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Note

EXCESS ENTHALPIES OF KETONES + DIETHER AT 298.15 K

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ABSTRACT

The excess molar enthalpy H_m^E has been determined as a function of mole fraction x at atmospheric pressure and 298.15 K for several binary mixtures of the type ketones (symmetrical and asymmetrical) + diether (1-2 dimethoxyethane). The ketones were 2-pentanone, 2-hexanone, 2-heptanone, 2-octanone, 2-nonanone, 3-pentanone, 4-heptanone, 5-nonanone.

For all mixtures the excess molar enthalpies are positive except for the systems 2-pentanone, 3-pentanone, and 2-hexanone with 1,-2-dimethoxyethane.

The values of H_m^E increase as the aliphatic chain of the ketone molecule increases.

INTRODUCTION

The purpose of this work has been to study the binary mixtures containing the oxygen (–O–) and carbonyl (–CO–) functional groups. We report experimental excess molar enthalpies of 1,2-dimethoxyethane (diether with two –O– groups) asymmetrical ketones (2-pentanone, 2-hexanone, 2-heptanone, 2-octanone, 2-nonanone) and symmetrical ketones (3-pentanone, 4-heptanone, 5,-nonanone) at 298.15 K and atmospheric pressure.

The aim of this work is to provide quantities for the characterization of the molecular interactions between ketones and ethers and the application of engineering data.

EXPERIMENTAL

A standard Calvet microcalorimeter [1] was used to determine the excess enthalpies. The microcalorimeter was calibrated using measured electrical energy and the calibration was checked by determining for the whole mole fraction range.

The excess molar enthalpies of (hexane + cyclohexane), (benzene + cyclohexane), and (tetrachloromethane + benzene) were measured at 298.15 K. Our results differ by less than 1% from those of the literature [2,3] near $x = 0.5$. The experimental technique of Paz-Andrade et al. [4] in which a small gas phase is present was used by the authors [5].

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TABLE 1

Excess molar enthalpy for asymmetrical and symmetrical ketones + 1, + 1,2-dimethoxyethane at 298.15 K

x	H_m^E (J mol^{-1})	x	H_m^E (J mol^{-1})	x	H_m^E (J mol^{-1})	x	H_m^E (J mol^{-1})
x2-Pentanone + (1 − x)1,2-dimethoxyethane							
0.1125	−30	0.3218	−83	0.5649	−97	0.8031	−62
0.1539	−42	0.3545	−88	0.6068	−95	0.8474	−51
0.2119	−59	0.3876	−94	0.6642	−88	0.8927	−37
0.2461	−67	0.4699	−99	0.7488	−74	0.9317	−26
0.2667	−73	0.5135	−99	0.7562	−73		
x2-Hexanone + (1 − x)1,2-dimethoxyethane							
0.1048	−4	0.2961	−30	0.4583	−46	0.7225	−39
0.1850	−14	0.3332	−34	0.5113	−46	0.7593	−36
0.2128	−19	0.3547	−35	0.5463	−46	0.8096	−31
0.2371	−22	0.3604	−36	0.5651	−47	0.8615	−25
0.2456	−24	0.3917	−40	0.6091	−45	0.9019	−18
0.2700	−25	0.3964	−40	0.6660	−44		
x2-Heptanone + (1 − x)1,2-dimethoxyethane							
0.0982	29	0.3064	31	0.6009	17	0.8030	5
0.1288	31	0.3566	30	0.6405	15	0.8111	4
0.1341	33	0.3893	27	0.6439	14	0.8499	3
0.1936	36	0.4444	25	0.6491	15	0.8909	1
0.2470	34	0.4930	20	0.6995	12	0.9064	1
0.2937	32	0.4970	20	0.7036	11	0.9480	−1
						0.9542	−1
x2-Octanone + (1 − x)1,2-dimethoxyethane							
0.1066	65	0.2773	94	0.4344	91	0.6704	63
0.1415	74	0.3152	96	0.4822	87	0.7248	54
0.1711	81	0.3556	94	0.5480	82	0.7916	40
0.2142	88	0.3629	94	0.5735	79	0.8982	19
0.2562	94	0.3767	94	0.5896	75		
x2-Nonanone + (1 − x)1,2-dimethoxyethane							
0.0962	92	0.2500	155	0.4556	167	0.6564	125
0.1648	129	0.2850	161	0.5105	157	0.7140	109
0.2347	151	0.3414	168	0.5152	159	0.7653	89
0.2392	153	0.4222	167	0.5522	152	0.8350	66
0.2406	152	0.4270	167	0.6004	140	0.9157	31
x3-Pentanone + (1 − x)1,2-dimethoxyethane							
0.0962	−22	0.2975	−70	0.5216	−90	0.7509	−69
0.1327	−34	0.3460	−79	0.5685	−91	0.8085	−59
0.1866	−45	0.3982	−85	0.5969	−89	0.8631	−45
0.2215	−56	0.4458	−90	0.6464	−84	0.8932	−35
0.2541	−63	0.4645	−90	0.7078	−77	0.9733	−10
x4-Heptanone + (1 − x)1,2-dimethoxyethane							
0.1318	71	0.3146	111	0.4590	112	0.5911	99
0.1855	90	0.3647	114	0.4609	113	0.6492	91
0.2113	98	0.3770	115	0.5012	110	0.7088	77
0.2131	98	0.4093	114	0.5159	110	0.7535	67
0.2229	100	0.4188	113	0.5746	101	0.8062	54
0.2492	104	0.4214	115	0.5863	100	0.8586	41
						0.9364	18

TABLE 1 (continued)

x	H_m^E (J mol^{-1})	x	H_m^E (J mol^{-1})	x	H_m^E (J mol^{-1})	x	H_m^E (J mol^{-1})
x5-Nonanone + $(1-x)$1,2-dimethoxyethane							
0.1028	135	0.3728	268	0.5537	247	0.7707	153
0.1614	189	0.3943	268	0.5619	245	0.8214	125
0.1924	206	0.4479	267	0.6231	226	0.8393	113
0.2672	247	0.4811	264	0.6660	209	0.8921	75
0.3183	261	0.5277	253	0.7195	185		

Nevertheless for the liquids considered, the corrections to the excess molar enthalpy and mole fraction due to the gas phase were always smaller than 0.1 J mol^{-1} and 0.0002, respectively. The calorimeter was thermostatted to ± 0.005 K, and the measurements were carried out at 298.15 K.

All the chemicals used were from Fluka, 2-pentanone (purum > 99 mol%), 2-hexanone (purum > 98 mol%), 2-heptanone (purum > 98 mol%), 2-octanone (purum > 98 mol%), 2-nonanone (purum > 97 mol%), 3-pentanone (purum > 99 mol%), 4-heptanone (purum > 98 mol%), 5-nonanone (purum > 97 mol%) and 1,2-dimethoxyethane (purum > 99 mol%) were used without further purification.

Prior to actual measurements, all liquids were dried using molecular sieve (Union Carbide Type 4A from Fluka).

Measurements of their densities and refractive indices at 293.15 were in good agreement with published values [6,7]. The ether used passed the peroxides test.

Conversion to molar quantities is based on the relative atomic-mass table of 1975 issued by IUPAC [8].

RESULTS AND DISCUSSION

The results of our measurements of H_m^E as a function of mole fraction of ketones for mixtures of 1,2-dimethoxyethane with asymmetrical and symmetrical ketones are presented in Table 1.

Each set of results has been fitted to the expression

$$H_m^E = x(1-x)\sum A_i(2x-1)^i \qquad (\text{J mol}^{-1}) \tag{1}$$

by least-square regression, all points having been weighted equally. Values of the coefficients A_i and standard deviations $s(H_m^E)$ are given in Table 2.

For almost all the mixtures $s(H_m^E)/H_m^E(\text{max}) < 0.01$ where $H_m^E(\text{max})$ denotes the maximum value of the excess molar enthalpy with respect to mole fraction.

TABLE 2

Coefficients A and standard deviations $s(H_m^E)$ for representation of the excess molar enthalpies of ketones + 1,2-dimethoxyethane at 298.15 K from equation (1)

Ketone	A_0 (J mol^{-1})	A_1 (J mol^{-1})	A_2 (J mol^{-1})	A_3 (J mol^{-1})	$s(H_m^E)$
2-Pentanone	−398.1	−5.4	80.2	−91.6	0.6
2-Hexanone	−183.5	−54.0	89.1	−75.2	0.8
2-Heptanone	83.2	−99.1	125.0	−150.3	0.8
2-Octanone	342.9	−187.7	141.8	−173.0	1.0
2-Nonanone	638.7	−273.5	131.2	−170.5	1.0
3-Pentanone	−364.9	−28.7	62.7	−63.7	0.9
4-Heptanone	439.6	−173.5	80.4	−66.9	0.9
5-Nonanone	1041.4	−358.9	150.0	−104.6	2.0

A graphical representation of the experimental points together with the smoothing curves is shown in Figs. 1 and 2. No literature results were found for comparison.

In all the systems investigated the excess molar enthalpy is positive except for binary mixtures 2-pentanone, 3-pentanone, 2-hexanone with 1,2-dimethoxyethane.

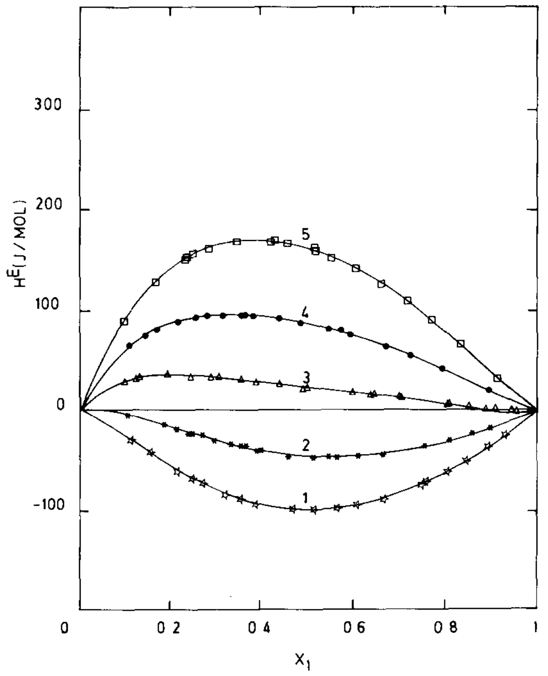

Fig. 1. Plot of H_m^E versus mole fraction for various mixtures of ketone + 1,2-dimethoxyethane. Ketones: ☆, 2-pentanone; •, 2-hexanone; △, 2-heptanone; ●, 2-octane; □, 2-nonanone.

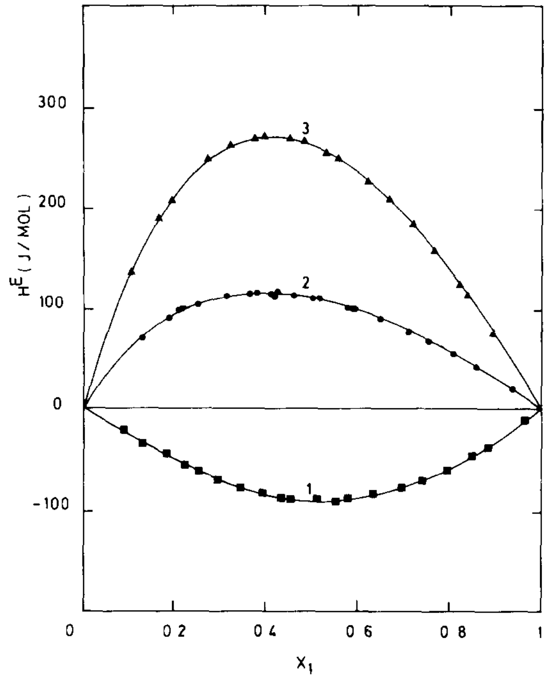

Fig. 2. Plot of H_m^E versus mole fraction for various mixtures of ketone + 1,2-dimethoxyethane. Ketones: ■, 3-pentanone; ●, 4-heptanone; ▲, 5-nonanone.

For all systems, the value of H_m^E increases as the aliphatic chain of the ketone molecule increases, moving from an exothermic effect to an endothermic effect.

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