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Densities and volumetric properties of binary mixtures of methyl acrylate with 1-alkanols (C_4–C_{10}) at different temperatures

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ABSTRACT

The densities, ρ of binary mixtures of methyl acrylate with 1-butanol, 1-hexanol, 1-octanol and 1-decanol, including those of pure liquids, over the entire composition range were measured at temperatures 288.15, 293.15, 298.15, 303.15, 308.15, 313.15, and 318.15 K and atmospheric pressure. From the experimental data, the excess molar volume, V_m^E, partial molar volumes, $V_{m,1}^{\circ\infty}$ and $V_{m,2}^{\circ\infty}$, and excess partial molar volumes, $V_{m,1}^{\circ E,\infty}$ and $V_{m,2}^{\circ E,\infty}$ at infinite dilution were calculated. The V_m^E values were found positive over the whole composition range for all the mixtures and at each temperature studied, except for methyl acrylate + 1-butanol which exhibit negative V_m^E values, indicating the presence of specific interactions between methyl acrylate and 1-alkanol molecules. The deviations in V_m^E values follow the order: 1-butanol<1-hexanol<1-octanol<1-decanol. It is observed that V_m^E values depend upon the length of alkyl chain in 1-alkanols and the interactions between methyl acrylate and 1-alkanols decrease with increase in alkyl chain length.

1. Introduction

The knowledge of physicochemical properties of non-aqueous binary liquid mixtures has relevance in theoretical and applied areas of research, and such results are frequently used in process design (flow, mass transfer, or heat transfer calculations) of many chemical and industrial processes [1–5]. In continuation to our earlier work [6–11] on the volumetric, ultrasonic and transport properties of non-aqueous binary liquid mixtures, here we report the results of our study on volumetric, ultrasonic and transport behaviour of binary mixtures of methyl acrylate (MA) with 1-butanol, 1-hexanol, 1-octanol and 1-decanol, over the entire composition range at different temperatures.

Methyl acrylate is a very important industrial chemical and is widely used commercially for the production of technically important high polymeric and latex compounds. It is polar (dipole moment, $\mu = 1.77$ D at 298.15 K) [12], aprotic and unassociated liquid [12]. Alkanols are protic, highly associated through hydrogen bonding and this association decreases with increase in alkyl chain length in 1-alkanol [13]. Therefore, the study of intermolecular interactions in methyl acrylate + 1-alkanol mixtures would be interesting owing to their industrial applications [14]. To the best of our knowledge, volumetric, ultrasonic and viscometric studies on binary mixtures of methyl acrylate (MA) with 1-butanol, 1-hexanol, 1-octanol and 1-decanol, are not reported in the literature. However, we have reported the densities of methyl acrylate + 1-butanol mixtures [10], and Sastry et al. [15] reported densities and ultrasonic speeds for methyl acrylate + 1-butanol mixtures at 308.15 and 318.15 K.

In the present paper, we report densities, ρ of binary mixtures of methyl acrylate with 1-butanol, or 1-hexanol, or 1-octanol, or 1-decanol, including those of pure liquids at temperatures 288.15, 293.15, 298.15, 303.15, 308.15, 313.15, and 318.15 K and atmospheric pressure, covering the entire composition range expressed by the mole fraction x_1 of methyl acrylate. The experimental values of ρ are used to calculate the excess molar volumes, V_m^E, partial molar volumes, $V_{m,1}^{\circ\infty}$ and $V_{m,2}^{\circ\infty}$, and excess partial molar volumes, $V_{m,1}^{\circ E,\infty}$ and $V_{m,2}^{\circ E,\infty}$ at infinite dilution. The variations of V_m^E with composition and temperature of the mixtures have been discussed in terms of molecular interaction in these mixtures. The effect alkyl chain length of 1-alkanol molecules on V_m^E has also been discussed.

2. Experimental

Methyl acrylate, 1-butanol, 1-hexanol, 1-octanol and 1-decanol used in the study were the AR grade products from S. D. Fine Chemicals, India and were purified by using the methods described in the literature [16,17]; the mass fraction purities as determined by gas chromatography are: methyl acrylate >0.995, 1-butanol >0.994, 1-hexanol >0.994, 1-octanol >0.993, and 1-decanol >0.993. Before use, the chemicals were stored over 0.4 nm molecular sieves for 72 h to remove water content, if any, and were degassed at low pressure. The mixtures were prepared by mass and were kept in special airtight stopper glass bottles to avoid evaporation. The weighings were done by using an electronic balance (model: GR-202, AND, Japan) with a

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precision of ±0.01 mg. The uncertainty in the mole fraction was estimated to be less than $\pm 1 \cdot 10^{-4}$.

The densities of pure liquids and their binary mixtures were measured by using a single-capillary pycnometer (made of Borosil glass) having a bulb capacity of ~10 mL. The capillary, with graduated marks, had a uniform bore and could be closed by a well-fitting glass cap. The marks on the capillary were calibrated by using triply distilled water. The uncertainty in density measurements was within $\pm 2 \cdot 10^{-5}$ g cm^{-3}. The temperature of the test liquids during the measurements was maintained within an uncertainty of ±0.01 K in an electronically controlled thermostatic water bath (model: ME-31A, JULABO, Germany). The reliability of experimental measurements of ρ was ascertained by comparing the experimental data of pure liquids with the corresponding values, which were available in the literature [15,17–19] at various temperatures. This comparison is given in Table 1 and the agreement between the experimental and the literature values is found good in general.

3. Results and discussion

The experimental values of densities, ρ of binary mixtures of methyl acrylate with 1-butanol, 1-hexanol, 1-octanol and 1-decanol, with methyl acrylate as a common component, over the entire composition range, expressed in mole fraction x_1 of methyl acrylate at different temperatures are listed in Tables 2–5. The values of V_m^E for the mixtures at each temperature were calculated by using the following relation

$$V_m^E = x_1 M_1 (1/\rho - 1/\rho_1) + x_2 M_2 (1/\rho - 1/\rho_2) \quad (1)$$

where M is the molar Mass; the subscripts 1 and 2 stand for pure components, methyl acrylate and alkanol, respectively. The values of V_m^E are listed in Tables 2–5. The values of V_m^E were fitted to a Redlich–Kister type [20] polynomial equation

$$V_m^E = x_1 x_2 \sum_{i=0}^{j} A_i (1-2x_1)^i. \quad (2)$$

The values of coefficients, A_i were evaluated by using the method of least squares, with all points weighted equally. The coefficients A_0, A_1, A_2, A_3 and A_4 along with standard deviations σ of fit for all the mixtures are listed in Table 6. The variations of V_m^E with x_1 of methyl acrylate for the mixtures at 298.15 and 318.15 K, along with the smoothed values by using Eq. (2) are presented graphically in Fig. 1.

The results presented in Fig. 1 indicate that V_m^E values are negative for methyl acrylate + 1-butanol and positive for methyl acrylate + 1-hexanol/1-octanol/1-decanol binary mixtures over the entire mole fraction range and at all investigated temperatures. The observed negative values of V_m^E for methyl acrylate + 1-butanol mixtures indicate the presence of specific interactions between methyl acrylate and 1-butanol molecules, whereas positive values of V_m^E for methyl acrylate + 1-hexanol/1-octanol/1-decanol binary mixtures indicate weak interactions between the components of the

Table 1
Experimental values of density, ρ of pure liquids along with the corresponding values available in the literature at various temperatures.

Liquid	T/(K)	ρ/(kg m^{-3})	
		Experimental	Literature
Methyl acrylate	293.15	953.51	953.5[a]
	298.15	947.56	947.5[a]
	308.15	935.66	935.6[a]; 935.62[b]
1-Butanol	293.15	809.17	809.56[a]
	298.15	805.54	805.75[a]; 805.4[c]
1-Hexanol	293.15	818.67	818.75[a]
	298.15	815.1	815.34[a]; 815.1[c]
1-Octanol	293.15	825.37	824.99[a]; 825.8[d]
	298.15	821.91	821.57[a]; 821.6[c]
1-Decanol	293.15	830.14	829.7[d]
	298.15	826.98	826.3[c]

[a] Ref. [17].
[b] Ref. [15].
[c] Ref. [18].
[d] Ref. [19].

Table 2
Densities, ρ (kg m^{-3}) and excess molar volumes, V_m^E (10^{-6} m^3 mol^{-1}) as functions of mole fraction, x_1 of methyl acrylate for methyl acrylate + 1-butanol mixtures at the temperatures 288.15 to 318.15 K and atmospheric pressure.

x_1	ρ	V_m^E	x_1	ρ	V_m^E
T = 288.15 K					
0.0000	812.80	0.000	0.6095	902.51	−0.089
0.0777	824.32	−0.032	0.6789	912.66	−0.080
0.1555	835.82	−0.057	0.7483	922.79	−0.067
0.2273	846.41	−0.075	0.8099	931.77	−0.054
0.2990	856.97	−0.087	0.8715	940.75	−0.039
0.3791	868.76	−0.095	0.9358	950.11	−0.020
0.4593	880.53	−0.098	1.0000	959.46	0.000
0.5344	891.53	−0.096			
T = 293.15 K					
0.0000	809.17	0.000	0.6095	897.49	−0.086
0.0777	820.51	−0.030	0.6789	907.47	−0.076
0.1555	831.84	−0.055	0.7483	917.44	−0.064
0.2273	842.27	−0.072	0.8099	926.28	−0.052
0.2990	852.67	−0.084	0.8715	935.10	−0.036
0.3791	864.28	−0.092	0.9358	944.31	−0.019
0.4593	875.86	−0.094	1.0000	953.51	0.000
0.5344	886.69	−0.093			
T = 298.15 K					
0.0000	805.54	0.000	0.6095	892.47	−0.082
0.0777	816.70	−0.029	0.6789	902.28	−0.072
0.1555	827.86	−0.052	0.7483	912.09	−0.061
0.2273	838.13	−0.069	0.8099	920.78	−0.049
0.2990	848.37	−0.081	0.8715	929.45	−0.034
0.3791	859.79	−0.088	0.9358	938.51	−0.018
0.4593	871.19	−0.091	1.0000	947.56	0.000
0.5344	881.84	−0.088			
T = 303.15 K					
0.0000	801.91	0.000	0.6095	887.45	−0.079
0.0777	812.89	−0.027	0.6789	897.09	−0.069
0.1555	823.88	−0.050	0.7483	906.74	−0.058
0.2273	833.99	−0.066	0.8099	915.28	−0.046
0.2990	844.07	−0.078	0.8715	923.80	−0.031
0.3791	855.30	−0.084	0.9358	932.71	−0.016
0.4593	866.52	−0.087	1.0000	941.61	0.000
0.5344	876.99	−0.084			
T = 308.15 K					
0.0000	798.28	0.000	0.6095	882.42	−0.074
0.0777	809.08	−0.025	0.6789	891.90	−0.065
0.1555	819.90	−0.048	0.7483	901.38	−0.054
0.2273	829.85	−0.064	0.8099	909.78	−0.043
0.2990	839.76	−0.074	0.8715	918.15	−0.029
0.3791	850.81	−0.080	0.9358	926.91	−0.015
0.4593	861.85	−0.083	1.0000	935.66	0.000
0.5344	872.14	−0.080			
T = 313.15 K					
0.0000	794.65	0.000	0.6095	877.39	−0.070
0.0777	805.27	−0.023	0.6789	886.71	−0.061
0.1555	815.91	−0.044	0.7483	896.02	−0.050
0.2273	825.70	−0.060	0.8099	904.27	−0.040
0.2990	835.45	−0.070	0.8715	912.50	−0.026
0.3791	846.32	−0.076	0.9358	921.11	−0.014
0.4593	857.17	−0.079	1.0000	929.71	0.000
0.5344	867.29	−0.076			
T = 318.15 K					
0.0000	791.02	0.000	0.6095	872.36	−0.065
0.0777	801.46	−0.021	0.6789	881.52	−0.057
0.1555	811.92	−0.041	0.7483	890.66	−0.046
0.2273	821.55	−0.056	0.8099	898.76	−0.036
0.2990	831.14	−0.066	0.8715	906.85	−0.024
0.3791	841.83	−0.073	0.9358	915.30	−0.011
0.4593	852.49	−0.074	1.0000	923.76	0.000
0.5344	862.44	−0.072			