ELSEVIER

Thermochimica Acta 269/270 (1995) 371–379

thermochimica
acta

Common intersection point independent of temperature for compressed liquid mixtures[☆]

A. Boushehri *, E.K. Goharshadi

Shiraz University, Shiraz, Iran

Received 16 September 1994; accepted 27 May 1995

Abstract

There exists a common intersection point for the isotherms of the reduced bulk modulus of each compressed liquid mixture as a function of density from triple point up to the critical temperature. A theoretical analysis of this empirical regularity is presented in terms of a statistical–mechanical equation of state (EOS) with accuracy near that of experiment. The results indicate that an effective van der Waals covolume $b(T)$ seems weakly temperature-dependent in agreement with molecular theory, thus the reduced bulk modulus versus volume shows the crossover. The better corresponding state for the volumetric properties of compressed liquids recently showed the successful extension of the previous equation of state to molecular liquids; the present results for LJ (12, 6) mixture, Ar + Kr, Kr + Xe, and $CO_2 + C_2H_6$ show the further capability of the equation of state for predicting the volumetric properties of liquid mixtures. Finally, we look at the pressure-dependence of the excess molar volume of Kr + Xe, Ar + N_2, Ar + C_2H_6, and $CO_2 + C_2H_6$. In general, V^E gets closer to 0 as P increases and the (EOS) reproduces this effect.

Keywords: Bulk modulus; Equation of state; Excess molar volume; Liquid mixtures

1. Introduction

Knowledge of the equation of state (EOS) is necessary to obtain densities and other thermodynamic properties under high pressure. An analytical equation of state based on the statistical–mechanical perturbation theory, has recently been proposed [1, 2].

---

* Corresponding author.

[☆] Presented at the 6th European Symposium on Thermal Analysis and Calorimetry, Grado, Italy, 11–16 September 1994.

SSDI 0040-6031(95)02540-5

This equation of state shows how the successful results of the past century for the compressibility of liquids could be obtained from statistical–mechanical theory [3]. The extension of Ref. [2] to molecular liquids, for which the second virial coefficients are not known, gives accurate P–V–T results at all liquid densities and temperatures [4].

There are many interesting regularities in physical properties of dense fluids. Seven of the better known ones are the following:

(1) Near linearity of ρ vs T at constant density, over the entire range from the perfect gas to the compressed liquid [5].

(2) Near linearity of a Clausius–Clapeyron plot of $\ln \rho_{\text{vap}}$ vs $1/T$ from the triple point to the critical point [6].

(3) Near linearity of the mean density of a saturated liquid and its equilibrium vapor as a function of temperature. This is the so-called "law of rectilinear diameters" [7].

(4) Near linearity of the bulk modulus of a liquid as a function of pressure [8–10].

(5) Linearity of the Zeno contour and its correlation with the line of rectilinear diameter. The Zeno contour is the locus of T vs ρ points at which the compression factor, $Z \equiv PV/RT$, is unity [11, 12].

(6) The common bulk modulus point, in which all the liquid isotherms of the reduced bulk modulus as a function of density intersect at essentially a single point [13, 14].

(7) Linearity $(Z-1)v^2$ vs ρ^2, where $\rho = 1/v$ is the molar density for both compressed liquids and dense supercritical fluids [15].

In Ref. [14] it has been shown how the existence of the common bulk modulus point for compressed liquids can be given a theoretical basis in terms of a statistical–mechanical equation of state. Analysis of this reference also indicates the limits of validity of the regularity, namely from triple point up to critical point. For simplicity only CH_4 and n-C_8H_{18} were considered in Ref. [14]. However, the arguments are not essentially changed for other molecules. In summary, the equation of state shows the behavior of the reduced bulk modulus in agreement with Huang and O'Connell's crossing plot [13]. This equation of state also shows how this generalized technique can be used in its present form for even the most complex systems. The results show further capability of the equation of state for predicting the volumetric properties of liquid substances with quite different acentric factors. Furthermore, we consider the treatments of mixtures in this report. The present work shows the successful extension of previous studies to molecular liquid mixture. Finally, we look at the pressure-dependence of the excess molar volume. In general, V^E gets closer to 0 as P increases, regardless of its sign at low P, and the EOS reproduces this effect.

2. Basic expressions and application

The corresponding state equation can be written as [2]

$$\frac{\rho}{\rho KT} = 1 + (B_2 - \alpha)\frac{\rho}{1 + \delta b\rho} + \alpha\frac{\rho}{1 - \lambda b\rho} \tag{1}$$

where ō = 0.22 λ, ρ is the number (molar) density, kT has its usual meaning, and λ is a constant. Three temperature-dependent quantities are needed to use the strong principle: the second virial coefficient B_2, an effective van der Waals covolume b, and a scaling factor α, which is equivalent to the contribution to B_2 from just the repulsive branch of the intermolecular forces. The strong principle may also be characterized by three constants: the Boyle volume V_B, the Boyle temperature T_B, and an empirical constant λ reflecting the spheracy of the molecule. It fortunately turns out that $\alpha(T)$ and $b(T)$ are rather insensitive to the shape of the intermolecular potential, so they appear nearly universal functions of temperature in terms of suitable reducing unit such as T_B and V_B. The numerical tables for B_2, α, and b for (12, 6) potential and Aziz–Slaman potential are given in Refs. [1] and [2], respectively. The bulk modulus (reciprocal of the isothermal compressibility) can be calculated from Eq. (1), that is

$$B=\rho\left(\frac{\partial P}{\partial \rho}\right)_T=\rho K T\left[1+\frac{(B_2-\alpha)\rho(2+\delta b\rho)}{(1+\delta b\rho)^2}+\frac{\alpha\rho(2-\lambda b\rho)}{(1-\lambda b\rho)^2}\right] \tag{2}$$

The reduced bulk modulus, $\underline{B}=B/\rho kT$, can be related to the equation of state

$$1-\underline{B}=\frac{(\alpha-B_2)\rho(2+\delta b\rho)}{(1+\delta b\rho)^2}-\frac{\alpha\rho(2-\lambda b\rho)}{(1-\lambda b\rho)^2} \tag{3}$$

The statistical–mechanical equation of state for a liquid LJ mixture has the following form [16]

$$\frac{P}{\rho kT}=1+\rho\sum_{ij}x_i x_j B_{ij}+\rho\sum_{ij}x_i x_j \alpha_{ij}[g_{ij}(d_i,d_j)-1] \tag{4}$$

where all the parameters of this equation are similar to those of Eq. 1, and the summations apply to all the components of the mixture.

We have used Eq. (4) to obtain the reduced bulk modulus for equimolar liquid mixtures of LJ molecules at three different temperatures in which one component has a fixed parameter value ($\epsilon_1/k=34$ K and $\sigma_1=2.85$ Å), and the parameter values of the other component are $\epsilon_2/\epsilon_1=3.5$ and $\sigma_2/\sigma_1=2$. The unlike parameters ϵ_{12} and σ_{12} were taken to follow simple combining rules: $\sigma_{12}=1/2(\sigma_1+\sigma_2)$ and $\epsilon_{12}=(\epsilon_1\epsilon_2)^{1/2}$.

Fig. 1 shows that the isotherms of $1-\underline{B}$ vs $(1/\rho V_B)$ cross at one point. Eq. (4) involves pairwise additivity, g_{ij}, where many-body forces are included in Eq. (3), x_i and x_j are mole fractions and the quantities B_{ij} and α_{ij} are related to pair potential $U_{ij}(r)$ in a manner similar to Eqs. 2 and 3 in Ref. [16].

The equation of state for 0.485 Ar + 0.515 Kr and 0.556 Kr + 0.444 Xe has been shown to be of the form [17]

$$\frac{\rho}{\rho kT}=1+\rho\sum_{ij}x_i x_j(B_{ij}-\alpha_{ij})F_{ij}+\rho\sum_{ij}x_i x_j\alpha_{ij}G_{ij} \tag{5}$$

where F_{ij} and G_{ij} are defined in Ref. [17], and other parameters are the same as those of Eq. (4). We have used the best available intermolecular potentials of the HFD-B or HFD-C form given by Aziz et al. [17–19], since the pair potentials for Ar–Ar, Kr–Kr,

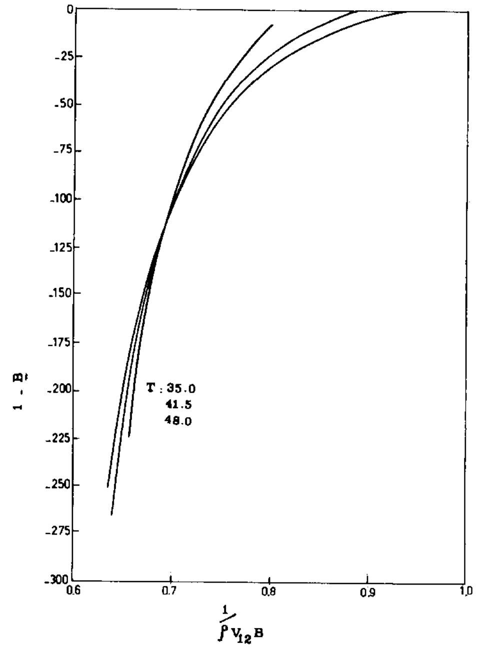

Fig. 1. Isotherms of $1-\underline{B}$ vs $1/\rho V_B$ for a (12, 6) mixture predicted from Eq. (4). The scale is made dimensionless with V_B for 1, 2.

Xe–Xe, Ar–Kr, Ar–Xe, and Kr–Xe are accurately known. We have taken $\lambda = 0.454$. No mixing rules are needed, and similar results are shown in Figs. 2 and 3. For convenience the scales in Figs. 2 and 3 are made dimensionless with the V_B for Ar and Kr, respectively. It is true that the isotherms don't intersect at exactly the same density, but they are within 5% of a common point. Even the slightly supercritical isotherms conform. Our examination of the behavior of the reduced bulk modulus reveals that its crossover occurs for liquid mixture isotherms using Eq. (5).

Data for pure CO_2, N_2, and C_2H_6 have previously been analyzed using mean effective L–J (12, 6) potentials, and the resulting potential parameters together with the values of λ are listed in Ref. [2]. The Boyle constants can be estimated by $T_B = 3.418\epsilon/k$ and $V_B = 1.201\, r_m^3$. The values of α and b for CO_2, N_2, and C_2H_6 can then be calculated [1]. It is important to use accurate values of $B(T)$ in the calculation, and for B_{12} we have adapted the fairly elaborate combination rules developed by Bzowski et al. [20] for use in a correlation scheme for the properties of a low density gas mixture [21].

Fig. 2 shows the variations of $1-\underline{B}$ as a function of $1/\rho V_B$ for Ar + Kr. The crossover of Kr + Xe isotherms is clearly shown in Fig. 3. Because the phenomenon is in the dense liquid as shown in Fig. 4 for $0.5CO_2 + 0.5C_2H_6$, this behavior can be attributed to variations of repulsive forces corresponding to $r/r_m = 0.86$ to 0.89, where r_m represents the intermolecular distance at the well depth and $U\ (r/r_m = 0.89) \approx 0$. Figs. 1–4 show that $1-\underline{B}$ are insensitive to the nature of the intermolecular forces in the fluid. Their

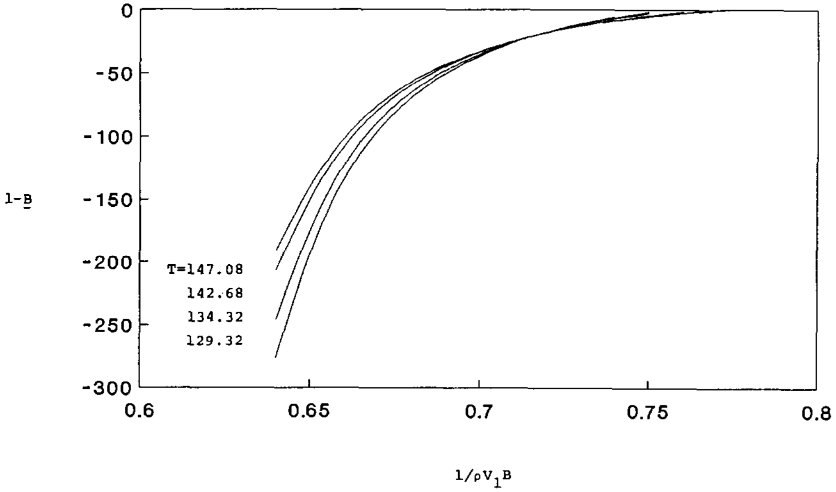

Fig. 2. The predicted reduced bulk modulus, $1-\underline{B}$, of Ar + Kr as a function of reduced volume for four temperatures.

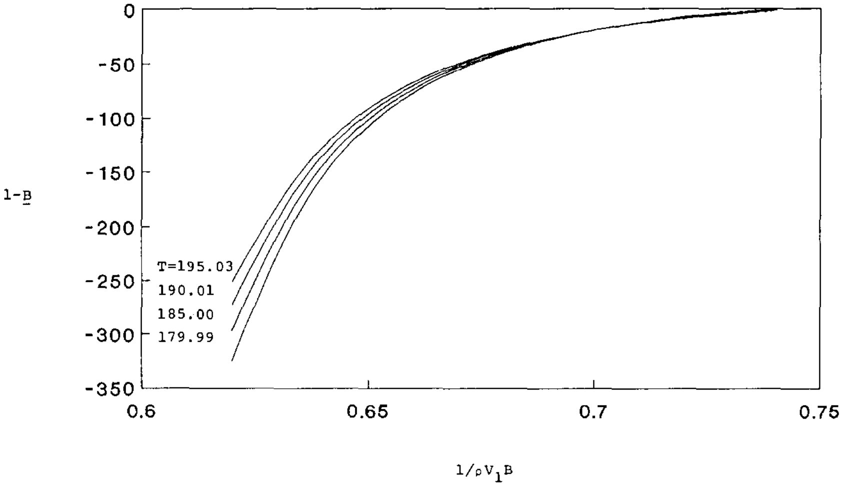

Fig. 3. Same as Fig. 2, for Kr + Xe.

universality can be attributed to the lack of importance of nonspherical forces in $(1-\underline{B})$. Careful examination of the $1-\underline{B}$ vs $1/\rho V_B$ plots in Figs. 1–4 leads to the following observations:

1. The isotherms intersect at nearly the same point in the plot of $1-\underline{B}$ vs the reduced volume $(1/\rho V_B)$ by a temperature-independent quantity $1/\rho_0 V_B$ (ρ_0 is the density at the point of intersection). This is consistent with the finding by Huang and O'Connell [13].

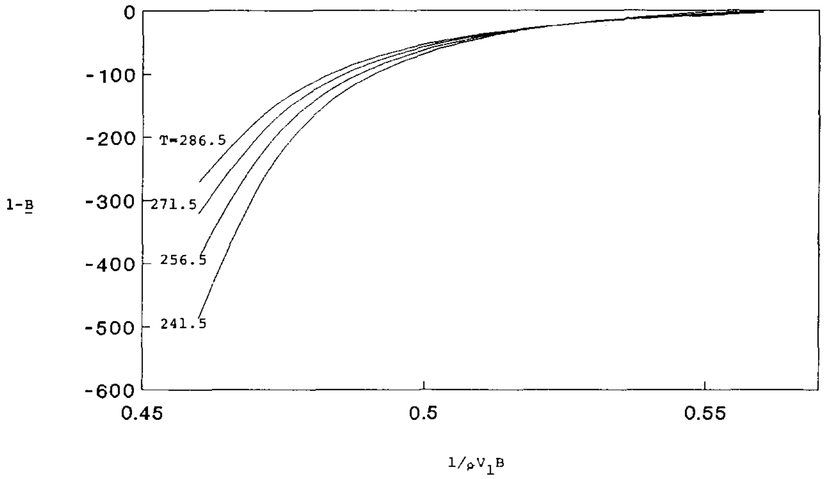

Fig. 4. Same as Fig. 2, for $CO_2 + C_2H_6$. The scale is made dimensionless with V_B for C_2H_6.

2. The common bulk modulus point is approximately valid in the liquid region. The lower temperature isotherms tend to intersect at the smaller volume and the higher temperature isotherms at the larger volume.

3. The existence of the intersection between the isotherms is associated with the temperature-dependence of the van der Waals covolume b. If b is temperature independent, the $1 - \underline{B}$ vs $1/\rho V_B$ plot will be equivalent to the $1 - \underline{B}$ vs $1/b\rho$ plot and so there will be no intersection of the isotherms. Huang and O'Connell noted that the van der Waals EOS does not lead to the intersection of the isotherms. This is primarily due to the temperature-independence of the covolume b in the van der Waals EOS.

4. The existence of the common bulk modulus point requires not only that covolume b be temperature-dependent but also that it have the correct choice of temperature-dependence. Apparently, the statistical–mechanical EOS allowing the existence of the common bulk modulus point indicates that the choice of b in this EOS is correct.

3. Results and discussion

The present work shows how the equation of state of compressed liquids can give a statistical–mechanical basis for application to real molecular liquids. The greatest source of liquid compression data is the work of Huang and O'Connell [13], in which is collected data on over 300 substances, but the present paper is only intended to assist users in judging the potential utility of the new equation of state for their purposes.

The similarity of the crossover behavior of all liquids is amazing. Figs. 1–4 show the behavior of LJ (12,6) mixture, Ar + Kr, Kr + Xe, and $CO_2 + C_2H_6$ in reduced coordinates of $1 - \underline{B}$ vs reduced volume, respectively. Figs. 1–4 indicate that variation of $1 - (B/\rho RT)$ with volume for both saturated and compressed liquids is similar. The present results also indicate that the strong principle of corresponding states for describing volumes of compressed liquid mixtures is valid. The most important result of the present work is that the unique modulus point of any liquid can be given a strong basis in statistical mechanics. This work shows to what extent the results for compressed liquids can be extended, namely from critical up to the freezing density [14].

In summary, theory indicates that $1-\underline{B}$ is a function of $1/\rho V_B$ for pure substance, and the fact that $1-\underline{B}$ is nearly a unique point in volume is consistent with the empirical findings of Huang and O'Connell [13]. Finally, the common compressibility

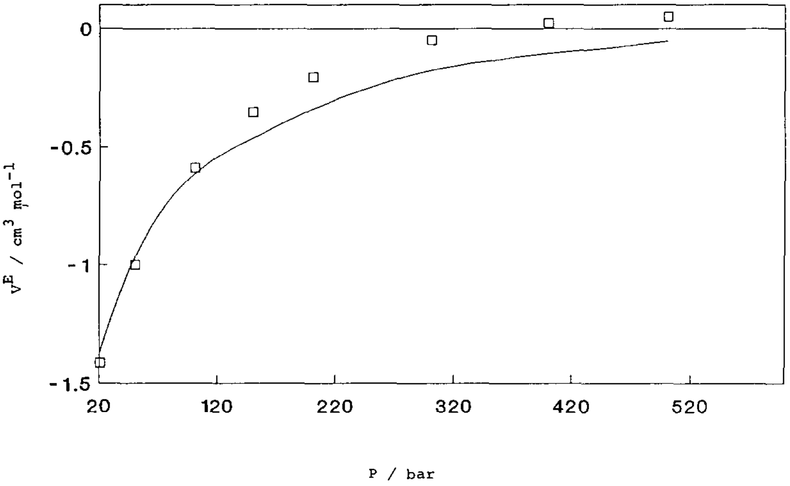

Fig. 5. Excess molar volume V_p^E for a 0.556Kr + 0.444Xe liquid mixture at 179.99 K as a function of pressure. The curve was calculated from the EOS and the symbols are the experimental values [22].

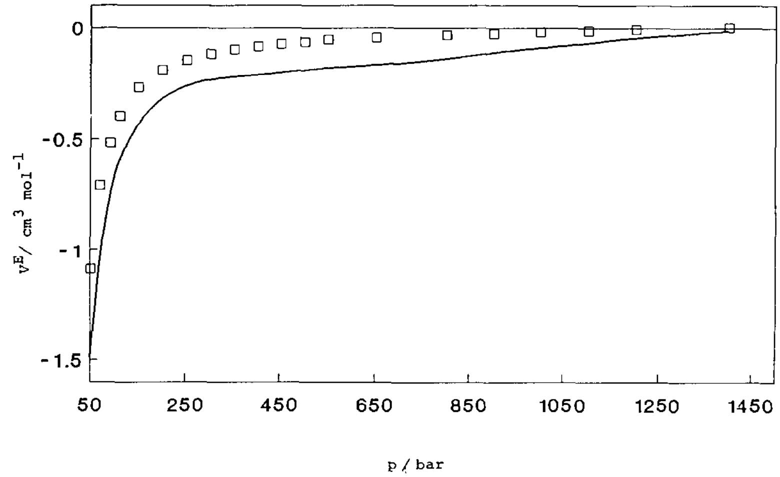

Fig. 6. Same as Fig. 5, for $0.476Ar + 0.524N_2$ at 119.33 K. The curve was calculated from the EOS and the symbols are the experimental values [23].

furnishes a constraint on the equation of state of the compressed liquid mixtures and the Song–Mason equation of state does give the unique modulus point. Furthermore, we look at the pressure-dependence of excess molar volume. In general, V^E gets closer to 0 as P increases, regardless of its sign at low P, and the equation of state reproduces this effect.

The excess molar volume, $1/\rho - \Sigma_i x_i/\rho_i$, at 179.99 K for the liquid mixture 0.556Kr + 0.444Xe [22] is shown as a function of pressure in Fig. 5. Figs. 6 and 7 show V_P^E as a function of P for 0.476Ar + 0.524N_2 at 119.33 K and 0.4983Ar + 0.5017C_2H_6 at

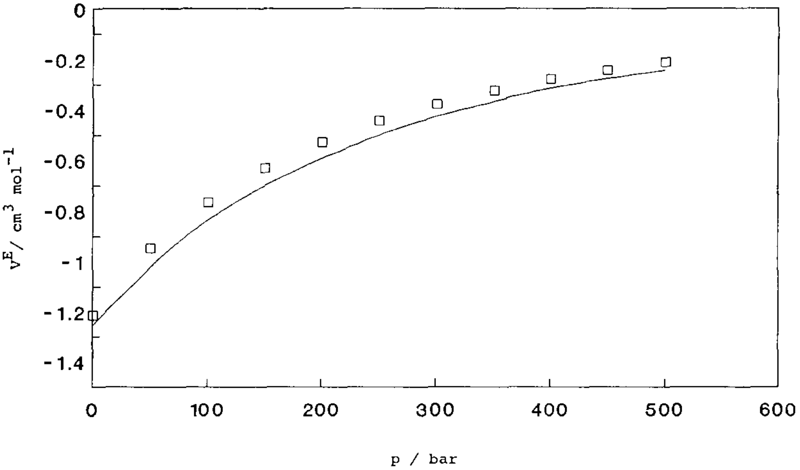

Fig. 7. Same as Fig. 5, for 0.4983Ar + 0.5017C_2H_6 at 115 K. The curve was calculated from the EOS and the symbols are the experimental values [24].

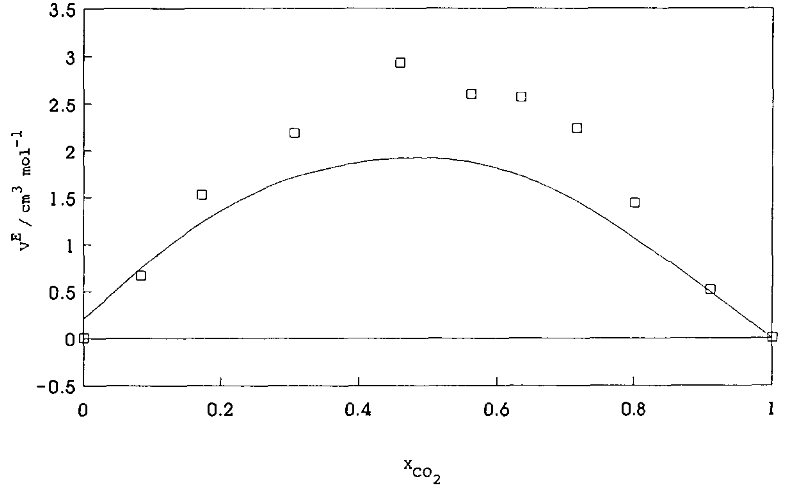

Fig. 8. The calculated excess molar volume of $CO_2 + C_2H_6$ liquid mixtures at their measured vapor pressures at 241.5 K with experimental V^E of Wallis et al. (□) [25].

115.0 K, respectively [23, 24]. Fig. 8 compares the calculated excess molar volume of $CO_2 + C_2H_6$ liquid mixtures at their measured vapor pressures at 241.5 K with the experimental V^E of Wallis et al. [25].

Acknowledgment

This research was supported in part by a Shiraz University Research Council Grant (No. 72-Sc-809-449).

References

[1] Y. Song and E.A. Mason, J. Chem. Phys., 91 (1989) 7840.
[2] G. Ihm, Y. Song and E.A. Mason, J. Chem. Phys., 94 (1991) 3839.
[3] Y. Song, B. Caswell and E.A. Mason, Int. J. Thermophys., 12 (1991) 855.
[4] A. Boushehri and E.A. Mason, Int. J. Thermophys., 14 (1993) 685.
[5] J.A. Beattie and W.H. Stockmayer, Rep. Prog. Phys., 7 (1940) 195.
[6] R.L. Scott, J. Chem. Educ., 30 (1953) 542.
[7] J.S. Rowlinson and F.L. Swinton, Liquids and Liquid Mixtures, Butterworth, London, 3rd edn., 1982.
[8] A.T.J. Hayward, Br. J. Appl. Phys., 18 (1967) 965.
[9] J.R. Macdonald, Rev. Mod. Phys., 41 (1969) 316.
[10] J.H. Dymond and R. Malhotra, Int. J. Thermophys., 9 (1988) 941.
[11] D. Ben-Amotz and D.R. Herschbach, Isr. J. Chem., 30 (1990) 59.
[12] J. Xu and D.R. Herschbach, J. Phys. Chem., 96 (1992) 2307.
[13] Y.H. Huang and J.P. O'Connell, Fluid Phase Equil., 37 (1987) 75.
[14] A. Boushehri, F.M. Tao and E.A. Mason, J. Phys. Chem., 97 (1993) 2711.
[15] G. Parsafar and E.A. Mason, J. Phys. Chem., 97 (1993) 9048.
[16] G. Ihm and E.A. Mason, Mol. Phys., 71 (1990) 109.
[17] G. Ihm, Y. Song and E.A. Mason, Mol. Phys., 75 (1992) 897.
[18] R.A. Aziz and M.J. Slaman, Mol. Phys., 57 (1986) 825.
[19] R.A. Aziz and A. van Dalen, J. Chem. Phys., 78 (1983) 2402.
[20] J. Bzowski, E.A. Mason and J. Kestin, Int. J. Thermophys., 9 (1988) 131.
[21] J. Bzowski, J. Kestin, E.A. Mason, and F.J. Uribe, J. Phys. Chem. Ref. Data, 19 (1990) 1179.
[22] J.C.G. Calado, H.J.R. Guedes, M. Nunes da Ponte, L.P. N. Rebelo and W.B. Streett, J. Phys. Chem., 90 (1986) 1892.
[23] A.A. Ricardo, S.F. Barreiros, M. Nunes da Ponte, G.M.N. Albuquerque and J.C.G. Calado, J. Chem. Thermodyn., 24 (1992) 1281.
[24] S.P. Singh and R.C. Miller, J. Chem. Thermodyn., 11 (1979) 395.
[25] K.P. Wallis, P. clancy, J.A. Zollweg and W.B. Streett, J. Chem. Thermodyn., 16 (1984) 811.