Volume-Based Thermodynamics of Ionic Liquids and Molten Salts:

Surface Tension and the Eötvös Equation

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7 Figures 1 Table ~2 900 words

Supplementary Files S1, S2, S3 and S4

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Abstract

The surface thermodynamics of *ionic fluids* (both ionic liquids and molten salts) are calculated from surface tension data by application of a modified Eötvös Equation, and the results compared with the corresponding values for *neutral organic liquids*.

As may be anticipated and here reported quantitatively, the coulombic interactions within the ionic fluids lead to smaller surface entropies and larger surface enthalpies because of tighter binding among the charged ions. For ionic liquids, an increase in formula volume leads to their surface properties tending towards those of neutral organic liquids, corresponding to a decrease in the strength of the coulombic interactions.

Unexpectedly large surface entropies for molten GaCl₃, BiBr₃, BiCl₃ and UF₆ suggest that these species may be behaving as freely-spinning pseudo-spherical molecules.

Introduction

"Volume-Based Thermodynamics" (VBT) are procedures by which colleagues and I have, over the last decade or so,¹⁻² related thermodynamic and physical properties of materials to some function of their formula volumes, V_m . In their most direct form, temperature-dependent entropies and heat capacities are closely correlated with formula volume itself, while energetic quantities such as lattice energy are correlated with the inverse cube-root of the formula volume, $V_m^{-1/3}$ (corresponding to the distances between atoms).

The bulk thermodynamics of ionic liquids has earlier been examined by the current author.³ We now explore the correlation between their surface tension thermodynamics and surface area, that is with $V_m^{2/3}$. Thus, VBT now covers the full possible range of volume-based thermodynamic correlations, from $V^{1/3}$ via $V^{2/3}$ to $V^{3/3} \equiv V!$

The current contribution extends recent coverage of the thermodynamics of surface tension from standard organic liquids⁴ to the currently significant ionic liquids and also to molten salts - which thereby introduces coulombic forces between the charged ions into the molecular interactions.

The Eötvös surface tension equation⁵ correlates surface tension, γ , with formula volume, $V_m^{2/3}$, introducing a temperature-independent constant, *k*:

$$\gamma V_m^{2/3} = k(T - T_c)$$
 (1)

It is also well-established that surface tension declines linearly with temperature:⁶⁻⁷

$$\gamma = a_0 - a_1 T \tag{2}$$

The Eötvös equation has the properties of a Gibbs energy

$$\Delta g = \gamma V_m^{2/3} \qquad (3a)$$

where lower-case g is used (rather than upper-case G) to represent *surface* Gibbs energy. However, the units are non-thermodynamic (with volume to the power 2/3) and so cannot conveniently be compared with standard thermodynamic quantities.

A simple modification⁸⁻¹⁰ generates the equation in units of Gibbs energy per mole. This consists only in multiplication by $N_A^{1/3}$ where N_A is the Avogadro Constant (6.022 × 10²³ mol⁻¹)

$$\Delta g = N_A^{1/3} \gamma V_m^{2/3}$$
 (3b)

From standard thermodynamics, using the definition of the Gibbs energy at fixed temperature and pressure:

$$\Delta g = \Delta h - T \Delta s \tag{4}$$

where Δh is a surface enthalpy and Δs is a surface entropy. From equations (2)-(4), the molar surface entropy is obtained as the temperature-derivative of the surface tension:⁹

$$\Delta s = -N_A^{1/3} V_m^{2/3} \left(\frac{\partial \gamma}{\partial T} \right)_p \tag{5}$$

The molar enthalpy, Δh , is determined by difference following Eq (4).

Example: $N_A = 6.022 \times 10^{23} \text{ mol}^{-1}$. Data for AgCl in Supporting Table S2: MW = 143.32 g mol^{-1}.

At 1.1 x melting point = 801 K; ρ = 4.77 g cm⁻³; γ = 176 mN m⁻¹ = 176 mJ m⁻²; $-(\partial \gamma / \partial T)_p$ = 0.052 mJ m⁻² K⁻¹.

$$N_{A}^{1/3} = (6.022 \text{ x } 10^{23} \text{ mol}^{-1})^{1/3} = 8.445 \text{ x } 10^{7} \text{ mol}^{-1/3}$$

$$V_{m} = 143.32 \text{ g mol}^{-1}/4.77 \text{ g cm}^{-3} = 30.05 \text{ cm}^{3} \text{ mol}^{-1} = (30.05/10^{6}) \text{ m}^{3} \text{ mol}^{-1}$$

$$\gamma = 176 \text{ mJ m}^{-2} = (176/10^{3}) \text{ J m}^{-2} = (176/10^{6}) \text{ kJ m}^{-2}$$

$$\left(\partial \gamma / \partial T\right)_{p} = 0.052 \text{ mJ m}^{-2} \text{ K}^{-1} = (0.052/10^{3}) \text{ J K}^{-1} \text{ m}^{-2}$$

$$\Delta g = N_{A}^{1/3} \gamma V_{m}^{2/3} = [6.022 \text{ x } 10^{23} \text{ mol}^{-1}]^{1/3} \text{ x } [(176/10^{6}) \text{ kJ m}^{-2}] \text{ x } [(30.05/10^{6}) \text{ m}^{3} \text{ mol}^{-1}]^{2/3}$$

$$= 14.3 \text{ kJ mol}^{-1}$$

$$\Delta s = -N_A^{1/3} \left(\frac{\partial \gamma}{\partial T} \right)_p V_m^{2/3}$$

= [6.022 x 10²³ mol⁻¹]^{1/3} x [(0.052/10³) J K⁻¹ m⁻²] x [(30.05/10⁶) m³ mol⁻¹]^{2/3}
= 4.24 J K⁻¹ mol⁻¹

 $\Delta h = \Delta g + T \Delta s = 14.3 + 801 \text{ x } 4.24 / 1000 = 17.7 \text{ kJ mol}^{-1}$

General Observations on Eötvös-Based Surface Thermodynamics

In our prior companion publication,⁴ we noted that this simple thermodynamic modification of the Eötvös surface tension equation had been independently introduced by Palit,⁸ by Lyklema¹¹ and by Myers.⁹ We have now identified even earlier reports: Skapski (1948) applied the modified equation to liquid metals,¹²⁻¹³ while Good (1957) applied Skapski's procedure to a more general group of liquids (including liquified gases).¹⁴ Good used his results (which he multiplied by an arbitrary 1.1 packing factor) in analysing surface orientations in polar liquids, and provided extensive data in an Appendix (which is now difficult to obtain).

Lyklema^{11, 15} and Myers,⁹ having examined a wide range of liquids, noted a Trouton's Rule of surface entropy, corresponding to an average value for the generation of surface entropy of about 20 J K⁻¹ mol⁻¹, with smaller values being observed for hydrogen-bonded liquids such as alcohols – implying some molecular order at the liquid surface – and larger values resulting from weakly-interacting liquids such as alkanes. The earlier analysis by Good¹⁴ also noted these relationships but did not relate them to Trouton's Rule.

In order to illustrate these conclusions, Fig. 1 plots surface entropy *versus* surface enthalpy for 52 organic liquids,⁴ ranging from alkanes to alcohols. A histogram of this data set may be found in Fig. 2 of the prior publication.⁴ There is a cluster of values in the central region, corresponding to the presumed Trouton's surface entropy constant of $20 \pm 6 \text{ J K}^{-1} \text{ mol}^{-1}$ but there is also a wide range of values, from 7.7 to 31.9 J K⁻¹ mol⁻¹ for the whole of this particular set of organic liquids. Another feature which may be noted in Fig. 1 is a weak linear correlation between surface entropy and surface enthalpy. This is often referred to as an Enthalpy-Entropy Compensation, where the simultaneous increase in both these quantities (with their opposite signs) appear to compensate each other thus reducing any changes in their combination in the Gibbs energy. However, this is unlikely to be a real effect, rather a statistical result arising from their evaluation from a single experimental value.¹⁶

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Figure 1: Surface entropy, $\Delta s / J K^{-1} mol^{-1}$, plotted against surface enthalpy, $\Delta h / kJ mol^{-1}$ for 52 organic liquids under ambient conditions.⁴ Data is listed in Supplementary File S1, Table S1.

Room-Temperature Ionic Liquids (RTILs)

Data Mining: There are a number of resources from which surface properties of RTILs may be obtained. ILThermo¹⁷⁻¹⁸ is a comprehensive IUPAC-supported ionic liquid database, published by NIST. Ordinarily, it provides responses to simple requests, but a Python-based command-line query for extended responses is available for local installation.¹⁹ Tariq, et al.,⁷ have performed a critical review of data published for RTIL's from 2001 to 2010. Surface tension data for RTILs have also been collected in a 2016 book by Marcus,⁶ while another comprehensive collection which covers much the same period is "lonic Liquids: Physicochemical Properties".²⁰

Data for the current publication have primarily been extracted from Marcus's book⁶ and the review by Tariq, et al.,⁷ supplemented by data from more recent publications. Structures of a number of the cations and anions constituting RTILs are listed in Supplementary file S3, while IUPAC names and CAS Registry Numbers of the currently-considered RTILs are listed in Supplementary file S4. For present purposes, a limitation in the data available is often a lack of values of temperature dependence which is required in order to evaluate surface entropy. The structures of a number of unfamiliar ions which comprise some RTILs appear in Supplementary file S3. *Observations:* Fig. 2 plots surface entropy *versus* surface enthalpy for 46 RTILs.⁴ Comparison with Fig. 1 shows much the same pattern of behavior as with the group of general organic liquids. The data is collected into a histogram in Fig. 3, while a histogram for their surface enthalpy appears in Fig. 4.



Figure 2: Surface entropy, $\Delta s / J K^{-1} mol^{-1}$, plotted against surface enthalpy, $\Delta h / kJ mol^{-1}$ for 44 ionic liquids under ambient conditions.⁴ Mean $\Delta s = 20.0 \pm 5.7 J K^{-1} mol^{-1}$. The large protic ionic liquid $[TOA]_2[nonanedioate]^{21}$ has been omitted as being out-of-range, lying at $\Delta s = 106.8 J K^{-1} mol^{-1}$ and $\Delta h = 58 kJ mol^{-1}$, on the extension to the apparent diagonal set of values, as can be seen in the smaller-scale inset to the Figure. In this inset, three hydrogen-bonded protic [TOA] ILs are shown in linear correlation as enlarged filled circles. Data is listed in Supplementary file S1, Table S2.

The data point for [C₄mim][SCN] has been omitted from Fig. 2 because seriously conflicting values have been reported for the temperature dependence of its surface tension:

 $(\partial \gamma / \partial T)$ /mJ m⁻² K⁻¹ = -0.0844²² and -0.202²³, yielding surface entropies of 22.3 and 53.8 J K⁻¹ mol⁻¹, respectively. Although the latter excessively large surface entropy seems faulty (cf. this value being out-of-range in Fig. 3), the reported experimental data²³ cannot currently be faulted.



Figure 3: Surface entropy, $\Delta s / J K^{-1} mol^{-1}$, for 44 ionic liquids under ambient conditions. Mean $\Delta s = 18.4 \pm 6 J K^{-1} mol^{-1}$. Data is listed in Supplementary file S1, Table S2.



Figure 4: Surface enthalpy, $\Delta h / kJ \text{ mol}^{-1}$, for 44 ionic liquids under ambient conditions. Mean $\Delta h = 20.9 \pm 3.7 \text{ kJ mol}^{-1}$. Data is listed in Supplementary file S1, Table S2.

Molten Salts

Data Mining: Molten salt surface tension data was selected from the 2016 book by Marcus⁶ Ionic Liquid Properties: From Molten Salts to RTILs, and from publications by Janz and colleagues.²⁴⁻²⁶ Again, the number of references which contained temperature dependence of surface tension was limited. *Observations:* In Fig. 5 surface entropy, $\Delta s / J K^{-1} mol^{-1}$, is plotted against surface enthalpy, $\Delta h / kJ mol^{-1}$ for 35 molten salts at the "corresponding state" of 1.1 times their melting temperatures, 1.1× T_m . The frequency distributions of surface entropy and surface enthalpy appear as histograms in Fig. 6 and Fig. 7, respectively.



Figure 5: Surface entropy, $\Delta s / J K^{-1} \text{ mol}^{-1}$, plotted against surface enthalpy, $\Delta h / kJ \text{ mol}^{-1}$ for 34 molten salts at the "corresponding state" of 1.1 times their melting temperatures, $1.1 \times T_m$. Orange diamonds represent the outliers GaCl₃, BiBr₃, BiCl₃ and UF₆. Data is listed in Supplementary file S2.



Figure 6: Surface entropy, $\Delta s / J K^{-1} mol^{-1}$, for 34 molten salts at the "corresponding state" of 1.1 times their melting temperatures, $1.1 \times T_m$. Mean $\Delta s = 8.1 \pm 6 J K^{-1} mol^{-1}$. The outlier data for GaCl₃, BiBr₃, BiCl₃ and UF₆ have been omitted. Data is listed in Supplementary file S2.



Figure 7: Surface enthalpy, $\Delta h / kJ \text{ mol}^{-1}$, for 34 molten salts at the "corresponding state" of 1.1 times their melting temperatures, $1.1 \times T_m$. Mean $\Delta h = 21.2 \pm 9 \text{ kJ mol}^{-1}$. The outlier data for GaCl₃, BiBr₃, BiCl₃ and UF₆ have been omitted. Data is listed in Supplementary file S2.

Discussion

The most interesting information which may be extracted from the current study is the differences among the mean values for the thermodynamic functions for different classes of liquids, as listed in Table 1. These values are approximately independent of temperature.

Table 1: Comparison of mean values of molar surface entropy, Δs , and molar surface enthalpy, Δh , among organic liquids, ionic liquids, and molten salts.

Thermodynamic	Organic	Ionic	Molten
Function	Liquids ⁴	Liquids	Salts
Δs / J K ⁻¹ mol ⁻¹	20.0 ± 6	18.4 ± 6	8.1±6
Δh / kJ mol ⁻¹	11.8±3	20.8±4	21.2 ± 9
Count	52	34	34

It is seen that the ionic materials are readily differentiated from the neutral organic liquids with respect to both surface enthalpy and surface entropy. This is indeed what might be expected since the charge interactions in the ionic fluids are significant additions to the van der Waals interactions in neutral fluids. Thus, the surface enthalpies of the ionic fluids (that is, ionic liquids and molten salts) are on average nearly twice as large as for the neutral organic liquids arising from the coulombic interactions. The mean surface entropies of molten salts are less than half as large as those of the other fluids, suggesting that the ions remain held strongly in place by coulombic forces, even in the surface.

The molar surface entropy has been related to a Trouton surface constant,⁴ with the surface entropy of neutral organic liquids increasing by roughly 20 J K⁻¹ mol⁻¹ on forming surface from bulk, compared with the Trouton constant increase in entropy of ~80 J K⁻¹ mol⁻¹ on transitioning from the bulk to gas phase. The smaller increase in surface entropy for RTILs and considerably smaller increase for

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molten salts suggests that the introduced coulombic interactions maintain a greater degree of order in these surfaces.²⁷

Comments

It is interesting to consider the outliers in these groups of liquids. It has already been noted (Fig. 2) that the large protic ionic liquid $[TOA]_2[nonanedioate]^{21}$ has exceedingly large surface thermodynamic parameters, and that the group of protic [TOA] ionic liquids has a strong linear correlation between surface entropies and surface enthalpies. The trioctyl ammonium groups of these cations are exceedingly flexible, leading to a large surface entropy which is amplified by the extreme size of the nonanedioate anion. Although an enthalpy-entropy compensation is generally discounted, the size of this effect and its differentiation from the pattern for other ionic liquids suggests further consideration should be given to the behaviour in this instance. The case of $[C_4mim][SCN]$, with strikingly different surface tension temperature dependencies reported, shows that the possibilities of experimental discrepancies must also be considered.

Among the molten salts, a few outliers have been noted, namely GaCl₃, BiBr₃, BiCl₃ and UF₆. Their exceptionally large surface entropies compared to other molten salts suggest that the groups may act as freely-rotating, near-spherical entities rather than independent ions. It is unclear why these cations behave in this rather specific way.

Conclusions

The surface thermodynamic properties of both neutral and charged fluids have been examined. A Trouton's Rule for surface entropy has been identified. The surfaces of charged fluids are more constrained than are those of neutral fluids, as is to be anticipated. As the volumes of the materials forming ionic fluids increase, the influence of the coulombic forces correspondingly decreases. A number of anomalous values have been identified and deserve further investigation.

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Supplementary Files: (S1) Surface thermodynamics of organic liquids (Table S1) and of RTILs (Table S2) (docx); (S2) Surface thermodynamics of Molten Salts (docx); (S3) Structures of some ions used for RTILs (pdf); (S4) RTIL names and CAS Registry Numbers (docx).

References

1. Glasser, L.; Jenkins, H. D. B., Predictive thermodynamics for ionic solids and liquids. *Phys. Chem. Chem. Phys.* **2016**, *18*, 21226-21240.

2. Glasser, L.; Jenkins, H. D. B., Predictive thermodynamics for condensed phases. *Chem. Soc. Rev.* **2005**, *34*, 866-874.

3. Glasser, L., Lattice and phase transition thermodynamics of ionic liquids. *Thermochim. Acta* **2004**, *421*, 87-93.

4. Glasser, L., Volume-based thermodynamics of organic liquids: Surface tension and the Eötvös equation. *J. Chem. Thermodynam.* **2021**, *157*, 106391.

5. Eötvös, L., Ueber den Zusammenhang der Oberflächenspannung der Flüssigkeiten mit ihrem Molecularvolumen. *Annalen der Physik* **1886**, *27*, 448-459.

6. Marcus, Y., *Ionic Liquid Properties: From Molten Salts to RTILs*. Springer International Publishing: New York, 2016.

7. Tariq, M.; Freire, M. G.; Saramago, B.; Coutinho, J. A. P.; Lopes, J. N. C.; Rebelo, L. P. N., Surface tension of ionic liquids and ionic liquid solutions. *Chem. Soc. Rev.* **2012**, *41*, 829-868.

8. Palit, S. R., Thermodynamic Interpretation of the Eötvös Constant. *Nature* **1956**, *177*, 1180.

9. Myers, R. T., True molar surface energy and alignment of surface molecules. *Journal of Colloid and Interface Science* **2004**, *274*, 229-236.

10. Wei, J.; Fan, B.-H.; Pan, Y.; Xing, N.-N.; Men, S.-Q.; Tong, J.; Guan, W., Vaporization enthalpy and the molar surface Gibbs free energy for ionic liquids [C_nDmim][NTF₂] (n=2, 4). *J. Chem. Thermodynam.* **2016**, *101*, 278-284.

11. Lyklema, J., A discussion on surface excess entropies. *Colloids and Surfaces a-Physicochemical and Engineering Aspects* **2001**, *186*, 11-16.

12. Skapski, A. S., The Temperature Coefficient of the Surface Tension of Liquid Metals. *J. Chem. Phys.* **1948**, *16*, 386-389.

13. Skapski, A. S., The Surface Tension of Liquid Metals. J. Chem. Phys. 1948, 16, 389-393.

14. Good, R. J., Surface entropy and surface orientation of polar liquids. *J. Phys. Chem.* **1957**, *61*, 810-813.

15. Lyklema, J., The surface tension of pure liquids. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* **1999**, *156*, 413-421.

16. Khrapunov, S., The Enthalpy-entropy Compensation Phenomenon. Limitations for the Use of Some Basic Thermodynamic Equations. *Curr Protein Pept Sci* **2018**, *19*, 1088-1091.

17. Dong, Q.; Muzny, C. D.; Kazakov, A.; Diky, V.; Magee, J. W.; Widegren, J. A.; Chirico, R. D.; Marsh, K. N.; Frenkel, M., ILThermo: A Free-Access Web Database for Thermodynamic Properties of Ionic Liquids. *J. Chem. Eng. Data* **2007**, *52*, 1151-1159.

18. Kazakov, A.; Magee, J. W.; Chirico, R. D.; Paulechka, E.; Diky, V.; Muzny, C. D.; Kroenlein, K.; Frenkel, M., NIST Standard Reference Database 147: NIST Ionic Liquids Database - (ILThermo), Version 2.0. National Institute of Standards and Technology: Gaithersburg MD, 20899.

19. Roemer, F. A library to access the ILThermo v2.0 database: pyilt2 0.9.8.

https://pypi.org/project/pyilt2/ (accessed February, 2021).

20. Zhang, S.; Lu, X.; Zhou, Q.; Li, X.; Zhang, X.; Li, S., Ionic Liquids: Physicochemical Properties. **2009**.

21. Al Kaisy, G. M. J.; Abdul Mutalib, M. I.; Rao, T. V. V. L. N., Novel halogen free hydrophobic trioctylammonium-based protic ionic liquids with carboxylate anions: Synthesis, characterization, and thermophysical properties. *J. Mol. Liq.* **2017**, *242*, 349-356.

22. Domańska, U.; Królikowska, M.; Królikowski, M., Phase behaviour and physico-chemical properties of the binary systems {1-ethyl-3-methylimidazolium thiocyanate, or 1-ethyl-3-methylimidazolium tosylate+water, or+an alcohol}. *Fluid Phase Equilibria* **2010**, *294*, 72-83.

23. Sánchez, L. G.; Espel, J. R.; Onink, F.; Meindersma, G. W.; Haan, A. B. d., Density, Viscosity, and Surface Tension of Synthesis Grade Imidazolium, Pyridinium, and Pyrrolidinium Based Room Temperature Ionic Liquids. *J. Chem. Eng. Data* **2009**, *54*, 2803-2812.

24. Janz, G. J.; Tomkins, R. P. T., Molten Salts: Volume 5, Part 2. Additional Single and Multi-Component Salt Systems. Electrical Conductance, Density, Viscosity and Surface Tension Data. *J. Phys. Chem. Ref. Data* **1983**, *12*.

25. Janz, G. J., Molten Salts Data as Reference Standards for Density, Surface Tension, Viscosity, and Electrical Conductance: KNO3 and NaCl. *J. Phys. Chem. Ref. Data* **1980**, *9*, 791-830.

26. Janz, G. J.; Lakshminarayanan, G. R.; Tomkins, R. P. T.; Wong, J., Molten Salts: Volume 2. Section 2. Surface Tension Data. NSRDS-NBS: 1969; Vol. 28.

27. Krimizis-Tsatsoulis, C., Trouton's rule mysteries: An attempt to a better understanding. *J. Chem. Thermodynam.* **2021**, *152*, 106256.

Table of Contents Graphic



A recently-rediscovered modified Eötvös equation generates molar Gibbs energies, Trouton-like molar surface entropies and molar surface enthalpies from surface tension data for ionic liquids and molten salts. Compared with neutral organic liquids, coulombic forces reduce the freedom of surface molecules as demonstrated by reduced surface entropies with correspondingly increasing surface enthalpies.