Estimation and interpretation of infinite dilution solute–solvent interaction enthalpies in non-electrolyte aqueous solutions

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ABSTRACT

An empirical strategy has been developed for estimating the enthalpy and the volume requirement for the formation of cavities in liquid water from purely thermodynamic experimental data. The ultimate objective was to complete a scheme for determining the enthalpies of solute–solvent interaction, from experimental enthalpies of mixing of water with non-ionic organic amphiphiles. Results are given for the analysis of several sets of enthalpy of mixing data, taken from the literature. These results were subjected to a group additivity analysis. The results of these analyses were judged to be consistent with the existence of a substantial enthalpy contribution that is derived from molecular reorganization of the aqueous solvent sheath in addition to the hydrogen bonding between the solute species and solvent water.

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1. Introduction

A powerful motivation, for measuring enthalpies of solution, is the anticipation of being in a position to extract information about the strength and nature of solute–solvent interactions. Values of the molar enthalpies of mixing for homogeneous binary liquid mixtures, $\Delta_{mix}H_m$, are obtainable from solution (or mixing) calorimetry. Since the ideal molar enthalpy of mixing of two liquids, $\Delta_{mix}H_m^{id}$, is zero, the measured molar enthalpy of mixing is identical to the excess molar enthalpy of the mixture, H_m^E.

It is frequently found to be desirable to translate excess molar enthalpies into the corresponding *apparent excess molar enthalpies* of the solute $\Phi_{H,A}^E$:

$$\Phi_{H,A}^E = \frac{H_m^E}{x_A} \tag{1}$$

Identifying this quantity as a property of the solute alone is tantamount to attributing all of the deviations from Raoult's Law ideality to the solute species. Extrapolation, to zero solute concentration, of a plot of $\Phi_{H,A}^E$ against mole fraction (or molality) provides a value for the *apparent excess molar enthalpy* of the solute species at *infinite dilution*, $\Phi_{H,A}^{E,\infty}$. The same quantity can also be evaluated by using any one of a number of appropriate data fitting strategies.

It should be noted that, at infinite dilution, the apparent and *partial excess molar enthalpies* of the solute are identical. They are also equal to the limiting value of the derivative function (dH_m^E/dx_A).

2. Thermodynamic model for estimating molar enthalpies of insertion of a solute into water

$\Phi_{H,A}^{E,\infty}$ is the enthalpy change that results when 1 mol of the solute molecules are taken from their own pure state and infinitely widely dispersed in the solvent. In order to attain a meaningful interpretation of such properties, it is helpful to treat solute dissolution as a three-step process. We shall be limiting our attention, on this occasion, to non-electrolyte aqueous solutions.

Step 1: *Vaporization of the solute.* The experimental molar enthalpy of vaporization of a liquid solute, at a specific temperature, is that of the transformation of 1 mol of liquid to 1 mol of vapor at the saturation vapor pressure for that temperature. Insofar as it is realistic to assume that the vapor behaves ideally, there would be no enthalpy difference associated with isothermally changing that pressure to the standard (0.1 MPa) value.

Step 2: *Formation of one mole of cavities of the appropriate shape and size in the solvent.* There are actually two components of this step since the solvent molecules that are removed to form cavities must be reconstituted into a continuous bulk.

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Step 3: *Insertion of the solute molecules into the cavities.* There are two contributing factors to the enthalpy change associated with this step. One is the contribution due to direct interactions between the solute molecules and their solvent "sheaths". The other is anticipated to be the significant contribution arising from the aggregative rearrangement of the proximal solvent molecules.

2.1. Step 1: Implementation of Hess' law

The enthalpy change for the first step is roughly approximated by the standard molar enthalpy of vaporization at the normal boiling temperature. Correction to give the molar enthalpy of vaporization, at the mixing temperature, is possible in either of two ways.

(1) From a knowledge of the molar heat capacities of the substance in both its liquid and gaseous states.
(2) From the temperature derivative of the natural logarithm of the vapor pressure at the mixing temperature, $d \ln p/dT = \Delta_{vap}H_m/RT^2$.

2.2. Step 2: Enthalpy of formation of a cavity

2.2.1. Cavity in ice

Since the ultimate objective is to determine the enthalpy of insertion of the monomeric solute molecules into their aqueous solvent cages, it is essential to be able to make a credible estimate of enthalpies of cavity formation.

In the simplest process of cavity formation, Avogadro's number of well-separated water molecules is removed from the bulk of crystalline ice. In terms of the enthalpy change, this step is dominated by the breaking of four times Avogadro's number of hydrogen bonds. The water molecules that have been removed from the ice are not left in a perfect gas state but are reconstituted as a new crystalline mass. This second stage is the reverse of sublimation (i.e. deposition) and restores 2 mol of hydrogen bonds.

This simple bookkeeping leads to the conclusion that the molar enthalpy of formation of uni-molecular cavities in ice is essentially equal to the molar enthalpy of sublimation. Thus:

$$\Delta_{cav}H_m(n = 1) = \Delta_{sub}H_m \tag{2}$$

Each water molecule, in an ice lattice, participates in four hydrogen bonds. Since two water molecules share each hydrogen bond, there is total of 2 mol of hydrogen bonds broken. We may thus consider the hydrogen bond enthalpy to have a value approximately equal to one half of the molar enthalpy of sublimation of ice.

The molar enthalpy of sublimation at 25 °C is the sum of the enthalpies of fusion and vaporization at that temperature [1]. The molar enthalpy of fusion at 25 °C is given by [1,2]:

$$\Delta_{fus}H_m(25) = \Delta_{fus}H_m(0) + 25(C_{p,m}(l) - C_{p,m}(s))$$
$$= 6007 + 25(75.15 - 37.98) = 6936 \, J \, mol^{-1}$$
$$= 6.94 \, kJ \, mol^{-1} \tag{3}$$

The molar enthalpy of vaporization at 25 °C, as determined using the Clausius–Clapeyron equation, is [1]:

$$\Delta_{vap}H_m(25) = 44.10 \, kJ \, mol^{-1} \tag{4}$$

Thus the molar enthalpy of sublimation at 25 °C is

$$\Delta_{sub}H_m(25) = 51.04 \, kJ \, mol^{-1} \tag{5}$$

That gives an estimate of 25.52 kJ mol^{-1} for the effective *bond enthalpy of an aqueous hydrogen bond* which compares favorably

with published estimates [3]. Hence, from Eqs. (2) and (5):

$$\Delta_{cav}H_m(n = 1) = \Delta_{sub}H_m = 51.0 \, kJ \, mol^{-1} \tag{6}$$

We consider next the enthalpy required for the formation of a *bimolecular cavity*. In this process Avogadro's number of adjacent molecular pairs is removed from the crystalline lattice. Each of the two water molecules originally possessed four hydrogen bonds but the one joining the two molecules remains intact. It follows that $2 \times 3 = 6$ hydrogen bonds are broken to form the cavities, but $6/2 = 3$ will be reconstituted in the new ice bulk. With a net loss of 3 mol of hydrogen bonds, we end up with the equation:

$$\Delta_{cav}H_m(n = 2) = 1.5 \, \Delta_{sub}H_m = 76.5 \, kJ \, mol^{-1} \tag{7}$$

If the number of linked ice molecules, being removed to form cavities, is increased to three, there are eight hydrogen bonds broken per cavity and thus:

$$\Delta_{cav}H_m(n = 3) = 2.0 \, \Delta_{sub}H_m = 102 \, kJ \, mol^{-1} \tag{8}$$

The general formula for the molar enthalpy of formation of cavities, each created by removing n linked ice molecules, is:

$$\Delta_{cav}H_m(n) = [1 + 0.5(n - 1)] \, \Delta_{sub}H_m \tag{9}$$

This formula only applies if the ice molecules are linked together to form either a straight or a branched chain. If the cluster of ice molecules contains one or more rings, the molar enthalpy of cavity formation is predicted to be smaller by 0.5 $\Delta_{sub}H_m$ per ring.

2.2.2. Cavity in liquid water

We are obviously not concerned with the insertion of solute molecules into cavities that have been made in ice, but into cavities produced in liquid water. We may, however, still think in terms of breaking hydrogen bonds to form the cavities and restoring one half of them when the detached water molecules condense to form a new bulk liquid sample.

In liquid water, there appears to be a distribution of the molecules among sites that possess differing numbers of hydrogen bonds. As has been convincingly demonstrated by both molecular dynamics and Monte-Carlo computer simulations, the average number of hydrogen bonds, at 25 °C, is somewhere between three and four per molecule. That number, n_{HB}, decreases with increasing temperature. Opinions differ, however, as to how one should actually count the hydrogen bonds [4,5].

A tolerable estimate of n_{HB} at 25 °C is given by:

$$n_{HB} = 4 \left(\frac{\Delta_{vap}H_m}{\Delta_{sub}H_m} \right) = 3.45 \tag{10}$$

In the same vein as Eqs. (6) and (9), we might write, for cavity formation in liquid water:

$$\Delta_{cav}H_m(n = 1) = \Delta_{vap}H_m \tag{11}$$

and

$$\Delta_{cav}H_m(n) = [1 + 0.5(n - 1)] \, \Delta_{vap}H_m \tag{12}$$

In the section dealing with ice, it was assumed that an integer number, n_W, of water molecules need to be removed to form the cavity. When the solvent is a liquid, however, it seems to be more appropriate to think in terms of an average number of moles of water molecules that need to be removed to provide room for 1 mol of solute. One method of predicting n_W that seemed to have merit is:

$$n_W = \frac{\Phi_{V,A}^{\infty}}{V_{m,W}^*} \tag{13}$$

Table 1
Solute–solvent interaction enthalpies for C_mE_n in water at 25 °C.

Solute	$\Phi_{H,A}^{E,\infty}$ (kJ mol^{-1})	$\Delta_{vap}H_{m,A}$ (kJ mol^{-1})	$\Phi_{V,A}^{\infty}$ (cm^3 mol^{-1})	$\Delta_{cav}H_m$ (kJ mol^{-1})	$\Delta_{insertion}H_{A.W}$ (kJ mol^{-1})
MeOH	−7.35[a]	37.83	38.22[b]	68.53	−113.71
EtOH	−10.24[c]	42.46	55.15[b]	89.14	−141.84
1-PrOH	−9.9[d]	47.50	70.84[b]	108.25	−165.55
2-PrOH	−13.23[e]	45.48	71.72[f]	109.32	−168.03
t-BuOH	−16.9[g]	46.74	88.41[h]	139.64	−193.28
MeOEtOH	−13.8[i]	45.20	75.12[j]	113.46	−172.46
EtOEtOH	−17.77[i]	48.23	91.18[j]	133.01	−199.01
BuOEtOH	−15.89[k]	56.59	123.18[k]	171.97	−244.45
BuOEtOEtOH	−26.02[l]	(61.60)	160.23[m]	217.08	−304.62

[a] Ref. [7].
[b] Ref. [8].
[c] Ref. [9].
[d] Ref. [10].
[e] Ref. [11].
[f] Ref. [12].
[g] Ref. [13].
[h] Ref. [14].
[i] Ref. [15].
[j] Ref. [16].
[k] Ref. [17].
[l] Ref. [18].
[m] Ref. [19].

where $\Phi_{V,A}^{\infty}$ is the partial molar volume of the solute at infinite dilution and $V_{m,W}^{*}$ is the molar volume of pure water at 25 °C (=18.07 cm^3 mol^{-1}).

Thus:

$$\Delta_{cav}H_m(n_W) = \left[1 + 0.5\left\{\left(\frac{\Phi_{V,A}^{\infty}}{V_{m,W}^{*}}\right) - 1\right\}\right] \Delta_{vap}H_{m,W} \qquad (14)$$

or

$$\Delta_{cav}H_m(n_W) = \left[0.5\left\{\left(\frac{\Phi_{V,A}^{\infty}}{V_{m,W}^{*}}\right) + 1\right\}\right] \Delta_{vap}H_{m,W} \qquad (15)$$

2.3. Step 3: Enthalpy of insertion of a solute into a cavity

Reverting to the partition, of the infinite dilution apparent molar enthalpy of solution, into three components leads to:

$$\Phi_{H,A}^{E,\infty} = \Delta_{vap}H_{m,A} + \left[0.5\left\{\left(\frac{\Phi_{V,A}^{\infty}}{V_{m,W}^{*}}\right) + 1\right\}\right] \Delta_{vap}H_{m,W}$$
$$+ \Delta_{insertion}H_{A.W} \qquad (16)$$

Here $\Delta_{insertion}H_{A.W}$ is the enthalpy of insertion of 1 mol of solute molecules into their solvent cavities. It follows that:

$$\Delta_{insertion}H_{A.W} = \Phi_{H,A}^{E,\infty} - \Delta_{vap}H_{m,A} - \left[0.5\left\{\left(\frac{\Phi_{V,A}^{\infty}}{V_{m,W}^{*}}\right) + 1\right\}\right]$$
$$\times \Delta_{vap}H_{m,W} \qquad (17)$$

And, using literature values for $V_{m,W}^{*}$ and $\Delta_{vap}H_{m,W}$:

$$\Delta_{insertion}H_{A.W} = \Phi_{H,A}^{E,\infty} - \Delta_{vap}H_{m,W} - \left[0.5\left\{\left(\frac{\Phi_{V,A}^{\infty}}{18.07}\right) + 1\right\}\right]$$
$$= 44.0 \text{ kJ mol}^{-1} \qquad (18)$$

3. Analysis of experimental data

3.1. Enthalpy of insertion of various solute series in water

Our first set of calculations was an extension of our ongoing studies of aqueous mixtures of small amphiphiles with the general formula $C_mH_{2m+1}-(OCH_2)_n-OH$.

Most of the values of the standard enthalpies of vaporization, that we needed, were to be found in the electronic literature [6].

Table 1 contains values calculated using Eq. (18) for $\Delta_{insertion}H_{A.W}$ for non-ionic amphiphiles with the general formula $C_mH_{2m+1}-(OCH_2)_n-OH$ (abbreviated to C_mE_n) and the enthalpic and volumetric data from which they were calculated.

Evidently, the enthalpy of mixing represents a relatively small difference between the more substantial endothermic (cavity formation) and exothermic (solute–solvent interaction) processes.

In the case of 2-(2-butoxyethoxy)ethanol it was not possible to find a value for the standard enthalpy of vaporization. Both 2-butoxyethanol and butan-1-ol and 2-ethoxyethanol and ethanol differ structurally by a CH_2-O-CH_2 group. That led to the following estimate of:

$$\Delta_{vap}H_{m,A}(\text{BuOEtOEtOH}) = 61.60 \text{ kJ mol}^{-1}$$

Table 1 contains two molecules differing only by CH_2 groups and two by CH_2OCH_2 groups.

For $\Delta_{insertion}H_{A.W}$ (kJ mol^{-1}), we find the following averages: $CH_2 = -23.05$ and $CH_2OCH_2 = -58.67$.
For $\Delta_{vap}H_{m,A}$ (kJ mol^{-1}), we find: $CH_2 = 4.47$ and $CH_2OCH_2 = 5.01$.

Acceptance of these values leads to:

For $\Delta_{insertion}H_{A.W}$, $CH_3 + CH_2OH = -140.86$ kJ mol^{-1}.
For $\Delta_{vap}H_{m,A}$, $CH_3 + CH_2OH = 42.81$ kJ mol^{-1}.

To provide a supplementary basis for performing this type of group additivity study, we added to the results obtained for the C_mE_n + water mixtures with calculations that made use of data reported by Abraham [20].

From the values reported for the limiting partial molar enthalpies of solution for the linear alkanes, we were able to

Table 2
Solute–solvent interaction enthalpies for linear alkanes (C_nH_{2n+2}) in water at 25 °C.

Solute	$\Phi_{H,A}^{E,\infty}$ (kJ mol^{-1})	$\Delta_{vap}H_{m,A}$ (kJ mol^{-1})	$\Phi_{V,A}^{\infty}$ (cm^3 mol^{-1})	$\Delta_{cav}H_m$ (kJ mol^{-1})	$\Delta_{insertion}H_{A,W}$ (kJ mol^{-1})
Methane	−13.81		36.45	66.38	−80.19
Ethane	−19.74		52.32	85.70	−105.44
Propane	−22.50		68.19	105.02	−127.52
Butane	−25.98		84.06	124.34	−150.32
Pentane	−0.46	26.73	99.43	143.66	−170.85
Hexane	0.17	31.54	115.80	162.99	−194.36
Heptane	2.68	36.57	131.67	182.31	−216.20
Octane	1.76	41.50	147.54	201.63	−241.37

Table 3
Solute–solvent interaction enthalpies for linear primary alkanols ($C_nH_{2n+1}OH$) in water at 25 °C.

Solute	$\Phi_{H,A}^{E,\infty}$ (kJ mol^{-1})	$\Delta_{vap}H_{m,A}$ (kJ mol^{-1})	$\Phi_{V,A}^{\infty}$ (cm^3 mol^{-1})	$\Delta_{cav}H_m$ (kJ mol^{-1})	$\Delta_{insertion}H_{A,W}$ (kJ mol^{-1})
MeOH	−7.28	37.45	38.22	68.53	−113.26
EtOH	−10.24	42.26	55.15	89.1	−141.64
1-PrOH	−9.9	47.84	70.84	108.25	−165.99
1-BuOH	−9.29	52.34	86.53	127.35	−188.98
1-PentOH	−7.74	56.94	102.22	146.45	−211.13
1-HexOH	−6.48	61.71	117.91	165.55	−233.74
1-HeptOH	−5.31	66.82	133.6	184.66	−256.79
1-OctOH	−3.18	70.96	149.19	203.64	−277.78

Table 4
Solute–solvent interaction enthalpies for linear primary alkanamines ($C_nH_{2n+1}NH_2$) in water at 25 °C.

Solute	$\Phi_{H,A}^{E,\infty}$ (kJ mol^{-1})	$\Delta_{vap}H_{m,A}$ (kJ mol^{-1})	$\Phi_{V,A}^{\infty}$ (cm^3 mol^{-1})	$\Delta_{cav}H_m$ (kJ mol^{-1})	$\Delta_{insertion}H_{A,W}$ (kJ mol^{-1})
MeNH$_2$	−21.00	24.26	41.68	72.74	−118.0
EtNH$_2$	−27.07	26.61	58.37	93.06	−146.7
1-PrNH$_2$	−24.64	31.33	74.12	112.24	−168.2
1-BuNH$_2$	−23.35	35.69	89.8	131.33	−190.4
1-PentNH$_2$	−22.04	40.08	105.7	150.69	−212.8
1-HexNH$_2$	−20.66	45.1	121.6	170.05	−235.8

construct Table 2. Estimates of the infinite dilution partial molar volumes were made using previously reported values for CH$_2$ and CH$_3$ together with an extrapolation to give that for CH$_4$.

Table 2 provides, by means of linear least squares optimization, the following average group contributions to $\Delta_{insertion}H_{A,W}$ (kJ mol^{-1}): CH$_4$ = −80.19, CH$_3$ = −52.44 and CH$_2$ = −22.47. The group contributions to $\Delta_{vap}H_{m,A}$ (kJ mol^{-1}) are CH$_3$ = 11.88 and CH$_2$ = 4.93.

Values of $\Delta_{insertion}H_{A,W}$ were also obtainable using Abraham's data [20] for linear alkanols (Table 3).

Table 3 provides the following average group contributions to $\Delta_{insertion}H_{A,W}$ (kJ mol^{-1}): CH$_3$ + CH$_2$OH = −142.85 and CH$_2$ = −22.67 kJ mol^{-1}. Using the value of −52.44 for the CH$_3$ group leads to −90.41 for CH$_2$OH.

Table 1 provided CH$_3$ + CH$_2$OH = −140.86 and CH$_2$ = −23.05 kJ mol^{-1}. Using the value of −52.44 for the CH$_3$ group leads to −88.42 for CH$_2$OH.

Table 3 provides the following average group contributions to $\Delta_{vap}H_{m,A}$ (kJ mol^{-1}): CH$_3$ + CH$_2$OH = 42.69 and CH$_2$ = 4.76. Using the value of 11.88 for the CH$_3$ contribution gives 30.81 for CH$_2$OH.

Table 1 gave CH$_3$ + CH$_2$OH = 42.81 and CH$_2$ = 4.47 kJ mol^{-1}. Using the value of 11.88 for the CH$_3$ contribution gives 30.93 for CH$_2$OH.

The Abraham paper [20] further provides values for the enthalpies of vaporization and the limiting partial molar enthalpies of solution of the first six straight chain amines.

An article by Cabani et al. [21] provided values for the limiting apparent molar volumes. These data and the calculated enthalpies of cavity formation and solute insertion are summarized in Table 4.

Table 4 yielded the following group contributions to $\Delta_{insertion}H_{A,W}$ (kJ mol^{-1}): CH$_2$ = −22.27 and CH$_3$ + CH$_2$NH$_2$ = −146.24. Using the value of −52.44 for the CH$_3$ group leads to CH$_2$NH$_2$ = −93.80.

For $\Delta_{vap}H_{m,A}$ (kJ mol^{-1}): CH$_2$ = 4.57 and CH$_3$ + CH$_2$NH$_2$ = 26.62. Using the value of 11.88 for the CH$_3$ contribution gives CH$_2$NH$_2$ = 14.74.

3.2. Summary of group-contribution results

Present results for average group contributions to the molar enthalpy of insertion and to the molar enthalpy of vaporization are collected in Table 5.

Both the hydroxyl and amine contributions are quite substantial reflecting hydrogen bonding to the solvent water; more than double the enthalpy of a single hydrogen bond.

The methyl and methylene contributions are negative and non-trivial. There is no question of hydrogen bonding between those solute groups and proximal water. The result is almost certainly

Table 5
Average group contributions (values in kJ mol^{-1}).

Group	$\Delta_{insertion}H_{A,W}$	$\Delta_{vap}H_{A,W}$	Sub-group	$\Delta_{insertion}H_{A,W}$	$\Delta_{vap}H_{A,W}$
CH$_3$	−52.44	11.88			
CH$_2$	−22.61	4.73			
CH$_3$OH	−113.48	37.83	OH	−67.13	25.99
CH$_2$OH	−89.16	30.87	Ether O	−8.63	−3.31
CHOH	−61.15	21.72	NH$_2$	−68.87	9.76
COH	−35.96	11.1			
CH$_3$–O–CH$_2$	−82.55	14.44			
CH$_2$–O–CH$_2$	−58.67	5.01			
CH$_3$NH$_2$	−118.00	24.26			
CH$_2$NH$_2$	−93.80	14.74			

derived from induced enhancement of the solvent hydrogen bonding; referred to as clathrate formation, structure making or the iceberg effect.

The ether oxygen atoms also appear to play a modest role in solute–solvent hydrogen bonding.

Evidently the hydroxyl groups contribute the equivalent of a hydrogen bond enthalpy to the enthalpies of vaporization of the alkanols. In this case, the amine group contribution is substantially smaller.

Dispersion forces are all that are available in alkanes.

It appears that this approach predicts that the ether oxygen atoms actually facilitate vaporization.

4. Scaled particle theory

It would be inappropriate to discuss the general topic of cavity formation, without making some mention of Scaled Particle Theory and its application to the estimation of thermodynamic properties of cavity formation [22–24].

Both solute and solvent molecules are treated as hard spheres. Each is assigned what is considered to be an appropriate radius. The cavity volume is that of the solute species. A statistical thermodynamic strategy has been devised to determine the changes in Gibbs energy, enthalpy and entropy of the solvent that result from the formation of a cavity of the solute molecular size in the solvent bulk. The literature reveals that there is a parallel strategy devised by Sinanoglu and that it is also possible to use Monte-Carlo techniques for computer simulation of the same quantities [25].

Having determined the enthalpy of cavity formation it is necessary to introduce the solute into its new home and estimate the enthalpy of interaction with the solvent. This is, of course, what our strategy also sets out to do. In Scaled Particle Theory there is a need to choose an appropriate potential function. That becomes a questionable venture for pairs of non-isotropic spheres, and requires allowances for directional features such as hydrogen bonding [26,27]. In the computer simulations, one comes closer to mimicking real molecules with the various derivatives of Jorgensen's potentials.

5. Conclusions

We conclude that, in determining enthalpies of cavity formation, one is best served by making use of as much appropriate thermodynamic data as is available. Careful use of group additivity schemes can widen considerably the thermodynamic database.

We believe that the numbers obtained for the contributions of the various functional groups to the enthalpy of interaction between the amphiphilic solute species and solvent water support the notion that solute–solvent hydrogen bonding and hydrophobic inducement of enhanced solvent hydrogen bonding are the principal considerations at play.

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