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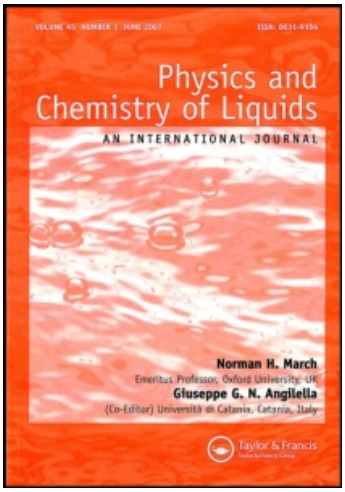

Physics and Chemistry of Liquids
Publication details, including instructions for authors and subscription information:
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Excess Molar Volumes of Binary Mixtures of Propyl Ethanoate with some *n*-Alkanes at 298.15 K and 308.15 K

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To cite this Article Lorenzana, M. T. , Jimenez, E. , Legido, J. L. , Fernandez, J. and Andrade, M. I. Paz(1991) 'Excess Molar Volumes of Binary Mixtures of Propyl Ethanoate with some *n*-Alkanes at 298.15 K and 308.15 K', Physics and Chemistry of Liquids, 24: 1, 13 — 20
To link to this Article: DOI: 10.1080/00319109108030644
URL: http://dx.doi.org/10.1080/00319109108030644

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Phys. Chem. Liq., 1991, Vol. 24, pp. 13–20
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EXCESS MOLAR VOLUMES OF BINARY MIXTURES OF PROPYL ETHANOATE WITH SOME *n*-ALKANES AT 298.15 K AND 308.15 K

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(Received 14 January 1991)

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Excess molar volumes v^E have been measured for the binary liquid mixtures of propyl ethanoate with five *n*-alkanes (*n*-hexane, *n*-heptane, *n*-octane, *n*-nonane and *n*-decane) at 298.15 and 308.15 K, using an Anton Paar densimeter. All the mixtures studied present positive v^E values that increase with the length of the chain of the alkane and with the temperature. The experimental results are compared with the predictions of the Nitta–Chao model.

KEY WORDS: Excess molar volumes, density, ester + alkane, Nitta–Chao model.

INTRODUCTION

In previous papers experimental results for excess molar enthalpies and excess molar volumes of binary mixtures containing propyl propanoate or propyl butanoate with *n*-alkanes were presented[1,2]. We now report the excess molar volumes of propyl ethanoate with *n*-alkane (from hexane to decane) at 298.15 K and 308.15 K. The purpose of this investigation is to know the influence of the alkyl radical of the propyl esters on the excess properties of their mixtures with *n*-alkanes.

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Group-contribution models are very useful to predict excess molar properties of binary mixtures. Among the usual group-contribution models the only capable to predict excess molar volumes is the Nitta–Chao model[3] which is based in Carnahan–Starling[4] hard-sphere equation of state. This model also predicts vaporization energies of pure compounds and excess enthalpies and activity coefficients of mixtures. The characteristic parameters corresponding to the ester + *n*-alkane mixtures of the Nitta–Chao model were calculated by us previously[5,6]. The measured excess molar volumes were used to test this model.

EXPERIMENTAL SECTION

Propyl ethanoate was supplied by Aldrich and *n*-alkanes by Sigma, all with a guaranteed purity >99 moles%. All the chemicals were degassed, dried with molecular sieves (Union Carbide type 4A from Fluka) and used without further purification. The densities of the pure liquids agree well with the literature values as Table 1 shows[7–15].

Excess molar volumes were determined from densities of the pure liquids and mixtures measured with an Anton Paar DMA 60/602 densimeter and thermostatted to within ±0.01 K in a Haake F3 circulating-water bath. The experimental technique has been described previously[1]. Mixtures were prepared by weighing with an estimated precision of 1.10^{-4} in mole fraction; the precision of v^E was estimated better than ±0.003 $cm^3\ mol^{-1}$.

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Table 1 Densities of the pure liquids at 298.15 and 308.15 K

Substance	$\rho \times 10^{-3}/kg.m^{-3}$			
	Experimental		*Literature*	
	298.15	308.15	298.15	308.15
Propyl ethanoate	0.88258	0.87135	0.8826[a] 0.88303[c]	0.87116[b]
n-hexane	0.65503	0.64598	0.65489[d] 0.65508[e]	0.64578[d] 0.64586[e]
n-heptane	0.67951	0.67102	0.67951[f] 0.67946[c]	0.67105[g] 0.67107[j]
n-octane	0.69843	0.69042	0.69844[i] 0.69849[j]	0.69042[h] 0.69050[g]
n-nonane	0.71364	0.70596	0.71375[c] 0.71381[j]	0.70591[g] 0.70596[i]
n-decane	0.72614	0.71854	0.72615[d] 0.72615[d]	0.71854[g] 0.71872[d]

[a] Ref. 7. [b] Interpolated from values in Ref. 7. [c] Ref. 8. [d] Ref. 9. [e] Ref. 10. [f] Ref. 11. [g] Ref. 12. [h] Ref. 13. [i] Ref. 14. [j] Ref. 15.

RESULTS AND DISCUSSION

The experimental results for the excess molar volumes at 298.15 K and 308.15 K are listed in Tables 2 and 3. To each set of v^E values, a Redlich–Kister function.

$$v^E = x(1 - x) \sum_{i=0}^{n} A_i(2x - 1)^i \quad (1)$$

was fitted, where x is the mole fraction of propyl ethanoate. The coefficients A_i and the standard deviation given in Table 4 were calculated by the unweighted least-squares method, the degree of the polynomial having been optimized by applying

Table 2 Excess molar volumes at 298.15 K.

x	v^E $cm^3.mol^{-1}$	x	v^E $cm^3.mol^{-1}$	x	v^E $cm^3.mol^{-1}$	x	v^E $cm^3.mol^{-1}$
			Propyl ethanoate + *n*-hexane				
0.0622	0.1864	0.3387	0.5982	0.5300	0.5997	0.7910	0.3428
0.0899	0.2578	0.3505	0.6088	0.5926	0.5577	0.8296	0.2870
0.1591	0.4034	0.3895	0.6215	0.6538	0.5061	0.8843	0.2035
0.1974	0.4650	0.4528	0.6151	0.6937	0.4638	0.9308	0.1284
0.2442	0.5233	0.4911	0.6119	0.7207	0.4302	0.9497	0.0960
			Propyl ethanoate + *n*-heptane				
0.0799	0.2941	0.3800	0.7833	0.5415	0.7859	0.7138	0.6201
0.1480	0.4763	0.4600	0.8036	0.6288	0.7168	0.7765	0.5235
0.2429	0.6589	0.4948	0.8012	0.6508	0.7009	0.8359	0.4185
0.3095	0.7366	0.5284	0.7889	0.6600	0.6864	0.8929	0.2826
			Propyl ethanoate + *n*-octane				
0.0543	0.2138	0.3009	0.7969	0.5486	0.8960	0.7477	0.6761
0.1175	0.4221	0.3549	0.8517	0.6038	0.8617	0.7951	0.5893
0.1698	0.5583	0.4365	0.9042	0.6371	0.8292	0.8888	0.3586
0.1785	0.5773	0.4382	0.9004	0.6912	0.7666	0.9145	0.2885
0.2632	0.7388	0.4989	0.9081	0.7300	0.7089	0.9518	0.1701
			Propyl ethanoate + *n*-nonane				
0.0790	0.3031	0.3196	0.8564	0.5529	0.9703	0.7971	0.6546
0.1091	0.4025	0.3455	0.8892	0.5950	0.9490	0.8412	0.5457
0.1574	0.5428	0.4037	0.9470	0.6465	0.9016	0.8988	0.3769
0.2157	0.6807	0.4437	0.9682	0.7056	0.8314	0.9438	0.2234
0.2641	0.7736	0.5087	0.9792	0.7510	0.7487		
			Propyl ethanoate + *n*-decane				
0.0622	0.2531	0.3634	0.9392	0.6044	1.0019	0.8241	0.6297
0.1177	0.4333	0.4464	1.0181	0.6501	0.9588	0.8540	0.5592
0.1554	0.5452	0.4964	1.0304	0.6931	0.9004	0.8924	0.4381
0.2182	0.7013	0.5478	1.0173	0.7167	0.8677	0.9434	0.2503
0.2700	0.8054	0.5717	1.0217	0.7792	0.7471		

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Table 3 Excess molar volumes at 308.15 K.

x	v^E $cm^3.mol^{-1}$	x	v^E $cm^3.mol^{-1}$	x	v^E $cm^3.mol^{-1}$	x	v^E $cm^3.mol^{-1}$
			Propyl ethanoate + *n*-hexane				
0.0837	0.2786	0.3281	0.6367	0.5723	0.5806	0.8063	0.3267
0.1259	0.3810	0.3820	0.6506	0.6348	0.5272	0.8596	0.2539
0.2007	0.5200	0.4309	0.6519	0.6973	0.4632	0.9014	0.1826
0.2326	0.5588	0.4844	0.6327	0.7249	0.4317	0.9397	0.1149
0.2770	0.6055	0.5250	0.6135	0.7767	0.3680		
			Propyl ethanoate + *n*-heptane				
0.1044	0.3795	0.3146	0.7894	0.5057	0.8487	0.7855	0.5268
0.1178	0.4162	0.3621	0.8348	0.5515	0.8260	0.8248	0.4450
0.1931	0.6054	0.4078	0.8494	0.6239	0.7653	0.9295	0.1985
0.2567	0.7096	0.4619	0.8564	0.7033	0.6716	0.9560	0.1244
			Propyl ethanoate + *n*-octane				
0.0954	0.3694	0.4211	0.9659	0.7254	0.7719	0.9181	0.2973
0.1944	0.6535	0.5303	0.9740	0.7647	0.7012	0.9544	0.1720
0.2499	0.7684	0.5677	0.9568	0.8007	0.6244		
0.3219	0.8796	0.6347	0.8992	0.8432	0.5189		
0.3769	0.9403	0.6810	0.8454	0.8759	0.4286		
			Propyl ethanoate + *n*-nonane				
0.0962	0.3729	0.4474	1.0190	0.7034	0.8730	0.8905	0.4289
0.1666	0.5899	0.5059	1.0326	0.7600	0.7750	0.9265	0.3001
0.2950	0.8680	0.5385	1.0304	0.7868	0.7193	0.9555	0.1880
0.3337	0.9258	0.6039	0.9958	0.8181	0.6361		
0.4061	0.9992	0.6538	0.9428	0.8438	0.5737		
			Propyl ethanoate + *n*-decane				
0.1006	0.4256	0.4357	1.0546	0.7099	0.9363	0.8717	0.5329
0.1718	0.6417	0.4900	1.0730	0.7563	0.8423	0.9289	0.3219
0.2493	0.8235	0.5726	1.0652	0.7925	0.7654	0.9632	0.1712
0.3099	0.9231	0.6271	1.0356	0.8234	0.6858		
0.3517	0.9757	0.6814	0.9696	0.8698	0.5458		

the F-test[16]. Figures 1 and 2 show the measured values of v^E together with the fitted curves $v^E(x)$.

As far as we know only the v^E's of propyl ethanoate + *n*-heptane system were measured before. Our value for $x = 0.5$ is 0.4% greater than the one of Grolier *et al.*[17] and 1.1% lower than that of Dusart *et al.*[18] All these experimental values are represented in Figure 3.

Figures 1 and 2 show that the characteristics of the excess volumes of propyl ethanoate + *n*-alkane follow the general behaviour of those of the ester + *n*-alkane mixtures: the $v^E(x)$ curves shift to the ester-rich region and v^E increases more rapidly for small than for longer alkanes[1,2,11,17–21].

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Table 4 Coefficients A_i for Eq. (1) and standard deviations s determined by the method of least squares.

System	A_0	A_1	A_2	A_3	s
$T = 298.15$ K					
Propyl ethanoate					
+ *n*-hexane	2.4336	−0.7160	0.1825	—	0.0025
+ *n*-heptane	3.1912	−0.5013	0.4157	−0.1205	0.0031
+ *n*-octane	3.6300	−0.2475	0.3666	—	0.0021
+ *n*-nanone	3.9162	0.0159	0.3553	—	0.0021
+ *n*-decane	4.1123	2.0938	0.3873	—	0.0050
$T = 308.15$ K					
Propyl ethanoate					
+ *n*-hexane	2.5035	−0.9489	0.4710	—	0.0019
+ *n*-heptane	3.4036	−0.6151	0.2235	—	0.0034
+ *n*-octane	3.9217	−0.2122	0.3046	—	0.0015
+ *n*-nonane	4.1324	0.0447	0.3376	—	0.0026
+ *n*-decane	4.3027	0.2815	0.7270	−0.3174	0.0031

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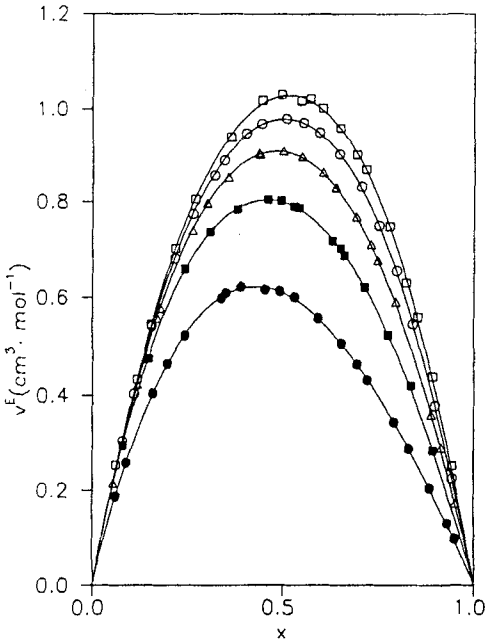

Figure 1 Excess molar volumes for propyl ethanoate + *n*-hexane (●), + *n*-heptane (■), + *n*-octane (△), + *n*-nonane (○), + *n*-decane (□) at 298.15 K. Continuous curves were calculated from Eq. (1).

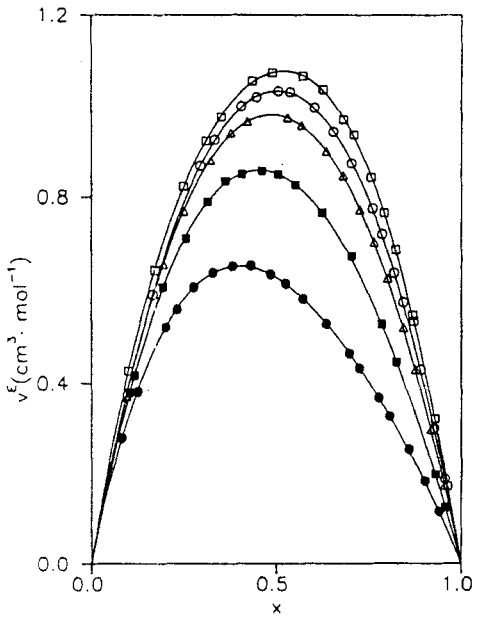

Figure 2 Excess molar volumes for propyl ethanoate + *n*-hexane (●), + *n*-heptane (■), + *n*-octane (△), + *n*-nonane (○), + *n*-decane (□) at 308.15 K. Continuous curves were calculated from Eq. (1).

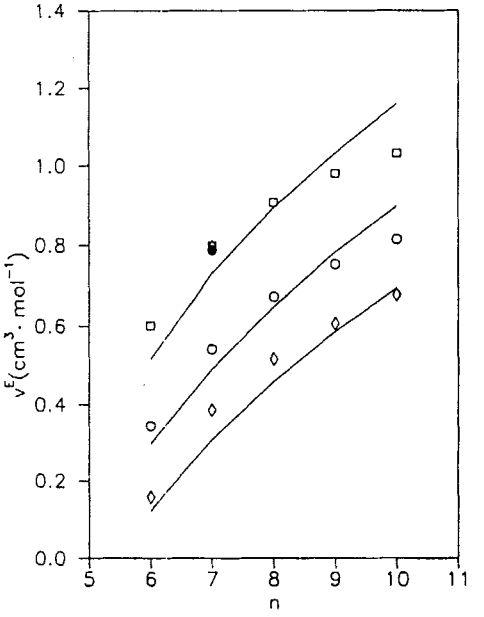

Figure 3 Plots of excess molar volumes at 298.15 K and $x = 0.5$ of $\{xC_mH_{2m+1}COOC_3H_7 + (1-x)C_nH_{2n+2}\}$ against *n*. $m = 1$: (□) this work, (●) Grolier *et al.*[17] and (△) Dusart *et al.*[18] $m = 2$ (○) Lorezana *et al.*[1] $m = 3$ (◇) Lorenzana *et al.*[2] Continuous curves are the predicted value with the Nitta–Chao model[3–6].

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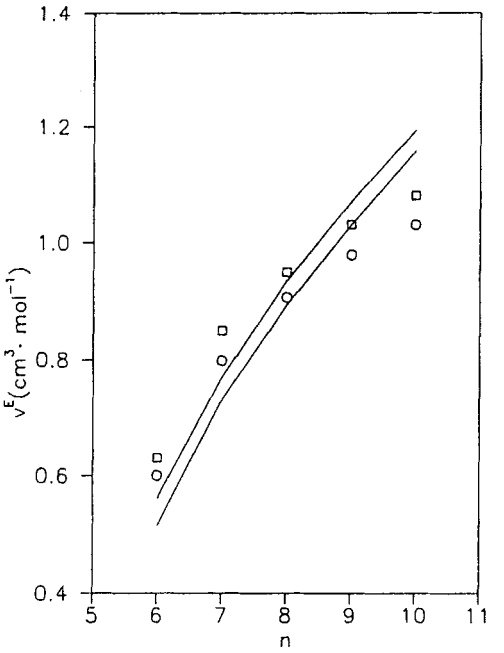

Figure 4 Excess molar volumes for equimolar propyl ethanoate + *n*-alkane mixtures against *n*, the number of carbons of the *n*-alkane at 298.15 (○) and at 308.15 K (□). Continuous curves are the predicted values with the Nitta–Chao model[3–6].

Figure 3 shows the excess molar volumes at equimolar composition of the present systems together with another propyl alkanoate + *n*-alkane systems from the literature[17,18]. As usual, excess molar volumes decrease as the length of the ester chain increases[1,2,11,17–21]. This decrease, in a given series of alkanoates corresponds to a dilution of the ester group.

The excess molar volumes increase when the temperature grows in all the concentration range. We have not found in the literature any v^E data for ester + *n*-alkane systems at temperature different from 298.15 K. Therefore it is not possible at the present stage to draw a definitive conclusion about the general behaviour with the temperature for the type of mixtures studied.

Figure 4 show the experimental excess volumes together with those predicted with the Nitta–Chao model with the parameters calculated by Navarro[5,6] for the ester–alkane interaction. The model predicts well the dependence of the excess molar volumes with the ester and alkane length and with the temperature. The differences between predicted and experimental values at $x = 0.5$ for the systems with propyl ethanoate are 8.0% at 298.15 K and 7.2% at 308.15 K. For all the systems presented in Figure 3 the mean deviation is 8.7%.

References

1. M. T. Lorenzana, J. L. Legido, E. Jiménez, J. Fernández, L. Pías, J. Ortega and M. I. Paz Andrade, *J. Chem. Thermodyn.*, **21**, 1017 (1989).

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2. M. T. Lorenzana, J. L. Legido, E. Jiménez, J. Fernández, L. Pías, J. Ortega and M. I. Paz Andrade, *J. Chem. Thermodyn.*, **22**, 1017 (1990).
3. T. Nitta, E. Turek, R. A. Greenkorn and K. C. Chao, *AIChE J.*, **23**, 144 (1977).
4. N. F. Carnahan and K. E. Starling, *J. Chem. Phys.*, **51**, 635.
5. J. M. Navarro, Doctoral Thesis, Facultad de Física, Universidad de Santiago, Spain. 1983.
6. J. Ortega, J. S. Matos, M. I. Paz-Andrade, J. Fernández, L. Pías, *Fluid Phase Equilibria*, **43**, 295 (1988).
7. *Selected Values of Properties of Hydrocarbons and Related Compounds.* Thermodynamics Research Center: Texas A & M University, College Station Texas, Table 23-2-1, (1969).
8. J. A. Riddick, W. B. Bunger, and T. K. Sakano, *Techniques of Chemistry, Vol. II, Organic Solvents*, 4th edn. (Wiley, New York, 1986).
9. M. Diaz Peña and G. Tardajos, *J. Chem. Thermodyn.*, **10**, 19 (1978).
10. A. Heintz, B. Schmittecker, D. Wagner and R. Lichtenthaler, *J. Chem. Eng. Data*, **31**, 487 (1986).
11. M. Pintos, R. Bravo, M. C. Baluja, M. I. Paz Andrade, G. Roux-Desgranges, J.-P. E. Grolier, *Can. J. Chem.*, **66**, 1179 (1988).
12. J. L. Legido, M. T. Lorenzana, E. Jiménez, J. Fernandez, A. Amigo and M. I. Paz Andrade, *J. Sol. Chem.*, **19**, 1095 (1990).
13. M. Garcia, C. Rey, V. P. Villar and J. Rodriguez, *J. Chem. Eng. Data*, **31**, 481 (1986).
14. J. Ortega and J. S. Matos, *Mat. Chem. Phys.*, **15**, 415 (1986).
15. R. R. Dreissbach, *Physical Properties of Chemical Compounds* (American Chemical Society, Washington, D.C., 1950).
16. P. Bevington, *Data Reduction and Error Analysis for the Physical Sciences* (McGraw-Hill, New York 1969).
17. J.-P. E. Grolier, D. Ballet and A. Viallard, *J. Chem. Thermodyn.*, **6**, 895 (1974).
18. O. Dusart, C. Piekarski, S. Piekarski and A. Viallard, *J. Chim. Phys.*, **73**, 837 (1976).
19. A. W. Awwad, K. A. Jbara and A. H. Al-Dujaili, *Thermochimica Acta*, **129**, 249 (1988).
20. A. W. Awwad, K. A. Jbara and A. H. Al-Dujaili, *Fluid Phase Equilibria*, **41**, 277 (1988).
21. P. V. Ilic, E. Jiménez, J. L. Legido, J. Fernández, and M. I. Paz Andrade, *J. Chem. Thermodyn*, **22** 865 (1990).

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