



Partial molar volumes partial molar adiabatic compressibilities and molar Gibbs energies of anisaldehyde with some alkoxyethanols – Insights through plots showing compositional, volumetric and temperature dependence



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ABSTRACT

Partial molar volumes (\bar{V}_i) and their excess values, apparent (V_ϕ) and reduced molar volumes have been derived from the measured density values for the binary liquid mixtures of Anisaldehyde (AA) + Methoxy ethanol (MOE), Ethoxy ethanol (EOE), and Butoxy ethanol (BOE) at 303.15 K, 308.15 K, 313.15 K and 318.15 K over the entire composition range and at atmospheric pressure. An analytical method based on Redlich–Kister fitting equations for V_m^E as a function of the mole fraction has been used to obtain partial molar volumes at infinite dilutions (\bar{V}_i^∞). Comparison has also been made by analyzing the apparent molar volumes, and reduced molar volume graphs for infinite values. The derivatives, $(\frac{\partial V_m^E}{\partial x_1})_{T,P}$ in PMV equations, substituted with β_{ad}^E values in place of V^E to obtain the partial molar adiabatic compressibility ($\phi^0 k_s$) deviation in molar Gibbs energies ($\Delta G^* E$) have also been derived from the measured viscosity values to further substantiate the thermodynamic and PMV analysis.

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1. Introduction: partial molar properties

A partial molar property is a thermodynamic quantity which indicates how an extensive property of a solution or mixture varies with changes in the molar composition of the mixture at constant temperature and pressure. Essentially it is the partial derivative with respect to the quantity (number of moles) of the component of interest. Every extensive property of a mixture has a corresponding partial molar property. Partial molar properties can often be determined because chemical mixtures are often maintained at constant temperature and pressure, and under these conditions, the value of any extensive property can be obtained from its partial molar property. They are especially useful when considering specific properties of pure substances (that is, properties of 1 mol of pure substance) and properties of mixing.

The present paper is an extension of the molecular interaction study of three binary liquid mixtures (Anisaldehyde (AA) + 2-Methoxyethanol (MOE) + 2-Ethoxyethanol (EOE) + 2-Butoxyethanol (BOE), AA being the common component, at 303.15 K, 308.15 K, 313.15 K and 318.15 K. In our previous work [1], we had presented the data from the studied effects of AA on the behavior of alkoxyethanols (MOE, EOE and BOE) by computing certain thermodynamic parameters like excess molar volume, intermolecular free length, adiabatic compressibility, and

deviation in viscosity. In continuation of our work, we are now presenting excess Gibbs energies of the activation of flow ($\Delta G^* E$), partial molar volumes $\bar{V}_{m,1}$, $\bar{V}_{m,2}$, and partial molar adiabatic compressibilities $\phi^0 k_{s,1}^E$, $\phi^0 k_{s,2}^E$, derived from the values of coefficients from Redlich–Kister polynomial equations. Values of these partial molar quantities at infinite dilution were also computed to get a focus on the in-depth behavior of each participating component as these quantities are very sensitive to interactions between solute and solvent and to changes induced in the solvent by the solute as the concentration of the latter tends to zero. Trends in these properties with changes in temperature and composition were also studied and discussed as they give some qualitative assessment of solution behavior in the intermediate composition range.

2. Results and discussions

2.1. Partial molar volumes

The partial molar volumes of the components of a mixture vary with the composition of the mixture, since, the environment of the molecules in the mixture changes with the composition. It is the changing molecular environment (and the consequent alteration of the interactions between molecules) that results in the thermodynamic properties of a mixture changing as its composition is altered.

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Table 1Partial molar volumes and excess partial molar volumes of AA ($\bar{V}_{m,1}$) and alkoxyethanols ($\bar{V}_{m,2}$) under study at all four temperatures (303.15 K–318.15 K).

x_1	$\bar{V}_{m,1}/\text{cm}^3 \text{ mol}^{-1}$				$\bar{V}_{m,1}^E/\text{cm}^3 \text{ mol}^{-1}$				$\bar{V}_{m,2}/\text{cm}^3 \text{ mol}^{-1}$				$\bar{V}_{m,2}^E/\text{cm}^3 \text{ mol}^{-1}$			
	303.15 K	308.15 K	313.15 K	318.15 K	303.15 K	308.15 K	313.15 K	318.15 K	303.15 K	308.15 K	313.15 K	318.15 K	303.15 K	308.15 K	313.15 K	318.15 K
<i>AA + MOE</i>																
0.000	124.3	123.5	123.2	122.9	2.77	1.27	0.16	−0.93	79.77	79.98	80.38	80.68	0.00	0.00	0.00	0.00
0.075	124.1	123.3	123.3	123.2	2.53	1.12	0.29	−0.63	79.78	79.98	80.37	80.67	0.01	0.01	−0.01	−0.01
0.155	123.8	123.3	123.4	123.5	2.24	1.04	0.38	−0.38	79.82	79.99	80.36	80.64	0.05	0.02	−0.02	−0.04
0.239	123.5	123.2	123.5	123.7	1.93	0.98	0.43	−0.18	79.90	80.01	80.35	80.59	0.12	0.03	−0.03	−0.09
0.328	123.1	123.1	123.5	123.8	1.61	0.88	0.44	−0.03	80.03	80.04	80.34	80.53	0.25	0.07	−0.03	−0.15
0.423	122.8	123.0	123.4	123.9	1.27	0.75	0.42	0.07	80.23	80.13	80.36	80.47	0.46	0.15	−0.02	−0.21
0.524	122.5	122.8	123.4	124.0	0.94	0.58	0.36	0.13	80.53	80.28	80.41	80.42	0.76	0.30	0.04	−0.26
0.631	122.1	122.6	123.3	124.0	0.62	0.39	0.28	0.14	80.97	80.53	80.53	80.41	1.20	0.56	0.16	−0.27
0.746	121.8	122.4	123.2	123.9	0.32	0.22	0.17	0.10	81.62	80.93	80.78	80.50	1.85	0.95	0.40	−0.18
0.868	121.6	122.3	123.1	123.9	0.10	0.07	0.06	0.04	82.58	81.55	81.25	80.77	2.81	1.57	0.87	0.09
1.000	121.5	122.2	123.0	123.8	0.00	0.00	0.00	0.00	84.00	82.67	82.09	81.37	4.23	2.69	1.71	0.69
<i>AA + EOE</i>																
0.000	125.2	124.9	125.1	125.2	3.63	2.65	2.04	1.33	98.11	98.39	99	99.39	0.00	0.00	0.00	0.00
0.082	124.8	124.6	124.9	125.1	3.29	2.41	1.85	1.28	98.12	98.43	99.01	99.46	0.02	0.01	0.01	0.00
0.168	124.5	124.4	124.7	125.0	2.95	2.18	1.69	1.21	98.17	98.43	99.03	99.41	0.06	0.04	0.03	0.01
0.257	124.1	124.2	124.5	124.9	2.59	1.93	1.52	1.11	98.27	98.57	99.08	99.43	0.16	0.11	0.08	0.04
0.350	123.7	123.9	124.3	124.8	2.20	1.66	1.32	0.98	98.44	98.62	99.17	99.49	0.33	0.23	0.17	0.10
0.447	123.3	123.6	124.1	124.7	1.78	1.35	1.09	0.82	98.72	98.82	99.32	99.61	0.62	0.44	0.32	0.20
0.548	122.9	123.2	123.9	124.5	1.33	1.02	0.83	0.64	99.16	99.15	99.57	99.78	1.06	0.76	0.57	0.39
0.653	122.4	122.9	123.6	124.3	0.88	0.69	0.57	0.45	99.84	99.66	99.98	100.1	1.74	1.27	0.98	0.68
0.764	122.0	122.6	123.3	124.1	0.47	0.37	0.31	0.25	100.9	100.4	100.6	100.6	2.75	2.05	1.61	1.16
0.879	121.7	122.3	123.1	123.9	0.14	0.12	0.10	0.08	102.4	101.6	101.6	101.4	4.27	3.24	2.60	1.96
1.000	121.5	122.2	123.0	123.8	0.00	0.00	0.00	0.00	104.7	103.5	103.2	102.7	6.59	5.12	4.21	3.27
<i>AA + BOE</i>																
0.000	124.8	124.7	125.1	125.3	3.30	2.49	2.08	1.44	132.5	133.2	134.0	134.3	0.00	0.00	0.00	0.00
0.090	124.7	124.6	125.0	125.2	3.15	2.35	1.95	1.33	132.5	133.2	134.0	134.4	0.01	0.01	0.01	0.00
0.181	124.6	124.5	124.9	125.1	3.09	2.31	1.92	1.31	132.5	133.2	134.0	134.4	0.02	0.01	0.01	0.01
0.275	124.5	124.4	124.9	125.1	2.95	2.21	1.84	1.26	132.5	133.3	134.0	134.4	0.07	0.05	0.04	0.03
0.371	124.2	124.2	124.7	125.0	2.69	2.02	1.68	1.16	132.7	133.4	134.1	134.4	0.23	0.17	0.14	0.09
0.470	123.8	124.0	124.5	124.8	2.32	1.75	1.45	1.00	133.0	133.6	134.3	134.6	0.57	0.42	0.35	0.24
0.571	123.4	123.6	124.2	124.6	1.85	1.40	1.16	0.80	133.7	134.1	134.7	134.9	1.20	0.90	0.74	0.51
0.674	122.8	123.2	123.9	124.4	1.31	0.99	0.82	0.57	134.8	135.0	135.4	135.3	2.33	1.74	1.44	0.99
0.780	122.3	122.8	123.5	124.2	0.74	0.56	0.47	0.32	136.7	136.4	136.6	136.2	4.25	3.18	2.64	1.81
0.889	121.8	122.4	123.2	123.9	0.23	0.18	0.15	0.10	139.9	138.8	138.6	137.6	7.45	5.61	4.67	3.21
1.000	121.5	122.2	123.0	123.8	0.00	0.00	0.00	0.00	145.1	142.8	142.0	139.9	12.6	9.59	8.00	5.54

The uncertainties are $0.01 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1}$.

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