Glossary

A	symbols subscripted A refer to $HClO_4$
B	symbols subscripted B refer to $Ba(ClO_4)_2$
m	molal concentration, mol/kg
I	total ionic strength, mol/kg
y	ionic strength fraction
ϕ	molal osmotic coefficient
$\gamma_\pm$	mean molal activity coefficient
a, $a(1)$, $a(2)$, $a(3)$, $a(4)$	parameters in Scatchard equations for single electrolytes, see ref *1*
$b(01)$, $b(02)$, $b(03)$, $b(12)$, $b(13)$	parameters in Scatchard equations for electrolyte mixtures, see ref *1*
$\sigma(\phi)$	standard deviation for osmotic coefficients

Registry No. $HClO_4$, 7601-90-3; $Ba(ClO_4)_2$, 13465-95-7.

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

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Excess molar volumes of *n*-octane + *n*-undecane have been determined from density measurements at 288.15, 293.15, 298.15, 303.15, and 308.15 K, and an approximation to $(\partial V_m^E/\partial T)_p$ in the neighborhood of 298.15 K has been calculated.

Introduction

This article reports excess volumes of $\{xn\text{-}C_8H_{18} + (1-x)C_{11}H_{24}\}$ determined from density measurements at 288.15, 293.15, 298.15, 303.15, and 308.15 K for $0 \le x \le 1$. Three-parameter empirical equations have been fitted to the results for each temperature. By fitting a quadratic in T to the five values obtained for each parameter, an approximate expression for $(\partial V_m^E/\partial T)_p$ in the neighborhood of 298.15 K has been obtained.

Experimental Section

Densities were measured with an Anton Paar D.M.A. 60/602 densimeter with 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 theromostat. The operational technique has been described elsewhere (*1*). The *n*-octane (Fluka purum >99 mol %) and *n*-undecane (Merck, >99 mol %) were carefully dried with molecular sieves (Union Carbide type 4A, from Fluka) and used directly without further purification. The densities of *n*-octane and *n*-undecane at the various temperatures employed are given in Table I along with values at 293.15 and 298.15 K from the literature for comparison (*2*, *3*).

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

	T/K				
	288.15	393.15	298.15	303.15	308.15
		Experimental			
n-octane	0.70660	0.70256	0.69853	0.69448	0.69042
n-undecane	0.74429	0.74059	0.73690	0.73320	0.72951
		Literature			
n-octane		0.70252^a	0.69849^a		
n-undecane		0.74017^b			

^{a} Reference *2*. ^{b} Reference *3*.

Results and Discussion

Table II lists the excess molar volumes V_m^E calculated from the densities for each x and T. For each T, equations of the form

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

were fitted (*4*) to the experimental results. The parameters A_k and standard deviations of fit are listed in Table III. Figure 1 shows the fitted V_m^E curves.

Once the A_k has been estimated, quadratics in T were fitted

$$A_k(T) = A_{k0} + A_{k1}(T/k) + A_{k2}(T/k)^2 \qquad (2)$$

The values so obtained for the A_{kj} are listed in Table IV. Equations 1 and 2 allow an approximation to $(\partial V_m^E/\partial T)_p$ to be

Table II. Excess Molar Volumes at Various Temperatures for $\{xC_8H_{16} + (1 - x)C_{11}H_{24}\}$; $\partial V_m^E = V_m^E(\text{obsd}) - V_m^E(\text{calcd})$

x	V_m^E/ (cm^3·mol^{-1})	∂V_m^E/ (cm^3·mol^{-1})	x	V_m^E/ (cm^3·mol^{-1})	∂V_m^E/ (cm^3·mol^{-1})	x	V_m^E/ (cm^3·mol^{-1})	∂V_m^E/ (cm^3·mol^{-1})	x	V_m^E/ (cm^3·mol^{-1})	∂V_m^E/ (cm^3·mol^{-1})
	288.15 K		0.2954	−0.0440	0.0006	0.4813	−0.0617	0.0008	0.6860	−0.0665	−0.0016
0.0886	−0.0150	0.0004	0.3256	−0.0478	−0.0001	0.5134	−0.0632	0.0000	0.7317	−0.0601	0.0001
0.1485	−0.0242	0.0001	0.3448	−0.0504	−0.0009	0.5428	−0.0631	0.0003	0.7800	−0.0535	0.0001
0.1946	−0.0305	−0.0001	0.3835	−0.0516	0.0011	0.5902	−0.0629	−0.0002	0.8034	−0.0491	0.0007
0.2601	−0.0377	0.0003	0.4444	−0.0557	0.0008	0.6448	−0.0614	−0.0010	0.8444	−0.0421	0.0000
0.3051	−0.0434	−0.0010	0.4897	−0.0579	0.0003	0.6823	−0.0575	0.0002	0.8786	−0.0347	−0.0001
0.3588	−0.0454	0.0013	0.5259	−0.0598	−0.0009	0.7327	−0.0524	0.0005			
0.4078	−0.0511	−0.0012	0.5599	−0.0592	−0.0002	0.7883	−0.0454	0.0003		308.15 K	
0.4383	−0.0513	0.0001	0.5997	−0.0585	−0.0002	0.8068	−0.0426	0.0003	0.0796	−0.0180	0.0009
0.4623	−0.0539	−0.0015	0.6320	−0.0579	−0.0007	0.8676	−0.0321	−0.0001	0.1617	−0.0371	−0.0010
0.5070	−0.0522	0.0014	0.6748	−0.0552	−0.0004	0.8980	−0.0261	−0.0004	0.2183	−0.0462	−0.0462
0.5349	−0.0540	0.0000	0.7102	−0.0523	−0.0003				0.2642	−0.0539	−0.0000
0.5719	−0.0537	0.0002	0.7284	−0.0489	0.0014		303.15 K		0.2988	−0.0589	−0.0000
0.5930	−0.0530	0.0007	0.7828	−0.0442	−0.0002	0.1151	−0.0252	−0.0003	0.3255	−0.0618	0.0006
0.6482	−0.0517	0.0003	0.8551	−0.0332	−0.0003	0.1574	−0.0328	0.0000	0.3797	−0.0690	−0.0005
0.6813	−0.0502	0.0001	0.8841	−0.0268	0.0006	0.2033	−0.0410	−0.0002	0.3949	−0.0699	0.0000
0.7349	−0.0473	−0.0010				0.2505	−0.0480	0.0001	0.4559	−0.0738	0.0007
0.7603	−0.0439	−0.0001		298.15 K		0.3013	−0.0545	0.0004	0.4920	−0.0774	−0.0011
0.8021	−0.0394	−0.0003	0.0859	−0.0176	−0.0011	0.3471	−0.0599	0.0002	0.5403	−0.0774	0.0001
0.8408	−0.0335	0.0001	0.1467	−0.0273	−0.0002	0.3909	−0.0645	−0.0002	0.5541	−0.0767	0.0009
0.8940	−0.0240	0.0005	0.2012	−0.0351	0.0007	0.3997	−0.0650	−0.0000	0.6063	−0.0771	−0.0004
			0.2375	−0.0403	0.0007	0.4311	−0.0672	−0.0000	0.6509	−0.0752	−0.0006
	293.15 K		0.2755	−0.0459	0.0001	0.4733	−0.0692	0.0002	0.6852	−0.0717	0.0002
0.0898	−0.0164	−0.0006	0.3038	−0.0499	−0.0005	0.5153	−0.0709	−0.0003	0.6966	−0.0698	0.0011
0.1503	−0.0262	−0.0007	0.3445	−0.0530	0.0007	0.5507	−0.0714	−0.0005	0.7441	−0.0667	−0.0014
0.1998	−0.0320	0.0008	0.3918	−0.0586	−0.0009	0.6004	−0.0684	0.0017	0.7991	−0.0557	0.0008
0.2488	−0.0397	−0.0005	0.4545	−0.0622	−0.0007	0.6494	−0.0681	−0.0004	0.8390	−0.0483	0.0001
									0.9034	−0.0326	−0.0003

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

	T/K				
	288.15	293.15	298.15	303.15	308.15
A_0	−0.213863	−0.233880	−0.251962	−0.281003	−0.306413
A_1	−0.042625	−0.046154	−0.043109	−0.052945	−0.068299
A_2	−0.017047	0.003170	0.009825	−0.006343	−0.012818
s	0.0008	0.0007	0.0006	0.0006	0.0007

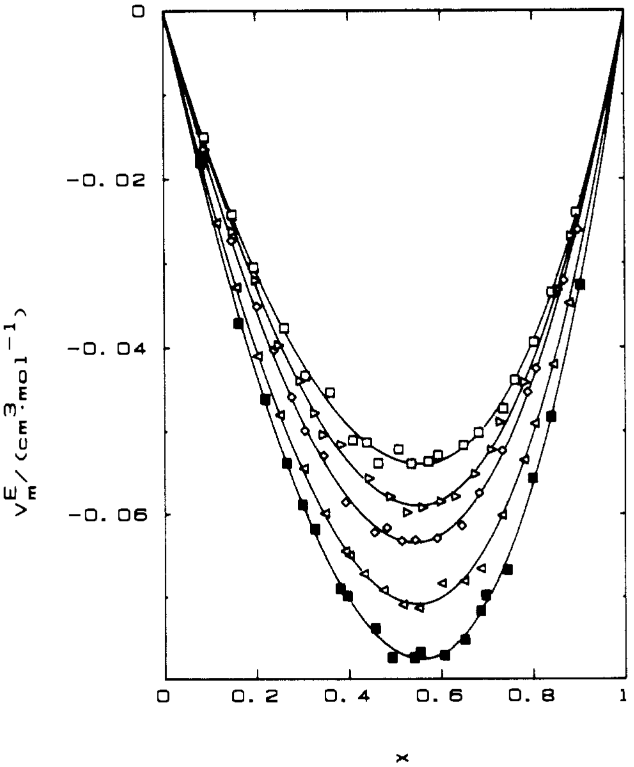

Figure 1. V_m^E of $\{xC_8H_{16} + (1 - x)C_{11}H_{24}\}$ at 288.15 (□), 293.15 (▷), 298.15 (◇), 303.15 (◁), and 308.15 K (■).

Table IV. Parameters A_{kj} of Eq 2

	j		
	0	1	2
A_{0j}	−4.39248	0.03240	−0.00006
A_{1j}	−8.97689	0.06107	−0.00010
A_{2j}	−19.34216	0.12981	−0.00021

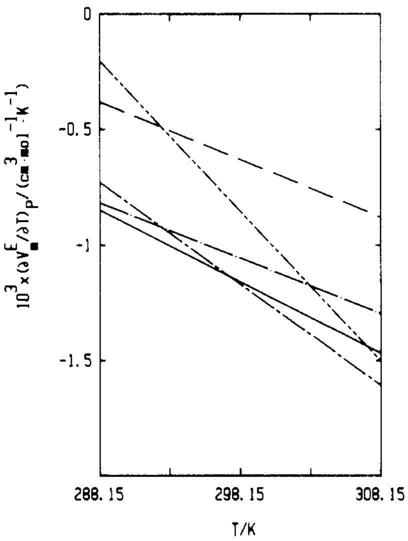

Figure 2. $(\partial V_m^E/\partial T)_p$ for $\{xC_8H_{16} + (1 - x)C_{11}H_{24}\}$: (- - -) $x = 0.2$; (-·-·-) $x = 0.4$; (—) $x = 0.5$; (- - - -) $x = 0.6$; (- -- -- -) $x = 0.8$.

calculated. Figure 2 shows the resulting graphs of $(\partial V_m^E/\partial T)_p$ against T for various values of x.

Figure 1 shows that V_m^E is in all cases negative and the V_m^E curve asymmetric, with a minimum at $x = 0.55$. The absolute value of V_m^E increases with T. Figure 2 shows that in the neighborhood of 298.15 K the first-order temperature dependence of $(\partial V_m^E/\partial T)_p$ has a negative slope for all mole fractions.

Registry No. *n*-Octane, 111-65-9; *n*-undecane, 1120-21-4.

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Excess Volumes of Binary 1-Alkanol/Nonane Mixtures at Temperatures between 293.15 and 333.15 K

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Excess volumes V^E of 1-propanol, 1-hexanol, 1-octanol, 1-decanol, and 1-dodecanol + nonane binary mixtures have been measured at 293.15, 298.15, and 333.15 K with a vibrating tube densitometer. The temperature dependence of V^E is discussed qualitatively in terms of a chemical and a physical contribution to V^E. The data can be used to test a quantitative theoretical approach published recently which allows one to describe not only G^E, H^E, and $C_p{}^E$ but also V^E for alkanol/alkane mixtures.

Introduction

Thermodynamic excess properties of alkanol/alkane mixtures have gained large interest during the last years. Since 1984 regular workshop meetings sponsored by the IUPAC have been held annually in order to coordinate research activities in thermodynamics of 1-alkanol/*n*-alkane mixtures.

Systematic studies of the excess Gibbs energy G^E, the excess enthalpy H^E, and the excess volume V^E provide important information for better understanding of the molecular liquid structure and intermolecular interactions predominated by the association of alkanol molecules due to hydrogen bonding. With the exception of mixtures containing methanol and ethanol, only a few systematic data of V^E for higher 1-alkanol/*n*-alkane mixtures existed in literature before 1977 (*1–4*). More recently precise measurements of V^E have been performed for quite a number of such mixtures whereby the chain length of the alkanol and/or the alkane has been changed systematically (*5–12*). Most of these data, however, have been obtained only at 298.15 K. In this work new data of V^E are presented for mixtures of 1-propanol, 1-hexanol, 1-octanol, 1-decanol, and 1-dodecanol + nonane at different temperatures between 293.15 and 333.15 K. Such data allow one to test sensitively the applicability of theoretical concepts which not only describe G^E and H^E but also V^E. Recently such a theoretical approach has been developed by Heintz (*13*), which combines a free volume model with an association model.

Experimental Section

Excess volumes are measured by using a vibrating tube densitometer. This method has become a widely used technique for measuring densities of liquids and liquid mixtures. V^E data can be determined with a precision comparable with that obtained by using the more conventional dilatometric technique. The principal experimental procedure of measuring V^E by this method has already been described previously (*14*). Water and dry air have been used for calibrating the apparatus and the constancy of the parameters of the vibrating tube has been checked with the liquids hexane and cyclohexane for which the densities are accurately known from literature. In applying this densitometric method for determining V^E special care has to be taken to correct for losses of liquid into the vapor space when the liquid mixtures are prepared by weighing the components into a flask. Since V^E is determined as the small difference of large values of volumes an exact knowledge not only of the density but also of the composition of the mixture is indispensable.

Table I. Experimental Densities of 1-Alkanols and Nonane

		$\rho/(\mathrm{g\ cm^{-3}})$	
substance	T/K	this work	lit.
1-propanol	293.15	0.803 78	0.80375 (*16*), 0.80386 (*17*)
	298.15	0.799 81	0.79975 (*16*), 0.79991 (*17*)
	333.15	0.770 58	0.7704 (*16*), 0.77080 (*17*)
1-hexanol	293.15	0.818 90	0.8198 (*16*), 0.81914 (*17*)
	298.15	0.815 34	0.8162 (*16*), 0.81565 (*17*)
	333.15	0.789 40	0.7903 (*16*), 0.78995 (*17*)
1-octanol	293.15	0.825 16	0.8258 (*16*), 0.82610 (*17*)
	298.15	0.821 79	0.8223 (*16*), 0.82259 (*17*)
	333.15	0.796 94	0.7970 (*16*), 0.79758 (*17*)
1-decanol	293.15	0.829 82	0.8297 (*16*), 0.82957 (*17*)
	298.15	0.826 44	0.8263 (*16*), 0.82623 (*17*)
	333.15	0.802 02	0.8017 (*16*), 0.80203 (*17*)
1-dodecanol	298.15	0.823 00	0.8308 (*16*), 0.82995 (*17*)
	333.15	0.805 81	0.8063 (*16*), 0.80606 (*17*)
nonane	293.15	0.717 93	0.7177 (*18*), 0.71799 (*19*)
	298.15	0.714 10	0.7139 (*18*), 0.71412 (*19*)
	333.15	0.686 42	0.6864 (*18*), 0.68652 (*19*)

The nonane mixtures containing the alkanols studied in this work are prepared at 25 °C. Since the components have sufficiently low vapor pressures at this temperature the corrections for losses into the vapor space are negligible compared with other experimental error sources which influence the accuracy of V^E. Therefore the procedure of correcting for the effect of evaporation on the liquid composition is discussed in more detail in a forthcoming paper (*15*) which deals with 1-alkanol/hexane mixtures where these effects play a much more dominant role.

The accuracy of the V^E measurements depends on the error limits of the densities of the liquid samples and their composition. The accuracy of the measured densities is essentially determined by the constancy of the temperature in the cell which contains the vibrating tube. In order to minimize the influence of fluctuations in temperature a special method has been applied by using a second cell which serves as a reference cell. Cell 1 contains the mixture under study and cell 2 is filled with water. The frequency of cell 1 is determined electronically by using the frequency of cell 2 as the basis for

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