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Excess molar volumes of *N*,*N*-dimethylformamide + 2-pentanone + alkan-1-ols mixed solvent systems at 303.15 K

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Abstract

Accurate excess molar volumes (V^E), at ambient pressure and 303.15 K, have been determined in the ternary liquid mixtures of *N*,*N*-dimethylformamide (DMF) + 2-pentanone (PE) + 1-alkan-1-ols (C_3–C_6) and in the binary mixtures of PE + alkan-1-ols (C_3–C_6) as a function of composition. The alkanols include 1-propanol, 1-butanol, 1-pentanol and 1-hexanol. The intermolecular interactions and structural effects were analyzed on the basis of the measured and derived properties. Excess molar volumes increase in magnitude with increase in chain length of alcohol. Valuable information on the behavior and governing factors of the liquid structure of the strongly associated solvents studied were inferred from the parameters deduced. The V^E results were correlated and fitted by the Redlich–Kister equation for binary mixtures and by the Cibulka equation for ternary mixtures, as a function of mole fraction. Several predictive empirical relations were applied to predict the excess volumes of ternary mixtures from the binary mixing data. An analysis of the data indicates a good agreement between experimental results and predicted values in all ternary systems. A discussion is presented and deviations are interpreted in terms of size, shape, the position of ketone group, the chain length of alkanol and hydrogen bond effects in the liquid mixtures studied to explain chemical and thermophysical behavior.

Keywords: Excess molar volumes; DMF; 2-Pentanone; Alkan-1-ols; Molecular interactions; Correlation

1. Introduction

The interaction between the carbonyl carbon group of ketone and solvents with polar groups, such as amide and alkanols, play a crucial role in the structural effects, molecular level and for practical applications. The considerable interest in the thermophysical properties of polar molecules containing amide, hydroxyl and carbonyl groups (ketones) and dissolved both in pure solvents and mixtures has been noted. In particular, mixtures containing carbonyl and amide groups, which can serve as a model of the peptide bond, and also containing alcohol (hydroxyl) groups, are being investigated in order to characterize intermolecular effects related to the presence of carbonyl groups and the chain length of the alkanols. When two or more solvent molecules are associated with one another to form a liquid mixture, it brings about a marked effect on the properties of the resulting system and differences in the intermolecular interactions of the solvents. This fact is well known as the transport phenomenon and thermophysical properties of mixed solvents. Numerous models of solutions [1–5] have been proposed to describe these effects and the molecular interactions between compounds forming a mixture. Volumetric properties of mixed solvents provided by the intrinsic volume of the molecules have been considered to be a good measure of solute–solvent interactions. The volumetric properties of binary liquid mixtures have been extensively studied, as they can contribute to a clarification of the various intermolecular interactions between the different species existing in solution. In particular, much effort has gone into the determination of molar excess volumes at infinite dilution where only the solute–solvent and the solvent–solvent

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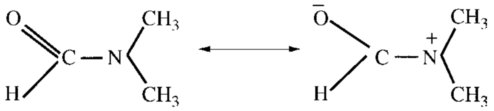
interactions are present. Furthermore, thermophysical properties of binary mixtures have vastly appeared in the literature [6–10], however, those pertaining to ternary mixtures have been rather scarcely investigated up to now. As the literature was scrutinized with respect to the factors affecting the thermophysical properties of ternary mixtures, it was seen that there are few systematic studies governing these factors [11–15].

The amides are interesting compounds in view of their technological importance and are expected to play as important solvents in chemical industry for practical purposes. They possess the –CO–NH– donor–acceptor group which is very common in nature as a peptide bond and exhibit the property of self-association by the H-bond. The amides appear to be the very polar solvents, forming hydrogen bonds both through oxygen and nitrogen atoms. *N*,*N*-Dimethylformamide (DMF) is a colorless, high-boiling, mobile, highly polar liquid with a faint, characteristic odor. It does not decompose on distillation and is freely miscible with water, alcohols, ethers, ketones, esters, carbon disulfide, and chlorinated and aromatic hydrocarbons. It is either immiscible or only partly miscible with aliphatic hydrocarbons. Even at elevated temperatures, aqueous solutions of DMF have very little tendency to hydrolyze.

DMF is a stable compound with a strong electron-pair donating and accepting ability and, is widely used in settings such as solvent reactivity relationships [16–20]. DMF is of particular interest because any significant structural effects are absent due to the lack of hydrogen bonds and therefore it may be applied as an aprotic protophilic solvent with a large dipole moment and a high dielectric constant ($\mu = 3.24$ Debye and $\varepsilon = 36.71$ at 298.15 K) [21] which is an efficient solvent for ketones as well as alkanols. It has been confirmed by Colaianni and Faurskov Nielsen [22] by low-frequency Raman spectroscopy studies that the hydrogen bonded interactions (N–H. . .O) exist in liquid formamide and in *N*-methylformamide, but not in *N*,*N*-dimethylformamide. DMF is an eminently suitable solvent for salts or compounds with a high molecular weight owing to the combined action of its small molecule, and its ability to form complexes. The resonance structure of DMF is shown below:



The negative pole in DMF is on an oxygen atom that juts out from the rest of the molecule and this oxygen atom is the best hydrogen bond acceptor. Through unshared pairs of electrons on these negatively charged, well exposed atoms are solvated very strongly. The positive pole on the other hand, is buried within the molecule. In DMF, the presence of two electron-repelling-CH_3 groups make the lone pair at nitrogen still more perceptible towards donation. Thus, it may be argued that the DMF is actually the donator of nitrogen–electron pairs.

Alkanols are polar liquids, strongly self-associated by hydrogen bonding to the extent of polymerization that may differ depending on temperature, chain length and position of the OH group. For the alcohols which are highly associated in the pure state, breaking of the H-bonds followed by specific interactions occurs upon mixing with highly polar solvents. The alkanol chain length, and shifting the position of the hydroxyl group of the alkanol are important parameters that must be taken into account to explain the behavior interaction of the amide + alkan-1-ol mixtures. It is well known that amides interact with water or alcohols by dipole–dipole interactions, and form some hydrogen-bonded complexes or hetero-associates [23–26]. The structure of the amide–water and amide–alcohol hetero-associations is different. The water molecule can participate in four hydrogen bonds, while alcohol molecules may create only two hydrogen bonds, forming linear polymeric structures [27]. On the basis of those studies, it will be interesting to explore the thermodynamic results of the addition of the amide carbonyl group mixtures with alcohols to obtain some information on the molecular interactions.

A comparison of the dipole moments of ketones with the corresponding alcohol shows that the ketones have higher dipole moments than the corresponding alcohols. Therefore, ketones are also polar and so the dipole–dipole interactions are strong; of course they form weaker hydrogen bonds than the alcohols. Since ketones lack hydroxyl groups, they are incapable to create intermolecular hydrogen bonds, but due to the presence of oxygen, they can form hydrogen bonds with alcohol or water molecules which lead to the complete solubility of low molecular weight ketones in the former solvents. On the other hand, their boiling points are considerable higher than for ethers or alkanes, indicating the presence of significant intermolecular dipole–dipole forces. The carbonyl group is polar since oxygen is more electronegative than carbon and forms a partially charged dipole. To study the object of changing the carbonyl functionalities [28–31] in the ketone groups, we have chosen 2-pentanone (PE) (dipole moment, $\mu = 2.70$ Debye and dielectric constant, $\varepsilon = 15.38$ at 298.15 K) [21] in order to study the molecular interactions in the polar group mixed solvents.

Zielkiewicz [14] studied the preferential solvation of the *N*-methylacetamide (NMA) molecule in the binary and ternary mixtures containing NMA or DMF, aliphatic alcohol and water by using the Kirkwood–Buff theory of solutions. He estimated the local mole fractions around the amide molecule, the orientation effects of molecules within the solvation shell, and a possibility of the formation of complexes. As already concluded [15], it seems reasonable to assume extensive hydrogen bonding in aqueous solutions, between water molecules (W) and the amide groups of DMF and *N*-methylformamide (NMF). In other words, the formation of ternary complex species is not significant for (DMF + NMF + W) mixtures. In order to extend the study of polar groups, such as amide with alkanols containing ketone, to characterize the type and magnitude of molecular interactions between the polar group solvents and also to study the effect of chain length of alkanols, we report here the excess molar volumes of four binary mixtures of 2-pentanone with 1-alkanols and also excess molar volumes of ternary mixtures containing *N*,*N*-dimethylformamide and 2-pentanone with 1-propanol, 1-butanol, 1-pentanol and 1-hexanol at 303.15 K at atmospheric pressure.

Table 1
Densities, ρ, at 303.15 K and refractive indices, n, at 298.15 K of pure components

Compound	ρ (g cm^{-3})		n	
	This work	Literature [21,32]	This work	Literature [21,32]
N,*N*-Dimethylformamide	0.94118	0.94120	1.4283	1.4282
2-Pentanone	0.79657	0.79660	1.3886	1.3885
1-Propanol	0.79659	0.79600	1.3836	1.3837
1-Butanol	0.80203	0.80206	1.3973	1.3974
1-Pentanol	0.80762	0.80764	1.4080	1.4080
1-Hexanol	0.81200	0.81201	1.4156	1.4157

2. Experimental

2.1. Materials

N,*N*-Dimethylformamide (99.9% of purity), 2-pentanone (99.5% of purity), 1-propanol (99.5% of purity) and 1-butanol (99.8% of purity) were obtained from Aldrich and 1-pentanol (≥99.5 of purity) and 1-hexanol (≥99.5 of purity) were purchased from Fluka. All chemicals were used without further purification. The purities of all the substances were checked by comparing the measured densities (ρ) at 303.15 K and refractive indices (n) at 298.15 K of the components with those reported in the literature [21,32]. Densities of pure components were determined with a capacity 12 cm^3 bicapillary-type pycnometer. The densities of the pure liquids were accurate to two parts in 10^5. Refractive index was determined using an Abbe's refractometer with an accuracy of ± 0.0002. The purities of the samples were further confirmed by GLC single sharp peaks. Densities and refractive indices of pure substances and their comparison with literature values are listed in Table 1.

2.2. Measurements

The experimental excess molar volumes for binary and ternary mixtures were measured by using the dilatometer technique delineated by Rao and Naidu [33] and Naidu and Naidu [34], respectively. More details on the experimental procedure were depicted in our previous papers [35,36]. One of the two or three bulbs was fitted with a capillary, and the other one or two were fitted with ground-glass stoppers. Each bulb of the dilatometer was filled with a component which mass was determined directly by weighing. The filled dilatometer was placed in a temperature controlled water bath maintained at 303.15 ± 0.01 K. The measured excess molar volume values were accurate to ± 0.003 cm^3 mol^{-1}. The uncertainty in solution composition expressed in mole fraction was found to be less than 5×10^{-5}.

3. Results and discussion

The excess molar volume data (V^E) for the binary (PE + 1-alkanol) and ternary (DMF + PE + 1-alkanol, where 1-alkanol is 1-propanol or 1-butanol or 1-pentanol or 1-hexanol) mixtures were determined at 303.15 K under atmospheric pressure and are reported in Tables 2 and 3, respectively. Fig. 1 summarizes details of the experimental binary excess molar volume data over the entire range of composition. The experimental V^E_{123} for ternary mixtures of DMF + PE + 1-alkanols at 303.15 K are illustrated in Fig. 2. The binary V^E data for DMF with 1-alkanols [37] and DMF with PE [38] were reported earlier.

Table 2
Excess molar volumes V^E_{23} for 2-pentanone with 1-alkanols at 303.15 K and at ambient pressure as function of the first component (x_1)

x_1	V^E_{23}(cm^3 mol^{-3})	x_1	V^E_{23}(cm^3 mol^{-3})
2-Pentanone + 1-propanol			
0.0849	−0.012	0.5834	−0.020
0.1342	−0.016	0.6318	−0.017
0.2023	−0.022	0.7032	−0.011
0.2591	−0.027	0.7836	−0.008
0.3239	−0.028	0.8324	−0.006
0.4042	−0.028	0.8732	−0.005
0.4832	−0.026	0.9149	−0.004
0.5342	−0.025	0.9548	−0.002
2-Pentanone + 1-butanol			
0.0842	−0.005	0.5673	−0.009
0.1426	−0.006	0.6218	−0.008
0.2025	−0.007	0.6842	−0.006
0.2642	−0.008	0.7341	−0.005
0.3218	−0.008	0.8017	−0.004
0.4022	−0.009	0.8624	−0.003
0.5112	−0.010	0.9418	−0.002
2-Pentanone + 1-pentanol			
0.0742	0.004	0.5621	0.012
0.1336	0.005	0.6112	0.010
0.1982	0.007	0.6632	0.009
0.2543	0.008	0.7036	0.008
0.3041	0.009	0.7512	0.007
0.3672	0.010	0.8024	0.005
0.4002	0.011	0.8903	0.004
0.4531	0.012	0.9406	0.002
0.5029	0.014		
2-Pentanone + 1-hexanol			
0.0812	0.012	0.5616	0.034
0.1526	0.017	0.6219	0.031
0.2014	0.022	0.7025	0.028
0.2624	0.027	0.7843	0.022
0.3242	0.030	0.8432	0.016
0.4024	0.032	0.9046	0.009
0.4605	0.034	0.9528	0.005
0.5012	0.036		

Table 3
Excess molar volumes V^{E}_{123} of ternary mixtures of *N*,*N*-dimethylformamide (1) + 2-pentanone (2) + 1-alkanols (3) at 303.15 K and at ambient pressure

x_1	x_2	V^E_{123}(exp) (cm^3 mol^{-1})
N,*N*-Dimethylformamide (1) + 2-pentanone (2) + 1-propanol (3)		
0.0062	0.8918	−0.036
0.0105	0.9087	−0.047
0.0218	0.4021	−0.034
0.0252	0.4722	−0.042
0.0283	0.0338	−0.028
0.0297	0.9001	−0.059
0.0352	0.0820	−0.030
0.0568	0.3577	−0.052
0.0655	0.8832	−0.068
0.0752	0.7792	−0.074
0.1026	0.1124	−0.038
0.1107	0.0293	−0.039
0.1153	0.7129	−0.092
0.1158	0.2239	−0.059
0.1179	0.4105	−0.074
0.1189	0.8011	−0.088
0.1200	0.5056	−0.082
0.1218	0.6017	−0.089
0.1234	0.7501	−0.086
0.1267	0.1548	−0.051
0.1301	0.3018	−0.065
0.1308	0.8154	−0.091
0.1441	0.4657	−0.092
0.1499	0.8027	−0.119
0.1602	0.1288	−0.059
0.1689	0.6969	−0.119
0.1703	0.5528	−0.093
0.1791	0.7920	−0.128
0.2044	0.0696	−0.049
0.2067	0.7624	−0.136
0.2156	0.6480	−0.125
0.2201	0.5081	−0.123
0.2346	0.1285	−0.066
0.2362	0.2558	−0.090
0.2471	0.7221	−0.158
0.2520	0.4011	−0.120
0.2524	0.6860	−0.149
0.2569	0.6317	−0.139
0.2629	0.0885	−0.061
0.2822	0.2813	−0.099
0.2917	0.0417	−0.053
0.3042	0.6736	−0.166
0.3089	0.1186	−0.073
0.3099	0.2948	−0.118
0.3102	0.5891	−0.155
0.3318	0.1586	−0.091
0.3660	0.3839	−0.144
0.3665	0.1859	−0.089
0.3685	0.5188	−0.169
0.3829	0.2905	−0.126
0.3868	0.5824	−0.182
0.3973	0.5207	−0.170
0.4036	0.2179	−0.120
0.4123	0.5145	−0.183
0.4139	0.4107	−0.153
0.4226	0.1236	−0.090
0.4514	0.2995	−0.143
0.4515	0.4419	−0.184
0.4632	0.4403	−0.173
0.4808	0.2327	−0.131
0.5002	0.3819	−0.171
0.5225	0.1415	−0.098
0.5609	0.3098	−0.159
0.5660	0.3449	−0.169
0.5683	0.1859	−0.122
0.6118	0.2640	−0.151
0.6253	0.1309	−0.101
0.6409	0.2371	−0.143
0.6572	0.2984	−0.180
0.6722	0.2792	−0.166
0.7019	0.2603	−0.161
0.7125	0.1804	−0.121
0.7146	0.2006	−0.128
0.7259	0.1245	−0.100
0.7313	0.2306	−0.151
0.7607	0.2052	−0.139
0.7821	0.1838	−0.132
0.7899	0.1649	−0.124
0.8014	0.1020	−0.091
0.8016	0.1349	−0.096
0.8326	0.0826	−0.071
0.8649	0.0796	−0.073
0.8806	0.0568	−0.062
0.9324	0.0295	−0.047
N,*N*-Dimethylformamide (1) + 2-pentanone (2) + 1-butanol (3)		
0.0112	0.3212	−0.009
0.0130	0.5267	−0.011
0.0133	0.8776	−0.012
0.0235	0.8776	−0.019
0.0241	0.9291	−0.039
0.0263	0.1335	−0.007
0.0337	0.4906	−0.021
0.0364	0.8989	−0.047
0.0407	0.2303	−0.013
0.0505	0.6718	−0.049
0.0536	0.8805	−0.056
0.0565	0.0731	−0.009
0.0627	0.5116	−0.041
0.0677	0.8835	−0.067
0.0771	0.0216	−0.007
0.0841	0.8825	−0.078
0.0859	0.1821	−0.018
0.0952	0.7811	−0.080
0.1011	0.1448	−0.015
0.1017	0.8684	−0.089
0.1104	0.2213	−0.026
0.1112	0.4142	−0.049
0.1115	0.5978	−0.073
0.1132	0.1024	−0.012
0.1142	0.8121	−0.092
0.1191	0.7022	−0.081
0.1201	0.3112	−0.038
0.1202	0.5112	−0.061
0.1223	0.8533	−0.108
0.1348	0.7425	−0.085
0.1509	0.0941	−0.008
0.1527	0.8080	−0.120
0.1594	0.4329	−0.059
0.1722	0.7899	−0.129
0.1732	0.3058	−0.052
0.1734	0.2060	−0.040
0.1858	0.7837	−0.147
0.1892	0.6961	−0.106
0.2047	0.0375	−0.009
0.2050	0.7731	−0.159
0.2055	0.6820	−0.116

Table 3 (*Continued*)

x_1	x_2	V^E_{123}(exp) (cm^3 mol^{-1})
0.2248	0.1122	−0.017
0.2378	0.4178	−0.073
0.2458	0.6114	−0.111
0.2604	0.2940	−0.061
0.2618	0.6374	−0.133
0.2716	0.2244	−0.051
0.2759	0.6872	−0.169
0.2857	0.6522	−0.160
0.3126	0.1044	−0.021
0.3202	0.5611	−0.130
0.3287	0.1365	−0.037
0.3349	0.5400	−0.151
0.3483	0.3695	−0.083
0.3505	0.2970	−0.073
0.3703	0.3938	−0.090
0.3827	0.5167	−0.161
0.3834	0.4722	−0.123
0.4002	0.4743	−0.131
0.4008	0.1759	−0.058
0.4134	0.1246	−0.046
0.4136	0.4118	−0.113
0.4233	0.4823	−0.170
0.4450	0.2182	−0.069
0.4746	0.4210	−0.157
0.4916	0.2454	−0.084
0.5048	0.3683	−0.131
0.5085	0.3482	−0.123
0.5153	0.3816	−0.161
0.5219	0.1259	−0.059
0.5628	0.3198	−0.152
0.5655	0.2756	−0.112
0.5770	0.2425	−0.094
0.6014	0.0160	−0.009
0.6098	0.2792	−0.133
0.6334	0.0823	−0.039
0.6524	0.2309	−0.122
0.7006	0.2727	−0.169
0.7118	0.1937	−0.113
0.7447	0.2327	−0.159
0.7248	0.1052	−0.068
0.7482	0.2093	−0.133
0.7488	0.2182	−0.149
0.7708	0.1850	−0.122
0.7971	0.1637	−0.112
0.8090	0.1047	−0.071
0.8181	0.1427	−0.091
0.8408	0.1184	−0.075
0.8450	0.0367	−0.023
0.8540	0.0187	−0.013
0.8801	0.0761	−0.063
0.8993	0.0429	−0.043
0.9146	0.0524	−0.046
N,*N*-Dimethylformamide (1) + 2-pentanone (2) + 1-pentanol (3)		
0.0188	0.6357	−0.004
0.0211	0.9172	−0.009
0.0223	0.3665	0.022
0.0226	0.1395	0.068
0.0247	0.1649	0.059
0.0262	0.0974	0.077
0.0266	0.3058	0.028
0.0279	0.4027	0.009
0.0326	0.1942	0.050
0.0377	0.9276	−0.024
0.0452	0.9276	−0.033

Table 3 (*Continued*)

x_1	x_2	V^E_{123}(exp) (cm^3 mol^{-1})
0.0536	0.8959	−0.039
0.0614	0.9018	−0.059
0.0641	0.8805	−0.046
0.0650	0.4542	−0.004
0.0661	0.9078	−0.072
0.0689	0.5315	−0.008
0.0773	0.0157	0.079
0.0822	0.5930	−0.022
0.0911	0.8402	−0.069
0.0917	0.8776	−0.080
0.0998	0.3022	0.009
0.1089	0.7816	−0.063
0.1109	0.0844	0.060
0.1110	0.6309	−0.033
0.1117	0.1548	0.025
0.1124	0.2239	0.015
0.1124	0.4122	−0.009
0.1126	0.7911	−0.073
0.1129	0.5022	−0.024
0.1193	0.6839	−0.043
0.1195	0.8532	−0.089
0.1342	0.3212	−0.004
0.1366	0.6780	−0.052
0.1399	0.0187	0.071
0.1424	0.1004	0.051
0.1474	0.8293	−0.099
0.1532	0.7339	−0.076
0.1624	0.4255	−0.020
0.1721	0.6481	−0.061
0.1741	0.8021	−0.120
0.1808	0.4764	−0.032
0.1857	0.5691	−0.051
0.1948	0.0228	0.062
0.1989	0.7053	−0.091
0.2144	0.3174	−0.009
0.2231	0.4489	−0.038
0.2233	0.6143	−0.069
0.2366	0.1427	0.021
0.2458	0.6688	−0.096
0.2459	0.6114	−0.082
0.2476	0.7233	−0.142
0.2600	0.3363	−0.017
0.2721	0.0400	0.050
0.2733	0.4512	−0.053
0.2738	0.7053	−0.149
0.2941	0.5933	−0.090
0.3094	0.5742	−0.133
0.3248	0.3683	−0.040
0.3273	0.4403	−0.063
0.3294	0.3408	−0.031
0.3438	0.5569	−0.122
0.3455	0.5480	−0.103
0.3525	0.1519	0.011
0.3632	0.4391	−0.073
0.3772	0.5717	−0.149
0.3799	0.0761	0.032
0.3903	0.1759	−0.004
0.3911	0.5001	−0.141
0.3947	0.4814	−0.092
0.4163	0.3331	−0.051
0.4264	0.2093	−0.010
0.4366	0.4027	−0.083
0.4536	0.4420	−0.123
0.4632	0.0249	0.052
0.4687	0.4118	−0.102

Table 3 (*Continued*)

x_1	x_2	V^{E}_{123}(exp) (cm^3 mol^{-1})
0.4750	0.2771	−0.042
0.4796	0.2496	−0.030
0.4920	0.3754	−0.091
0.5037	0.4403	−0.153
0.5265	0.3695	−0.123
0.5289	0.2028	−0.019
0.5322	0.0278	0.033
0.5604	0.2644	−0.062
0.5515	0.3288	−0.103
0.5659	0.2697	−0.074
0.5925	0.2274	−0.052
0.6041	0.0308	0.022
0.6118	0.2600	−0.094
0.6140	0.3151	−0.142
0.6271	0.2366	−0.081
0.6315	0.1175	0.004
0.6874	0.0216	0.013
0.7011	0.2327	−0.120
0.7032	0.2152	−0.101
0.7046	0.1940	−0.078
0.7080	0.1711	−0.062
0.7191	0.0971	−0.01
0.7439	0.1543	−0.067
0.7666	0.2007	−0.147
0.8010	0.1098	−0.038
0.8027	0.1649	−0.141
0.8366	0.1013	−0.059
0.8392	0.1287	−0.098
0.8512	0.1267	−0.119
0.8531	0.0882	−0.047
0.8746	0.0974	−0.087
0.8806	0.0716	−0.042
0.8877	0.0609	−0.029
0.9007	0.0462	−0.022
0.9027	0.0731	−0.077
0.9039	0.0127	−0.004
0.9043	0.0314	−0.012
0.9087	0.0631	−0.068
N,*N*-Dimethylformamide (1) + 2-pentanone (2) + 1-hexanol (3)		
0.0111	0.9151	−0.020
0.0113	0.8409	−0.010
0.0153	0.7816	0.003
0.0198	0.0865	0.097
0.0201	0.9152	−0.031
0.0203	0.9471	−0.040
0.0214	0.6925	0.011
0.0218	0.1522	0.080
0.0220	0.1925	0.070
0.0227	0.2644	0.057
0.0241	0.8302	−0.019
0.0268	0.4571	0.029
0.0279	0.3816	0.040
0.0303	0.3153	0.048
0.0306	0.1012	0.090
0.0312	0.5483	0.020
0.0418	0.8240	−0.032
0.0499	0.9140	−0.052
0.0700	0.0187	0.098
0.0756	0.8959	−0.060
0.0786	0.0864	0.081
0.0789	0.7564	−0.042
0.0887	0.7011	−0.022
0.0912	0.7073	−0.029
0.0928	0.6522	−0.012
0.0940	0.1139	0.070
0.0956	0.8410	−0.063
0.0975	0.3517	0.027
0.1006	0.7657	−0.051
0.1008	0.5822	0.003
0.1011	0.0228	0.091
0.1112	0.4856	0.010
0.1122	0.2124	0.045
0.1183	0.4008	0.018
0.1201	0.2815	0.038
0.1259	0.8471	−0.080
0.1324	0.1156	0.056
0.1415	0.7467	−0.057
0.1434	0.6327	−0.041
0.1591	0.0207	0.082
0.1648	0.4826	0.001
0.1741	0.7944	−0.090
0.1792	0.5273	−0.023
0.1798	0.5039	−0.011
0.1799	0.7012	−0.068
0.1850	0.6176	−0.051
0.1891	0.5335	−0.032
0.2058	0.0228	0.071
0.2086	0.6630	−0.075
0.2421	0.2152	0.030
0.2430	0.0293	0.061
0.2440	0.7242	−0.112
0.2602	0.6298	−0.092
0.2709	0.3260	0.010
0.2719	0.4542	−0.040
0.2855	0.4065	−0.022
0.2991	0.3535	−0.001
0.3013	0.6650	−0.113
0.3062	0.2369	0.021
0.3160	0.4891	−0.060
0.3182	0.0293	0.051
0.3248	0.5623	−0.099
0.3284	0.3725	−0.031
0.3418	0.3342	−0.010
0.3436	0.6354	−0.121
0.3563	0.5146	−0.090
0.3680	0.4764	−0.081
0.3835	0.3725	−0.052
0.4005	0.4987	−0.112
0.4029	0.1254	0.105
0.4185	0.2984	−0.021
0.4226	0.2496	0.002
0.4243	0.0187	0.041
0.4315	0.3790	−0.061
0.4328	0.1106	0.116
0.4350	0.2028	0.010
0.4371	0.4520	−0.100
0.4452	0.4912	−0.121
0.4459	0.3001	−0.042
0.4592	0.4041	−0.090
0.4744	0.0338	0.032
0.4918	0.1091	0.119
0.5022	0.3514	−0.077
0.5218	0.1186	0.111
0.5330	0.3852	−0.111
0.5468	0.1924	−0.012
0.5525	0.3535	−0.098
0.5587	0.2899	−0.062
0.5651	0.2072	−0.033
0.5677	0.0441	0.022

Table 3 (*Continued*)

x_1	x_2	V^E_{123}(exp) (cm^3 mol^{-1})
0.5734	0.3153	−0.089
0.5786	0.2182	−0.041
0.5912	0.1477	0.003
0.5984	0.3790	−0.123
0.6002	0.1776	−0.020
0.6218	0.1009	0.113
0.6276	0.2730	−0.080
0.6309	0.2182	−0.050
0.6423	0.0672	0.011
0.6659	0.3067	−0.112
0.7114	0.2164	−0.055
0.7134	0.2517	−0.110
0.7224	0.0207	0.012
0.7584	0.2135	−0.092
0.7719	0.2007	−0.082
0.7896	0.1839	−0.061
0.8125	0.0207	0.002
0.8187	0.1519	−0.051
0.8529	0.1095	−0.041
0.9004	0.0249	−0.011
0.9123	0.0631	−0.030
0.9502	0.0207	−0.021

The binary excess molar volume data were correlated by means of the Redlich–Kister type equation, i.e.

$$V^{\mathrm{E}}_{ij}(x_i, x_j) = x_i x_j \sum_{s=0}^{n-1} a_s (x_i - x_j)^s \qquad (1)$$

where n is the number of coefficients. Its determination depended on the data sets. For the data presented in this paper (PE + 1-alkanol), its value was accepted if the higher order coefficient was found to be statistically insignificant, what was deduced from the changes of the remainder variance and additionally supported by the residual analysis. For the remaining binary data sets composed of the less numerous experimental data points, it was additionally imposed that the number of parameters could not exceed three. The values of coefficients and standard deviations are given in Table 4.

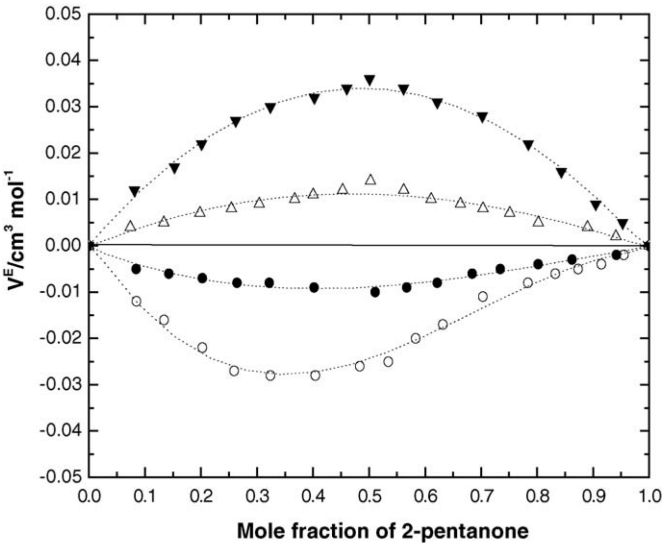


Fig. 1. Excess molar volumes, V^{E}_{23}, at 303.15 K and atmospheric pressure for 2-pentanone + 1-propanol, (o); +1-butanol, (●); + 1-pentanol, (△); +1-hexanol, (▲.) dotted lines (. . .) correlated by Redlich–Kister equation.

The ternary data were correlated by Cibulka [39] equation. It contains three parameters (b_0, b_1, b_2) included in the last term of Eq. (2) which is a correction over the three binary contributions. The latter ones are usually expressed by the Redlich–Kister Eq. (1):

$$V^{\mathrm{E}}_{123} = \sum_{i,j=1,2;1,3;2,3} V^{\mathrm{E}}_{ij}(x_i, x_j) + x_1 x_2 x_3 (b_0 + b_1 x_1 + b_2 x_2) \qquad (2)$$

where x_1, x_2 and x_3 are the mole fractions of DMF, PE and alkanol, respectively. The results of the ternary correlations, i.e. the values of the parameters of the Cibulka equation and the standard deviations, are listed in Table 5.

There exist a lot of algorithms which enable to predict ternary (or multicomponent) data on the base of binary correlations only. For the excess molar volume data, for which an equation-of-state must be included in any theoretically justified model, usually some empirical rules are used for this purpose [40,41]. They are based on two sets of assumptions: (i) the definition of a functional form of binary contributions and (ii) the definition of mole fractions used as parameters in these contributions ($x_i^{(ij)}$). In the simplest case one can assume that

$$x_i^{(ij)} = x_i \quad x_j^{(ij)} = x_j \qquad (3)$$

and a ternary function is a simple sum of binary dependencies

$$V^{\mathrm{E}}_{123} = \sum_{i,j=1,2;1,3;2,3} V^{\mathrm{E}}_{ij}(x_i, x_j) \qquad (4)$$

which are usually given by the Redlich–Kister equations. Such a procedure is sometimes termed as the Redlich–Kister method to predict ternary data from the binary ones.

Among more elaborated methods, one can define a group of symmetric algorithms which apply the same functional form for all the binary contributions. Two of them have been tested in this paper—the method of Kohler [42] and the method of Jacob and Fitzner [43].

The Kohler method is based on the following expressions:

$$V^{\mathrm{E}}_{123} = \sum_{i,j=1,2;1,3;2,3} (x_i + x_j)^2 V^{\mathrm{E}}_{ij}(x_i^{(ij)}, x_j^{(ij)}) \qquad (5)$$

where

$$x_i^{(ij)} = \frac{x_i}{x_i + x_j} \qquad (6)$$

while that of Jacob and Fitzner

$$V^{\mathrm{E}}_{123} = \sum_{i,j=1,2;1,3;2,3} \frac{x_i x_j}{x_i^{(ij)} x_j^{(ij)}} V^{\mathrm{E}}_{ij}(x_i^{(ij)}, x_j^{(ij)}) \qquad (7)$$

and

$$x_i^{(ij)} = \frac{1}{2}(1 + x_i - x_j) \quad x_j^{(ij)} = \frac{1}{2}(1 + x_j - x_i) \qquad (8)$$

The asymmetric methods, which differentiate between binary contributions, are used for the systems when one binary pair

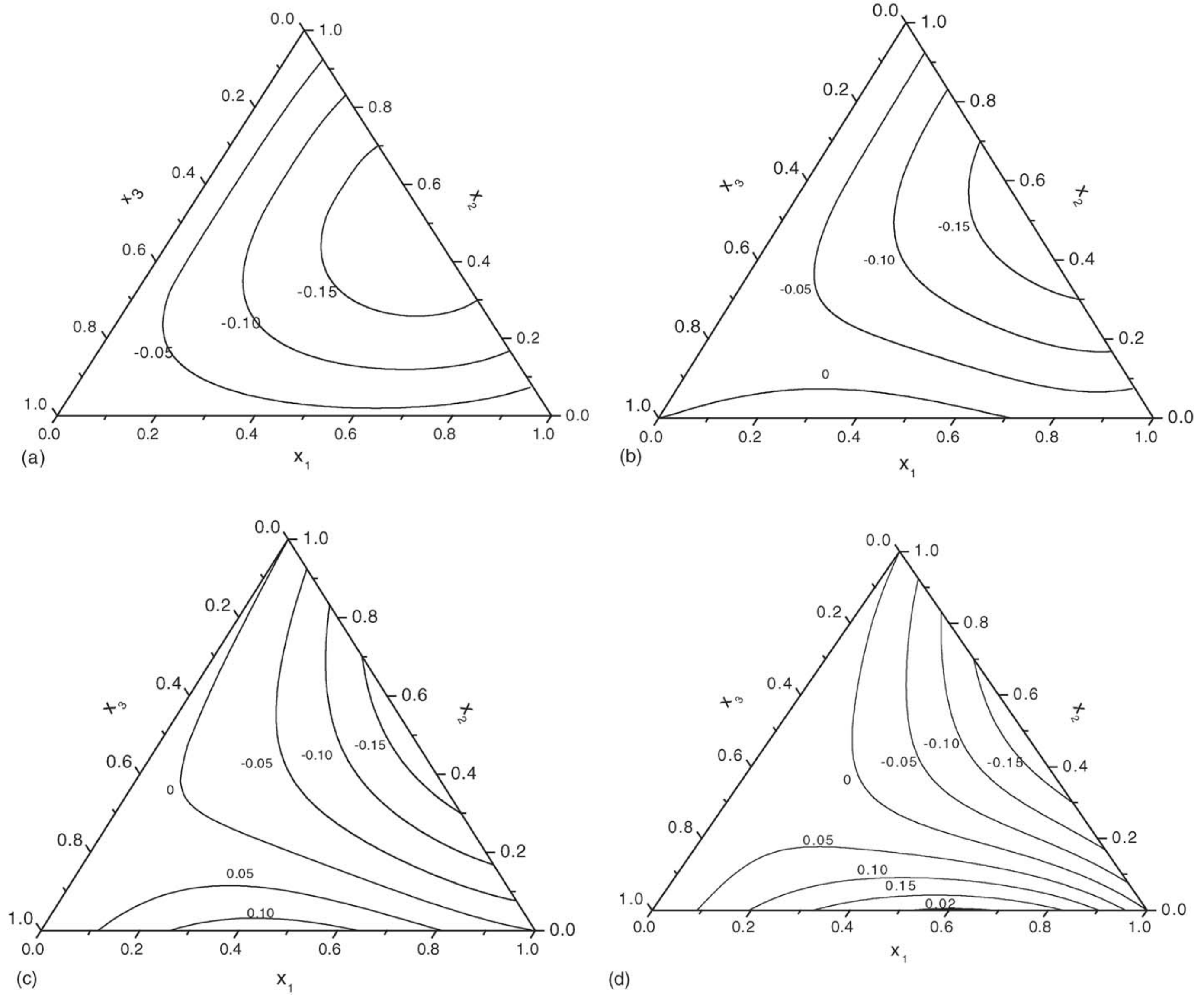


Fig. 2. The ternary excess molar volumes, V^E_{123}, for (a) DMF (1) + PE (2) + 1-propanol (3); (b) DMF (1) + PE (2) + 1-butanol (3); (c) DMF (1) + PE (2) + 1-pentanol (3); (d) DMF (1) + PE (2) + 1-hexanol (3) at 303.15 K and at atmospheric pressure. Lines showing the equal excess molar volume values were calculated by Eq. (2) with the parameters given in Tables 4 and 5.

Table 4

The values of the coefficients of the Redlich–Kister equation and standard deviations $\sigma(V^E)$ at 303.15 K

	a_0 (cm^3 mol^{-1})	a_1 (cm^3 mol^{-1})	a_2 (cm^3 mol^{-1})	$\sigma(V^E)$ (cm^3 mol^{-1})
DMF + PE	−0.7152	–	–	0.003[a]
DMF + 1-propanol	−0.1465	−0.0881		0.001[b]
DMF + 1-butanol	0.1019	−0.1425	−0.2296	0.003[b]
DMF + 1-pentanol	0.4921	−0.1465	−0.1913	0.004[b]
DMF + 1-hexanol	0.7817	0.3313	0.1456	0.005[b]
PE + 1-propanol	−0.0974	0.0792	–	0.001[c]
PE + 1-butanol	−0.0360	0.0149	–	0.001[c]
PE + 1-pentanol	0.0442	–	–	0.001[c]
PE + 1-hexanol	0.1354	−0.0098	–	0.001[c]

[a] [38].

[b] [37].

[c] This work.

Table 5
The correlation and the prediction of ternary data-values of the coefficients b_0, b_1 and b_2 of the Cibulka Eq. (2) with the standard deviations including predictive methods

	b_0 (cm^3 mol^{-1})	b_1 (cm^3 mol^{-1})	b_2 (cm^3 mol^{-1})	$\sigma(V^E)$ (cm^3 mol^{-1})			
DMF + PE + 1-propanol	−0.0866	−0.8399	−1.2520	0.012[a]	0.020[b]	0.020[c]	0.020[d]
DMF + PE + 1-butanol	−0.6038	0.8146	−0.5522	0.015[a]	0.018[b]	0.017[c]	0.018[d]
DMF + PE + 1-pentanol	−1.3490	0.4536	2.1500	0.022[a]	0.023[b]	0.023[c]	0.023[d]
DMF + PE + 1-hexanol	−0.9374	−2.7920	2.2480	0.037[a]	0.045[b]	0.046[c]	0.045[d]

[a] [39].
[b] Redlich–Kister equation.
[c] [42].
[d] [43].

differs significantly as to polarity or deviations from ideality. It is not a case for the systems studied. The standard deviations of the ternary predictions are given in Table 5. The prediction accuracy may be considered as fair good and only for the DMF + PE + 1-propanol system significantly lower than the correlation accuracy. Surprisingly, the simplest Redlich–Kister method gives almost the same results as the Kohler and the Jacob and Fitzner methods.

Usually, the extent of deviation of liquid mixtures from ideal behavior is best expressed by the excess functions. Among them, the excess molar volumes can be interpreted as composed from three contributions, namely of physical, chemical and structural effects. The physical effects involve dispersion forces and non-specific interactions in the mixture, adding positive contributions to V^E. The chemical and specific interactions result in decrease in volume, which includes charge transfer type forces and other complex forming interactions between the two species, thereby these chemical effects contribute negative values to V^E. The structural effects that arise from the geometrical fitting of one component into the other are due to the different molar volumes and free volumes of pure components, and add negative contributions to V^E.

Fig. 1 shows that the experimental excess molar volumes at 303.15 K and at ambient for the binary mixtures of PE + 1-propanol, and 1-butanol are negative over the entire composition range and increasingly positive values were found for the larger alkanols, i.e. 1-pentanol and 1-hexanol. A similar trend has been observed by Prieto et al. [44] and Letcher and Nevines [45] for the same systems at 298.15 K. On the basis of those studies, the V^E values can be interpreted in terms of solvent polarity, the number of alcohol carbon atoms, and molecular size [46]. The negative V^E values in the lower chain alkanols, correspond to strong self-association of the pure alcohols, which reflects the existence of different types of association. The fact that the dipole moment ($\mu = 3.09$ Debye) and high dielectric constant ($\varepsilon = 20.45$ at 298. 15 K) for 1-propanol are noticeably higher compared to the other alcohols ($\mu = 1.55$ Debye, $\varepsilon = 13.30$ at 298. 15 K, for 1-hexanol) [21], leads to an increase in alcohol polarity that results in stronger heteroassociates. Therefore, the longer the chain of the alkanol, the polarity of –OH decreases and the weaker the corresponding dipole–dipole interactions. Moreover, increasing the alkanol chain length reduces the concentration of OH groups in higher alkanols and thereby lower dipole moment in higher alkanols, which must likewise results in weaker interactions. The positive effects in higher alkanols are due to the rupture of alkanol–alkanol hydrogen bonds and ketone–ketone dipole interactions and these are physical interactions among like molecules. In addition, the positive values reveal which a shielding effect on the higher alkanol hydroxyl group proton by the two adjacent methyl groups, thus preventing any association between the PE and alkanol species [45]. The V^E_{23} values for 2-pentanone + 1-alkanols mixtures are found to vary in the following order:

1-hexanol > 1-pentanol > 1-butanol > 1-propanol

The fact that V^E increases with the length of the alkanol may be due to the steric hindrance of the –CH_3 group in higher alcohols. These observations can be explained in terms of ease with which the alkanol chains can fit into the volume left free by the ketone molecules.

The extreme V^E_{23} values for PE + 1-alkanols systems are as follows: 1-propanol (−0.026 cm^3 mol^{-1} at $x_1 = 0.4832$, minimum), 1-butanol (−0.010 cm^3 mol^{-1} at $x_1 = 0.5112$, minimum), 1-pentanol (0.014 cm^3 mol^{-1} at $x_1 = 0.5029$, maximum) and 1-hexanol (0.036 cm^3 mol^{-1} at $x_1 = 0.5012$, maximum). The negative V^E_{12} values are observed at 303.15 K over the whole composition range for the system of DMF + PE, the minimum V^E value (−0.179 cm^3 mol^{-1}) was observed at $x_1 = 0.5174$ and it may be concluded that the polar nature of the two components leads to dipolar interactions that act between the electron deficient carbon of PE and negatively charged oxygen of DMF and also the electron rich oxygen of PE and positively polarized nitrogen of DMF [38]. On the other hand, the V^E_{13} values were negative in the mixture of DMF + 1-propanol, with the extreme values (−0.035 cm^3 mol^{-1} at $x_1 = 0.4898$), and positive in the DMF + 1-butanol (0.025 cm^3 mol^{-1} at $x_1 = 0.4450$), +1-pentanol (0.120 cm^3 mol^{-1} at $x_1 = 0.5154$), +1-hexanol (0.197 cm^3 mol^{-1} at $x_1 = 0.5029$) over the entire composition range [37]. It is well known that amides interact with water or alcohol as solutions by dipole–dipole interactions, and form some hydrogen-bonded complexes or hetero-associates [23–26].

The data included in Table 3 and Fig. 2 show that the excess molar volumes, V^E_{123}, for the ternary mixtures of DMF + PE + 1-propanol and +1-butanol at 303.15 K are negative over the entire composition range. The negative values indicate that the interactions among DMF, PE and 1-propanol or 1-butanol molecules in ternary mixtures are obviously similar to those in binary ones, however, the lower positive values are observed in DMF + 1-butanol (0.025 $\mathrm{cm^3\,mol^{-1}}$ at $x_1 = 0.4450$), which cannot be affected in DMF + PE + 1-butanol mixtures. Interactions between the DMF molecule with PE and 1-propanol or 1-butanol can occur through the free electron pair of DMF oxygen or nitrogen atoms and carbon or oxygen of PE, and engage the hydrogen atoms of alkanol. The negative V^E values suggest that the factors influencing structure making effects formation of interactions between unlike molecules are dominant in these mixtures. It is noteworthy to compare between the negative excess molar volumes in the present study (1-propanol or 1-butanol mixtures) with the positive excess volume data reported for the ternary systems (DMF + cyclopentanone (CP) [28] or cyclohexanone (CH) [29] +1-alkanols at 303.15 K), which indicates a radical difference between an aliphatic ketone and cyclic ketone. Positive V^E excess volumes are observed in DMF + CP (0.108 $\mathrm{cm^3\,mol^{-1}}$ at $x_1 = 0.5337$) [28] or DMF + CH (0.132 $\mathrm{cm^3\,mol^{-1}}$ at $x_1 = 0.5214$) [38], CP + 1-alkanols [47] or CH + 1-alkanols [48] and DMF + 1-pentanol or 1-hexanol [37] and thereby, positive excess molar volumes were observed in DMF + CP or CH + 1-alkanols.

The results in Table 3 show that the measured ternary excess molar volumes exhibit an inversion in sign in the mixtures containing 1-pentanol and 1-hexanol, what suggests that forming and breaking of interactions between unlike molecules compete with each other to varying degrees. The results indicate that, the negative V_{12}^E and positive V_{13}^E (for 1-pentanol or 1-hexanol mixtures) or V_{23}^E (for 1-pentanol or 1-hexanol mixtures) contributions are affected in these ternary mixtures and are compensation effect on expansion and contraction in volume. In earlier papers, we found the same trend in the ternary mixtures of DMF + methyl ethyl ketone (MEK) [30] or diethyl ketone (DEK) [31] +1-pentanol or 1-hexanol at 303.15 K. These results demonstrate that interactions between +ketone + alkanol mixture involving ketones with methyl, ethyl, cyclo or propyl side chains V_{123}^E is only strongly dependent on the nature of the ketone side chain. Conversely, the V_{123}^E is weakly dependent on the alkyl chain of the alkanol. However, the structural effects and a detailed evaluation of orientational effects are difficult to interpret in ternary mixtures [14,15].

References

[1] G.M. Wilson, J. Am. Chem. Soc. 86 (1964) 127–130.

[2] H. Renon, J.M. Prausnitz, AIChE J. 14 (1968) 135–144.

[3] Aa. Fredenslund, R.J. Jones, J.M. Prausnitz, AIChE J. 21 (1975) 1086–1099.

[4] U. Weidlich, J. Gmehling 26 (1987) 1372–1381.

[5] T. Hofman, J. Phys. Chem. B 108 (2004) 2383–2397.

[6] M.I. Davis, G. Douhéret, J.R. Reis, M.J. Blandamer, Phys. Chem. Chem. Phys. 3 (2001) 4555–4559.

[7] E.F.G. Barbosa, S.M.C. Sousa, M.S.C.S. Santos, I.M.S. Lampreia, Phys. Chem. Chem. Phys. 3 (2001) 556–561.

[8] U. Domańska, J. Łachwa, T.M. Letcher, J. Chem. Thermodyn. 34 (2002) 885–893.

[9] I.M.S. Lampreia, F.A. Dias, Â.F.S.S. Mendonça, Phys. Chem. Chem. Phys. 5 (2003) 4869–4874.

[10] B. García, S. Aparicio, A.M. Navarro, R. Alcalde, J.M. Leal, J. Phys. Chem. B 108 (2004) 15841–15850.

[11] M.T. Lorenzana, E. Jiménez, J.L. Legido, J. Fernández, M.I. Paz Andrade, J. Chem. Thermodyn. 25 (1993) 1041–1047.

[12] E.R. López, J. García, J.L. Legido, A. Coronas, J. Fernández, J. Chem. Soc. Faraday Trans. 91 (1995) 2071–2079.

[13] L. Lepori, E. Matteoli, Fluid Phase Equilib. 145 (1998) 69–87.

[14] J. Zielkiewicz, Phys. Chem. Chem. Phys. 2 (2000) 2925–2932.

[15] B. García, R. Alcalde, S. Aparicio, J.M. Leal, J.S. Matos, Phys. Chem. Chem. Phys. 3 (2001) 2866–2871.

[16] E. Žagar, M. Žigon, Polymer 41 (2000) 3513–3521.

[17] Y.K. Kang, H.S. Park, J. Mol. Struct. (Theochem.) 676 (2004) 171–176.

[18] H. Borrmann, I. Persson, M. Sandström, C.M.V. Stålhandske, J. Chem. Soc. Perkin Trans. 2 (2000) 393–402.

[19] Y. Umebayashi, K. Matsumoto, M. Watanabe, S. Ishiguro, Phys. Chem. Chem. Phys. 3 (2001) 5475–5481.

[20] B. García, R. Alcalde, J.M. Leal, J.S. Matos, J. Phys. Chem. B 101 (1997) 7991–7997.

[21] J.A. Riddick, W.B. Bunger, T.K. Sakano, Organic Solvents, fourth ed., Wiley-Inter Science, New York, 1986.

[22] S.E.M. Colaianni, O. Faurskov Nielsen, J. Mol. Struct. 347 (1995) 267–283.

[23] E.D. Schmid, E. Brodbek, Can. J. Chem. 63 (1985) 1365–1376.

[24] G. Eaton, M.C.R. Symons, P.P. Rastogi, J. Chem. Soc. Faraday Trans. 85 (1989) 3257–3271.

[25] E.S. Eberhardt, R.T. Raines, J. Am. Chem. Soc. 116 (1994) 2149–2150.

[26] L. Pikkarainen, Thermochim. Acta 178 (1991) 311–315.

[27] W. Acree, Thermodynamic Properties of Nonelectrolyte Solutions, Academic Press, New York, 1984 (Chapter 8).

[28] P. Venkatesu, M.V.P. Rao, J. Chem. Thermodyn. 30 (1998) 207–213.

[29] P. Venkatesu, M.V.P. Rao, J. Chem. Eng. Data 42 (1997) 90–92.

[30] P. Venkatesu, D. Venkatesulu, M.V.P. Rao, J. Chem. Eng. Data 39 (1994) 140–142.

[31] P. Venkatesu, M.V.P. Rao, Fluid Phase Equilib. 120 (1996) 205–210.

[32] J. Timmermans, Physico-Chemical Constants of Pure Organic Compounds, Elsevier, Amsterdam, 1962.

[33] M.V.P. Rao, P.R. Naidu, Can. J. Chem. 52 (1974) 788–790.

[34] G.R. Naidu, P.R. Naidu, J. Chem. Eng. Data 26 (1981) 197–200.

[35] P. Venkatesu, M.V.P. Rao, Fluid Phase Equilib. 93 (1994) 369–376.

[36] P. Venkatesu, M.V.P. Rao, Fluid Phase Equilib. 98 (1994) 173–178.

[37] K.P. Rao, K.S. Reddy, Phys. Chem. Liq. 15 (1985) 147–154.

[38] P. Venkatesu, M.V.P. Rao, J. Chem. Eng. Data 41 (1996) 1059–1060.

[39] I. Cibulka, Collect. Czech. Chem. Commun. 47 (1982) 1414.

[40] G.L. Bertrand, W.E. Acree Jr., G.L. Burchfield, J. Sol. Chem. 12 (1983) 327–336.

[41] C. Pando, J.A.R. Renuncio, J.A.G. Calzon, J.J. Christensen, R.M. Izatt, J. Sol. Chem. 16 (1987) 503–512.

[42] F. Kohler, Monatsh. Chem. 91 (1960) 738.

[43] K.T. Jacob, K. Fitzner, Thermochim. Acta 18 (1977) 197–208.

[44] G. Prieto, P. Nogueira, R. Bravo, F. Sarmiento, M.I. Paz Andrade, J. Chem. Thermodyn. 24 (1992) 905–912.

[45] T.M. Letcher, J.A. Nevines, J. Chem. Eng. Data 40 (1995) 293–295.

[46] R.J. Fort, W.R. Moore, Trans. Faraday Soc. 62 (1966) 1112–1119.

[47] M.V.P. Rao, P.R. Naidu, J. Chem. Thermodyn. 8 (1976) 73–76.

[48] M.V.P. Rao, P.R. Naidu, J. Chem. Thermodyn. 8 (1976) 96–98.