Mixing Properties of the System Methyl Acetate + Methanol + Ethanol at 298.15 K

Ana Rodríguez, Jose Canosa, Beatriz Orge, Miguel Iglesias, and José Tojo*

Departamento de Ingeniería Química, Universidad de Vigo, Aptdo. 874, 36200 Vigo, Spain

This paper reports measurements of the densities and refractive indices of the ternary system methyl acetate + methanol + ethanol and the corresponding binary systems methyl acetate + methanol, methyl acetate + ethanol, and methanol + ethanol at 298.15 K and atmospheric pressure. A vibrating tube digital densimeter and a refractometer of synthetic sapphire prism (sodium D wavelengh) were used, the whole mole fraction range being covered. Excess molar volumes and deviations of the refractive indices on mixing were determined. Polynomials have been fitted to the results, the computed parameters being shown.

1. Introduction

Knowledge of the mixing properties of multicomponent ternary mixtures has relevance in both theoretical and applied areas of research because such results are useful in the general design and simulation of processes in the chemical and petrochemical industries and specific applications like thermodynamic study of potential separation agents in extractive distillation. This work is related to a project to determine thermophysical properties of solutions of short chain aliphatic alcohols like entrainers for binary minimum azeotropes. This article reports values of densities and refractive indices for the mixture methyl acetate + methanol + ethanol measured at 298.15 K, over the entire mole fraction range at atmospheric pressure. Comparison has been made between the measured values and those predicted by different methods. An estimation of excess partial molar volumes is made using a modified Heller equation (Heller, 1965) which depends on the refractive indices of the mixture.

2. Experimental Section

All chemicals were Lichrosolv quality (Merck Farma y Química S. A.). The pure components were recently acquired and kept in an inert argon atmosphere after the bottles were opened. The materials were degassed ultrasonically and dried over molecular sieves Type 4A or 3A, $^1/_{16}$ in. Precautions were taken such as cooling chemicals before sample preparation or reducing to a minimum the vapor space in the vessels, in order to avoid losses by evaporation during manipulation and possible errors in molar fraction calculations. Chromatographic (GLC) analysis gave purities of 0.998 for methyl acetate, methanol, and ethanol, with maximum water contents of 6.8×10^{-3}, 1.5×10^{-2}, and 2.2×10^{-2} mass % (Metrohm 737 KF coulometer), respectively. The densities and refractive indices at 298.15 K agreed within recommended values (Table 1).

A PolyScience controller bath model 9010 with a temperature stability of $\pm 10^{-2}$ K was used for the measurements. Samples were prepared by mass using a Mettler AT-261 Delta Range balance with a precision of 10^{-5} g. The densities of the mixtures and pure liquids were measured with an Anton Paar DMA-60/602 densimeter with an uncertainty of 10^{-5} g·cm^{-3} and the refractive indices were measured by the automatic refractometer ABBEMAT-HP Dr. Kernchen with an uncertainty of 10^{-5}. The apparatus was calibrated periodically using degassed Millipore quality water and degassed and dried Fluka quality *n*-heptane. The chromatographic (GLC) analysis gave a purity of 0.990 for *n*-heptane. The uncertainty in the calculation of excess

* To whom correspondence should be addressed. E-mail: jtojo@uvigo.es.

Table 1. Comparison of Data with Literature Data for Pure Liquids at 298.15 K

	ρ(298.15 K)/g·cm^{-3}		n^D(298.15 K)	
component	exptl	lit.	exptl	lit.
methyl acetate	0.926 74	0.927 3[a]	1.358 50	1.358 9[a]
		0.927 9[b]		1.361 4[b]
		0.927 03[c]		
methanol	0.786 65	0.786 64[a]	1.326 45	1.326 52[a]
		0.786 64[b]		1.326 52[b]
ethanol	0.785 02	0.785 09[a]	1.359 22	1.359 41[a]
		0.785 04[b]		1.359 41[b]

[a] TRC Thermodynamic Tables (1994). [b] Riddick and Bunger (1986). [c] Ortega (1995).

Table 2. Densities, Refractive Indices, Excess Molar Volumes, and Deviations of Refractive Indices on Mixing for Binary Mixtures at 298.15 K

x_1	ρ/g·cm^{-3}	n^D	V_m^E/cm^3·mol^{-1}	$\Delta_{mix}n^D$
Methyl Acetate (1) + Methanol (2)				
0.0973	0.811 47	1.332 03	−0.020	0.0025
0.2035	0.834 12	1.337 23	−0.040	0.0043
0.2986	0.851 35	1.341 38	−0.057	0.0054
0.3944	0.866 28	1.344 96	−0.067	0.0059
0.4909	0.879 36	1.348 04	−0.072	0.0059
0.6007	0.892 30	1.350 97	−0.072	0.0053
0.6927	0.901 79	1.353 14	−0.066	0.0045
0.7711	0.909 01	1.354 75	−0.053	0.0036
0.8651	0.916 88	1.356 57	−0.037	0.0024
Methyl Acetate (1) + Ethanol (2)				
0.1124	0.804 72	1.358 49	0.087	−0.0006
0.1928	0.818 07	1.358 28	0.133	−0.0008
0.2686	0.830 18	1.358 12	0.163	−0.0009
0.3562	0.843 55	1.358 03	0.187	−0.0009
0.4604	0.858 71	1.357 97	0.198	−0.0009
0.5754	0.874 54	1.357 95	0.195	−0.0009
0.6856	0.888 97	1.358 01	0.171	−0.0007
0.7908	0.902 06	1.358 12	0.137	−0.0005
0.8699	0.911 54	1.358 20	0.100	−0.0004
Methanol (1) + Ethanol (2)				
0.0990	0.785 11	1.356 67	0.002	0.0007
0.2249	0.785 23	1.353 45	0.004	0.0016
0.3059	0.785 32	1.351 10	0.005	0.0019
0.4016	0.785 43	1.348 43	0.007	0.0024
0.5021	0.785 57	1.345 44	0.008	0.0027
0.5578	0.785 65	1.343 63	0.008	0.0027
0.7063	0.785 90	1.338 45	0.008	0.0024
0.7562	0.786 00	1.336 46	0.007	0.0020
0.7967	0.786 09	1.334 82	0.007	0.0017
0.9010	0.786 34	1.330 40	0.005	0.0007

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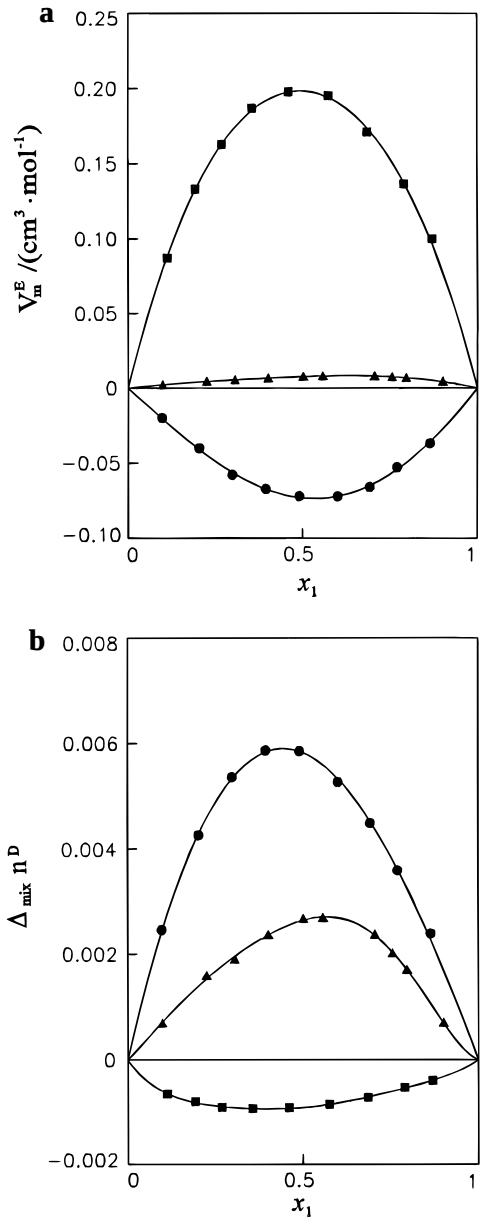

Figure 1. Variation of the (a) excess molar volumes and (b) deviations of refractive indices on mixing with mole fraction at 298.15 K for (●) methyl acetate (1) + methanol (2), (■) methyl acetate (1) + ethanol (2), and (▲) methanol (1) + ethanol (2).

molar volumes and refractive indices deviation was estimated as better than 8.6×10^{-4} cm^3·mol^{-1} and 2×10^{-5}, respectively. The accuracy in the determination of the molar fraction of the measured samples is 5×10^{-5}. The experimental technique and mode of operation have been described previously (Iglesias *et al.*, 1995).

3. Results and Discussion

The excess molar volumes and refractive indices deviation for the binary and ternary mixtures were calculated from eqs 1 and 2, respectively. In these equations, ρ is the

$$V_m^E = \sum_{i=1}^{N} x_i M_i (\rho^{-1} - \rho_i^{-1}) \quad (1)$$

$$\Delta_{mix} n^D = n^D - \sum_{i=1}^{N} x_i n_i^D \quad (2)$$

density of the mixture, n^D is the refractive index of the mixture, and ρ_i and n_i^D are the values for the pure components. The value of N represents the number of components in the mixture. Parts a and b of Figure 1 show the excess volumes and deviations of the refractive indices for methyl acetate + methanol, methyl acetate + ethanol, and methanol + ethanol, respectively.

Densities and refractive indices of the mixture are given in Tables 2 and 3. No values of these properties for the investigated ternary system have been published, as far as we know, in open literature.

The excess ternary mixtures which are presented in Table 3 were correlated with the Cibulka equation (Cibulka, 1982):

$$\Delta Q_{123} = \Delta Q_{12} + \Delta Q_{13} + \Delta Q_{23} + x_1 x_2 (1 - x_1 - x_2)(C_1 + C_2 x_1 + C_3 x_2) \quad (3)$$

Table 3. Densities, Refractive Indices, Excess Molar Volumes, and Deviations of Refractive Indices on Mixing for Methyl Acetate (1) + Methanol (2) + Ethanol (3) at 298.15 K

x_1	x_2	ρ/g·cm^{-3}	n^D	V_m^E/cm^3·mol^{-1}	$\Delta_{mix} n^D$
0.0824	0.1485	0.800 51	1.355 21	0.060	0.0009
0.0761	0.2806	0.800 28	1.351 83	0.046	0.0019
0.0762	0.3813	0.801 02	1.349 17	0.041	0.0025
0.0725	0.5002	0.801 22	1.345 77	0.030	0.0030
0.0695	0.5979	0.801 32	1.342 72	0.026	0.0031
0.0655	0.6788	0.801 15	1.339 94	0.018	0.0030
0.0646	0.7690	0.801 75	1.336 70	0.011	0.0027
0.0491	0.8722	0.798 85	1.332 46	0.006	0.0019
0.1480	0.1643	0.812 52	1.354 68	0.084	0.0009
0.1458	0.2744	0.813 35	1.352 15	0.073	0.0020
0.1342	0.4053	0.812 79	1.348 67	0.049	0.0028
0.1372	0.4987	0.814 62	1.346 08	0.036	0.0033
0.1314	0.6099	0.814 98	1.342 72	0.019	0.0036
0.1227	0.7048	0.814 39	1.339 58	0.010	0.0035
0.1205	0.7847	0.815 10	1.336 78	−0.002	0.0034
0.1852	0.7151	0.828 28	1.339 88	−0.010	0.0042
0.1936	0.6260	0.828 22	1.342 74	0.009	0.0042
0.2018	0.5251	0.827 88	1.345 63	0.032	0.0038
0.2145	0.4098	0.828 17	1.348 93	0.055	0.0033
0.2204	0.2899	0.827 11	1.351 75	0.082	0.0022
0.2319	0.1490	0.826 71	1.354 98	0.116	0.0008
0.2643	0.6353	0.842 61	1.343 11	−0.012	0.0049
0.2751	0.5368	0.842 24	1.345 91	0.013	0.0045
0.2921	0.4084	0.842 27	1.349 26	0.048	0.0036
0.2950	0.3007	0.840 33	1.351 76	0.081	0.0026
0.3097	0.1618	0.839 78	1.354 80	0.124	0.0011
0.3469	0.5464	0.855 73	1.346 20	−0.013	0.0051
0.3663	0.4302	0.855 80	1.349 17	0.023	0.0043
0.3816	0.3050	0.854 89	1.351 86	0.069	0.0029
0.3959	0.1672	0.853 54	1.354 75	0.122	0.0013
0.4410	0.4421	0.868 73	1.349 26	−0.009	0.0048
0.4698	0.3163	0.869 30	1.352 19	0.040	0.0037
0.4791	0.1755	0.866 37	1.354 85	0.108	0.0017
0.5425	0.3285	0.880 79	1.352 14	0.009	0.0041
0.5926	0.1705	0.882 56	1.355 16	0.080	0.0019
0.6938	0.1760	0.896 58	1.355 28	0.036	0.0023
0.0409	0.0731	0.792 61	1.357 04	0.033	0.0002
0.1060	0.0888	0.804 35	1.356 54	0.074	0.0003
0.1980	0.0854	0.820 14	1.356 52	0.114	0.0002
0.2780	0.0840	0.833 18	1.356 46	0.140	0.0002
0.3620	0.0823	0.846 30	1.356 47	0.152	0.0002
0.4543	0.0869	0.860 19	1.356 46	0.154	0.0004
0.5636	0.0697	0.875 15	1.356 91	0.152	0.0004
0.6501	0.1034	0.888 02	1.356 44	0.108	0.0011
0.7705	0.0917	0.903 20	1.356 80	0.065	0.0011
0.8299	0.0975	0.910 87	1.356 91	0.026	0.0015
0.1111	0.0841	0.805 19	1.356 62	0.079	0.0002
0.6694	0.2601	0.896 58	1.353 87	−0.014	0.0037
0.5341	0.3940	0.881 89	1.350 75	−0.025	0.0048
0.4355	0.5007	0.869 75	1.347 79	−0.032	0.0053
0.2660	0.6918	0.844 44	1.341 41	−0.031	0.0050
0.3446	0.6035	0.857 11	1.344 52	−0.039	0.0053
0.2280	0.2097	0.827 05	1.353 70	0.102	0.0015
0.3011	0.2299	0.839 80	1.353 38	0.104	0.0019
0.3882	0.2361	0.854 10	1.353 38	0.096	0.0022
0.4724	0.2418	0.867 31	1.353 45	0.080	0.0025

Table 4. Parameters of Equations 3 and 4 and Standard Deviations σ

			Methyl Acetate (1) + Methanol (2)			
V_m^E/cm^3·mol^{-1}	$B_0 = -0.2920$	$B_1 = -0.0461$	$B_2 = 0.0367$			$\sigma = 0.0010$
$\Delta_{mix}n^D$	$B_0 = 0.0233$	$B_1 = -0.0053$				$\sigma = 0.00005$
			Methyl Acetate (1) + Ethanol (3)			
V_m^E/cm^3·mol^{-1}	$B_0 = 0.7942$	$B_1 = -0.0144$	$B_2 = 0.1367$			$\sigma = 0.0017$
$\Delta_{mix}n^D$	$B_0 = -0.0036$	$B_1 = 0.0011$	$B_2 = -0.0006$	$B_3 = 0.0013$	$B_4 = -0.0027$	$\sigma = 0.00001$
			Methanol (2) + Ethanol (3)			
V_m^E/cm^3·mol^{-1}	$B_0 = 0.0308$	$B_1 = 0.0151$	$B_2 = 0.0099$			$\sigma = 0.0001$
$\Delta_{mix}n^D$	$B_0 = 0.0106$	$B_1 = 0.0036$	$B_2 = -0.0008$	$B_3 = -0.0059$	$B_4 = -0.0051$	$\sigma = 0.00004$
			Methyl Acetate (1) + Methanol (2) + Ethanol (3)			
V_m^E/cm^3·mol^{-1}	$C_1 = -0.1007$	$C_2 = -0.0566$	$C_3 = 0.7243$			$\sigma = 0.0017$
$\Delta_{mix}n^D$	$C_1 = -0.0031$	$C_2 = -0.0064$	$C_3 = -0.0030$			$\sigma = 0.00006$

where ΔQ_{12}, ΔQ_{13}, and ΔQ_{23} are the binary contributions expressed by the Redlich−Kister expression (Redlich and Kister, 1948) for every binary mixture:

$$\Delta Q_{ij} = x_i x_j \sum_{p=0}^{M} B_p (x_i - x_j)^p \qquad (4)$$

in this equation ΔQ_{ij} is the excess property, x is the molar fraction, B is a parameter, and M is the degree of the polynomic expansion. The unweighted least-squares method was used to fit the polynomials to the data. The degree was optimized by applying the F-test (Bevington, 1969). Curves of excess molar volumes and deviations of the refractive indices have been plotted in Figure 2.

Methyl acetate + methanol shows negative deviations, and methanol + ethanol and methyl acetate + ethanol show positive deviations. Relatively high concentrations of ethanol for ternary mixtures show positive deviations.

The parameters of fitting eqs 3 and 4 and corresponding standard deviations are given in Table 4. The standard deviations were calculated using eq 5. In this equation z

$$\sigma = \left(\frac{\sum_{i}^{n_{DAT}} (z_{exp} - z_{pred})^2}{n_{DAT}} \right)^{1/2} \qquad (5)$$

is the value of the property and n_{DAT} is the number of experimental data. No significantly better standard deviations were obtained by trying different fitting models to correlate excess values.

Several methods to predict density, refractive indices, and the excess properties of mixtures were applied to test their validity, which are compilated by Iglesias *et al.*, 1996.

The density of binary and ternary mixtures was estimated by the Hankinson−Brobst−Thompson, Rackett, Spencer and Danner modified Rackett, Bradford−Thodos, Riedel, Narsimham, and Yen−Woods methods. The Narsimham equation gives the smaller deviation in ternary estimations, as well as in the methyl acetate + methanol mixture. Bradford−Thodos and Yen−Woods equations present the best results in methyl acetate + ethanol and methanol + ethanol mixtures, respectively.

The refractive indices were compared with the predicted results for the mixing rules proposed by Lorentz−Lorenz, Dale−Gladstone, Arago−Biot, Eykman, Newton, Oster, and Eyring−John equations. The lower deviations in the ternary mixture were determined by the Newton rule for the methyl acetate + methanol system and Lorenz−Lorentz rule for the methanol + ethanol and methyl acetate + methanol + ethanol systems. Very similar results were obtained for all the rules in the methyl acetate+ethanol mixture.

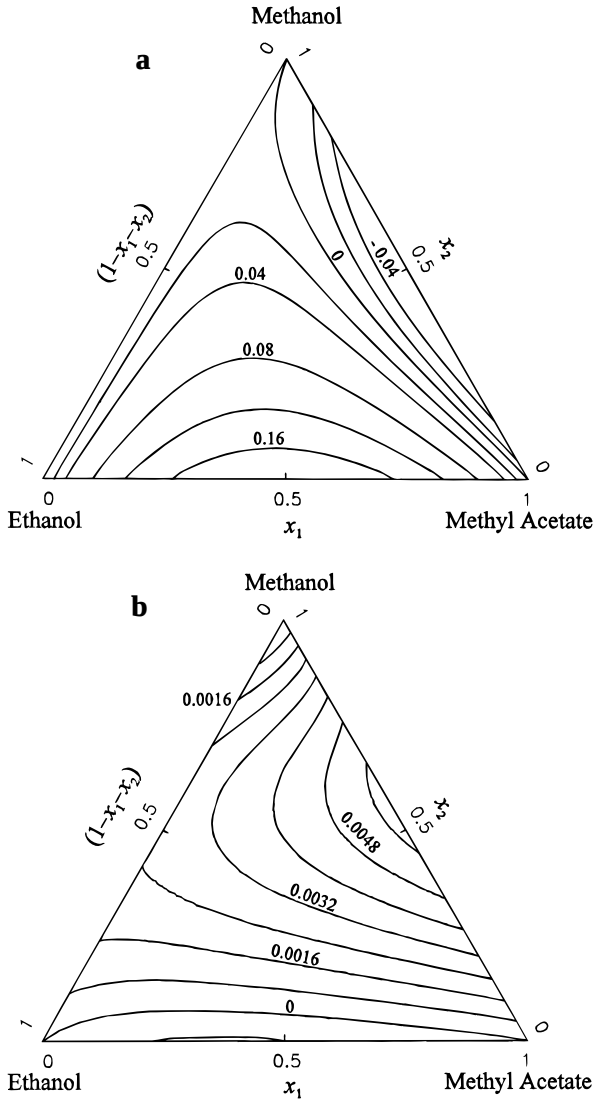

Figure 2. Curves of (a) excess molar volume and (b) deviations of refractive indices on mixing for methyl acetate (1) + methanol (2) + ethanol (3) mixture at 298.15 K.

The predictive methods for excess properties (Köhler, Jacob and Fitzner, Colinet, Tsao and Smith, Toop, Scatchard) determine ternary excess properties by means of additive binary contributions, using different rules to determine them. In the estimation of excess volumes, symmetric equations and type a asymmetric equations show lower deviations with respect to experimental results. For deviations of refractive indices on mixing estimation, the better results were obtained by symmetric equations and type b asymmetric equations.

The excess partial molar volumes were predicted (Nakata and Sakurai, 1987; Arancibia and Katz, 1993; Heller,

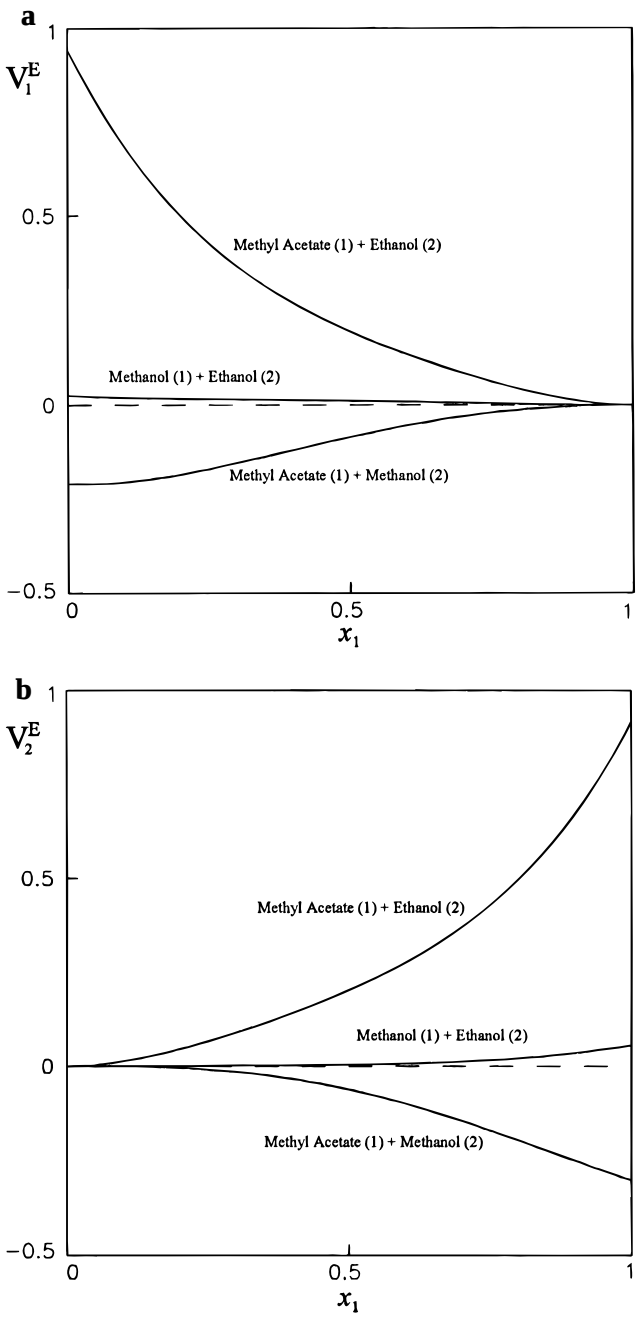

Figure 3. Partial excess molar volumes of methyl acetate (1) + methanol (2), methyl acetate (1) + ethanol (2), and methanol (1) + ethanol (2) mixtures at 298.15 K for (a) V_1^E and (b) V_2^E.

1965) from refractive index mixing rules (Lorentz−Lorenz, Dale−Gladstone, Eykman, and Oster) and the relation of excess volumes with density of pure components for binary mixtures. Parts a and b of Figure 3 show the trends of excess partial molar volumes with the corresponding molar fraction for the three binary mixtures. It is important to underline the lack of variation in the interaction between the two alcohols, indicating a slightly and fairly constant value in the entire composition range. The positive trend in the curve corresponding to the methyl acetate + ethanol mixture and the negative trend of the methyl acetate + methanol suggest the different closeness of the packing of the solvent molecules around the solute due to the different chain molecular lengths of the alcohols.

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Registry Nos. Supplied by the Author: Methyl acetate, 79-20-9; methanol, 67-56-1; ethanol, 64-17-5.

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