Excess Molar Volumes and Speed of Sound of Ethyl Acetate and Butyl Acetate with 2-Alkoxyethanols at 308.15 K

Gandi Chandrasekhar, Pannuru Venkatesu, and Murari Venkata Prabhakara Rao*

Department of Chemistry, Sri Venkateswara University, Tirupati-517 502, Andhra Pradesh, India

Excess molar volumes (V^E) and speed of sound (u) of the binary liquid mixtures of ethyl acetate and butyl acetate with 2-alkoxyethanols at 308.15 K have been measured over the entire range of composition. The 2-alkoxyethanols are 2-methoxyethanol, 2-ethoxyethanol, and 2-butoxyethanol. The V^E values are positive in mixtures of ethyl acetate and butyl acetate with 2-methoxyethanol, 2-ethoxyethanol, and 2-butoxyethanol. The speed of sound data were used to compute isentropic compressibilities (κ_s) and excess isentropic compressibilities (κ_s^E). The κ_s^E values are negative over the entire range of composition for all the systems of 308.15 K.

Introduction

In the chemical industry, a knowledge of the thermodynamic properties of nonelectrolyte solutions are essential in the design involving chemical separations, heat transfer, mass transfer and fluid flow. This paper forms part of our program on the measurement of thermodynamic properties of binary liquid mixtures (Venkatesu and Rao, 1994; Goud et al., 1995; Venkatesu et al., 1996). We report in this paper excess molar volumes and excess isentropic compressibilities for ethyl acetate and butyl acetate with 2-methoxyethanol, 2-ethoxyethanol, and 2-butoxyethanol at 308.15 K. The study of 2-alkoxyethanols is of interest because of the effect of the simultaneous presence of ether and alcoholic oxygen atoms on the molecular interactions. The molecules of the alkoxyethanols are self-associated like the alcohols (Cobos and Casanova, 1987). The effect of the simultaneous presence of ether and alcoholic oxygen atoms in the same molecule of alkoxyethanol and the presence of the etheric oxygen enhances the ability of the −OH group to form hydrogen bonds, and we can expect intramolecular hydrogen bonds to be formed in the alkoxyethanol molecules. The main purpose of this work is to provide information on the molecular interactions between acetates and 2-alkoxyethanols from the measurements of V^E and κ_s^E data.

Experimental Section

Procedure. The methods of V^E used in our laboratory have been described previously (Rao and Naidu, 1974; Ramadevi and Rao, 1995). The V^E values were measured with a dilatometer technique. The V^E values are accurate to ± 0.003 cm^3 mol^{-1}. Speed of sound values were measured by a single-crystal ultrasonic interferometer (Mittal Enterprises, model no. M81) at 4 MHz frequency at 308.15 K. These were accurate to 0.2%. A thermostatically controlled, well-stirred water bath with temperature controlled to ± 0.01 K was used for all the measurements. The value of κ_s was calculated using the relation

$$\kappa_s = u^{-2}\rho^{-1} \tag{1}$$

$$\rho = \frac{x_1 M_1 + x_2 M_2}{x_1 V_1{}^0 + x_2 V_2{}^0 + V^E} \tag{2}$$

* To whom correspondence should be addressed.

Table 1. Densities of Pure Components at 298.15 K

component	ρ/g·cm^{-3} expt	ρ/g·cm^{-3} lit.
ethyl acetate	0.894 53	0.894 55[a]
butyl acetate	0.876 33	0.876 36[a]
2-methoxyethanol	0.960 05	0.960 02[b]
2-ethoxyethanol	0.925 18	0.925 20[a]
2-butoxyethanol	0.896 23	0.896 25[a]

[a] Venkatesulu et al., 1997. [b] Das and Hazra, 1993.

where u and ρ denote speed of sound and density of binary mixtures, x_1 and x_2 denote the mole fractions, $V_1{}^0$ and $V_2{}^0$ are molar volumes, and M_1 and M_2 are molar masses of components 1 and 2, respectively, and V^E is the excess volume of the binary mixtures. The excess isentropic compressibilities (κ_s^E) were evaluated from the equation

$$\kappa_s{}^E = \kappa_s - \phi_1\kappa_{s1} - \phi_2\kappa_{s2} \tag{3}$$

where κ_s, κ_{s1}, and κ_{s2} are the isentropic compressibilities of the mixture and the pure components 1 and 2, respectively, and ϕ_1 and ϕ_2 are volume fractions of the components.

Materials. All the chemicals used were of analytical grade and purchased from commercial sources of ethyl acetate (Fluka), butyl acetate (Aldrich), and 2-alkoxyethanols (BDH). Ethyl acetate and butyl acetate were purified by the methods described by Iloukhani et al. (1984), and 2-alkoxyethanols were further purified by the methods described by Venkatesulu et al. (1994, 1997). The purities of the samples were checked by comparing the measured densities of the components with those reported in the literature (Venkatesulu et al., 1997; Das and Hazra, 1993). Densities of pure components were determined with a bicapillary type pycnometer, which offers an accuracy of 2 parts in 10^5. The experimental densities for pure liquids are reported in Table 1, together with literature values. Care was taken to prevent evaporation.

Results and Discussion

The measured excess molar volumes, V^E, as function of mole fraction (x_1) of ethyl acetate with 2-alkoxyethanols, and of butyl acetate with 2-alkoxyethanols at 308.15 K are reported in Tables 2 and 3 and are represented graphically in Figures 1 and 2, respectively. The u, ρ, κ_s, and κ_s^E values

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Table 2. Excess Molar Volumes for Ethyl Acetate (1) + 2-Alkoxyethanols (2) at 308.15 K

x_1	V^E / $cm^3 \cdot mol^{-1}$	x_1	V^E / $cm^3 \cdot mol^{-1}$
Ethyl Acetate (1) + 2-Methoxyethanol (2)			
0.1156	0.052	0.6271	0.140
0.2223	0.090	0.7420	0.119
0.2802	0.104	0.7810	0.111
0.4494	0.131	0.8269	0.084
0.5367	0.133		
Ethyl Acetate (1) + 2-Ethoxyethanol (2)			
0.1236	0.100	0.5934	0.211
0.1667	0.129	0.7654	0.173
0.2822	0.171	0.8179	0.151
0.4296	0.206	0.8576	0.127
0.4800	0.213		
Ethyl Acetate (1) + 2-Butoxyethanol (2)			
0.1310	0.103	0.5729	0.305
0.2036	0.164	0.6730	0.275
0.3018	0.235	0.7714	0.220
0.4131	0.290	0.9217	0.085
0.5282	0.306		

Table 3. Excess Molar Volumes for Butyl Acetate (1) + 2-Alkoxyethanols (2) at 308.15 K

x_1	V^E / $cm^3 \cdot mol^{-1}$	x_1	V^E / $cm^3 \cdot mol^{-1}$
Butyl Acetate (1) +2-Methoxyethanol (2)			
0.0756	0.073	0.5528	0.248
0.1677	0.131	0.7049	0.232
0.3393	0.209	0.7949	0.191
0.4498	0.235	0.8396	0.171
0.5116	0.243		
Butyl Acetate (1) + 2-Ethoxyethanol (2)			
0.1346	0.217	0.6583	0.316
0.2091	0.301	0.7042	0.285
0.3596	0.374	0.8052	0.210
0.3912	0.388	0.9143	0.102
0.5463	0.369		
Butyl Acetate (1) + 2-Butoxyethanol (2)			
0.1534	0.050	0.6104	0.168
0.2558	0.090	0.7260	0.132
0.3108	0.128	0.7903	0.109
0.3642	0.143	0.8531	0.070
0.4898	0.179		

of ethyl acetate with 2-alkoxyethanols are listed in Tables 4 and 5. The $\kappa_s{}^E$ values with volume fraction are graphically presented in Figures 3 and 4. The V^E values are fitted by the method of least squares using the polynomial

$$V^E = x_1x_2[a_0 + a_1(x_1 - x_2) + a_2(x_1 - x_2)^2] \qquad (4)$$

where x_1 and x_2 are the mole fractions of components 1 and 2. a_0, a_1, and a_2 are the adjustable parameters obtained by the least-squares method and are listed in Table 6 along with the standard deviation $\sigma(V^E)$.

The depencence of $\kappa_s{}^E$ on volume fraction has been expressed by polynomial form:

$$\kappa^E{}_s = \phi_1\phi_2[b_0 + b_1(\phi_1 - \phi_2) + b_2(\phi_1 - \phi_2)^2] \qquad (5)$$

Here b_0, b_1, and b_2 are constants obtained by the method of least squares and are given in Table 7 along with standard deviations.

The data included in Table 2 and 3 show that V^E values are positive in the mixtures of ethyl acetate or butyl acetate with 2-methoxyethanol, 2-ethoxyethanol, and 2-butoxyethanol over the whole range of composition. Further the curves in Figures 2 and 3 show that V^E versus mole fraction of ethyl acetate and of butyl acetate curves are symmetric. The positive molar excess volumes can be ascribed to breaking of hydrogen bonds in 2-alkoxyethanols by the addition of ethyl acetate or butyl acetate. The observed positive excess volume on mixing indicates that the dis-

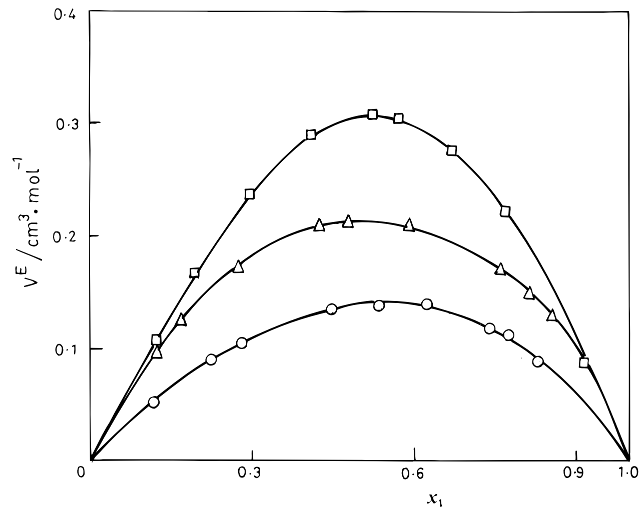

Figure 1. Excess volumes (**V^E**) for ethyl acetate (1) + 2-methoxyethanol (○), + 2-ethoxyethanol (△), and + 2-butoxyethanol (□) at 308.15 K.

Table 4. Volume Fraction (ϕ_1) of Ethyl Acetate and ρ, u, κ_s, and $\kappa_s{}^E$ for the Binary Mixtures of Ethyl Acetate with 2-Alkoxyethanols at 308.15 K

ϕ_1	ρ / $g \cdot cm^3$	u / $m \cdot s^{-1}$	κ_S / TPa^{-1}	$\kappa^E{}_S$ / TPa^{-1}
Ethyl Acetate + 2-Methoxyethanol				
0.0000	0.951 54	1312	611	
0.1403	0.941 27	1291	637	−17
0.2630	0.932 36	1265	670	−21
0.3271	0.927 80	1252	688	−23
0.5047	0.915 38	1216	739	−26
0.5912	0.909 37	1198	766	−25
0.6774	0.903 33	1180	795	−23
0.7822	0.896 30	1160	829	−21
0.8166	0.894 03	1153	841	−19
0.8564	0.891 61	1146	854	−18
0.9204	0.887 39	1133	878	−14
1.0000	0.882 39	1112	916	
Ethyl Acetate + 2-Ethoxyethanol				
0.0000	0.916 71	1268	678	
0.1253	0.911 48	1254	698	−10
0.1689	0.909 86	1247	707	−11
0.2854	0.905 45	1228	732	−14
0.4334	0.900 02	1205	765	−16
0.4839	0.898 17	1198	776	−17
0.5972	0.894 23	1181	802	−18
0.7682	0.888 72	1154	845	−16
0.8202	0.887 22	1145	860	−13
0.8595	0.886 14	1138	871	−12
0.9136	0.884 59	1130	885	−10
1.0000	0.882 39	1112	916	
Ethyl Acetate + 2-Butoxyethanol				
0.0000	0.888 09	1274	694	
0.1016	0.886 80	1264	708	−9
0.1610	0.886 02	1254	718	−12
0.2449	0.885 00	1240	735	−13
0.3456	0.883 97	1224	755	−16
0.4565	0.883 15	1207	777	−18
0.5016	0.882 87	1198	789	−16
0.6070	0.882 44	1180	814	−15
0.7169	0.882 20	1162	839	−14
0.8004	0.882 17	1149	859	−13
0.8983	0.882 24	1133	883	−10
1.0000	0.882 39	1112	916	

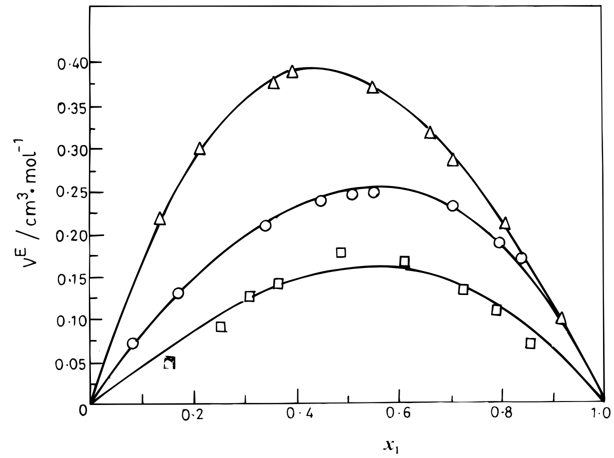

Figure 2. Excess volumes (**V^E**) for butyl acetate (1) + 2-methoxyethanol (○), + 2-ethoxyethanol (△), and + 2-butoxyethanol (□) at 308.15 K.

Table 5. Volume Fraction (ϕ_1) of Butyl Acetate and ρ, u, κ_s, and κ_s^E for the Binary Mixtures of Butyl Acetate with 2-Alkoxyethanols at 308.15 K

ϕ_1	ρ / g·cm^{-3}	u / m·s^{-1}	κ_s / TPa^{-1}	κ^E_s / TPa^{-1}
	Butyl Acetate + 2-Methoxyethanol			
0.0000	0.951 54	1312	611	
0.1206	0.940 43	1302	627	−13
0.2525	0.928 70	1281	656	−16
0.3113	0.923 39	1272	669	−18
0.4627	0.909 97	1250	703	−19
0.5782	0.900 18	1232	732	−18
0.6372	0.895 15	1223	747	−17
0.6746	0.891 97	1216	758	−15
0.8002	0.881 62	1199	789	−14
0.8666	0.876 24	1190	806	−13
0.8977	0.873 67	1185	815	−11
1.0000	0.866 22	1165	851	
	Butyl Acetate + 2-Ethoxyethanol			
0.0000	0.916 71	1268	678	
0.1750	0.906 01	1254	702	−6
0.2651	0.900 17	1246	716	−8
0.3558	0.895 84	1237	730	−10
0.4337	0.891 91	1229	742	−11
0.4671	0.889 89	1225	749	−10
0.6216	0.882 39	1208	777	−9
0.7244	0.877 86	1197	795	−8
0.7646	0.876 16	1192	803	−7
0.8494	0.872 62	1182	817	−5
0.9355	0.868 95	1173	836	−4
1.0000	0.866 22	1165	851	
	Butyl Acetate + 2-Butoxyethanol			
0.0000	0.888 09	1274	694	
0.1544	0.884 38	1263	709	−9
0.2573	0.881 87	1252	723	−11
0.3125	0.880 39	1247	730	−13
0.3660	0.879 14	1242	737	−14
0.4917	0.876 14	1229	756	−15
0.5247	0.875 45	1224	762	−14
0.6122	0.873 64	1213	778	−12
0.7275	0.871 32	1199	798	−10
0.7916	0.870 07	1195	811	−7
0.8541	0.868 96	1183	823	−5
1.0000	0.866 22	1165	851	

sociation of the self-associated species of the alkoxyethanol on dilution with acetates is the dominating feature. It has been ascertained that the mixed liquids are probably due to strong dipolar interactions and hydrogen bonds which occur between the, π-electrons of the acetates and oxygen (−O−) in 2-alkoxyethanols.

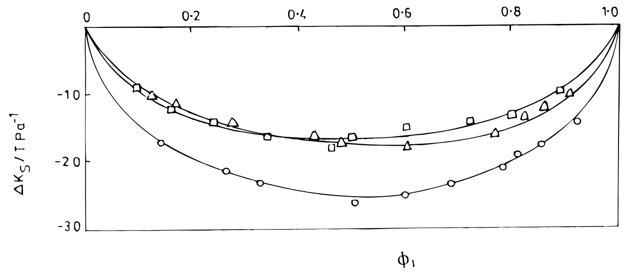

Figure 3. Excess isentropic compressibilities (κ_S^E) as a function of volume fraction (ϕ_1) for ethyl acetate (1) + 2-methoxyethanol (○), + 2-ethoxyethanol (△), and + 2-butoxyethanol (□) at 308.15 K.

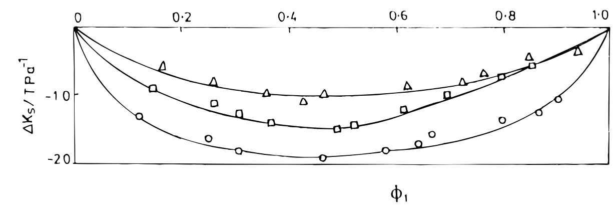

Figure 4. Excess isentropic compressibilities (κ_S^E) as a function of volume fraction (ϕ_1) for butyl acetate (1) + 2-methoxyethanol (○), + 2-ethoxyethanol (△), and + 2-butoxyethanol (□) at 308.15 K.

Table 6. Coefficients of Eq. 4 and Standard Deviations $\sigma(V^E)$ for the Binary Systems at 308.15 K[a]

system	a_0	a_1	a_2	$\sigma(V^E)$
ethyl acetate +				
2-methoxyethanol	0.5487	0.0865	0.0426	0.004
2-ethoxyethanol	0.8503	0.0762	0.2432	0.002
2-butoxyethanol	1.2285	0.1945	−0.3072	0.002
butyl acetate +				
2-methoxyethanol	0.9663	0.2173	0.3349	0.002
2-ethoxyethanol	1.5192	−0.3904	0.1455	0.003
2-butoxyethanol	0.7056	0.1442	−0.4709	0.003

[a] All units cm^3·mol^{-1}.

Table 7. Values of the Parameters of Eq 5 and Standard Deviation $\sigma(\kappa_s^E)$ for the Binary Systems at 308.15 K[a]

system	b_0	b_1	b_2	$\sigma(\kappa_s^E)$
ethyl acetate +				
2-methoxyethanol	−92.9	−7.7	−105.5	2
2-ethoxyethanol	−65.6	−13.4	−58.0	1
2-butoxyethanol	−62.8	−2.9	−59.8	1
butyl acetate +				
2-methoxyethanol	−68.2	6.0	−83.8	1
2-ethoxyethanol	−37.9	−1.0	−23.3	1
2-butoxyethanol	−56.2	17.1	6.0	1

[a] All units TPa^{-1}.

The data included in Figure 1 show that excess volumes increase with increase in chain length of the 2-alkoxyethanol; i.e., the interaction between ethyl acetate and alkoxyethanol decreases with increase in chain length of alkoxyethanol. The observed excess volumes for the systems of butyl acetate with 2-alkoxyethanols suggest that the interactions are stronger because of the presence of two bulky groups in the system of butyl acetate + 2-butoxyethanol other than alkoxyethanols.

A close examination of results included in Table 4 and 5 show that κ_s^E values are negative over the whole range of composition for all the systems. The negative κ_s^E values may be attributed to the existance of dispersion and dipolar interactions between unlike molecules. The observed negative κ_s^E indicates that dipolymerization of self-associated species of alkoxyethanols, on dilution with acetates, is dominating.

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