Excess Volumes of (Ketone + Alkanol) at the Temperature 298.15 K

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Excess molar volumes V_m^E were measured as a function of mole fraction at the temperature 298.15 K and atmospheric pressure for the 12 mixtures {$x(CH_3COC_2H_5$ or $CH_3COC_3H_7$ or $C_2H_5COC_2H_5) + (1 - x)C_jH_{2j+1}$-OH} where $j = 1$, 2, or 3. A vibrating tube densitometer (Paar DMA 601) was used to determine V_m^Es. The results are discussed in terms of the length of the ketone carbon chain, the position of the keto group, and the chain length of the alkanol.

Introduction

In this work we have investigated the interaction between a ketone and a short-chain alkanol by measuring the excess molar volumes of mixing. Our results show the effects of increasing the carbon chain length of the ketone, increasing the carbon chain length of the alkanol, shifting the position of the keto group, and shifting the position of the hydroxy group of the alkanol.

Experimental Section

The ketones were purified as specified by Perrin and Armarego (*1*) and stored in a dry glovebox. The alcohols were dried and distilled as previously described (*2*) and also stored in a glovebox prior to use. An analysis by the Karl–Fisher technique showed the water impurity to be less than 0.02 mol %.

An Anton-Paar DMA 602 vibrating-tube density meter, thermostated at the temperature 298.15 ± 0.005 K was used to measure the densities of the pure liquids and the mixtures. Mole fractions were accurate to 10^{-3} and excess volumes to 1×10^{-3} cm^3·mol^{-1}.

Results

The measured excess molar volumes V_m^E and the residuals δV_m^E are given in Table 1. To each set of experimental values a polynomial

$$\delta V_m^E/(\text{cm}^3\cdot\text{mol}^{-1}) = V_m^E/(\text{cm}^3\cdot\text{mol}^{-1}) - x(1-x)\sum_{r=0}^{r=k} A_r(1-2x)^r$$

was fitted by the method of least squares. The parameters A_r are given in Table 2.

Discussion

V_m^E results for the mixtures discussed here have not previously been reported in the literature. V_m^Es at 298.15 K for (propanone + methanol or ethanol or propan-1-ol or propan-2-ol) have however been reported earlier (*3-5*). Winnick and Kong (*3*) evaluated V_m^E for (propanone + methanol) mixtures and showed that V_m^E was negative over the measured range of mole fraction, although this did not include the very dilute alkanol region. Miyano and Hayduk (*4*) investigated (propanone + ethanol and propanone + propan-1-ol) mixtures and showed that V_m^Es ($x = 0.5$) are negative for both system but positive in the dilute alkanol region. (Propanone + propan-2-ol) mixtures were studied by Thacker and Rowlinson (*5*); they showed that the V_m^E was positive over the whole mole fraction range. Our results also show negative V_m^Es ($x = 0.5$) for each of the (ketone + methanol or ethanol or propan-1-ol) mixtures and positive V_m^Es for each of the (ketone + propan-2-ol) mixtures.

The results demonstrate that for (ketone + alkanol) mixture involving ketones with methyl, ethyl, or propyl side chains the V_m^E is only weakly dependent on the nature of the ketone side chain. Conversely, the V_m^E is strongly dependent on the alkyl chain of the alkanol. The most negative V_m^Es are attributable to the smaller chain alkanols. These effects are clearly noticeable by comparing the V_m^E ($x = 0.5$) values in Table 3.

A comparison of V_m^E ($x = 0.5$) for some of the mixtures discussed here with V_m^E ($x = 0.5$) for heptane + ethanol or propan-1-ol) mixtures succors an understanding of the interaction involved. For (heptane + ethanol or propan-1-ol) mixtures V_m^Es ($x = 0.5$) are positive. The origin of the positive nature of the V_m^E is most likely due to the breakdown of the hydrogen bonding between the alkanol molecules by the hydrocarbon. Conversely, V_m^E ($x = 0.5$) for (ketone + ethanol or propan-1-ol) are negative for the ketone $CH_3COC_2H_5$, $CH_3COC_3H_7$, or $C_2H_5COC_2H_5$. This negative effect is most likely due to the association between the keto group of the ketone and the proton of the alkanol hydroxy group. This effect apparently outweighs the effect due to the dissociation of the alcohol.

The positive V_m^E values for (ketone + propan-2-ol) mixtures is probably attributable to a shielding effect on the alkanol hydroxy group proton by the two adjacent methyl groups, thus preventing any association between the ketone and alkanol species.

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Table 1. Excess Molar Volumes, V_m^E, for (Ketone + Alkanol) and the Deviations, δV_m^E, Calculated from Equation 1 and Table 2 at the Temperature 298.15 K

x	V_m^E/cm^3·mol^{-1}	10^3·δV_m^E/cm^3·mol^{-1}	x	V_m^E/cm^3·mol^{-1}	10^3·δV_m^E/cm^3·mol^{-1}	x	V_m^E/cm^3·mol^{-1}	10^3·δV_m^E/cm^3·mol^{-1}
				$xCH_3COC_2H_5 + (1-x)CH_3OH$				
0.050	−0.0637	0.9	0.268	−0.2306	−4.3	0.628	−0.2492	−2.9
0.077	−0.0922	2.0	0.312	−0.2420	0.5	0.716	−0.2125	0.5
0.098	−0.1139	1.0	0.355	−0.2541	0.1	0.785	−0.1773	−1.6
0.130	−0.1452	−2.1	0.395	−0.2606	1.2	0.823	−0.1504	0.5
0.163	−0.1670	1.3	0.454	−0.2670	0.5	0.893	−0.0977	0.0
0.199	−0.1931	−1.5	0.511	−0.2661	0.8	0.989	−0.0047	6.1
0.231	−0.2075	1.8	0.575	−0.2567	2.2	0.998	0.0034	5.4
				$xCH_3COC_3H_7 + (1-x)CH_3OH$				
0.065	−0.0638	−1.6	0.268	−0.1805	−0.6	0.530	−0.2198	−2.8
0.086	−0.0808	−1.6	0.318	−0.1934	2.3	0.582	−0.2084	2.9
0.114	−0.1004	−0.4	0.367	−0.2057	1.3	0.659	−0.1918	2.8
0.136	−0.1142	0.6	0.408	−0.2132	0.2	0.735	−0.1679	0.4
0.168	−0.1344	−0.3	0.471	−0.2213	−3.1	0.789	−0.1426	0.8
0.201	−0.1506	0.9	0.499	−0.2208	−2.5	0.871	−0.0985	−2.5
0.233	−0.1648	1.4						
				$xC_2H_5COC_2H_5 + (1-x)CH_3OH$				
0.042	−0.0389	0.1	0.286	−0.1682	2−0.1	0.662	−0.1787	2.3
0.068	−0.0600	−0.1	0.320	−0.1771	0.0	0.711	−0.1676	0.2
0.118	−0.0932	1.2	0.362	−0.1865	−0.6	0.782	−0.1430	−1.8
0.138	−0.1050	1.3	0.424	−0.1938	0.8	0.822	−0.1237	−1.5
0.173	−0.1249	−0.1	0.476	−0.1977	0.5	0.877	−0.0933	−2.2
0.208	−0.1426	−1.9	0.544	−0.1986	−1.1	0.955	−0.0309	5.8
0.243	−0.1549	−0.6	0.590	−0.1928	0.7	0.993	0.0002	6.2
				$xCH_3COC_2H_5 + (1-x)C_2H_5OH$				
0.040	−0.0186	0.8	0.282	−0.0691	2.0	0.550	−0.0622	0.4
0.059	−0.0268	0.3	0.311	−0.0721	0.2	0.599	−0.0584	−0.8
0.093	−0.0412	−2.1	0.347	−0.0742	−1.3	0.657	−0.0499	1.0
0.108	−0.0456	−2.0	0.387	−0.0743	−1.8	0.677	−0.0483	0.0
0.144	−0.0517	1.1	0.437	−0.0710	−0.2	0.701	−0.0445	0.7
0.182	−0.0586	1.7	0.486	−0.0675	0.4	0.790	−0.0333	−0.9
0.218	−0.0654	0.1						
				$xCH_3COC_3H_7 + (1-x)C_2H_5OH$				
0.034	−0.0162	−1.0	0.230	−0.0534	2.4	0.561	−0.0411	1.4
0.053	−0.0229	−0.5	0.272	−0.0554	2.2	0.680	−0.0292	0.6
0.080	−0.0329	−1.8	0.304	−0.0570	0.9	0.742	−0.0231	−0.4
0.114	−0.0400	−0.1	0.334	−0.0574	0.2	0.836	−0.0116	0.7
0.123	−0.0432	−1.4	0.396	−0.0561	−0.8	0.860	−0.0104	−0.6
0.162	−0.0469	1.9	0.443	−0.0529	−0.4	0.896	−0.0070	−0.6
				$xC_2H_5COC_2H_5 + (1-x)C_2H_5OH$				
0.031	−0.0110	3.2	0.228	−0.0620	0.5	0.622	−0.0501	−0.7
0.036	−0.0142	2.0	0.312	−0.0680	0.6	0.656	−0.0432	1.2
0.060	−0.0234	2.0	0.361	−0.0695	0.0	0.679	−0.0393	1.5
0.091	−0.0362	−0.6	0.409	−0.0680	0.8	0.753	−0.0285	−0.1
0.132	−0.0489	−2.5	0.457	−0.0657	0.8	0.833	−0.0183	−3.2
0.163	−0.0546	−1.7	0.573	−0.0582	−2.3	0.895	−0.0034	2.9
				$xCH_3COC_2H_5 + (1-x)C_3H_7OH$				
0.043	−0.0091	−1.3	0.210	−0.0278	1.7	0.502	−0.0287	1.0
0.079	−0.0147	−0.9	0.269	−0.0335	−0.4	0.553	−0.0256	0.9
0.097	−0.0167	−0.1	0.306	−0.0358	−1.5	0.600	−0.0235	−0.3
0.112	−0.0177	−1.0	0.350	−0.0365	−1.8	0.759	−0.0137	−1.3
0.125	−0.0211	−0.6	0.408	−0.0341	−0.3	0.826	−0.0090	−0.4
0.184	−0.0258	1.4	0.462	−0.0309	0.9	0.879	−0.0047	1.3
				$xCH_3COC_3H_7 + (1-x)C_3H_7OH$				
0.046	−0.0095	−0.8	0.189	−0.0243	−0.9	0.625	−0.0078	0.6
0.065	−0.0130	−1.3	0.222	−0.0251	−0.4	0.733	0.0006	−0.3
0.084	−0.0140	0.3	0.354	−0.0263	−1.2	0.783	0.0033	−1.2
0.108	−0.0155	1.6	0.366	−0.0253	−0.4	0.815	0.0053	−1.1
0.131	−0.0187	0.6	0.414	−0.0224	0.7	0.935	0.0084	1.5
0.146	−0.0197	0.9	0.573	−0.0116	1.2	0.962	0.0062	1.4
				$xC_2H_5COC_2H_5 + (1-x)C_3H_7OH$				
0.048	−0.0114	−0.1	0.267	−0.0378	−0.7	0.604	−0.0302	−0.3
0.063	−0.0130	1.3	0.367	−0.0389	0.3	0.682	−0.0244	−0.3
0.114	−0.0223	0.7	0.414	−0.0388	−0.1	0.735	−0.0197	0.0
0.140	−0.0270	0.5	0.448	−0.0373	0.6	0.787	−0.0159	−0.7
0.153	−0.0291	−1.0	0.518	−0.0347	0.4	0.842	−0.0102	0.3
0.218	−0.0341	0.1	0.566	−0.0324	0.0	0.868	−0.0079	0.5
0.240	−0.0355	0.2						
				$xCH_3COC_2H_5 + (1-x)CH_3C(OH)CH_3$				
0.065	0.0606	1.0	0.418	0.2284	0.4	0.726	0.1856	−2.6
0.138	0.1173	2.2	0.466	0.2335	0.7	0.771	0.1663	−1.6
0.186	0.1438	−1.5	0.527	0.2334	0.4	0.833	0.1376	4.0

Table 1 (Continued)

x	V_m^E/cm^3·mol^{-1}	10^3·δV_m^E/cm^3·mol^{-1}	x	V_m^E/cm^3·mol^{-1}	10^3·δV_m^E/cm^3·mol^{-1}	x	V_m^E/cm^3·mol^{-1}	10^3·δV_m^E/cm^3·mol^{-1}
				xCH$_3$COC$_3$H$_7$ + (1 − x)CH$_3$C(OH)CH$_3$				
0.226	0.1659	−1.0	0.569	0.2322	2.8	0.897	0.0947	4.9
0.257	0.1803	−1.2	0.614	0.2203	−1.8	0.940	0.0537	−1.6
0.322	0.2053	−0.7	0.664	0.2085	−1.3	0.955	0.0360	−6.3
0.365	0.2191	1.2						
				xCH$_3$COC$_3$H$_7$ + (1 − x)CH$_3$C(OH)CH$_3$				
0.045	0.0474	0.8	0.364	0.2130	1.7	0.668	0.2131	0.1
0.077	0.0756	0.9	0.424	0.2217	−1.0	0.732	0.1933	1.2
0.107	0.0963	−1.6	0.448	0.2252	−0.7	0.802	0.1584	−0.3
0.147	0.1258	1.3	0.512	0.2307	0.4	0.852	0.1290	1.4
0.193	0.1473	−2.9	0.555	0.2277	−2.1	0.923	0.0715	−1.4
0.265	0.1826	0.9	0.604	0.2256	0.2	0.949	0.0488	−1.0
0.319	0.2010	1.4						
				xC$_2$H$_5$COC$_2$H$_5$ + (1 − x)CH$_3$C(OH)CH$_3$				
0.033	0.0225	−0.9	0.273	0.1360	1.2	0.627	0.1746	−3.0
0.057	0.0383	−0.5	0.331	0.1520	0.6	0.700	0.1634	−0.7
0.116	0.0725	0.9	0.378	0.1620	−0.5	0.743	0.1523	0.9
0.158	0.0903	−1.3	0.418	0.1697	−0.4	0.794	0.1339	2.2
0.194	0.1067	0.0	0.507	0.1811	0.5	0.863	0.0996	3.0
0.238	0.1234	0.2	0.563	0.1826	0.7	0.927	0.0502	−5.5

Table 2. Coefficients A_r and Standard Deviations σ[a] for x(CH$_3$COC$_2$H$_5$ or CH$_3$COC$_3$H$_7$ or C$_2$H$_5$COC$_2$H$_5$) + (1 − x)ROH at the Temperature 298.15 K by Equation 1

	A_0	A_1	A_2	A_3	10^3·σ/cm^3·mol^{-1}
			CH$_3$OH		
xCH$_3$COC$_2$H$_5$	−1.0698	−0.0872	−0.1403	−0.1339	2.7
xCH$_3$COC$_3$H$_7$	−0.8731	−0.0395	−0.0812	−0.0825	2.0
xC$_2$H$_5$COC$_2$H$_5$	−0.7945	0.0074	−0.1398	−0.0826	2.4
			CH$_3$CH$_2$OH		
xCH$_3$COC$_2$H$_5$	−0.2675	−0.1511	−0.0727	−0.0461	1.3
xCH$_3$COC$_3$H$_7$	−0.1900	−0.1618	−0.0734	−0.0808	1.2
xC$_2$H$_5$COC$_2$H$_5$	−0.2537	−0.1688	0.0155	−0.0885	2.0
			CH$_3$(CH$_2$)$_2$OH		
xCH$_3$COC$_2$H$_5$	−0.1191	−0.1151	−0.0050	0.0494	1.2
xCH$_3$COC$_3$H$_7$	−0.0731	−0.1339	0.0443	−0.0547	1.1
xC$_2$H$_5$COC$_2$H$_5$	−0.1437	−0.0896	−0.0080	−0.0217	0.6
			CH$_3$CH(OH)CH$_3$		
xCH$_3$COC$_2$H$_5$	0.9349	0.0037	0.0600	−0.0036	2.8
xCH$_3$COC$_3$H$_7$	0.9197	−0.0799	0.1663	0.1333	1.5
xC$_2$H$_5$COC$_2$H$_5$	0.7205	−0.1428	0.0659	0.1082	2.1

[a] $\sigma = [\Sigma(V_{m(exptl)}^E - V_{m(calcd)}^E)^2/(n - k)]^{1/2}$, where n is the number of experimental points.

Table 3. Excess Molar Volumes, V_m^E, at $x = 0.5$

mixture	$V_m^E(x = 0.5)$/ cm^3·mol^{-1}	mixture	$V_m^E(x = 0.5)$/ cm^3·mol^{-1}
CH$_3$COC$_2$H$_5$ + CH$_3$OH	−0.2675	CH$_3$COC$_2$H$_5$ + CH$_3$(CH$_2$)$_2$OH	−0.0298
CH$_3$COC$_3$H$_7$ + CH$_3$OH	−0.2183	CH$_3$COC$_3$H$_7$ + CH$_3$(CH$_2$)$_2$OH	−0.0183
C$_2$H$_5$COC$_2$H$_5$ + CH$_3$OH	−0.1986	C$_2$H$_5$COC$_2$H$_5$ + CH$_3$(CH$_2$)$_2$OH	−0.0359
CH$_3$COC$_2$H$_5$ + CH$_3$CH$_2$OH	−0.0669	CH$_3$COC$_2$H$_5$ + CH$_3$CH(OH)CH$_3$	0.2337
CH$_3$COC$_3$H$_7$ + CH$_3$CH$_2$OH	−0.0475	CH$_3$COC$_3$H$_7$ + CH$_3$CH(OH)CH$_3$	0.2299
C$_2$H$_5$COC$_2$H$_5$ + CH$_3$CH$_2$OH	−0.0634	C$_2$H$_5$COC$_2$H$_5$ + CH$_3$CH(OH)CH$_3$	0.1801

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