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Volumetric Properties of Chloroalkanes + Amines Mixtures: Theoretical Analysis Using the ERAS-Model

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Abstract In this study, experimental data of excess molar volumes of {dichloromethane (DCM), or trichloromethane (TCM) + *n*-butylamine (*n*-BA), or +*s*-butylamine (*s*-BA), or +*t*-butylamine (*t*-BA), or +diethylamine (DEA), or +triethylamine (TEA)} mixtures as a function of composition have been used to test the applicability of the extended real associated solution model (ERAS-Model). The values of the excess molar volume were negative for (DCM + *t*-BA, or +DEA, or +TEA and TCM + *n*-BA, or +*s*-BA, or +DEA, or +TEA) mixtures and present sigmoid curves for (DCM + *n*-BA, or +*s*-BA) mixtures over the complete mole-fraction range. The agreement between theoretical and experimental results is discussed in terms of cross-association between the components present in the mixtures.

Keywords Amines · Chloroalkanes · ERAS-Model · Volumetric properties

1 Introduction

Excess properties, such as excess molar-volume ($V_{\mathrm{m}}^{\mathrm{E}}$), excess molar enthalpy ($H_{\mathrm{m}}^{\mathrm{E}}$), and excess molar Gibbs energy ($G_{\mathrm{m}}^{\mathrm{E}}$), have been used to develop and to test solution models and theories. The excess molar-volume behavior is a result of physical, structural, and chemical effects. Consequently, the complexity associated with the origin of $V_{\mathrm{m}}^{\mathrm{E}}$ coupled with the relative ease to determine it experimentally with good precision,

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make this function a sensitive tool for testing molecular theories or models of solution and to extend our understanding about molecular interactions between components.

Following up our thermodynamic study of binary mixtures [1–5], in this study excess molar volumes of {dichloromethane (DCM) or trichloromethane (TCM) + *n*-butylamine (*n*-BA), or +*s*-butylamine (*s*-BA), or +*t*-butylamine (*t*-BA), or +diethylamine (DEA), or +triethylamine (TEA)} mixtures as a function of composition have been used to test the applicability of the extended real associated solution model (ERAS-Model) [6,7]. It combines the Kretschmer–Wiebe model of linear successive association [8] with Flory's equation of state [9]. Developed originally to describe excess functions of binary alkane–alkanol mixtures, it has been used to describe excess properties of other type of systems. However, to the best of our knowledge, the ERAS-Model has not yet been tested for the mixtures in this study. Thermodynamic properties of binary mixtures of chloroalkanes with amines have been studied by other authors [10–21].

2 ERAS-Model

$V_{\rm m}^{\rm E}$ was correlated by means of the ERAS-Model using the following equations [7]:

$$V_{\rm ERAS}^{\rm E} = V_{\rm phys}^{\rm E} + V_{\rm chem}^{\rm E}, \tag{1}$$

with

$$V_{\rm phys}^{\rm E} = \left(x_{\rm A} V_{\rm A}^{*} + x_{\rm B} V_{\rm B}^{*}\right)\left(\tilde{V}_{\rm M} - \Phi_{\rm A}\tilde{V}_{\rm A} - \Phi_{\rm B}\tilde{V}_{\rm B}\right) \tag{2}$$

and

$$\begin{aligned} V_{\rm chem}^{\rm E} &= \tilde{V}_{\rm M}\Bigg[x_{\rm A}\Delta v_{\rm A}^{*}K_{\rm A}\left(\phi_{\rm A1} - \phi_{\rm A1}^{\rm o}\right) + x_{\rm B}\Delta v_{\rm B}^{*}K_{\rm B}\left(\phi_{\rm B1} - \phi_{\rm B1}^{o}\right) \\ &\quad + \frac{x_{\rm A}K_{\rm AB}\Delta v_{\rm AB}^{*}\phi_{\rm B1}\left(1 - K_{A}\phi_{A1}\right)}{V_{\rm B}/V_{\rm A} + (1 - K_{\rm B}\phi_{\rm B1})K_{\rm AB}\phi_{\rm B1}}\Bigg]. \end{aligned} \tag{3}$$

The value of $\tilde{V}_{\rm M}$ is obtained by iterative solution of Flory's equation of state, which holds not only for pure components (i = A, B) but also for mixtures (i = M):

$$\frac{\tilde{P}_i\tilde{V}_i}{\tilde{T}_i} = \frac{\tilde{V}_i^{1/3}}{\tilde{V}_i^{1/3} - 1} - \frac{1}{\tilde{V}_i\tilde{T}_i} \tag{4}$$

The reduction parameters $T_{\rm M}^{*}$ and $P_{\rm M}^{*}$ are obtained using the following equations:

$$T_{\rm M}^{*} = \frac{P_{\rm M}^{*}}{P_{\rm A}^{*}\Phi_{\rm A}/T_{\rm A}^{*} + P_{\rm B}^{*}\Phi_{\rm B}/T_{\rm B}^{*}}, \tag{5}$$

and

$$P_{\rm M}^{*} = P_{\rm A}^{*}\Phi_{\rm A} + P_{\rm B}^{*}\Phi_{\rm B} - \Phi_{\rm A}\Theta_{\rm B}\chi_{\rm AB}. \tag{6}$$

Θ_{B} is the surface fraction of the component B in the mixtures, defined as

$$\Theta_{\mathrm{B}} = 1 - \Theta_{\mathrm{A}} = \frac{(S_{\mathrm{B}}/S_{\mathrm{A}})\Phi_{\mathrm{B}}}{(S_{\mathrm{B}}/S_{\mathrm{A}})\Phi_{\mathrm{B}} + \Phi_{\mathrm{A}}} \tag{7}$$

and the hard-core volume fractions are defined as

$$\Phi_{\mathrm{A}} = 1 - \Phi_{\mathrm{B}} = \frac{x_{\mathrm{A}} V_{\mathrm{A}}^{*}}{x_{\mathrm{A}} V_{\mathrm{A}}^{*} + x_{\mathrm{B}} V_{\mathrm{B}}^{*}}. \tag{8}$$

S_i values can be estimated using Bondi's method [22]. χ_{AB} in Eq. 6 is the energetic interaction parameter characterizing the difference of dispersive interactions between the molecules in the mixture and pure compounds. It is the only adjustable parameter of the physical contribution for the excess volume.

The characteristic parameters $V_i^*$and $P_i^*$are obtained from experimental data of the molar volume V_i, the thermal expansion coefficient α_i, and the isothermal compressibility κ_i of the pure liquids using the following equations:

$$V_i^* = V_i \left[\frac{1 + \left(\alpha_i - \alpha_i^*\right) T}{1 + 4/3 \left(\alpha_i - \alpha_i^*\right) T} \right]^3 \tag{9}$$

and

$$P_i^* = \left(\alpha_i - \alpha_i^*\right) T \tilde{V}_i^2 \left(\kappa_i - \alpha_i^* T \frac{\Delta v_i^*}{\Delta h_i^*} \right)^{-1}. \tag{10}$$

ϕ_{i1} and ϕ_{i1}^{o} ($i =$ A, B) are the volume fractions of the monomeric species in the mixture and pure components, respectively.

$$\Phi_{\mathrm{A}} = \frac{\phi_{\mathrm{A}1}}{(1 - K_{\mathrm{A}}\phi_{\mathrm{A}1})^2} \left(1 + \frac{V_{\mathrm{A}} K_{\mathrm{AB}} \phi_{\mathrm{B}1}}{V_{\mathrm{B}}\,(1 - K_{\mathrm{B}}\phi_{\mathrm{B}1})} \right) \tag{11}$$

$$\Phi_{\mathrm{B}} = \frac{\phi_{\mathrm{B}1}}{(1 - K_{\mathrm{B}}\phi_{\mathrm{B}1})^2} \left(1 + \frac{K_{\mathrm{AB}} \phi_{\mathrm{A}1}}{(1 - K_{\mathrm{A}}\phi_{\mathrm{A}1})} \right), \tag{12}$$

with ϕ_{i1} equal to ϕ_{i1}^{o} if $\Phi_i = 1$.

The cross-association parameters χ_{AB}, K_{AB}, and Δv_{AB}^* were adjusted to excess volume data by using a least-squares fit.

3 Results and Discussion

Figures 1, 2, 3, 4, 5, 6, 7, 8, and 9 show the composition dependence of $V_{\mathrm{m}}^{\mathrm{E}}$ for the systems. The $V_{\mathrm{m}}^{\mathrm{E}}$ curves for (DCM + *n*-BA, or +*s*-BA) mixtures is a sigmoid curve with a contraction at a high concentration of the amine (Figs. 1, 2). The same behavior in the literature [12,14] explains this tendency by the fact that butylamines are hydrogen-bonded-associated liquids [23] and the addition of dichloromethane

Fig. 1 Values of V_m^E as a function of the mole fraction of DCM at 25 °C for the system (DCM + *n*-BA). (◯) experimental [1], (—) ERAS-Model, (- - -) physical contribution, (– –) chemical contribution

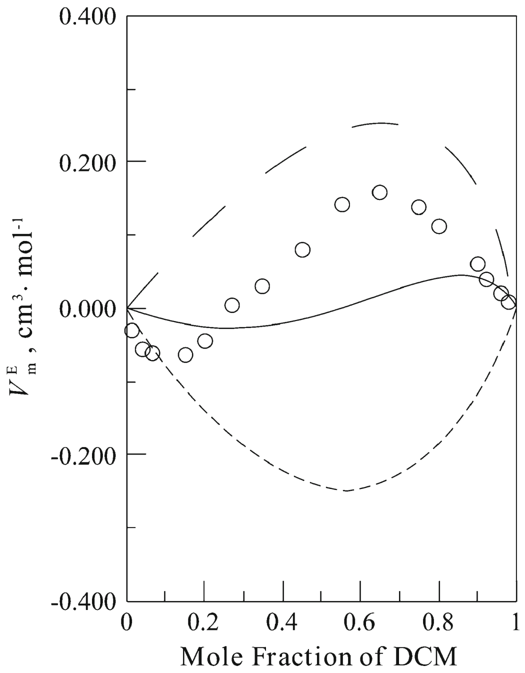


Fig. 2 Values of V_m^E as a function of the mole fraction of DCM at 25 °C for the system (DCM + *s*-BA). (◯) experimental [1], (—) ERAS-Model, (- - -) physical contribution, (– –) chemical contribution

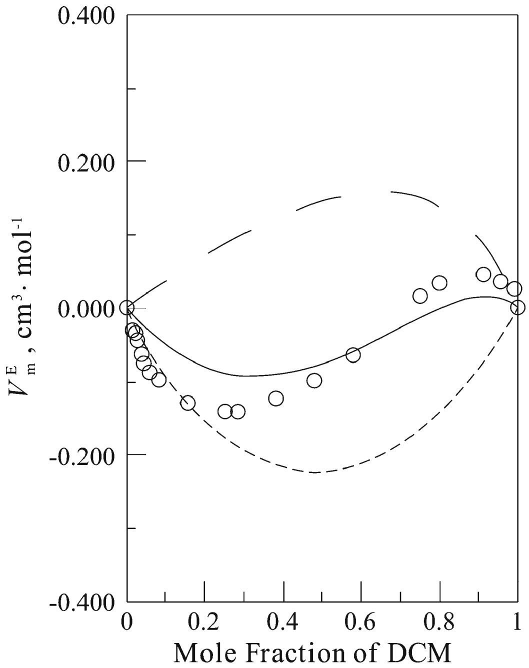


Fig. 3 Values of V_m^E as a function of the mole fraction of DCM at 25 °C for the system (DCM + *t*-BA). (◯) experimental [1], (—) ERAS-Model, (- - -) physical contribution, (– –) chemical contribution

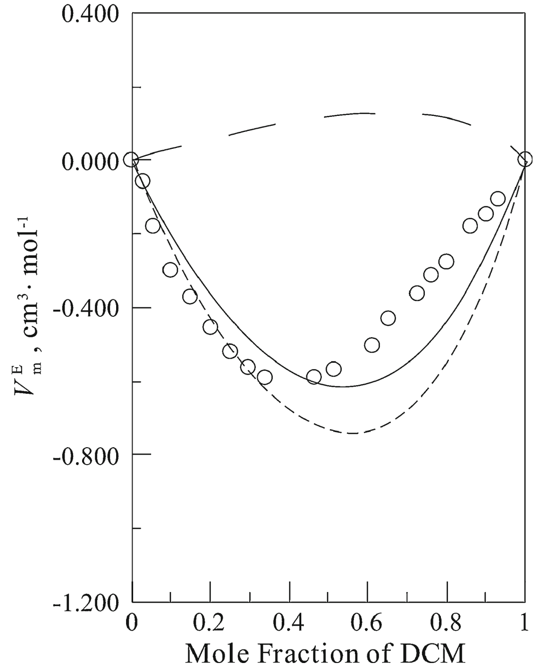


Fig. 4 Values of V_m^E as a function of the mole fraction of DCM at 25 °C for the system (DCM + DEA). (◯) experimental [1], (—) ERAS-Model, (- - -) physical contribution, (– –) chemical contribution

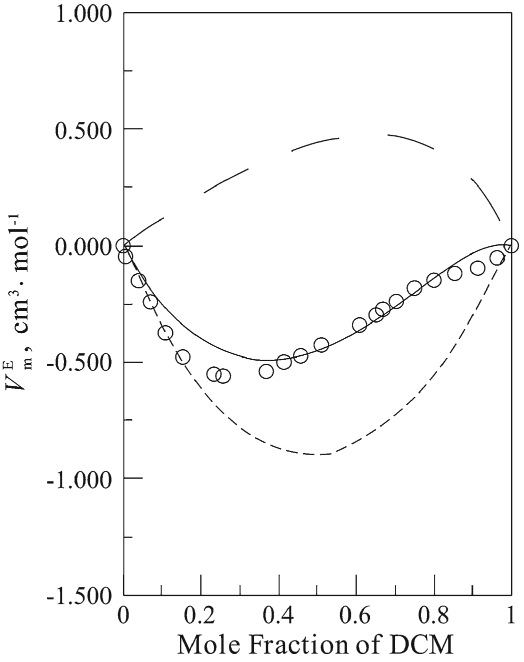


Fig. 5 Values of V_m^E as a function of the mole fraction of DCM at 25 °C for the system (DCM + TEA). (◯) experimental [1], (—) ERAS-Model, (- - -) physical contribution, (– –) chemical contribution

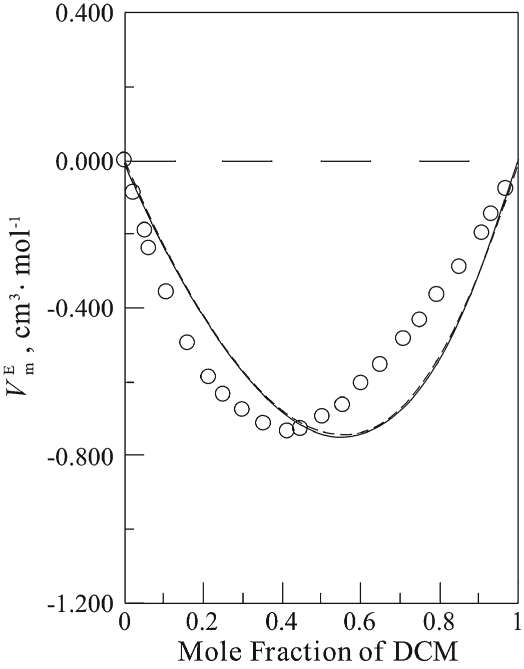


Fig. 6 Values of V_m^E as a function of the mole fraction of TCM at 25 °C for the system (TCM + *n*-BA). (◯) experimental [2], (—) ERAS-Model, (- - -) physical contribution, (– –) chemical contribution

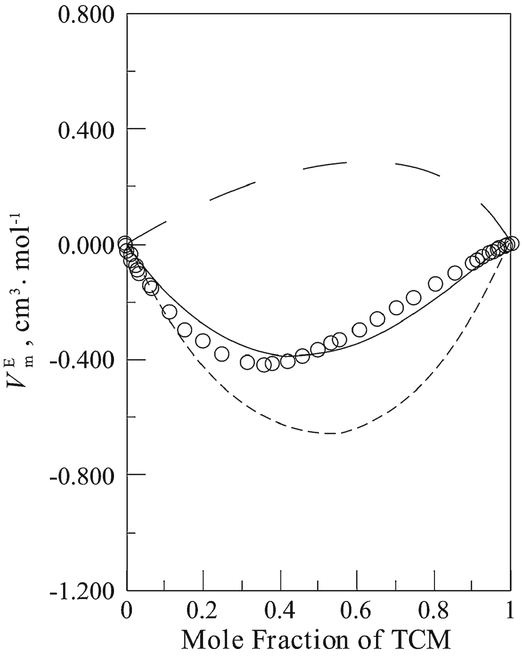


Fig. 7 Values of V_m^E as a function of the mole fraction of TCM at 25 °C for the system (TCM + *s*-BA). (◯) experimental [2], (—) ERAS-Model, (- –) physical contribution, (– –) chemical contribution

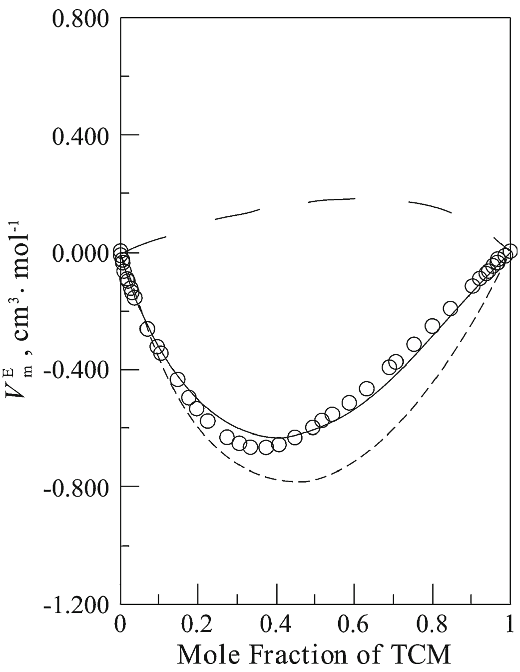
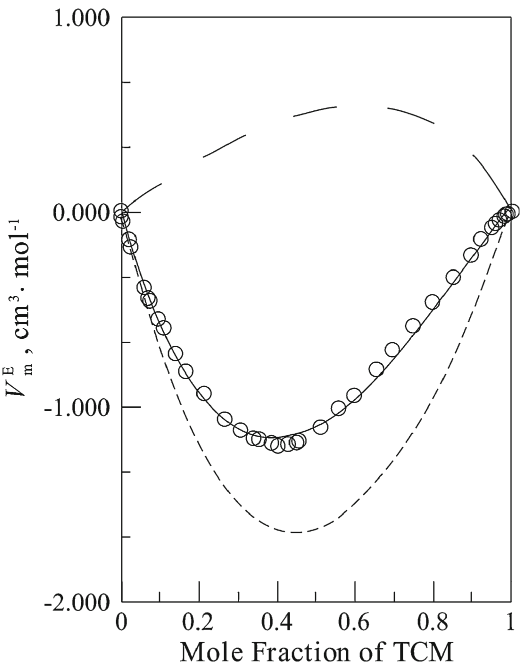


Fig. 8 Values of V_m^E as a function of the mole fraction of TCM at 25 °C for the system (TCM + DEA). (◯) experimental [2], (—) ERAS-Model, (- - -) physical contribution, (– –) chemical contribution



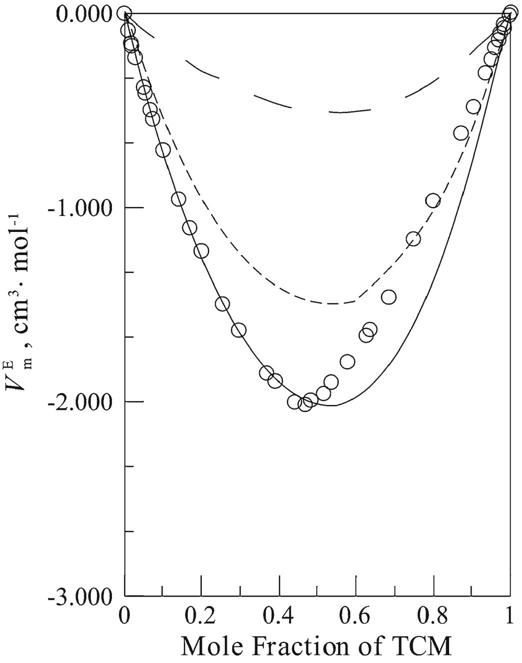


Fig. 9 Values of V_m^E as a function of the mole fraction of TCM at 25 °C for the system (TCM + TEA). (◯) experimental [2], (—) ERAS-Model, (- - -) physical contribution, (– –) chemical contribution

produces a rupture of the hydrogen bond of butylamines causing a volume expansion. At higher concentration of amines, it is possible that complex association by hydrogen bonds is formed between monomers of amines and molecules of dichloromethane, causing a volume contraction. For the remaining systems, V_m^E is negative over the entire composition range (Figs. 3, 4, 5, 6, 7, 8, 9). Spectroscopic evidence in the literature indicates the possibility of two types of interactions present in the system studied (1) hydrogen bonding between the C–H hydrogen of the chloroalkanes with the n-donor atom of amines [24–28] and (2) charge transfer complex between the π-electrons of chlorine atoms with the lone pair in amines [29–36]. In this way, we believe that the negative V_m^E values for the mixtures are a consequence of the presence of interactions between the chloroalkanes and amines, attributed to the formation of complexes by charge transfer and hydrogen bonding, simultaneously. Moreover, there is a considerable difference between the molar volume of the compounds [1,2], and this fact can also help to explain the negative V_m^E values by considering the interstitial accommodation of the chloroalkane molecules into clusters of the amines. This possibility has been considered by other authors [15,37].

Experimental results were correlated by means of the ERAS-Model. Pure component quantities used in the calculation are given in Table 1. In all the systems studied here, the chloroalkanes were assumed to be inert components without self association ($K_\mathrm{A} = 0$), but cross association between a chloroalkane and an amine was possible ($K_\mathrm{AB} \neq 0$). Since it was not possible to find in the literature experimental results of excess molar enthalpies (H_m^E) for the systems studied here, the ERAS parameter Δv_AB^*, K_AB, and χ_AB were adjusted to the experimental V_m^E data. The adjustable parameters for all the binary mixtures are listed in Table 2. For all the sys-

Table 1 Properties and parameters of pure components at 25 °C and $p = 0.1$ MPa

Component	K	P^*(J · cm^{-3})	V (cm^3 · mol^{-1})	V^*(cm^3 · mol^{-1})	$\alpha \times 10^4$ (K^{-1})	$\kappa \times 10^4$ (MPa^{-1})	S (nm^{-1})	$\triangle v^*$ (cm^3 · mol^{-1})	$\triangle h^*$ (kJ · mol^{-1})
DCM	0	707[a]	64.54	48.80[a]	13.91[a]	10.26[a]	14.34[a]	0	0
TCM	0	635[a]	80.71	62.20[a]	12.60[a]	9.98	14.34[a]	0	0
n-BA	0.96[b]	468[b]	99.19	78.51[b]	11.45[b]	13.14[b]	14.41[b]	−4.5[b]	−13.8
s-BA	0.96[c]	303.5[c]	101.76	78.52[c]	13.11[c]	15.90[c]	14.41[c]	−2.8[c]	−13.2
t-BA	0.91	485	106.50	83.77	13.11[d]	13.90[d]	14.41[d]	−2.8[d]	−13.2
DEA	0.84[c]	396.4[c]	104.60	78.30[c]	15.30[c]	14.71[c]	14.19[c]	−8.5[c]	−8.5
TEA	0	467.6[e]	139.86	107.40[e]	12.85[e]	13.92[e]	13.99[e]	0	0

K association constant, P^* reduction pressure, V molar volume, V^* reduction volume, α thermal expansion coefficient, κ isothermal compressibility, S surface volume ratio, $\triangle v^*$ molar volume of association, $\triangle h^*$ molar enthalpy of association

[a] Ref. [12]

[b] Ref. [38]

[c] Ref. [4]

[d] Values of n-butylamine from Ref. [7]

[e] Ref. [7]

Table 2 ERAS-Model parameters adjustable to experimental V_m^E data at 25 °C and $p = 0.1$ MPa

System	K_{AB}	Δv^*_{AB} ($cm^3 \cdot mol^{-1}$)	χ_{AB} ($J \cdot cm^{-3}$)
DCM + *n*-BTA	0.01	−1.1	−40.9
DCM + *s*-BTA	0.01	−1.1	−32.6
DCM + *t*-BTA	0.09	−1.9	−80.1
DCM + DEA	0.02	−1.8	−49.2
DCM + TEA	0.01	−1.1	−57.1
TCM + *n*-BTA	0.01	−1.1	−55.9
TCM +*s*-BTA	0.01	−1.2	−43.6
TCM + DEA	0.01	−1.2	−75.6
TCM + TEA	0.09	−3.8	−87.4

tems studied Δv^*_{AB} and K_{AB} have values smaller than the amines. Although these adjustable parameters present small values, they have an important contribution in chemical terms. This possibility has been considered by other authors [12]. These authors have found for (di-*n*-butylamine + dichloromethane, or +trichloromethane, or +tetrachloromethane) mixtures the following values, respectively, $\Delta v^*_{AB} = -7.2\,cm^3 \cdot mol^{-1}$, $K_{AB} = 0.02$, and $\chi_{AB} = -18.9\,J \cdot cm^{-3}$; $\Delta v^*_{AB} = -1.7\,cm^3 \cdot mol^{-1}$, $K_{AB} = 0.09$, and $\chi_{AB} = -54.5\,J \cdot cm^{-3}$; $\Delta v^*_{AB} = -3.1\,cm^3 \cdot mol^{-1}$, $K_{AB} = 0.04$, and $\chi_{AB} = -85.6\,J \cdot cm^{-3}$. The results of both studies show the model is able to take into account the cross association between the chloroalkanes and amines due to hydrogen bonding. Excluding the Δv^*_{AB} and K_{AB} values, the model fails to describe the experimental data.

Figures 1, 2, 3, 4, 5, 6, 7, 8, and 9 compare the experimental results with values calculated from ERAS-Model. The dotted lines represent the physical contribution, and the dashed lines represent the chemical contribution. In the light of the model, both contributions (physical and chemical) are important to represent the experimental results. However, for the (DCM + TEA and TCM + TEA) systems the chemical term seems to not contribute to predict the experimental data. For the (DCM + DEA and TCM + *n*-BA, or +*s*-BA, or DEA) mixtures, the ERAS-Model predicts quite well the experimental results. For the (TCM + TEA) systems the ERAS-Model predicts accurately the experimental results for a mole fraction of TCM less than 0.5. At $x_A > 0.5$, the model overestimates the experimental V_m^E curve. For the (DCM + DEA, or +TEA) systems, the model is able to predict qualitatively the experimental results, but the asymmetry of the experimental results seems to affect the V_m^E prediction curves. The model qualitatively predicts the S-shaped composition dependence of V_m^E for (DCM + *n*-BA, or +*s*-BA) mixtures. Nevertheless, for (DCM + *n*-BA) systems the model underestimates the experimental results, and the correlation fails to predict the V_m^E data. A comparison of the systems in this study shows that the (DCM + *n*-BA) presents the worst V_m^E predictions with symmetry, size, and shape of the ERAS-Model in disagreement with the experimental data.

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References

1. R.B. Tôrres, H.E. Hoga, J. Mol. Liquids **143**, 17 (2008)
2. J.G. Magalhães, R.B. Tôrres, P.L.O. Volpe, J. Chem. Thermodyn. **40**, 1402 (2008)
3. R.B. Tôrres, A.Z. Francesconi, P.L.O. Volpe, Fluid Phase Equilib. **210**, 287 (2003)
4. R.B. Tôrres, A.Z. Francesconi, Fluid Phase Equilib. **200**(2), 317 (2002)
5. R.B. Tôrres, A.Z. Francesconi, P.L.O. Volpe, Fluid Phase Equilib. **200/1**, 1 (2002)
6. A. Heintz, Ber. Bunsenges. Phys. Chem. **89**, 172 (1985)
7. H. Funke, M. Wetzel, A. Heintz, Pure Appl. Chem. **61**, 1429 (1989)
8. C.B. Kretschmer, R. Wiebe, J. Chem. Phys. **22**, 1697 (1954)
9. P.J. Flory, R.A. Orwoll, A. Vrij, J. Am. Chem. Soc. **86**, 3507 (1964)
10. S.L. Oswal, J.S. Desai, S.P. Ijardar, N.I. Malek, Thermochim. Acta **427**, 51 (2005)
11. J.M. Resa, C. González, S.O. Landaluce, J. Lanz, J. Chem. Eng. Data **45**, 867 (2000)
12. I.L. Acevedo, E.L. Arancibia, M. Katz, J. Solution Chem. **22**, 191 (1993)
13. I.L. Acevedo, E.L. Arancibia, M. Katz, Thermochim. Acta **195**, 129 (1992)
14. I.L. Acevedo, M. Katz, J. Solution Chem. **19**, 1041 (1990)
15. I.L. Acevedo, M. Katz, Thermochim. Acta **156**, 199 (1989)
16. R.P. Schutte, T.C. Liu, L.H. Hepler, Can. J. Chem. **67**, 446 (1989)
17. L.G. Hepler, Z.S. Kooner, G. Roux-Desgranges, J.P.E. Grolier, J. Solution Chem. **14**, 579 (1985)
18. M.M. Kopečni, S.K. Milonjić, N.M. Djordjević, J. Chromatogr. **139**, 1 (1977)
19. Y.P. Handa, D.V. Fenby, D.E. Jones, J. Chem. Thermodyn. **7**, 337 (1975)
20. A. Chand, Y.P. Handa, D.V. Fenby, J. Chem. Thermodyn. **7**, 401 (1975)
21. L.G. Hepler, D.V. Fenby, J. Chem. Thermodyn. **5**, 471 (1973)
22. A. Bondi, J. Phys. Chem. **68**, 441 (1946)
23. J.C. Schug, W.M. Chang, J. Phys. Chem. **75**, 938 (1971)
24. D.E. Martire, J.P. Sheridan, J.W. King, S.E. O'Donnell, J. Am. Chem. Soc. **98**, 3101 (1976)
25. C.M. Huggins, G.C. Pimentel, J.N. Shoolery, J. Chem. Phys. **23**, 1244 (1955)
26. B.N. Khare, S.S. Mitra, G. Lengyel, J. Chem. Phys. **47**, 5173 (1967)
27. H. Ratajczak, J. Chem. Phys. **76**, 3000 (1972)
28. M. Tamres, S. Searles, E.M. Leighly, D.W. Mohrman, J. Am. Chem. Soc. **76**, 3983 (1954)
29. P. Data, G.M. Barrow, J. Am. Chem. Soc. **87**, 3053 (1965)
30. W.J. Lautenberger, E.N. Jones, J.G. Miller, J. Am. Chem. Soc. **90**, 1110 (1968)
31. C.J. Biaselle, J.G. Miller, J. Am. Chem. Soc. **96**, 3813 (1974)
32. D.P. Stevenson, G.M. Coppinger, J. Am. Chem. Soc. **84**, 149 (1962)
33. R. Erra-Balsells, A.R. Frasca, Aust. J. Chem. **41**, 103 (1988)
34. J.P. Sheridan, D.E. Martire, F.P. Banda, J. Am. Chem. Soc. **95**, 4788 (1973)
35. D.E. Martire, J.P. Sheridan, J.W. King, S.E. O'Donnell, J. Am. Chem. Soc. **98**, 3101 (1976)
36. J.G. Dawber, J. Chem. Soc. Faraday Trans. I **75**, 370 (1979)
37. C.M. Kinart, W.J. Kinart, D. Checińska-Majak, A. Ćwiklińska, J. Mol. Liquids **109**, 19 (2004)
38. S.L. Oswal, Thermochim. Acta **425**, 59 (2005)