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EXCESS VOLUMES OF TRIMETHYLPHOSPHITE AND TRIBUTYLPHOSPHATE WITH BRANCHED AND LINEAR ALKANES

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ABSTRACT

Excess volumes are reported at 298.15 K for trimethylphosphite and tributylphosphate with n-alkanes (from n-hexane to n-hexadecane), and with two branched alkanes: 2,2,4-trimethylpentane and 2,2,4,4,6,8,8-heptamethylnonane. The positive contribution due to disordering of the longer alkanes increases with the presence of the (PO) group in the tributylphosphate molecule.

INTRODUCTION

Continuing the study of excess molar volumes of globular molecules (like tributylphosphite) with n-alkanes [1] to show the presence of short-range orientational order in the liquid phase of long-chain n-alkanes and the loss of this order when n-alkanes are mixed with a second component of more globular shape [2,3], we report here the excess volumes of mixing at 298.15 K of trimethylphosphite and tributylphosphate with n-alkanes (from n-hexane to n-hexadecane) and also with two branched alkanes: 2,2,4-trimethylpentane and 2,2,4,4,6,8,8-heptamethylnonane. Measurements with trimethylphosphate are not possible because the mixtures with n-alkanes are not miscible at this temperature. Moreover the choice of this system shows the influence of the size of methyl and butyl chains of phosphite molecules, and also the possibility of correlation of n-alkanes between these chains. The comparison of excess volumes of tributylphosphite [1] and tributylphosphate with alkanes demonstrates a specific contribution due to the (PO) group of the tributylphosphate molecule.

EXPERIMENTAL

The solvents used in this work are trimethylphosphite (EGA Chemie, > 97 mol%), tributylphosphate (Fluka, puriss > 99%), and the others are the same as those used in ref. 1. Excess molar volumes were calculated at 298.15 K from density measurements of pure liquids and their mixtures made with a vibrating-tube densimeter DMA 60 (Anton Paar, Graz, Austria).

RESULTS

The experimental values of V_m^E for the different systems are summarized in Tables 1 and 2. The polynomial form

$$V_m^E\ (\text{cm}^3\ \text{mol}^{-1}) = x(1-x)\sum_{j=0}^{4} A_j(2x-1)^j \qquad (1)$$

was fitted to each set of results by the least-squares method. The coefficient A_j and the standard deviation

$$\sigma\left(V_m^E\right) = \left[\Sigma\left(V_{m(\text{cal})}^E - V_m^E\right)^2/(N-M)\right]^{1/2}$$

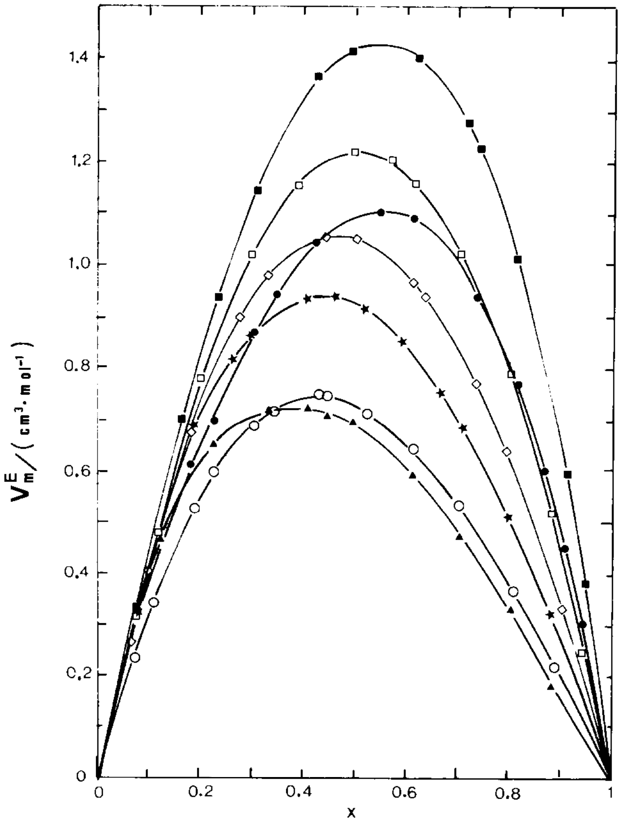

Fig. 1. Excess molar volumes V_m^E for $\{x[CH_3O]_3P+(1-x)C_nH_{2n+2}\}$ at 298.15 K. ▲, n-hexane; ★, n-heptane; ◇, n-octane; □, n-decane; ■, n-hexadecane; ○, 2,2,4-trimethylpentane; ●, 2,2,4,4,6,8,8-heptamethylnonane.

TABLE 1

Experimental excess molar volumes V_m^E at 298.15 K of $\{x[CH_3O]_3P+(1-x)C_nH_{2n+2}\}$

x	V_m^E ($cm^3\ mol^{-1}$)	x	V_m^E ($cm^3\ mol^{-1}$)	x	V_m^E ($cm^3\ mol^{-1}$)	x	V_m^E ($cm^3\ mol^{-1}$)	x	V_m^E ($cm^3\ mol^{-1}$)
$C_nH_{2n+2} = C_6H_{14}$									
0.1233	0.470	0.3297	0.714	0.4460	0.701	0.6090	0.590	0.8054	0.335
0.2268	0.652	0.4094	0.725	0.4964	0.697	0.7028	0.470	0.8819	0.176
C_7H_{16}									
0.0716	0.321	0.2999	0.864	0.5222	0.910	0.7094	0.685		
0.1929	0.681	0.3996	0.933	0.5930	0.857	0.7955	0.510		
0.2610	0.814	0.4583	0.937	0.6611	0.750	0.8778	0.319		
C_8H_{18}									
0.0645	0.268	0.2734	0.899	0.5036	1.047	0.7328	0.769		
0.0948	0.415	0.3290	0.977	0.6081	0.965	0.7933	0.638		
0.1846	0.678	0.4414	1.056	0.6356	0.941	0.9023	0.333		
$C_{10}H_{22}$									
0.0753	0.312	0.3000	1.020	0.5651	1.199	0.8024	0.785		
0.1168	0.479	0.3915	1.150	0.6150	1.157	0.8844	0.515		
0.2001	0.777	0.4975	1.219	0.7032	1.024	0.9455	0.244		
$C_{16}H_{34}$									
0.0727	0.328	0.3103	1.141	0.6211	1.398	0.8145	1.012		
0.1626	0.699	0.4256	1.364	0.7190	1.274	0.9138	0.593		
0.2354	0.937	0.4956	1.410	0.7439	1.227	0.9482	0.381		
$CH_3C(CH_3)_2CH_2CH(CH_3)CH_3$									
0.0743	0.229	0.2269	0.597	0.4301	0.749	0.6113	0.642	0.8868	0.218
0.1058	0.340	0.3032	0.686	0.4421	0.737	0.7004	0.531		
0.1876	0.525	0.3402	0.713	0.5229	0.711	0.8043	0.368		
$CH_3C(CH_3)_2CH_2C(CH_3)_2CH_2CH(CH_3)CH_2C(CH_3)_2CH_3$									
0.1804	0.604	0.3462	0.944	0.6054	1.089	0.8668	0.600		
0.2240	0.689	0.4231	1.045	0.7342	0.939	0.9057	0.451		
0.3036	0.870	0.5461	1.107	0.8141	0.769	0.9419	0.303		

TABLE 2

Experimental excess molar volumes V_m^E at 298.15 K of $\{x[CH_3(CH_2)_3O]_3PO+(1-x)C_nH_{2n+2}\}$

x	V_m^E (cm^3 mol^{-1})	x	V_m^E (cm^3 mol^{-1})	x	V_m^E (cm^3 mol^{-1})	x	V_m^E (cm^3 mol^{-1})	x	V_m^E (cm^3 mol^{-1})
$C_nH_{2n+2} = C_6H_{14}$									
0.0835	−0.096	0.2575	−0.224	0.4591	−0.276	0.6595	−0.239	0.8130	−0.158
0.1863	−0.158	0.3050	−0.231	0.5018	−0.260	0.7035	−0.266	0.8716	−0.110
0.2002	−0.166	0.4150	−0.260	0.5509	−0.256	0.7598	−0.191		
C_7H_{16}									
0.1026	0.047	0.3073	0.070	0.5581	0.029	0.7485	−0.034		
0.1531	0.054	0.4107	0.058	0.6164	0.024	0.8307	−0.036		
0.2012	0.076	0.5067	0.040	0.6796	−0.006	0.8983	−0.026		
C_8H_{18}									
0.0745	0.152	0.3037	0.295	0.4551	0.278	0.7144	0.181		
0.1195	0.188	0.3519	0.301	0.5159	0.274	0.8073	0.117		
0.1992	0.269	0.4056	0.281	0.6068	0.247	0.8431	0.099		
$C_{10}H_{22}$									
0.0618	0.213	0.3081	0.584	0.5081	0.597	0.7903	0.334		
0.1052	0.315	0.4029	0.591	0.6239	0.524	0.8897	0.196		
0.2047	0.476	0.4612	0.597	0.7051	0.452				

$C_{12}H_{26}$									
0.0703	0.284	0.2471	0.663	0.4641	0.765	0.5812	0.718	0.8109	0.451
0.1063	0.390	0.3121	0.718	0.5120	0.761	0.6038	0.715	0.8678	0.332
0.1994	0.592	0.4099	0.743	0.5130	0.764	0.7059	0.609	0.9028	0.245
$C_{16}H_{34}$									
0.0599	0.297	0.3017	0.941	0.6057	0.993	0.9169	0.360		
0.1295	0.554	0.4118	1.032	0.7074	0.871				
0.1973	0.750	0.5011	1.048	0.8182	0.674				
$CH_3C(CH_3)_2CH_2CH(CH_3)CH_3$									
0.1028	−0.105	0.3106	−0.260	0.4993	−0.308	0.8228	−0.168		
0.1868	−0.180	0.4054	−0.305	0.6181	−0.272	0.8716	−0.106		
0.2519	−0.229	0.4099	−0.301	0.7192	−0.233	0.9045	−0.083		
$CH_3C(CH_3)_2CH_2C(CH_3)_2CH_2CH(CH_3)CH_2C(CH_3)_2CH_3$									
0.0973	0.231	0.4044	0.532	0.7024	0.456	0.9317	0.137		
0.2027	0.390	0.5047	0.557	0.7849	0.365				
0.3063	0.488	0.6044	0.518	0.8339	0.299				

TABLE 3

Parameters A_j of eqn. (1) and standard deviation $\sigma(V_m^E)$ for $\{x[CH_3O]_3P+(1-x)C_nH_{2n+2}\}$

$x[CH_3O]_3P+$	A_0	A_1	A_2	A_3	A_4	$\sigma(V_m^E)$ (cm^3 mol^{-1})
$(1-x)C_6H_{14}$	2.7326	−1.1965	0.6716	−0.8676	−0.1420	0.010
$(1-x)C_7H_{16}$	3.6966	−0.9592	0.0824	−0.2222	0.1750	0.004
$(1-x)C_8H_{18}$	4.2014	−0.6500	0.1188	0.1938	−0.1678	0.009
$(1-x)C_{10}H_{22}$	4.8543	0.0370	0.3842	0.2559	−0.8000	0.006
$(1-x)C_{16}H_{34}$	5.6742	0.9745	0.5897	0.8105	0.2667	0.007
$(1-x)CH_3C(CH_3)_2CH_2CH(CH_3)CH_3$	2.8937	−0.9329	0.1313	0.1217	−0.4107	0.006
$(1-x)CH_3C(CH_3)_2CH_2C(CH_3)_2CH_2CH(CH_3)CH_2C(CH_3)_2CH_3$	4.3907	0.8132	0.1496	−0.0348	0.4997	0.006

TABLE 4

Parameters A_j of eqn. (1) and standard deviation $\sigma(V_m^E)$ for $\{x[CH_3(CH_2)_3O]_3PO+(1-x)C_nH_{2n+2}\}$

$x[CH_3(CH_2)_3O]_3PO+$	A_0	A_1	A_2	A_3	A_4	$\sigma(V_m^E)$ (cm^3 mol^{-1})
$(1-x)C_6H_{14}$	−1.0744	0.0204	−0.0004	0.0945	0.0322	0.008
$(1-x)C_7H_{16}$	0.1815	−0.4773	−0.3377	−0.1048	0.3227	0.007
$(1-x)C_8H_{18}$	1.0951	−0.4871	0.4419	−0.6215	−0.2491	0.008
$(1-x)C_{10}H_{22}$	2.3726	−0.5986	0.2643	−0.4687	0.3270	0.008
$(1-x)C_{12}H_{26}$	3.0302	−0.4082	0.8809	−0.6743	−0.2297	0.006
$(1-x)C_{16}H_{34}$	4.1783	−0.3275	1.0623	0.1999	0.0930	0.005
$(1-x)CH_3C(CH_3)_2CH_2CH(CH_3)CH_3$	−1.2242	0.1042	0.1316	−0.0451	0.2328	0.006
$(1-x)CH_3C(CH_3)_2CH_2C(CH_3)_2CH_2CH(CH_3)CH_2C(CH_3)_2CH_3$	2.2010	−0.1059	0.1767	−0.2870	0.1914	0.004

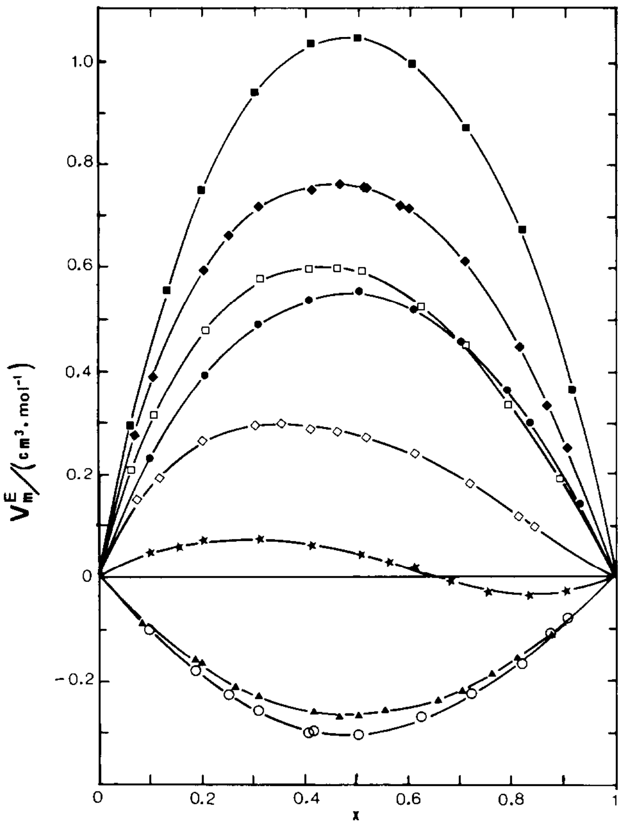

Fig. 2. Excess molar volumes V_m^E for $\{x[CH_3(CH_2)_3O]_3PO+(1-x)C_nH_{2n+2}\}$ at 298.15 K. ▲, n-hexane; ★, n-heptane; ◇, n-octane; □, n-decane; ◆, n-dodecane; ■, n-hexadecane; ○, 2,2,4-trimethylpentane; ●, 2,2,4,4,6,8,8-heptamethylnonane.

where N is the number of direct experimental values and M the number of coefficients A_j, which are listed in Tables 3 and 4. The smoothed representations and the experimental points are shown in Figs. 1 and 2.

In the two groups of mixtures the excess volumes become more symmetrical with the longer alkanes and there are no large differences in symmetry between systems containing hexadecane and the branched isomer. As in the previous work [1] the values of V_m^E of mixing increase with the chain-length of linear alkanes: this positive effect on V_m^E is due to the disruption of correlation of molecular orientations existing in the long chains of pure alkanes when these are mixed with a second component of more globular shape. For branched alkanes, for example heptamethylnonane, which has a globular shape covered with methyl groups, the orientational order is absent; moreover, molecular models show that heptamethylnonane may be considered as a cylinder with a length/diameter ratio of 1.9, while n-hexadecane is chain-like with a length/diameter ratio of 5.0 [4]. Conse-

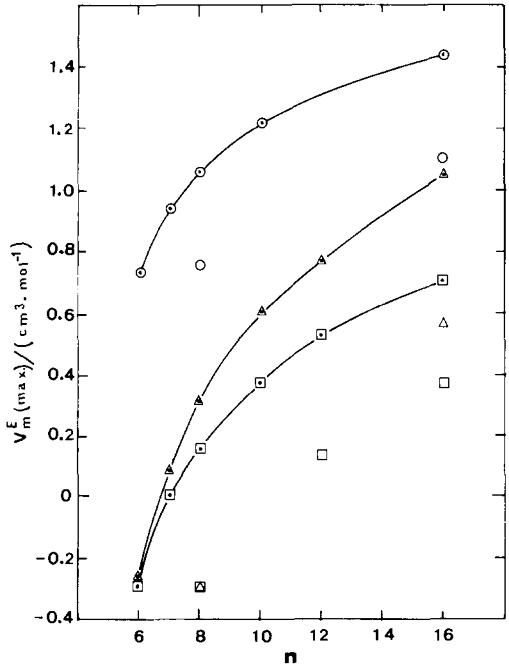

Fig. 3. V_m^E(max) plotted against chain length n of alkanes at 298.15 K. $[CH_3O]_3P$ with: ⊙, n-alkanes; ○, branched alkanes. $[CH_3(CH_3)_3O]_3P$ with: ⊡, n-alkanes; □, branched alkanes. $[CH_3(CH_3)_3O]_3PO$ with: ◬, n-alkanes; △, branched alkanes.

quently the values of V_m^E of mixing for branched alkanes are smaller than those of n-alkane isomers.

For trimethylphosphite mixtures, all the V_m^E of mixing are positive and large; because of the smallness of the methyl chains of trimethylphosphite, no interstitial accommodation of molecules in mixtures with shorter alkanes occurs, and this gives a least compact structure to this system, while in the tributylphosphite or tributylphosphate mixtures with n-alkanes the shorter alkane molecules can correlate their orientations with the butyl chains, giving a packing effect, and the V_m^E of mixing can be negative with n-hexane and 2,2,4-trimethylpentane.

A comparison of the V_m^E of mixing of tributylphosphate and tributylphosphite molecules with n-alkanes shows the influence of the (PO) group of tributylphosphate molecules, since the other part of the molecule is the same. In Fig. 3 one can see that the V_m^E of mixing with n-hexane are approximately equal in the two systems, but when the chain length of alkane is greater the V_m^E of mixing is larger with tributylphosphate molecules; moreover the differences between the V_m^E values of n-alkanes and of their branched isomers with phosphate and phosphite molecules are larger with tributylphosphate than with tributylphosphite. These measurements point out that perhaps the (PO) group of the tributylphosphate molecules increases the disruption of molecular order existing in the pure n-alkanes.

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