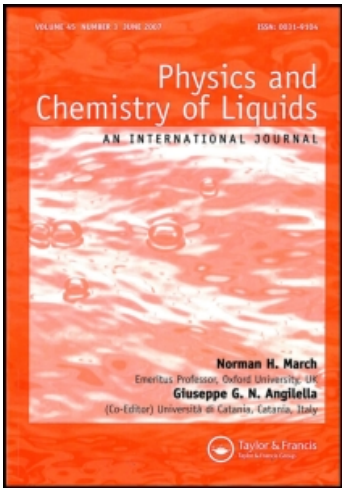

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Analysis of Excess Molar Volumes of the Ternary Systems Containing a Propyl Alkanoate and Two Alkanes with Some Predictive Methods

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ANALYSIS OF EXCESS MOLAR VOLUMES OF THE TERNARY SYSTEMS CONTAINING A PROPYL ALKANOATE AND TWO ALKANES WITH SOME PREDICTIVE METHODS

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Excess molar volumes at 298.15 *K* of the ternary mixtures (propyl ethanoate + *n*-heptane + *n*-decane), (propyl propanoate + *n*-heptane + *n*-decane) and (propyl butanoate + *n*-heptane + *n*-decane) were determined using a DMA 60/602 Anton Paar densimeter. All the experimental values were compared with the results obtained with empirical expressions for estimating ternary properties from binary data and with the Nitta-Chao group-contribution model. For these ternary mixtures the same behaviour that had been observed in ester + *n*-alkane binary systems was found: excess volumes decrease when the ester length increases.

KEY WORDS: Excess molar volumes, ternary mixtures, density, ester, alkane, Nitta-Chao model.

INTRODUCTION

In previous papers we have presented theoretical and experimental results for excess molar enthalpies and excess molar volumes of ester + *n*-alkane binary mixtures (see Lorenzana *et al.*[1–3] and Ortega *et al.*[4] and references therein). Subsequently, we have started an investigation program about the excess molar volumes of ternary mixtures containing a ester and two alkanes[5]. In this work, excess molar volumes of the ternary mixtures of propyl ethanoate (PRET) or propyl propanoate (PRPR) or

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propyl butanoate (PRBU) with *n*-heptane ($n-C_7$) and *n*-decane ($n-C_{10}$) at 298.15 K are reported.

The obtained excess molar volumes were used to test the group-contribution model of Nitta-Chao[6] and the empirical methods of Kohler[7], Jacob-Fitzner[8], Colinet[9], Tsao-Smith[10], Toop[11] and Scatchard *et al.*[12]. These methods predict excess properties of the ternary mixtures from those of the involved binary mixtures. The Cibulka[13] equation has been used to correlate the experimental values of ternary mixtures.

EXPERIMENTAL SECTION

Propyl propanoate and propyl butanoate (Fluka, 99%), propyl ethanoate (Aldrich, 99%) and *n*-alkanes (Sigma, 99%) were stored over Fluka Union Carbide Type 4A molecular sieves and degassed before use. The densities agreed well with published values[1-3,14]. The chemicals were the same as those of previous papers where we had measured the excess volumes of the binary mixtures[1-3,5].

Excess volumes were calculated from density measurements performed using an Anton Paar 60/602 densimeter thermostatted to within 0.01 *K* in Haake F3 circulating water bath. Immediately prior to each series of measurements, thrice distilled water and *n*-heptane were used to calibrate the densimeter. Mixtures were prepared by weighing with an estimated precision of $\pm 10^{-4}$ mole fractions; the precision of excess molar volumes was estimated as better that $\pm 0.003\,\mathrm{cm^3 \cdot mol^{-1}}$. The experimental technique has been described previously[15].

EXPERIMENTAL RESULTS

Excess molar volumes of the binary mixtures were taken from the references[1-3,5]. A variable-degree Redlich-Kister polynomial of the form

$$\frac{v^E(x_i, x_j)}{(\mathrm{cm^3 \cdot mol^{-1}})} = x_i x_j \sum_{p=0}^{q} A_p (x_i - x_j)^p \tag{1}$$

where x_i and x_j are the mole fractions of the components i and j respectively, was fitted to each binary system. The coefficients A_p calculated by unweighted least squares method are given in Table 1.

The experimental excess molar volumes, v^E_{123}, of the ternary mixtures are shown in Tables 2, 3 and 4. No excess volumes for these systems were found in the literature.

The Cibulka[13] equation has been used to correlate the experimental values of the excess molar volumes of the ternary mixtures:

$$\frac{v^E_{123}}{(\mathrm{cm^3 \cdot mol^{-1}})} = v^E_{\mathrm{bin}} + x_1 x_2 x_3 (A_1 + A_2 x_1 + A_3 x_2) \tag{2}$$

where v^E_{bin}, known as the binary contribution to the excess ternary volumes is given by

$$v^E_{\mathrm{bin}} = v^E_{12}(x_1, x_2) + v^E_{13}(x_1, x_3) + v^E_{23}(x_2, x_3) \tag{3}$$

Table 1 Coefficients A_p for Eq. (1) determined by the least squares method.

System	A_0	A_1	A_2
propyl ethanoate + *n*-heptane[3]	3.191	−0.501	0.182
propyl ethanoate + *n*-decane[3]	4.112	2.094	0.387
propyl propanoate + *n*-heptane[1]	2.162	−0.564	0.242
propyl propanoate + *n*-decane[1]	3.258	−0.084	0.210
propyl butanoate + *n*-heptane[2]	1.540	−0.425	0.221
propyl butanoate + *n*-decane[2]	2.712	−0.038	0.156
n-heptane + *n*-decane[5]	−0.407	−0.046	−0.091

Table 2 Excess molar volumes of x_1 propyl ethanoate + x_2 *n*-heptane + x_3 *n*-decane at 298.15 K.

x_1	x_2	v^E $cm^3 \cdot mol^{-1}$	x_1	x_2	v^E $cm^3 \cdot mol^{-1}$
0.0620	0.6150	0.1419	0.3137	0.3712	0.7556
0.0630	0.7880	0.1669	0.3590	0.3291	0.8113
0.0647	0.4103	0.1558	0.3742	0.1370	0.8923
0.0677	0.1877	0.2100	0.4042	0.1561	0.9062
0.1186	0.7332	0.3523	0.4545	0.2393	0.8924
0.1220	0.5573	0.3364	0.4712	0.0461	0.9923
0.1252	0.1509	0.3960	0.4824	0.3744	0.8369
0.1305	0.3636	0.3788	0.4845	0.3911	0.8249
0.1478	0.3249	0.4279	0.4891	0.2092	0.9087
0.1667	0.5152	0.4749	0.5236	0.3300	0.8456
0.1824	0.0900	0.5810	0.5397	0.1617	0.9247
0.2082	0.6368	0.5585	0.5683	0.2933	0.8245
0.2119	0.4687	0.5796	0.5830	0.1221	0.9291
0.2242	0.2703	0.6228	0.6080	0.2510	0.8250
0.2406	0.0475	0.7194	0.6253	0.0828	0.9109
0.2617	0.5884	0.6588	0.6619	0.0453	0.8945
0.2717	0.4147	0.6898	0.6748	0.1816	0.7784
0.2760	0.2252	0.7338	0.7538	0.1112	0.6965
0.3006	0.5565	0.7141	0.7891	0.0768	0.6532

where $v_{ij}^E(x_i, x_j)$ are given by Eq. (1). In this equation the binary mixtures have no physical sense, i.e. $x_i + x_j = 1$ does not hold here.

The A_i parameters calculated by the unweighted least-squares method are given in Table 5 and standard deviations in Table 6 Curves of constant v_{123}^E have been plotted in Figures 1, 2 and 3.

DISCUSSION

Predictive methods from binary mixtures data

Some of the predictive methods we are going to utilize were not originally proposed to reproduce excess molar volumes. Although they were designed to predict excess

Table 3 Excess molar volumes of x_1 propyl propanoate + x_2 *n*-heptane + x_3 *n*-decane at 298.15 K.

x_1	x_2	v^E $cm^3 \cdot mol^{-1}$	x_1	x_2	v^E $cm^3 \cdot mol^{-1}$
0.0479	0.8288	0.0861	0.3183	0.5951	0.5403
0.0507	0.4597	0.0639	0.3419	0.2238	0.6537
0.0518	0.6548	0.0704	0.3507	0.5882	0.5525
0.0804	0.6500	0.1528	0.3702	0.4140	0.6093
0.0895	0.8152	0.2026	0.3816	0.5839	0.5609
0.0982	0.4488	0.2047	0.3938	0.1963	0.6958
0.1092	0.2473	0.2613	0.4127	0.4058	0.6137
0.1337	0.8065	0.3019	0.4255	0.2186	0.7004
0.1467	0.4443	0.3193	0.4470	0.4024	0.6181
0.1507	0.6194	0.3153	0.4718	0.2106	0.7035
0.1867	0.7741	0.3878	0.4845	0.3909	0.6116
0.1893	0.6090	0.3820	0.5215	0.3869	0.5922
0.2071	0.4395	0.4243	0.5483	0.2050	0.6785
0.2222	0.2151	0.5086	0.5521	0.3883	0.5621
0.2412	0.6041	0.4614	0.5898	0.3804	0.5335
0.2467	0.2256	0.5418	0.6236	0.1878	0.6299
0.2543	0.6127	0.4689	0.6540	0.1993	0.5850
0.2835	0.4282	0.5322	0.6863	0.1943	0.5445
0.3043	0.2164	0.6257	0.7679	0.1800	0.4125

Table 4 Excess molar volumes of x_1 propyl butanoate + x_2 *n*-heptane + x_3 *n*-decane at 298.15 K.

x_1	x_2	v^E $cm^3 \cdot mol^{-1}$	x_1	x_2	v^E $cm^3 \cdot mol^{-1}$
0.0255	0.1098	0.0402	0.2153	0.4549	0.3024
0.0450	0.1936	0.0673	0.2251	0.1376	0.4325
0.0636	0.0660	0.1478	0.2281	0.0210	0.4827
0.0683	0.2936	0.0964	0.2294	0.2379	0.3979
0.0804	0.0491	0.1980	0.2434	0.5143	0.3235
0.0809	0.1710	0.1480	0.2696	0.5695	0.3313
0.0878	0.3775	0.1130	0.2813	0.2917	0.4333
0.1028	0.4423	0.1358	0.2907	0.1777	0.4975
0.1116	0.0334	0.2734	0.3273	0.0301	0.5963
0.1164	0.2458	0.2028	0.3524	0.2154	0.5254
0.1248	0.0115	0.3054	0.3607	0.1080	0.5801
0.1250	0.5375	0.1679	0.4083	0.2495	0.5295
0.1303	0.1351	0.2715	0.4214	0.0388	0.6503
0.1401	0.6026	0.1887	0.4603	0.2813	0.5074
0.1484	0.0907	0.3199	0.5212	0.0480	0.6475
0.1485	03138	0.2452	0.5959	0.1784	0.5349
0.1568	0.6746	0.2113	0.6069	0.0559	0.6130
0.1807	0.1874	0.3452	0.6901	0.0635	0.5269
0.1860	0.3930	0.2864	0.8329	0.0767	0.2953

molar enthalpies or excess Gibbs energies, they should be applicable to any other excess property.

Before comparing the predictions of the different equations with the experimental values, let us display some of them. We shall represent by $x_i (i = 1, 2, 3)$ the mole fractions of the ternary mixtures.

Table 5 Coefficients A_i for Eq. 2.

System	A_0	A_1	A_2
PRET + $n-C_7$ + $n-C_{10}$	1.2685	−2.0718	−0.3051
PRPR + $n-C_7$ + $n-C_{10}$	1.3268	0.0537	0.3972
PRBU + $n-C_7$ + $n-C_{10}$	1.8507	−0.3924	−2.9251

Table 6 Standard deviations for the correlation and the prediction models for the systems studied.

	PRET + $n-C_7$ + $n-C_{10}$	*PRPR* + $n-C_7$ + $n-C_{10}$	*PRBU* + $n-C_7$ + $n-C_{10}$
Redlich-Kister	0.0139	0.0330	0.0192
Khöler	0.0113	0.0314	0.0188
Colinet	0.0092	0.0304	0.0173
Tsao(a)	0.0171	0.0330	0.0205
Tsao(b)	0.1413	0.0889	0.0709
Tsao(c)	0.1186	0.0464	0.0475
Toop(a)	0.0069	0.0172	0.0118
Toop(b)	0.0218	0.0423	0.0245
Toop(c)	0.0105	0.0336	0.0206
Scatchard(a)	0.0073	0.0166	0.0129
Scatchard(b)	0.0230	0.0439	0.0250
Scatchard(c)	0.0130	0.0329	0.0201
Cibulka	0.0056	0.0046	0.0044
Nitta-Chao	0.0460	0.0263	0.0123

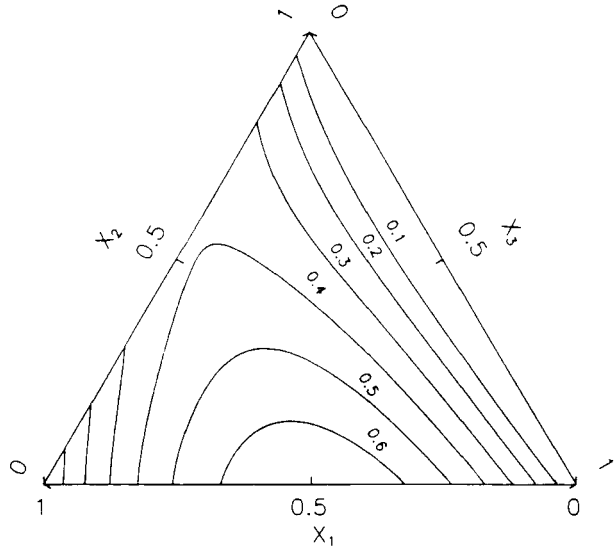

Figure 1 Curves of constant $v^E_{m,123}/(\text{cm}^3\cdot\text{mol}^{-1})$ for (ethyl propanoate + *n*-heptane + *n*-decane) at 298.15 K.

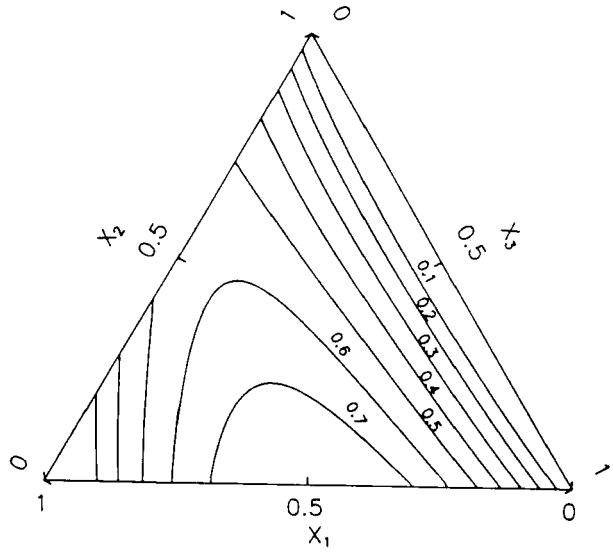

Figure 2 Curves of constant $v^E_{m,123}/(\mathrm{cm}^3\cdot\mathrm{mol}^{-1})$ for (propyl propanoate + *n*-heptane + *n*-decane) at 298.15 K.

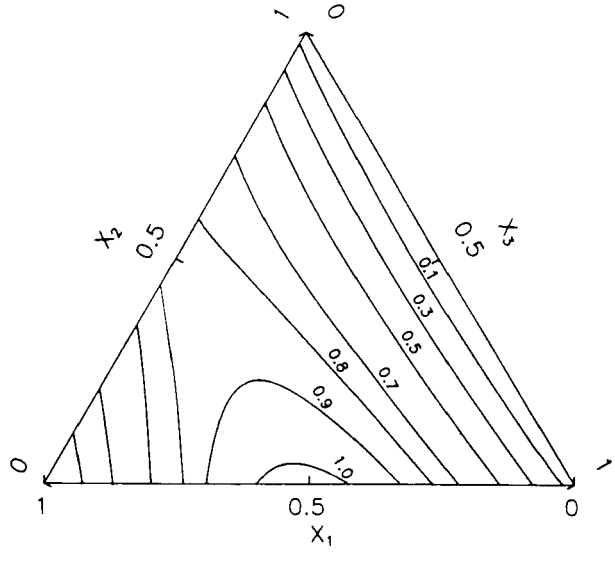

Figure 3 Curves of constant $v^E_{m,123}/(\mathrm{cm}^3\cdot\mathrm{mol}^{-1})$ for (butyl propanoate + *n*-heptane + *n*-decane) at 298.15 K.

According to the Kohler[7] expression, the excess molar volume for a ternary mixture is given by

$$v^E_{123} = (x_1 + x_2)^2 v^E(x'_1, x'_2) + (x_1 + x_3)^2 v^E(x'_1, x'_3) + (x_2 + x_3)^2 v^E(x'_2, x'_3) \tag{4}$$

in which $v^E(x'_i, x'_j)$ is the excess molar volume for the binary mixtures at composition (x'_1, x'_2), such that $x'_i = 1 - x'_j = x_i/(x_i + x_j)$. Jacob and Fitzner[8] have proposed the following expression:

$$v^E_{123} = \left[\frac{x_1 \cdot x_2}{\left(x_1 + \frac{x_3}{2}\right)\cdot\left(x_2 + \frac{x_3}{2}\right)}\right] v^E(x'_1, x'_2) + \left[\frac{x_1 \cdot x_3}{\left(x_1 + \frac{x_3}{2}\right)\cdot\left(x_3 + \frac{x_2}{2}\right)}\right] v^E(x'_1, x'_3)$$

$$+ \left[\frac{x_2 \cdot x_3}{\left(x_2 + \frac{x_1}{2}\right)\cdot\left(x_3 + \frac{x_1}{2}\right)}\right] v^E(x'_2, x'_3) \tag{5}$$

where the mole fractions $x'_i - x'_j = x_i - x_j$. When Redlich-Kister expressions are used for the binary mixtures Eq. (5) leads to Eq. (3). So, v^E_{123} is equal to the so-called binary contribution to excess ternary volumes, v^E_{bin}.

Colinet[9] suggested an equation to predict v^E_{123} of ternary mixtures in which six different binary compositions appear:

$$v^E_{123} = \frac{1}{2}\left(\frac{x_2}{(1-x_1)} v^E_{12}(x_1, 1-x_1) + \frac{x_1}{(1-x_2)} v^E_{12}(1-x_2, x_2)\right.$$

$$+ \frac{x_3}{(1-x_1)} v^E_{13}(x_1, 1-x_1) + \frac{x_1}{(1-x_3)} v^E_{13}(1-x_3, x_3)$$

$$\left. + \frac{x_3}{(1-x_2)} v^E_{23}(x_2, 1-x_2) + \frac{x_2}{(1-x_3)} v^E_{23}(1-x_3, x_3)\right) \tag{6}$$

Eq. (2–5) are symmetric in the sense that all the three binary mixtures are treated identically. Their numerical predictions do not depend on the arbitrary designation of component numbering. Unlike Tsao and Smith[10] who proposed an asymmetric equation:

$$v^E_{123} = \frac{x_2}{(1-x_1)} v^E(x'_1, x'_2) + \frac{x_3}{(1-x_1)} v^E(x'_1, x'_3) + (1-x_1) v^E(x'_2, x'_3) \tag{7}$$

in which $x'_i = (1 - x'_j) = x_1$ for the 1,3 and 1,3 binary systems, and $x'_2 = x_2/(x_2 + x_3)$ for the 2,3 binary systems.

Toop[11] proposed an assymetric equation which is very similar to that of Tsao and Smith.

$$v^E_{123} = \frac{x_2}{(1-x_1)} v^E(x'_1, x'_2) + \frac{x_3}{(1-x_1)} v^E(x'_1, x'_3) + (1-x_1)^2 v^E(x'_2, x'_3) \tag{8}$$

The only difference between the above equations is the exponent 2 of the third term.

Scatchard *et al.*[12] modified Eq. (3) for the mixtures of a polar substance with two apolar liquids, obtaining another asymmetric equation whose first two terms are equal to those of Eq. (6) and (7) and whose third term coincides with the last one of Eq. (4)

$$v^E_{123} = \frac{x_2}{(1-x_1)} v^E(x'_1, x'_2) + \frac{x_3}{(1-x_1)} v^E(x'_1, x'_3) + v^E_{23}(x'_2, x'_3) \tag{9}$$

The mean deviations between experimental and predicted values are given in Table 6. We can see that the deviations from the predictions range between 1.5 and 30 times larger than the Standard deviation of the correlation.

For asymmetric equations we must specify which is component 1. Table 6, *a* indicates that component 1 is propyl alkanoate, *b n*-heptane and *c n*-decane. The most accurate predictions are due to the Toop[11] and Scatchard *et al.*[12] equations when alkyl propanoate is chosen as component 1. Tsao and Smith's equation lead to higher deviations. This agrees with the conclusions of Pando *et al.*[16], about the predictions of excess enthalpies for ternary mixtures. Among the symmetric equations the best results are due to Colinet's equation[9].

Nitta-Chao group contribution model

This model does not use the properties of the involved binary mixtures to predict the excess properties of ternary mixtures. It is based on the concept of group contribution. Nitta *et al.*[6] adopt the cell theory for molecular chains of Flory *et al.*[17] adapted to a group model by Lee *et al.*[18] in order to obtain the partition function of a given liquid. Some of the advantages of this model with respect to the group-contribution methods are its greater theoretical rigour, its capacity to predict a larger number of thermodynamic properties. It is the only group contribution model capable of predicting excess molar volumes.

Navarro[19,20] determined the parameters corresponding to the COO ester group, and those of interaction with methyl and methylene groups from vaporization enthalpies and densities of esters and from v^E, h^E and g^E experimental data of ester + alkane binary systems.

Figure 4 shows the comparison between the predicted values of the Nitta-Chao model and the fitted values for three pseudobinary systems with propyl alkanoates. This model predicts well the magnitude and the symmetry of the curves. The mean percentage deviations is about 8% for the studied ternary systems. Furthermore the decreasing of v^E when the length of the propyl alkanoate increases is also well predicted. This behaviour is similar to the one found for the excess volumes of

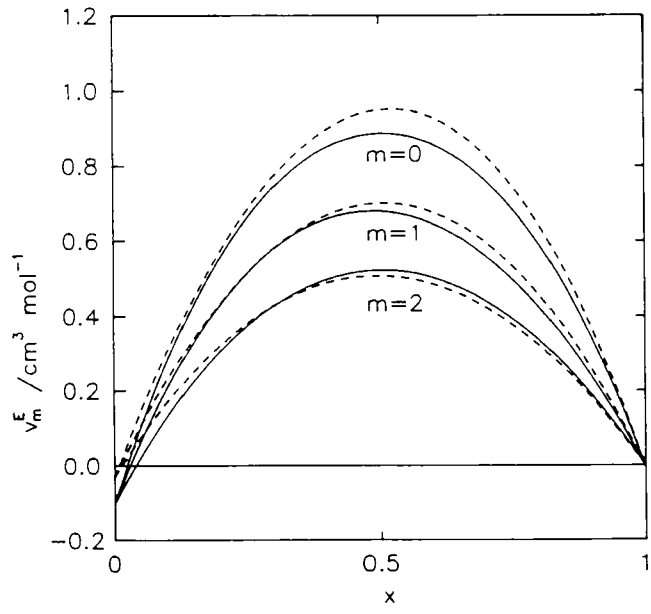

Figure 4 Curves of excess molar volumes at 298.15 K of the pseudobinary system ($x CH_3(CH_2)_m CO_2 C_3H_7 + (1-x)(0.5 C_7H_{16} + 0.5 C_{10}H_{22})$). ------- Cibulka equation.——— Nitta-Chao model.

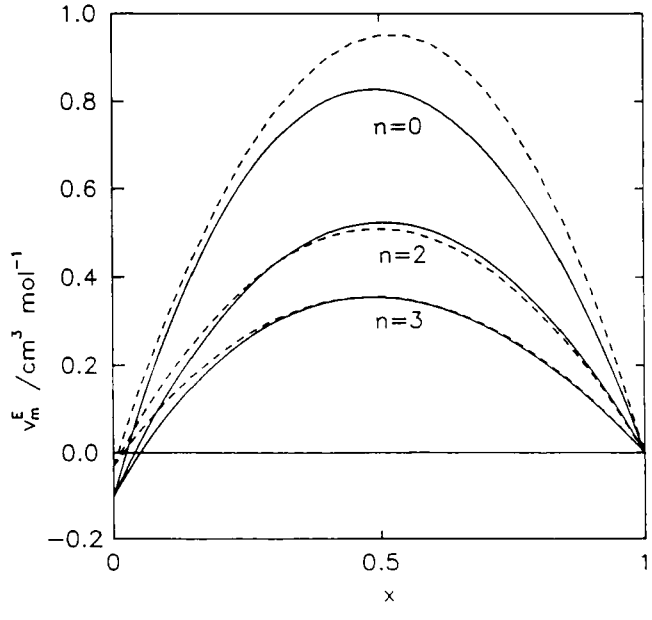

Figure 5 Curves of excess molar volumes at 298.15 K of the pseudobinary systems ($x C_3H_7CO_2 (CH_2)_n CH_3 + (1-x)(0.5 C_7H_{16} + 0.5 C_{10}H_{22})$), $n = 0$[5], $n = 2$(this work), $n = 3$[5]. ------- Cibulka equation. ——— Nitta-Chao model.

ester + alkane binary systems[1-3]. Thus, if we represent a given ester by R_1 $COOR_2$ it results that v^E decreases when the length of the radicals R_1 or R_2 increase.

In order to analyze the variation of v^E with the length of the radical R_2 of the alkyl alkanoate, three pseudobinary systems containing different alkyl butanoates taken from this work and from the literature[5], were plotted in Figure 5. The v^E also increases when the length of the alkyl butanoate decreases and this behaviour is well predicted by the Nitta-Chao model.

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