Excess Enthalpies of Ketone + Alkanol at the Temperature 298.15 K

Trevor M. Letcher* and J. Ashley Nevines

Department of Chemistry, University of Natal, King George V Avenue, Durban 4001, Republic of South Africa

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The excess molar enthalpies, H^E_m of pentan-2-one or pentan-3-one + methanol, ethanol, propan-1-ol, or propan-2-ol were measured over the whole composition range at the temperature 298.15 K and atmospheric pressure. These results, together with results from the literature, are discussed in terms of the ketone and alkanol carbon numbers and the position of the OH group on the alkanol.

Introduction

We have previously reported the excess molar volumes of mixing, V^E_m, of butanone, pentan-2-one, or pentan-3-one + methanol, ethanol, propan-1-ol, or propan-2-ol (Letcher and Nevines, 1995). In this work we have complemented the earlier work by measuring the excess molar enthalpies of mixing, H^E_m, of pentan-2-one or pentan-3-one + methanol, ethanol, propan-1-ol, propan-2-ol at 298.15 K. These results also complement other previously reported H^E_m results for propanone + methanol (Coomber and Wormald, 1976), ethanol (Nicolaides and Eckert, 1978), propan-1-ol, or propan-2-ol (Christiansen et al., 1982) and for butanone + methanol, ethanol, propan-1-ol, or propan-2-ol (Christiansen et al., 1982). The H^E_m's for a ketone + an alkanol are also compared with the H^E_m's of hexane + propanone (Christiansen et al., 1982), butanone, pentan-1-one, or pentan-2-one (Kiyohara et al., 1977) and also with the H^E_m's of hexane + methanol (Savini et al., 1965), ethanol (DeQ. Jones and Lu, 1966), propan-1-ol (Brown et al., 1964), or propan-2-ol (Christiansen et al., 1982).

Experimental Section

The ketones were purified as directed by Perrin and Armarego (1988). The alcohols were dried and distilled as previously described by Letcher et al. (1990) and stored in a dry glovebox prior to use. The alcohols were analyzed for possible water contamination by the Karl-Fisher technique and were found to have a water impurity of less than 0.02 mol %.

A ThermoMetric 2277 thermal activity monitor was used to determine the excess molar enthalpies. Our technique and calibrations were checked by comparing our results for H^E_m of butanone + propan-1-ol with the reported literature values (Christiansen et al., 1982). Our results were always within 5 J mol^{-1} of the interpolated results.

Results and Discussion

The measured excess molar enthalpies H^E_m and the residuals δH^E_m are given in Table 1. To each set of experimental values of polynomial

$$\delta H^E_m/(\mathrm{J{\cdot}mol^{-1}}) = H^E_m/(\mathrm{J{\cdot}mol^{-1}}) - x(1-x)\sum_{r=0}^{r=k} A_r(1-2x)^r \qquad (1)$$

was fitted by the method of least squares. The parameters A_r are given in Table 2. The H^E_m's for the mixtures discussed in this work are all positive, with H^E_m (maximum) occurring at approximately $x = 0.5$.

Table 1. Excess Molar Enthalpies, H^E_m, for Ketone + Alkanol and the Deviations, δH^E_m, Calculated from Eq 1 and Table 2 at the Temperature 298.15 K

x	H^E_m/(J·mol^{-1})	δH^E_m/(J·mol^{-1})	x	H^E_m/(J·mol^{-1})	δH^E_m/(J·mol^{-1})	x	H^E_m/(J·mol^{-1})	δH^E_m/(J·mol^{-1})
$x\ CH_3COCH_2CH_2CH_3 + (1-x)\ CH_3OH$								
0.081	185.8	0.6	0.296	536.8	−3.3	0.624	669.0	1.5
0.108	239.1	−1.4	0.462	672.9	−2.0	0.702	606.9	−0.5
0.146	312.3	−0.7	0.549	690.3	0.6	0.790	491.0	−0.3
0.267	504.8	5.2						
$x\ CH_3CH_2COCH_2CH_3 + (1-x)\ CH_3OH$								
0.111	255.0	−1.4	0.432	694.3	−1.0	0.567	730.0	−2.1
0.148	335.8	4.2	0.468	722.0	8.2	0.690	673.7	−9.9
0.308	581.6	−2.8	0.511	734.3	6.7	0.810	545.3	5.1
0.401	665.9	−8.7	0.546	735.2	3.0			
$x\ CH_3COCH_2CH_2CH_3 + (1-x)\ CH_3CH_2OH$								
0.100	344.0	−3.8	0.330	793.8	−1.7	0.590	856.9	3.6
0.131	435.9	2.4	0.404	859.1	0.3	0.635	817.4	2.4
0.187	566.3	0.0	0.514	879.5	−5.2	0.738	669.4	−1.9
0.273	724.7	3.1						
$x\ CH_3CH_2COCH_2CH_3 + (1-x)\ CH_3CH_2OH$								
0.076	265.2	0.7	0.520	984.2	−5.5	0.754	813.0	−4.0
0.139	452.1	−3.7	0.572	979.9	−4.8	0.802	730.6	5.5
0.331	864.2	7.6	0.679	922.9	5.9	0.854	589.3	−6.3
0.428	953.5	−1.8	0.683	917.7	4.9			
$x\ CH_3COCH_2CH_2CH_3 + (1-x)\ CH_3(CH_2)_2OH$								
0.097	409.2	2.0	0.359	1130.3	−5.3	0.690	1018.9	−1.3
0.186	733.6	−2.0	0.436	1210.6	8.7	0.764	867.2	−4.8
0.226	863.1	4.4	0.580	1163.6	−1.1	0.823	726.0	4.8
0.293	1019.4	−4.9	0.611	1133.9	0.7			
$x\ CH_3CH_2COCH_2CH_3 + (1-x)\ CH_3(CH_2)_2OH$								
0.120	487.3	2.2	0.352	1090.3	9.3	0.676	1033.5	−6.9
0.156	618.6	3.4	0.516	1154.3	−3.4	0.752	937.9	10.2
0.221	810.1	−7.8	0.596	1121.4	2.8	0.792	843.6	−5.3
0.292	981.3	−3.8						
$x\ CH_3COCH_2CH_2CH_3 + (1-x)\ CH_3CH(OH)CH_3$								
0.121	715.9	1.0	0.421	1470.0	2.6	0.667	1352.1	1.1
0.169	910.2	−3.1	0.512	1500.5	−3.8	0.753	1137.1	3.7
0.233	1125.8	2.5	0.604	1448.8	0.1	0.792	998.6	−3.5
0.308	1304.2	−0.7						
$x\ CH_3CH_2COCH_2CH_3 + (1-x)\ CH_3CH(OH)CH_3$								
0.157	827.9	3.8	0.418	1447.3	−0.4	0.687	1275.2	0.2
0.221	1062.1	−5.0	0.525	1458.4	1.4	0.763	1112.9	2.6
0.287	1254.1	−0.3	0.614	1380.6	−3.4	0.807	984.2	−1.3
0.389	1426.7	2.9						

Table 2. Coefficients A_r and Standard Deviations σ^a for $x\ CH_3COCH_2CH_3$ or $CH_3CH_2COCH_2CH_3 + (1-x)ROH$ at the Temperature 298.15 K from Eq 1

ketone	A_0	A_1	A_2	A_3	σ/(J·mol^{-1})
CH_3OH					
$CH_3COCH_2CH_2CH_3$	2745.9	−403.4	14.6	119.4	2.8
$CH_3CH_2COCH_2CH_3$	2899.7	−542.2	485.4	−368.5	7.1
CH_3CH_2OH					
$CH_3COCH_2CH_2CH_3$	3544.1	89.5	62.6	408.0	3.7
$CH_3CH_2COCH_2CH_3$	3947.8	−406.1	692.0	−548.4	6.3
$CH_3(CH_2)_2OH$					
$CH_3COCH_2CH_2CH_3$	4836.6	398.4	145.6	−1152.4	5.4
$CH_3CH_2COCH_2CH_3$	4641.4	210.9	895.8	−1652.0	7.9
$CH_3CH(OH)CH_3$					
$CH_3COCH_2CH_2CH_3$	6018.0	−106.5	598.3	1011.1	3.3
$CH_3CH_2COCH_2CH_3$	5860.3	409.1	1092.2	−1325.3	3.4

[a] $\sigma = [\sum(H^E_{m,\mathrm{exptl}} - H^E_{m,\mathrm{calcd}})^2/(n-m)]^{1/2}$ where n is the number of experimental points and m is the number of coefficients.

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* To whom correspondence should be addressed.

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Table 3. Excess Molar Enthalpies: $A = H^E_m(0.5\ RCOR' + 0.5\ C_jH_{2j+1}OH)$; $B = H^E_m(0.5\ RCOR' + 0.5\ C_6H_{14})$; $C = H^E_m(0.5\ C_6H_{14} + 0.5\ C_jH_{2j+1}OH)$ for j = 1, 2, or 3[a]

	H^E_m(X = 0.5)/J·mol^{-1}						
ketone	*A*	ref	*B*	ref	*C*	ref	*A* − *B* − *C*
			CH_3OH				
CH_3COCH_3	710	Coomber and Wormald (1976)	1600	Christiansen et al. (1982)	600	Savini et al. (1965)	−1490
$CH_3COCH_2CH_3$	715	Christiansen et al. (1982)	1250	Kiyohara et al. (1977)	600	Savini et al. (1965)	−1135
$CH_3COCH_2CH_2CH_3$	687	this work	1040	Kiyohara et al. (1977)	600	Savini et al. (1965)	−953
$CH_3CH_2COCH_2CH_3$	725	this work	1000	Kiyohara et al. (1977)	600	Savini et al. (1965)	−875
			C_2H_5OH				
CH_3COCH_3	1110	Nicolaides and Eckert (1978)	1600	Christiansen et al. (1982)	550	DeQ. Jones and Lu (1966)	−1040
$CH_cOCH_2CH_3$	1075	Christiansen et al. (1982)	1250	Kiyohara et al. (1977)	550	DeQ. Jones and Lu (1966)	−725
$CH_3COCH_2CH_2CH_3$	886	this work	1040	Kiyohara et al. (1977)	550	DeQ. Jones and Lu (1966)	−704
$CH_3CH_2COCH_2CH_3$	987	this work	1000	Kiyohara et al. (1977)	550	DeQ. Jones and Lu (1966)	−563
			$CH_3(CH_2)_2OH$				
CH_3COCH_3	1380	Christiansen et al. (1982)	1600	Christiansen et al. (1982)	560	Brown et al. (1964)	−780
$CH_3COCH_2CH_3$	1310	Christiansen et al. (1982)	1250	Kiyohara et al. (1977)	560	Brown et al. (1964)	−500
$CH_3COCH_2CH_2CH_3$	1209	this work	1040	Kiyohara et al. (1977)	560	Brown et al. (1964)	−391
$CH_3CH_2COcH_2CH_3$	1160	this work	1000	Kiyohara et al. (1977)	560	Brown et al. (1964)	−400
			$CH_3CH(OH)CH_3$				
CH_3COCH_3	1600	Christiansen et al. (1982)	1600	Christiansen et al. (1982)	620	Christiansen et al. (1982)	−620
$CH_3COCH_2CH_3$	1495	Christiansen et al. (1982)	1250	Kiyohara et al. (1977)	620	Christiansen et al. (1982)	−375
$CH_3COCH_2CH_2CH_3$	1505	this work	1040	Kiyohara et al. (1977)	620	Christiansen et al. (1982)	−155
$CH_3CH_2COCH_2CH_3$	1465	this work	1000	Kiyohara et al. (1977)	620	Christiansen et al. (1982)	−155

[a] The value of *C* for CH_3OH has been obtained by extrapolating the H^E_m data from the miscible mixtures to $x = 0.5$.

The results for pentan-2-one or pentan-3-one + methanol, ethanol, propan-1-ol, or propan-2-ol at 298.15 K together with the results for propanone or butanone + methanol, ethanol, propan-1-ol, or propan-2-ol (Coomber and Wormald, 1976; Nicolaides and Eckert, 1978; Christiansen et al., 1982) show a weak dependence on the type of ketone but a strong dependence on the type of alkanol. This can readily be seen in the $H^E_m(x = 0.5)$ results given in Table 3. The $V^E_m\{x$ butanone, pentan-1-one, or pentan-2-one + $(1 - x)$ alkanol$\}$ results reported earlier also reflect a weak dependency on the type of ketone but a strong dependency on the type of alkanol.

The magnitude of the interaction between a ketone and an alkanol at a mole fraction x of ketone can be obtained by subtracting from $A = H^E_m\{x$ ketone + $(1 - x)$ alkanol$\}$ the enthalpy contribution resulting from the dissociation of ketone on the one hand and the alkanol on the other. This contribution can be estimated very roughly from $B = H^E_m\{x$ ketone + $(1 - x)$ butane$\}$ and $C = H^E_m\{x$ butane + $(1 - x)$ alkanol$\}$. The more negative the value of $A - B - C$ the greater will be the association between the ketone and the alkanol. The results of such an analysis at $x = 0.5$ are given in Table 3 and indicate that the degree of association is dependent on the alkyl chain length of the species involved, with the greatest association between the ketone and the alkanol with the shortest carbon chain.

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