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Temperature and composition dependence of the density and viscosity of binary mixtures of (1-decanol + fragrance material)

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ABSTRACT

Density and viscosity were determined for binary mixtures containing 1-decanol and three fragrance raw materials based on cyclohexane: cyclohexyl carboxylic acid (CCA), or cyclohexyl acetate (CA), or 2-cyclohexyl ethyl acetate (2CEA) in wide range of temperatures from 300 to 340 K and atmospheric pressure. Excess molar volumes were calculated and correlated by the Redlich–Kister polynomial expansions involving parameters dependent on temperature for the mixtures. The polynomial correlations describe the variation of density and viscosity with composition. The coefficient of thermal expansion, α was described for all pure fragrance raw materials and their mixtures and related excess property has been calculated. The temperature dependence of density and viscosity for these systems can be described by an empirical second-order polynomial and by the Vogel–Fulcher–Tammann equation, respectively. Comparison of the results for three binary systems elucidates the influence of the substituent at the cyclohexane ring on their physical and volumetric properties.

1. Introduction

Fragrance materials (FMs) are used in a variety of consumer products ranging from perfumes to skin products such as creams, lotions, detergents, and various other personal and household products. The potential for exposure to these materials in our society is, therefore, very high, particularly for those products that come into direct contact with the skin. The list of a large number of diverse chemicals used as fragrance ingredients and safety evaluation of these materials is wide known [1–3]. The process of organic liquid mixtures containing compounds including, aromatics, aliphatics and oxygenates with alcohols and water is an important consideration in all industries involving FM. The hundreds of substances—acids, esters and alcohols, in FM have been accepted as "generally recognize as safe substances" and have become the leading preservatives for food as well as for pharmaceutical and cosmetic preparations [4,5].

The esters of cyclohexanol and carboxylic acids used as a FM are formed as byproducts in the process of the commercial oxidation of cyclohexane into cyclohexanone [6]. The data of isobaric heat capacities, densities, speed of sound, enthalpies of vaporization and enthalpies of phase transitions for ester based on cyclohexanol and carboxylic acids have been just published [6,7]. Cyclohexyl acetate was also tested as an entrainer for the solvent extraction and separation of butyric acid from water [8]. There is a pressing need to have more physico-chemical information about mixtures of the FM with different solvents, for example as alkanols. Both, 1-decanol and FM used in these work are used as additives for many different cosmetic and preservatives for food compositions and the density and viscosity of these mixtures are very important.

Until now, we have focused on the determination of phase equilibria, (solid + liquid) phase equilibria of FM based on cyclohexane base with 1-octanol at ambient and high pressure [9]. To our best knowledge the densities and viscosities of these substances were not measured. The experimental measurements of these properties were carried out at atmospheric pressure of FMs: {1-decanol (1) + cyclohexyl carboxylic acid (CCA) (2)} at temperatures 310, 320, 330 and 340 K, and of {1-decanol (1) + cyclohexyl acetate (CA), or 2-cyclohexyl ethyl acetate (2CEA) (2)} at temperatures 300, 310, 320, 330 and 340 K. The chemical names and the abbreviations of substances under study are presented in Table 1. CCA in nature is in coffee and as odor and/or flavor in blueberry, cherry, fruit tropical fruit, pineapple, raisin and raspberry [1]. CA in nature is in sauerkraut and as odor and/or flavor in apple, banana, blackberry, raspberry and rum [1]. 2CEA is used as odor and/or flavor in balsam, floral, raspberry and rose [1].

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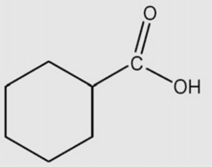
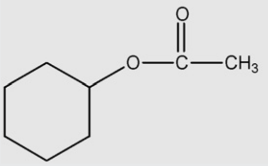
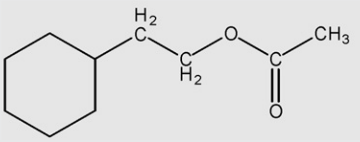
Table 1
Investigated compounds: structure, name, abbreviation of name and values of molar mass.

Name of compound	Structural formula	Abbreviation, M/g mol^{-1}
Cyclohexyl carboxylic acid		CCA 128.17
Cyclohexyl acetate		CA 142.20
2-Cyclohexyl ethyl acetate		2CEA 170.24

2. Experimental

2.1. Materials

Investigated compounds were: cyclohexyl carboxylic acid, $C_7H_{12}O_2$ (CCA), (Sigma–Aldrich Chemie GmbH, Stenheim, Germany, CAS No. 98-89-5), cyclohexyl acetate, $C_8H_{14}O_2$, (CA), (Sigma–Aldrich Chemie GmbH, Stenheim, Germany, CAS No. 622-45-7), and 2-cyclohexyl ethyl acetate, $C_{10}H_{18}O_2$, (2CEA), (SAFC Supplay Solutions, St Louis, USA CAS No. 21722-83-8). The purity of compounds was ≥98 mass%. Chemicals were used without any purification.

1-Decanol was delivered from Sigma–Aldrich Chemie GmbH, Stenheim, Germany. Before direct use solvent was purified by fractional distillation to the mass fraction purity ≥99.8 mass%. All compounds were checked by GLC analysis and no significant impurities were found. The thermophysical characterization of the compounds was obtained by the differential scanning microcalorimetry (DSC) in our previous work [9].

2.2. Methods

2.2.1. Density measurements

The densities of all the chemicals were measured using an Anton Paar GmbH 4500 vibrating-tube densimeter (Graz, Austria), thermostated at different temperatures. Two integrated Pt 100 platinum thermometers provided good precision of the internal control of temperature ($T \pm 0.01$ K). Densimeter includes an automatic correction for the viscosity of the sample. The apparatus is precise to within 1×10^{-5} g cm^{-3}, and the uncertainty of the measurements was estimated to be better than $\pm 5 \times 10^{-5}$ g cm^{-3}. The densimeter's calibration was performed at atmospheric pressure using doubly distilled and degassed water, specially purified benzene (CHEMIPAN, Poland 0.999) and dried air. The information about the calibration with water and benzene over the entire range of temperature together with the literature data of density are presented in Table 1S in the Supplementary Data (SD). Mixtures were prepared by weighing; the error in mole fraction being estimated as less than 5×10^{-4}. The densities of 1-decanol and FM given in Table 2 were measured at higher temperature (310 K). Our values at higher temperature (310 K) are lower than those reported in literature at $T = 298.15$ K. The uncertainty of the excess molar volumes depend on the uncertainties of the density measurements and can be assumed as ± 0.0005 cm^3 mol^{-1}.

2.2.2. Viscosity measurements

Viscosity measurements were carried out in an Anton Paar BmbH AMVn (Graz, Austria) programmable viscometer, with a nominal uncertainty of ±0.1% and reproducibility <0.5% for viscosities from 0.3 to 2500 mPa s. The internal control of temperature was with a precision of ±0.01 K in a range from 283.15 to 373.15 K. The diameter of the capillary was 1.8 mm for viscosities from 2.5 to 70 mPa s and the diameter of the ball was 1.5 mm. The calibration procedure included 1-hexanol at $T = 298.15$ K (4.49 mPa s) which is in satisfactory agreement with the literature value 4.52 mPa s [13] as well as for 1-decanol at $T = 298.15$ K (experimental value 11.29 mPa s) in comparison with the literature value (11.32 mPa s [13]). More information about calibration is included in the SD as GRS 1.

3. Results and discussion

The experimental data of density, ρ and dynamic viscosity, η versus x_1, the mole fraction of the 1-decanol of the {1-decanol (1) + CCA, or CA, or 2CA (2)} mixtures at different temperatures are listed in Tables 3–5. The densities are higher for FM than for 1-decanol and decrease with increasing 1-decanol content. Only the viscosity of CCA is higher than that for 1-decanol and decrease with increasing 1-decanol mole fraction. As usual, both density and viscosity decrease with an increasing temperature. We found no previous data as a function of temperature for these systems for comparison.

Experimental densities at ambient pressure, investigated in this work, for the FM becomes distinctly nonlinear in function of temperature, especially at high 1-decanol content. A second-order polynomial was found to satisfactorily correlate, the change of density of pure substances with temperature:

$$\rho = a_2 T^2 + a_1 T + a_0 \qquad (1)$$

where T is the absolute temperature, a_2, a_1 and a_0 refer to the fit coefficients. Fit parameters are listed in Table 2S in the SD. The accuracy of the fit is with $R^2 = 1$.

Table 2
Thermophysical constants of pure substances: melting temperature, T_{fus}; enthalpy of fusion, $\Delta_{fus}H$; solid–solid phase transition temperature, T_{tr}; enthalpy of the solid–solid phase transition, $\Delta_{tr}H$; measured densities, $\rho^{310.00}$; densities from literature, $\rho^{298.15}$.

Compound	T_{fus}/K	$\Delta_{fus}H$/kJ mol^{-1}	T_{tr}/K	$\Delta_{tr}H$/kJ mol^{-1}	$\rho^{310.00}$/g cm^{-3}	$\rho^{298.15}$/g cm^{-3}
1-Decanol	279.1[a]	28.79[b]			0.81826	0.8261[c]
Cyclohexyl carboxylic acid	301.9[d]	9.197[d]	–	–	1.01717	1.033[e]
Cyclohexyl acetate	221.4[d], 224.6[f]	3.384[d], 7.994[f]	221.8[f], 154 (g)[d], 151.8 (g)[f]	5.230[f]	0.95390	0.970[e], 0.9654[g]
2-Cyclohexyl ethyl acetate	–	–	–	–	0.93503	0.950[e]

[a] From Ref. [10].
[b] From Ref. [11].
[c] From. Ref. [12].
[d] From Ref. [9].
[e] Densities/Aldrich.
[f] From Ref. [6].
[g] From Ref. [7].

The effect of composition on density is presented in Figs. 1–3 together with the correlation lines calculated with polynomial:

$$\rho = b_3x_1^3 + b_2x_1^2 + b_1x_1 + b_0 \tag{2}$$

The densities are highest for pure FM, with decreasing values with increasing 1-decanol content. The parameters of correlation with $R^2 = 1$ are shown in Table 3S in the SD.

The densities of three pure fragrance material increases in all temperatures in the order: CCA > CA > 2CEA. For example at $T = 310$ K

Table 3
Experimental density ρ, excess molar volume V_m^E, dynamic viscosity η for the {1-decanol (1) + cyclohexyl carboxylic acid (2)} binary system.

x_1	T/K			
	310	320	330	340
ρ/g cm^{-3}				
0.0000	1.01717	1.00877	1.00040	0.99203
0.0377	1.00593	0.99764	0.98937	0.98110
0.0625	0.99887	0.99064	0.98242	0.97422
0.1776	0.96818	0.96023	0.95228	0.94431
0.2753	0.94478	0.93702	0.92925	0.92145
0.4103	0.91549	0.90793	0.90036	0.89275
0.4952	0.89867	0.89124	0.88377	0.87625
0.5659	0.88548	0.87813	0.87074	0.86329
0.6678	0.86776	0.86052	0.85323	0.84589
0.7657	0.85198	0.84486	0.83765	0.83036
0.8462	0.83980	0.83274	0.82561	0.81836
0.9063	0.83111	0.82411	0.81702	0.80982
0.9593	0.82373	0.81678	0.80974	0.80260
1.0000	0.81826	0.81133	0.80431	0.79715
V_m^E/cm^3 mol^{-1}				
0.000	0.000	0.000	0.000	0.000
0.038	−0.005	−0.009	−0.013	−0.018
0.062	−0.021	−0.027	−0.031	−0.041
0.178	−0.077	−0.091	−0.107	−0.127
0.275	−0.134	−0.153	−0.174	−0.201
0.410	−0.178	−0.196	−0.220	−0.253
0.495	−0.182	−0.203	−0.226	−0.257
0.566	−0.176	−0.194	−0.215	−0.246
0.668	−0.163	−0.177	−0.195	−0.227
0.766	−0.139	−0.154	−0.166	−0.188
0.846	−0.106	−0.115	−0.126	−0.139
0.906	−0.066	−0.073	−0.079	−0.090
0.959	−0.029	−0.034	−0.039	−0.053
1.000	0.000	0.000	0.000	0.000
η/mPa s				
0.0000	13.2	9.26	6.76	5.07
0.0377	12.1	8.54	6.29	4.81
0.0625	11.8	8.32	6.13	4.70
0.1776	10.6	7.57	5.65	4.35
0.2753	9.61	6.94	5.19	4.04
0.4103	8.79	6.39	4.80	3.72
0.4952	8.45	6.15	4.63	3.58
0.5659	8.15	5.94	4.47	3.45
0.6678	7.86	5.72	4.30	3.32
0.7657	7.70	5.60	4.20	3.23
0.8462	7.48	5.48	4.12	3.17
0.9063	7.43	5.36	4.00	3.07
0.9593	7.41	5.30	3.99	3.06
1.0000	7.09	5.00	3.67	2.74

Table 4
Experimental density ρ, excess molar volume V_m^E, dynamic viscosity η for the {1-decanol (1) + cyclohexyl acetate (2)} binary system.

x_1	T/K				
	300	310	320	330	340
ρ/g cm^{-3}					
0.0000	0.96357	0.95390	0.94417	0.93441	0.92464
0.0746	0.94918	0.93980	0.93036	0.92089	0.91139
0.1275	0.93964	0.93043	0.92120	0.91192	0.90257
0.1840	0.92988	0.92086	0.91180	0.90271	0.89357
0.2015	0.92689	0.91791	0.90894	0.89991	0.89081
0.2425	0.92006	0.91124	0.90238	0.89348	0.88452
0.2741	0.91503	0.90631	0.89762	0.88882	0.87996
0.4169	0.89364	0.88538	0.87706	0.86870	0.86025
0.4886	0.88366	0.87561	0.86750	0.85933	0.85109
0.6055	0.86847	0.86073	0.85293	0.84510	0.83714
0.6993	0.85706	0.84955	0.84199	0.83437	0.82663
0.8435	0.84097	0.83383	0.82658	0.81926	0.81181
0.8806	0.83703	0.82995	0.82279	0.81555	0.80817
1.0000	0.82513	0.81826	0.81133	0.80431	0.79715
V_m^E/cm^3 mol^{-1}					
0.0000	0.000	0.000	0.000	0.000	0.000
0.0746	0.200	0.204	0.207	0.209	0.212
0.1275	0.298	0.307	0.310	0.314	0.324
0.1840	0.388	0.400	0.408	0.414	0.422
0.2015	0.421	0.437	0.441	0.447	0.458
0.2425	0.488	0.501	0.511	0.519	0.528
0.2741	0.516	0.531	0.529	0.537	0.546
0.4169	0.602	0.613	0.624	0.630	0.640
0.4886	0.618	0.627	0.636	0.644	0.649
0.6055	0.578	0.586	0.594	0.593	0.598
0.6993	0.517	0.524	0.528	0.529	0.531
0.8435	0.319	0.312	0.316	0.318	0.320
0.8806	0.261	0.258	0.259	0.259	0.261
1.0000	0.000	0.000	0.000	0.000	0.000
η/mPa s					
0.0000	1.95	1.61	1.36	1.16	1.01
0.0746	2.01	1.65	1.38	1.17	1.02
0.1275	2.11	1.72	1.43	1.21	1.05
0.1840	2.26	1.82	1.51	1.27	1.09
0.2015	2.30	1.86	1.55	1.30	1.10
0.2425	2.42	1.95	1.60	1.34	1.14
0.2741	2.54	2.03	1.66	1.39	1.18
0.4169	3.15	2.47	1.98	1.63	1.36
0.4886	3.61	2.81	2.23	1.81	1.49
0.6055	4.41	3.35	2.62	2.09	1.70
0.6993	5.27	3.95	3.04	2.39	1.92
0.8435	7.56	5.49	4.10	3.14	2.47
0.8806	8.17	5.85	4.37	3.34	2.61
1.0000	10.30	7.09	5.00	3.67	2.74

the density of CA is 0.95390 g cm^{-3} whilst the density of 2CEA including a double CH$_2$ group in the molecule in comparison with CA is much lower, 0.93503 g cm^{-3}. Thus, two CH$_2$ groups change the structure of the liquid phase, separate the molecules and decrease the density.

Figs. 4–6 show the experimental dynamic viscosities for the three binary systems studied, as a function of temperature, for different compositions together with the well-known Vogel–Fulcher–Tammann, VFT equation [14–16]. This equation has been used to correlate variations of viscosity with temperature in a measured system:

$$\eta = CT^{0.5} \exp\left(\frac{D}{T - T_0}\right) \tag{3}$$

The fit parameters, determined empirically are in general C, D and T_0 when the linear relation is observed between logarithmic value of $\eta T^{0.5}$ and $(T - T_0)^{-1}$ according to the Eq. (3) with three adjustable parameters. However, for the glass-forming liquids, the refined value for T_0 (called the ideal transition temperature) can be found from the glass transition temperature. The difference between T_0 and $T_{\mathrm{tr(g)}}$ is approximately 50–60 K [17]. It is known that T_0 is lower than that observed from DSC glass transition temperature. For the FM under study only the temperature of CA glass transition was determined by DSC (see Table 2) and the values are 154.0 K [9] and 151.8 K [6]. Using the value of T_0 equals to 99 K the nice correlation of the experimental curves of all FM can be obtained. However, the possible values of T_0 may be also obtained from the viscosity at 10^{15} mPa s [18]. The new values of the glass transition temperatures, defined as the temperature at which the

Table 5
Experimental density ρ, excess molar volume V_m^E, dynamic viscosity η for the {1-decanol (1) + cyclohexyl ethyl acetate (2)} binary system.

x_1	T/K				
	300	310	320	330	340
ρ/g cm^{-3}					
0.0000	0.94364	0.93503	0.92643	0.91782	0.90917
0.1066	0.92942	0.92100	0.91257	0.90411	0.89564
0.1534	0.92337	0.91503	0.90667	0.89829	0.88987
0.2863	0.90656	0.89844	0.89031	0.88213	0.87390
0.3370	0.90031	0.89231	0.88426	0.87616	0.86798
0.4105	0.89139	0.88351	0.87559	0.86762	0.85959
0.4983	0.88090	0.87320	0.86544	0.85761	0.84971
0.5476	0.87509	0.86747	0.85981	0.85205	0.84424
0.6306	0.86545	0.85795	0.85045	0.84285	0.83515
0.7020	0.85732	0.84992	0.84253	0.83503	0.82746
0.7382	0.85332	0.84602	0.83868	0.83125	0.82373
0.8402	0.84212	0.83500	0.82783	0.82058	0.81321
0.9332	0.83217	0.82520	0.81817	0.81105	0.80380
1.0000	0.82513	0.81826	0.81133	0.80431	0.79715
V_m^E/cm^3 mol^{-1}					
0.0000	0.000	0.000	0.000	0.000	0.000
0.1066	0.172	0.178	0.187	0.198	0.204
0.1534	0.221	0.230	0.243	0.255	0.268
0.2863	0.332	0.349	0.365	0.385	0.392
0.3370	0.359	0.370	0.388	0.409	0.422
0.4105	0.380	0.394	0.412	0.432	0.451
0.4983	0.395	0.404	0.419	0.439	0.463
0.5476	0.397	0.407	0.419	0.440	0.459
0.6306	0.385	0.399	0.406	0.420	0.432
0.7020	0.355	0.373	0.380	0.396	0.387
0.7382	0.322	0.330	0.338	0.350	0.356
0.8402	0.223	0.226	0.229	0.233	0.242
0.9332	0.099	0.099	0.101	0.104	0.108
1.0000	0.000	0.000	0.000	0.000	0.000
η/mPa s					
0.0000	2.54	2.07	1.72	1.46	1.26
0.1066	2.65	2.14	1.77	1.49	1.28
0.1534	2.74	2.20	1.82	1.53	1.31
0.2863	2.94	2.34	1.91	1.59	1.34
0.3370	3.14	2.46	2.01	1.65	1.39
0.4105	3.47	2.72	2.15	1.76	1.44
0.4983	3.91	3.02	2.41	1.94	1.61
0.5476	4.25	3.26	2.56	2.07	1.70
0.6306	4.92	3.76	2.93	2.32	1.88
0.7020	5.57	4.15	3.18	2.50	2.01
0.7382	5.93	4.40	3.37	2.64	2.12
0.8402	7.22	5.25	3.94	3.02	2.38
0.9332	8.92	6.35	4.67	3.53	2.72
1.0000	10.30	7.09	5.00	3.67	2.74

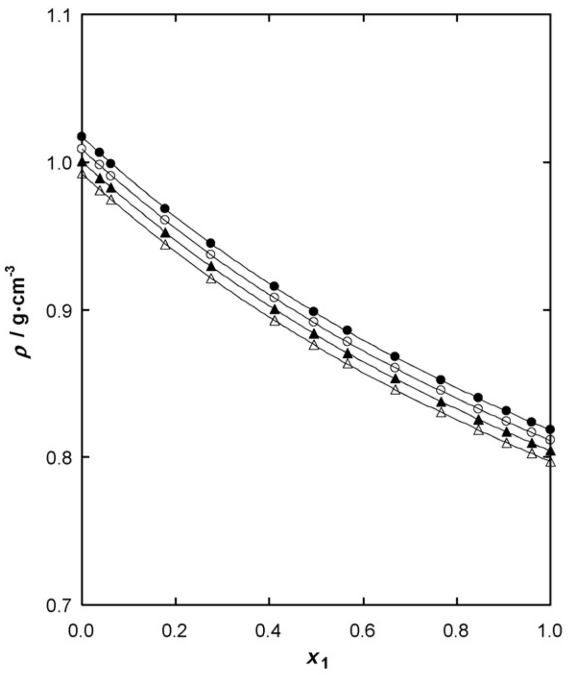


Fig. 1. Density ρ for the {1-decanol (1) + cyclohexyl carboxylic acid (2)} binary systems as a function of mole fraction at different temperatures: (●) 310 K; (○) 320 K; (▲) 330 K and (△) 340 K. Solid line represents the polynomial correlation.

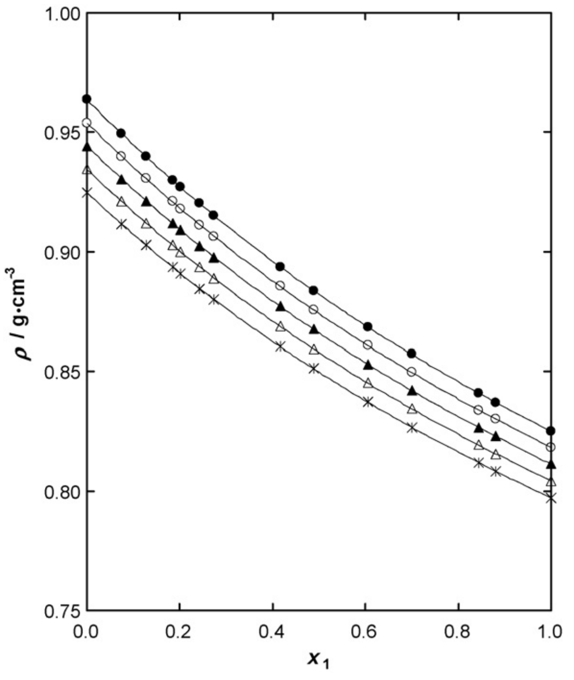


Fig. 2. Density ρ for the {1-decanol (1) + cyclohexyl acetate (2)} binary systems as a function of mole fraction at different temperatures: (●) 300 K; (○) 310 K; (▲) 320 K; (△) 330 K and (✳) 340 K. Solid line represents the polynomial correlation.

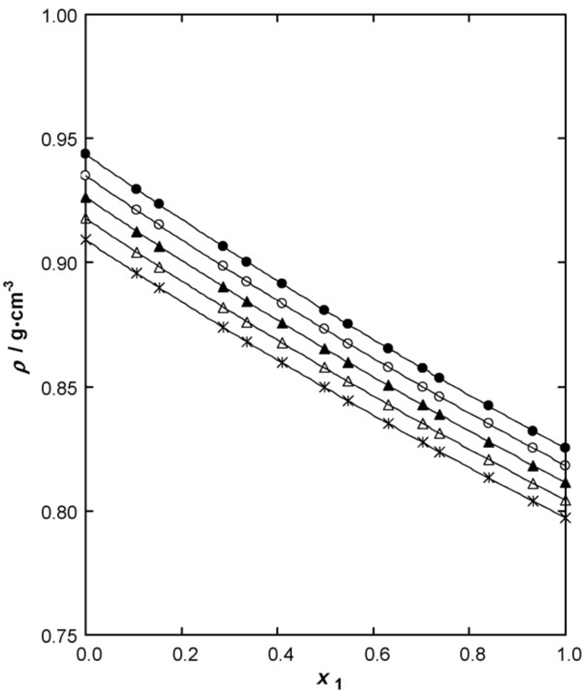


Fig. 3. Density ρ for the {1-decanol (1) + cyclohexyl ethyl acetate (2)} binary systems as a function of mole fraction at different temperatures: (●) 300 K; (○) 310 K; (▲) 320 K; (△) 330 K and (✳) 340 K. Solid line represents the polynomial correlation.

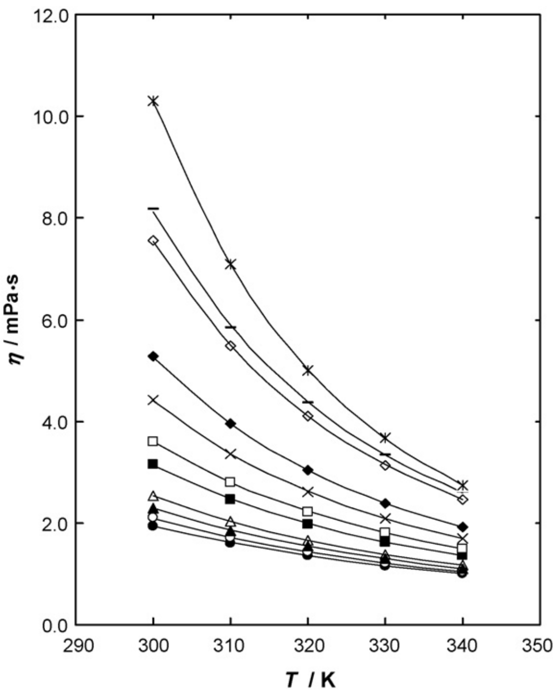


Fig. 5. Dynamic viscosity η for the {1-decanol (1) + cyclohexyl acetate (2)} binary systems as a function of temperature at different mole fractions of 1-decanol: (●) 0.0000; (○) 0.1275; (▲) 0.2015; (△) 0.2741; (■) 0.4166; (□) 0.4886; (×) 0.6055; (♦) 0.6993; (◊) 0.8435; (–) 0.8806; (✳) 1.0000. Solid lines represent the corresponding correlations by the VFT equation.

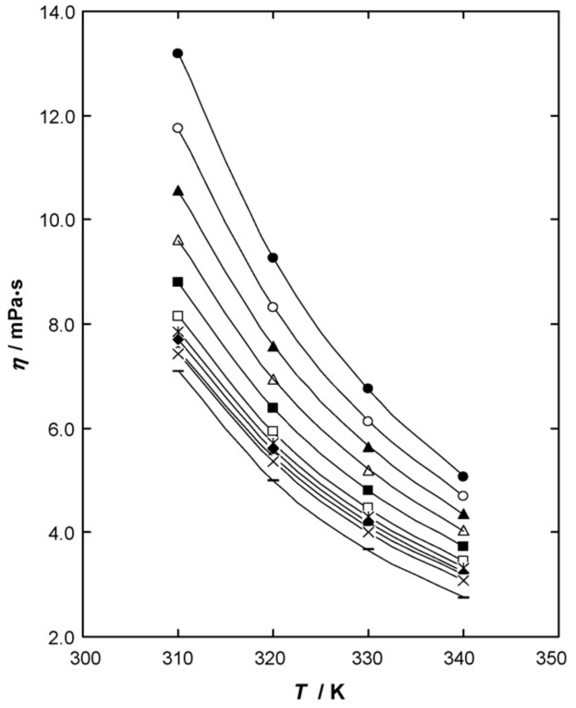


Fig. 4. Dynamic viscosity η for the {1-decanol (1) + cyclohexyl carboxylic acid (2)} binary systems as a function of temperature at different mole fractions of 1-decanol: (●) 0.0000; (○) 0.0625; (▲) 0.1776; (△) 0.2753; (■) 0.4103; (□) 0.5659; (✳) 0.6678; (♦) 0. 7657; (◊) 0.8462; (×) 0.9063; (–) 1.0000. Solid lines represent the corresponding correlations by the VFT equation.

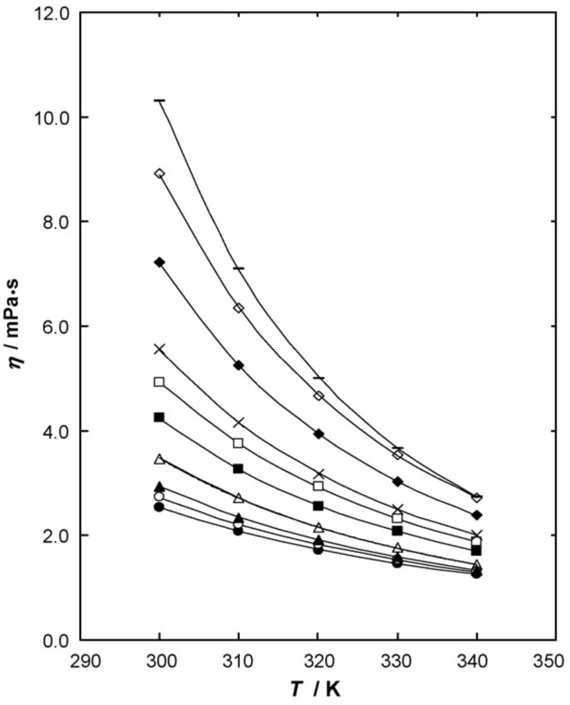


Fig. 6. Dynamic viscosity η for the binary systems {1-decanol (1) + cyclohexyl ethyl acetate (2)} as a function of temperature at different mole fractions of 1-decanol: (●) 0.0000; (○) 0.1534; (▲) 0.2863; (△) 0.4105; (■) 0.5476; (□) 0.6306; (×) 0.7020; (♦) 0.8402; (◊) 0.9332; (–) 1.0000. Solid lines represent the corresponding correlations by the VFT equation.

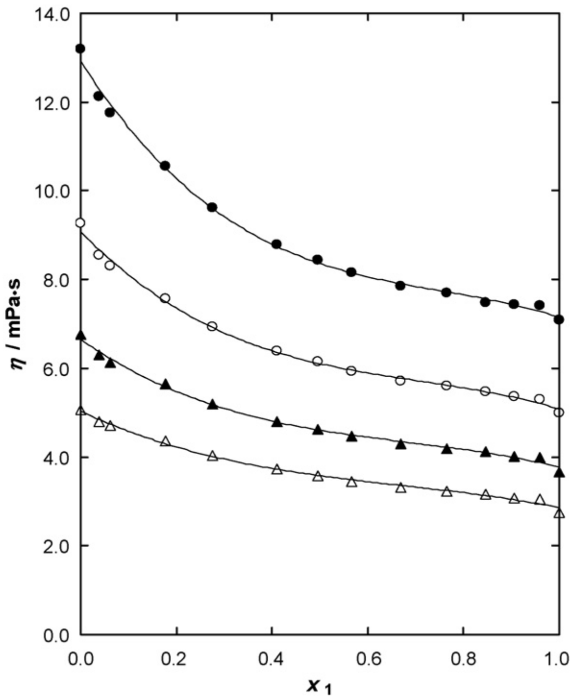


Fig. 7. Dynamic viscosity η for the {1-decanol (1) + cyclohexyl carboxylic acid (2)} binary systems as a function of mole fraction at different temperatures: (●) 310 K; (○) 320 K; (▲) 330 K and (△) 340 K. Solid line represents the polynomial correlation.

viscosity reaches the value of 10^{15} mPa s are 141.7, 122.4 and 123.7 K, for CCA, CA and 2CEA, respectively. Finally, the values of T_0 were developed from the experimental glass transition temperature for CCA (154 K) and from the viscosity of 10^{15} mPa s for CA (122.4 K) and for 2CEA (123.7 K). The values of T_0 used in the correlation were lower ($\Delta T = 55$ K): 99, 67.4 and 68.7 K, for CCA, CA and 2CEA, respectively. One value of parameter T_0 was used for different concentrations, because the FM is here the most important and ΔT_0 discuss by many authors may be about 10 K. The results of correlation are presented in Tables 4S and 5S in the SD. The VFT equation suitably correlates, as a function of the temperature, not only the viscosities of pure FM but also the viscosities of the mixtures for the binary systems through the composition range. These parameters are strongly sensitive to the choice of T_0. The standard deviations are listed in Table 5S.

The character of changes of dynamic viscosities with composition is presented in Figs. 7–9 for three FM together with solid lines calculated with polynomial:

$$\eta = c_3x_1^3 + c_2x_1^2 + c_1x_1 + c_0 \qquad (4)$$

The parameters of correlation are shown in Table 6S in the SD. It is easy to observe that the character of changes is different for acid (CCA) and for esters (CA, 2CEA). For CCA the viscosity decreases with an increase of 1-decanol mole fraction because viscosity of pure CCA is very high (13.2 mPa s at $T = 310$ K).

3.1. The excess molar volume

From the density, the excess molar volume, (V_m^E/cm^3 mol^{-1}) of any mixture with mole fraction, x_1 of 1-decanol is obtained from:

$$\begin{aligned} V_m^E &= V_m - \{x_1(V_{m1} + V_{m2})\} \\ &= x_1M_1\left(\frac{1}{\rho} - \frac{1}{\rho_1}\right) + (1 - x_1)M_2\left(\frac{1}{\rho} - \frac{1}{\rho_1}\right) \end{aligned} \qquad (5)$$

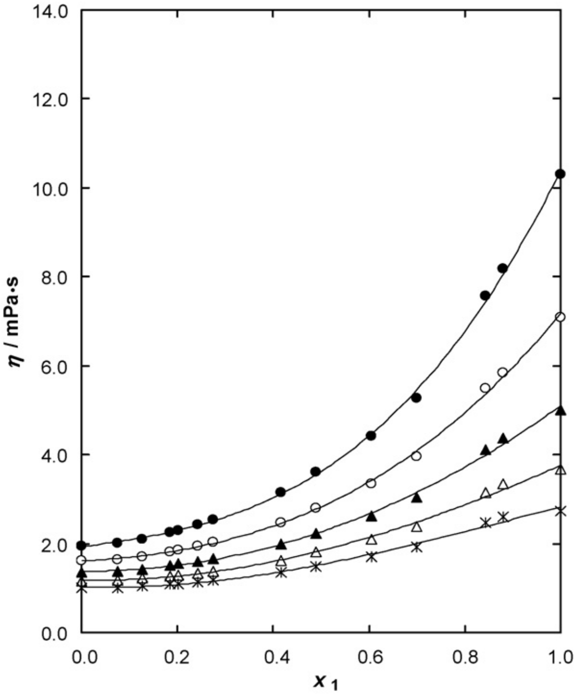


Fig. 8. Dynamic viscosity η for the {1-decanol (1) + cyclohexyl acetate (2)} binary systems as a function of mole fraction at different temperatures: (●) 300 K; (○) 310 K; (▲) 320 K; (△) 330 K and (✳) 340 K. Solid line represents the polynomial correlation.

Here, M_i, V_{mi} and ρ_i denote, respectively the molar mass, the molar volume and the density of pure component $i = 1$ (1-decanol), or 2 (FM), and V_m is the molar volume of the mixture.

Experimental excess molar volumes V_m^E data of {1-decanol (1) + FM (2)} are recorded in Table 3 for CCA, in Table 4 for CA and

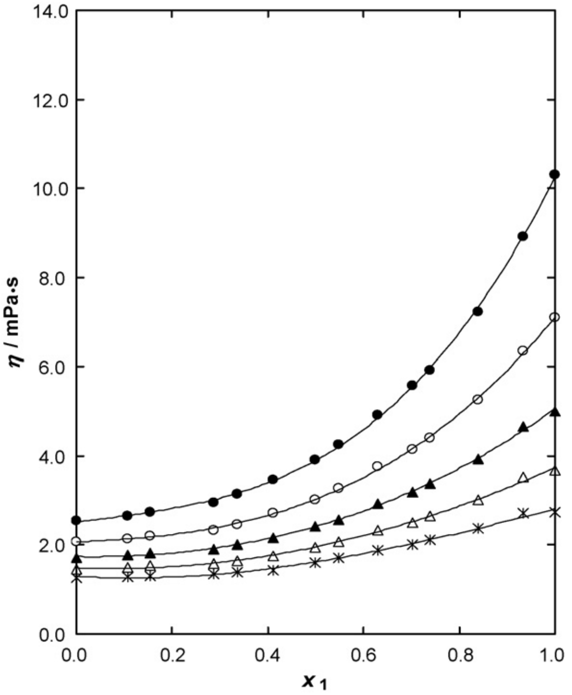


Fig. 9. Dynamic viscosity η for the {1-decanol (1) + cyclohexyl ethyl acetate (2)} binary systems as a function of mole fraction at different temperatures: (●) 300 K; (○) 310 K; (▲) 320 K; (△) 330 K and (✳) 340 K. Solid line represents the polynomial correlation.

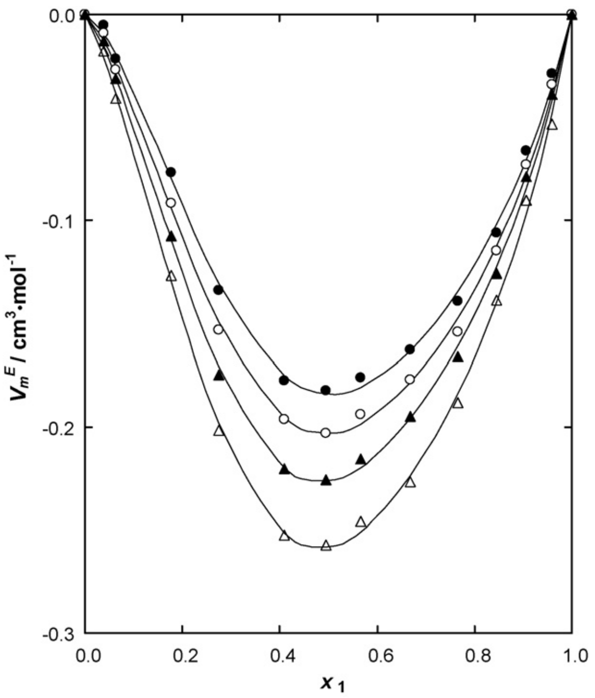


Fig. 10. Excess molar volume V_m^E versus x_1 for the {1-decanol (1) + cyclohexyl carboxylic acid (2)} binary systems at different temperatures: (●) 310 K; (○) 320 K; (▲) 330 K and (△) 340 K. The solid lines represent the corresponding correlations by the Redlich–Kister equation.

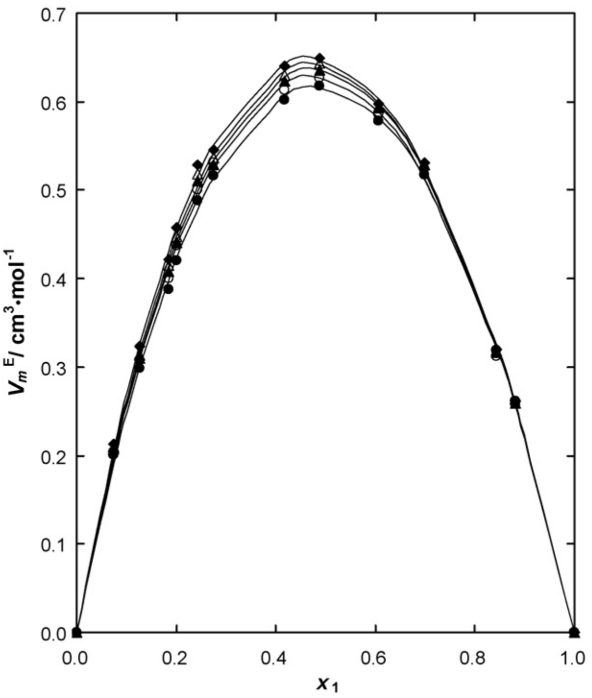


Fig. 11. Excess molar volume V_m^E versus x_1 for the {1-decanol (1) + cyclohexyl acetate (2)} binary systems at different temperatures: (●) 300 K; (○) 310 K; (▲) 320 K; (△) 330 K and (♦) 340 K. The solid lines represent the corresponding correlations by the Redlich–Kister equation.

in Table 5 for 2CEA. The data were calculated by the smoothing Redlich–Kister equation:

$$V_m^E = x_1(1 - x_1)\sum_{i=1}^{4} A_i(T)(2x_1 - 1)^{i-1} \tag{6}$$

with temperature dependence parameters

$$A_i(T) = b_i + c_i T \tag{7}$$

where x_1 is the mole fraction of the 1-decanol and $V_m^E/(\mathrm{cm^3\,mol^{-1}})$ is the molar excess volume and i is the number of parameters. The values of the parameters (A_i), for V_m^E have been determined using a method of least-squares. The fit parameters are summarized in Table 7S in the SD.

The values of V_m^E as well as the Redlich–Kister fits are plotted in Figs. 10–12 for the concentration dependence of the excess molar volumes. The graphs of V_m^E indicate that only the mixtures of {1-decanol (1) + CCA (2)} exhibit negative deviations from ideality over the entire composition range. The minimum of V_m^E is $-0.20\,\mathrm{cm^3\,mol^{-1}}$ at mole fraction range 0.5 (at $T = 320$ K). Fig. 10 shows that the values of the excess volume are quite symmetrical with the mole fraction with the increasing temperature and are more negative when the temperature increases. Data of the V_m^E for esters CA and 2CEA are positive with maximum of V_m^E equal to 0.64 and $0.42\,\mathrm{cm^3\,mol^{-1}}$ at mole fraction range 0.5 (at $T = 320$ K). The excess molar volume data become more positive in the following order: CCA < 2CEA < CA. The small negative deviations from ideality were observed for CCA; the probable explanation can be attributed to the specific interactions of CCA as an acid with 1-decanol. The differences for CA and 2CEA can be only explain by the packing effects being better for the longer aliphatic chain (substituent at the cyclohexane ring) at 2CEA molecule.

3.2. Volume expansivity of the pure FM and their mixtures

From the density–temperature dependence one can calculate the volume expansivity (coefficient of thermal expansion), α,

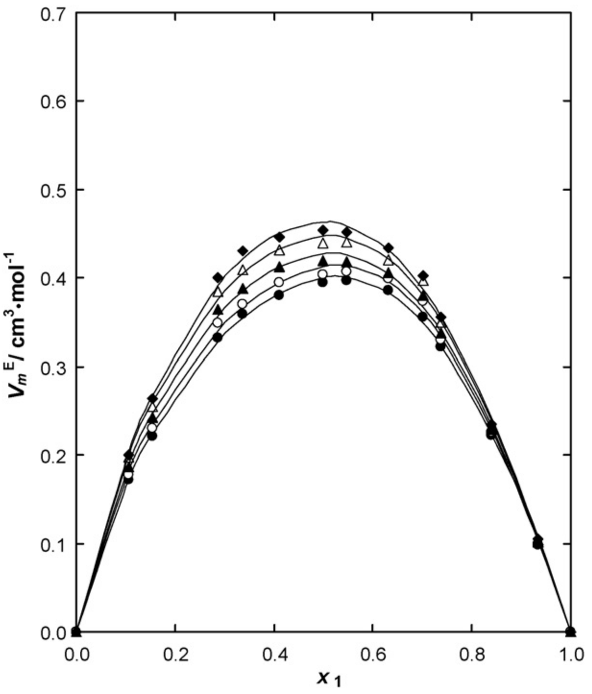


Fig. 12. Excess molar volume V_m^E versus x_1 for the {1-decanol (1) + cyclohexyl ethyl acetate (2)} binary systems at different temperatures: (●) 300 K; (○) 310 K; (▲) 320 K; (△) 330 K and (♦) 340 K. Solid line represented Redlich–Kister equation.

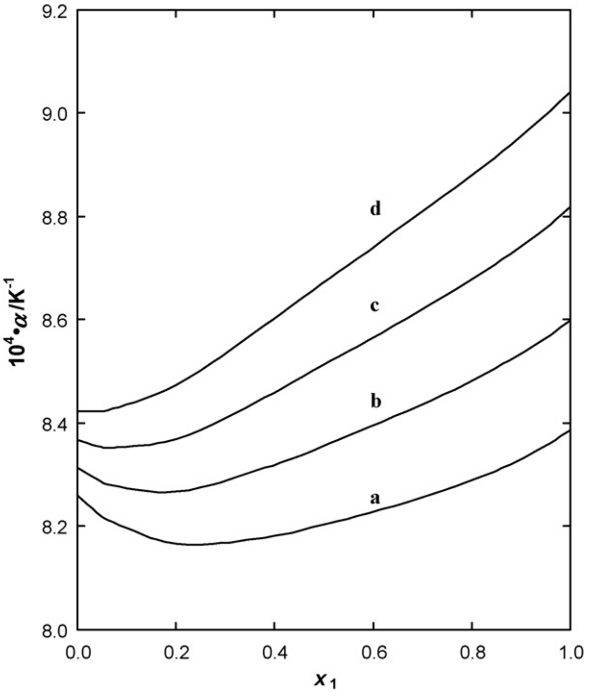


Fig. 13. Plot of volume expansivity α of the {1-decanol (1) + cyclohexyl carboxylic acid (2)} system against mole fraction x_1 at different temperatures: (a) 310 K; (b) 320 K; (c) 330 K; (d) 340 K.

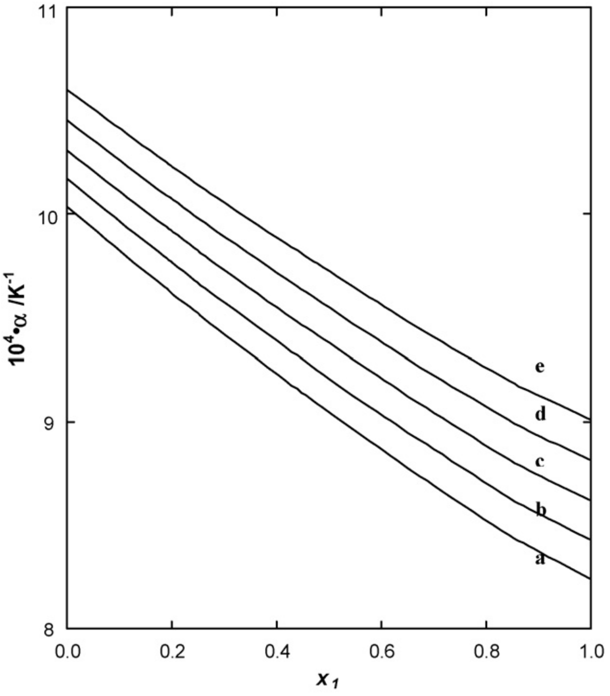


Fig. 14. Plot of volume expansivity α of the {1-decanol (1) + cyclohexyl acetate (2)} system against mole fraction x_1 at different temperatures: (a) 300 K; (b) 310 K; (c) 320 K; (d) 330 K; (e) 340 K.

defined as:

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p = -\frac{1}{\rho}\left(\frac{\partial \rho}{\partial T}\right)_p \quad (8)$$

where subscript p indicates constant pressure. If one considers a plot of ρ versus T to be linear, then the magnitude of α increases with increasing temperature. A more careful analysis reveals that the densities of the pure FM measured here actually do not increase linearly with temperature. Using Eqs. (6)–(8), the volume expansivity can be presented in a function of the composition and temperature. The results of our analysis for pure substances and their mixtures are listed in Tables 8S to 10S. The errors of derived values of parameters calculated through the statistical analysis depend significantly on the form of an equation chosen to represent density as a function of temperature at constant pressure. As a result the increasing volume expansivity with increasing temperature was observed. This is a typical behavior for fluids in general. Plots of volume expansivity α of the binary {1-decanol (1) + FM (2)} systems against mole fraction x_1 at different temperatures (300, 310, 320, 330 and 340 K) are shown in Figs. 13–15. The trends of the volume expansivity with the composition of the mixtures is totally different for CCA, for which the parameter α increases with an increase of the mole fraction of 1-decanol, and for CA and 2CEA, for which this trend is the opposite. The volume expansivity of these mixtures are considerably less dependent on temperature than it was observed for typical organic mixtures [19]. Moving along the concentration scale, the expansivity for CA systems fall from a high value for pure CA to the considerably lower one for 1-decanol. This decrease is nonlinear being less regular at low mole fraction of 1-decanol. Similar trend was observed for 2CEA with stronger nonlinear dependence at low 1-decanol concentration. Thus, a solutions reveal the volumetric properties typical for mixtures of two compounds.

Next the corresponding excess function was determined. The excess volume expansivity was calculated by the equation:

$$\alpha^E = \alpha - \varphi_1^{id}\alpha_1 - \varphi_2^{id}\alpha_2 \quad (9)$$

where φ_i^{id} is an ideal volume fraction given by the following relation:

$$\varphi_1^{id} = \frac{x_i V_{mi}}{x_1 V_{m1} + x_2 V_{m2}} \quad (10)$$

in which V_{mi} stands for a molar volume for a pure component i.

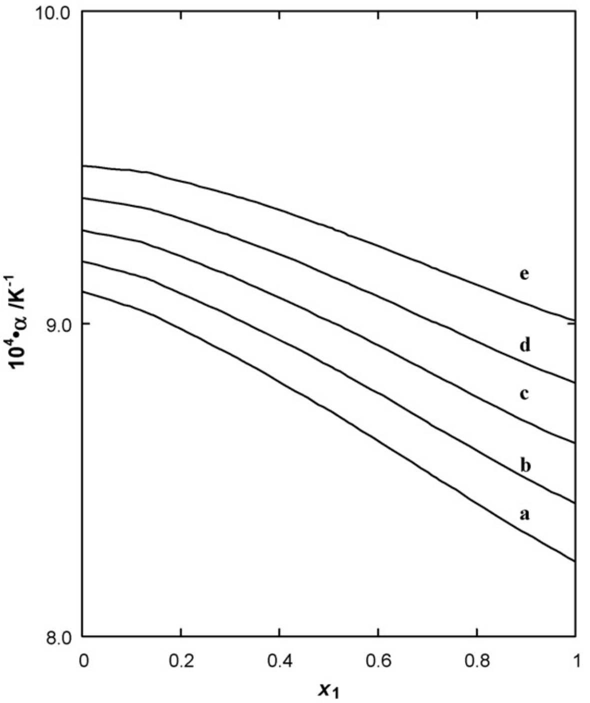


Fig. 15. Plot of volume expansivity α of the {1-decanol (1) + cyclohexyl ethyl acetate (2)} system against mole fraction x_1 at different temperatures: (a) 300 K; (b) 310 K; (c) 320 K; (d) 330 K; (e) 340 K.

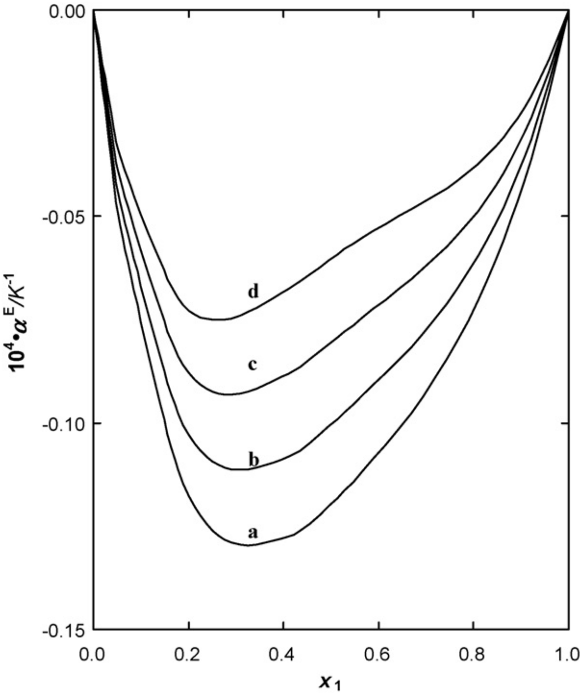


Fig. 16. Plot of excess volume expansivity α^E of the {1-decanol (1) + cyclohexyl carboxylic acid (2)} system against mole fraction x_1 at different temperatures: (a) 310 K; (b) 320 K; (c) 330 K; (d) 340 K.

Typical concentration dependencies of excess expansivity are given in Figs. 16–18. The first two mixtures including CCA and CA reveal minimum of α^E with absolute minimum values at the same order of magnitude (about $-0.1\,K^{-1}$) as was usually observed in organic mixtures [19]. The curves are asymmetrical, especially for CCA and 2CEA with the maximum for the 2CEA located at the 1-decanol mole fraction about 0.3.

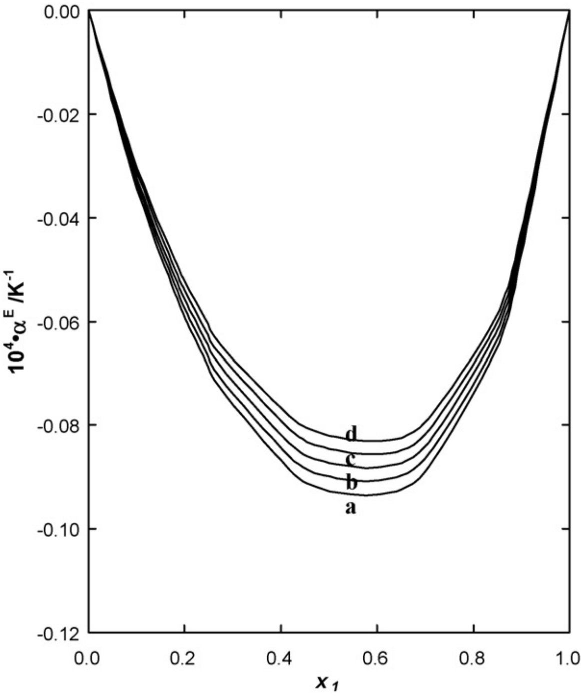


Fig. 17. Plot of excess volume expansivity α^E of {1-decanol (1) + cyclohexyl acetate (2)} system against mole fraction x_1 at different temperatures: (a) 300 K; (b) 310 K; (c) 320 K; (d) 330 K; (e) 340 K.

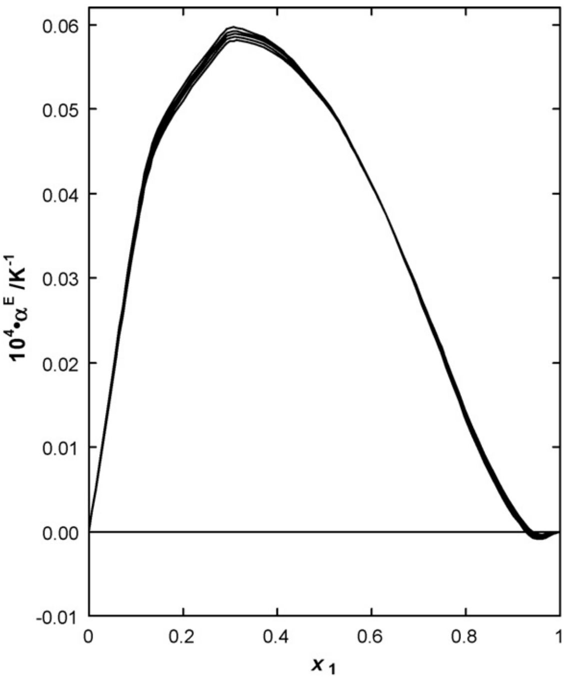


Fig. 18. Plot of excess volume expansivity α^E of the {1-decanol (1) + cyclohexyl ethyl acetate (2)} system against mole fraction x_1 at different temperatures.

4. Concluding remarks

New data on densities and viscosities of pure three polar fragrance raw materials based on the cyclohexane and their binary mixtures with 1-decanol were measured. In this work the noticeable interaction was expected between all FM, possessing different polar groups in their molecules with 1-decanol. The lower V_m^E of FM with 1-decanol means possible stronger interaction between FM and solvent. The highest interaction with 1-decanol was observed for acid (CCA). From the density–temperature dependence the volume expansivity, α was described for three pure FM and their mixtures. The highest value was found for cyclohexyl carboxylic acid.

The results of the correlations with the second-order polynomial, Redlich–Kister equation, and VFT equation of density, excess molar volumes, and viscosity were with very low standard deviations.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tca.2009.02.013.

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