Densities, Excess Molar Volumes, Viscosities, Speeds of Sound, Excess Isentropic Compressibilities, and Relative Permittivities for Alkyl (Methyl, Ethyl, Butyl, and Isoamyl) Acetates + Glycols at Different Temperatures

Nandhibatla V. Sastry* and Mitesh C. Patel

Department of Chemistry, Sardar Patel University, Vallabh Vidyanagar, 388120 Gujarat, India

New experimental data on densities at (298.15 to 313.15) K, viscosities, speeds of sound, and relative permittivities at (298.15 and 308.15) K for the 10 binary mixtures of alkyl (methyl, ethyl, butyl, and isoamyl) acetates + glycols (ethylene, diethylene, triethylene, and propylene) have been measured as a function of the composition. Deviation functions, such as deviations in speeds of sound and deviations in relative permittivities, and excess functions, such as excess molar volumes and excess isentropic compressibilities, were calculated and fitted to a Redlich−Kister type equation. Grunberg−Nissan, McAllister, and Auslander equations correlated the mixture viscosities adequately. The values of speeds of sound in these mixtures, as predicted by collision factor theory, matched well with experimental data. The variation of the Kirkwood correlation factor with the ester mole fraction was examined. A qualitative analysis of the deviation and excess functions was made to ascertain the nature and type of bulk state interactions.

1. Introduction

The thermophysical behavior in aliphatic alkyl alkanoates + 1-alcohols and branched alcohols has been extensively studied in terms of excess molar enthalpies, H_m^E,[1−4] excess molar volumes, V_m^E,[5−11] and dynamic viscosities and viscosity deviations.[12−15] A literature survey showed that there exists very limited reports on ester + glycol mixtures, although glycols are interesting molecules, as they offer a wide variety of molecular architectures. Aminabhavi and Banerjee[15] have reported that the V_m^E values at T = (298.15 to 308.15) K for the binary mixture of methyl acetate + poly(ethylene glycol) were three times more negative than those for methyl acetate + ethylene glycol. The authors envisaged that ester + ether weak linkages coupled with ester + hydroxyl group interactions exist together in the former system. The present study reports the experimental data of various theromophysical properties of aliphatic ester + glycol binary mixture systems over the whole composition range. The aliphatic esters chosen are methyl, ethyl, butyl, and isoamyl acetates. The glycol components are ethylene glycol, propylene glycol, diethylene glycol, and triethylene glycols. The selection of some of the above components for the mixture preparation is hampered by immiscibility. Hence, we could do measurements on a total of 10 binary mixtures in the whole composition range. These 10 mixtures are methyl acetate + ethylene glycol, + diethylene glycol, + trietheylene glycol and + propylene glycol; ethyl acetate + diethylene glycol, + triethylene glycol, and + propylene glycol; butyl acetate + triethylene glycol and + propylene glycol; and isoamyl acetate + propylene glycol. The densities of these binary mixtures were measured at the four temperatures (298.15, 303.15, 308.15, and 313.15) K, while the other properties such as dynamic viscosities, speeds of sound, and relative permittivities were measured at T = (298.15 and 308.15) K.

* Corresponding author. Fax: 0091-2692-236475. E-mail: nvsastry_ad1@sancharnet.in.

2. Experimental Section

Materials. The laboratory reagent grade methyl, ethyl, butyl, and isoamyl acetates were purchased from Chiti-Chem, India, and have a stated purity of 99% on a mole basis. Methyl acetate was washed with saturated sodium chloride solution, dried with anhydrous magnesium sulfate, and then distilled. Ethyl acetate was dried over potassium carbonate, filtered, and distilled, and the first and last portions of the distillate were discarded. The entire center fraction was then distilled over phosphorus pentoxide. Butyl acetate and isoamyl acetate were purified by drying over calcium carbonate overnight, filtered, and freshly distilled. Ethylene and propylene glycols were purchased from Sisco-Chem Pvt. Ltd., India, and di- and triethylene glycols were from Chiti-Chem, India. Ethylene, diethylene, and triethylene glycols were fractionally distilled in a vacuum, and the middle fractions were collected and dried over sodium sulfate. After decantation, the liquids were fractionally distilled. Propylene glycol was dried with anhydrous sodium sulfate and fractionally distilled. The gas chromatographic analysis of treated glycols revealed that various impurities, such as free acid (as acetic acid) and water, in general, and peroxides (as H_2O_2) in diethylene and triethylene glycols and ethylene glycol in diethylene glycol, in particular, were reduced and the final purity of glycols was found to be greater than 99.5% on a mole basis.

Methods. The pure liquids were extensively degassed by repeated distillations before binary mixtures were prepared by mass in hermetically sealed glass vials. The mass measurements accurate to ±0.01 mg were made on a single pan balance (Dhona 100 DS, India). The estimated accuracy in the mole fractions was ±0.0001. Densities of pure liquids and liquid mixtures were measured using an

10.1021/je0340248 CCC: $25.00
Published on Web 05/23/2003

Table 1. Densities, ρ, Viscosities, η, Speeds of Sound, v, and Relative Permittivities, ϵ_r, for Pure Components

	T = 298.15 K		T = 303.15 K		T = 308.15 K		T = 313.15 K	
	exp	lit.	exp	lit.	exp	lit.	exp	lit.
				Methyl Acetate				
ρ/g·cm^{-3}	0.926 80(3)	0.926 84[38]	0.919 70(0)	0.919 67[42]	0.915 22(2)	0.9152[15]	0.908 33(5)	
η/mPa·s	0.384	0.380[14]			0.351	0.355[15]		
v/m·s^{-1}	1150	1149.53[39]			1103	1102.99[39]		
ϵ_r	6.864	6.861[40]			6.648	6.649[40]		
				Ethyl Acetate				
ρ/g·cm^{-3}	0.894 55(6)	0.894 55[41]	0.888 48(1)	0.8885[13]	0.882 50(1)	0.8825[12]	0.875 97(5)	
η/mPa·s	0.428	0.424[12]			0.387	0.385[12]		
v/m·s^{-1}	1138	1138.62[39]			1095	1093.28[39]		
ϵ_r	5.990	5.987[40]			5.784	5.783[40]		
				Butyl Acetate				
ρ/g·cm^{-3}	0.876 19(1)	0.876 19[43]	0.871 27(6)	0.871 29[41]	0.865 43(5)	0.8654[44]	0.860 48(6)	
η/mPa·s	0.674	0.675[44]			0.594	0.593[44]		
v/m·s^{-1}	1190	1190[4]			1150	1148.98[39]		
ϵ_r	5.001	4.994[40]			4.842	4.846[40]		
				Isoamyl Acetate				
ρ/g·cm^{-3}	0.866 21(8)	0.8664[41]	0.861 05(8)		0.855 85(5)		0.852 95(7)	0.8529[41]
η/mPa·s	0.781	0.7895[41]			0.747			
v/m·s^{-1}	1195				1154			
ϵ_r	5.346				4.982			
				Ethylene Glycol				
ρ/g·cm^{-3}	1.110 00(7)	1.1100[41]	1.106 63(8)	1.106 64[41]	1.103 08(0)		1.099 64(3)	
η/mPa·s	14.820				10.478			
v/m·s^{-1}	1662	1664[15]			1635	1632.1[45]		
ϵ_r	40.252	40.250[40]			38.229	38.225[40]		
				Diethylene Glycol				
ρ/g·cm^{-3}	1.113 51(2)	1.1135[46]	1.109 56(4)	1.1095[45]	1.106 22(3)	1.1062[45]	1.103 02(0)	1.1030[47]
η/mPa·s	30.012	30.0[41]			16.972			
v/m·s^{-1}	1580	1577[46]			1550			
ϵ_r	30.921	30.925[40]			29.163	29.160[40]		
				Triethylene Glycol				
ρ/g·cm^{-3}	1.119 59(9)	1.1195[42]	1.115 88(9)		1.111 96(4)		1.109 53(8)	
η/mPa·s	34.398				21.306			
v/m·s^{-1}	1612				1586			
ϵ_r	23.049	23.047[40]			21.856	21.850[40]		
				Propylene Glycol				
ρ/g·cm^{-3}	1.032 75(2)	1.0328[41]	1.029 02(1)	1.0290[39]	1.025 40(6)		1.021 53(5)	1.0215[47]
η/mPa·s	43.434				24.244			
v/m·s^{-1}	1492				1454			
ϵ_r	28.373	28.378[40]			26.742	26.747[40]		

Anton Paar, Austria, density meter model DMA 5000. The density meter was calibrated using liquid density standards supplied by the manufacturer. The instrument has a built-in thermostat for maintaining the desired temperatures with a precision of ±0.003 °C and an accuracy of ±0.01 °C. The repeatability in the density measurements of four time distilled water was found to be better than 3 × 10^{-6} g·cm^{-3}. For estimating the accuracies in the reported densities, we calculated the deviations of our measured values for the three esters and four glycols from the literature data at different temperatures. The densities reported in the present study have accuracies better than 3.3 × 10^{-5} g·cm^{-3}. Two different Ubbelohde viscometers were used to determine the viscosities for covering wide range values of either pure liquids or their binary mixtures. Each of the viscometers was calibrated with four time distilled water (ρ_{25} = 0.997 047 g·cm^{-3}, ρ_{35} = 0.994 031 g·cm^{-3}; η_{25} = 0.890 mPa·s, η_{35} = 0.719 mPa·s) and purified and triple distilled cyclohexane (ρ_{25} = 0.773 891 g·cm^{-3}, ρ_{35} = 0.764 461 g·cm^{-3}; η_{25} = 0.898 mPa·s, η_{35} = 0.748 mPa·s) to estimate the viscometer constants, A and B, at respective temperatures by solving the simultaneous equations of type

$$\eta/\text{mPa·s} = \rho/\text{g·cm}^{-3}\{A(t/\text{s}) - B/(t/\text{s})\} \quad (1)$$

The flow times, t, were measured with a stopwatch capable of registering time accurate to ±0.1 s. To avoid evaporation losses during viscosity measurements, the openings of the glass tubes were plugged with cotton and the flow times were measured just after the fresh mixture was made. The precision and accuracy in the measured viscosities are estimated to be 0.001 and 0.003 mPa·s, respectively. An ultrasonic interferometer supplied by Mittal Enterprise, New Delhi, was used to estimate the speeds of sound (with a precision of ±0.8 m·s^{-1}) in liquids and their binary mixtures. The accuracy in the measured speeds of sound was found to be ±1.3 m·s^{-1}. A Universal Dielectrometer, model OH-301 (Radelkis, Hungary), was used to measure the capacitance in pure liquids and binary mixtures. The capacitances were converted to the relative permittivities after performing the calibration of the dielectric cells.[16] The precision and accuracy of the relative permittivities have been estimated to be 0.001 and 0.004 units. The temperature during the viscosity, speeds of sound, and capacitance measurements was maintained accurately to 0.01 °C by employing a thermostatically controlled circulator (ISREF, model 017 A (India)). The measured properties for the pure liquids at different temperatures along with the literature comparison are given in Table 1.

Table 2. Experimental Densities, ρ, for Esters (1) + Glycols (2) at T = (298.15 to 313.15) K

	ρ/g·cm^{-3}					ρ/g·cm^{-3}			
x_1	T = 298.15 K	T = 303.15 K	T = 308.15 K	T = 313.15 K	x_1	T = 298.15 K	T = 303.15 K	T = 308.15 K	T = 313.15 K
Methyl Acetate (1) + Ethylene Glycol (2)					Methyl Acetate (1) + Diethylene Glycol (2)				
0.0444	1.100 26(9)	1.096 48(3)	1.092 85(8)	1.089 11(5)	0.0406	1.107 83(7)	1.103 83(9)	1.100 41(8)	1.097 07(9)
0.1488	1.077 91(5)	1.073 64(9)	1.070 12(4)	1.065 97(8)	0.1512	1.091 77(3)	1.087 47(0)	1.083 89(0)	1.080 13(4)
0.2505	1.056 96(7)	1.052 60(1)	1.049 33(5)	1.045 05(8)	0.2516	1.076 55(1)	1.071 84(8)	1.068 15(9)	1.063 99(7)
0.3485	1.037 61(0)	1.033 23(8)	1.030 22(3)	1.025 91(8)	0.3488	1.061 26(8)	1.056 15(1)	1.052 35(4)	1.047 79(9)
0.4411	1.020 06(8)	1.015 63(8)	1.012 78(0)	1.008 44(6)	0.4400	1.046 36(5)	1.040 88(3)	1.036 96(6)	1.032 05(9)
0.4856	1.011 89(1)	1.007 39(2)	1.004 56(7)	1.000 19(8)	0.4926	1.037 46(1)	1.031 79(1)	1.027 79(4)	1.022 69(3)
0.5507	1.000 20(9)	0.995 55(2)	0.992 71(8)	0.988 26(1)	0.5504	1.027 35(5)	1.021 49(8)	1.017 40(7)	1.012 10(0)
0.6503	0.982 94(1)	0.977 90(4)	0.974 92(2)	0.970 21(8)	0.6509	1.008 76(1)	1.002 63(1)	0.998 36(4)	0.992 71(6)
0.7489	0.966 49(2)	0.960 93(5)	0.957 65(6)	0.952 55(0)	0.7510	0.988 53(2)	0.982 17(4)	0.977 74(3)	0.971 76(6)
0.8498	0.950 22(1)	0.944 03(9)	0.940 33(1)	0.934 64(0)	0.8504	0.966 18(0)	0.959 59(0)	0.955 04(9)	0.948 73(7)
0.9453	0.935 24(0)	0.928 45(5)	0.924 26(7)	0.917 85(8)	0.9429	0.942 76(8)	0.935 89(8)	0.931 35(4)	0.924 70(0)
Methyl Acetate (1) + Triethylene Glycol (2)					Methyl Acetate (1) + Propylene Glycol (2)				
0.0455	1.115 19(3)	1.111 41(4)	1.107 51(2)	1.105 03(0)	0.0465	1.027 72(1)	1.023 69(9)	1.020 09(8)	1.015 96(0)
0.1522	1.103 73(7)	1.099 72(2)	1.095 80(2)	1.093 05(0)	0.1493	1.016 80(5)	1.012 28(8)	1.008 63(7)	1.004 03(1)
0.2512	1.091 78(8)	1.087 49(1)	1.083 50(1)	1.080 38(4)	0.2510	1.006 23(2)	1.001 34(6)	0.997 58(0)	0.992 61(7)
0.3504	1.078 53(3)	1.073 91(6)	1.069 84(1)	1.066 30(3)	0.3512	0.995 96(4)	0.990 75(8)	0.986 86(0)	0.981 59(2)
0.4457	1.064 43(7)	1.059 49(7)	1.055 35(1)	1.051 39(5)	0.4412	0.986 79(9)	0.981 30(7)	0.977 29(8)	0.971 76(6)
0.4900	1.057 35(2)	1.052 25(8)	1.048 08(8)	1.043 93(8)	0.4906	0.981 76(8)	0.976 11(3)	0.972 05(1)	0.966 37(3)
0.5519	1.046 77(6)	1.041 46(7)	1.037 27(2)	1.032 85(4)	0.5499	0.975 70(8)	0.969 85(1)	0.965 73(2)	0.959 87(8)
0.6512	1.027 79(8)	1.022 13(9)	1.017 92(6)	1.013 08(2)	0.6483	0.965 55(1)	0.959 34(6)	0.955 15(3)	0.949 00(4)
0.7516	1.005 30(6)	0.999 28(1)	0.995 06(0)	0.989 76(5)	0.7483	0.955 01(1)	0.948 45(8)	0.944 20(6)	0.937 77(0)
0.8513	0.978 49(8)	0.972 08(1)	0.967 82(7)	0.962 01(3)	0.8499	0.943 97(0)	0.937 10(9)	0.932 79(4)	0.926 10(7)
0.9424	0.948 80(2)	0.941 98(5)	0.937 63(0)	0.931 21(6)	0.9447	0.933 26(5)	0.926 21(0)	0.921 80(8)	0.914 96(3)
Ethyl Acetate (1) + Diethylene Glycol (2)					Ethyl Acetate (1) + Triethylene Glycol (2)				
0.0441	1.103 89(7)	1.100 06(3)	1.096 40(5)	1.092 83(2)	0.0466	1.112 15(6)	1.108 39(1)	1.104 32(5)	1.101 76(4)
0.1491	1.081 32(6)	1.077 52(2)	1.073 43(1)	1.069 24(5)	0.1482	1.095 30(5)	1.091 27(9)	1.086 97(6)	1.084 07(3)
0.2504	1.059 83(6)	1.055 84(6)	1.051 57(3)	1.047 06(0)	0.2500	1.077 40(3)	1.073 02(7)	1.068 55(6)	1.065 26(1)
0.3491	1.039 00(8)	1.034 73(1)	1.030 34(0)	1.025 66(0)	0.3499	1.058 65(0)	1.053 94(5)	1.049 34(7)	1.045 63(8)
0.4487	1.017 94(8)	1.013 34(6)	1.008 79(5)	1.004 01(7)	0.4493	1.038 63(5)	1.033 67(9)	1.028 96(4)	1.024 82(7)
0.5011	1.006 80(2)	1.002 03(1)	0.997 36(1)	0.992 53(8)	0.4995	1.027 95(3)	1.022 90(8)	1.018 12(9)	1.013 77(4)
0.5485	0.996 65(9)	0.991 74(1)	0.986 94(0)	0.982 07(0)	0.5503	1.016 71(8)	1.011 60(8)	1.006 75(9)	1.002 18(3)
0.6492	0.974 85(1)	0.969 64(4)	0.964 50(6)	0.959 48(8)	0.6497	0.993 40(0)	0.988 21(9)	0.983 20(8)	0.978 19(8)
0.7505	0.952 44(8)	0.946 98(7)	0.941 47(0)	0.936 20(1)	0.7490	0.968 18(2)	0.962 95(0)	0.957 73(0)	0.952 29(0)
0.8492	0.930 05(8)	0.924 36(7)	0.918 52(8)	0.912 88(1)	0.8503	0.940 27(4)	0.934 90(2)	0.929 41(5)	0.923 53(8)
0.9445	0.907 81(9)	0.901 89(7)	0.895 89(6)	0.889 73(8)	0.9417	0.913 03(0)	0.907 33(0)	0.901 55(5)	0.895 28(4)
Ethyl Acetate (1) + Propylene Glycol (2)					Butyl Acetate (1) + Triethylene Glycol (2)				
0.0451	1.024 21(9)	1.020 33(7)	1.016 53(1)	1.012 46(7)	0.0452	1.108 89(1)	1.105 14(4)	1.101 13(4)	1.098 60(7)
0.1493	1.005 58(2)	1.001 36(1)	0.997 21(4)	0.992 76(9)	0.1515	1.083 49(6)	1.079 63(7)	1.075 41(2)	1.072 59(1)
0.2515	0.988 63(2)	0.984 09(1)	0.979 68(1)	0.974 90(8)	0.2488	1.060 06(2)	1.056 08(6)	1.051 65(3)	1.048 53(8)
0.3514	0.973 20(0)	0.968 36(1)	0.963 71(4)	0.958 63(5)	0.3493	1.035 73(3)	1.031 63(6)	1.026 98(5)	1.023 57(7)
0.4393	0.960 46(6)	0.955 37(8)	0.950 52(2)	0.945 17(5)	0.4464	1.012 14(6)	1.007 94(0)	1.003 07(9)	0.999 41(7)
0.5000	0.952 10(1)	0.946 85(1)	0.941 84(5)	0.936 31(3)	0.4953	1.000 24(4)	0.995 98(7)	0.991 02(1)	0.987 24(5)
0.5497	0.945 49(7)	0.940 12(1)	0.934 99(0)	0.929 30(9)	0.5495	0.987 03(6)	0.982 72(3)	0.977 64(5)	0.973 75(1)
0.6505	0.932 74(8)	0.927 13(9)	0.921 75(4)	0.915 78(2)	0.6493	0.962 66(7)	0.958 25(5)	0.952 97(8)	0.948 88(7)
0.7495	0.921 01(9)	0.915 21(8)	0.909 59(5)	0.903 37(2)	0.7488	0.938 29(5)	0.933 77(7)	0.928 31(6)	0.924 03(5)
0.8499	0.909 87(8)	0.903 92(6)	0.898 10(1)	0.891 68(3)	0.8515	0.913 02(6)	0.908 37(8)	0.902 74(6)	0.898 24(4)
0.9487	0.899 61(8)	0.893 57(0)	0.887 61(7)	0.881 09(7)	0.9421	0.890 60(4)	0.885 80(7)	0.880 04(2)	0.875 29(3)
Butyl Acetate (1) + Propylene Glycol (2)					Isoamyl Acetate (1) + Propylene Glycol (2)				
0.0445	1.020 01(0)	1.016 10(6)	1.012 28(7)	1.008 28(6)	0.0455	1.017 21(4)	1.013 29(3)	1.009 48(3)	1.005 69(1)
0.1493	0.993 58(9)	0.989 44(2)	0.985 19(2)	0.980 98(9)	0.1457	0.988 00(0)	0.983 78(4)	0.979 64(5)	0.976 02(7)
0.2487	0.972 28(4)	0.968 01(6)	0.963 42(7)	0.959 09(8)	0.2483	0.963 53(3)	0.959 11(8)	0.954 73(8)	0.951 27(9)
0.3511	0.953 32(0)	0.948 95(9)	0.944 08(9)	0.939 65(1)	0.3508	0.943 13(8)	0.938 57(7)	0.934 01(4)	0.930 68(7)
0.4460	0.937 92(4)	0.933 47(3)	0.928 39(7)	0.923 85(8)	0.4520	0.926 02(1)	0.921 33(8)	0.916 63(1)	0.913 40(8)
0.4973	0.930 34(2)	0.925 83(6)	0.920 66(7)	0.916 07(1)	0.4959	0.919 36(1)	0.914 62(9)	0.909 86(8)	0.906 68(2)
0.5491	0.923 15(4)	0.918 58(8)	0.913 33(6)	0.908 68(1)	0.5551	0.911 01(5)	0.906 21(9)	0.901 38(9)	0.898 24(7)
0.6504	0.910 32(1)	0.905 62(9)	0.900 23(9)	0.895 46(8)	0.6523	0.898 71(2)	0.893 81(6)	0.888 88(7)	0.885 80(3)
0.7495	0.899 15(9)	0.894 34(8)	0.888 84(1)	0.883 97(0)	0.7497	0.887 92(1)	0.882 93(1)	0.877 91(2)	0.874 87(8)
0.8489	0.889 19(5)	0.884 29(5)	0.878 67(0)	0.873 72(7)	0.8495	0.878 28(0)	0.873 20(6)	0.868 10(7)	0.865 12(0)
0.9460	0.880 55(5)	0.875 62(2)	0.869 86(7)	0.864 90(2)	0.9426	0.870 47(9)	0.865 34(5)	0.860 17(8)	0.857 24(3)

3. Results and Discussion

Densities, ρ, and Excess Molar Volumes, V_m^E. The experimental densities, ρ, of methyl acetate + ethylene glycol, + diethylene glycol, + triethylene glycol, and + propylene glycol; ethyl acetate + diethylene glycol, + triethylene glycol, and + propylene glycol; butyl acetate + triethylene glycol and + propylene glycol; and isoamyl acetate + propylene glycol at T = (298.15, 303.15, 308.15, and 313.15) K are listed in Table 2. The V_m^E values were calculated from the measured densities of pure (1 = ester or 2 = glycol) and mixture (12) components, using the relation

$$V_m^E/\text{cm}^3\cdot\text{mol}^{-1} = \frac{x_1M_1 + x_2M_2}{\rho_{12}} - \left\{\frac{x_1M_1}{\rho_1} + \frac{x_2M_2}{\rho_2}\right\} \quad (2)$$

The compositional variation of V_m^E values for the 10 binary mixtures was mathematically expressed by the equation

Table 3. Dynamic Viscosities, η, Speeds of Sound, v, and Relative Permittivities, ϵ_r, for Esters (1) + Glycols (2) at T = (298.15 and 308.15) K

	η/mPa·s		v/m·s^{-1}		ϵ_r			η/mPa·s		v/m·s^{-1}		ϵ_r	
x_1	298.15 K	308.15 K	298.15 K	308.15 K	298.15 K	308.15 K	x_1	298.15 K	308.15 K	298.15 K	308.15 K	298.15 K	308.15 K
Methyl Acetate (1) + Ethylene Glycol (2)							Methyl Acetate (1) + Diethylene Glycol (2)						
0.0444	11.857	8.678	1627	1600	37.941	36.016	0.0406	26.415	14.199	1562	1533	29.447	27.941
0.1488	7.177	5.649	1550	1521	32.667	31.152	0.1512	18.265	8.812	1513	1485	25.989	24.809
0.2505	4.535	3.788	1482	1452	27.826	26.819	0.2516	12.721	5.780	1472	1441	23.302	22.190
0.3485	2.996	2.623	1424	1391	23.526	22.980	0.3488	8.747	3.883	1431	1398	20.890	19.829
0.4411	2.078	1.882	1374	1338	19.849	19.639	0.4400	6.023	2.698	1392	1357	18.683	17.748
0.4856	1.758	1.614	1351	1315	18.225	18.132	0.4926	4.811	2.196	1370	1334	17.407	16.599
0.5507	1.390	1.296	1320	1282	16.036	16.046	0.5504	3.728	1.757	1345	1308	16.000	15.374
0.6503	0.994	0.941	1276	1237	13.109	13.148	0.6509	2.345	1.203	1301	1260	13.555	13.321
0.7489	0.734	0.697	1237	1196	10.726	10.672	0.7510	1.440	0.834	1258	1213	11.196	11.356
0.8498	0.554	0.522	1199	1157	8.809	8.615	0.8504	0.866	0.586	1214	1168	9.087	9.456
0.9453	0.435	0.404	1167	1122	7.455	7.195	0.9429	0.527	0.426	1174	1127	7.527	7.718
Methyl Acetate (1) + Triethylene Glycol (2)							Methyl Acetate (1) + Propylene Glycol (2)						
0.0455	32.014	19.446	1598	1572	22.068	21.202	0.0465	34.285	19.206	1472	1434	26.542	25.109
0.1522	25.742	15.145	1559	1533	20.129	19.660	0.1493	20.441	11.620	1429	1391	23.096	21.905
0.2512	19.759	11.485	1521	1493	18.613	18.218	0.2510	12.351	7.189	1388	1350	20.163	19.082
0.3504	14.274	8.336	1482	1452	17.211	16.763	0.3512	7.576	4.553	1350	1313	17.452	16.478
0.4457	9.869	5.882	1446	1414	15.867	15.356	0.4412	4.915	3.063	1318	1281	15.046	14.222
0.4900	8.158	4.935	1428	1396	15.223	14.698	0.4906	3.887	2.478	1301	1264	13.731	13.017
0.5519	6.128	3.806	1402	1369	14.293	13.773	0.5499	2.939	1.932	1281	1244	12.164	11.613
0.6512	3.687	2.422	1357	1323	12.719	12.274	0.6483	1.859	1.294	1249	1211	9.695	9.454
0.7516	2.075	1.467	1305	1268	11.035	10.727	0.7483	1.176	0.875	1218	1178	7.575	7.631
0.8513	1.103	0.854	1246	1206	9.317	9.146	0.8499	0.744	0.598	1189	1147	6.217	6.433
0.9424	0.587	0.501	1188	1143	7.779	7.640	0.9447	0.489	0.425	1164	1119	6.149	6.220
Ethyl Acetate (1) + Diethylene Glycol (2)							Ethyl Acetate (1) + Triethylene Glycol (2)						
0.0441	26.538	14.599	1557	1527	29.415	27.891	0.0466	30.140	18.654	1592	1567	22.281	21.191
0.1491	19.331	10.139	1501	1467	26.107	24.943	0.1482	22.048	13.708	1547	1523	20.621	19.692
0.2504	13.792	7.076	1444	1410	23.206	22.225	0.2500	15.585	9.818	1499	1473	18.957	18.146
0.3491	9.631	4.946	1393	1358	20.577	19.710	0.3499	10.731	6.905	1452	1426	17.301	16.604
0.4487	6.504	3.420	1346	1311	18.062	17.307	0.4493	7.167	4.749	1408	1379	15.621	15.054
0.5011	5.226	2.808	1322	1287	16.785	16.095	0.4995	5.775	3.896	1386	1356	14.758	14.267
0.5485	4.257	2.345	1301	1267	15.650	15.029	0.5503	4.602	3.168	1363	1333	13.876	13.465
0.6492	2.692	1.591	1261	1226	13.299	12.851	0.6497	2.881	2.076	1318	1286	12.128	11.881
0.7505	1.645	1.068	1223	1188	11.026	10.755	0.7490	1.748	1.329	1271	1236	10.365	10.258
0.8492	0.988	0.719	1189	1151	8.916	8.778	0.8503	1.015	0.823	1220	1181	8.569	8.536
0.9445	0.587	0.487	1157	1116	7.016	6.888	0.9417	0.604	0.523	1171	1130	6.979	6.894
Ethyl Acetate (1) + Propylene Glycol (2)							Butyl Acetate (1) + Triethylene Glycol (2)						
0.0451	32.316	19.383	1463	1429	26.908	25.360	0.0452	31.196	18.956	1586	1559	22.136	21.031
0.1493	16.843	11.715	1401	1371	23.637	22.302	0.1515	24.062	14.161	1524	1498	19.897	18.991
0.2515	9.278	7.280	1343	1317	20.629	19.513	0.2488	18.288	10.622	1470	1446	17.842	17.106
0.3514	5.396	4.653	1294	1268	17.923	17.008	0.3493	13.276	7.731	1420	1395	15.808	15.23
0.4393	3.463	3.184	1255	1229	15.752	14.992	0.4464	9.402	5.575	1375	1350	13.981	13.536
0.5000	2.597	2.469	1232	1205	14.374	13.704	0.4953	7.798	4.694	1355	1329	13.119	12.734
0.5497	2.075	2.014	1215	1186	13.316	12.712	0.5495	6.273	3.856	1334	1307	12.209	11.882
0.6505	1.357	1.351	1186	1153	11.359	10.861	0.6493	4.084	2.642	1298	1267	10.637	10.398
0.7495	0.930	0.928	1164	1128	9.658	9.240	0.7488	2.566	1.776	1265	1232	9.149	8.972
0.8499	0.661	0.645	1149	1109	8.112	7.763	0.8515	1.528	1.153	1233	1197	7.595	7.448
0.9487	0.491	0.459	1140	1098	6.704	6.438	0.9421	0.936	0.774	1207	1168	6.089	5.943
Butyl Acetate (1) + Propylene Glycol (2)							Isoamyl Acetate (1) + Propylene Glycol (2)						
0.0445	31.874	18.512	1467	1429	26.269	24.784	0.0455	31.606	18.401	1460	1425	26.057	24.589
0.1493	16.098	10.192	1407	1372	21.899	20.754	0.1457	16.423	10.429	1398	1369	21.589	20.423
0.2487	8.935	6.083	1355	1322	18.412	17.56	0.2483	8.962	6.168	1346	1320	17.773	16.862
0.3511	5.175	3.762	1310	1280	15.381	14.787	0.3508	5.224	3.864	1304	1281	14.600	13.914
0.4460	3.295	2.523	1276	1246	13.007	12.603	0.4520	3.269	2.574	1270	1248	12.009	11.526
0.4973	2.638	2.071	1260	1230	11.878	11.552	0.4959	2.721	2.196	1258	1235	11.038	10.635
0.5491	2.141	1.719	1247	1217	10.837	10.575	0.5551	2.165	1.802	1243	1220	9.864	9.563
0.6504	1.489	1.241	1226	1194	9.058	8.885	0.6523	1.560	1.357	1223	1199	8.255	8.095
0.7495	1.106	0.947	1210	1178	7.616	7.476	0.7497	1.191	1.075	1211	1182	7.014	6.938
0.8489	0.870	0.759	1200	1165	6.418	6.279	0.8495	0.961	0.893	1202	1169	6.098	6.02
0.9460	0.727	0.640	1194	1155	5.456	5.304	0.9426	0.831	0.788	1197	1160	5.548	5.343

of the type

$$A^E = x_1(1 - x_1)\sum_{i=0}^{i=n} a_i(2x_1 - 1)^i \qquad (3)$$

where $A^E = V_m^E$, a_i are the parameters, and x_1 is the ester mole fraction. The a_i were estimated using multiple regression analysis based on a least-squares method. The values of a_i along with the standard deviations, σ, are given in Table 6. The V_m^E versus x_1 profiles at different temperatures, in general, have several common features. A representative plot showing the variation of V_m^E as a function of mole fractions of esters at T = 298.15 K is shown in Figure 1. The V_m^E values of the binary mixtures except for the ethyl acetate, butyl acetate, and isoamyl acetate + propylene glycol systems were negative over the whole mole fraction, and the profiles were skewed toward the ester rich region. In contrast, the V_m^E values for the esters + propylene glycol were small and positive. For a given ester, the V_m^E values, especially in the mole fraction range ≈0.4−0.5, became more negative from ethylene glycol to its dimeric and trimeric forms. Similarly, the increase in the length

Table 4. Adjustable Parameters of Eqs 4−6 for the Correlation of Mixture Viscosities at T = (298.15 and 308.15) K

T/K	G_{12}	σ	Mc_{12}	Mc_{21}	σ	A_{21}	B_{21}	B_{12}	σ
Methyl Acetate (1) + Ethylene Glycol (2)									
298.15	−1.433	0.001	−0.194	0.965	0.001	0.101	0.579	0.509	0.001
308.15	−0.887	0.001	−0.181	0.894	0.001	0.138	0.660	0.584	0.001
Methyl Acetate (1) + Diethylene Glycol (2)									
298.15	−1.266	0.001	0.871	2.343	0.001	0.283	0.186	0.836	0.002
308.15	−0.537	0.001	0.031	1.337	0.001	0.142	0.454	0.617	0.001
Methyl Acetate (1) + Triethylene Glycol (2)									
298.15	3.056	0.001	1.550	2.996	0.001	0.354	0.257	0.480	0.002
308.15	2.198	0.001	1.055	2.367	0.001	0.387	0.259	0.710	0.001
Methyl Acetate (1) + Propylene Glycol (2)									
298.15	−0.376	0.001	0.527	2.073	0.001	0.107	0.272	0.538	0.001
308.15	−0.811	0.01	0.140	1.517	0.001	0.105	0.420	0.526	0.001
Ethyl Acetate (1) + Diethylene Glycol (2)									
298.15	1.528	0.001	1.101	2.454	0.001	0.332	0.221	0.852	0.002
308.15	0.383	0.001	0.474	1.666	0.001	0.239	0.430	0.784	0.001
Ethyl Acetate (1) + Triethylene Glycol (2)									
298.15	1.626	0.001	1.170	2.560	0.001	0.309	0.204	0.819	0.002
308.15	1.212	0.001	0.814	2.078	0.001	0.311	0.303	0.838	0.001
Ethyl Acetate (1) + Propylene Glycol (2)									
298.15	−2.028	0.001	0.094	1.562	0.001	0.060	0.320	0.390	0.001
308.15	−0.863	0.001	0.234	1.537	0.001	0.106	0.478	0.527	0.001
Butyl Acetate (1) + Triethylene Glycol (2)									
298.15	1.855	0.001	1.575	2.777	0.001	0.429	0.276	0.858	0.001
308.15	1.041	0.001	1.067	2.153	0.001	0.379	0.384	0.943	0.001
Butyl Acetate (1) + Propylene Glycol (2)									
298.15	−2.918	0.001	0.130	1.458	0.001	0.054	0.308	0.373	0.001
308.15	−2.463	0.001	0.015	1.187	0.001	0.070	0.442	0.431	0.001
Isoamyl Acetate (1) + Propylene Glycol (2)									
298.15	−3.110	0.001	0.170	1.496	0.001	0.056	0.267	0.386	0.001
308.15	−2.703	0.001	0.095	1.237	0.001	0.075	0.362	0.456	0.001

Table 5. Physicochemical Properties at T = (298.15 and 308.15) K for the Pure Components

	V_T/cm³·mol⁻¹	V_0/cm³·mol⁻¹	V_a/cm³·mol⁻¹	L_f/Å	Y	S	B/cm³·mol⁻¹	r_j/Å	$C_p{}^a$/J·K⁻¹·mol⁻¹	α^b/k·K⁻¹
T = 298.15 K										
methyl acetate	79.930	62.108	17.821	0.557	64.04	2.890	19.881	1.990	140.6[48]	1.400
ethyl acetate	98.494	76.480	22.012	0.599	73.57	2.858	24.509	2.134	170.6[49]	1.379
butyl acetate	132.574	106.736	25.838	0.562	91.88	2.986	33.023	2.357	228.1[49]	1.185
isoamyl acetate	150.292	122.487	27.805	0.552	100.71	2.998	37.444	2.458	248.5[40]	1.138
ethylene glycol	55.917	47.601	8.215	0.310	53.632	4.169	13.931	1.768	150.8[41]	0.637
diethlene glycol	95.303	82.765	12.538	0.323	77.55	3.961	23.762	2.112	244.7[50]	0.653
triethylene glycol	134.320	117.678	16.454	0.336	98.06	4.039	33.458	2.367	328.2[50]	0.702
propylene glycol	73.682	62.418	11.263	0.351	64.24	3.743	18.358	1.938	190.8[40]	0.729
T = 308.15 K										
methyl acetate	80.941		18.833	0.588		2.773	20.125	1.998	143.9[48]	1.450
ethyl acetate	99.837		23.357	0.635		2.751	24.838	2.144	172.8[49]	1.418
butyl acetate	134.222		27.485	0.598		2.886	33.424	2.367	230.6[49]	1.208
isoamyl acetate	152.112		29.625	0.588		2.896	37.889	2.468	251.3[40]	1.158
ethylene glycol	56.268		8.667	0.323		4.102	14.019	1.772	154.1[41]	0.646
diethlene glycol	95.931		13.170	0.340		3.886	23.915	2.117	249.1[50]	0.658
triethylene glycol	135.053		17.375	0.354		3.974	33.688	2.373	334.0[50]	0.707
propylene glycol	74.210		11.791	0.367		3.648	18.486	1.943	193.6[40]	0.745

[a] The values for methyl acetate, isoamyl acetate, and propylene glycol at T = 308.15 K are interpolated from temperature-dependent data. [b] α_i interpolated values using a linear equation relating α_i and T = (298.15 to 348.15 K). The individual values for each temperature were calculated from the measured densities at two successive temperatures using the relation $\alpha_i = ((\rho_1/\rho_2) - 1)/\Delta T$.

of the alkyl chain from methyl to ethyl and to butyl in the respective esters drastically decreased the negative magnitude of V_m^E in di- and triethylene glycol containing mixtures. The rise in the temperature has been found to increase the negative magnitudes of V_m^E values in all the mixtures. As far as we are aware, there exists only one report[15] for the V_m^E values of methyl acetate + ethylene glycol at T = 298.15 K. Our calculated $(V_m^E)_{0.5}$ value of −0.476 cm³·mol⁻¹ for methyl acetate + ethylene glycol at (T = 298.15 K) is 0.006 cm³·mol⁻¹ more negative than the literature value of −0.470 cm³·mol⁻¹ for the same system and at the same temperature.[15] We believe that our V_m^E values are more accurate than the pycnometrically derived data of Aminabhavi and Banerjee.[15] At equimolar composition, our calculated $(V_m^E)_{0.5}$ value of −0.476 cm³·mol⁻¹ (at T = 298.15 K) for methyl acetate + diethylene glycol is not only in sign disagreement but also 3.4 times lower in magnitude than the value of 0.2020 cm³·mol⁻¹ for methyl acetate + ethanol[7] at the same temperature. Similarly, our reported equimolar V_m^E values of −0.462, −0.510, and −0.537 for ethylene glycol + diethylene glycol mixtures (at 298.15, 303.15, and 308.15) K, respectively, have been found to differ not only in sign but also less in magnitude by 2.4, 2.7, and 2.5 times from 0.3415,[8] 0.303,[13] and 0.269[10]

Table 6. Parameters of Eq 3 for the Mathematical Representation of Excess and Deviation Functions for Esters (1) + Glycols (2) at Different Temperatures

	T/K	a_0	a_1	a_2	σ	a_0	a_1	a_2	σ
		Methyl Acetate (1) + Ethylene Glycol (2)				Methyl Acetate (1) + Diethylene Glycol (2)			
V_m^E/cm^3·mol^{-1}	298.15	−1.902	−0.051	−0.230	0.001	−2.651	−2.148	−1.082	0.001
	303.15	−2.262	−0.336	0.082	0.001	−2.643	−2.149	−1.334	0.001
	308.15	−2.648	−0.577	0.249	0.001	−2.641	−2.094	−1.213	0.001
	313.15	−3.033	−0.973	0.324	0.001	−2.662	−2.155	−1.320	0.001
δv/m·s^{-1}	298.15	−66.7	13.1	2.1	0.5	−68.9	−2.2	−25.1	0.5
	308.15	−54.6	10.7	23.4	0.5	−62.4	−34.6	−18.8	0.7
κ_s^E/TPa^{-1}	298.15	−472.8	74.3	−25.9	0.4	−395.8	−156.5	−34.6	0.2
	308.15	−589.7	64.2	−38.1	0.5	−476.3	−171.4	−23.4	0.3
$\delta\epsilon_r$	298.15	−11.535	−4.523	2.366	0.001	−10.881	−0.867	−7.787	0.001
	308.15	−7.764	−4.199	−1.957	0.001	−9.676	1.813	−0.104	0.001
		Methyl Acetate (1) + Triethylene Glycol (2)				Methyl Acetate (1) + Propylene Glycol (2)			
V_m^E/cm^3·mol^{-1}	298.15	−3.280	−2.297	−1.592	0.001	−0.999	−0.678	−0.107	0.001
	303.15	−3.332	−2.311	−1.717	0.001	−0.982	−0.687	0.054	0.001
	308.15	−3.368	−2.361	−1.895	0.001	−0.999	−0.669	−0.043	0.001
	313.15	−3.462	−2.407	−2.172	0.001	−0.962	−0.680	0.091	0.001
δv/m·s^{-1}	298.15	−64.4	−12.4	3.3	2.7	−66.7	−1.9	0.4	0.4
	308.15	−53.8	−11.8	7.3	3.3	−42.3	9.9	−4.1	0.5
κ_s^E/TPa^{-1}	298.15	−366.0	−306.9	−171.3	0.3	−292.5	−19.7	5.0	0.3
	308.15	−445.7	−375.8	−233.1	0.5	−369.7	−52.2	1.0	0.4
$\delta\epsilon_r$	298.15	−7.723	0.682	−4.788	0.001	−14.806	−10.162	−13.800	0.001
	308.15	−6.431	−1.295	−0.082	0.001	−13.873	−7.853	−8.738	0.001
		Ethyl Acetate (1) + Diethylene Glycol (2)				Ethyl Acetate (1) + Triethylene Glycol (2)			
V_m^E/cm^3·mol^{-1}	298.15	−1.848	−1.308	−0.072	0.001	−1.598	−0.558	0.179	0.001
	303.15	−2.038	−1.137	−0.274	0.001	−1.547	−0.784	−0.325	0.001
	308.15	−2.148	−1.191	0.196	0.001	−1.654	−0.972	−0.263	0.001
	313.15	−2.300	−1.702	−0.243	0.001	−1.721	−0.947	−0.320	0.001
δv/m·s^{-1}	298.15	−133.3	−9.4	66.0	0.8	−103.5	11.7	36.4	1.1
	308.15	−123.7	8.6	77.5	1.5	−85.3	0.21	46.8	1.6
κ_s^E/TPa^{-1}	298.15	−377.9	−41.8	−51.1	0.2	−383.6	−226.6	−114.7	0.3
	308.15	−456.4	−87.4	−88.1	0.4	−471.7	−280.2	−148.7	0.5
$\delta\epsilon_r$	298.15	−5.759	1.515	−2.025	0.001	−4.308	−1.231	−0.982	0.001
	308.15	−4.480	1.146	0.903	0.001	−3.067	−0.019	0.862	0.001
		Ethyl Acetate (1) + Propylene Glycol (2)				Butyl Acetate (1) + Triethylene Glycol (2)			
V_m^E/cm^3·mol^{-1}	298.15	0.577	0.078	0.062	0.001	−0.264	0.016	−0.249	0.001
	303.15	0.609	0.149	0.074	0.001	−0.368	0.043	−0.329	0.001
	308.15	0.587	0.194	0.204	0.001	−0.425	−0.007	−0.340	0.001
	313.15	0.597	0.288	0.321	0.001	−0.493	−0.093	−0.534	0.001
δv/m·s^{-1}	298.15	−228.4	−32.4	21.4	0.5	−197.5	20.9	52.3	0.9
	308.15	−174.9	−75.0	23.9	0.4	−166.3	21.2	16.7	0.4
κ_s^E/TPa^{-1}	298.15	−125.8	176.4	−18.9	0.4	−206.3	−26.3	−36.0	0.3
	308.15	−221.8	214.4	21.1	0.8	−275.4	−38.9	−23.6	0.3
$\delta\epsilon_r$	298.15	−4.784	−0.024	1.962	0.001	−4.158	1.804	4.033	0.001
	308.15	−4.063	−0.067	1.163	0.001	−2.864	2.022	3.977	0.001
		Butyl Acetate (1) + Propylene Glycol (2)				Isoamyl Acetate (1) + Propylene Glycol (2)			
V_m^E/cm^3·mol^{-1}	298.15	0.960	0.101	0.310	0.001	1.094	0.233	0.580	0.001
	303.15	0.945	0.128	0.482	0.001	1.086	0.218	0.654	0.001
	308.15	0.960	0.083	0.416	0.001	1.090	0.202	0.687	0.001
	313.15	0.951	0.123	0.541	0.001	1.090	0.212	0.729	0.001
δv/m·s^{-1}	298.15	−156.6	−26.5	97.1	1.3	−145.3	4.7	22.6	0.6
	308.15	−115.1	−20.4	68.3	0.8	−74.5	−2.7	25.6	0.7
κ_s^E/TPa^{-1}	298.15	−84.0	172.0	−108.7	0.4	−68.8	180.9	−76.1	0.4
	308.15	−143.8	167.7	−100.2	0.3	−165.2	176.8	−9.5	0.4
$\delta\epsilon_r$	298.15	−6.116	1.031	0.075	0.001	−7.877	−1.243	0.473	0.001
	308.15	−4.557	1.074	−0.589	0.001	−6.243	0.052	1.588	0.003

for the ethyl acetate + 1-pentanol mixtures at the corresponding temperatures. The IR and microwave spectroscopic studies[17−20] on gas and liquid phases of glycol molecules and the gas-phase electron diffraction experimental[21,22] and theoretical ab initio molecular orbital and molecular mechanics calculations[23−25] indicated that the gauche form with an intramolecular hydrogen bond in the glycols is more stable energetically than the trans form. Not only this, the theoretical quantum solvation calculations[26−28] further unambiguously revealed that the intramolecular hydrogen bonds in glycols were still retained upon hydration. So, it is clear that the positive contributions emanating from the depolymerization effects as observed for 1-alcohols are supposed to be the bare minimum in esters + glycol systems while formation of ester···glycol complexes is quite likely. The observed positive V_m^E values in ethyl acetate, butyl acetate, and isoamyl acetate + propylene glycol indicate that the $-CH_3$ group of the latter causes steric hindrance. The large and negative V_m^E values for esters + glycols over esters + 1-alcohols mixtures, in general, indicate the presence of weak interactions between the carbonyl oxygen of the ester and the two −OH groups of the glycols on one hand and the carbonyl carbon of the ester and the etheric oxygen of the dimeric/trimeric glycols on the other hand.[29,30]

Viscosities and Their Correlation. The experimental data of dynamic viscosities, η_{12}, for the 10 binary mixtures

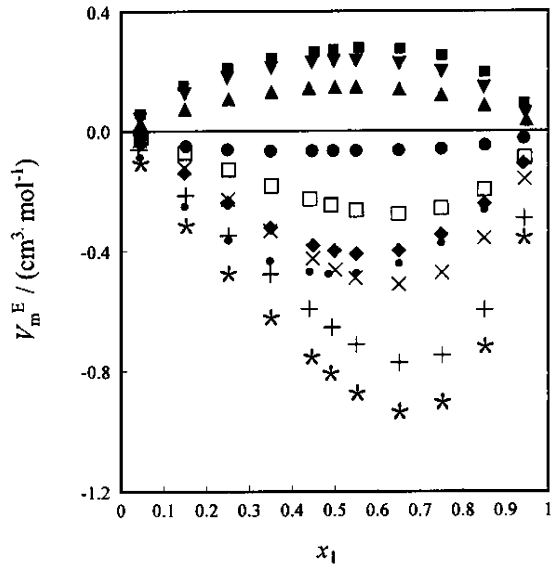

Figure 1. Variation of excess molar volumes, V_m^E, with ester mole fraction for the binary mixtures of esters + glycols at T = 298.15 K: methyl acetate + (·) ethylene glycol, + (+) diethylene glycol, + (∗) triethylene glycol, + (□) propylene glycol; ethyl acetate + (×) diethylene glycol, + (◆) triethylene glycol, + (▲) propylene glycol; butyl acetate + (●) triethylene glycol, + (▼) propylene glycol; and isoamyl acetate + (■) propylene glycol.

at T = (298.15 and 308.15) K are listed in Table 3. The mixture viscosities were also correlated through one parameter Grunberg−Nissan,[31] two parameter McAllister,[32] and three parameter Auslander[33] equations:

$$\ln \eta_{12} = x_1 \ln \eta_1 + x_2 \ln \eta_2 + x_1 x_2 G_{12} \tag{4}$$

$$\ln \nu_{12} = {x_1}^3 \ln \nu_1 + 3{x_1}^2 x_2 \ln Mc_{12} + 3x_1{x_2}^2 \ln Mc_{21} + {x_2}^3 \ln \nu_2 - \ln\left(x_1 + \frac{x_2 M_2}{M_1}\right) + 3{x_1}^2 x_2 \ln\left(\frac{2}{3} + \frac{M_2}{3M_1}\right) + 3x_1{x_2}^2 \ln\left(\frac{1}{3} + \frac{2M_2}{3M_1}\right) + {x_2}^3 \ln\left(\frac{M_2}{M_1}\right) \tag{5}$$

$$x_1(x_1 + B_{12}x_2)(\eta_{12} - \eta_1) + A_{21}x_2(B_{21}x_1 + x_2)(\eta_{12} - \eta_2) = 0 \tag{6}$$

where ν is the kinematic viscosity. The terms G_{12}, Mc_{12}, Mc_{21}, A_{21}, B_{21}, and B_{12} in the above equations were treated as adjustable parameters, and their values were estimated using a nonlinear regression analysis based on a least-squares method. The summary of the analysis along with the standard deviations, σ, between experimental and correlated values is given in Table 4. The σ values ranged from 0.001 to 0.002, indicating that these three equations adequately correlate the mixture viscosities.

Speeds of Sound, v, and Excess Isentropic Compressibilities, κ_s^E. The experimental values for the speeds of sound, v, in the binary mixtures are listed in Table 3. The v values were also calculated using free length[34] and collision factor[35] theories and the Junjie (as given in ref 36) and Nomoto equations.[37] Various characteristic properties (needed in the calculations) such as molar volume, V_T, molar volume at absolute zero, V_0, available volume, V_a, free length, L_f, surface area, Y, actual volume per mole, B_i, molecular radius, r_j, and molar heat capacities, C_p, for the pure components at both the temperatures are listed in Table 5. The percentage standard deviations, σ/%, between experimental and calculated values ranged from

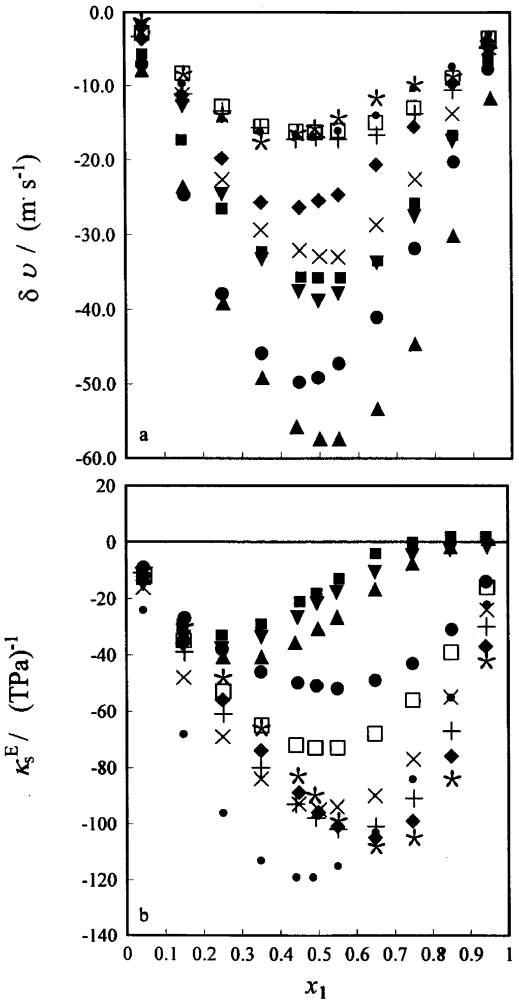

Figure 2. Variation of (a) deviation in speeds of sound, δv, and (b) excess isentropic compressibilities, κ_s^E, with ester mole fraction for the binary mixtures of esters + glycols at T = 298.15 K. (The symbols are same as those shown in Figure 1.)

0.3 to 4.5 for the collision factor theory and Nomoto equations while other approaches yielded large deviations. The deviations in speeds of sound, δv, and κ_s^E were calculated using the relations

$$\delta v / \mathrm{m \cdot s^{-1}} = v_{12} - (\phi_1 v_1 + \phi_2 v_2) \tag{7}$$

$$\kappa_s^E / \mathrm{TPa^{-1}} = \kappa_s - \kappa_s^{id} \tag{8}$$

where κ_s is the isentropic compressibility and was calculated using the Laplace equation, that is, $\kappa_s = 1/v^2\rho$ and κ_s^{id} was calculated from the relation

$$\kappa_s^{id} = \sum_{i=1}^{2} \phi_i[\kappa_{s,i} + TV_i({a_i}^2)/C_{p,i}] - \{T(\sum_{i=1}^{2} x_i V_i)(\sum_{i=1}^{2} \phi_i a_i)^2 / \sum_{i=1}^{2} x_i C_{p,i}\} \tag{9}$$

and ϕ_i is the ideal state volume fraction and is defined by the relation

$$\phi_i = x_i V_i / (\sum_{i=1}^{2} x_i V_i) \tag{10}$$

These functions were also expressed mathematically to

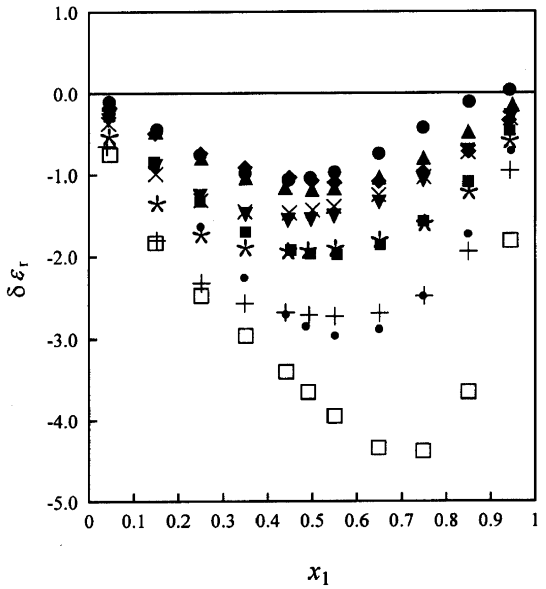

Figure 3. Variation of relative permittivity deviations, $\delta\epsilon_r$, with ester mole fraction for the binary mixtures of esters + glycols at $T = 298.15$ K. (The symbols are same as those shown in Figure 1.)

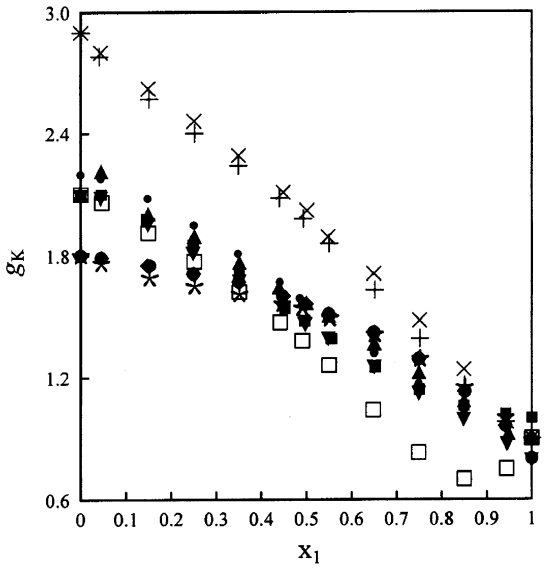

Figure 4. Variation of Kirkwood correlation factor, g_K, with ester mole fraction for the binary mixtures of esters + glycols at $T = 298.15$ K. (The symbols are same as those shown in Figure 1.)

judge the internal consistency of the data using eq 3. The values of the least-squares coefficients, a_i, and standard deviations, σ, are listed in Table 6. A representative graphical variation of δv and κ_s^E values as a function of ester mole fraction at $T = 298.15$ K is shown in Figure 2. It can be seen that δv and κ_s^E values in these mixtures in general are large and negative over the whole composition. However, for the ethyl acetate, butyl acetate, and isoamyl acetate + propylene glycol mixtures, the κ_s^E versus x_1 profiles were asymmetric and sigmoidal with negative values over most of the composition range followed by a few close to zero or slight positive values in the ester rich region. The rise in the temperature from $T = 298.15$ to 308.15 K always resulted in more negative κ_s^E values. The observed large and negative κ_s^E values indicate that the mixed components have molecular species that occupy smaller volumes in space and hence have less compressions.

Relative Permittivities, ϵ_r, and Deviations in Relative Permittivities, $\delta\epsilon_r$. The experimental relative permittivities, ϵ_r, for the 10 binary mixtures of esters + glycols are listed in Table 3. The deviations in relative permittivities, $\delta\epsilon_r$, were calculated using the relation

$$\delta\epsilon_r = \epsilon_{r,12} - \sum \phi_i \epsilon_{r,i} \tag{11}$$

The compositional variation of $\delta\epsilon_r$ was mathematically expressed by eq 3, and the calculated values for the parameters, a_i, along with the σ values are summarized in Table 6. The graphical representation of $\delta\epsilon_r$ as a function of ester mole fraction is given in Figure 3. The profiles for the binary mixtures except for that of butyl acetate + triethylene glycol are large and negative over the whole composition and at both the temperatures. The latter system was, however, characterized by an asymmetric profile with negative $\delta\epsilon_r$ values followed by small and positive values in the ester rich region.

Further examination of $\delta\epsilon_r$ versus x_1 profiles showed that the negative magnitudes around equimolar composition systematically become less in a given acetate (methyl or ethyl) with the increase in the number of oxyethylene units in the glycols. The same is found to be true for a given glycol (diethylene or triethylene) with the increase in the alkyl chain length of the esters (from methyl to butyl). No systematic trend in $\delta\epsilon_r$ values was observed for esters + propylene glycol mixtures. The rise in temperature also resulted in less negative $(\delta\epsilon_r)_{0.5}$ values.

The Kirkwood correlation parameter, g_K, which depends only on the number of neighbors of a molecule and their relative configuration, was calculated from the relation

$$g_K = \left\{\frac{(\epsilon_{r,12} - \epsilon_\alpha)(2\epsilon_{r,12} + \epsilon_\alpha)}{\epsilon_{r,12}(\epsilon_\alpha + 2)^2}\right\}\left\{\frac{9kT}{4\pi N(x_1\mu_1 + x_2\mu_2)^2}\right\}V_{m,12} \tag{12}$$

where k and μ_i are the Boltzmann constant and the dipole moment of the pure components. ϵ_α is equated to $1.1n_D^2$, where n_D is the refractive index. The variation of g_K with the ester mole fraction has been depicted in Figure 4. It can be seen from the figure that the g_K values of pure esters are around unity, which is expected of normal polar liquids. The variations in g_K versus x_1 profiles in the binary mixtures of ester + glycols are found to be typical. The initial invariance in g_K values indicates that the addition of a small amount of any of the four esters to ethylene, propylene, and triethylene glycols does not alter the associate structures in the latter. The linear decrease of g_K values over the whole composition in methyl and ethyl acetate + diethylene glycol mixtures indicates that the dipolar alignment in the mixed species gets systematically perturbed. The lower g_K values at ester rich composition for the esters + propylene glycol mixtures hint that the mixed species in these mixtures are structureless.

Acknowledgment

The authors thank Prof. Dr. R. M. Patel, head, Department of Chemistry, Sardar Patel University, for providing necessary laboratory facilities.

Literature Cited

(1) Fernandez, J.; Pintos, M.; Baluja, M. C.; Jimenez, E.; Paz Andrade, M. I. Excess Enthalpies of Some Ester + Alcohol Binary Mixtures. *J. Chem. Eng. Data* **1985**, *30*, 318−320.

(2) Navarro, J. M.; Baloira, M.; Bravo, R.; Paz Andrade, M. I.; Pintos, M. Excess Enthalpies of (*n*-Alkanol + Ethyl Ethanoate or Ethyl propanoate) at 298.15 K. *J. Chem. Thermodyn.* **1985**, *17*, 447−451.

(3) Lopez, M.; Paz Andrade, M. I.; Fernandez, J.; Rodriguez-Nunez, E.; Ortega, J. Excess Molar Enthalpies at 298.15 K of (an *n*-Alkyl Formate + an *n*-Alkanol) I. {xHCO_2 $(CH_2)_2$ CH_3 + (1-x) C_nH_{2n+1} OH} (n = 3 to 10). *J. Chem. Thermodyn.* **1986**, *18*, 1003−1006.

(4) Sarmiento, F.; Lopez, M.; Paz Andrade, M. I.; Fernandez, J.; Ortega, J.; Pena, J. A. Excess Enthalpies at 298.15 K of (an *n*-Alkyl Formate + an *n*-Alkanol) III. {xHCO_2 $(CH_2)_2$ CH_3 + (1-x) $C_nH_{2\ n+1}$ OH} (n = 3 to 10). *J. Chem. Thermodyn.* **1988**, *20*, 1315−1319.

(5) Ortega, J.; Bravo, R.; Jimenez, E.; Paz Andrade, M. I. Excess Molar Volumes of (Ethyl Formate + Each of Several Alkanols at 298.15 K. *J. Chem. Thermodyn.* **1986**, *18*, 403−406.

(6) Ortega, J. Excess Molar Volumes of Binary Mixtures of Butyl Formate with Normal Alcohols at 298.15 K. *J. Chem. Eng. Data* **1985**, *30*, 465−467.

(7) Ortega, J.; Susial, P. Excess Molar Volumes of Mixtures Containing Methyl Alkanoates (Acetate, Propanoate, and Butanoate) with Normal Alkanols (from Ethanol to Pentan-1-ol). *Can. J. Chem.* **1989**, *67*, 1120−1124.

(8) Ortega, J.; Pena, J. A.; Paz Andrade, M. I. Excess Molar Volumes of Binary Mixtures of Ethyl Acetate and Propyl Acetate with Normal Alkanols. *Aust. J. Chem.* **1986**, *39*, 1685−1690.

(9) Ortega, J. Excess Molar Volumes of Ethyl Propanoate or Ethyl Butanoate + *n*-Alkanol at 298.15 K. *J. Indian Chem. Soc.* **1986**, *LXIII*, 961−964.

(10) Qin, A.; Hoffman, D. E.; Munk, P. Excess Volumes of Mixtures of Some Alkyl Esters and Ketones with Alkanols. *Collect. Czech. Chem. Commun.* **1993**, *58*, 2625−2641.

(11) Ortega, J.; Matos, J. S.; Paz Andrade, M. I.; Jimenez, E. Excess Molar Volumes of (Ethyl Formate or Ethyl Acetate + an Isomer of Hexanol) at 298 K. *J. Chem. Thermodyn.* **1985**, *17*, 1127−1132.

(12) Nikam, P. S.; Mahale, T. R.; Hasan, M. Density and Viscosity of Binary Mixtures of Ethyl Acetate with Methanol, Ethanol, Propan-1-ol, Propan-2-ol, Butan-1-ol, 2-Methylpropan-1-ol, and 2-Methylpropan-2-ol at (298.18, 303.15 and 308.15) K. *J. Chem. Eng. Data* **1996**, *41*, 1055−1058.

(13) Nikam, P. S.; Mahale, T. R.; Hasan, M. Densities and Viscosities for Ethyl Acetate + Pentan-1-ol, + Hexan-1-ol, + 3, 5, 5-Trimethylhexan-1-ol, + Heptan-1-ol, + Octan-1-ol, and + Decan-1-ol at (298.15, 303.15, and 308.15) K. *J. Chem. Eng. Data* **1998**, *43*, 436−440.

(14) Canosa, J.; Rodriguez, A.; Tojo, J. Dynamic Viscosities of (Methyl Acetate or Methanol) with (Ethanol, 1-Propanol, 2-Propanol, 1-Butanol, and 2-Butanol) at 298.15 K. *J. Chem. Eng. Data* **1998**, *43*, 417−421.

(15) Aminabhavi, T. M.; Banerjee, K. Density, Viscosity, Refractive Index and Speed of Sound in Binary Mixtures of Methyl Acetate + Ethylene Glycol or + Poly(ethylene glycol) in the Temperature Interval (298.15−308.15) K. *J. Chem. Eng. Data* **1998**, *43*, 852−855.

(16) Sastry, N. V.; Raj, M. M. Dielectric Constants, Molar Polarizations, and Refractive Indices for 2-Butoxyethanol + Hexane and + Heptane at 30 °C and 40 °C. *J. Solution Chem.* **1996**, *25*, 1137−1149.

(17) Buckley, P.; Giguere, P. A. Infrared Studies on Rotational Isomerism. *Can. J. Chem.* **1967**, *45*, 397−407.

(18) Caminati, W.; Corbelli, G. Conformation of Ethylene Glycol from the rotational Spectra of the Non-Tunneling o-Monodeuterated Species. Conformation and Hydrogen Bond in 1,2-propanediols. *J. Mol. Spectrosc.* **1981**, *90*, 572−578.

(19) Krueger, P. J.; Mettee, H. D. Spectroscopic Studies of Alcohols. Part VII. Intramolecular Hydrogen Bonds in Ethylene Glycol and 2-Methoxyethanol. *J. Mol. Spectrosc.* **1965**, *18*, 131−140.

(20) Matsuura, H.; Hiraishi, M.; Miyazawa, T. Raman Spectra and Energy Difference Between Rotational Isomers of Ethylene Glycol. *Spectrochim. Acta* **1972**, *28A*, 2299−2304.

(21) Caminati, W. Conformation and Hydrogen Bond in 1,2-Propanediol. *J. Mol. Spectrosc.* **1981**, *86*, 193−201.

(22) Bastiansen, O. Intramolecular Hydrogen Bonds in Ethylene Glycol, Glycerol and Ethylene Chlorohydrin. *Acta Chem. Scand.* **1949**, *3*, 415−421.

(23) Kazeorouni, M. R.; Hedberg, L.; Hedberg, K. Conformational Analysis. 21. Ethane-1,2-diol. An Electron-Diffraction Investigation, Augmented by Rotation Constants and ab Initio Calculations of the Molecular Structure, Conformational Composition, SQM Vibrational Field, and Anti-Gauche Energy Difference with Implicit Internal Hydrogen Bonding. *J. Am. Chem. Soc.* **1997**, *119*, 8324−8331.

(24) Yeh, T.-S.; Chang, Y.-P.; Su, T.-M.; Chao, I. Global Conformational Analysis of 1,2-Ethanediol. *J. Phys. Chem.* **1994**, *98*, 8921−8929.

(25) Nagy, P. I.; Dunn, W. I., III; Alagona, G.; Ghio, C. Theoretical Calculations in 1,2-Ethanediol. 2. Equilibrium of the Gauche Conformers with and without an Intramolecular Hydrogen Bond in Aqueous Solution. *J. Am. Chem. Soc.* **1992**, *114*, 4752−4758.

(26) Van Alsenoy, C.; Van Den Enden; Schafer, L. Ab Initio Studies of Structural Features not Easily Amenable to Experiment. Part 31. Conformational Analysis and Molecular Structures of Ethylene Glycol. *J. Mol. Strut. (THEOCHEM)* **1984**, *108*, 121−128.

(27) Ikuta, S.; Nomura, O. An ab Initio study on the Intramolecular Hydrogen Bond of Protonated Ethylene Glycol and Ethylenediamine. *Chem. Phys. Lett.* **1989**, *154*, 71−77.

(28) Cramer, C. C.; Truhlar, D. G. Quantum Chemical Conformational Analysis of 1,2-Ethanediol: Correlation and Solvation Effects on the Tendency To Form Internal Hydrogen Bonds in the Gas Phase and in Aqueous Solution. *J. Am. Chem. Soc.* **1994**, *116*, 3892−3900.

(29) Francesconi, R.; Acrelli, A.; Comelli, F. Excess properties of Binary Mixtures Containing 2-Methoxy-2-methylpropane (MTBE) and Alkyl Alkanoates at 298.15 K. *J. Chem. Eng. Data* **1998**, *43*, 329−332.

(30) Comelli, F.; Francesconi, R.; Ottani, S. Excess Molar Enthalpies and Excess Molar Volumes of Binary Mixtures Containing 1, 3-Dioxolane + Four Pairs of Alkyl Alkanoate Isomers at 298.15 K. *J. Chem. Eng. Data* **1998**, *43*, 815−818.

(31) Grunberg, L.; Nissan, A. H. The Viscosities of Liquid Mixtures. *Trans. Faraday Soc.* **1949**, *45*, 125−137.

(32) McAllister, R. A. The Viscosities of Liquid Mixtures. *AIChE J.* **1960**, *6*, 427−431.

(33) Auslander, I. G. Properties of Mixtures. *Br. Chem. Eng.* **1964**, *9*, 610−615.

(34) Jacobson, B. Intermolecular Free Lengths in the Liquid State. *Acta Chem. Scand.* **1952**, *8*, 1485−1495.

(35) Mishra, R. L.; Pandey, J. D. Comparison of Collision Factor Theory & Free Length Theory for Binary Liquid Mixtures. *Ind. J. Pure Appl. Phys.* **1977**, *15*, 505−506.

(36) Mehta, S. K.; Chauhan, R. K.; Dewan, R. K. Excess Volumes and Isentropic Compressibilities of Pyrrolidin-2-one-alkanol (C_s-C_5) Binary Mixtures. *J. Chem. Soc., Faraday Trans.* **1996**, *92*, 1167−1173.

(37) Nomoto, O. Empirical Formula for Sound Velocity in Liquid Mixtures. *J. Phys. Soc. Jpn.* **1958**, *13*, 1528−1532.

(38) Monton, J. B.; Burguet, M. C.; Munoz, R.; Wisnaik, J.; Seguru, H. Non-Azeotropy in the System Methyl Ethanoate + 1,2-Epoxybutane. *J. Chem. Eng. Data* **1997**, *42*, 1195−1200.

(39) Sakurai, M.; Nakamura, K.; Nitta, K. Partial Molar Isentropic Compressions of Alkyl Acetate in Water. *J. Chem. Eng. Data* **1998**, *43*, 249−254.

(40) Lide, D. R., Ed. *Handbook of Physics and Chemistry*, 75th ed.; CRC Press: Boca Raton, FL, 1994.

(41) Riddick, J. A.; Bunger, W. B.; Sakano, T. K. *Organic Solvents*, 4th ed.; Wiley-Interscience: New York, 1986; Vol. II.

(42) Oswal, S. L.; Patel, N. B. Speed of Sound, Isentropic Compressibility, Viscosity and Excess Volumes of Binary Mixtures. I. Acetonitrile with Alkyl acetate. *J. Chem. Eng. Data* **1995**, *40*, 840−844.

(43) Comelli, F.; Francesconi, R. Excess Molar Enthalpies of Binary Mixtures Containing Propylene Carbonate + 23 Alkanoates at 298.15 K. *J. Chem. Eng. Data* **1998**, *43*, 333−336.

(44) Aminabhavi, T. M.; Banerjee, K. Density, Viscosity, Refractive Index and Speed of Sound in Binary Mixtures of Acrylonitrile with Methyl Acetate, Ethyl Acetete, *n*-Propyl Acetate, *n*-Butyl Acetate and 3-Methyl Butyl 2-Acetate in the Temperature Interval (298.15−308.15) K. *J. Chem. Eng. Data* **1998**, *43*, 514−518.

(45) Pal, A.; Singh, W. Speeds of Sound and Viscosities in Aqueous Poly(ethylene glycol) Solutions at 303.15 and 308.15 K. *J. Chem. Eng. Data* **1997**, *42*, 234−237.

(46) Aminabhavi, T. M.; Gopalakrishna, B. Densities, Viscosities, Refractive Index, and Speed of Sound in Aqueous Mixtures of *N*,*N*-Dimethylformamide, Dimethyl Sulfoxide, *N*,*N*-Dimethylacetamide, Acetonitrile, Ethylene Glycol, Diethylene Glycol, 1,4-Dioxane, Tetrahydrofuran, 2-Methoxyethanol, and 2-Ethoxyethanol at 298.15 K. *J. Chem. Eng. Data* **1995**, *40*, 856−861.

(47) Pal, A.; Singh, W.; Sharma, H. Excess Molar Volumes, and Excess Partial Molar Volumes for Binary Mixtures of 2-Butoxy Ethanol with Ethylene Glycol, Diethylene Glycol, Triethylene Glycol, Propylene Glycol and Dimethylsulphoxide at 313.15 K. *Ind. J. Chem.* **1998**, *37A*, 507−511.

(48) Costas, M.; Patterson, D. Self-association of Alcohols in Inert Solvents. *J. Chem. Soc., Faraday Trans.* **1985**, *81*, 635−654.

(49) Zabransky, M.; Hyzick, V.; Finkeova, J.; Vesely, F. Heat Capacities of Six Liquid Esters as a Function of Temperature. *Collect. Czech. Chem. Commun.* **1987**, *25*, 25−34.

(50) Stephens, M. A.; Tamplin, W. S. Saturated Liquid Specific Heats of Ethylene Glycol Homologues. *J. Chem. Eng. Data* **1979**, *24*, 81−82.

Received for review January 28, 2003. Accepted April 23, 2003.

JE0340248