2. It is preferable to use the N_2O analogy to estimate the diffusivity of CO_2 in aqueous AMP solutions rather than the Stokes-Einstein relation.
3. An empirical correlation, based on the experimental data, is presented for calculating the density of aqueous AMP solutions over the temperature range 20-90 °C and the complete range of concentration.

Nomenclature

a	parameter of eq 10
b	parameter of eq 11
C_1	constant defined by eq 1
D	diffusivity, m^2/s
H	Henry's coefficient, $(kPa{\cdot}m^3)/kmol$
M	molarity of amine solution, $kmol/m^3$
t	temperature, °C
T	temperature, K
y	volume fraction
η	viscosity, $(N{\cdot}s)/m^2$
ρ	density, kg/m^3

Subscripts

am	alkanolamine
AMP	2-amino-2-methyl-1-propanol
CO_2	carbon dioxide
m	mixture
N_2O	nitrous oxide
sol.	amine solution
water	pure water

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Excess Volumes of *n*-Hexane + *n*-Undecane between 288.15 and 308.15 K

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Excess molar volumes of *n*-hexane + *n*-undecane have been determined from density measurements at 288.15, 293.15, 298.15, 303.15, and 308.15 K. The densities were obtained with an Anton Paar densimeter. The minimum values of V_m^E for the systems *n*-hexane, *n*-heptane, *n*-octane, and *n*-nonane + *n*-undecane are plotted against temperature.

Introduction

In previous works (*1-3*) the excess volumes of *n*-heptane + *n*-undecane, *n*-octane + *n*-undecane, and *n*-nonane + *n*-undecane at 288.15, 293.15, 298.15, 303.15, and 308.15 K have been determined. This article reports similar measurements for $(x)n\text{-}C_6H_{14} + (1 - x)n\text{-}C_{11}H_{24}$, together with three-parameter empirical equations fitted to the results obtained at each temperature.

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 (*4*). The *n*-hexane (Fluka purum grade, >99 mol %) and *n*-undecane (Merk, >99 mol %) were carefully dried with Union Carbide Type 4A molecular sieve (from Fluka) and were used directly without purification. The observed densities of *n*-hexane and *n*-undecane at the various temperatures employed are given in Table I, along with published values (*5-10*) for comparison.

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

	288.15 K	293.15 K	298.15 K	303.15 K	308.15 K
			Experimental Values		
n-hexane	0.664 02	0.659 47	0.654 95	0.650 33	0.645 72
n-undecane	0.744 29	0.740 59	0.736 90	0.733 20	0.729 51
			Literature Values		
n-hexane	0.663 45[a]	0.659 33[b]	0.655 09[c]	0.650 18[b]	0.645 78[d]
n-undecane	0.743 55[a]	0.740 17[e]	0.736 50[f]	0.732 84[f]	0.729 07[d]

[a] Reference 5. [b] Reference 6. [c] Reference 7. [d] Reference 8. [e] Reference 9. [f] Reference 10.

Results and Discussion

Table II lists the excess molar volumes V_m^E calculated from the observed densities for each temperature T and each value

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Table II. Excess Molar Volumes at Various Temperatures for $(x)n\text{-}C_6H_{14} + (1-x)n\text{-}C_{11}H_{24}$[a]

x	V^E_m/ (cm^3 mol^{-1})	δV^E_m/ (cm^3 mol^{-1})	x	V^E_m/ (cm^3 mol^{-1})	δV^E_m/ (cm^3 mol^{-1})
		288.15 K			
0.0925	-0.0642	-0.0005	0.5617	-0.2466	0.0003
0.1747	-0.1131	0.0004	0.5748	-0.2473	0.0001
0.1846	-0.1194	-0.0003	0.5953	-0.2474	0.0003
0.2242	-0.1397	0.0007	0.6098	-0.2476	-0.0004
0.2694	-0.1627	0.0001	0.6517	-0.2434	-0.0001
0.3132	-0.1831	-0.0005	0.7140	-0.2298	-0.0001
0.3457	-0.1959	-0.0001	0.7753	-0.2054	0.0001
0.4147	-0.2202	-0.0006	0.8330	-0.1720	-0.0003
0.4396	-0.2266	0.0001	0.8655	-0.1472	0.0002
0.5011	-0.2397	0.0003	0.9339	-0.0824	0.0001
		293.15 K			
0.0823	-0.0621	0.0006	0.5257	-0.2685	0.0001
0.1106	-0.0832	-0.0005	0.5526	-0.2712	0.0003
0.1476	-0.1063	0.0013	0.5724	-0.2733	-0.0005
0.1747	-0.1248	-0.0000	0.6351	-0.2711	-0.0004
0.2318	-0.1597	-0.0009	0.6849	-0.2615	0.0004
0.2946	-0.1925	-0.0004	0.7352	-0.2453	0.0004
0.3224	-0.2053	-0.0001	0.7545	-0.2374	-0.0001
0.4355	-0.2482	0.0004	0.8562	-0.1709	-0.0000
0.4516	-0.2536	-0.0004	0.8959	-0.1338	-0.0001
0.5134	-0.2662	0.0005	0.9203	-0.1076	-0.0005
		298.15 K			
0.0902	-0.0745	0.0001	0.5264	-0.2953	-0.0007
0.0997	-0.0817	0.0001	0.5517	-0.2975	0.0002
0.1675	-0.1316	-0.0002	0.6058	-0.2993	-0.0002
0.2366	-0.1770	-0.0004	0.6488	-0.2941	0.0007
0.2904	-0.2083	-0.0004	0.6848	-0.2879	-0.0008
0.2613	-0.1912	0.0003	0.7460	-0.2640	0.0002
0.3277	-0.2268	0.0006	0.7935	-0.2373	-0.0002
0.4374	-0.2727	0.0003	0.8148	-0.2218	0.0002
0.4456	-0.2758	-0.0001	0.8573	-0.1862	-0.0000
0.4919	-0.2880	0.0001	0.9188	-0.1189	0.0002
		303.15 K			
0.0885	-0.0797	0.0001	0.5355	-0.3224	0.0002
0.1007	-0.0895	0.0006	0.5716	-0.3262	-0.0001
0.1684	-0.1439	0.0000	0.5912	-0.3267	-0.0002
0.1991	-0.1666	-0.0001	0.6390	-0.3225	0.0005
0.2454	-0.1987	-0.0002	0.6701	-0.3164	0.0006
0.2907	-0.2268	0.0001	0.7458	-0.2884	-0.0002
0.3640	-0.2668	-0.0000	0.7964	-0.2563	0.0001
0.4264	-0.2943	-0.0005	0.8369	-0.2227	0.0001
0.4761	-0.3103	-0.0002	0.8697	-0.1902	-0.0004
0.5034	-0.3168	-0.0000	0.9123	-0.1390	-0.0004
		308.15 K			
0.0887	-0.0859	0.0005	0.5491	-0.3517	0.0003
0.1247	-0.1196	-0.0009	0.5888	-0.3543	0.0001
0.1513	-0.1414	0.0001	0.6029	-0.3535	0.0006
0.2209	-0.1968	0.0003	0.6465	-0.3502	-0.0011
0.2762	-0.2368	-0.0003	0.6686	-0.3447	-0.0005
0.3364	-0.2740	0.0002	0.7010	-0.3337	-0.0001
0.3910	-0.3030	0.0001	0.7118	-0.3290	0.0002
0.4375	-0.3237	-0.0004	0.8064	-0.2691	0.0003
0.4758	-0.3364	0.0001	0.8703	-0.2045	0.0001
0.5274	-0.3484	0.0005	0.9269	-0.1282	0.0002

[a] $\delta V^E_m = V^E_m(\text{obsd}) - V^E_m(\text{calcd})$.

Table III. Parameters A_k of Equation 1 and Standard Deviations σ of Fit

T/K	A_0	A_1	A_2	σ
288.15	-0.959 324	-0.338 0011	-0.112 5578	0.000 35
293.15	-1.057 572	-0.375 7918	-0.124 0496	0.000 53
298.15	-1.159 443	-0.413 4080	-0.130 4254	0.000 40
303.15	-1.264 263	-0.450 5399	-0.141 8263	0.000 33
308.15	-1.372 379	-0.487 5558	-0.144 4249	0.000 47

of the mole fraction of *n*-hexane x. For each T, equations of the form

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

were fitted to the experimental results. The parameters A_k and the standard deviations are listed in Table III, and Figure 1 shows the fitted V^E_m curves, together with the experimental points. In all cases V^E_m is negative and the curves are asymmetric with a minimum at $x = 0.5900$. These results are in accordance with the work of Marsh and Ott (*11*) at 298.15 and 308.15 K.

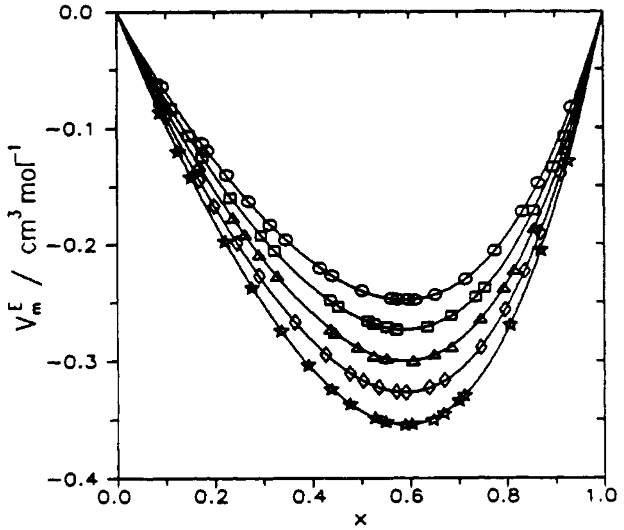

Figure 1. V^E_m of $(x)n\text{-}C_6H_{14} + (1-x)n\text{-}C_{11}H_{24}$ at 288.15 (○), 293.15, (□), 298.15 (◇), and 308.15 K (☆).

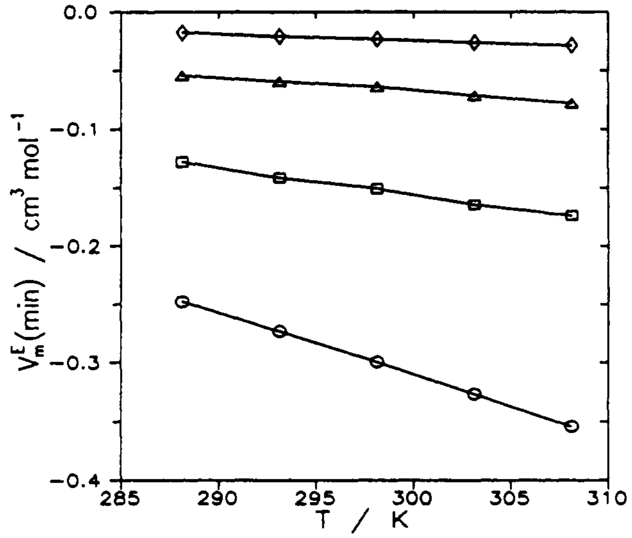

Figure 2. Minimum of V^E_m for the systems *n*-hexane (○), *n*-heptane (□), *n*-octane (△), and *n*-nonane (◇) + *n*-undecane, plotted versus temperature.

In Figure 2 we present the minimum of V^E_m versus temperature for the *n*-alkane + *n*-undecane mixtures studied in this and previous works. The absolute value of the excess volume decreases as the length of the *n*-alkane chain increases, showing a parallel reduction in the interactions in the mixture with respect to the pure components. On mixing, AA and BB interactions (where A is *n*-undecane and B the other *n*-alkane) are replaced by AB interactions, whose dispersive nature suggests that, in keeping with the relative sizes of the molecules involved, AA > AB > BB (though polarization of *n*-undecane should be greater with *n*-hexane than *n*-nonane). Though it is difficult to quantify this effect without further structural information, it nevertheless seems reasonable to attribute the variation in excess volume largely to the reduction of the coordination number of *n*-undecane as the length of the other component increases and the A/B size ratio decreases. This reduction in coordination number would be accompanied by a decrease in the magnitude of the AB interaction as a whole, as is reflected by the variation in the mole fraction at which the

Table IV. Mole Fraction at Which the Excess Volume Is Minimum[a]

	$x(V_m^E(\min))$	$V_m^E\min$	r_B/r_A
n-hexane	0.5900	−0.2995	0.8257
n-heptane	0.5684	−0.1506	0.8664
n-octane	0.5486	−0.0634	0.9036
n-nonane	0.5269	−0.0231	0.9380

[a] r_B/r_A is the ratio of molecular radius of B (*n*-undecane) and A (other *n*-alkane).

excess volume in minimum (see Table IV, which also lists approximate radii calculated from polarizabilities with use of molar refraction data (*12*)).

The absolute values of the excess volumes increased slightly with temperature. This effect too decreased as the length of the B chain increased. Temperature did not significantly affect the mole fraction at which the maximum absolute excess volume occurred. In interpreting these results, it must be borne in mind that at the working temperatures the molecules involved all have several significant conformations. Increasing temperature increases the proportion of higher energy conformations and so changes the feature of the intermolecular interactions. However, detailed explanation of our experimental results in these terms requires a conformational analysis that lies outside the scope of this article.

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Effect of Aluminum, Iron, and Magnesium upon the Solubility of α-Calcium Sulfate Hemihydrate in 40%, 45%, 50%, and 55% P_2O_5 Phosphoric Acid Solutions at 80, 90, 100, and 110 °C: Correlations with Water Concentration

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The influence of the common wet-process phosphoric acid impurities [Al_2O_3 (1.50%), Fe_2O_3 (2.15%), and MgO (0.50%)] upon the solubility of α-calcium sulfate hemihydrate in 40%, 45%, 50%, and 55% P_2O_5 phosphoric acid solutions at 80, 90, 100, and 110 °C, respectively, were measured. These additives were found to have very little influence upon α-$CaSO_4{\cdot}0.5H_2O$ solubility when the data are compared at equal water contents. The weight percent solubility in terms of anhydrous calcium sulfate is given by the equation $\%\ CaSO_4 = -0.39820685 + 0.00442936t + 0.00031947(\%\ H_2O)^2 + 0.00011517t(\%\ H_2O)$, where t is the temperature (°C) and % H_2O is the weight percent of water in the solution. Slight deviations in solubility are discussed in terms of enthalpy and entropy effects.

Introduction

Previously, we reported the solubility of α-calcium sulfate hemihydrate in phosphoric acid solutions ranging in concentrations from 40% to 55% P_2O_5 at temperatures of 80–110 °C (*1*). These are the concentration and temperature ranges of relevance for the production of concentrated wet-process phosphoric acid by "hemihydrate processes", i.e., processes in which phosphate rock is digested with sulfuric acid to produce phosphoric acid and insoluble byproduct calcium sulfate hemihydrate, $Ca(SO_4){\cdot}0.5H_2O$.

In the present publication, we describe the individual effects of typical concentrations of the phosphate rock derived impurities, Al, Fe, and Mg, upon the solubility of $CaSO_4{\cdot}0.5H_2O$ at P_2O_5 concentrations of 40–55% and temperatures of 80–110 °C. Limited work in this area has been conducted primarily by Russian investigators. For example, Kremenetskaya et al. (*2*) found that the combined effect of CaO and MgO was to lower the solubility of both $CaSO_4{\cdot}2H_2O$ and $CaSO_4{\cdot}0.5H_2O$ at P_2O_5 concentrations ranging from 30% to 40% and temperatures ranging from 60 to 90 °C. Shpunt et al. (*3*) obtained slight reductions in $CaSO_4{\cdot}0.5H_2O$ solubility with MgO alone at 80 °C and concentrations of 20–45% P_2O_5. Other investigators have studied the combined effect of Al_2O_3, F^-, and SiF_6^{2-} upon the solubilities and transition parameters for $CaSO_4{\cdot}2H_2O$–$CaSO_4{\cdot}0.5H_2O$–H_3PO_4 systems (*4*, *5*). In the cases investigated, the data were correlated in terms of P_2O_5 concentration rather than the total salt and acid content of the concentrated solutions.

In our previous publication (*1*), we also expressed the solubility data for the pure $CaSO_4{\cdot}0.5H_2O$–H_3PO_4–H_2O system in terms of weight percent P_2O_5 concentration and temperature. Since the concentration of water in an aqueous solution is inversely related to the concentrations of the remaining soluble components, it now appears of more general applicability to correlate the present and previous results in terms of water concentration and temperature, where "water concentration" (% H_2O) is defined as the calculated percentage of water present in the solutions, as determined by difference after as-