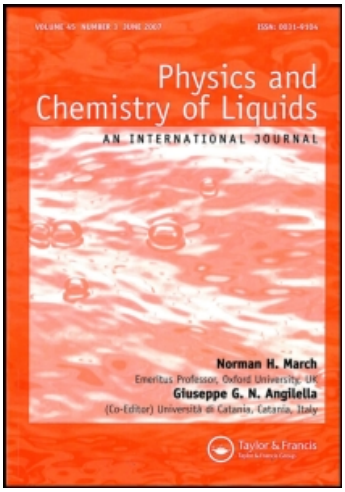

Physics and Chemistry of Liquids
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713646857

Volumetric and acoustic properties of butylacetate with some alkan-1-ols (C_1-C_6) at 298.15 K

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To cite this Article Iloukhani, H. and Nojini, Z. B.(2005) 'Volumetric and acoustic properties of butylacetate with some alkan-1-ols (C_1-C_6) at 298.15 K', Physics and Chemistry of Liquids, 43: 5, 429 — 440
To link to this Article: DOI: 10.1080/00319100500179159
URL: http://dx.doi.org/10.1080/00319100500179159

Physics and Chemistry of Liquids
Vol. 43, No. 5, October 2005, 429–440

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Volumetric and acoustic properties of butylacetate with some alkan-1-ols (C_1–C_6) at 298.15 K

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(*Received 22 January 2005; in final form 14 June 2005*)

Densities, ρ and speeds of sound, u data have been measured for binary mixtures of butylacetate with alkan-1-ols, namely, methanol, ethanol, propan-1-ol, butan-1-ol, pentan-1-ol and hexan-1-ol at 298.15 K and atmospheric pressure. From the experimental results, excess molar volumes, V_m^E and partial molar volumes, $\bar{V}_i$ were also calculated. V_m^E for butylacetate + methanol methanol mixtures is negative over the entire range of mole fractions and positive values are obtained for all the remaining mixtures. For $\bar{V}_i$ their values have been extrapolated to zero concentration to obtain the limiting value at infinite dilution, $\bar{V}_i^\circ$. Further, isentropic compressibilities, k_s and Rao's molar sound function, R_m of the mixtures were computed by combining sound velocity and density data. Deviation in isentropic compressibility, Δk_s were evaluated using volume fraction, ϕ weighing of the individual component properties to estimate ideal mixture behavior. The Δk_s values are positive over the whole of volume fraction for all the mixtures. An inversion of sign in Δk_s is observed in the system butylacetate + methanol, at around 0.65 volume fraction of butylacetate. For all mixtures the V^E and Δk_s results were satisfactorily correlated by the Redlich–Kister polynomial. The results are explained in terms of dissociation of the self-associated alkan-1-ol molecules and the formation of aggregates between unlike molecules.

Keywords: Excess molar volumes; Speeds of sound; Butylacetate; Alkan-1-ols; Redlich–Kister equation

1. Introduction

The volumetric and acoustic properties of mixing can be quite significant and give a measure of molecular interactions and, hence, can provide information needed to test existing theories of solutions. This article forms part of a series on the measurement of thermodynamic and acoustic properties of non-electrolyte solutions for binary mixtures with butylacetate as a component and alkan-1-ols, namely, methanol, ethanol, propan-1-ol, butan-1-ol, pentan-1-ol and hexan-1-ol in which specific interactions between unlike molecules can occur [1–5]. Excess molar volumes, V_m^E speed of sound, u isentropic compressibilities, k_s deviation in the isentropic compressibilities,

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Physics and Chemistry of Liquids
ISSN 0031-9104 print: ISSN 1029-0451 online © 2005 Taylor & Francis
DOI: 10.1080/00319100500179159

Δk_s and Rao's molar sound function, R_m, for butylacetate + ethanol, +ethanol, +propanol-1-ol, +butan-1-ol, +pentan-1-ol, +hexan-1-ol at 298.15 K are reported.

2. Experimental

2.1. *Materials*

The materials used in the study, suppliers, and their purities are listed in table 1. Butylacetate was purified by the standard method described by Perrin and Armarego [6]. All alkan-1-ols used were purified by distillation using a 1-m fractionation column. The purified compounds were stored in brown glass bottles and fractionally distilled immediately before use. Purity of each compound was ascertained by the constancy of the boiling point and also from the density and refractive index. Densities were measured at 293.15 K using a bicapillary pycnometer with an accuracy of 4 parts in 10^4. Refractive indices were measured at 293.15 K with an Abbe refractometer. Water was circulated to the refractometer from a constant temperature bath at 293.15 K. The accuracy of the refractive index measured is on the order of ±0.0002. Table 1 also gives the density and refractive index measurements, which agree with values obtained from the literature [7].

2.2. *Apparatus and procedure*

The speeds of sound velocity, u in pure liquids and the binary mixtures were measured with a single crystal multifrequency ultrasonic interferometer (Mittal Enterprise, New Delhi). In the present work, a steel cell fitted with a quartz crystal of 1 MHz frequency was employed. In these measurements the temperature was maintained constant by circulating water around a liquid cell from a thermostat controlled at 298.15 K. The densities of pure components and mixtures were measured with a bicapillary pycnometer with an accuracy of 4 parts in 10^4.

Mixtures were prepared by mixing known masses of pure component in air-tight, narrow-mouth ground-glass stoppered bottles. All the mass measurements were performed on an electronic balance (Mettler AE 163, Switzerland) accurate to 0.01 mg. The possible error in the mole fraction is estimated to be less than $\pm 1 \times 10^{-4}$. The accuracies in the values of speed of sound, u and density, ρ were estimated to be within $\pm 1.5\,m\,s^{-1}$, and 0.01%, respectively.

Table 1. Source, purity grades, densities, ρ and refractive indices, n_D of the pure components at 293.15 K.

			ρ (g cm^{-3})		n_D	
Component	Source	Purity (mass %)	Expt.	Lit.[a]	Expt.	Lit.[a]
Butylacetate	Merck	99	0.88124	0.8813	1.3937	1.3941
Methanol	Merck	99.8	0.79123	0.7913	1.3288	1.3284
Ethanol	Merck	99.5	0.78947	0.7894	1.3610	1.3614
Propanol-1-ol	Merck	99	0.80361	0.8037	1.3852	1.3856
Butan-1-ol	Merck	99	0.80979	0.8097	1.3990	1.3993
Pentan-1-ol	Fluka	99	0.81471	0.8148	1.4105	1.4100
Hexan-1-ol	Merck	98.5	0.81853	0.8186	1.4186	1.4182

[a]Ref. [7].

3. Results and discussion

At least 13 density measurements were performed (with repetition) for each binary system, in the full concentration range ($0 \leq x \leq 1$). The excess molar volumes V_m^E of the solution of molar composition x were calculated from the densities of the pure liquids and their mixtures according to the following equation:

$$V_m^E = [xM_1 + (1-x)M_2]/\rho - [xM_1/\rho_1 + (1-x)M_2/\rho_2] \quad (1)$$

where ρ, ρ_1 and ρ_2 are the densities of the solution and pure components 1 and 2, respectively, and M_1 and M_2 the molar masses of the pure components. The corresponding values of ρ and V_m^E of binary mixtures of [x butylacetate + $(1-x)$ alkan-1-ols] at 298.15 K are reported in table 2 and figure 1.

Each set of results was fitted using a Redlich–Kister polynomial [8] which, for binary mixtures, is

$$V_m^E(\text{cm}^3\,\text{mol}^{-1}) = x(1-x)\sum_{k=1} A_k(1-2x)^{k-1} \quad (2)$$

where x is the mole fraction of butylacetate, A_k is the polynomial coefficient obtained by a linear least-squares fitting procedure. In each case, the optimum number of coefficients was ascertained from an examination of the variation of the standard deviation $\sigma(V^E)$ with

$$\sigma(V^E) = \left[\sum (V_{\text{expt.}}^E - V_{\text{calcd.}}^E)^2/(n-p)\right]^{(1/2)} \quad (3)$$

in which n is the number of results and p is the number of parameters retained in equation (2). The values adopted for the coefficients A_k and the standard deviation $\sigma(V_m^E)$ are summarized in table 5.

Comparison of V_m^E for different systems recorded in figure 1 reveals several interesting features. It is observed that V_m^E for the binary mixtures of butylacetate with methanol is negative, while those with ethanol, propanol-1-ol, butan-1-ol, pentan-1-ol and hexan-1-ol are positive over the entire composition range. The V_m^E *versus* x curves for all mixtures show a simple minima or a maxima around 0.5–0.6 mole fraction of butylacetate. It can be observed that the V_m^E values at these concentrations increased with the number of $-CH_2-$ groups in the alkan-1-ol in the order

hexan-1-ol > pentan-1-ol > butan-1-ol
> propan-1-ol > ethan-1-ol > methanol.

For methanol, existence of strong hydrogen bonding and specific interaction between unlike molecules causes a decrease in volume. With longer-chain alkan-1-ols' attraction, interactions between unlike species decrease and repulsive interactions predominate, leading to positive excess molar volumes. This can be explained by the fact that alkan-1-ols are hydrogen bonded associated liquids and the addition of butylacetate, which is a polar molecule, but not an associated liquid, causes the rupture of the

Table 2. Densities, ρ (g cm^{-3}), excess molar volumes, V_m^E (cm^3 mol^{-1}) and partial molar volumes, $\bar{V}_i$ (cm^3 mol^{-1}) for the mixtures of x butylacetate + $(1-x)$ alkan-1-ols at 298.15 K.

x	ρ	V_m^E	$\bar{V}_1$	$\bar{V}_2$	x	ρ	V_m^E	$\bar{V}_1$	$\bar{V}_2$
				x butylacetate + $(1-x)$ methanol					
0.1056	0.8115	0.000	132.50	40.71	0.5555	0.8592	−0.051	132.53	40.75
0.1557	0.8203	0.000	132.49	40.71	0.6486	0.8642	−0.057	132.39	40.60
0.2160	0.8291	−0.001	132.50	40.72	0.7001	0.8665	−0.052	132.26	40.48
0.2743	0.8362	−0.001	132.52	40.74	0.7616	0.8689	−0.039	132.07	40.29
0.3388	0.8429	−0.008	132.55	40.77	0.8621	0.8724	−0.007	131.71	39.93
0.3965	0.8480	−0.018	132.57	40.79	0.9302	0.8744	−0.007	131.50	39.71
0.4569	0.8528	−0.031	132.58	40.80	0.9469	0.8765	−0.008	131.45	39.67
				x butylacetate + $(1-x)$ ethanol					
0.0653	0.7974	0.023	132.51	58.66	0.5642	0.8519	0.159	132.66	58.81
0.1177	0.8059	0.404	132.51	58.66	0.6200	0.8558	0.157	132.74	58.89
0.1758	0.8143	0.059	132.51	58.66	0.6915	0.8604	0.144	132.87	59.02
0.2447	0.8230	0.082	132.51	58.66	0.7790	0.8655	0.111	133.07	59.22
0.3246	0.8317	0.108	132.52	58.66	0.8306	0.8683	0.086	133.19	59.34
0.4364	0.8420	0.141	132.55	58.70	0.8886	0.8714	0.054	133.33	59.47
0.5049	0.8476	0.154	132.60	58.74	0.9510	0.8744	0.021	133.44	59.59
				x butylacetate + $(1-x)$ propan-1-ol					
0.0293	0.8031	0.025	133.35	76.26	0.5456	0.8504	0.162	132.80	76.39
0.1444	0.8163	0.085	133.07	76.29	0.6053	0.8544	0.174	132.74	76.45
0.2188	0.8239	0.108	132.93	76.31	0.6748	0.8587	0.167	132.69	76.57
0.2980	0.8313	0.127	132.89	76.32	0.7135	0.8611	0.159	132.63	76.66
0.3385	0.8348	0.136	132.84	76.32	0.7886	0.8654	0.132	132.60	76.88
0.3870	0.8388	0.146	132.84	76.33	0.8556	0.8691	0.096	132.55	77.13
0.4637	0.8446	0.161	132.84	76.34	0.9038	0.8717	0.065	132.52	77.34
				x butylacetate + $(1-x)$ butan-1-ol					
0.0872	0.8142	0.058	133.23	91.95	0.5846	0.8519	0.193	132.74	92.15
0.1666	0.8211	0.099	133.10	91.96	0.6397	0.8554	0.189	132.71	92.21
0.2777	0.8301	0.143	133.02	91.99	0.6933	0.8587	0.180	132.67	92.28
0.3344	0.8344	0.160	132.92	92.01	0.7523	0.8623	0.163	132.63	92.37
0.4317	0.8415	0.181	132.89	92.05	0.8101	0.8657	0.139	132.60	92.49
0.4801	0.8449	0.188	132.81	92.07	0.8802	0.8698	0.099	132.56	92.67
0.5328	0.8485	0.193	132.78	92.11	0.9336	0.8728	0.061	132.53	92.83
				x butylacetate + $(1-x)$ pentan-1-ol					
0.0888	0.8174	0.730	133.85	108.68	0.5177	0.8464	0.244	132.77	108.96
0.1352	0.8207	0.110	133.33	108.69	0.6302	0.8537	0.225	132.73	109.06
0.2270	0.8270	0.172	133.27	108.72	0.6734	0.8564	0.213	132.65	109.09
0.3217	0.8335	0.217	133.10	108.78	0.7172	0.8592	0.198	132.63	109.11
0.3734	0.8369	0.233	132.95	108.83	0.7886	0.8636	0.167	132.61	109.15
0.4182	0.8399	0.241	132.88	108.87	0.8448	0.8670	0.136	132.58	109.17
0.4675	0.8432	0.245	132.82	108.92	0.8137	0.8712	0.087	132.55	109.22
				x butylacetate + $(1-x)$ hexan-1-ol					
0.0412	0.0817	0.052	133.68	125.31	0.5422	0.8477	0.255	132.78	125.62
0.1014	0.8211	0.117	133.55	125.32	0.6559	0.8547	0.237	132.80	125.67
0.2136	0.8277	0.204	133.34	125.37	0.7178	0.8585	0.221	132.71	125.70
0.2876	0.8321	0.237	133.10	125.43	0.7833	0.8625	0.199	132.68	125.74
0.3417	0.8354	0.252	132.98	125.47	0.8789	0.8685	0.144	132.65	125.88
0.4380	0.8413	0.261	132.90	125.55	0.9071	0.8703	0.120	132.56	125.95
0.4888	0.8444	0.260	132.81	125.58	0.9677	0.8743	0.050	132.55	126.16

hydrogen bonds of ethanol, propan-1-ol, butan-1-ol, pentan-1-ol, and hexan-1-ol with resulting expansion and V_m^E is positive. For the lower molecular weight solute, methanol, the association between solvent–solute is stronger, which, therefore, causes a volume contraction $V_m^E < 0$. Negative values of V_m^E for methanol and positive values for remaining systems support this simple explanation.

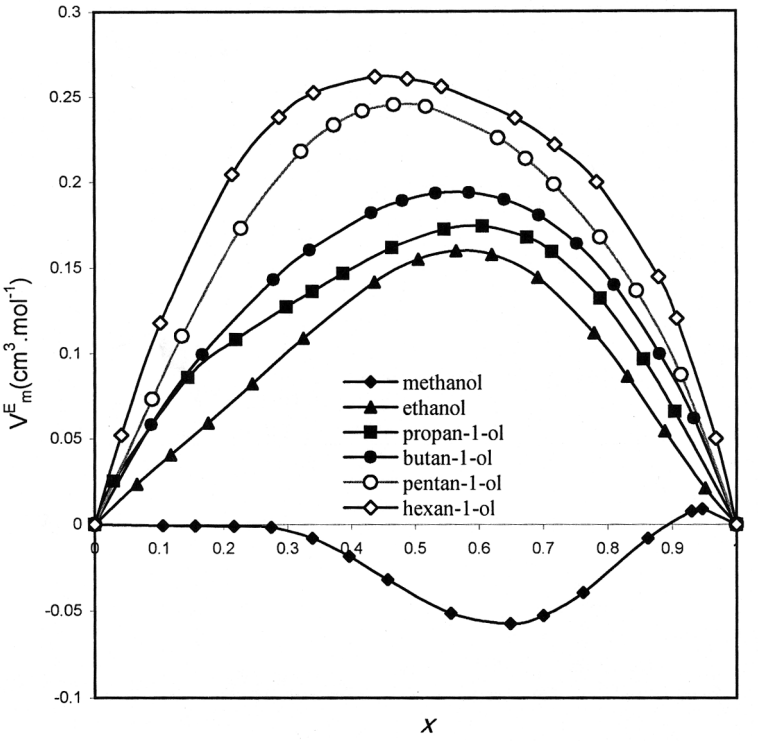

Figure 1. Excess molar volume for the binary mixtures of $\{x$ butylacetate $+ (1 - x)$ alkan-1-ols$\}$ at 298.15 K.

The partial molar volumes of components, $\bar{V}_i$ in binary mixture can be determined from excess molar volumes data as follows:

$$\bar{V}_1 = V_m^E + (1 - x)(\partial V^E/\partial x) \tag{4}$$

$$\bar{V}_2 = V_m^E - x(\partial V^E/\partial x) \tag{5}$$

in which $\bar{V}_1$ and $\bar{V}_2$ are excess partial molar volumes of butylacetate and alkan-1-ols, respectively, where x and $(1 - x)$ are the mole fraction of butylacetate and alkan-1-ols, respectively.

To obtain values of the partial molar volumes, $\bar{V}_i$, we start by differentiation of equation (2) with respect to x and substitution of the result in equations (4) and (5) leads to the following equations for the partial molar volumes of butylacetate, $\bar{V}_1$ and alkan-1-ol, $\bar{V}_2$

$$\bar{V}_1 = (1 - x)^2 \sum_{k=1} A_k(1 - 2x)^{k-1} - 2x(1 - x)^2 \sum_{k=1} A_k(k - 1)(1 - 2x)^{k-2} \tag{6}$$

$$\bar{V}_2 = x^2 \sum_{k=1} A_k(1 - 2x)^{k-1} - 2x^2(1 - x) \sum_{k=1} A_k(k - 1)(1 - 2x)^{k-2}. \tag{7}$$

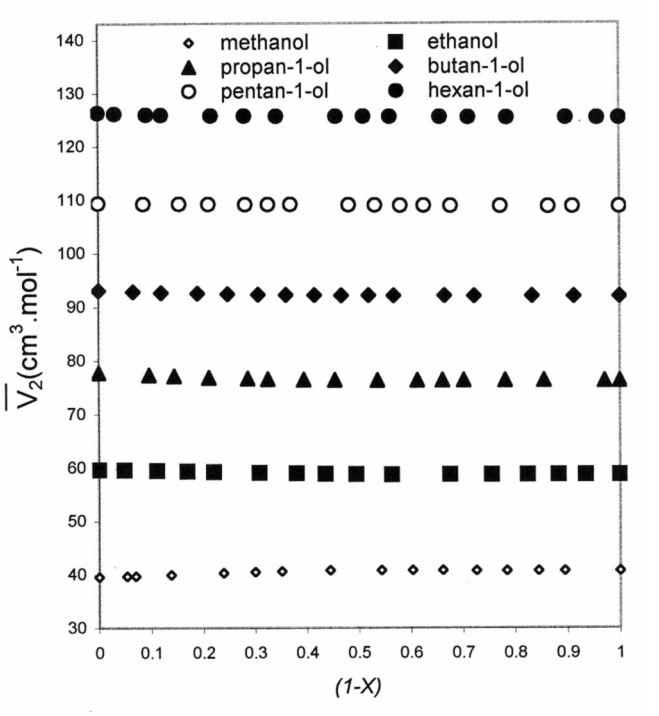

Figure 2. Partial molar volume alkan-1-ols mixtures of $\{x$ butylacetate $+ (1-x)$ alkan-1-ols$\}$ at 298.15 K.

Partial molar volumes of butylacetate, $\bar{V}_1$ and $\bar{V}_2$ for all compositions can be calculated by using the Redlich–Kister coefficients (table 5) in equations (6) and (7). Results at 298.15 K are also listed in table 2 and shown in figure 2.

The partial molar volume at infinite dilution $\bar{V}_i^\circ$ appears to be of interest. In the limit of infinite dilution, solute–solute interaction disappears. Thus, the values of the partial molar volumes at infinite dilution provide insight into solute–solvent interactions. We can consider butylacetate at infinite dilution ($x = 0$) in alkan-1-ol and of alkan-1-ol at infinite dilution ($x = 1$) in butylacetate. Setting $x = 0$ in equation (6) leads to

$$\bar{V}_1^\circ = \sum_{k=1} A_k. \tag{8}$$

Similary, setting $x = 1$ in equation (7) leads to

$$\bar{V}_2^\circ = \sum_{k=1} A_k(-1)^{k-1}. \tag{9}$$

In equations (8) and (9), $\bar{V}_1^\circ$ and $\bar{V}_2^\circ$ represent the partial molar volumes of butylacetate at infinite dilution in alkanols and the partial molar volume of alkan-1-ols at infinite dilution in butylacetate, respectively. All partial molar volumes at infinite dilution, $\bar{V}_i^\circ$ were calculated using the Redlich–Kister coefficients (table 5) in equations (8) and (9) and are listed in table 3.

Table 3. Partial molar volumes of butylacetate at infinite dilution in alkan-1-ols, $\bar{V}_1^\circ$ ($cm^3\,mol^{-1}$) and partial molar volumes of alkan-1-ols at infinite dilution in butylacetate, $\bar{V}_2^\circ$ ($cm^3\,mol^{-1}$) from equations (8) and (9), for x butylacetate + $(1-x)$ alkan-1-ols at 298.15 K.

System	$\bar{V}_1^\circ$	$\bar{V}_2^\circ$
x butylacetate + $(1-x)$ methanol	132.91	41.13
x butylacetate + $(1-x)$ etahanol	132.87	59.01
x butylacetate + $(1-x)$ propan-1-ol	133.17	76.92
x butylacetate + $(1-x)$ butan-1-ol	133.52	92.95
x butylacetate + $(1-x)$ pentan-1-ol	133.17	109.92
x butylacetate + $(1-x)$ hexan-1-ol	134.22	127.01

The specific compression of solution is defined as the partial derivative of specific volumes, V, with respect to pressure, p under isentropic conditions: $k_s = -(\partial V/\partial p)_s$. Then, the isentropic compressibility, k_s values can be estimated from the relation

$$k_s = (\rho u^2)^{-1} \tag{10}$$

where ρ and u are the density and speed of sound, respectively, of mixture.

Defining the ideal isentropic solution property, k_s^{id}, is not as straightforward as for the ideal molar volumes, V^{id} [9]. However, one may write the defining equation in terms of the volume fraction's average [10–12]

$$k_s^{id} = \sum_i (k_{s,i}^*)\phi_i \tag{11}$$

where $k_{s,i}^*$ is the isentropic compressibility of pure component i, and $\phi_i = x_i V_i^\circ / \Sigma x_j V_j$ is the volume fraction of component i. Then the deviation in isentropic compressibility, Δk_s from the ideal mixing values can be estimated from the following equation

$$\Delta k_s = k_s - \sum_i (k_{s,i}^*)\phi_i. \tag{12}$$

The values of u and k_s are fitted by

$$u \text{ or } k_s = \sum_{k=1}^{m} A_k x_1^i \tag{13}$$

where A_k is an adjustable parameter. The values of A_k along standard deviation σ for u and k_s are also given in table 5.

The Rao's molar sound function, R_m [13], has been obtained from the following equation:

$$R_m = u^{(1/3)}\left(\sum x_i M_i/\rho\right) \tag{14}$$

where x_i and M_i are the mole fraction and molecular weight of component i.

Table 4. Densities, ρ (kg m^{-3}), speeds of sound, u (m s^{-1}), isentropic compressibility, k_s (T Pa^{-1}), deviation isentropic compressibility, Δk_s (T Pa^{-1}), and Rao's molar sound function, R_m ($m^{10/3}\,s^{-1/3}\,mol^{-1}$) for binary mixtures of x butylacetate + $(1-x)$ alkan-1-ols at 298.15 K.

x	ϕ	ρ	u	k_s	Δk_s	$10^6\,R_m$	x	ϕ	ρ	u	k_s	Δk_s	$10^6\,R_m$
x butylacetate + $(1-x)$ methanol													
0.0626	0.1786	803.2	1083	1061	−3.4	477	0.4762	0.7473	854.2	1118	935	7.8	876
0.1420	0.3499	818.1	1099	1007	−15.5	554	0.5621	0.8067	859.7	1122	923	9.9	958
0.1853	0.4253	823.5	1106	989	−15.4	598	0.6588	0.8626	864.7	1127	909	9.7	1052
0.2618	0.5357	834.8	1113	969	−9.37	671	0.7248	0.8954	867.5	1131	900	8.5	1117
0.3137	0.5979	840.4	1114	959	−4.0	720	0.8052	0.9308	870.5	1136	889	6.3	1196
0.3768	0.6629	846.4	1115	949	1.81	781	0.8930	0.9644	873.3	1141	878	3.6	1282
0.3973	0.6820	848.1	1116	946	3.3	800	–	–	–	–	–	–	–
x butylacetate + $(1-x)$ ethanol													
0.0355	0.0768	798.4	1104	1061	15.0	628	0.4297	0.6299	841.5	1122	942	18.0	941
0.0480	0.1023	799.0	1104	1007	18.6	639	0.5034	0.6960	847.4	1125	930	16.7	998
0.0907	0.1839	801.7	1105	989	26.1	676	0.6336	0.7962	856.7	1130	913	15.3	1100
0.1282	0.2493	807.5	1105	969	28.5	704	0.7346	0.8621	863.0	1133	901	13.4	1178
0.1808	0.3327	815.0	1108	959	28.1	745	0.8545	0.9299	869.6	1138	886	9.1	1272
0.2838	0.4724	827.4	1114	949	23.3	826	0.9246	0.9651	873.1	1142	877	5.3	1327
0.3360	0.5334	832.8	1117	946	20.9	867	–	–	–	–	–	–	–
x butylacetate + $(1-x)$ propan-1-ol													
0.0332	0.0563	799.4	1160	1026	7.9	814	0.3463	0.4793	829.2	1144	920	23.3	1003
0.0593	0.0987	799.6	1157	1025	13.7	832	0.3994	0.5361	834.2	1145	913	19.6	1032
0.0880	0.1436	799.9	1156	1020	19.2	853	0.4623	0.5990	839.7	1146	905	15.5	1072
0.1191	0.1914	800.1	1154	1012	23.9	875	0.5293	0.6615	845.2	1147	898	12.2	1111
0.1471	0.2307	807.6	1148	999	26.7	886	0.6116	0.7567	853.7	1147	889	9.1	1178
0.2369	0.3504	818.0	1144	972	28.9	938	0.9283	0.8968	872.4	1144	875	6.8	1344
0.2879	0.4126	823.6	1144	960	26.9	968	–	–	–	–	–	–	–
x butylacetate + $(1-x)$ butan-1-ol													
0.0622	0.0873	811.9	1188	929	3.0	1001	0.4631	0.5542	843.7	1160	880	13.1	1165
0.0890	0.1235	813.8	1186	932	5.3	1012	0.5133	0.6031	847.2	1158	878	11.7	1186
0.1301	0.1773	818.0	1180	935	9.0	1028	0.5811	0.6666	851.6	1156	877	10.1	1214
0.1763	0.2354	821.9	1175	937	12.5	1046	0.6565	0.7336	856.4	1154	875	9.0	1245
0.2718	0.3498	829.6	1167	937	16.2	1085	0.7349	0.7998	861.2	1151	875	8.4	1278
0.3598	0.4475	836.2	1163	933	15.8	1121	0.8585	0.8974	868.5	1147	873	6.9	1328
0.4204	0.5100	840.7	1161	927	14.4	1147	0.9514	0.9657	873.8	1146	869	3.4	1366
x butylacetate + $(1-x)$ pentan-1-ol													
0.0726	0.0872	816.3	1230	871	4.1	1183	0.4926	0.5421	844.8	1181	847	11.9	1275
0.1318	0.1562	819.4	1222	873	6.3	1198	0.5585	0.6066	849.1	1175	851	11.8	1290
0.1586	0.1868	822.3	1218	877	7.3	1202	0.6252	0.6703	853.4	1170	855	11.4	1304
0.2294	0.2663	827.2	1209	880	9.1	1218	0.6934	0.7338	857.7	1164	859	10.6	1319
0.3123	0.3563	832.8	1200	883	10.5	1231	0.7663	0.7999	862.2	1159	862	9.2	1335
0.3716	0.4189	836.8	1193	883	11.2	1249	0.8434	0.8678	867.0	1155	864	7.0	1352
0.4324	0.4816	840.8	1187	881	11.7	1262	0.9428	0.9526	873.0	1149	866	3.0	1374
x butylacetate + $(1-x)$ hexan-1-ol													
0.0811	0.0854	819.1	1260	809	0.4	1362	0.5296	0.5435	846.9	1193	828	11.1	1372
0.1687	0.1767	825.1	1246	815	1.8	1363	0.5924	0.6059	850.8	1186	835	11.3	1374
0.2268	0.2367	828.5	1237	819	3.5	1365	0.6591	0.6715	854.9	1178	841	10.8	1376
0.2763	0.2876	830.4	1230	826	5.5	1368	0.7285	0.7394	859.1	1171	847	9.5	1378
0.3464	0.3592	835.7	1219	833	7.4	1368	0.7918	0.8008	863.0	1165	852	7.7	1380
0.4069	0.4204	839.4	1210	838	9.1	1369	0.8532	0.8600	866.9	1160	856	5.5	1383
0.4677	0.4816	843.1	1201	843	10.4	1370	0.9238	0.9276	871.4	1154	861	2.8	1385

The results for u, k_s, Δk_s and R_m are given in table 4 and dependence of k_s and Δk_s on composition and volume fraction, respectively, are shown in figures 3 and 4, respectively. The isentropic compressibility, k_s and deviations in isentropic compressibility, Δk_s values are believed to be reliable to within 1.0 T Pa^{-1}. The Δk_s values

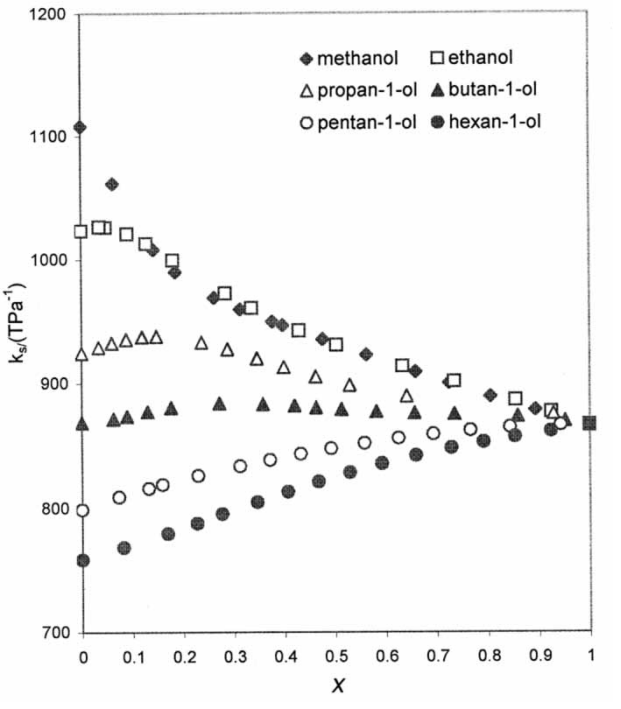

Figure 3. Dependence of isentropic compressibilities on mole fraction x for butylacetate containing binary mixtures with alkan-1-ols at 298.15 K.

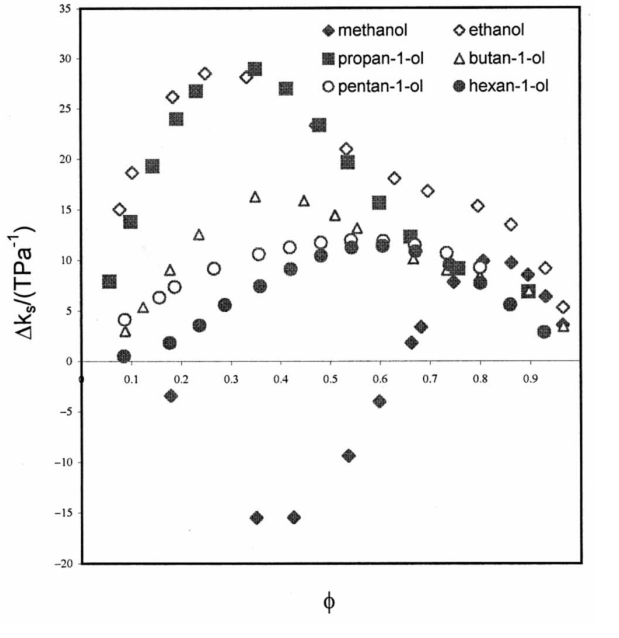

Figure 4. Dependence of deviation in isentropic compressibility on volume fraction ϕ for butylacetate mixtures with alkan-1-ols at 298.15 K.

Table 5. Coefficients, A_k and standard deviations, σ for equations (2), (13) and (15) and equations (3) and (16), respectively, for the binary mixtures of butylacetate with alkan-1-ols at 298.15 K.

Property	A_1	A_2	A_3	A_4	σ
		x butylacetate $+(1-x)$ methanol			
V_m^E ($cm^3\,mol^{-1}$)	−0.1770	0.4230	0.2336	−0.7691	0.005
u ($m\,s^{-1}$)	1068.8	225.9	−345.2	207.2	3.5
k_s ($T\,Pa^{-1}$)	1109.4	−696.0	896.1	−456.8	10.7
Δk_s ($T\,Pa^{-1}$)	−47.9	−131.7	170.8	145.7	2.4
		x butylacetate $+(1-x)$ ethanol			
V_m^E ($cm^3\,mol^{-1}$)	0.6160	−0.2942	−0.2421	0.3135	0.004
u ($m\,s^{-1}$)	1101.0	41.9	16.5	−16.4	1.2
k_s ($T\,Pa^{-1}$)	1039.8	−257.4	83.9	7.0	3.2
Δk_s ($T\,Pa^{-1}$)	88.8	78.7	119.8	−48.5	1.6
		x butylacetate $+(1-x)$ propan-1-ol			
V_m^E ($cm^3\,mol^{-1}$)	0.6683	−0.2753	0.1387	0.4237	0.003
u ($m\,s^{-1}$)	1165	−140.36	296.9	−183.7	1.3
k_s ($T\,Pa^{-1}$)	928.7	108.5	−489.1	335.6	2.3
Δk_s ($T\,Pa^{-1}$)	87.9	129.5	42.4	−124.9	2.0
		x butylacetate $+(1-x)$ butan-1-ol			
V_m^E ($cm^3\,mol^{-1}$)	0.7637	−0.1800	0.1230	0.0585	0.003
u ($m\,s^{-1}$)	1191.8	−92.3	48.2	0.0	1.8
k_s ($T\,Pa^{-1}$)	865.4	117.1	−237.4	127.1	1.3
Δk_s ($T\,Pa^{-1}$)	58.7	52.7	1.0	−115.9	1.6
		x butylacetate $+(1-x)$ pentan-1-ol			
V_m^E ($cm^3\,mol^{-1}$)	0.9805	−0.0753	0.0363	−0.2909	0.003
u ($m\,s^{-1}$)	1241.0	−149.3	61.1	−5.8	0.2
k_s ($T\,pa^{-1}$)	800.8	120.9	−50.2	−4.5	0.2
Δk_s ($T\,Pa^{-1}$)	47.1	−8.6	16.0	1.6	2.0
		x butylacetate $+(1-x)$ hexan-1-ol			
V_m^E ($cm^3\,mol^{-1}$)	1.0440	−0.0850	0.3977	−0.3478	0.007
u ($m\,s^{-1}$)	1247.2	−167.0	15.7	26.9	0.4
k_s ($T\,Pa^{-1}$)	756.3	139.7	18.9	−51.7	0.4
Δk_s ($T\,Pa^{-1}$)	42.8	−29.3	−30.1	5.0	2.0

were correlated with the composition data by means of the Redlich–Kister equation [8], which for binary mixtures is

$$\Delta k_s = \phi(1-\phi)\sum_{k=0} A_k(1-2\phi)^{k-1} \tag{15}$$

where ϕ is the volume fraction of butylacetate, A_k is the polynomial coefficient, and k is the number of the polynomial coefficient.

In each case, the optimum number of the polynomial coefficient was ascertained from an examination of the variation of the standard deviation, $\sigma(\Delta k_s)$ with

$$\sigma(\Delta k_s) = \left[\sum (\Delta k_{s(exp.)} - \Delta k_{s(calcd.)})^2/(n-p)\right]^{1/2} \tag{16}$$

where n and p are the number of results and number of adjustable parameters, A_k, retained in equation (15), respectively. The values adopted for the polynomial coefficient, A_k and the standard deviation, $\sigma(\Delta k_s)$ estimates associated with the use of equations (15) and (16) respectively, are also summarized in table 5.

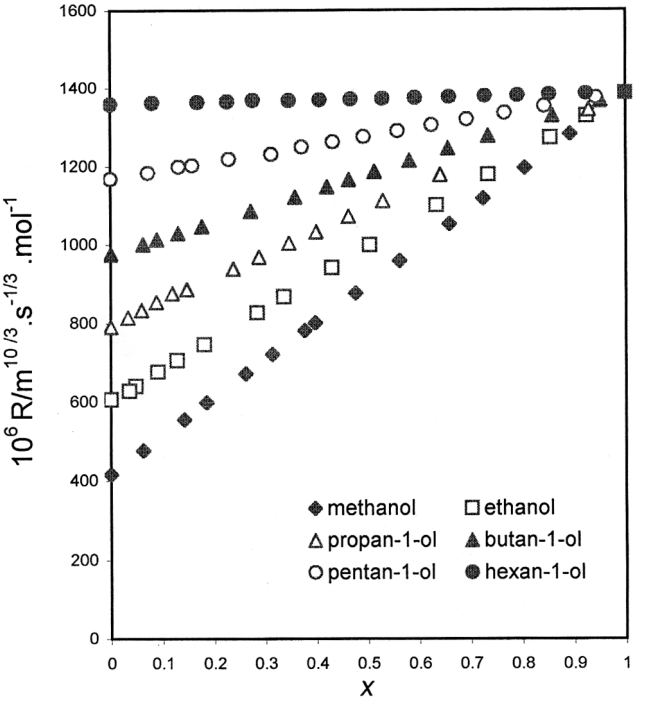

Figure 5. Rao's molar sound function of mole fraction x for butylacetate containing mixtures with alkan-1-ols at 298.15 K.

The deviations in isentropic compressibility, Δk_s are positive over the whole range of composition for all the binary mixtures formed by butylacetate with the alkan-1-ols. An inversion of the sign of Δk_s is observed over some volume fraction, ϕ for mixtures of butylacetate with methanol.

The positive values of Δk_s for four mixtures (C_2–C_6) mean that the mixture is more compressible than the corresponding ideal mixture. Therefore, in these systems, an expansion in free volume is considered to occur making the mixtures more compressible than the ideal mixture, which ultimately culminates into the positive values of Δk_s. For the mixture of butylacetate + methanol the Δk_s values at around 0.65 volume fraction of butylacetate indicate the opposite of the above explanation.

The dependence of Rao's molar sound functions, R_m on mole fractions x for all the binary mixtures is shown in figure 5. The plots show that for all the mixtures the values of R vary linearly with x except mixtures involving butylacetate with ethanol, where slight positive deviations are observed.

Acknowledgements

The authors are thankful to the university authorities for providing the necessary facilities to carry out the research.

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