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EXCESS MOLAR VOLUMES OF TRIBUTYL PHOSPHATE(TBP) + n-ALKANOL, n-ALKANOL + n-ALKANE MEASURED WITH A MODIFIED CONTINUOUS-DILUTION DILATOMETER *

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ABSTRACT

Excess molar volumes V_m^E as a function of mole fraction x for CH_3OH + TBP, n-$C_5H_{11}OH$ + TBP, n-C_4H_9OH + TBP, n-C_4H_9OH + n-C_8H_{18}, n-$C_5H_{11}OH$ + n-C_8H_{18}, n-$C_5H_{11}OH$ + n-$C_{10}H_{22}$, and n-$C_5H_{11}OH$ + n-$C_{12}H_{26}$ at 298.15 K and n-C_4H_9OH + TBP at 303.15 K were measured in a modified continuous-dilution dilatometer. Excess molar volumes are positive over the entire range of mole fraction x for eight binary systems. The values of V_m^E increase with increasing chain length of the molecule of n-alkanol or n-alkane.

INTRODUCTION

The systems for n-alkanol + TBP (tributyl phosphate) are important for the extraction industry. Many works on excess volumes of n-alkanol + n-alkane have been reported [1–3]. The present work was undertaken in order to study the interactions between polar and weak polar as well as polar and non-polar molecules and the effect of chain length of n-alkane or n-alkanol molecules on V_m^E values.

EXPERIMENTAL

Analytical reagents TBP, methanol, n-butanol, n-pentanol, n-octane, n-decane, n-dodecane, benzene and cyclohexane were purified by fractional distillation using a 1.5 m long column packed with fine copper rings. All of these distilled reagents were stored over 4 Å molecular sieves. Before loading them into the dilatometer, the compounds were degassed. The densities and refractive indices agree well with those reported in the literature [4,5].

Excess volumes were measured in a modified continuous-dilution dilatometer. The apparatus [6] is shown in Fig. 1 and is based on the Stokes and Levien dilatometer [8] and the Kumaran and McGlashan tilting dilution

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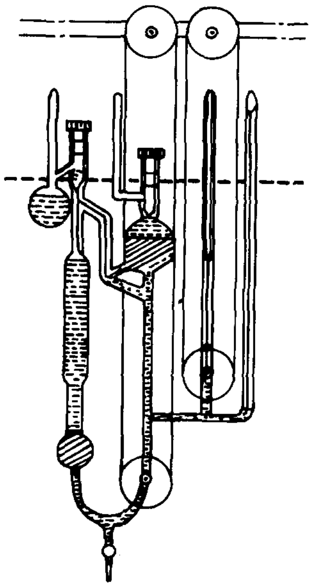

Fig. 1. The modified continuous-dilution dilatometer illustrated in detail in ref. 6.

dilatometer [7]. The proper working of the apparatus was checked by xc-C_6H_{12} + (1 − x)C_6H_6, where x is the mole fraction of cyclohexane (c-C_6H_{12}). The results were fitted to eqn. 1.

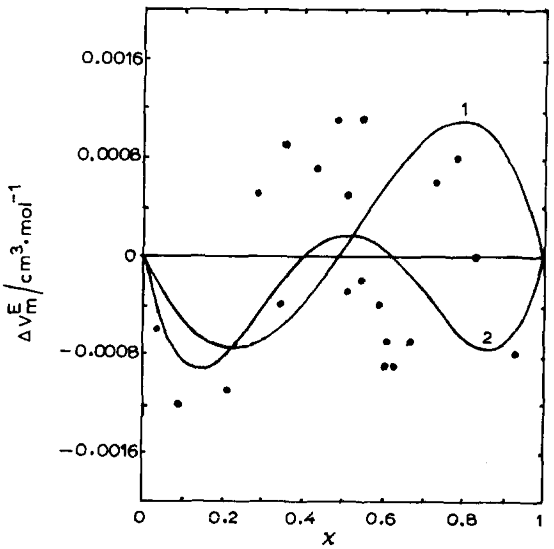

Fig. 2. Deviations of V_m^E of xc-C_6H_{12} + (1 − x)C_6H_6. ●, Experimental values; curve 1, Kumaran and McGlashan [7]; curve 2, Stokes et al. [8].

TABLE 1

The least-squares parameters and standard deviations s for xc-$C_6H_{12}+(1-x)C_6H_6$ at 298.15 K

a_0	a_1	a_2	s (cm^3 mol^{-1})	Reference
2.5981	−0.0893	0.0493	0.0007	This work, [6]
2.5983	−0.0990	0.0518	0.0006	[7]
2.5988	−0.0901	0.0345	0.0008	[8]

$$V_m^E = x(1-x)\left[a_0 + a_1(1-2x) + a_2(1-2x)^2 + a_3(1-2x)^3\right] \quad (1)$$

The least-squares parameters and standard deviations are given in Table 1 for comparison with the results of Kumaran and McGlashan and Stokes et al. [7,8]. The excess volumes were reproducible to 0.001 cm^3 mol^{-1}. Fig. 2 gives a comparison of measurements at 298.5 K between the present results and Kumaran et al. from the literature. Our results agree with those by Kumaran and McGlashan [7] as shown in Fig. 2 in the form of

$$\Delta V_m^E = V_{m,exp}^E - V_{m,calc.(eqn.(1))}^E \qquad \text{for } 298.5 \text{ K}$$

RESULTS

The experimental values of V_m^E measured for n-$C_nH_{2n+1}OH$ + TBP and n-$C_nH_{2n+1}OH$ + n-C_nH_{2n+2} are given in Tables 2 and 3, the parameters a_0,

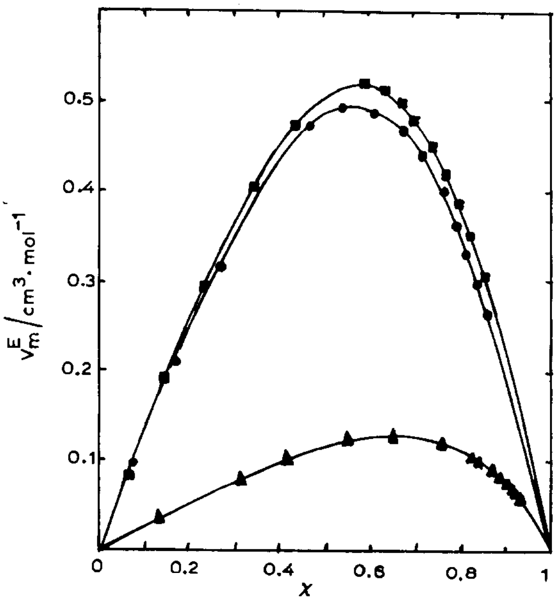

Fig. 3. Excess molar volumes V_m^E at 298.15 K. ——, Calculated from eqn. (1)., ▲, $xCH_3OH+(1-x)$TBP; ●, xn-$C_4H_9OH+(1-x)$TBP; ■, xn-$C_5H_{11}OH+(1-x)$TBP.

TABLE 2

Experimental excess molar volumes V_m^E for n-$C_nH_{2n+1}OH$+TBP at 298.15 K and 303.15 K, $S_m^E = V_{mexp}^E - V_{mcal}^E$

x	V_m^E (cm^3 mol^{-1})	S_m^E (cm^3 mol^{-1})	x	V_m^E (cm^3 mol^{-1})	S_m^E (cm^3 mol^{-1})
$x CH_3OH + (1-x)$TBP at 298.15 K					
0.1313	0.0335	0.0019	0.8691	0.0888	−0.0014
0.3180	0.0762	−0.0031	0.8883	0.0809	−0.0005
0.4203	0.1004	0.0000	0.9028	0.0740	0.0000
0.5567	0.1231	0.0033	0.9164	0.0681	0.0008
0.6549	0.1269	0.0012	0.9196	0.0667	0.0013
0.7649	0.1164	−0.0024	0.9258	0.0662	0.0018
0.8244	0.1037	−0.0022	0.9342	0.0585	0.0023
0.8464	0.0970	−0.0019	0.9371	0.0556	0.0026
x n-$C_4H_9OH + (1-x)$TBP at 298.15 K					
0.0733	0.1003	0.0010	0.6716	0.4729	−0.0001
0.1685	0.2143	−0.0008	0.7180	0.4417	−0.0010
0.2640	0.3188	0.0006	0.7630	0.4004	−0.0008
0.3679	0.4102	−0.0013	0.7930	0.3668	−0.0002
0.4694	0.4752	0.0008	0.8171	0.3354	−0.0004
0.5484	0.4974	0.0004	0.8407	0.3024	0.0004
0.6178	0.4940	0.0008	0.8635	0.2676	0.0012
x n-$C_5H_{11}OH + (1-x)$TBP at 298.15 K					
0.0649	0.0888	−0.0006	0.6701	0.4998	0.0007
0.1486	0.1965	−0.0005	0.7001	0.4818	0.0004
0.2313	0.2948	0.0007	0.7401	0.4494	0.0001
0.3426	0.4083	0.0017	0.7667	0.4223	−0.0002
0.4335	0.4279	−0.0025	0.7963	0.3869	−0.0005
0.5875	0.5219	0.0009	0.8207	0.3539	−0.0005
0.6330	0.5143	0.0004	0.8529	0.3054	0.0003
x n-$C_4H_9OH + (1-x)$TBP at 303.15 K					
0.0291	0.0401	0.0001	0.6050	0.5077	0.0009
0.0858	0.1124	−0.0013	0.6671	0.4874	−0.0003
0.1480	0.1900	0.0006	0.7281	0.4466	−0.0004
0.2012	0.2514	0.0001	0.7646	0.4109	−0.0010
0.3131	0.3660	0.0001	0.8068	0.3602	−0.0010
0.3879	0.4285	−0.0011	0.8361	0.3194	−0.0002
0.4630	0.4760	−0.0015	0.8610	0.2808	0.0007
0.5515	0.5090	0.0022	0.8709	0.2644	0.0011

a_1, a_2, a_3 are obtained by the least-squares method, and the standard deviations s are given in Table 4. The V_m^E vs. x plots are given in Figs. 3–5.

DISCUSSION

The excess molar volumes V_m^E for n-alkanol + TBP and n-alkanol + n-alkane are positive over the whole mole fraction x range and increase with

TABLE 3

Experimental excess molar volumes for n-$C_nH_{2n+1}OH$ + n-C_nH_{2n+2} at 298.15 K

x	V_m^E (cm^3 mol^{-1})	S_m^E (cm^3 mol^{-1})	x	V_m^E (cm^3 mol^{-1})	S_m^E (cm^3 mol^{-1})
xn-C_4H_9OH + (1 − x)n-C_8H_{18}					
0.1374	0.2125	0.0011	0.8123	0.1245	−0.0009
0.2973	0.2909	−0.0018	0.8477	0.1032	−0.0002
0.4347	0.2877	0.0005	0.8791	0.0834	0.0002
0.5535	0.2546	0.0016	0.9014	0.0688	0.0004
0.6551	0.2101	−0.0001	0.9213	0.0557	0.0007
0.7508	0.1598	−0.0012	0.9353	0.0463	0.0009
xn-$C_5H_{11}OH$ + (1 − x)n-C_8H_{18}					
0.1570	0.1740	0.0024	0.8089	0.0568	−0.0010
0.2708	0.2123	−0.0026	0.8553	0.0392	−0.0005
0.3994	0.2106	−0.0023	0.8797	0.0311	0.0008
0.5177	0.1862	0.0048	0.8983	0.0250	0.0009
0.6202	0.1419	0.0008	0.9136	0.0203	0.0010
0.7075	0.1002	−0.0021	0.9255	0.0168	0.0010
0.7628	0.0756	−0.0020			
xn-$C_5H_{11}OH$ + (1 − x)n-$C_{10}H_{22}$					
0.0772	0.1794	0.0141	0.7487	0.2022	−0.0038
0.1999	0.2749	−0.0129	0.8087	0.1603	−0.0005
0.3085	0.3218	0.0004	0.8454	0.1265	−0.0034
0.4957	0.3214	0.0080	0.8871	0.0950	0.0017
0.6013	0.2857	0.0013	0.9127	0.0748	0.0042
0.7076	0.2283	−0.0045	0.9350	0.0566	0.0054
xn-$C_5H_{11}OH$ + (1 − x)n-$C_{12}H_{26}$					
0.0789	0.1894	0.0115	0.7763	0.2499	−0.0054
0.2339	0.3313	−0.0126	0.8192	0.2135	−0.0029
0.3385	0.3824	0.0005	0.8666	0.1670	−0.0002
0.4370	0.3960	0.0063	0.8971	0.1349	0.0026
0.5525	0.3782	0.0044	0.9242	0.1034	0.0041
0.6646	0.3280	−0.0031	0.9434	0.0797	0.0046

TABLE 4

Values of the parameters a_0, a_1, a_2, a_3 of eqn. (1) and standard deviations s

Mixture	T(K)	a_0	a_1	a_2	a_3	s (cm^3 mol^{-1})
CH_3OH + TBP	298.15	0.4524	−0.2743	0.1508	−0.1378	0.0020
n-C_4H_9OH + TBP	298.15	1.9448	−0.6518	−0.1166	0.2536	0.0008
n-C_4H_9OH + TBP	303.15	1.9751	−0.7278	−0.1124	0.2703	0.0010
n-$C_5H_{11}OH$ + TBP	298.15	2.0361	−0.7128	−0.0778	0.1838	0.0009
n-C_4H_9OH + n-C_8H_{18}	298.15	1.0837	0.5989	0.3885	0.1613	0.0010
n-$C_5H_{11}OH$ + n-C_8H_{18}	298.15	0.7494	0.0534	0.1386	0.1057	0.0021
n-$C_5H_{11}OH$ + n-$C_{10}H_{22}$	298.15	1.2506	0.3881	0.4802	0.6000	0.0069
n-$C_5H_{11}OH$ + n-$C_{12}H_{26}$	298.15	1.5372	0.2949	0.5594	0.4466	0.0063

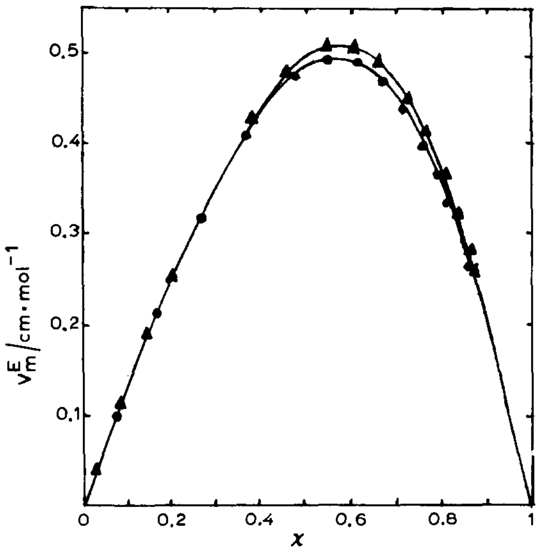

Fig. 4. Excess molar volumes V_m^E of xn-$C_4H_9OH + (1-x)$TBP. ———, Calculated from eqn. (1); ●, 298.15 K; ▲, 303.15 K.

increasing chain length of molecules of n-alkanol or n-alkane. The values of V_m^E increase in the sequence CH_3OH + TBP < n-C_4H_9OH + TBP < n-$C_5H_{11}OH$ + TBP; n-C_4H_9OH + TBP at 298.15 K < n-C_4H_9OH + TBP at

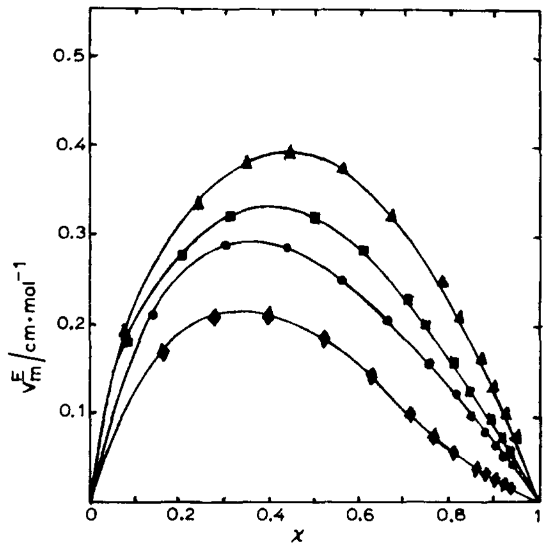

Fig. 5. Excess molar volumes V_m^E at 298.15 K. ———, Calculated from eqn. (1); ◆, xn-$C_5H_{11}OH + (1-x)$n-C_8H_{18}; ●, xn-$C_4H_9OH + (1-x)$n-C_8H_{18}; ■, xn-$C_5H_{11}OH + (1-x)$n-$C_{10}H_{22}$; ▲, xn-$C_5H_{11}OH + (1-x)$n-$C_{12}H_{26}$.

303.15 K; n-$C_5H_{11}OH$ + n-C_8H_{18} < n-C_4H_9OH + n-C_8H_{18} < n-$C_5H_{11}OH$ + n-$C_{10}H_{22}$ < n-$C_5H_{11}OH$ + n-$C_{12}H_{26}$.

The excess molar volumes obtained here can be explained as follows. Alkanols are self-associated due to H-bonding. The H-bondings are broken on dilution with a non-polar (e.g. n-alkane) or weak polar (e.g. TBP) solvent giving positive contributions to the excess volumes. The disruption of the original order of both the n-alkanol and TBP or both n-alkanol and n-alkane molecules might also make a contribution to the excess volumes, due to non-specific interactions between unlike molecules. The chain length of an alkane or an n-alkanol has a considerable effect on excess volumes, due to the steric structure. Because of these, the values of V_m^E increase with increasing chain length of the n-alkanol and n-alkane in n-alkanol + TBP systems and in n-alkanol + n-alkane systems, respectively.

It has been found [9] that the dimerization constant of TBP dimer is about 2.9 dm^3 mol^{-1}. This value is small, therefore the dissociation TBP dimer and the interaction between TBP and n-alcohol molecules are only providing a small contribution to V_m^E of the TBP + n-alcohol binary systems. It can be seen from Fig. 4 that values of V_m^E for n-C_4H_9OH + TBP at 298.15 K and 303.15 K are positive with a positive temperature coefficient. Perhaps the H-bonding breaking increases with increasing temperature of the mixture. The volume behavior summarized above can be explained. When a mixture is formed, changes in self-association and physical interaction of the van der Waals type lead to an increase in volume; changes of "free volume" and interstitial accommodation also lead to change of volume.

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