shown in Figures 1–6 as a function of the square root of molar concentrations $(c)^{1/2}$. The infinite dilute apparent molal volumes ($\Phi_V^\circ = \bar{V}_2^\circ$) for these solutions were obtained by extrapolation with the Redlich (*15, 16*) equation (below c = 0.2)

$$\Phi_V = \Phi_V^\circ + S_V c^{1/2} + b_V c \qquad (2)$$

where S_V is the Debye-Hückel limiting law slope (*8, 15*), c is the molar concentration [$c = md^\circ\, 10^3/(10^3 + \Phi_V\, md^\circ)$], and b_V is an empirical constant. As apparent from Figures 1–6, the Φ_V's of the NaF, Na_2SO_4, K_2SO_4, and $MgCl_2$ solutions all approach limiting law behavior in di-

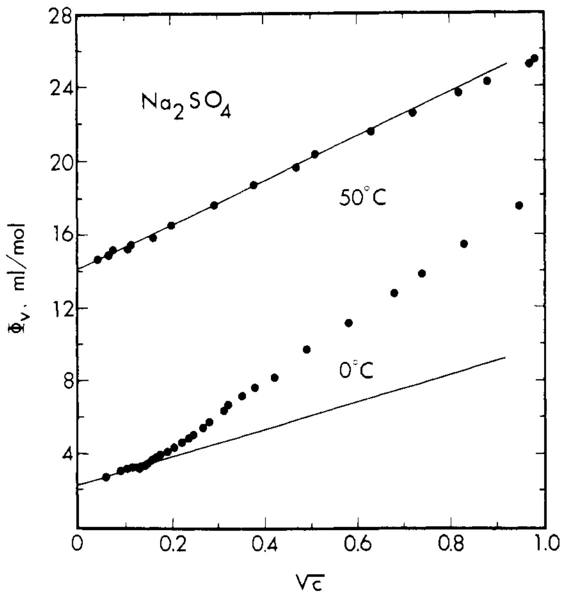

Figure 2. Apparent molal volumes, Φ_V, of Na_2SO_4 solutions as function of $\sqrt{c}$ at 0° and 50°C. Straight lines are Debye-Hückel theoretical limiting law slopes (*8, 15*)

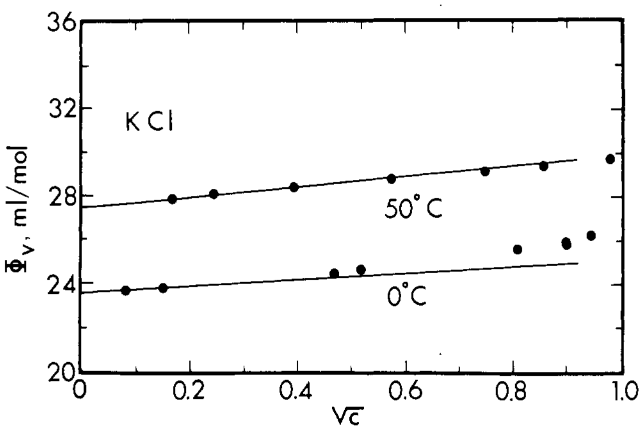

Figure 3. Apparent molal volumes, Φ_V, of KCl solutions as function of $\sqrt{c}$ at 0° and 50°C. 0°C data are taken from Dunn (*2*). Straight lines are Debye-Hückel theoretical limiting law slopes (*8, 15*)

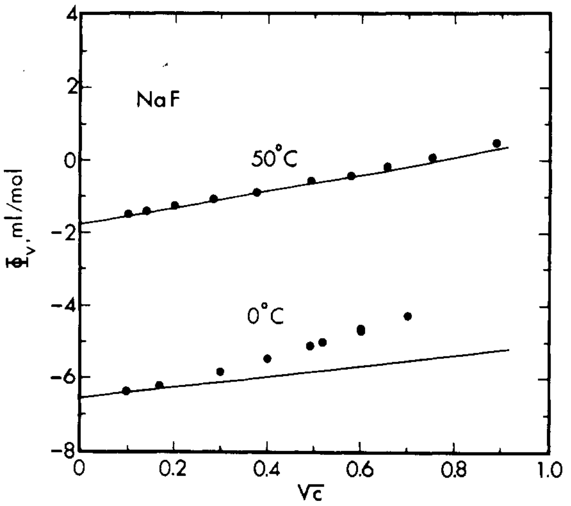

Figure 1. Apparent molal volumes, Φ_V, of NaF solutions as function of $\sqrt{c}$ at 0° and 50°C. Straight lines are Debye-Hückel theoretical limiting law slopes (*8, 15*)

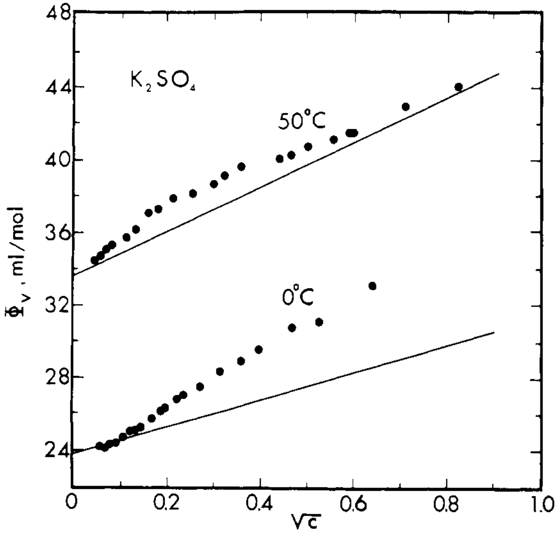

Figure 4. Apparent molal volumes, Φ_V, of K_2SO_4 solutions as function of $\sqrt{c}$ at 0° and 50°C. Straight lines are Debye-Hückel theoretical limiting law slopes (*8, 15*)

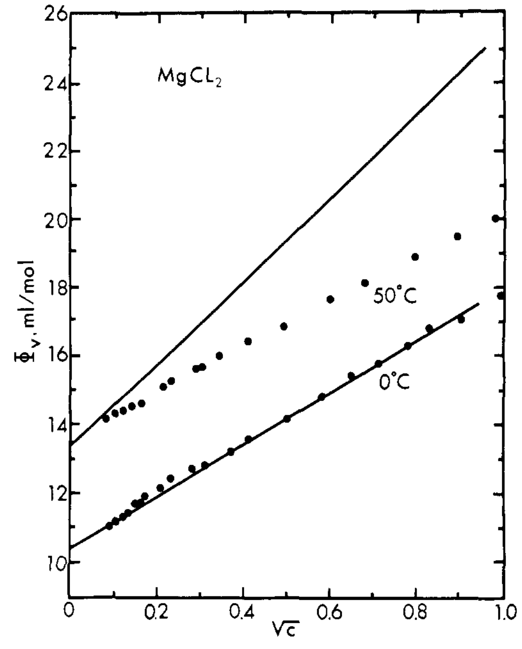

Figure 5. Apparent molal volumes, Φ_V, of $MgCl_2$ solutions as function of $\sqrt{c}$ at 0° and 50°C. Straight lines are Debye-Hückel theoretical limiting law slopes (*8, 15*)

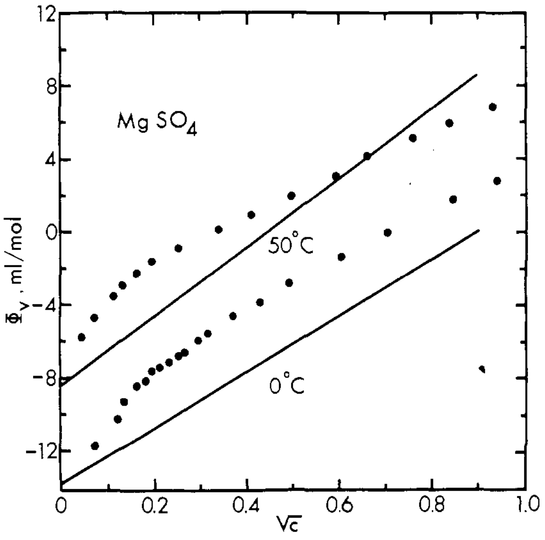

Figure 6. Apparent molal volumes, Φ_V, of $MgSO_4$ solutions as function of $\sqrt{c}$ at 0° and 50°C. Straight lines are Debye-Hückel theoretical limiting law slopes (*8, 15*)

Table II. Infinite Dilution Partial Molal Volumes of Aqueous NaF, Na_2SO_4, KCl, K_2SO_4, $MgCl_2$, and $MgSO_4$ Solutions at 0°, 25°, and 50°C

	$\bar{V}_2^\circ$, ml/mol		
Salt	0°C	25°C	50°C
NaF	$-6.51,^a -5.72^b$	2.37^b	$-1.77,^a -1.7^b$
Na_2SO_4	$2.33,^a 3.7^c$	11.56^b	$14.09,^a 15.5^d$
KCl	23.62^b	26.85^b	$27.57,^a 27.66,^e 27.64,^f 27.9^d$ $27.87,^g 27.12^h$
K_2SO_4	$23.79,^a 22.7^i$	32.02^b	$33.63,^a 35.1^d$
$MgCl_2$	$10.42,^a 12.7,^c 11.4^f$	14.49^b	$13.40,^a 14.70,^f 15.1^d$
$MgSO_4$	$-13.06,^a -10.0^c$	-7.19^b	$-8.14,^a -4.87^b$

[a] This study. [b] Millero's compilation (*14*). [c] Zen (*19*). [d] Ellis (*3-5*). [e] Scott (*18*). [f] Root (*17*). [g] Akerlof and Bender (*1*). [h] Redlich and Rosenfeld (*16*). [i] Jones and Calvin (*6*).

Table III. Partial Molal Expansibilities at Infinite Dilution for NaF, Na_2SO_4, KCl, K_2SO_4, and $MgSO_4$ at 12.5° and 37.5°C

	$\Phi_E^\circ = \bar{E}^\circ$, ml/mol^{-1} deg^{-1}	
Salt	12.5°C	37.5°C
NaF	0.1656	0.0240
NaCl[a]	0.1488	0.0484
Na_2SO_4	0.3716	0.0988
KCl	0.1288	0.0288
K_2SO_4	0.3280	0.0656
$MgCl_2$	0.1628	−0.0436
$MgSO_4$	0.2352	−0.0384

[a] Millero (*10*).

lute solutions. The large positive deviations from the limiting law for the $MgSO_4$ solutions make it difficult to use Equation 2 to obtain an infinite Φ_V°. We have thus used large plots of the Φ_V vs. $c^{1/2}$ to estimate the Φ_V°'s for $MgSO_4$.

The infinite dilution $\bar{V}_2^\circ$'s for these solutions at 0° and 50°C are given in Table II along with the results obtained by other workers (*1-6, 10, 15-19*). Also given in Table II are the $\bar{V}_2^\circ$'s for these salts at 25°C obtained by other workers (*1-6, 8-10, 14, 16*).

Our results at 0° and 50°C (except for KCl) cannot be directly compared to the work of others because of the error in extrapolation to infinite dilution made by earlier workers (*8, 14*). As pointed out elsewhere (*8*), the errors made by earlier workers are caused by neglecting to use the limiting law as an aid in the extrapolation and by using unreliable Φ_V's at low concentrations (i.e., unreliable densities). Note that an improper extrapolation to infinite dilution can give Φ_V°'s that are in error by as much as 3 ml/mol (*8*) for a 1-1 electrolyte.

By linearly extrapolating Dunn's (*2*) work at 45° and 55°C, one obtains Φ_V° (KCl) = 27.57 ml/mol, which is in excellent agreement with our extrapolated values.

The internal consistency of our values for Φ_V° can be tested by using the additivity principle. The differences between Φ_V° (1/2 K_2SO_4) and Φ_V° (1/2 Na_2SO_4) are 10.73 and 9.77 ml/mol, respectively, at 0° and 50°C compared to 10.68 and 9.87 obtained from the Φ_V°'s of KCl and NaCl (*2, 8, 10*). The Φ_V° of $MgSO_4$ can be calculated by the additivity principle using the Φ_V°'s of $MgCl_2$, Na_2SO_4, K_2SO_4, NaCl, and KCl. The additivity method gives Φ_V° ($MgSO_4$) = −13.05 and −13.03 ml/mol at 0° and −8.17 and −8.11 ml/mol at 50°C, respectively, from the Na^+ and K^+ salts.

The infinite dilution partial molal expansibilities, $\Phi_E^\circ = \bar{E}_2^\circ = \partial\Phi_V^\circ/\partial T$ at 12.5° and 37.5°C for these electrolytes, are given in Table III, along with the results for NaCl (*10*). The $\bar{E}_2^\circ$'s for all of the electrolytes decrease with increasing temperature (i.e., $\partial\bar{E}_2^\circ/\partial T$ is negative). As discussed elsewhere (*8, 14*), the decrease in $\bar{E}_2^\circ$ for electrolytes or the maximum in the $\bar{V}_2^\circ$ can be attributed to the decrease in volume owing to the increase in electrostriction with increasing temperature.

The deviations from the limiting law (b_V) of the Φ_V's at 0°C for all of the electrolytes, with the exception of $MgCl_2$, are positive. At 50°C, the positive deviations become smaller ($MgSO_4$ and K_2SO_4) or close to zero (NaF and Na_2SO_4). The deviations of Φ_V's for the $MgCl_2$ solutions are near zero at 0° and negative at 50°C. The effect of temperature on the b_V's for all the electrolytes is similar in that $\partial b_V/\partial T$ is negative. The large positive deviations for most of the electrolytes at 0° and K_2SO_4 and $MgSO_4$ at 50°C may be due to cation anion ion pair formation (*10*). The large negative deviations for $MgCl_2$ solutions at 50°C are what one might expect from the extended Debye-Hückel equation or if cation–cation and anion–anion interactions are more important than cation–anion interactions (*10*).

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Diffusion Coefficients of O_2, N_2, and CO_2 in Fluorinated Ethers

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Diffusion coefficients of O_2, N_2, and CO_2 in three fluorinated ethers are measured at 25° and 37°C. These coefficients are, in general, about twice as large as those in water.

Large gas solubilities in certain fluorinated ethers have stimulated considerable interest in their use as potential oxygen carriers in liquid breathing (5), in cardiopulmonary bypass machines (3), and as blood substitutes (8). To compute the mass-transfer rate during such processes, the diffusion coefficients of O_2, N_2, and CO_2 are needed. We have undertaken to measure these values for gases in fluorinated ethers at 25° and 37°C. The compounds studied were Caroxin-D (perfluoro-1,4 diisopropoxy butane) (Allied Chemical Corp., Morristown, N.J.), Caroxin-F (perfluoro-1-isopropoxy hexane) (Allied Chemical Corp., Morristown, N.J.), and FC-80 (perfluorobutyl perfluorotetrahydrofuran) (3M Co., St. Paul, Minn.).

Experimental

Materials. Minimum purities of O_2, N_2, and CO_2 were 99.6%. Caroxin-D and Caroxin-F were of greater than 99.9% purity as supplied, whereas FC-80 contains several isomers (*2*).

Procedure. Diffusion coefficients were measured with a modified Stokes' diaphragm cell (*9*). The procedure was described in detail by Tham and Gubbins (*11*), and we shall present only essential information here. The diaphragms were of porosity *D* (ASTM 10–20 μm), and stirring was accomplished with magnetic stirrers, rotating at 60 rpm. The diaphragm cells were immersed in a constant temperature bath controlled to within ±0.02° of the desired temperature with a proportional controller.

The cells were calibrated with 0.1*N* HCl, each cell being calibrated twice at the beginning of the work; cell constants were reproducible within ±0.5%. [The diffusion coefficients are known accurately for the $HCl-H_2O$ system (*10*).]

The solvent-filled diaphragm method was used for both the calibration and diffusion coefficient measurement runs. Diffusion coefficients were calculated from the equation (*1, 4*)

$$D_{12} = \frac{1}{\beta t} \ln \left[\frac{C_B^\circ}{C_B - C_T}\right]\left[1 - \frac{\lambda}{6}\right] \qquad (1)$$

where D_{12} is the differential diffusion coefficient of 1 in 2.

$$C_B^\circ = C_B \left[\frac{V_B + 1/2\, V_D}{V_D}\right] + C_T\left[\frac{V_T + 1/2\, V_D}{V_B}\right] \qquad (2)$$

$$\lambda = \frac{V_D}{V_B + V_T} \qquad (3)$$

β is the cell constant derived from calibration with HCl, and *t* is the time of diffusion; *C* is the concentration of diffusing substance, and *V* is the volume. Subscripts *B*, *T*, and *D* refer to bottom and top compartment and diaphragm, respectively.

The cell was first evacuated and then filled with the degassed fluorocarbon. It was equilibrated in a constant temperature bath for 2 hr with constant stirring; then, the bottom chamber was emptied and filled with solution containing the diffusing material. The method of preparing the gas solution and the precautions necessary in filling the cell have been described elsewhere (*7, 12*).

Solutions containing the dissolved gas were analyzed with a Perkin-Elmer Model 900 gas chromatograph equipped with a thermal conductivity detector. The column was a ⅛-in. × 12-ft Porapak Q column, which was kept at room temperature. The helium carrier gas flow rate was 40 ml/min; injector port and detector temperatures were kept at 100° and 200°C, respectively. Calibration of the chromatograph was done by injecting a known volume of pure gas into the chromatograph and measuring the peak area. Linear response was observed in the range of concentrations of interest. The chromatograph analyses were reproducible to ±0.6%.

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