Solution enthalpies – experimental determinations and thermodynamic modeling – with possible application in the new energetic nanotechnologies

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Available apparatus:

SETARAM C80 3D computer-controlled mixing and reaction calorimeter using reversal mixing cells (reference and sample) made of stainless steel

Measurements procedure:

Each reversal mixing vessel has two compartments. The smaller, lower recipient (0.6 cm^3) of the measuring cell contained a very small known amount of solid (solute) covered by the removable lid. The same amount of liquid (solvent) was added to the lower part of the reference cell. The larger, upper container (5.0 cm^3) of each cell was filled with a known high amount of solvent. The measuring and reference cells were placed inside the metallic block of the Calvet-type calorimeter. The working temperature was fixed and, when thermal equilibrium was reached (in cca. 3 hours), the components in the vessels were mixed by rotation of the calorimeter block using the rocking device. The differential heat-flux was then recorded, and integrated as a function of time to give the heat changes during mixing.

Calibrations:

- Electrically using the Joule effect by means of a special cell with calibrated heaters as recommended by IUPAC;
- Test measurements of the molar enthalpies of solution in infinite dilution region for KCl (crystals) in water. Our values were with 2 % lower than literature value determined at 30 ^{0}C. The reproducibility in determining the mixing enthalpy was 0.1 % from the measured value.

Experimental uncertainties:

$\sigma(t) = 0.05\ ^0C$; $\sigma(x) = 0.0001$; $\sigma(\Delta_{sol}H) = 0.005$ J.

Special precautions:

- Drying under high vacuum the solid solutes, at adequate temperatures, till constant mass, and storing at 25 ^{0}C under the same high vacuum during whole measurements period.
- Drying the solvent, if necessary and possible, on molecular sieves.

Examples of studied solutions

- 1-Butyl-3-methylimidazolium chloride (solid solute) + water (solvent)

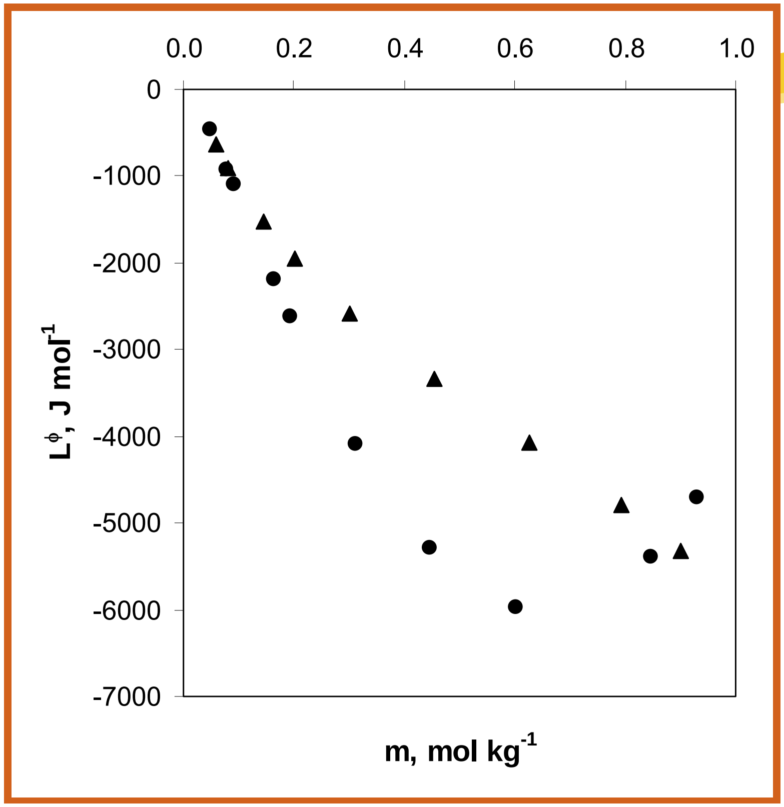
t = 30 ^{0}C
t = 45 ^{0}C

- 1-Butyl-3-methylimidazolium bromide (solid solute) + water (solvent)

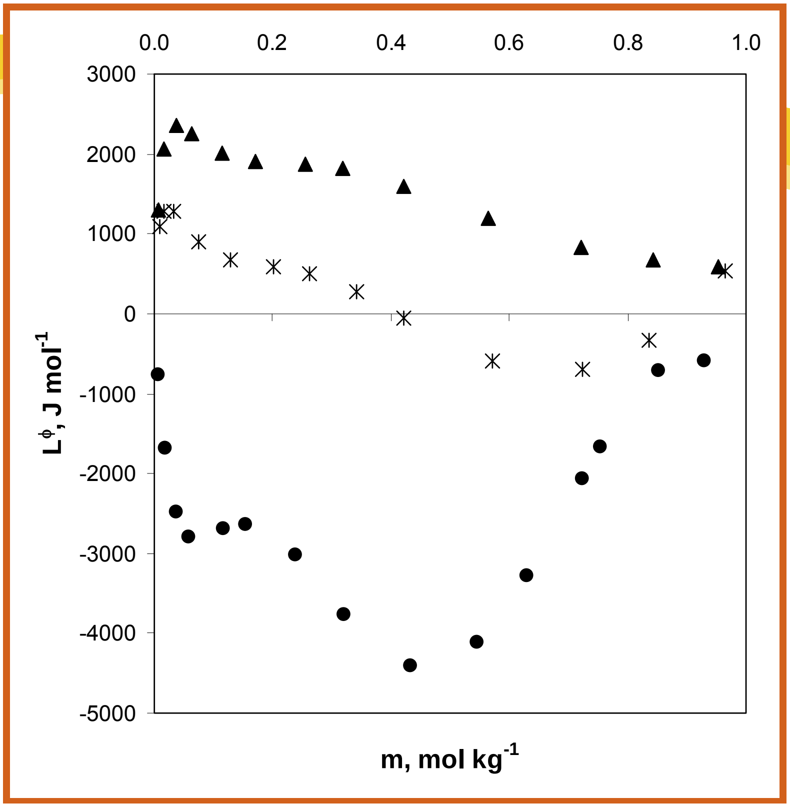
t = 30 ^{0}C
t = 37 ^{0}C
t = 45 ^{0}C

Concentration range:

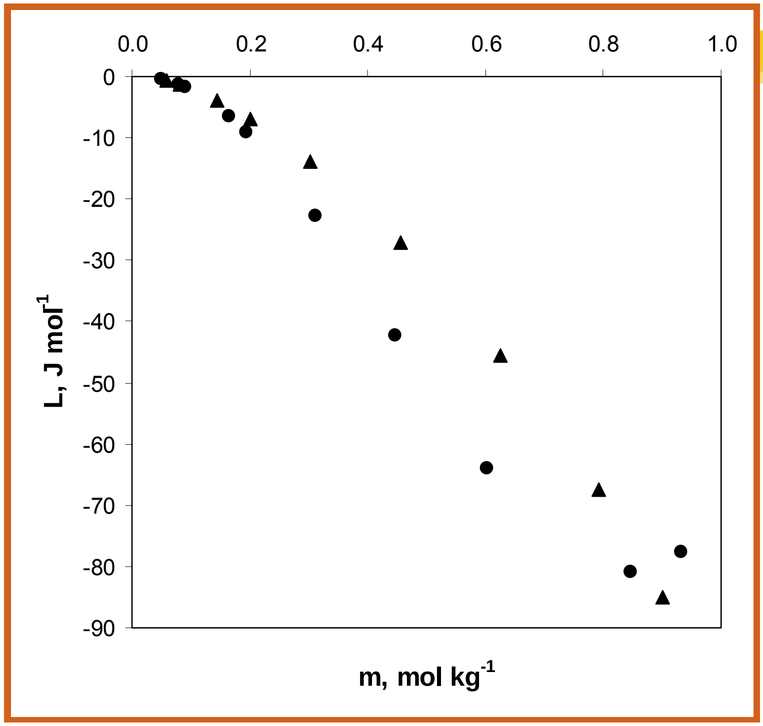
0.006 - 1 mol/kg (equivalent to 0.0001 – 0.02 mole fraction of IL)



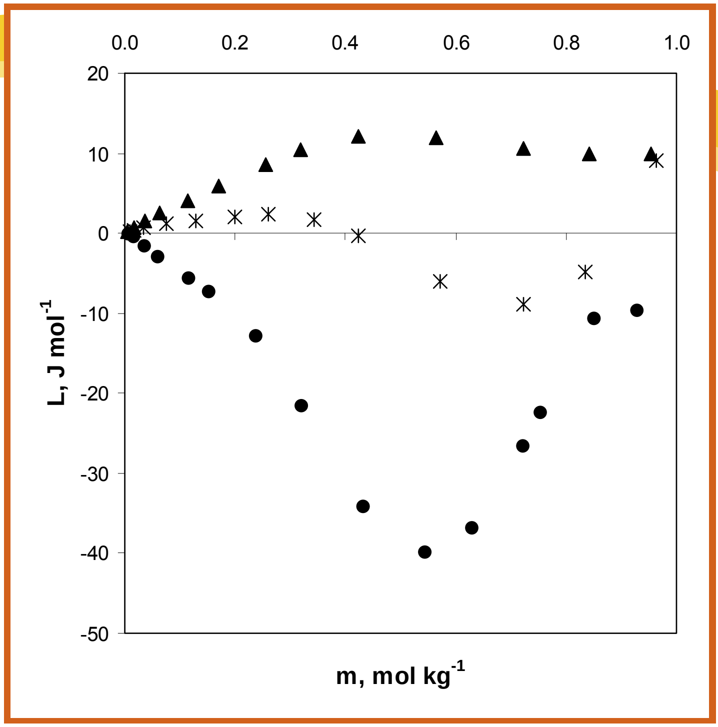
Apparent relative molar enthalpy for [bmim]Cl in water at 30 ^{0}C (•) and 45 ^{0}C (▲) resulted from the best correlation of the experimental $D_{sol}H_m$ vs. m data by means of 4-parameters Silvester and Pitzer (1977) model with absolute mean relative deviations of 3%, least squares optimization method and TableCurve 2D v5.01. software.



Apparent relative molar enthalpy for [bmim]Br in water at 30 ^{0}C (•), 37 ^{0}C, and 45 ^{0}C (▲) resulted from the best correlation of the experimental $D_{sol}H_m$ vs. m data by means of 7-parameters Archer and Rard (1998) model with absolute mean relative deviations of 22%, 9%, 7%, least squares optimization method and TableCurve 2D v5.01. software.



Relative molar enthalpy for [bmim]Cl + water system at 30 ^{0}C (●) and 45 ^{0}C (▲) resulted from the best correlation of the experimental $D_{sol}H_m$ vs. m data by means of 4-parameters Silvester and Pitzer (1977) model with absolute mean relative deviations of 3%, least squares optimization method and TableCurve 2D v5.01. software.



Relative molar enthalpy for [bmim]Br + water system at 30 ^{0}C (●), 37 ^{0}C, and 45 ^{0}C (▲) resulted from the best correlation of the experimental $D_{sol}H_m$ vs. m data by means of 7-parameters Archer and Rard (1998) model with absolute mean relative deviations of 22%, 9%, 7%, least squares optimization method and TableCurve 2D v5.01. software.

Conclusions

The results of the molar enthalpy of solution correlation for chloride proves that our laboratory is able to perform accurate measurements of enthalpy of solution in the infinite dilution region. Significant heats of mixing could be evidenced also for other solid solutes (eventually nano-sized) in liquid solvents in order to exploit the data in the new energetic nanotechnologies.

The experimental molar enthalpy of solution data for bromide have not been correlated within the estimated experimental uncertainties. Nevertheless, the electrolyte models are not sufficiently developed (Hendriks et al., 2010). More work has to be done in this direction by using also our new experimental data for the same ILs with 1-butanol systems.

However, the expected evolution with temperature of the apparent relative molar enthalpies of the solutes and relative molar enthalpies of the mixtures is evidenced qualitatively in the present results.

Cited references

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