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EXCESS MOLAR ENTHALPIES OF SOME *n*-ALKYLAMINE + CYCLOHEXANE OR + BENZENE BINARY MIXTURES *

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ABSTRACT

The excess molar enthalpies, H^E, were determined as a function of mole fraction, x, at 303.15 K and atmospheric pressure, for *n*-pentylamine, *n*-heptylamine, *n*-nonylamine and *n*-undecylamine + cyclohexane or + benzene binary mixtures. The results show that H^E of *n*-alkylamine + cyclohexane mixtures increases with decreasing chain length of the *n*-alkylamine, but that H^E of *n*-alkylamine + benzene mixtures decreases with decreasing chain length of the *n*-alkylamine.

INTRODUCTION

Following our study of the thermodynamic properties of binary mixtures containing an *n*-alkylamine with an odd number of carbon atoms, the excess enthalpies H^E, at 303.15 K and atmospheric pressure, of *n*-pentyl-, *n*-heptyl-, *n*-nonyl- and *n*-undecylamine with cyclohexane or benzene are reported here. The aim of this work is to complete our previous study [1] on *n*-alkylamine + *n*-dodecane or + *n*-hexadecane binary mixtures.

There are no known previous measurements on H^E of the mixtures studied here.

EXPERIMENTAL

All the *n*-alkylamines were the same as those used previously [1]. Cyclohexane and benzene were from Fluka AG, Buchs, with a purity of better than 99.5 mol%.

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Excess molar enthalpies were determined using an isobaric and quasi-isothermic calorimeter [2]. Electric energy was measured to better than 0.5% and the temperature of the water thermostat was controlled to within ±0.002 K.

TABLE 1

Excess molar enthalpies at 303.15 K and atmospheric pressure

x	H^E (J mol^{-1})	x	H^E (J mol^{-1})	x	H^E (J mol^{-1})	x	H^E (J mol^{-1})
n-pentylamine (1) + cyclohexane (2)				*n*-pentylamine (1) + benzene (2)			
0.0301	185	0.4384	1072	0.0335	89	0.4975	581
0.0648	364	0.4908	1053	0.0686	174	0.5487	559
0.1023	530	0.5478	1014	0.1358	314	0.6005	536
0.1658	753	0.6071	952	0.2007	424	0.6934	462
0.2343	913	0.6964	801	0.2654	506	0.7529	394
0.3024	1015	0.7932	597	0.3336	560	0.8006	338
0.3445	1057	0.8878	342	0.3801	579	0.8554	254
0.3484	1060	0.9511	149	0.4239	589	0.9039	174
0.3910	1070			0.4581	590		
n-heptylamine (1) + cyclohexane (2)				*n*-heptylamine (1) + benzene (2)			
0.0678	353	0.5035	925	0.0328	105	0.4937	591
0.0928	455	0.5671	866	0.0696	206	0.5684	562
0.1696	686	0.6618	747	0.1319	331	0.6628	485
0.2279	818	0.7373	609	0.2056	454	0.7335	411
0.2982	913	0.8264	433	0.2687	527	0.7967	330
0.3680	951	0.8795	313	0.3292	573	0.8643	230
0.4054	959	0.9357	169	0.3999	598	0.9395	101
0.4604	947			0.4478	601		
n-nonylamine(1) + cyclohexane (2)				*n*-nonylamine (1) + benzene (2)			
0.0482	256	0.4480	899	0.0510	193	0.4490	647
0.0989	465	0.4996	868	0.0979	325	0.4863	632
0.1616	673	0.5961	781	0.1642	472	0.5956	571
0.2320	790	0.7036	625	0.2366	572	0.6916	472
0.3079	879	0.7921	464	0.2981	626	0.7910	342
0.3355	895	0.8870	271	0.3490	648	0.8996	160
0.3994	909			0.3944	654		
n-undecylamine (1) + cyclohexane (2)				*n*-undecylamine (1) + benzene (2)			
0.0312	164	0.4512	872	0.0317	135	0.4454	688
0.0669	320	0.5069	833	0.0602	244	0.4846	682
0.1006	449	0.5899	755	0.0967	364	0.5813	611
0.1664	645	0.6876	625	0.1462	484	0.6752	511
0.2344	767	0.7960	427	0.2244	603	0.7495	412
0.3005	844	0.8839	255	0.3044	674	0.8386	277
0.3477	870	0.9351	143	0.3629	701	0.9042	169
0.4001	879			0.4059	700		

TABLE 2

Coefficients A_i and standard deviations $\sigma(H^E)$ for representation of excess molar enthalpies at 303.15 K and atmospheric pressure by eqn. (1)

n-alkylamine (1) + hydrocarbon (2)	A_1	A_2	A_3	A_4	$\sigma(H^E)$ (J mol^{-1})
n-alkylamine (1) + cyclohexane (2)					
n-pentylamine	4207	−1216	627	−446	4
n-heptylamine	3699	−1320	619	−312	4
n-nonylamine	3477	−1374	668	−325	3
n-undecylamine	3361	−1391	525	−310	3
n-alkylamine (1) + benzene (2)					
n-pentylamine	2331	−518	95	162	3
n-heptylamine	2364	−578	139	−199	3
n-nonylamine	2526	−895	377	−453	3
n-undecylamine	2673	−1083	522	−427	4

RESULTS AND DISCUSSION

The results of measurements of H^E, as a function of x, at 303.15 K and atmospheric pressure, are listed in Table 1. The composition dependence of H^E was fitted by least-squares to a Redlich–Kister-type polynomial

$$H^E(\text{J mol}^{-1}) = x(1-x)\sum_i A_i(2x-1)^{i-1} \quad (1)$$

where x is the mole fraction of *n*-alkylamine. The coefficients A_i and the corresponding standard deviations, σ, are given in Table 2.

The excess molar enthalpies of *n*-alkylamine + cyclohexane are all positive (Fig. 1) and decrease with increasing length of the aliphatic chain of the amine. This decrease (see Fig. 3) is slightly lower than in the case of *n*-alkylamine + *n*-alkane binary mixtures studied previously [1]; the maxima of the H^E–x curves shift gradually toward the cyclohexane-rich side. The partial molar enthalpies $H^{E\infty}$ obtained by extrapolating $H^E/x(1-x)$ to infinite dilution of amine tend to a value very close to (5.6 ± 0.1 kJ mol^{-1}), higher than the corresponding value obtained in the case of *n*-alkylamine + *n*-alkane (3.5 ± 0.2 kJ mol^{-1}) [1,3]

The excess molar enthalpies of *n*-alkylamine + benzene are all positive but show a noticeable exothermic effect relative to *n*-alkylamine + *n*-dodecane, + *n*-hexadecane, or + cyclohexane, which can be put down to the H_2N–π specific interaction. The H^E values of these mixtures increase with

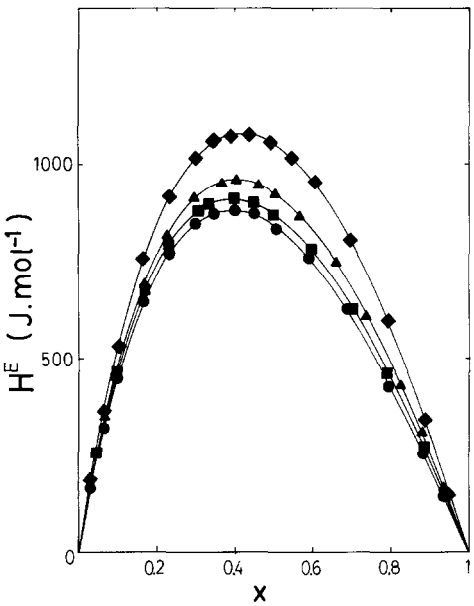

Fig. 1. Excess molar enthalpies H^E, at 303.15 K and atmospheric pressure, for cyclohexane + : *n*-pentylamine (◆), *n*-heptylamine (▲), *n*-nonylamine (■) and *n*-undecylamine (●). Full curves represent the smoothing eqn. (1).

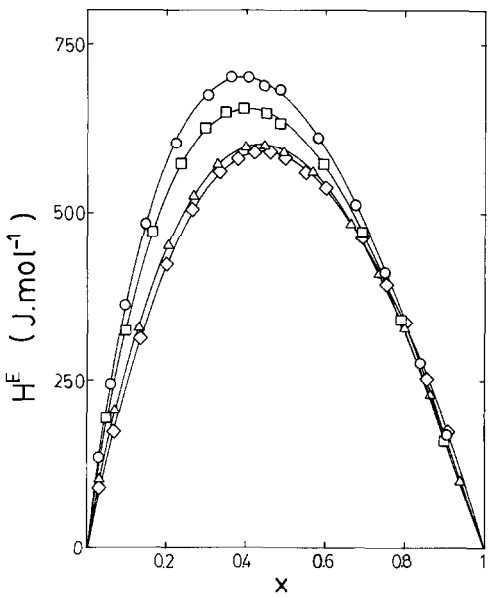

Fig. 2. Excess molar enthalpies H^E, at 303.15 K and atmospheric pressure, for benzene + : *n*-pentylamine (◇), *n*-heptylamine (△), *n*-nonylamine (□) and *n*-undecylamine (○). Full curves represent the smoothing eqn. (1).

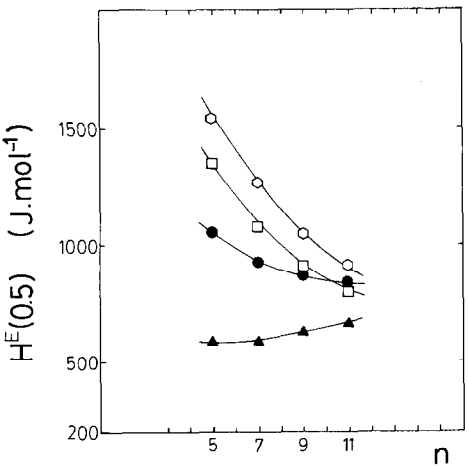

Fig. 3. Plots of excess molar enthalpies at equimolar fraction $H^E_{0.5}$ against the number n of C atoms of the chain of the n-alkylamine: (□) n-dodecane + n-alkylamine (ref. 1); (○) n-hexadecane + n-alkylamine (ref. 1); (●) cyclohexane + n-alkylamine (this work); (▲) benzene + n-alkylamine (this work).

increasing length of the aliphatic chain of the n-alkylamine and the maxima of the H^E–x curves shift gradually toward the benzene-rich side (Figs. 2 and 3).

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