Experimental enthalpies of mixtures of alkylfluoroethers + *n*-alkanes at 298.15 K

M.M. Elsa F. de Ruiz Holgado [a], Marta M. Mato [a], Manuel M. Piñeiro [b],
Eleuterio L. Arancibia [c], José Luis Legido [b],
María Inmaculada Paz Andrade [a,*]

[a] *Departamento de Física Aplicada, Campus Universitario Sur, Universidade de Santiago, E-15782 Santiago de Compostela, Spain*
[b] *Departamento de Física Aplicada, Facultade de Ciencias, Universidade de Vigo, E-36200 Vigo, Spain*
[c] *Departamento de Química, Facultad de Ciencias Exactas y Tecnología, Universidad Nacional de Tucumán, Tucumán, Argentina*

Abstract

In this work, excess molar enthalpies, H_m^E, at 298.15 K and atmospheric pressure of methylnonafluorobutylether + alkane (hexane, octane, decane, dodecane) and ethylnonafluorobutylether + alkane (hexane, octane, decane, dodecane) are reported. Values of excess molar enthalpies were measured using a Calvet microcalorimeter. The binary experimental data were fitted using a Redlich–Kister variable-degree polynomial. The excess molar enthalpy is positive for all the mixtures. Phase separation is found in the range of $0.3 < x < 0.8$ and $0.3 < x < 0.94$ for the mixtures methylnonafluorobutyl ether + (decane, or dodecane), respectively.
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1. Introduction

The purpose of this work is to report experimental excess molar enthalpies of methylnonafluorobutylether, (x), + (hexane, octane, decane, or dodecane), $(1 - x)$, and ethyl-nonafluorobutylether, (x), + (hexane, octane, decane, or dodecane), $(1 - x)$, mixtures at the temperature of 298.15 K and atmospheric pressure. These systems have been chosen because mixtures containing hydrofluoroethers and alkanes have been proposed recently as alternative environmentally friendly refrigerants, fire-extinguishers, foam blowing agents, solvents and vapour desiccants in the cleaning process of semiconductors [1,2]. From a theoretical point of view, the excess molar enthalpies can be used to study the energetic interactions between the molecules present in a mixture, such as dispersive forces, hydrogen bonding interactions, etc.

Values of excess molar enthalpies were measured using a Calvet microcalorimeter. The binary experimental data were fitted using a Redlich–Kister variable-degree polynomial [3].

2. Experimental section

2.1. Materials

The chemicals were commercial products of the best quality grade and were used without further purification except drying with Union Carbide 0.4 nm molecular sieves.

n-Hexane and *n*-octane were obtained from Fluka (pro-analysis >99%). Methyl nonafluorobutylether and ethylnonafluorobutyleter were provided by TCI (>99%). *n*-Decane (>99%) and *n*-dodecane (>99%) were obtained from Sigma–Aldrich.

2.2. Apparatus and procedure

The mixtures were prepared by weight using a Mettler H51 balance (precision $\pm 1 \times 10^{-5}$ g), ensuring the uncertainty in mole fraction to be less than 10^{-4}.

The experimental excess molar enthalpies were measured using a Calvet microcalorimeter (1 μW precission) equipped

with a device allowing operation in the absence of vapour phase (<1% vapour space), and having a calorimeter-cell volume of approximately $10\,cm^3$. A Philips PM2535 voltmeter and a data acquisition system were linked to the microcalorimeter. Calibration was performed electrically using a Setaram EJP30 stabilised current source. Further details about the experimental method of operation have been published previously [4,5].

3. Data correlation

Experimental values of H_m^E for the binary mixture {x-alkylnonafluorobutylether $+ (1 - x)$ alkane} are listed in Table 1. The excess molar enthalpy values for the binary mixtures were fitted by the Redlich–Kister fitting polinomial [3] of the form

$$H_m^E = x(1 - x)\sum_{i=1}^{n} A_i(2x - 1)^{i-1}, \tag{1}$$

where H_m^E is the excess molar enthalpy. The fitting parameters A_i were calculated by a least-squares fitting procedure and are listed in Table 2, together with the corresponding standard deviations (σ). The number of parameters used in Eq. (1) was determined in each case by applying the F-test [6].

Table 1
Experimental binary excess molar enthalpies, H_m^E 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})
x-Nonafluorobutyl methyl ether $+ (1 - x)$ hexane				x-Nonafluorobutyl ethyl ether $+ (1 - x)$ hexane			
0.0481	385	0.7710	1308	0.0243	179	0.4880	1470
0.0912	682	0.8426	1014	0.0557	390	0.5103	1468
0.1135	816	0.9067	674	0.0947	609	0.6263	1355
0.1458	973	0.9513	404	0.1422	827	0.6502	1317
0.1928	1199	–	–	0.1902	994	0.7068	1194
0.2822	1505	–	–	0.2249	1117	0.8138	901
0.3798	1706	–	–	0.2602	1191	0.8400	818
0.4960	1753	–	–	0.3292	1336	0.9078	482
0.6165	1664	–	–	0.3845	1393	0.9487	290
0.7152	1491	–	–	0.4290	1451	–	–
x-Nonafluorobutyl methyl ether $+ (1 - x)$ octane				x-Nonafluorobutyl ethyl ether $+ (1 - x)$ octane			
0.0180	162	0.5173	1902	0.0451	275	0.6319	1559
0.1051	796	0.5622	1866	0.0992	671	0.6836	1443
0.1555	1105	0.6195	1827	0.1736	1033	0.7377	1332
0.2072	1359	0.6616	1754	0.2315	1242	0.7886	1152
0.2655	1564	0.7062	1661	0.2639	1350	0.8415	950
0.2981	1660	0.7648	1486	0.3645	1559	0.8828	767
0.3282	1734	0.8047	1335	0.4036	1603	0.9384	437
0.3926	1857	0.8705	1023	0.5435	1649	0.9664	271
0.4405	1902	0.9129	725	0.5831	1611	–	–
x-Nonafluorobutyl methyl ether $+ (1 - x)$ decane[a]				x-Nonafluorobutyl ethyl ether $+ (1 - x)$ decane			
0.0352	317	0.3283	1699	0.0498	275	0.8168	1202
0.0766	652	0.3385	1689	0.1081	684	0.9074	727
0.0860	720	0.3973	1716	0.2056	1233	0.9626	320
0.1393	1084	0.6014	1563	0.2939	1527	–	–
0.1467	1143	0.6994	1509	0.4061	1740	–	–
0.1957	1391	0.8071	1417	0.5149	1779	–	–
0.2606	1595	0.9092	931	0.6017	1717	–	–
0.2841	1654	0.9480	609	0.7131	1555	–	–
x-Nonafluorobutyl methyl ether $+ (1 - x)$ dodecane[a]				x-Nonafluorobutyl ethyl ether $+ (1 - x)$ dodecane			
0.0261	246	0.5702	1108	0.0372	304	0.3726	1791
0.0586	506	0.6890	975	0.0889	692	0.4742	1849
0.1046	777	0.7239	952	0.1335	970	0.5931	1802
0.1331	944	0.8017	894	0.1758	1205	0.7148	1612
0.2058	1147	0.8964	763	0.1852	1234	0.7465	1533
0.2869	1300	0.9058	727	0.2306	1430	0.7916	1408
0.3964	1228	0.9534	631	0.2711	1555	0.8466	1213
0.4190	1233	0.9635	502	0.2780	1583	0.9003	887
0.5055	1145	0.9824	276	0.3196	1666	0.9527	465

[a] The nonafluorobutylmethylether + dodecane and the nonafluorobutylmethylether + decane systems show phase separation in the concentration range of $0.3 < x < 0.94$ and $0.3 < x < 0.8$, respectively. The points inside the demixing region were not included in the regression analysis.

Table 2
The parameters A_i ($\sigma(A_1)$ J mol^{-1}) and standard deviations, $\sigma(H_m^E)$ J mol^{-1} of Eq. (1)

	Hexane	Octane	Decane	Dodecane
Nonafluorobutyl methyl ether				
$A_1 \pm \sigma(A_1)$	7040 ± 28	7637 ± 18	7371 ± 59[b]	6223 ± 112[b]
$A_2 \pm \sigma(A_2)$	−135 ± 44	–	–	2605 ± 135[b]
$A_3 + \sigma(A_3)$	1587 ± 99	1986 ± 85	4277 ± 149[b]	6830 ± 210[b]
$A_4 + \sigma(A_4)$	–	535 ± 96	–	–
$A_5 + \sigma(A_5)$	–	–	–	–
$A_6 + \sigma(A_5)$	–	–	2636 ± 150[b]	–
$\sigma(H_m^E)$	12	11	11[b]	13[b]
Nonafluorobutyl ethyl ether				
$A_1 \pm \sigma(A_1)$	5826 ± 20	6619 ± 26	7093 ± 32	7385 ± 27
$A_2 \pm \sigma(A_2)$	−247 ± 79	–	–	−213 ± 82
$A_3 + \sigma(A_3)$	1002 ± 89	1159 ± 111	2800 ± 314	2796 ± 99
$A_4 + \sigma(A_4)$	−652 ± 192	−1140 ± 354	–	1684 ± 208
$A_5 + \sigma(A_5)$	–	–	−2837 ± 495	–
$A_6 + \sigma(A_6)$	–	2131 ± 609	2530 ± 203	–
$\sigma(H_m^E)$	12	14	12	12

[b] Parameters for the mixtures in the miscible range. The points inside the demixing region were not included in the regression analysis.

4. Results and discussion

Fig. 1 shows the measured values of H_m^E of the binary mixture containing methylnonafluorobutylether + (hexane, or octane) plotted against x, the mole fraction of methylnonafluorobutyl ether, together with the fitted curves.

Fig. 2 shows the excess molar enthalpies of ethylnonafluorobutylether + (hexane, or octane, or decane, or dodecane) mixtures against x, the mole fraction of ethylnonafluorobutylether, at 298.15 K.

Fig. 3 shows the measured values of H_m^E for $x = 0.5$ of methylnonafluorobutylether + (pentane, or hexane, or heptane, or octane, or nonane) systems versus n, the number of carbon atoms of the alkanes, at 298.15 K. The excess molar enthalpies of methylnonafluorobutylether + (pentane, or heptane, or nonane), included for comparison, were measured by Minamihounoki et al. [2].

In Fig. 4, the H_m^E of the binary mixtures of methylnonafluorobutylether + (decane, or dodecane) have been included, and in Fig. 5 the H_m^E ($x = 0.5$) of ethylnonafluorobutylether
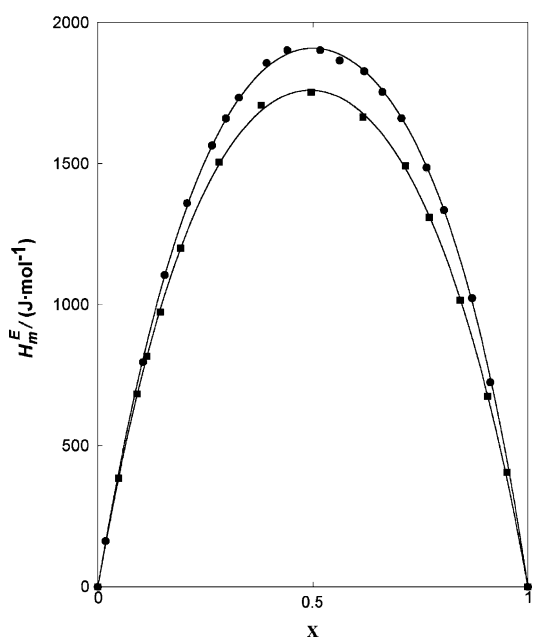

Fig. 1. Excess molar enthalpies H_m^E (J mol^{-1}) at 298.15 K of nonafluorobutyl methyl ether (x) + alkanes ($1 - x$). Experimental data: hexane (■), octane(●), solid line(—), fitted by Eq. (1) with the coefficients listed in Table 2.
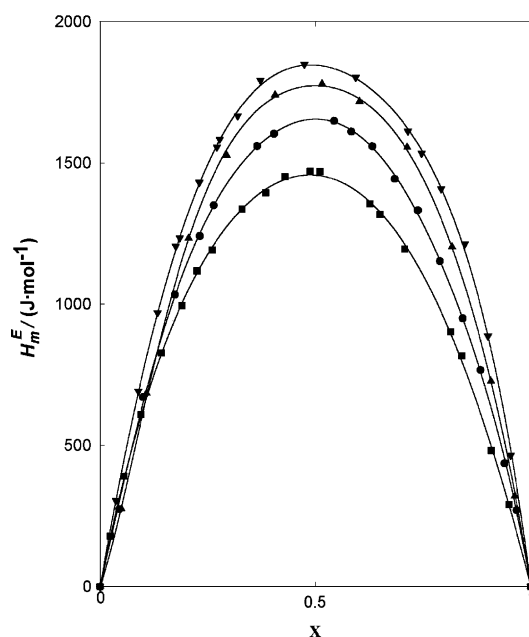

Fig. 2. Excess molar enthalpies H_m^E J mol^{-1} at 298.15 K of nonafluorobutyl ethyl ether (x) + alkanes ($1-x$). Experimental values: hexane (■); octane (●); decane (▲); dodecane (▼); solid line (—), results from the fitting Eq. (1) with the coefficients listed in Table 2.
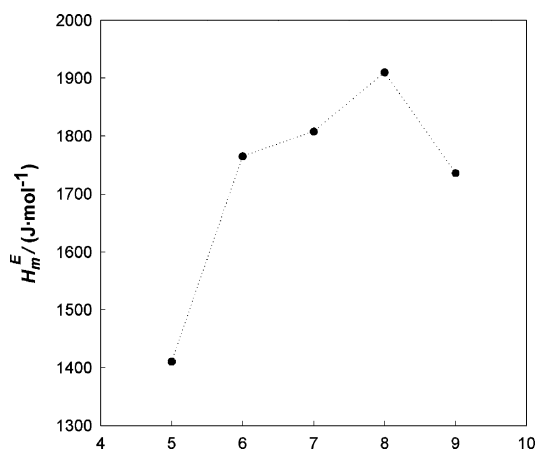
Fig. 3. Excess molar enthalpies $H_{\mathrm{m}}^{\mathrm{E}}$ J mol^{-1} at $x = 0.5$ and 298.15 K of nonafluorobutyl methyl ether + alkanes (pentane[2], or hexane, or heptane[2], or octane, or nonane[2]) systems vs. n, the number of carbon atoms of the alkanes.

Fig. 5. Excess molar enthalpies $H_{\mathrm{m}}^{\mathrm{E}}$ J mol^{-1} for $x = 0.5$ at 298.15 K against n, the number of carbon atoms of the alkanes, of ethylnonafluorobutylether + alkanes ($n = 6, 8, 10, 12$) mixtures.

+ (hexane, or octane, or decane, or dodecane) systems versus n, the number of carbon atoms of the alkanes, at 298.15 K were plotted.

As shown in Fig. 1, $H_{\mathrm{m}}^{\mathrm{E}}$ for the binary systems methyl-nonafluorobutylether + (hexane or octane) is positive over the whole range of composition. The obtained curves are symmetrical, with their maximum placed close to the equimolar composition. The endothermic character of these mixtures shows that the rupture, during the mixing process, of previous interactions present in the pure components, alkanes and hydrofluoroethers, is energetically more impor-
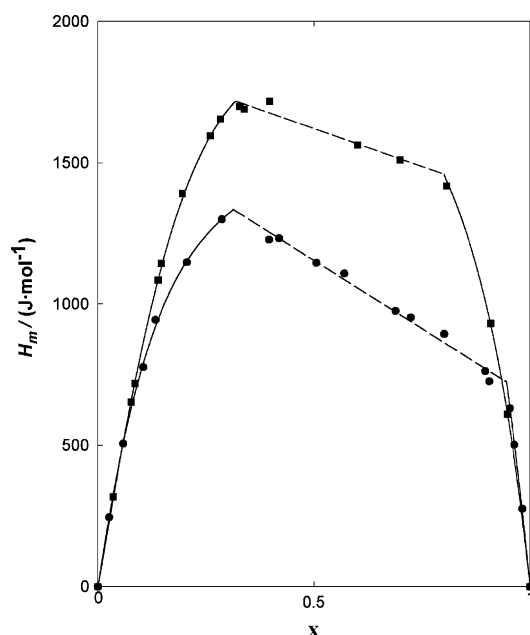
tant than the formation of molecular interactions between unlike molecules. This fact applies to all hydrofluoroether + alkane mixtures studied in this paper.

Fig. 2 shows $H_{\mathrm{m}}^{\mathrm{E}}$ values for the systems ethylnonafluorobutylether + (hexane, octane, decane or dodecane). In this case, for mixtures containing hexane or octane, $H_{\mathrm{m}}^{\mathrm{E}}$ values are slightly lower than those obtained for the systems methylnonafluorobutylether + (hexane or octane). This can be explained by means of weaker dipole–dipole interactions present in pure ethylnonafluorobutylether compared to pure methylnonafluorobutylether. The length increase of the non-fluorinated carbon chain makes the charge distribution by inductive effect to be less accused, and therefore a weaker dipole–dipole interaction will exist. When we compare systems containing ethylnonafluorobutylether + higher alkanes (decane or dodecane), we can see that maximum $H_{\mathrm{m}}^{\mathrm{E}}$ values lie over the same range as the systems methyl-nonafluorobutylether + (hexane or octane). As we increase the length of the alkane carbon chain, it can be seen that not only the strength of the ether–alkane interaction decreases, but also that the previous alkane–alkane interaction is stronger.

Fig. 3 shows that the excess enthalpies of methylnonafluorobutylether + (pentane, hexane, heptane, or octane) binary systems at $x = 0.5$ are positive, increasing with the alkane chain length, except for methylnonafluorobutylether + nonane.

Fig. 4 shows the values of $H_{\mathrm{m}}^{\mathrm{E}}$ of methylnonafluorobutylether + decane and methylnonafluorobutylether + dodecane. Both systems show phase separation in the concentration range $0.3 < x < 0.8$ and $0.3 < x < 0.94$, respectively. The endothermicity of these mixtures with decane and dodecane may also be due to the predominance of the rupture of previous interactions existing in the pure components, alkanes and ethers. Comparing $H_{\mathrm{m}}^{\mathrm{E}}$ values in the miscible regions of these two mixtures, we can see a different trend that in the case of lower alkanes. In this

Fig. 4. Excess molar enthalpies $H_{\mathrm{m}}^{\mathrm{E}}$ J mol^{-1} at 298.15 K for nonafluo-robutylmethyl ether (x) + alkanes ($1 - x$) mixtures. Experimental values: decane (■); dodecane (●); solid line (—), results from the fitting Eq. (1); (- - - - -) linear fitting with the points inside the demixing region.
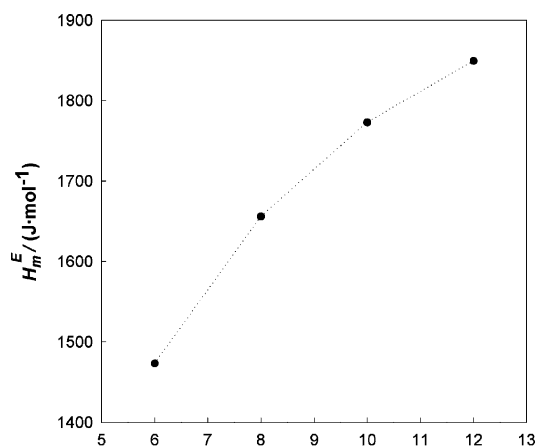
case, the mixture containing dodecane shows less positive H_m^E values that the one containing decane. This is probably due to underestimated values of H_m^E obtained for the methylnonafluorobutylether + dodecane mixture, because of inmiscibility matters.

Acknowledgements

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