

Application of the Graph Theory to Ternary Excess Molar Volumes of (an Ionic Liquid + Methanol + Water)

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Ternary excess molar volumes, V_{123}^E have been evaluated from density measurements over the entire composition range for {1-ethyl-3-methyl-imidazoliumdiethylenglycolmonomethyl ether sulfate [EMIM][CH₃(OCH₂CH₂)₂OSO₃] (1) + methanol (2) + water (3)} at $T = 298.15$ K, 303.15 K and 313.15 K. The V_{123}^E values were negative at $T = 298.15$ K and 303.15 K and became positive at $T = 313.15$ K. All the experimental data were evaluated for thermodynamic consistency by correlation with the Redlich–Kister equation. The results have also been analyzed in terms of Graph Theory. Atoms in the structural formula of a molecule are represented by letters and the bonds joining them by lines, the topology then provides the total information contained in that molecule [1-2]. The connectivity parameter of third degree, ${}^3\xi$ [3] of the molecule is defined by:

$${}^3\xi = \sum_{m < n < o < p} (\delta_m^v \delta_n^v \delta_o^v \delta_p^v)^{-0.5} \quad (1)$$

Where $\delta_i^v = Z_i - h$; where Z_i is the maximum valency of the atom and h is the number of hydrogen atoms attached to it. Kier [4] has suggested that information regarding the effect of branching in molecules can be obtained by evaluation of ${}^3\xi$. Since the addition of component 1 to (2+3) mixtures leads to a change in topology of the (1+2+3) ternary mixture the V_{123}^E results can be interpreted in terms of this change in topology. The overall change in the ternary excess molar volume can then be expressed by equation (2):

$$\begin{aligned} V_{123}^E = & [x_1 x_2 ({}^3\xi_1 / {}^3\xi_2) / x_1 + x_2 ({}^3\xi_1 / {}^3\xi_2)] [(1 + x_2) \chi_{12}^* + x_1 \chi^*] \\ & + [x_2 x_3 ({}^3\xi_2 / {}^3\xi_3) / x_2 + x_3 ({}^3\xi_2 / {}^3\xi_3)] [(1 + x_3) \chi_{23}^*] \\ & + [x_1 x_3 ({}^3\xi_3 / {}^3\xi_1) / x_3 + x_1 ({}^3\xi_3 / {}^3\xi_1)] [(1 + x_1) \chi_{13}^* + x_3 \chi^*] \end{aligned} \quad (2)$$

Equation (2) contains four unknown parameters (χ_{13}^* , χ_{23}^* , χ_{12}^* , and χ^*) and these were calculated by using experimental V_{123}^E data of the (1+2+3) ternary mixtures at four arbitrary compositions. These parameters were subsequently utilized to predict V_{123}^E values as functions of x_1 and x_2 . The predicted V_{123}^E values by Graph Theory, in general, compare well with their corresponding experimental V_{123}^E values. In the cases where agreement between experimental and calculated values is not good, the predicted values are of the same sign. The failure to correctly predict the magnitude of V_{123}^E values may be due to formation of ternary contacts which have not been considered.

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