Density and Viscosity of Several Aldehydes Fragrance Compounds in Their Binary Mixtures with Ethanol at (298.15 K, 308.15 K, and 318.15 K)

Hiannie Djojoputro and Suryadi Ismadji*

Department of Chemical Engineering, Widya Mandala Surabaya Catholic University, Kalijudan 37, Surabaya 60114, Indonesia

Density and viscosity for binary mixtures of hexanal, octanal, nonanal, and decanal with ethanol over the whole composition range have been measured at three different temperatures (298.15, 308.15, and 318.15) K and atmospheric pressure. Redlich−Kister-type polynomial equations were fitted to the calculated excess molar volumes and viscosity deviations.

Introduction

Density and viscosity are important basic data used in process simulation, equipment design, solution theory, and molecular dynamics.[1,2] In the fragrance industries, aliphatic aldehydes are among the most important materials in the manufacturing processes.[3] The most important and frequently used are hexanal (aldehyde C_6), octanal (aldehyde C_8), nonanal (aldehyde C_9), and decanal (aldehyde C_{10}). These aldehydes are frequently used in perfumery to create fruity and roast characteristics.

Systematic studies of the thermodynamic behavior and physical properties of several flavor and fragrance compounds in their binary mixtures have been performed.[4−7] In continuation of our ongoing research program on the properties of binary mixtures containing a flavor or fragrance compound as one component with a variety of alcohols, in this paper we present the experimental data on density and viscosity of binary mixtures of hexanal + ethanol, octanal + ethanol, nonanal + ethanol, and decanal + ethanol at 298.15 K, 308.15 K, and 318.15 K. To the best of our knowledge, no literature data are available for the density and viscosity of the binary systems reported here.

Experimental Section

Materials. High-purity and AR-grade samples of hexanal, octanal, nonanal, decanal, and ethanol used in this experiment were purchased from Sigma-Aldrich Asia. Octanal, decanal, and ethanol were used without further purification since the purity of these compounds was higher than 0.995 (analyzed by gas chromatography Shimadzu, GC-17A using a flame ionization detector with high-purity helium as the carrier gas). Hexanal and nonanal were purified by vacuum distillation. After purification, the purity of these compounds was higher than 0.995.

The binary mixture samples were prepared by mass in the airtight-stoppered glass bottles using a Mettler Toledo AE 240 balance with the uncertainty of ± 10^{-5} g. The uncertainty of the mole fraction for each binary mixture is less than 0.0001.

* Corresponding author. Telephone: +62 31 3891264. Fax: +62 31 3891267. E-mail: suryadi@mail.wima.ac.id.

Table 1. Comparison of the Experimental Density and Viscosity of Hexanal, Octanal, Nonanal, Decanal, and Ethanol with Literature Values at 298.15 K, 308.15 K, and 318.15 K

		ρ_L/(g·cm^{-3})		η_L/(mPa·s)	
compound	*T*/K	exp	lit	exp	lit
hexanal	298.15	0.83312	0.83400[3]	0.805	
	308.15	0.81894		0.716	
	318.15	0.80431		0.639	
octanal	298.15	0.82107	0.82000[3]	1.200	
	308.15	0.80734		1.074	
	318.15	0.79385		0.965	
nonanal	298.15	0.83104	0.82700[3]	1.392	
	308.15	0.81801		1.251	
	318.15	0.80472		1.127	
decanal	298.15	0.80124	0.80000[3]	1.560	
	308.15	0.78905		1.412	
	318.15	0.77618		1.281	
ethanol	298.15	0.78508	0.78529[8]	1.088	1.086[8]
			0.78490[10]		1.105[9]
	308.15	0.77809	0.77641[11]	0.897	0.893[11]
	318.15	0.76391		0.767	

Density Measurements. The measurements of the densities of the pure components and the binary mixtures were carried out using a Mettler Toledo density meter-type DE50 with the uncertainty about 10^{-5} g·cm^{-3}. Prior to measurement, the instrument was calibrated with double-distilled water at 298.15 K, 308.15 K, and 318.15 K. The temperature of the measuring cell was maintained at 298.15 K, 308.15 K, and 318.15 K using a Julabo refrigerated and heating circulator, model F12-MD, with an uncertainty of 0.1 K.

Viscosity Measurements. For the viscosity measurement, an automatic microviscosimeter Anton Paar type AMV$_n$, equipped with an automatic timer (±0.01 s), was used. This instrument uses the rolling ball principle according to DIN 53015 and ISO/DIS 12058, where gold-covered steel balls roll down inside an inclined, sample filled glass capillary. The uncertainty of time in the range of (0 to 250) s is less than 0.02 s with a precision of ±0.01 s. The temperature range of this viscosimeter is from (283.15 to 343.15) K with the uncertainty less than 0.05 K. The calibration of the instrument was performed periodically with double-distilled water. The uncertainty in the viscosity measurement was estimated be less than

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Table 2. Experimental Density and Viscosity and Excess Molar Volume for Binary Mixtures Hexanal (1) + Ethanol (2), Octanal (1) + Ethanol (2), Nonanal (1) + Ethanol (2), and Decanal (1) + Ethanol (2) at 298.15 K, 308.15 K, and 318.15 K

x_1	ρ_L / (g·cm^{-3})	η_L / (mPa·s)	V^E / (cm^3·mol^{-1})	x_1	ρ_L / (g·cm^{-3})	η_L / (mPa·s)	V^E / (cm^3·mol^{-1})	x_1	ρ_L / (g·cm^{-3})	η_L / (mPa·s)	V^E / (cm^3·mol^{-1})
Hexanal (1) + Ethanol (2) at 298.15 K											
0.0000	0.78508	1.088	0.000	0.4037	0.79869	0.963	1.497	0.8100	0.82030	0.852	1.044
0.1094	0.78800	1.053	0.560	0.5027	0.80322	0.935	1.592	0.9226	0.82769	0.824	0.494
0.2049	0.79101	1.023	0.962	0.6207	0.80924	0.902	1.539	1.0000	0.83312	0.805	0.000
0.3226	0.79533	0.987	1.331	0.7108	0.81429	0.878	1.368				
Hexanal (1) + Ethanol (2) at 308.15 K											
0.0000	0.77809	0.897	0.000	0.4037	0.78967	0.819	1.313	0.8100	0.80804	0.747	0.920
0.1094	0.78057	0.875	0.490	0.5027	0.79352	0.801	1.398	0.9226	0.81432	0.729	0.437
0.2049	0.78313	0.857	0.843	0.6207	0.79864	0.780	1.353	1.0000	0.81894	0.716	0.000
0.3226	0.78681	0.834	1.167	0.7108	0.80293	0.764	1.204				
Hexanal (1) + Ethanol (2) at 318.15 K											
0.0000	0.76391	0.767	0.000	0.4037	0.77536	0.712	1.347	0.8100	0.79353	0.662	0.943
0.1094	0.76636	0.752	0.503	0.5027	0.77917	0.700	1.433	0.9226	0.79974	0.648	0.448
0.2049	0.76890	0.739	0.864	0.6207	0.78423	0.685	1.387	1.0000	0.80431	0.639	0.000
0.3226	0.77253	0.723	1.197	0.7108	0.78847	0.674	1.236				
Octanal (1) + Ethanol (2) at 298.15 K											
0.0000	0.78508	1.088	0.000	0.3977	0.79508	1.131	1.586	0.7980	0.81090	1.176	1.186
0.1077	0.78723	1.100	0.580	0.4952	0.79840	1.142	1.702	0.9089	0.81630	1.189	0.625
0.2019	0.78945	1.110	1.004	0.6115	0.80281	1.155	1.669	1.0000	0.82107	1.200	0.000
0.3178	0.79262	1.122	1.401	0.7003	0.80651	1.165	1.508				
Octanal (1) + Ethanol (2) at 308.15 K											
0.0000	0.77809	0.897	0.000	0.3977	0.78622	0.964	1.328	0.7980	0.79907	1.036	0.998
0.1077	0.77983	0.915	0.486	0.4952	0.78892	0.981	1.426	0.9089	0.80346	1.057	0.527
0.2019	0.78164	0.930	0.840	0.6115	0.79250	1.001	1.401	1.0000	0.80734	1.074	0.000
0.3178	0.78421	0.950	1.174	0.7003	0.79550	1.018	1.267				
Octanal (1) + Ethanol (2) at 318.15 K											
0.0000	0.76391	0.767	0.000	0.3977	0.77223	0.840	1.407	0.7980	0.78539	0.921	1.056
0.1077	0.76570	0.786	0.514	0.4952	0.77499	0.859	1.512	0.9089	0.78988	0.945	0.557
0.2019	0.76754	0.803	0.890	0.6115	0.77866	0.883	1.483	1.0000	0.79385	0.965	0.000
0.3178	0.77018	0.825	1.243	0.7003	0.78174	0.901	1.340				
Nonanal (1) + Ethanol (2) at 298.15 K											
0.0000	0.78508	1.088	0.000	0.3939	0.79770	1.199	2.256	0.7855	0.81731	1.320	1.763
0.1034	0.78770	1.116	0.799	0.5045	0.80252	1.232	2.438	0.8980	0.82425	1.357	0.982
0.2039	0.79072	1.144	1.447	0.5943	0.80685	1.260	2.408	1.0000	0.83104	1.392	0.000
0.2930	0.79379	1.169	1.899	0.7116	0.81307	1.297	2.110				
Nonanal (1) + Ethanol (2) at 308.15 K											
0.0000	0.77809	0.897	0.000	0.3939	0.78905	1.023	2.016	0.7855	0.80608	1.165	1.581
0.1034	0.78037	0.928	0.712	0.5045	0.79324	1.061	2.180	0.8980	0.81211	1.209	0.882
0.2039	0.78299	0.960	1.291	0.5943	0.79700	1.093	2.155	1.0000	0.81801	1.251	0.000
0.2930	0.78565	0.989	1.696	0.7116	0.80240	1.137	1.891				
Nonanal (1) + Ethanol (2) at 318.15 K											
0.0000	0.76391	0.767	0.000	0.3939	0.77511	0.893	2.132	0.7855	0.79253	1.038	1.669
0.1034	0.76624	0.798	0.754	0.5045	0.77940	0.931	2.304	0.8980	0.79869	1.084	0.931
0.2039	0.76892	0.830	1.366	0.5943	0.78324	0.964	2.278	1.0000	0.80472	1.127	0.000
0.2930	0.77164	0.859	1.794	0.7116	0.78876	1.009	1.998				
Decanal (1) + Ethanol (2) at 298.15 K											
0.0000	0.78508	1.088	0.000	0.4120	0.78978	1.262	0.961	0.8008	0.79673	1.452	0.713
0.1011	0.78598	1.128	0.323	0.5105	0.79131	1.308	1.024	0.9145	0.79923	1.513	0.360
0.2102	0.78714	1.174	0.613	0.5836	0.79255	1.343	1.018	1.0000	0.80124	1.560	0.000
0.3013	0.78825	1.213	0.804	0.6889	0.79448	1.395	0.928				
Decanal (1) + Ethanol (2) at 308.15 K											
0.0000	0.77809	0.897	0.000	0.4120	0.78128	1.081	0.670	0.8008	0.78599	1.290	0.499
0.1011	0.77870	0.939	0.224	0.5105	0.78232	1.131	0.713	0.9145	0.78768	1.358	0.253
0.2102	0.77948	0.987	0.428	0.5836	0.78315	1.169	0.712	1.0000	0.78905	1.412	0.000
0.3013	0.78024	1.028	0.560	0.6889	0.78447	1.226	0.647				
Decanal (1) + Ethanol (2) at 318.15 K											
0.0000	0.76391	0.767	0.000	0.4120	0.76748	0.947	0.776	0.8008	0.77276	1.157	0.576
0.1011	0.76459	0.808	0.260	0.5105	0.76864	0.997	0.827	0.9145	0.77465	1.226	0.292
0.2102	0.76547	0.854	0.495	0.5836	0.76958	1.035	0.823	1.0000	0.77618	1.281	0.000
0.3013	0.76632	0.895	0.648	0.6889	0.77105	1.092	0.749				

0.004 mPa·s. The measuring temperature was kept at (298.15 K, 308.15 K, and 318.15 K) by placing the sample filled glass capillary in a block controlled by a Julabo refrigerated and heating circulator.

All measurements described above were performed at least three times, and the results were averaged to give the final values. A comparison between the experimental results of density and viscosity of pure liquids and those from literature is given in Table 1. From this table, it is clear that the experimental values of density and viscosity of pure liquids are generally in agreement with those from literature.

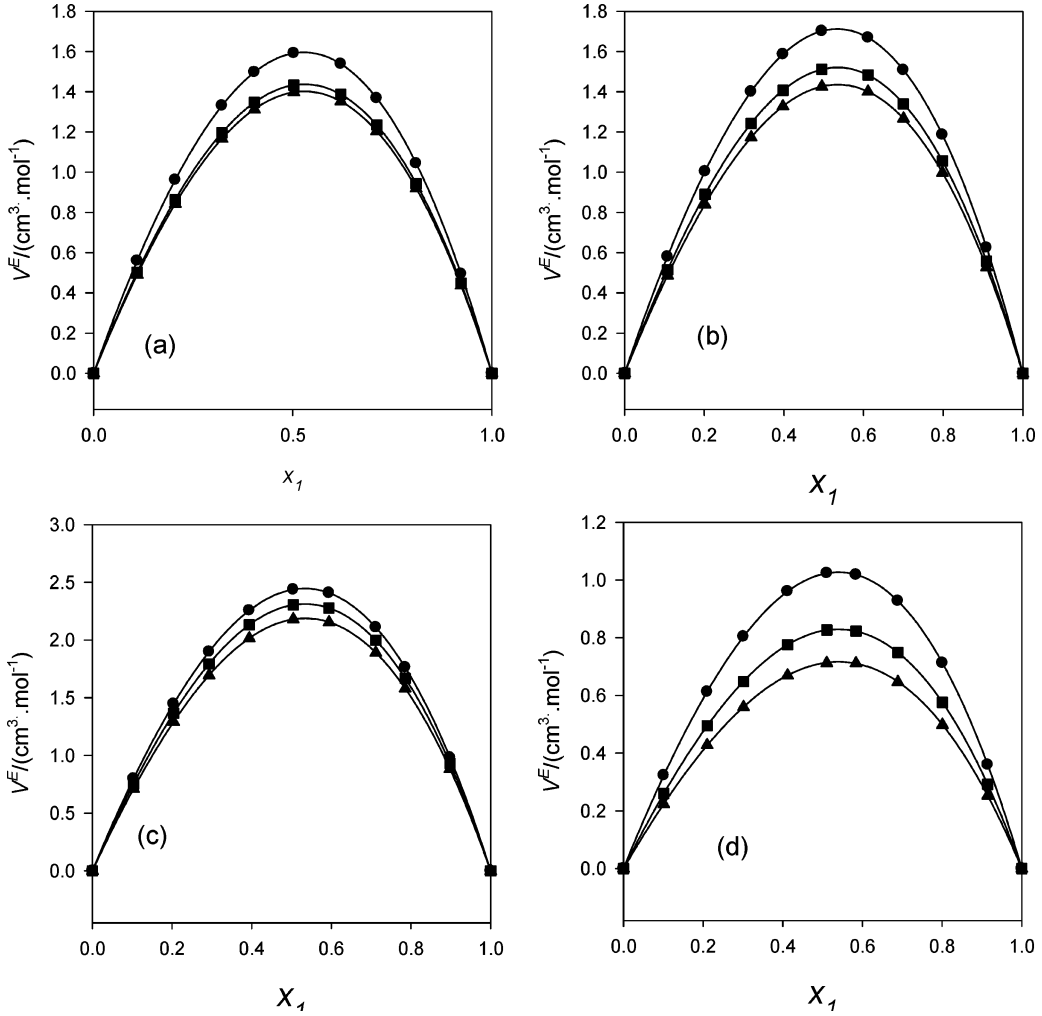

Figure 1. Excess molar volumes (V^E) for (a) hexanal (1) + ethanol (2), (b) octanal (1) + ethanol (2), (c) nonanal (1) + ethanol (2), and (d) decanal (1) + ethanol (2). ●, 298.15 K; ▲, 308.15 K; and ■, 318.15 K.

Results

The density and viscosity data of the binary mixtures hexanal (1) + ethanol (2), octanal (1) + ethanol (2), nonanal (1) + ethanol (2), and decanal (1) + ethanol (2) at (298.15, 308.15, and 318.15) K are given in Table 2. The excess molar volume (V^E) was calculated from density data according to the following equation:

$$V^E = \frac{x_1M_1 + x_2M_2}{\rho_L} - (x_1V_1 + x_2V_2) \qquad (1)$$

where ρ_L is the density of the mixture and x_1, V_1, M_1, x_2, V_2, and M_2 are the mole fraction, molar volume, and molecular weight of pure compounds 1 and 2, respectively. The average uncertainty for V^E is less than 0.001 cm^3·mol^{-1}. The excess molar volume values calculated from eq 1 are also summarized in Table 2. The values of this excess property are positive over the whole composition range. The excess volumes of the four binary systems at 298.15 K, 308.15 K, and 318.15 K are plotted in Figure 1. The maximum values are reached at mole fraction near 0.5. From Figure 1, it can be seen that the excess molar volume of the systems studied decreases with increasing temperature. The repulsive forces between the lone pair of electrons on oxygen atoms of both of the components (aldehyde and ethanol) in the mixture leads to positive deviation in excess molar volume (V^E) of the system.

Table 3. Parameter and Standard Deviations of the Redlich−Kister Polynomial Equation for Selected Aldehydes + Ethanol Systems

	T/K	A_0	A_1	A_2	A_3	σ
			Hexanal (1) + Ethanol (2)			
V^E/(cm^3·mol^{-1})	298.15	6.3632	0.7359	−0.0824	−0.0187	0.0001
	308.15	5.5867	0.6699	−0.0559	−0.0014	0.0001
	318.15	5.7292	0.6894	−0.0560	−0.0088	0.0001
$\Delta\eta$/(mPa·s)	298.15	−0.0440	0.0014	0.0026	−0.0035	0.0009
	308.15	−0.0204	−0.0019	0.0008	0.0053	0.0130
	318.15	−0.0117	0.0055	0.0032	−0.0105	0.0201
			Octanal (1) + Ethanol (2)			
V^E/(cm^3·mol^{-1})	298.15	6.8172	0.9468	−0.0653	−0.0022	0.0001
	308.15	5.7140	0.8193	−0.0281	−0.0024	0.0001
	318.15	6.0532	0.8562	−0.0488	0.0101	0.0001
$\Delta\eta$/(mPa·s)	298.15	−0.0065	0.0014	0.0011	−0.0123	0.0287
	308.15	−0.0156	−0.0018	0.0041	0.0065	0.0324
	318.15	−0.0230	0.0026	−0.0023	−0.0051	0.0075
			Nonanal (1) + Ethanol (2)			
V^E/(cm^3·mol^{-1})	298.15	9.7392	1.3372	−0.1120	−0.0228	0.0001
	308.15	8.7096	1.2287	−0.0865	−0.0032	0.0001
	318.15	9.2074	1.2874	−0.0954	−0.0170	0.0001
$\Delta\eta$/(mPa·s)	298.15	−0.0366	0.0039	−0.0056	−0.0144	0.0027
	308.15	−0.0576	−0.0041	−0.0037	0.0035	0.0015
	318.15	−0.0688	−0.0083	0.0047	0.0117	0.0010
			Decanal (1) + Ethanol (2)			
V^E/(cm^3·mol^{-1})	298.15	4.0827	0.6605	−0.0212	−0.0162	0.0001
	308.15	2.8470	0.4632	−0.0039	0.0130	0.0001
	318.15	3.2969	0.5350	−0.0178	0.0009	0.0001
$\Delta\eta$/(mPa·s)	298.15	−0.0838	−0.0049	−0.0002	0.0034	0.0007
	308.15	−0.1166	−0.0060	−0.0014	−0.0078	0.0003
	318.15	−0.1310	−0.0059	−0.0005	−0.0089	0.0004

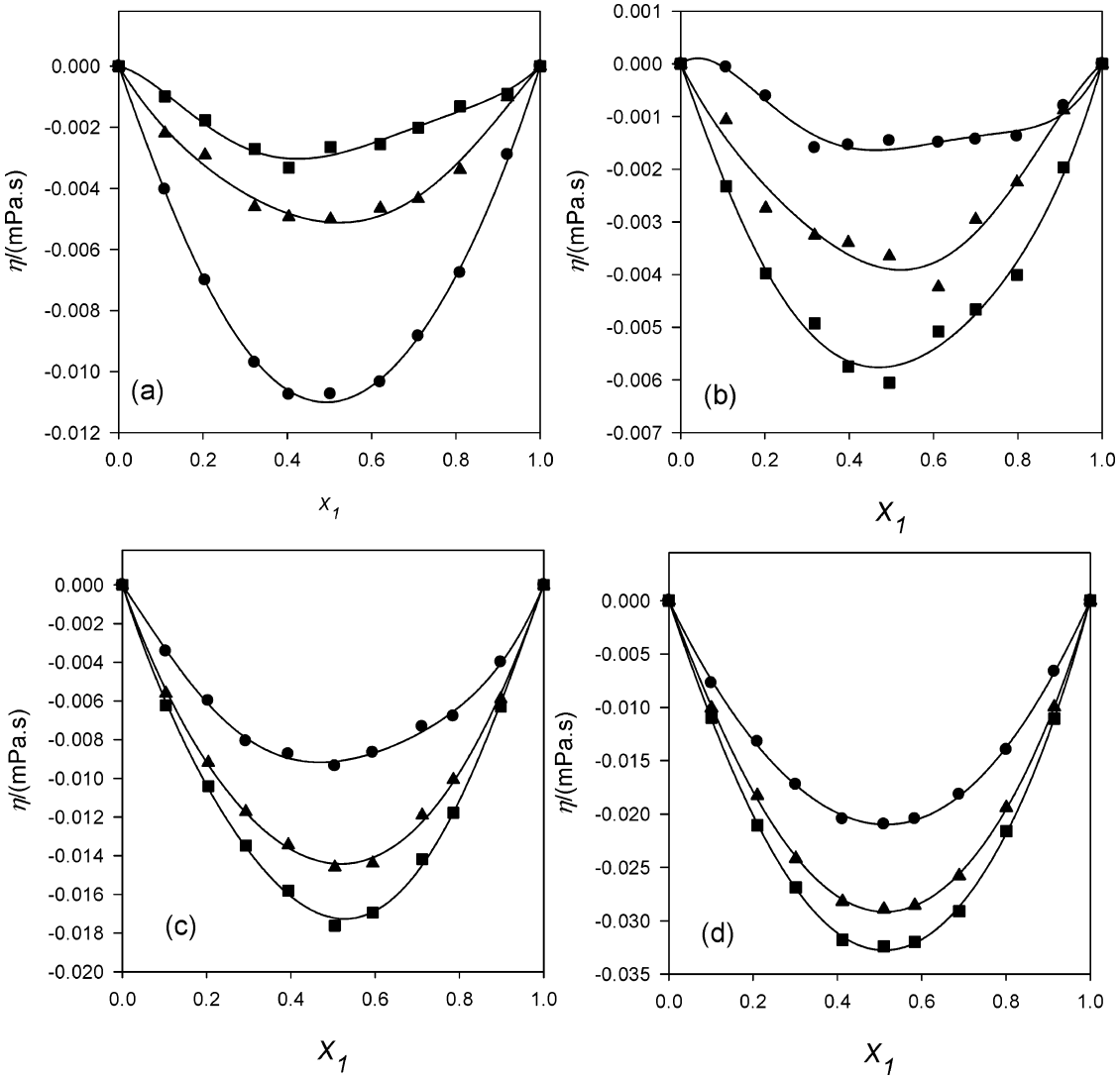

Figure 2. Viscosity deviation (η) for (a) hexanal (1) + ethanol (2), (b) octanal (1) + ethanol (2), (c) nonanal (1) + ethanol (2), and (d) decanal (1) + ethanol (2). ●, 298.15 K; ▲, 308.15 K; and ■, 318.15 K.

The viscosity deviations were also calculated using the experimental values of viscosity listed in Table 2. The following equation was used to obtain the viscosity deviations ($\Delta\eta$):

$$\Delta\eta = \eta_{\mathrm{L}} - x_1\eta_{\mathrm{L1}} - x_2\eta_{\mathrm{L2}} \tag{2}$$

where η_{L} is the measured mixture viscosity, and η_{L1} and η_{L2} represent the pure component viscosity. The viscosity deviations of all systems at 298.15 K, 308.15 K, and 318.18 K are given in Figure 2. The viscosity deviations for all systems are negative over the entire composition range.

The excess properties for the binary mixtures have been fitted to a Redlich−Kister-type equation:

$$V^{\mathrm{E}}/\mathrm{cm}^3\cdot\mathrm{mol}^{-1} = x_1x_2\sum_{i=0}^{n}A_i(x_1 - x_2)^i \tag{3}$$

or

$$\Delta\eta/\mathrm{mPa\cdot s} = x_1x_2\sum_{i=0}^{n}A_i(x_1 - x_2)^i \tag{4}$$

A_i are adjustable parameters evaluated by least-squares optimization, and n is the number of these parameters. The results together with the standard deviations (σ) are presented in Table 3. From this table, it is clear that Redlich−Kister polynomial equations can represent the excess molar volume and viscosity deviation very well, which is indicated by a low standard deviation.

Conclusions

Experimental data of the density and viscosity of several aldehyde fragrance compounds in their binary mixture with ethanol have been measured at several temperatures. These data have been used to compute excess properties of the systems. Positive and negative deviations are observed for V^{E} and $\Delta\eta$, respectively.

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