0.473 and 0.498 nm, respectively.

On the other hand, the polarizabilities α_+ divided by the cubes of the "real dimension" of the cations (*14*) yield values that decrease strongly with n_C: from 0.94 for $n_C = 1$, to 0.42 for $n_C = 7$. These "real dimensions" pertain to curled-up conformations of the alkyl chains in the unsolvated state, whereas those derived from the refractivities in both water and DMF pertain to straightened-out chains. This suggests that the tetra-*n*-alkylammonium cations are similarly solvated in water and in DMF.

Registry No. DMF, 68-12-2; $(CH_3)_4NBr$, 64-20-0; $(C_2H_5)_4NBr$, 71-91-0; $(C_2H_5)_4NI$, 68-05-3; $(C_3H_7)_4NBr$, 1941-30-6; $(C_4H_9)_4NBr$, 1643-19-2; $(C_5H_{11})_4NBr$, 866-97-7; $(C_6H_{13})_4NBr$, 4328-13-6; $(C_7H_{15})_4NBr$, 4368-51-8; NH_4Br, 12124-97-9.

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Received for review January 5, 1987. Accepted September 4, 1987. This research was supported by the U.S.–Israel Binational Science Fund, grant No. 84-00292.

Excess Volumes of (*n*-Nonane + *n*-Undecane) between 288.15 and 308.15 K

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Excess molar volumes of (*n*-nonane + *n*-undecane) have been determined from density measurements at 288.15, 293.15, 298.15, 303.15, and 308.15 K. Density was obtained with an Anton Paar densimeter. The molar volumes of (*n*-nonane + *n*-undecane), (*n*-octane + *n*-undecane), and (*n*-heptane + *n*-undecane) are given as functions of temperature and the mole fraction of *n*-undecane. For each of these three binary mixtures, the coefficient of thermal expansion is plotted against the mole fraction of *n*-undecane at three temperatures.

Introduction

In previous articles (*1*, *2*) the excess volumes of (*n*-heptane + *n*-undecane) and (*n*-octane + *n*-undecane) at 288.15, 293.15, 298.15, 303.15, and 308.15 K have been determined. This article reports similar measurements for $(x)n\text{-}C_9H_{20} + (1 - x)n\text{-}C_{11}H_{24}$ together with three-parameter empirical equations fitted to the results obtained at each temperature. Third-degree polynomials in the mole fraction of *n*-undecane $(1 - x)$ have been fitted, at each temperature T, to the molar volumes of all three binary mixtures; and a polynomial in T has been fitted to the coefficients of the molar volume equations to obtain an expression for the molar volume as a function of $(1 - x)$ and T, and hence an expression for the coefficient of thermal expansion as a function of the same variables for $0 \leqslant x \leqslant 1$ in the temperature range investigated.

Experimental Section

Densities were measured with an Anton Paar DMA 60/602 densimeter with a resolution of $\pm 1.5 \times 10^{-6}$ g cm^{-3}. The temperature of the water bath containing the oscillator tube was kept constant to within ±0.005 K with a Hetofrig thermostat. The operational technique has been described elsewhere (*3*). The *n*-nonane (Fluka purum >99 mol %) and *n*-undecane (Merk >99 mol %) were carefully dried with Union Carbide Type 4 A molecular sieve (from Fluka) and were used directly without further purification. The observed densities of *n*-nonane and *n*-undecane at the various temperatures employed are given in Table I along with published values (*4*–*6*) for comparison.

Table I. Experimental Densities (g cm^{-3}) at Various Temperatures and Comparison with Literature Values

	T/K				
	288.15	293.15	298.15	303.15	308.15
			Experimental		
n-nonane	0.721 76	0.717 85	0.713 96	0.710 07	0.706 17
n-undecane	0.744 29	0.740 59	0.736 90	0.733 20	0.729 51
			Literature		
n-nonane		0.717 63[a]	0.713 81[a]	0.709 76[c]	
n-undecane		0.740 17[b]	0.736 5[c]	0.732 84[c]	

[a] Reference *4*. [b] Reference *5*. [c] Reference *6*.

Results and Discussion

Table II list the excess molar volumes V_m^E calculated from the observed densities for each temperature T and each value of the mole fraction of *n*-nonane x. For each T, equations of the form

$$V_m^E/(\text{cm}^3\ \text{mol}^{-1}) = x(1 - x)\sum_{k<3} A_k(2x - 1)^k \qquad (1)$$

were fitted to the experimental results. The parameters A_k and the standard deviations of fit are listed in Table III, and Figure 1 shows the fitted V_m^E curves together with the experimental points. In all cases V_m^E is negative and the curves are asymmetric with a minimum at $x = 0.473$.

Third-degree polynomials

$$V_m = \sum_{k<4} B_k(1 - x)^k \qquad (2)$$

Table II. Excess Molar Volumes at Various Temperatures for $(x)n\text{-}C_9H_{20} + (1 - x)c\text{-}C_{11}H_{24}$; $\delta V_m^E = V_m^E(\text{obsd}) - V_m^E(\text{calcd})$

x	V_m^E/ (cm^3 mol^{-1})	δV_m^E/ (cm^3 mol^{-1})	x	V_m^E/ (cm^3 mol^{-1})	δV_m^E/ (cm^3 mol^{-1})	x	V_m^E/ (cm^3 mol^{-1})	δV_m^E/ (cm^3 mol^{-1})	x	V_m^E/ (cm^3 mol^{-1})	δV_m^E/ (cm^3 mol^{-1})
288.15 K											
0.0903	−0.0054	0.0005	0.2648	−0.0135	−0.0001	0.5072	−0.0181	−0.0006	0.7069	−0.0152	0.0005
0.1449	−0.0089	−0.0002	0.3064	−0.0151	−0.0005	0.5505	−0.0178	−0.0002	0.7777	−0.0141	−0.0004
0.1878	−0.0108	−0.0001	0.3679	−0.0164	−0.0004	0.5890	−0.0166	0.0008	0.8211	−0.0119	−0.0000
0.1997	−0.0115	−0.0004	0.4200	−0.0161	0.0007	0.6461	−0.0167	0.0001	0.8685	−0.0094	0.0002
0.2433	−0.0120	0.0007	0.4648	−0.0170	0.0003	0.6922	−0.0170	−0.0009	0.9106	−0.0069	0.0002
293.15 K											
0.1026	−0.0068	0.0004	0.3000	−0.0166	0.0002	0.5240	−0.0203	0.0005	0.7199	−0.0176	−0.0003
0.1413	−0.0097	−0.0002	0.3549	−0.0185	0.0000	0.5564	−0.0208	−0.0002	0.7702	−0.0160	−0.0007
0.1987	−0.0119	0.0007	0.4029	−0.0201	0.0005	0.5848	−0.0195	0.0009	0.8354	−0.0121	−0.0001
0.2308	−0.0144	−0.0002	0.4441	−0.0210	−0.0007	0.6399	−0.0198	−0.0003	0.8836	−0.0083	0.0008
0.2499	−0.0153	−0.0004	0.4903	−0.0206	0.0001	0.6854	−0.0178	0.0007	0.9141	−0.0076	−0.0006
298.15 K											
0.1106	−0.0075	0.0006	0.3047	−0.0191	−0.0004	0.5289	−0.0229	0.0001	0.6868	−0.0196	0.0006
0.1610	−0.0116	−0.0002	0.3480	−0.0196	0.0006	0.5524	−0.0225	0.0005	0.7312	−0.0187	−0.0001
0.1986	−0.0143	−0.0007	0.3667	−0.0208	0.0001	0.5887	−0.0227	−0.0001	0.7875	−0.0153	0.0005
0.2520	−0.0154	0.0009	0.4017	−0.0224	−0.0007	0.6425	−0.0220	−0.0005	0.8336	−0.0132	−0.0001
0.2755	−0.0175	0.0000	0.4561	−0.0233	−0.0006	0.6691	−0.0207	0.0002	0.8873	−0.0102	−0.0007
303.15 K											
0.0837	−0.0080	−0.0007	0.2923	−0.0201	0.0004	0.4909	−0.0249	0.0008	0.7519	−0.0198	0.0006
0.1216	−0.0102	0.0001	0.3533	−0.0229	0.0000	0.5314	−0.0264	−0.0005	0.7786	−0.0192	−0.0002
0.1679	−0.0127	0.0008	0.3824	−0.0235	0.0003	0.6039	−0.0257	−0.0004	0.8102	−0.0171	0.0000
0.2056	−0.0163	−0.0004	0.4039	−0.0240	0.0003	0.6544	−0.0251	−0.0009	0.8472	−0.0146	0.0000
0.2334	−0.0182	−0.0007	0.4406	−0.0254	−0.0003	0.6926	−0.0225	0.0005	0.9013	−0.0101	0.0001
308.15 K											
0.0689	−0.0078	−0.0003	0.3031	−0.0230	0.0006	0.5490	−0.0282	0.0001	0.7420	−0.0239	−0.0004
0.1045	−0.0118	−0.0009	0.3560	−0.0252	0.0004	0.6034	−0.0279	−0.0001	0.7961	−0.0198	0.0007
0.1497	−0.0143	0.0003	0.4008	−0.0274	−0.0006	0.6572	−0.0271	−0.0004	0.8434	−0.0171	0.0000
0.1939	−0.0173	0.0004	0.4545	−0.0283	−0.0005	0.7050	−0.0245	0.0006	0.8908	−0.0131	−0.0001
0.2452	−0.0208	0.0000	0.5013	−0.0281	0.0002	0.7210	−0.0246	−0.0001	0.9301	−0.0092	−0.0003

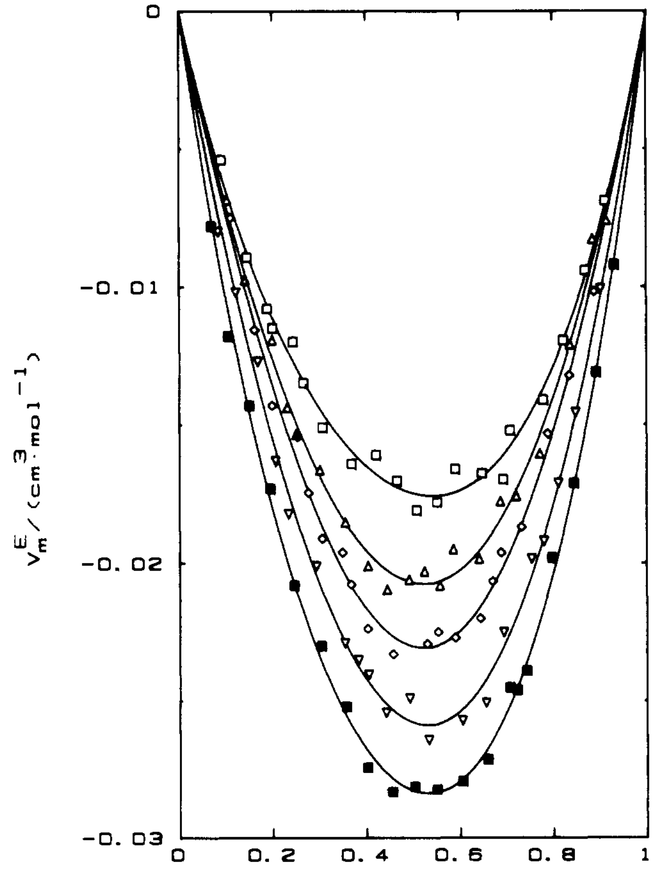

Figure 1. V_m^E of $(x)n\text{-}C_9H_{20} + (1 - x)c\text{-}C_{11}H_{24}$ at 288.15 (□), 293.15 (△), 298.15 (◇), 303.15 (▽), and 308.15 (■).

Table III. Parameters A_k of Eq 1 and Standard Deviations $s(V_m^E)/(\text{cm}^3\ \text{mol}^{-1})$

	T/K				
	288.15	293.15	298.15	303.15	308.15
A_0	−0.0700013	0.0828850	−0.0921431	−0.1031704	−0.1130709
A_1	−0.0088089	−0.0065207	−0.0076936	−0.0113176	−0.0110737
A_2	−0.0137567	−0.0006481	0.0063627	−0.0028520	−0.0188731
s	0.0005	0.0005	0.0005	0.0005	0.0005

Table IV. Parameters B_{kj} of Eq 3

	j		
	0	1	2
B_{0j}	117.1870	0.0195700	0.00027489
B_{1j}	42.8490	0.1250200	−0.00018230
B_{2j}	34.4532	−0.2451364	0.00044600
B_{3j}	−27.6409	0.1914965	−0.00033442

Table V. Thermal Expansion Coefficient α: Comparison of Values Calculated in This Paper with Those from the Literature at 293.15 K

	$10^3\alpha/K^{-1}$			
	n-heptane	n-octane	n-nonane	n-undecane
this paper	1.233	1.149	1.087	0.998
ref 7	1.238	1.151	1.085	1.006

where 1 − x is the mole fraction of n-undecane, have been fitted to the molar volumes calculated from the density data of Table II for (n-nonane + n-undecane), (n-octane + n-undecane), and (n-heptane + n-undecane). The coefficients B_k are assumed to be functions of temperature and have been fitted with polynomials of the form

$$B_k = \sum_{j<3} B_{kj} T^j \qquad (3)$$

The values of the B_{kj} are listed in Table IV.

The molar volumes obtained above can be used to calculate the coefficient of thermal expansion $\alpha = 1/V_m(\partial V_m/\partial T)_P$ of each of the three binary systems considered in the range of temperatures investigated. In Table V the values obtained in

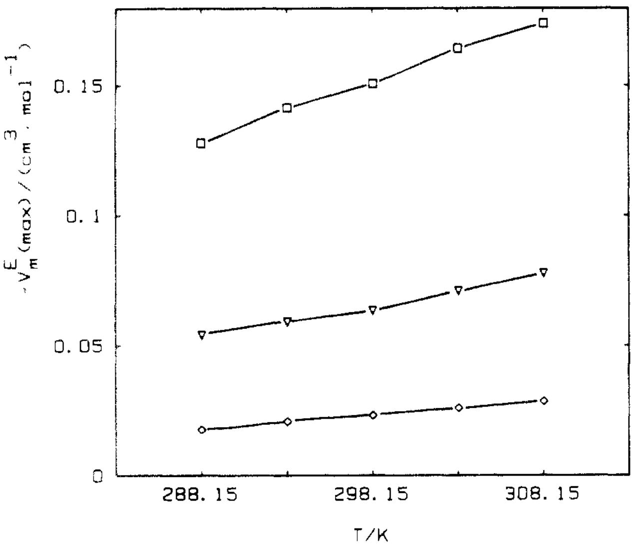

Figure 2. Maximum values of V_m^E: (□) n-heptane + n-undecane, (▽) n-octane + n-undecane, (◇) n-nonane + n-undecane.

the present study are compared with previously published values (*7*).

In Figure 2 we present the maxima of V_m^E versus temperature for the three mixtures studied. These results allow to draw qualitative conclusions concerning the dependence of excess molar entropy S_m^E on pressure. Note that the maximum values of $-V_m^E$ increase with the difference between the chain lengths of the mixture's components and with the temperature.

According to Maxwell's equation

$$(\partial S_m^E/\partial P) = -(\partial V_m^E/\partial T) \quad (4)$$

and the previous paragraph, we get a positive derivative $(\partial S_m^E/\partial P)$, and the deviation from ideal behavior thus increases with pressure and with the difference in chain length of the components.

Registry No. Nonane, 111-84-2; undecane, 1120-21-4.

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Received for review January 30, 1987. Accepted October 1, 1987.

Estimation of Ion Product of Water in Sea Water

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The equations of Sweeton, Mesmer, and Baes, of Marshall and Mesmer, and of Marshall and Franck, which were found useful in estimating the ion product of pure water at different temperatures and pressures, have now been applied for predicting the ion product of water in sea water at 0 and 25 °C and up to 1000 bar pressure. By introduction of the density of sea water at a given pressure, the equation of Marshall and Franck describes some reliably calculated values for the ion product of water in sea water. The equation of Sweeton, Mesmer, and Baes with an added density relationship based on the equation of Marshall and Franck also provides these values.

Introduction

The self-ionization of water is a fundamental property for aqueous systems and is frequently used by electrolyte chemists, chemical oceanographers, and geochemists in their evaluations. In the past few years, a large number of equations representing the self-ionization of water in pure water and in aqueous NaCl solution under different conditions have been proposed. However, equations are not available for estimating the ion product of water in sea water up to high pressures. In this note, we examine two sets of equations given by (1) Sweeton, Mesmer, and Baes (*1*) and Marshall and Mesmer (*2*) and by (2) Marshall and Franck (*3*) for estimating values of the ion product of water in sea water (log K_w), applicable to high pressures. Throughout this study, we refer to K_w on the molality scale.

Equations

The equation of Sweeton, Mesmer, and Baes (SMB) (*1*) for the ionization of pure water at temperatures from 25 to 300 °C and at saturated pressure is given as

$$\ln K_w^0(\mathrm{SMB}) = 2.303(-606.52 - 2.1710 \times 10^6 T^{-2} + 3.1286 \times 10^4 T^{-1} - 9.7610 \times 10^{-2} T + 94.973 \ln T) \quad (1)$$

This expression can be combined with the equation of Marshall and Mesmer (SMARME) (*2*) to give

$$\ln K_w^0(\mathrm{SMARME}) = \ln K_w^0(\mathrm{SMB}) + 2.303(k - 1) \log \rho_p/\rho_1 \quad (2)$$

where according to Marshall and Franck (*3*)

$$k = 13.957 - 1.2623 \times 10^3 T^{-1} + 8.5641 \times 10^5 T^{-2} \quad (3)$$

and where ρ_p and ρ_1 are the densities at pressure p and 1 bar, respectively.

Marshall and Mesmer (*2*) expressed the ion product of pure water in terms of density at various pressures. According to Quist (*4*) and also Sweeton, Mesmer, and Baes (*1*), the density (ρ) describes the ion product of water more simply than pressure.

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