A corresponding states approach for the prediction of surface tension of molten alkali halides

N. Galamba[a], C.A. Nieto de Castro[a,*], I. Marrucho[b], J.F. Ely[c]

[a] *Departamento de Química e Bioquímica e Centro de Ciências Moleculares e Materiais,*
Faculdade de Ciências da Universidade de Lisboa, 1749-016 Lisboa, Portugal
[b] *Departamento de Química, Universidade de Aveiro, Campus de Santiago, 3810 Aveiro, Portugal*
[c] *Chemical Engineering and Petroleum Refining Department, Colorado School of Mines, Golden, CO 80401-1887, USA*

Abstract

The extended corresponding states principle has been applied on the prediction of the surface tension of pure molten alkali halides. The model uses liquid density and vapour pressure data of the salts of interest and of the reference salt, chosen to be NaCl, as the input for the calculation of temperature-dependent equivalent substance reducing ratios (ESRR). The model here described was already applied on the prediction of the viscosity and thermal conductivity of pure molten alkali halides [High Temp.-High Pressures, 2000]. Calculations were also made using the simple two-parameter corresponding states principle, with the melting temperature and corresponding density as scaling factors. Agreement between calculated and experimental data is within 10–15% for most of the salts studied. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Extended corresponding states principle; Alkali halides; Surface tension

1. Introduction

Molten salts, alkali halides and their mixtures in particular, have industrially important characteristics, in addition to a scientifically interesting behaviour, which justify the need for accurate thermophysical property data and the development of theoretical models for these systems. The viscosity, thermal conductivity and surface tension of high temperature melts, in general, are the most needed for industry purposes and unfortunately still the most poorly established properties [2].

Although, considerable effort has been devoted in the past to the experimental measurement of these properties at high temperatures, the existent data is still very limited due to experimental difficulties related with some of the characteristics of these systems (e.g. strong chemical activity, high melting points, etc.). With the complexity of these experimental measurements in mind, in addition to the great

* Corresponding author.

number of systems of interest existent, it becomes especially important to develop models capable of predicting these properties given a minimum amount of information as input.

The corresponding states principle is still one of the most powerful tools in this respect and has already been applied to equilibrium [3–9] and transport [1,8–15] properties prediction of pure molten salts and their mixtures.

In this paper, the application of the extended corresponding states model on the prediction of the surface tension of pure molten alkali halides is discussed. The model here described was already applied on the prediction of viscosity and thermal conductivity for these molten salts [1]. It has then been showed that agreement between predicted viscosity and thermal conductivity with experimental data was within 10% for viscosity and within experimental accuracy in the case of thermal conductivity for most of the salts studied. The present work seeks to understand the capability of the model on predicting data for an equilibrium property for the same set of molten salts, thus complementing the previous calculations, as a part of a more general attempt of implementation of a simple but still accurate extended corresponding states approach for prediction of thermophysical properties of pure molten alkali halides and their mixtures.

The basic idea of the extended corresponding states theory [16–19] results from the assumption that the intermolecular potential parameters are not constants, but instead functions of the temperature and density of the system, while the potential itself is conformal to the potential of some reference fluid. This temperature and density dependence is then introduced in the equivalent substance reducing ratios (ESRR) through the use of molecular shape factors. The accuracy of this approach lies in the accuracy of the shape factors, which are used in the definition of the equivalent substance state point, and in the accuracy of the data for the properties of the reference fluid, which will be used in the prediction of the same properties for the fluids of interest. In addition, this approach eliminates the need for detailed knowledge of the intermolecular potential.

In this work, as in the previous calculations for viscosity and thermal conductivity, saturation liquid density and vapour pressure data were used for the reference salt, chosen to be NaCl, and for the salts of interest. The ESRR were determined and found to be temperature dependent only. These ESRR along with the use of a corresponding states relationship for the surface tension were then used to predict this property for the salts under study. In addition, surface tension has been calculated using the simple two-parameter corresponding states theory, through the use of the melting temperature and the corresponding density as reducing parameters, thus permitting the observation of the effect of the use of shape factors in the predicted surface tension. Despite of not being a true corresponding states point, the melting point has been used as an approximation of the triple point, thus expecting the melting temperature and the corresponding density to be similar to the corresponding triple-point values for the alkali halides. This approach is justified by the non-existence of triple-point data for most of these salts.

2. Model description

2.1. The simple two-parameter corresponding states principle

The corresponding states principle for simple spherical fluids was first proposed by van der Waals in an empirical form and later demonstrated by Pitzer [20] through dimensional analysis of the configuration integral. The basic result is that if two pure fluids "j" and "o" are conformal (obey the same reduced

intermolecular potential), it then becomes possible through the use of scaling arguments to show that

$$A_j^r(T_j, \rho_j) = f_j A_o^r(T_o, \rho_o) = f_j A_o^r\left(\frac{T_j}{f_j}, \rho_j h_j\right) \tag{1}$$

In this equation, $A^r = A(T, \rho) - A^*(T, \rho)$ is the residual Helmholtz energy (the $*$ indicates an ideal gas value), ρ the molar density, T the absolute temperature, and f_j and h_j scale factors called equivalent substance reducing ratios. The subscripts "j" and "o" indicate a fluid of interest and a reference fluid, respectively. The scaling arguments used in the derivation of Eq. (1) permit the determination of a relation between the temperature and molar density of the fluid of interest "j" and the corresponding values for the reference fluid "o", namely $T_o = T_j/f_j$ and $\rho_o = \rho_j h_j$. The equivalent substance reducing ratios are related on a microscopic scale to the ratios of the intermolecular potential parameters, and on a macroscopic scale to the critical parameters of the two fluids, namely, $f_j = \varepsilon_j/\varepsilon_o = T_j^c/T_o^c$ and $h_j = \sigma_j^3/\sigma_o^3 = \rho_o^c/\rho_j^c$. Here ε and σ are the intermolecular potential energy and distance parameters, respectively, and the superscript "c" denotes a critical point value. Alternatively, the triple point can be used as the corresponding states point, thus making $f_j = T_j^t/T_o^t$ and $h_j = \rho_o^t/\rho_j^t$, where the superscript "t" denotes a triple-point value.

2.2. The extended corresponding states principle

The simple two-parameter corresponding states principle, whose basic result was discussed above, is only obeyed by spherically symmetric molecules whose intermolecular potentials are conformal. In an attempt to extend the principle to other molecules, Leland et al. [16,17] proposed the use of shape factors that are introduced in the equivalent substance reducing ratios and in principle are allowed to be functions of temperature and density. As discussed earlier, the use of shape factors results from the assumption that the intermolecular potential parameters are not constant but in fact may change with temperature and density, while the potential is itself conformal to the potential of some reference fluid.

In the extended corresponding states principle, the equivalent substance reducing ratios become $f_j = \varepsilon_j(T, \rho)/\varepsilon_o = (T_j^c/T_o^c)\theta_j(T, \rho)$ and $h_j = \sigma_j(T, \rho)^3/\sigma_o^3 = (\rho_o^c/\rho_j^c)\phi_j(T, \rho)$, where θ and ϕ are called shape factors. If the two fluids "j" and "o" are conformal, θ and ϕ are unity, and the original equivalent substance reducing ratios developed for the simple corresponding states principle are recovered. The assumption that the potential parameters are temperature dependent, results originally from angle-average calculations on non-spherical potentials [16], and permitted to join in the same class, in terms of corresponding states, polar fluids and simple non-polar fluids. In the case of molten salts, the corresponding states approach developed by Harada et al. [6] uses an effective diameter, determined by a perturbation method which is temperature and density dependent, thus suggesting that this temperature and density dependence of the shape factors is also correct for molten alkali halides. The shape factor approach has the advantage of not having to use any potential parameters to scale the properties.

In the extended corresponding states principle, the basic thermodynamic relation, Eq. (1), found for the simple corresponding states principle remains the same. It is found however that due to the density and temperature dependence of the shape factors, other thermodynamic relationships between various properties become more complex, becoming dependent on the derivatives of the equivalent substance reducing ratios with respect to density and temperature.

2.3. Equivalent substance reducing ratios calculation

Ideally, the shape factors θ and ϕ could be calculated "exactly" for each molten salt of interest through the use of high-accuracy equations of state for these salts and for the reference salt. Using any two thermodynamic property corresponding states relationships between the two fluids "j" and "o", in addition to the critical temperature and density for each salt. Unfortunately, this critical data has not been measured yet, nor has the experimental PVT data for these systems permitted the development of these high-accuracy equations of state. Despite this limitation in terms of shape factors calculation, at least using any experimental critical data, the properties of the salt "j" can be calculated once the equivalent substance reducing ratios for that salt have been determined, given the knowledge of the same properties for the reference salt.

Most of the data that are available for molten alkali halides are for the saturation boundary, viz. vapour pressures and saturated liquid densities. In this work, vapour pressure and saturation liquid density-fitted equations, available in literature, have been used to calculate the equivalent substance reducing ratios. Since the saturation boundary only depends upon temperature, density independent equivalent substance reducing ratios are found. The vapour pressure and saturated liquid density of any salt of interest are related to the reference salt properties through the equations

$$p_j^s(T_j) = \frac{p_o^s(T_o) f_j}{h_j} = \frac{p_o^s(T_j/f_j) f_j}{h_j} \tag{2}$$

$$\rho_j^s(T_j) = \frac{\rho_o^s(T_o)}{h_j} = \frac{\rho_o^s(T_j/f_j)}{h_j} \tag{3}$$

Simultaneous solution of Eqs. (2) and (3) provides the equivalent substance reducing ratios along the saturation boundary.

The liquid density-fitted equations used in the calculation of the ESRR were taken from the NIST database [21] for all the molten alkali halides, with the exception of NaCl whose density equation used is available in the [28] (1982 and onwards). The vapour pressure-fitted equations were taken from Janz [22] for LiF and NaF, Topor [23] for CsF, DIPPR database [28] for KCl and NaBr, Topor [24] for NaI, and Lange [25] for all the other molten alkali halides.

Because of the limited temperature range of the density and vapour pressure correlation equations available, these have been extrapolated in the calculation of f_j and h_j, thus increasing the uncertainty on the estimated properties.

2.4. Surface tension prediction

The surface tension for each of the molten salts of interest "j" has been calculated using the following equation:

$$\gamma_j(T_j) = \gamma_o(T_o) = \gamma_o\left(\frac{T_j}{f_j}\right) \frac{f_j}{h_j^{2/3}} \tag{4}$$

where γ is the surface tension. This equation can be derived from the equality of the reduced surface tension $\gamma^* = \gamma \sigma^2 / \varepsilon$ for the molten salt of reference "o" and the molten salt of interest "j" at the same reduced temperature, or alternatively through the statistical mechanical relation for surface tension using the same type of argument which lead to Eqs. (1)–(3).

The following correlation equation has been used for the surface tension of NaCl (reference fluid):

$$\gamma = 0.20133 \left(1 - \frac{T}{3400}\right)^{1.4978} \tag{5}$$

where γ is the surface tension ($N\,m^{-1}$) and T the absolute temperature. Eq. (5) is available in the [28] (1982 and onwards). This equation, along with Eq. (4), have been used for the semi-theoretical estimation of the surface tension of the molten alkali halides, using the simple two-parameter corresponding states theory, with the melting temperature and the corresponding density [26] as scale factors. In addition, the use of Eqs. (2) and (3) permitted the calculation of shape factors, introduced in the equivalent substance reducing ratios, thus trying to force the salts to conformity in an extended corresponding states approach.

3. Results

The surface tension data predicted with the two corresponding states schemes have been compared with experimental data taken from the [28] (1982 and onwards) for NaF, the NIST database [21] for LiF, KF, RbF and CsF, and [27] for all the other molten alkali halides.

Table 1 shows the average absolute percent deviation (AAD) and the average percentage error (BIAS) for the predicted surface tension for each of the alkali halides obtained with the simple corresponding

Table 1
Average absolute percent deviation (AAD) and average percentage error (BIAS) values for surface tension of molten alkali halides[a]

SALT (T_m–T_b)	n	ΔT (K)	SCST		ECST	
			AAD	BIAS	AAD	BIAS
LiF (1121–1954)	Correlation	1290.0–1533.0	9.8	−9.8	14.9	+14.9
NaF (1268–1977)	8	1290.0–1360.0	4.4	+4.4	7.2	+7.2
KF (1131–1775)	Correlation	1185.0–1583.0	4.2	−4.2	2.7	−2.7
RbF (1068–1681)	Correlation	1068.0–1218.0	7.1	−7.1	8.6	−8.6
CsF (986–1524)	Correlation	1048.0–1253.0	5.6	−5.6	15.1	−15.1
LiCl (883–1655)	12	974.5–1194.8	16.2	−16.2	0.83	+0.83
KCl (1043–1680)	15	1049.3–1185.6	4.8	−4.8	8.2	−8.2
RbCl (990–1654)	9	1057.3–1179.0	10.9	−10.9	2.1	−2.1
CsCl (918–1573)	12	943.3–1162.6	18.9	−18.9	16.4	−16.4
LiBr (823–1583)	10	931.0–1158.6	22.9	−22.9	2.7	−2.7
NaBr (1020–1665)	16	1033.5–1184.1	3.8	−3.8	5.3	−5.3
KBr (1007–1656)	13	1012.1–1193.2	9.0	−9.0	9.9	−9.9
RbBr (953–1625)	15	974.0–1183.0	15.4	−15.4	14.5	−14.5
CsBr (909–1573)	14	922.9–1185.0	20.7	−20.7	20.0	−20.0
LiI (723–1444)	4	893.7–984.2	26.7	−26.7	3.0	+3.0
NaI (935–1577)	12	944.1–1164.8	11.2	−11.2	10.6	−10.6
KI (958–1597)	15	969.9–1185.7	12.2	−12.2	15.8	−15.8
RbI (913–1577)	11	921.1–1125.2	21.2	−21.2	17.8	−17.8
CsI (894–1573)	9	983.3–1147.5	25.3	−25.3	11.4	−11.4

[a] Calculated in the temperature range ΔT, using the simple corresponding states theory (SCST) and the extended corresponding states theory (ECST), together with their melting (T_m) and boiling (T_b) temperatures.
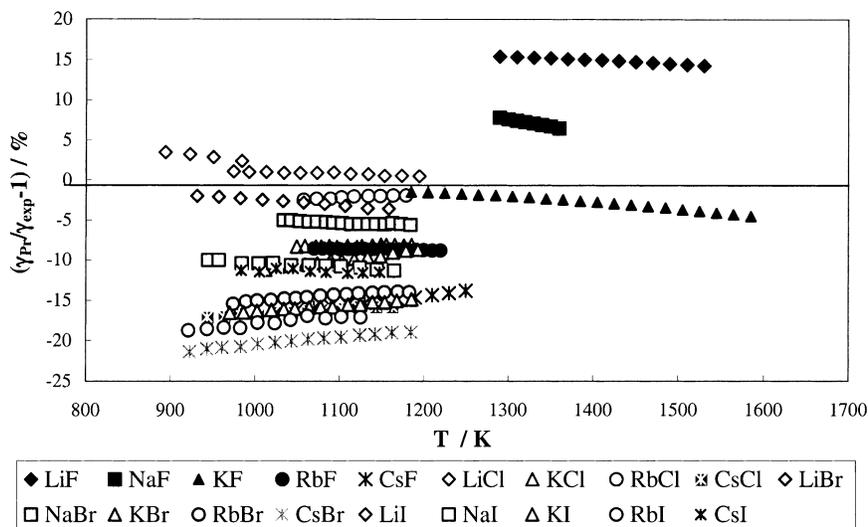
Fig. 1. Surface tension deviations calculated as a function of temperature for all the molten alkali halides studied.

states theory (SCST) and the extended corresponding states theory (ECST). The n represents the number of experimental data points used for the comparisons. Fig. 1 shows a plot of the surface tension deviations as a function of temperature for all the molten alkali halides.

In the case of the alkali fluorides (except for NaF), the estimated surface tensions have been compared with the data calculated through the use of the correlation equations available in the NIST database [21], using a temperature step equal to 1 K. It can be seen from Table 1 that the SCST fails completely on the prediction of surface tension for the molten lithium and cesium halides (with the "exception" of LiF and CsF), the smallest and largest cations, respectively, from the molten alkali halides set. The introduction of shape factors on the ESRR seems to be capable of solving only the problem of the lithium halides (with the exception of LiF). In addition, it introduces additional errors on the predictions for other molten salts, thus becoming very difficult to establish a pattern that could suggest any possible corrections to the model. In general, the ECST under-predicts the surface tension of the salts (Fig. 1), with the exception of LiF, NaF, LiCl and LiI. The major sources of error of this model are the extrapolations of the vapour pressure correlation equations used in the calculation of the shape factors.

4. Conclusions

The simple and the extended corresponding states have been applied to the semi-theoretical estimation of the surface tension of molten alkali halides. The results showed that the scheme proposed works satisfactorily only for some of the molten salts studied. The major uncertainty arose from the lack of vapour pressure curves covering all the temperature ranges used.

The shape factors used were obtained empirically. Ideally, shape factors correlation equations in terms of characteristic molecular parameters should be developed, thus permitting the use of the corresponding states principle in a predictive form. In addition, it should then be possible to understand the way a

corresponding states scheme would or would not fail for some of the molten alkali halides. However, and because of the lack of experimental data for molten salts, these correlation equations are still very difficult to develop. In general, a molecular approach of the corresponding states principle for molten salts rises the problem of having to use some specific intermolecular potential model, for which it is still very difficult to find parameters for all the systems of interest.

References

[1] N. Galamba, C.A. Nieto de Castro, I. Marrucho, J.F. Ely, High Temp.-High Pressures, 2001, in press.
[2] A. Nagashima, Int. J. Thermophys. 11 (2) (1990).
[3] H. Reiss, S.W. Mayer, J.L. Katz, J. Chem. Phys. 35 (3) (1961) 820–826.
[4] B.B. Owens, J. Chem. Phys. 44 (8) (1966) 3144–3145.
[5] L.V. Woodckock, Proc. R. Soc., Lond. A 348 (1976) 187–202.
[6] M. Harada, M. Tanigaki, Y. Tada, Ind. Eng. Chem. Fundam. 22 (1983) 116–121.
[7] Y. Tada, S. Hiraoka, T. Uemura, M. Harada, Ind. Eng. Chem. Res. 29 (1990) 1509–1516.
[8] Y. Tada, S. Hiraoka, Katsumura, C.Y. Park, Ind. Eng. Res. 32 (1993) 2873–2880.
[9] Y. Tada, S. Hiraoka, T. Achiwa, S. Koh, Ind. Eng. Chem. Res. 34 (1995) 1461–1470.
[10] R.E. Young, J.P. O'Connel, Ind. Eng. Chem. Fundam. 10 (3) (1971) 418–423.
[11] L.R. White, H.T. Davis, J. Chem. Phys. 47 (12) (1967) 5433–5439.
[12] Y. Abe, A. Nagashima, J. Chem. Phys. 75 (8) (1981) 3977–3985.
[13] Y. Tada, S. Hiraoka, T. Uemura, M. Harada, Ind. Eng. Chem. Res. 27 (1988) 1042–1049.
[14] M. Harada, A. Shioi, T. Miura, S. Okumi, Ind. Eng. Chem. Res. 31 (10) (1992) 2400–2407.
[15] Y. Nagasaka, A. Nagashima, Int. J. Thermophys. 14 (4) (1993) 923–936.
[16] T.W. Leland, P.S. Chappelear, Ind. Eng. Chem. 60 (7) (1968a) 15–43.
[17] T.W. Leland, J.S. Rowlinson, G.A. Sather, I.D. Watson, Trans. Faraday Soc. 64 (1968) 2034–2043.
[18] J.W. Leach, P.S. Chappelear, T.W. Leland, AIChE J. 14 (4) (1968) 568–576.
[19] G.D. Fisher, T.W. Leland, Ind. Eng. Chem. Fundam. 9 (4) (1970) 537–544.
[20] K.S. Pitzer, J. Chem. Phys. 7 (1939) 583–590.
[21] G.J. Janz, NIST Properties of Molten Salts Database, NIST SRD 27, Version 2.0, 1992.
[22] G.J. Janz, Molten Salts Handbook, Academic Press, New York, 1967.
[23] L. Topor, J. Chem. Thermodyn. 8 (1976) 777–783.
[24] L. Topor, J. Chem. Thermodyn. 4 (1972) 739–744.
[25] N.A. Lange, Lange's Handbook of Chemistry, 11th Edition, McGraw-Hill, New York, 1973.
[26] J.S.M.E. Thermophysical Properties Handbook, Tokyo, 1990.
[27] Y. Sato, T. Ejima, M. Fukasawa, K. Abe, J. Phys. Chem. 94 (1990) 1991–1996.
[28] Design Institute for Physical Property Data, DIPPR Database, AIChE, New York, 1982.