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Excess Enthalpies of Some Binary Mixtures. *n*-Alkane + Aliphatic Ether, *n*-Alkane + Hydroxy Ether, Aliphatic Ether + Hydroxy Ether[†]

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Measurements of excess enthalpies in a Picker flow microcalorimeter were carried out at 298.15 K for binary mixtures of *n*-heptane with di-*n*-butyl ether, diethylene glycol dimethyl ether, and 2-butoxyethanol and for 2-butoxyethanol with di-*n*-butyl ether, diethyl ether, and diethylene glycol dimethyl ether. In all cases the excess enthalpies are positive; for binary mixtures containing an ether their magnitude depends upon the molecular surface fraction of the oxygen group in the ether molecule.

Molar excess enthalpies have been reported for alcohol + ether mixtures (*1*); their interpretation in terms of a group contribution model (*2–4*) necessitates evaluation of the interchange energy parameters for the pair of contacts oxygen (–O–)/aliphatic (–CH_3 or –CH_2–) from mixtures of aliphatic ether + *n*-alkane. Also a good check for the prediction of the thermodynamic properties of mixtures containing the three functional groups oxygen, hydroxyl (–OH), and aliphatic, particularly with molecules having simultaneously the oxygen and hydroxyl groups, is thus to have available the excess enthalpies for the mixtures hydroxy ether + *n*-alkane as well as hydroxy ether + aliphatic ether. Furthermore, since cellosolves, typified here by 2-butoxyethanol, are solvents of highly technical importance, then accumulation of further information about the thermodynamic properties of such mixtures is essential to a more complete understanding of their behavior.

We report here the excess enthalpies H^E for the following systems: di-*n*-butyl ether ($CH_3(CH_2)_3O(CH_2)_3CH_3$) + *n*-heptane, diethylene glycol dimethyl ether (or diglyme, $CH_3O(CH_2)_2O(CH_2)_2OCH_3$) + *n*-heptane; 2-butoxyethanol ($CH_3(CH_2)_3O(CH_2)_2OH$) + *n*-heptane, + di-*n*-butyl ether, + diethyl ether ($CH_3CH_2OCH_2CH_3$), and + diethylene glycol dimethyl ether.

Experimental Section

Excess enthalpies were determined in a Picker flow microcalorimeter (from Setaram, France). Details of the auxilliary equipment and of the operating procedure have been described previously (*1*). The calorimeter was thermostated to ±0.005 K, and the measurements were carried out at 298.15 K.

Ethers used in this work were the same as in previous works (*1*, *5*); their densities and heat capacities are given in ref *1* and *5*, respectively. *n*-Heptane (puriss.) was purchased from Fluka with a reported purity of ≥99.5 mol %, its measured density being 679.5 kg m^{-3}; 2-butoxyethanol obtained from Merck was pure grade with a reported purity of >99 mol % and had a measured density of 896.0 kg m^{-3}. Before actual measurements all liquids were dried with molecular sieves (Union Carbide Type 4 A, 2.5–1.4-mm beads from Fluka).

Results and Discussion

Experimental values of the excess enthalpies are listed in Table I; in all binaries *x* is the mole fraction of the first cited component.

Each set of results was fitted with a polynomial form

$$H^E = x(1 - x) \sum_{i=0}^{n-1} A_i \{U(x)\}^i \qquad (1)$$

Values of the coefficients A_i were determined by the method of (unweighted) least squares. It was found that the best fit was obtained by using two different functions $U(x)$ depending on the shape of the H^E curves: $U = 2x - 1$, $U = x^{1/2}c$. The *U* function used for each system is indicated in Table II, where the corresponding values of A_i, standard deviation $\sigma(H^E)$, and *x* range of fitting are listed.

For all of the mixtures $\sigma(H^E)/H^E_{max} < 0.013$, H^E_{max} being the maximum value of the molar excess enthalpy with respect to mole fraction *x*.

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Table I. Experimental Values of the Molar Excess Enthalpies H^E at 298.15 K

x	H^E/ (J mol^{-1})	x	H^E/ (J mol^{-1})
$CH_3(CH_2)_3O(CH_2)_3CH_3$ (x) + $CH_3(CH_2)_5CH_3$ ($1-x$)			
0.0145	8.4	0.5269	120.7
0.0233	10.9	0.5769	116.7
0.0320	17.2	0.6275	111.3
0.0496	25.5	0.6787	103.5
0.0673	34.1	0.7306	93.0
0.0850	41.4	0.7831	79.0
0.1029	48.8	0.8363	63.0
0.1478	66.0	0.8686	52.6
0.1932	79.8	0.8902	44.9
0.2392	91.9	0.9119	37.1
0.2858	102.5	0.9338	28.3
0.3328	110.4	0.9557	18.7
0.3805	116.2	0.9668	15.6
0.4287	119.9	0.9778	11.2
0.4775	121.2	0.9889	5.2
$CH_3O(CH_2)_2O(CH_2)_2OCH_3$ (x) + $CH_3(CH_2)_5CH_3$ ($1-x$)			
0.0219	156.4	0.5702	1502.4
0.0320	217.3	0.6193	1446.7
0.0421	287.5	0.6683	1361.8
0.0522	355.4	0.7172	1254.9
0.0623	429.5	0.7660	1135.9
0.0824	558.1	0.8146	969.7
0.1026	674.9	0.8631	775.6
0.1227	778.2	0.8922	654.2
0.1729	989.1	0.9116	552.9
0.2230	1165.3	0.9309	439.5
0.2730	1293.6	0.9502	315.5
0.3228	1400.7	0.9695	193.2
0.3725	1464.8	0.9791	126.0
0.4221	1519.5	0.9888	71.0
0.4716	1542.4	0.9984	3.8
0.5210	1527.4		
$CH_3(CH_2)_3O(CH_2)_2OH$ (x) + $CH_3(CH_2)_5CH_3$ ($1-x$)			
0.0068	69.7	0.4743	872.7
0.0171	170.0	0.5247	842.8
0.0273	277.8	0.5751	799.3
0.0375	358.7	0.6254	749.1
0.0477	432.8	0.6756	690.1
0.0580	473.2	0.7257	613.1
0.0784	553.9	0.7757	527.2
0.0988	617.5	0.8257	440.1
0.1192	671.1	0.8756	335.7
0.1702	758.1	0.9254	218.8
0.2211	818.0	0.9453	162.7
0.2717	855.5	0.9652	105.3
0.3226	877.8	0.9851	41.7
0.3732	893.8		
$CH_3(CH_2)_3O(CH_2)_2OH$ (x) + $CH_3(CH_2)_3O(CH_2)_3CH_3$ ($1-x$)			
0.0041	23.8	0.5567	648.5
0.0164	71.4	0.6059	604.9
0.0286	137.1	0.6541	553.3
0.0528	288.8	0.7014	497.1
0.0769	374.6	0.7478	440.5
0.1007	457.1	0.7933	375.6
0.1243	512.1	0.8379	306.6
0.1824	601.4	0.8817	229.7
0.2393	664.3	0.9246	148.9
0.2950	697.4	0.9416	116.0
0.3496	718.2	0.9584	81.0
0.4030	724.3	0.9752	44.9
0.4553	706.1	0.9918	14.2
0.5065	682.4		
$CH_3(CH_2)_3O(CH_2)_2OH$ (x) + $CH_3CH_2OCH_2CH_3$ ($1-x$)			
0.0028	6.6	0.4706	382.9
0.0195	53.3	0.6012	334.0
0.0366	98.6	0.8239	152.1
0.0539	138.5	0.8897	87.1
0.0715	174.9	0.9066	73.2
0.0985	223.6	0.9236	57.2
0.1449	288.4	0.9409	41.5
0.2439	360.4	0.9584	25.7
0.2967	388.7	0.9761	6.8
0.3520	395.8		
$CH_3(CH_2)_3O(CH_2)_2OH$ (x) + $CH_3O(CH_2)_2O(CH_2)_2OCH_3$ ($1-x$)			
0.0052	7.5	0.4606	585.5
0.0156	36.0	0.5120	583.2
0.0260	63.8	0.5635	573.5
0.0364	86.3	0.6148	559.5
0.0572	137.2	0.6661	538.0
0.0779	183.6	0.7174	486.9
0.0987	226.2	0.7686	419.2
0.1506	321.0	0.8197	341.9
0.2024	401.0	0.8708	252.3
0.2714	468.8	0.9219	170.8
0.3058	518.3	0.9422	127.3
0.3574	554.9	0.9626	84.6
0.4090	577.4	0.9836	36.5

Table II. Coefficients A_i,[c] Standard Deviations $\sigma(H^E)$,[c] and Fitting Ranges of Concentration for Representation of Molar Excess Enthalpies at 298.15 K by Eq 1

systems	A_0	A_1	A_2	A_3	$\sigma(H^E)$	range
$CH_3(CH_2)_3O(CH_2)_3CH_3$ (x) + $CH_3(CH_2)_5CH_3$[a] ($1-x$)	484.2	−30.5	15.0	−23.8	0.3	0.0443 0.9680
$CH_3O(CH_2)_2O(CH_2)_2OCH_3$ (x) + $CH_3(CH_2)_5CH_3$[a] ($1-x$)	6126	−337	1362		6	0.0691 0.9377
$CH_3(CH_2)_3O(CH_2)_2OH$ (x) + $CH_3(CH_2)_5CH_3$[b] ($1-x$)	16653	−44690	50720	−19824	10	0.0273 0.9851
$CH_3(CH_2)_3O(CH_2)_2OH$ (x) + $CH_3(CH_2)_3O(CH_2)_3CH_3$[b] ($1-x$)	9261	−18517	17539	−6226	5	0.0528 0.9416
$CH_3(CH_2)_3O(CH_2)_2OH$ (x) + $CH_3CH_2OCH_2CH_3$[a] ($1-x$)	1507	−616	281	−633	2	0.0539 0.9409
$CH_3(CH_2)_3O(CH_2)_2OH$ (x) + $CH_3O(CH_2)_2O(CH_2)_2OCH_3$[a] ($1-x$)	2368	−91.2	105		7	0.0260 0.9626

[a] $U = 2x - 1$. [b] $U = x^{1/2}$. [c] In J mol^{-1}.

Ether + n-alkane mixtures have been successfully interpreted in terms of group contribution theory (*3*, *6*) taking into account the "etheric character" of the ether expressed by the molecular surface fraction (*3*) α_e of the oxygen group in the molecule. The H^E values obtained here in n-heptane with two homomorphic ethers —di-n-butyl ether (α_e = 0.0464) and diethylene glycol dimethyl ether (α_e = 0.1573)—confirm that the higher α_e is, the more positive is the H^E. The observed dif-

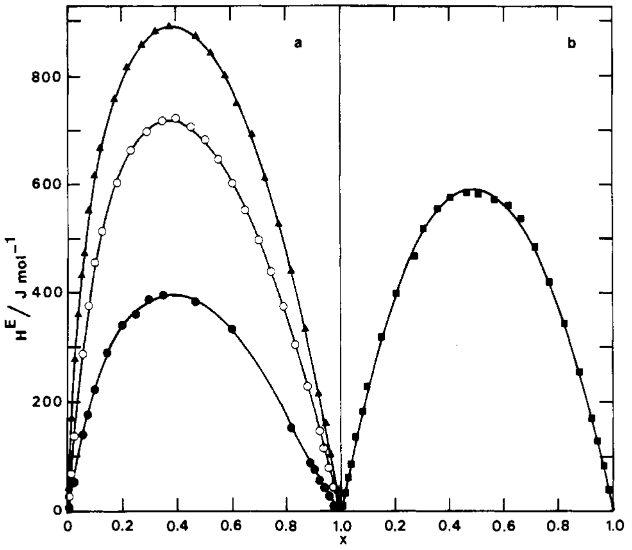

Figure 1. Molar excess enthalpies at 298.15 K of 2-butoxyethanol with various solvents vs. the mole fraction, x, of the cellosolve. Points are experimental results; curves are smoothed representations by eq 1. Part a: (▲) with *n*-heptane; (○) with di-*n*-butyl ether; (●) with diethyl ether. Part b: (■) with diethylene glycol dimethyl ether.

ference in H^E_{max} between these two mixtures, which is rather large ($\simeq$ 1400 J mol^{-1}, see Table I), is reasonably predicted by the theory (*7*).

Excess-enthalpy curves of mixtures containing 2-butoxyethanol indicate that these mixtures behave similarly to mixtures containing an alcohol: i.e., the large and unsymmetric H^E curve with *n*-heptane (Figure 1a), which decreases in magnitude when *n*-alkane is replaced by a more "active" solvent like an ether. When a monoether is replaced by another one, the decrease of H^E corresponds with an increase of the etheric molecular surface fraction α_e. As a matter of fact, the change in H^E ($|\Delta H^E_{max}| \simeq 300$ J mol^{-1}), observed in Figure 1, is due to the augmentation of OH/O interactions (*1*) between the oxygen and hydroxyl groups between unlike molecules when α_e varies from 0.0464 (di-*n*-butyl ether) to 0.0796 (diethyl ether). When 2-butoxyethanol is mixed with a polyether like diethylene glycol dimethyl ether, we also observe a large decrease of H^E resulting from an increase of the interactions between unlike molecules. However, the symmetry of the H^E curve in this later case (see Figure 1b) shows that the competition of interactions between like and unlike molecules is most probably rather complex. A theoretical interpretation of all of these systems has been tentatively proposed (*7*) and will be given in a forthcoming paper.

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Isobaric Vapor–Liquid Equilibria of the 1-Octanol–Tetralin System at Subatmospheric Pressures

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The vapor–liquid equilibria of the 1-octanol–Tetralin system were measured at 50, 100, 200, 400, and 760 mmHg. All of the results could be correlated by the Wilson equation with the parameters at 50 mmHg pressure, up to the atmospheric pressure.

Introduction

Knowledge of the effect of pressure on vapor–liquid equilibria is important for the designing of low-pressure distillation units. The vapor–liquid equilibria of the system 1-octanol (1)–Tetralin (1,2,3,4-tetrahydronaphthalene) (2) were measured at 50, 100, 200, 400, and 760 mmHg. The effect of pressure was examined and the results were correlated by the Wilson equation (*1*).

Experimental Section

The experimental apparatus was the same as the one which was described elsewhere (*2*). The pressures were measured within ±0.4 mmHg by a mercury manometer. The temperatures were measured by a standardized mercury thermometer having an accuracy of 0.02 °C. The compositions of the liquid and vapor phases were determined by the refractive indexes, an Abbe refractometer being used with the sodium lamp at 298.15 K. The compositions were evaluated within an error of ±0.002 mole fraction.

Commercial-grade 1-octanol and Tetralin were distilled in a wetted wall column with 1-m length and 10-mm i.d. at 10 mmHg. The refractive indexes of each distillate were read by the Abbe refractometer with an error of ±0.0002 refractive units. The intermediate distillates with refractive indexes close to the values reported in the literature were used for this work. The purity of both compounds was estimated to be 99.8% by gas chromatography at 230 °C, using a column of 2.2-m length and 3-mm i.d. with Porapak-s. The physical properties of the compounds are summarized in Table I.

After each of the pure compounds was heated in an equilibrium still at atmospheric pressure for 3 h, we determined whether the refractive indexes of the contents had changed. No change of refractive index was found in either compound, but the color of the Tetralin in the still turned to brown during the heating. It was found that 1.5 wt % of the Tetralin was

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