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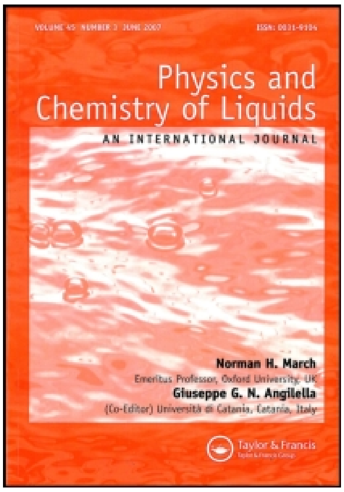

Physics and Chemistry of Liquids

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713646857

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To cite this Article Gallego, L. J. , Somoza, J. A. and Alonso, J. A.(1985) 'Concentration Fluctuations in Binary Mixtures of Inert-Gas Fluids', Physics and Chemistry of Liquids, 15: 1, 41 — 48
To link to this Article: DOI: 10.1080/00319108508081002
URL: http://dx.doi.org/10.1080/00319108508081002

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Phys. Chem. Liq., 1985, Vol. 15, pp. 41–48
0031-9104/85/1501-0041$18.50/0

Printed in the United Kingdom

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(Received February 7, 1985)

The non-random two-liquid theory developed by Renon and Prausnitz has been used to study the concentration fluctuations in binary Ar–Kr and Kr–Xe liquid mixtures. The concept of local composition on which this theory is based is very helpful in interpreting the tendency for phase separation exhibited by both systems.

1 INTRODUCTION

The study of the concentration fluctuations $S_{cc}(0)$ in binary liquid mixtures provides information about the nature of the interactions between the components of the system. $S_{cc}(0)$ is related to the thermodynamic properties of a binary mixture via the expression[1]

$$S_{cc}(0) = \frac{RT}{(\partial^2 g_M/\partial c_1^2)_{T,P}}, \tag{1}$$

where c_1 is the concentration of component 1, g_M is the molar Gibbs free energy of mixing, R is the gas constant, T is the absolute temperature and P is the pressure. The characteristic features of $S_{cc}(0)$ have been studied by Bhatia and coworkers on the basis of several theories of mixtures (for a survey, see the review article by Bhatia[2]). In the case of an ideal solution, that is, when the two components of the mixture are distributed at random, $S_{cc}(0) = c_1 c_2$. Deviations from ideal behaviour show up very clearly in $S_{cc}(0)$. Specifically, when the system presents a tendency towards segregation or phase separation, then $S_{cc}(0) > c_1 c_2$; if on the contrary the system has a tendency towards compound formation, then $S_{cc}(0)$ dips below the ideal line. Most work on concentration fluctuations has been restricted to binary liquid alloys,[1-16] with little mention of non-metallic systems (Ratti and Bhatia,[6] for example, have studied Ar–Kr mixtures using perturbation theory on a hard-sphere reference system). However, Joarder and Silbert[17] have recently performed an interesting study of $S_{cc}(0)$ for a binary mixture of model polar fluids within the framework of a van der Waals-type theory, and we expect their article to motivate more exhaustive studies of the concentration fluctuations in complex non-metallic mixtures.

In the present paper we study Ar–Kr and Kr–Xe liquid mixtures. For this purpose we shall use a semiempirical model developed by Renon and Prausnitz[18,19] known as the non-random two-liquid (NRTL) theory. This model has recently been employed by us[15,20] in the study of binary liquid alloys formed between alkali metals. Our concern now is to show that the NRTL theory allows an interesting interpretation of the interatomic forces and the characteristic features of $S_{cc}(0)$ in binary mixtures of liquified inert gases.

2 EXPRESSION FOR $S_{cc}(0)$ IN THE NRTL THEORY

The NRTL theory is based on the concept of local composition originally introduced by Wilson.[21] This concept is expressed by Renon and Prausnitz through the formula

$$\frac{c_{21}}{c_{11}} = \frac{c_2 \exp(-\alpha g_{21}/RT)}{c_1 \exp(-\alpha g_{11}/RT)}. \tag{2}$$

In this equation c_{11} and c_{21} are the local concentrations of molecules of types 1 and 2 respectively around a molecule of type 1; g_{11} and g_{21} are energy parameters associated with 1–1 and 2–1 interactions, respectively; and α is a constant characterizing the tendency of the components to mix in a nonrandom fashion. Equation (2) thus relates the local concentrations and the overall concentrations c_1 and c_2 through Boltzmann factors. When $\alpha = 0$, these two classes of quantities coincide. Interchanging subscripts 1 and 2, we also have

$$\frac{c_{12}}{c_{22}} = \frac{c_1 \exp(-\alpha g_{12}/RT)}{c_2 \exp(-\alpha g_{22}/RT)}. \tag{3}$$

The local concentrations obey the conservation equations

$$c_{21} + c_{11} = 1 \tag{4}$$

and

$$c_{12} + c_{22} = 1. \tag{5}$$

By incorporating the concept of local composition into Scott's two-liquid model of mixtures,[22] Renon and Prausnitz derived the following expression for the molar excess Gibbs free energy;

$$g_E = RTc_1c_2\left[\frac{\tau_1 \exp(-\alpha\tau_1)}{c_1 + c_2 \exp(-\alpha\tau_1)} + \frac{\tau_2 \exp(-\alpha\tau_2)}{c_2 + c_1 \exp(-\alpha\tau_2)}\right], \tag{6}$$

where

$$\tau_1 = \frac{g_{12} - g_{11}}{RT} \tag{7}$$

and

$$\tau_2 = \frac{g_{12} - g_{22}}{RT}. \tag{8}$$

Thus, from Eqs (1) and (6), plus the relation between g_E and g_M

$$g_M = g_E + RT(c_1 \ln c_1 + c_2 \ln c_2), \tag{9}$$

the following expression for $S_{cc}(0)$ is obtained:

$$S_{cc}(0) = \frac{c_1c_2}{1\text{-}2c_1c_2\left[\dfrac{\tau_1 \exp(-2\alpha\tau_1)}{(c_1 + c_2 \exp(-\alpha\tau_1))^3} + \dfrac{\tau_2 \exp(-2\alpha\tau_2)}{(c_2 + c_1 \exp(-\alpha\tau_2))^3}\right]}. \tag{10}$$

This equation contains the three adjustable parameters τ_1, τ_2 and α. However, after applying their theory to thermodynamic data of a large number of liquid mixtures, Renon and Prausnitz[18] have established rules of thumb for the a priori determination of the non-randomness parameter α. In particular, for systems such as those considered in this paper which differ little from ideal behaviour, they recommend the value $\alpha = 0.3$. Accordingly, we shall use this value for α throughout, thus considering (10) as a two-parameter equation.

3 APPLICATION TO Ar–Kr AND Kr–Xe SYSTEMS

We have applied Eq. (10) to Ar–Kr and Kr–Xe liquid mixtures. The experimental $S_{cc}(0)$ data have been obtained from Eq. (1) using measurements of g_E published by Davies *et al.*[23] for Ar–Kr at 115.8 K and by Calado and

TABLE I

Optimal values of the parameters τ_1 and τ_2 and standard deviations of the fits of Eq. (10) to the experimental $S_{cc}(0)$ data for Ar–Kr and Kr–Xe systems

System	Values of the parameters		Standard deviation
Ar–Kr	$\tau_1 = -0.0016$	$\tau_2 = 0.3679$	0.00031
Kr–Xe	$\tau_1 = -0.044$	$\tau_2 = +0.396$	0.0017

Staveley[24] for Kr–Xe at 161.4 K. Equation (10) was then fitted to the experimental data by using the nonlinear optimum-seeking procedure developed by Marquardt.[25] The results are presented in Table I and Figure 1. The Table contains the optimal values of the parameters τ_1 and τ_2 and the standard deviations of the curves fitted. The fit is very good in both cases, as can be seen in Figure 1. That the curves are nearly symmetrical about $c = \frac{1}{2}$ is a consequence of the small differences between the molar volumes of the components in both systems: 2.7% and 8.5% for Ar–Kr and Kr–Xe respectively.[23, 24] It can also be appreciated that for these two systems the $S_{cc}(0)$ curve lies above that corresponding to an ideal mixture. This means, according to the discussion at the beginning of this paper, that there is a tendency (although small) towards phase separation. Indeed, this may be deduced directly from the fact that the quantity $w \equiv (\tau_1 + \tau_2)/2 = (2g_{12} - g_{11} - g_{22})/2RT$ is in both cases positive (0.183 and 0.176 for Ar–Kr and Kr–Xe respectively), which, bearing in mind the meaning ascribed to the parameters g_{ij}, indicates a preference for like-atom pairs in the mixture. The much larger value of τ_2 with respect to τ_1 (see Table I) implies that in the case of the Ar–Kr mixture, the Kr–Kr interaction is large compared to both Ar–Ar and Ar–Kr interactions, and in the case of the Kr–Xe mixture, the Xe–Xe interaction is large compared to the Kr–Kr and Kr–Xe interactions. It may also be noted that the quantity $\Delta \equiv \tau_2 - \tau_1 = (g_{11} - g_{22})/RT$ has the values Δ(Ar–Kr) = 0.37 and Δ(Kr–Xe) = 0.44. These values are not too dissimilar from the differences in the energy parameter ε/kT (k being the Boltzmann constant) describing the depth of the Lennard-Jones potential for like-atom pairs, which according to the data of Ref. 26 are $(\varepsilon(\text{Kr–Kr}) - \varepsilon(\text{Ar–Ar}))/kT \simeq 0.44$ and $(\varepsilon(\text{Xe–Xe}) - \varepsilon(\text{Kr–Kr}))/kT \simeq 0.31$.

The NRTL theory offers an interesting way of explaining the tendency to phase separation in Ar–Kr and Kr–Xe systems based on the concept of local composition. According to the definition of the local concentration c_{ij}, the quantity

$$\Delta c_i = c_{ij} - c_{ii} \tag{11}$$

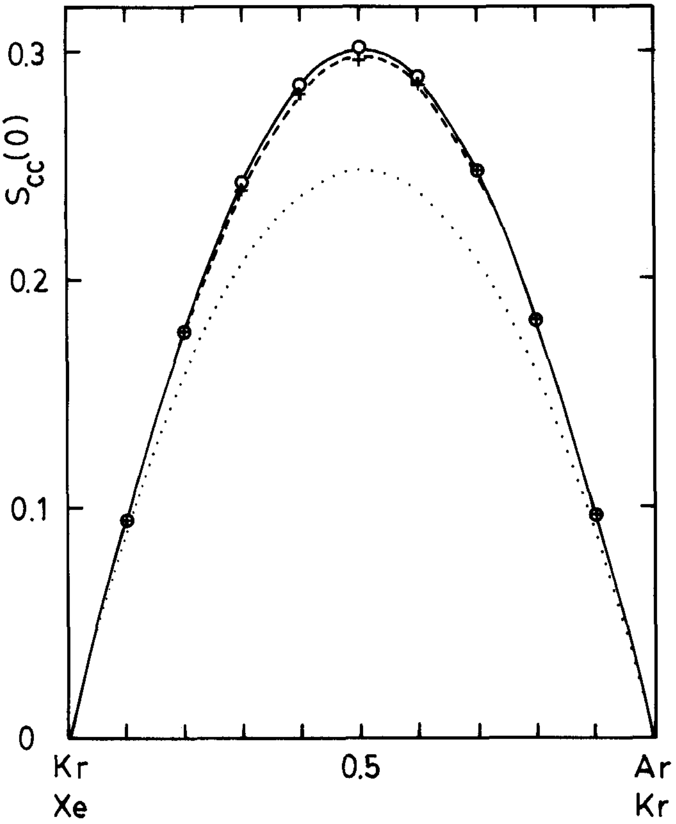

FIGURE 1 $S_{cc}(0)$ for Ar-Kr (——— NRTL theory, ○ experimental data[23]) and for Kr-Xe (- - - NRTL theory, + experimental data[24]). For reference, the ideal solution curve (· · ·) is also shown.

is a measure of the difference between the distribution of i atoms surrounding a j atom and the distribution of i atoms surrounding an i atom. Using Eqs (2)-(5), the explicit form of Δc_i becomes

$$\Delta c_i = \frac{c_1 \exp(-\alpha\tau_2)}{c_2 + c_1 \exp(-\alpha\tau_2)} + \frac{c_2 \exp(-\alpha\tau_1)}{c_1 + c_2 \exp(-\alpha\tau_1)} - 1 \qquad (i = 1, 2). \quad (12)$$

Figure 2 shows the behavior of Δc_i as a function of concentration in Ar-Kr and Kr-Xe mixtures. The negative values obtained in all cases for Δc_i are an indication of the higher probability of finding a like atom near a given atom than of finding an unlike atom. A similar interpretation has been given by Crozier *et al.*[27] in a study of the partial structure factors of these systems in the long wavelength limit.

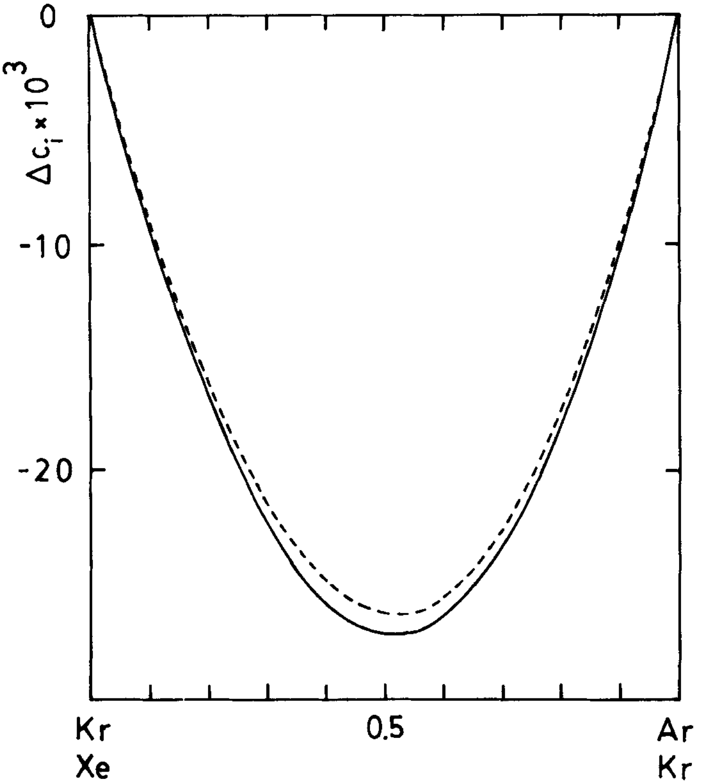

FIGURE 2 Variation of Δc_i ($i = 1$ or 2) with composition for the Ar–Kr (———) and Kr–Xe (– – –) systems.

In conclusion, the NRTL theory provides a simple and useful approach for studying the behaviour of $S_{cc}(0)$ in non-metallic as well as metallic binary liquid mixtures, and it can be considered as an alternative to more fundamental theories such as those using perturbation of a hard-sphere potential.[6] For the systems considered in this paper, the Ar–Kr and Kr–Xe liquid mixtures, the NRTL theory neatly brings out the preference for like-atom nearest-neighbour pairs rather than unlike-atom pairs.

Acknowledgements

The authors wish to thank Drs M. Silbert and R. N. Joarder for a preprint of Ref. 17, and the CAICYT of Spain for financial support.

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