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EXCESS MOLAR ENTHALPIES OF SOME n-ALKYLAMINE + n-ALKANE BINARY MIXTURES

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ABSTRACT

The excess molar enthalpies, H^E, are determined as a function of the mole fraction, x, at 303.15 K and atmospheric pressure, for n-pentylamine, n-heptylamine, n-nonylamine and n-undecylamine + n-dodecane or + n-hexadecane binary mixtures. The H^E values obtained decrease with increasing length of the aliphatic chain of the amine and with decreasing number of carbon atoms in the n-alkane.

INTRODUCTION

The application of the thermodynamics of liquid mixtures to systems of biological interest have confirmed the importance of the study of some interactions existing between the amino group and other functional groups. However, no suitable data are available in the literature for amines with aliphatic chains longer than seven or eight carbon atoms.

This work presents the excess enthalpies, H^E, at 303.15 K and atmospheric pressure, of binary mixtures containing an n-alkylamine with an odd number of carbon atoms (n-pentyl-, n-heptyl-, n-nonyl-, and n-undecylamine) with n-dodecane or n-hexadecane. The aim of this work was to complete previous studies [1,2] carried out in our laboratory on binary mixtures containing n-alkylamines and n-alkanes. As far as we know, no data have been published on the H^E of the mixtures studied here.

EXPERIMENTAL

All the alkylamines used were from Fluka AG (Buchs) and better than 98 mol% pure. The materials were used without further purification, although they were kept over an activated molecular sieve to avoid moisture contamination.

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TABLE 1

Refractive index, n_D, of the pure alkylamine at 298.15 K and atmospheric pressure

Component	Exp.	Lit. [3]
n-Pentylamine	1.40860	1.4093
n-Heptylamine	1.42216	1.4228
n-Nonylamine	1.43162	1.4318
n-Undecylamine	1.43762	1.4381

Refractive index measurements for the sodium D line were carried out to ± 0.00002 using an Abbe refractometer, and the experimental values for the pure amines, at 298.15 K (Table 1) agreed satisfactorily with the literature values [3].

Excess molar enthalpies were determined using an isobaric and quasi-isothermic calorimeter [4]. Electrical energy was measured to better than 0.5% and the temperature of the water thermostat was controlled to within ± 0.002 K. The calorimeter was checked with n-hexane + cyclohexane, the agreement with the reported data [5] being better than 0.5% over the central range of the concentrations used.

RESULTS AND DISCUSSION

The results of the measurements of H^E, as a function of x, at 303.15 K and atmospheric pressure, are listed in Table 2. The composition depen-

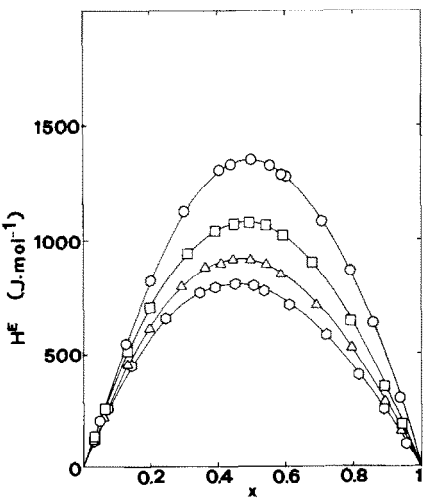

Fig. 1. Excess molar enthalpies, H^E, at 303.15 K and atmospheric pressure, for n-dodecane + : n-pentylamine (○), n-heptylamine (□), n-nonylamine (△), n-undecylamine (⬡). Full curves represent the smoothing eqn. (1).

TABLE 2

Excess molar enthalpies at 303.15 K and atmospheric pressure

x	H^E (J mol^{-1})	x	H^E (J mol^{-1})
n-Pentylamine(1) + n-dodecane (2)			
0.0537	224	0.5563	1325
0.1297	545	0.5914	1288
0.2036	820	0.6052	1278
0.3028	1125	0.7116	1083
0.4065	1306	0.7930	865
0.4390	1328	0.8582	638
0.4981	1352	0.9398	302
n-Heptylamine(1) + n-dodecane (2)			
0.0325	134	0.4929	1078
0.0666	272	0.5430	1064
0.1335	514	0.5952	1022
0.1988	702	0.6818	903
0.3082	939	0.7925	648
0.3920	1039	0.8934	363
0.4497	1071	0.9450	188
0.4651	1077		
n-Nonylamine(1) + n-dodecane(2)			
0.0328	121	0.4971	913
0.0619	223	0.5451	896
0.1341	454	0.5887	850
0.1992	616	0.6965	716
0.2966	798	0.7983	528
0.3647	880	0.8968	290
0.4116	901	0.9428	162
0.4466	915		
n-Undecylamine(1) + n-dodecane(2)			
0.0342	118	0.5075	799
0.0763	260	0.5387	778
0.1476	448	0.6150	716
0.2487	657	0.7232	582
0.3506	769	0.8216	404
0.3934	793	0.8927	253
0.4539	808	0.9583	102
n-Pentylamine(1) + n-hexadecane (2)			
0.0331	170	0.5877	1522
0.0652	330	0.6037	1508
0.1338	645	0.6356	1474
0.2042	922	0.7015	1351
0.2829	1186	0.7914	1094
0.3838	1421	0.8703	761
0.4405	1500	0.9244	480
0.4922	1538	0.9622	252
0.5357	1542		

TABLE 2 (continued)

x	H^E (J mol^{-1})	x	H^E (J mol^{-1})
n-Heptylamine(1) + n-hexadecane(2)			
0.0335	150	0.5034	1262
0.0663	284	0.5456	1256
0.1341	546	0.5863	1230
0.2060	793	0.6942	1090
0.2983	1038	0.7922	842
0.3269	1098	0.8871	509
0.3936	1201	0.9526	225
0.4423	1244		
n-Nonylamine(1) + n-hexadecane(2)			
0.0350	124	0.5460	1033
0.0687	246	0.6008	996
0.1308	462	0.6799	892
0.2125	708	0.7647	740
0.2961	886	0.8739	475
0.3936	1014	0.9207	316
0.4416	1043	0.9675	147
0.5047	1046		
n-Undecylamine(1) + n-hexadecane(2)			
0.0325	106	0.5184	905
0.0666	220	0.5649	887
0.1405	450	0.6149	832
0.2277	659	0.7074	718
0.3276	836	0.8029	535
0.4195	908	0.8797	347
0.4710	918	0.9485	161

TABLE 3

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

n-Alkylamine(1) + n-alkane(2)	A_1	A_2	A_3	A_4	$\sigma(H^E)$ (J mol^{-1})
n-Alkylamine(1) + n-dodecane (2)					
n-Pentylamine	5398	−177	−652	891	4
n-Heptylamine	4312	−321	−353	−139	4
n-Nonylamine	3644	−575	−224	162	4
n-Undecylamine	3194	−663	−87	80	3
n-Alkylamine(1) + n-hexadecane(2)					
n-Pentylamine	6164	694	−22	223	2
n-Heptylamine	5067	157	−275	168	4
n-Nonylamine	4194	−339	−60	882	4
n-Undecylamine	3660	−483	−289	445	5

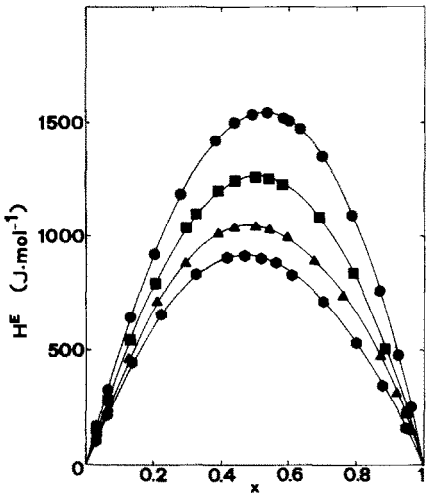

Fig. 2. Excess molar enthalpies, H^E, at 303.15 K and atmospheric pressure, for n-hexadecane + : n-pentylamine (●), n-heptylamine (■), n-nonylamine (▲), n-undecylamine (⬢). Full curves represent the smoothing eqn. (1).

dence of H^E was fitted by least squares to a Redlich-Kister type polynomial

$$H^E = x(1-x)\sum_i A_i(2x-1)^{i-1} \qquad (1)$$

where x is the mole fraction of n-alkylamine. The coefficients A_i and the corresponding standard deviations, σ, are given in Table 3.

The excess molar enthalpies of n-alkylamine + n-dodecane or + n-hexadecane are all positive (Figs. 1 and 2) and decrease with increasing

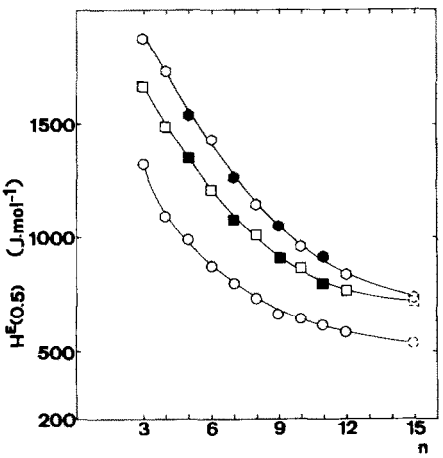

Fig. 3. Plots of excess molar enthalpies at the equimolar fraction $H^E_{0.5}$ versus the number of carbon atoms in the chain of the n-alkylamine: (○) n-hexane + n-alkylamine [6]; (□) n-dodecane + n-alkylamine (this work and [1]); (⬡) n-hexadecane + n-alkylamine (this work and [2]).

length of the aliphatic chain of the amine and with decreasing number of carbon atoms of the n-alkane. The maxima of the H^E versus x curves shift gradually toward the n-alkane rich side; this effect is most noticeable in the case of n-dodecane.

In Fig. 3, the values of the excess enthalpies at equimolar fractions, $H^E_{x=0.5}$, for the n-alkylamines + n-hexadecane studied in this work, are plotted against the chain length of the n-alkylamine, together with previous results obtained by us for n-alkylamine + n-alkane mixtures.

The partial molar excess enthalpies, $H^{E\infty}$, obtained by extrapolating $H^E/x(1-x)$ to infinite dilution of amine, appears, in principle, to be independent of the chain length for amines longer than n-octylamine. The $H^{E\infty}$ values, at 303.15 K, are very close to 3.5 ± 0.2 kJ mol^{-1} in both n-hexane, and n-dodecane or n-hexadecane.

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