Excess Enthalpies of Binary Mixtures of Methanol with Heptanone Isomers at 298.15 and 323.15 K

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The excess molar enthalpies, H_m^E, for methanol + 2-heptanone, 3-heptanone, and 4-heptanone have been measured as a function of mole fraction at 298.15 and 323.15 K by means of an isothermal flow calorimeter. Values for H_m^E are endothermic with a maximum value occurring at a mole fraction close to 0.5. The temperature effect on the excess enthalpy values is important. Maximum values at 298.15 K range from 725 to 744 J·mol^{-1}. Maximum values at 323.15 K range from 908 to 955 J·mol^{-1}. The position of the ketone group has little effect on the measured H_m^E.

Introduction

In a previous paper, Rubio *et al.* (1983, 1984) reported vapor−liquid equilibrium (VLE) measurements for methanol + 2-heptanone, 3-heptanone, and 4-heptanone at 298.15 and 323.15 K. These kind of oxygenated compound mixtures are interesting from the theoretical point of view because the alcohol presents amphoteric behavior and the ketone is a Lewis base, and therefore the interaction due to the hydrogen bond has to be taken into account. As part of a program underway at our laboratory to provide excess molar enthalpies (H_m^E) and VLE data for mixtures in which association effects are very important (Coto *et al.*, 1995a,b, 1996a,b, Renuncio *et al.*, 1995, 1996; Mössner, 1996), H_m^E data for the binary mixtures formed by methanol and heptanone isomers at 298.15 and 323.15 K are reported in this paper.

Experimental Section

The high-pressure flow calorimeter from Hart Scientific (model 7501) used for the experiments and the experimental procedure have been described by Christensen *et al.* (1976) and by Gmehling (1993). The chemicals were pumped into the calorimeter by two thermostated ISCO pumps (model LC2600). The calorimeter cell was thermostated in a silicon oil bath (±0.0005 K), and the pressure was controlled by a back-pressure regulator. A manually controlled piston acts as a fine adjustment of the nitrogen pressure over the back-pressure regulator. Oscillations in pressure were smaller than ±0.01 MPa.

The materials employed were methanol (Carlo Erba, purity 99.9 mole %), 2-heptanone (Sigma-Aldrich, purity 99.9 mole %), 3-heptanone (Sigma-Aldrich, purity 99.8 mole %), and 4-heptanone (Sigma-Aldrich, purity 99.4 mole %). Measurements of the methanol + 3-heptanone system at 323.15 K were carried out using 3-heptanone from Fluka, purity greater than 97 mole %. Chemicals were used without further purification. Methanol was handled under inert nitrogen atmosphere to prevent water condensation.

All runs were made in the steady-state fixed composition mode. Flow rates were selected to cover the whole mole fraction range. In most cases, the measurements were carried out at a total flow rate of 0.005 cm^3·s^{-1}. A few measurements were carried out at a total flow rate of 0.010 cm^3·s^{-1}. Reproducibility of results was estimated to be ±(1 + 0.01H_m^E) J·mol^{-1}. The flow rates measured in cm^3·s^{-1} were converted to mol·s^{-1} and to mole fractions using the densities of the two materials estimated as follows. For methanol, the densities at the temperature of the pump and at 4 MPa were calculated from the density at atmospheric pressure given in the *TRC Thermodynamics Tables* (1994) and the isothermal compressibility reported by Diaz Peña and Tardajos (1979). For heptanone isomers, the densities at the temperature of the pump and at 4 MPa were calculated from the densities at atmospheric pressure given in the *TRC Thermodynamics Tables* (1994) using the method of Thomson *et al.* (1982).

Results and Discussion

Excess molar enthalpies were determined for methanol + 2-heptanone, 3-heptanone, and 4-heptanone over the entire composition range at 298.15 and 323.15 K and at a pressure of 4.00 MPa. The results obtained are given in Table 1. Values for H_m^E at each temperature studied were fitted to a Padé approximant given by the equation

$$H_m^E/(\mathrm{J \cdot mol^{-1}}) = x(1 - x)\frac{\sum_{n=0} A_n(2x-1)^n}{1 + \sum_{k=1} B_k(2x-1)^k} \qquad (1)$$

where A_n and B_k are adjustable coefficients and x is the methanol mole fraction. The coefficients A_n and B_k and standard deviations between experimental and calculated values of H_m^E are given in Table 2. Figures 1−3 are plots of H_m^E against x at the two temperatures studied for the methanol + 2-heptanone, methanol + 3-heptanone, and methanol + 4-heptanone systems, respectively.

Mixtures show endothermic mixing at the two temperatures studied. The temperature effect on the excess enthalpy values is important. Values of H_m^E exhibit a maximum at a mole fraction close to 0.5 and become more endothermic as temperature increases. Maximum values at 298.15 K range from 725 to 744 J·mol^{-1}. Maximum values at 323.15 K range from 908 to 955 J·mol^{-1}. The position of the ketone group has little effect in the H_m^E values. Previously, Renuncio *et al.* (1995) have shown that the pressure effect on the excess enthalpy for the ethanol + propanal system in the range from 2.00 to 8.00 MPa is of the same order as the experimental uncertainty. A similar dependence for H_m^E with pressure may be expected

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Table 1. Experimental Excess Molar Enthalpies H_m^E for Methanol (x) + Heptanone Isomer ($1 - x$)

x	$H_m^E/(J{\cdot}mol^{-1})$	x	$H_m^E/(J{\cdot}mol^{-1})$	x	$H_m^E/(J{\cdot}mol^{-1})$
		Methanol + 2-Heptanone, 298.15 K			
0.103	217	0.397	722	0.793	483
0.118	285	0.434	736	0.802	461
0.147	346	0.450	735	0.821	432
0.177	408	0.493	740	0.827	415
0.203	447	0.522	744	0.899	277
0.265	569	0.597	713	0.918	227
0.304	624	0.697	621	0.924	212
0.320	650	0.754	538	0.975	83
0.354	669				
		Methanol + 3-Heptanone, 298.15 K			
0.147	293	0.372	689	0.749	517
0.204	424	0.400	701	0.802	439
0.301	601	0.454	725	0.849	348
0.319	615	0.552	704	0.898	269
0.351	656	0.678	602	0.947	153
0.359	671	0.696	573	0.975	70
		Methanol + 4-Heptanone, 298.15 K			
0.069	180	0.402	716	0.722	565
0.103	279	0.478	731	0.754	525
0.126	358	0.493	730	0.802	448
0.147	416	0.521	719	0.827	409
0.178	474	0.548	708	0.849	367
0.198	507	0.597	685	0.899	270
0.210	560	0.630	657	0.951	145
0.348	678	0.679	612	0.962	121
0.378	705				
		Methanol + 2-Heptanone, 323.15 K			
0.103	268	0.377	886	0.673	801
0.126	323	0.397	900	0.714	728
0.170	471	0.424	906	0.748	673
0.200	564	0.493	925	0.802	566
0.222	608	0.500	924	0.819	540
0.257	700	0.552	900	0.853	457
0.273	728	0.599	870	0.899	329
0.305	785	0.647	822	0.950	193
0.353	848				
		Methanol + 3-Heptanone, 323.15 K			
0.049	131	0.378	941	0.775	637
0.076	235	0.447	954	0.802	575
0.096	310	0.478	958	0.826	520
0.125	462	0.521	926	0.849	464
0.177	630	0.572	889	0.875	407
0.203	681	0.629	960	0.898	344
0.230	760	0.669	799	0.924	266
0.248	781	0.722	730	0.948	194
0.272	841	0.753	661	0.958	167
0.347	919				
		Methanol + 4-Heptanone, 323.15 K			
0.075	338	0.305	826	0.722	720
0.103	409	0.348	866	0.754	645
0.126	480	0.417	904	0.802	583
0.147	550	0.450	908	0.826	516
0.172	623	0.493	901	0.849	454
0.198	663	0.521	904	0.860	419
0.210	686	0.557	881	0.899	328
0.222	707	0.573	876	0.932	235
0.248	753	0.619	841	0.951	165
0.277	788	0.679	784		

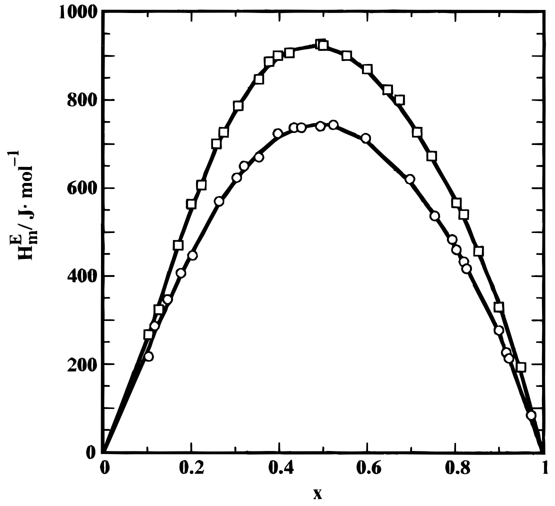

Figure 1. Excess molar enthalpies H_m^E for methanol (x) + 2-heptanone ($1 - x$): ○, 298.15 K; □, 323.15 K; —, calculated from eq 1.

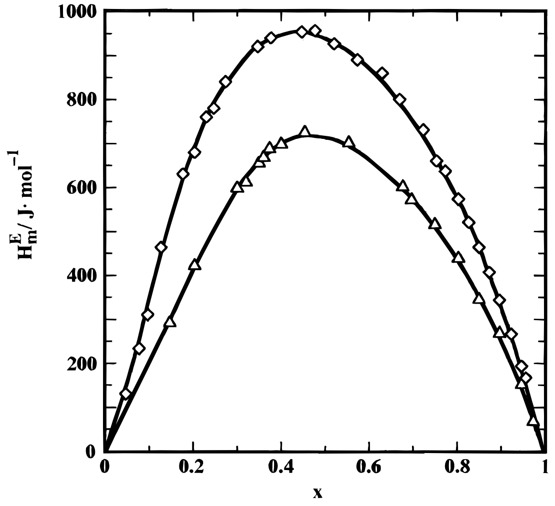

Figure 2. Excess molar enthalpies H_m^E for methanol (x) + 3-heptanone ($1 - x$): △, 298.15 K; ◇, 323.15 K; —, calculated from eq 1.

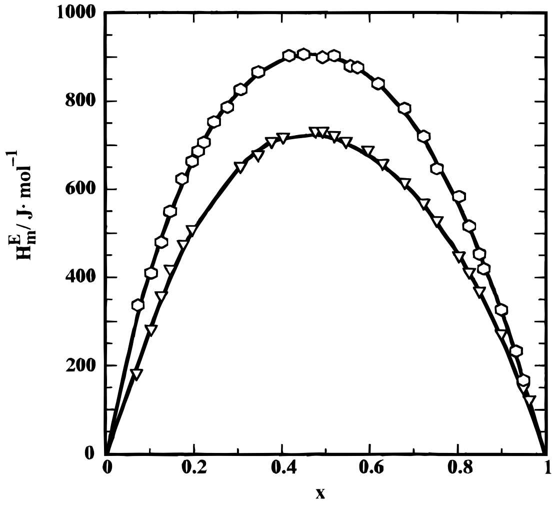

Figure 3. Excess molar enthalpies H_m^E for methanol (x) + 4-heptanone ($1 - x$): ▽, 298.15 K; ⬡, 323.15 K; —, calculated from eq 1.

for methanol + heptanone isomers, and H_m^E values reported in this paper may be compared with those previously determined for binary mixtures formed by methanol and other ketones at atmospheric pressure.

Excess enthalpies of methanol + ketone have been determined mostly at 298.15 K. Nogueira *et al.* (1994) reviewed excess enthalpies for binary mixtures of a 2-ketone (from acetone to 2-heptanone) + an 1-alkanol (from ethanol or 1-propanol to 1-octanol or 1-decanol) at 298.15 K. These H_m^E values are endothermic over the entire composition range with a maximum value occurring at a mole fraction close to 0.5. These maximum values range from 1250 J·mol^{-1} for 2-heptanone + 1-propanol to 1500 J·mol^{-1} for 2-heptanone + 1-octanol. Nogueira *et al.* (1994) concluded that H_m^E values decrease as the aliphatic chain

Table 2. Coefficients and Standard Deviation, σ, for Least-Squares Representation of H_m^E for Methanol (x) + Heptanone Isomer ($1 - x$) by Eq 1

	298.15 K methanol +			323.15 K methanol +		
	2-heptanone	3-heptanone	4-heptanone	2-heptanone	3-heptanone	4-heptanone
A_0	2979.5	2893.0	2890.1	3695.5	3775.4	3621.1
A_1	136.57	342.30	−1756.1	−1230.1	−2603.6	364.52
A_2	−307.20	−650.46	151.83	−407.35	−1.8598	706.26
A_3	−648.14	−1319.7	−653.31	−1136.3	−1220.3	388.85
B_1			−0.75082	−0.43106	−0.90406	
σ/J·mol^{-1}	7.8	5.7	8.1	7.0	10	8.1

Table 3. Excess Molar Enthalpies H_m^E for Methanol + Ketone Mixtures at 298.15 K and $x = 0.5$

ketone	H_m^E/(J·mol^{-1})	ref
acetone	710	Coomber and Wormald (1976)
butanone	720	Nagata *et al.* (1976)
	679	Garriga *et al.* (1996)
2-pentanone	687	Letcher and Nevines (1995)
3-pentanone	725	Letcher and Nevines (1995)
2-heptanone	745	this work
3-heptanone	723	this work
4-heptanone	723	this work

length of the ketone increases for a given 1-alkanol and that they increase as the aliphatic chain length of the alcohol increases for a given ketone. Letcher and Nevines (1995) reviewed excess enthalpies for binary mixtures of a ketone (acetone, butanone, 2-pentanone, or 3-pentanone) + an alkanol (methanol, ethanol, 1-propanol, or 2-propanol) at 298.15 K. H_m^E values are endothermic over the entire composition range with a maximum value occurring at a mole fraction close to 0.5. The H_m^E ($x = 0.5$) values reflect a weak dependence on the type of ketone and a strong dependence on the type of alkanol. Results reported in this paper confirm the conclusions of Nogueira *et al.* (1994) and Letcher and Nevines (1995). The composition dependence of H_m^E for methanol + 2-heptanone, 3-heptanone, and 4-heptanone is very similar to that previously reported for other methanol + ketone mixtures. H_m^E values for methanol + 2-heptanone at 298.15 K are considerably less endothermic than those reported by Nogueira *et al.* (1994) for 1-propanol + 2-heptanone at the same temperature, thus indicating a strong dependence on the type of alkanol. Table 3 compares H_m^E values at 298.15 K and $x = 0.5$ for methanol + 2-heptanone, 3-heptanone, and 4-heptanone with those previously reported for methanol + acetone, butanone, 2-pentanone, and 3-pentanone at the same temperature. These values are very similar to each other, thus indicating a very weak dependence of H_m^E on the type of ketone for the methanol + ketone mixtures at 298.15 K. The H_m^E dependence on the type of ketone at 298.15 K becomes more important as the aliphatic chain length of the alcohol increases. H_m^E values at 323.15 K and $x = 0.5$ are 924, 944, and 905 J·mol^{-1} for methanol + 2-heptanone, 3-heptanone, and 4-heptanone, respectively. These values indicate that the effect of the ketone-group position becomes more important as the temperature increases.

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