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Internal pressure, free volume and excess thermodynamic properties of methyl acrylate+1-alkanols (C_4–C_{10}) binary mixtures from ultrasonic speed and density

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The experimental values of ultrasonic speeds and densities, of binary mixtures of methyl acrylate with 1-butanol, 1-hexanol, 1-octanol and 1-decanol have been used to calculate the internal pressures, free volumes, excess internal pressures, excess free volumes, excess free energy, excess enthalpy and excess entropy of mixing over the entire composition range at 298.15 K using regular solution theory. The results have been interpreted in terms of intermolecular interactions between the component molecules in the mixture. The variations of these excess properties with composition indicate that the methyl acrylate-alkanol interaction in these mixtures follows the order: 1-butanol > 1-hexanol > 1-octanol > 1-decanol. It is observed that the order of interactions in these mixtures depends upon the length of alkyl chain in the studied 1-alkanol molecules. In addition, the values of ultrasonic speeds have also been calculated theoretically for these mixtures using scaled particle theory and found to be in good agreement with experimental findings.

Keywords: Solution chemistry, Thermodynamics, Excess properties, Methyl acrylate, Alkanols, Molecular interactions, Regular solution theory, Scaled particle theory

The ultrasonic speed may be considered as a thermodynamic property, provided that a negligible amount of ultrasonic absorption of the acoustic waves of low frequency and of low amplitude is observed; in which case, the ultrasonic absorption of the acoustic waves is negligible[1]. The excess thermodynamic properties derived from ultrasonic velocity have been found to provide useful information regarding intermolecular interactions[2–4] between the component molecules of the binary liquid mixtures. The cohesive forces are of primary importance irrespective of any model chosen for the liquid state. Internal pressure, π_i [= $(\partial E/\partial V)_T$] of a fluid is the volume derivative of its internal energy at constant temperature. It has been subject of interest among researchers in the past[5–18], as it provides a measure of molecular interactions, internal structure, clustering phenomenon, ionic interactions, dipolar interactions, etc., in the liquid mixtures.

Many empirical, semi-empirical and statistical models such as free length theory[19], collision factor theory[20], Nomoto relation[21], van Deal-Vangeel relation[22,23], etc. have been used by various researchers to evaluate the ultrasonic speeds in mixtures. Scaled particle theory (SPT) is a statistical model[24], which assumes liquids molecules as hard spheres. It relates microscopic parameters such as radius, surface area and hard core volume of a molecule with the macroscopic parameters such as ultrasonic speed. The propagation of ultrasonic wave through a solution depends upon its molecular structure as well as the molecular interactions prevailing in the solution. It is the only model developed that considers the shape of constituent molecules of binary mixtures in calculating their theoretical ultrasonic speeds[25]. Seven different shapes, viz., sphere, cube, tetrahedron, disc A, disc B, disc C and disc D have been taken into consideration. When the correct shapes are assigned to the participating components of the mixture, the theoretical ultrasonic speeds are close to experimental values.

In continuation to our ongoing research[26–29] on binary mixtures containing acrylate monomers, here we report the results of our study on binary mixtures of methyl acrylate with 1-butanol, 1-hexanol, 1-octanol and 1-decanol. Methyl acrylate is polar (dipole moment, μ = 1.77 D at 298.15 K)[23], aprotic and unassociated liquid[30]. Alkanols are protic, highly associated through hydrogen bonding and this association decreases with increase in alkyl chain length in 1-alkanol[31]. Therefore, the study of intermolecular interactions in methyl acrylate+

1-alkanol mixtures would be interesting owing to their industrial applications[32].

In the present article, the internal pressures (π_i), free volumes (V_f), internal pressures (π_i), free volumes (V_f), excess internal pressures (π_i^E), excess free volumes (V_f^E), excess free energy (G^E), excess enthalpy (H^E) and excess entropy (S^E) of mixing for these methyl acrylate+1-alkanol binary mixtures have been calculated from experimental ultrasonic speeds (u) and densities (ρ) over the whole composition range expressed by mole fraction (x_1) of methyl acrylate at 298.15 K by using regular solution theory. The experimental data of ultrasonic speeds (u) and densities (ρ) of these binary mixtures have been taken from our previous studies[26,27]. The variations of these excess parameters with composition of the mixtures are discussed in terms of molecular interactions in these mixtures. Furthermore, the values of ultrasonic speeds have been calculated theoretically from pure component data of these mixtures using scaled particle theory and the results were compared with experimental findings. The deviations for each system have been discussed in terms of capability of molecules to attain a particular shape in the binary mixture.

Theoretical

Regular solution theory

The internal pressure of a fluid is related to the thermal pressure coefficient $(\partial P/\partial T)_V$ by the following well-known thermodynamic equation of state,

$$\pi_\mathrm{i} = \left(\frac{\partial E}{\partial V}\right)_\mathrm{T} = T\left(\frac{\partial P}{\partial T}\right)_\mathrm{V} - P = T\left(\frac{\alpha_\mathrm{p}}{k_\mathrm{T}}\right) - P \quad \dots (1)$$

where α_p is the isobaric expansivity and k_T is the isothermal compressibility of the mixture. For most of the liquids, the thermal pressure coefficient multiplied by absolute temperature, i.e., $T(\alpha_p/k_T)$ is very high so that the external pressure (P) becomes negligible in comparison[16,33,34], therefore it may be neglected in the Eq. (1) in the present calculations. Thus, the internal pressure can be shown to be equal to the following relationship[33,34].

$$\pi_{nt} = \alpha_p T/k_T \quad \dots (2)$$

The free volume, V_f, of the mixtures is calculated from the relationship[33–36],

$$V_\mathrm{f} = \frac{RT}{(P+\pi_i)} \quad \dots (3)$$

since P is very small as compared to π_i, it has been neglected in the Eq. (3) in the present calculations. k_T, is calculated using the well-known thermodynamic relationship,

$$k_\mathrm{T} = k_\mathrm{s} + \frac{TV\alpha_\mathrm{p}^2}{C_\mathrm{p}} \quad \dots (4)$$

where k_s [$= 1/(u^2\rho)$] is isentropic compressibility, V is the molar volume and C_p is the heat capacity of the mixture. The α_p values for the mixtures were evaluated from temperature dependence of density data[19]. The C_p values of pure liquids at 298.15 K have been taken from the literature[37] and the C_p values for the mixtures have been calculated by using the following relationship.

$$C_\mathrm{p} = x_1 C_{\mathrm{p},1} + x_2 C_{\mathrm{p},2} \quad \dots (5)$$

The values of various parameters, C_p, α_p, k_s and k_T of pure liquids at 298.15 K used in the calculations are given as supplementary data (Table S1). The π_i^E and V_f^E of binary mixtures have been calculated using the relationship,

$$Y^E = Y - \left(x_1 Y_1 + x_2 Y_2\right) \quad \dots (6)$$

where Y is π_i or V_f and subscripts 1 and 2 refers to pure methyl acrylate and 1-alkanol, respectively. The excess enthalpies (H^E) and excess entropies (S^E) are calculated from π_i and V_f by using the following relations based on regular solution theory[35,36]

$$-H^\mathrm{E} = \pi_i V - \left[x_1 \pi_{i,1} V_1 + x_2 \pi_{i,2} V_2\right] \quad \dots (7)$$

$$S^\mathrm{E} = R\left[x_1 \ln V_{\mathrm{f},1} + x_2 \ln V_{\mathrm{f},2} - \ln V_\mathrm{f}\right] \quad \dots (8)$$

The excess free energy (G^E) of mixtures is given by the relation

$$G^\mathrm{E} = H^\mathrm{E} - TS^\mathrm{E} \quad \dots (9)$$

The values of u, ρ, π_i, V_f, π_i^E, V_f^E, G^E, H^E and S^E for the binary mixtures of methyl acrylate with 1-butanol, 1-hexanol, 1-octanol and 1-decanol as functions of mole fraction, x_1 of methyl acrylate at 298.15 K are listed in Table 1. The values of π_i^E, V_f^E, H^E, S^E and G^E were fitted to a Redlich-Kister[38] type polynomial equation,

Table 1—The values of u, ρ, π_i, V_f, π_i^E, V_f^E, G^E, H^E and S^E as a function of mole fraction (x_1) of methyl acrylate for methyl acrylate+1-alkanol binary mixtures at 298.15 K

x_1	u ($m\ s^{-1}$)	ρ ($kg\ m^{-3}$)	π_i ($10^8\ N\ m^{-2}$)	V_f ($10^{-6}\ m^3\ mol^{-1}$)	π_i^E ($10^8\ N\ m^{-2}$)	V_f^E ($10^{-6}\ m^3\ mol^{-1}$)	G^E ($kJ\ mol^{-1}$)	H^E ($kJ\ mol^{-1}$)	S^E ($kJ\ mol^{-1}\ K^{-1}$)
Methyl acrylate+1-butanol									
0.0000	1242.6	805.54	2.8899	8.5776	0.0000	0.0000	0.0000	0.0000	0.0000
0.0777	1230.5	816.70	2.9357	8.4437	-0.0155	0.0090	0.1364	0.1439	0.0075
0.1555	1220.1	827.86	2.9854	8.3030	-0.0271	0.0114	0.2400	0.2524	0.0124
0.2273	1212.2	838.13	3.0357	8.1656	-0.0334	0.0060	0.2978	0.3117	0.0139
0.2990	1205.9	848.37	3.0902	8.0214	-0.0354	-0.0063	0.3180	0.3307	0.0127
0.3791	1200.2	859.79	3.1543	7.8585	-0.0346	-0.0218	0.3135	0.3233	0.0098
0.4593	1195.7	871.19	3.2209	7.6961	-0.0313	-0.0367	0.2869	0.2928	0.0060
0.5344	1192.4	881.84	3.2847	7.5465	-0.0266	-0.0483	0.2476	0.2498	0.0022
0.6095	1189.9	892.47	3.3498	7.3999	-0.0208	-0.0568	0.1971	0.1956	-0.0015
0.6789	1188.2	902.28	3.4106	7.2681	-0.0148	-0.0609	0.1443	0.1398	-0.0045
0.7483	1186.9	912.09	3.4711	7.1413	-0.0090	-0.0600	0.0929	0.0862	-0.0066
0.8099	1186.0	920.78	3.5242	7.0338	-0.0045	-0.0543	0.0518	0.0445	-0.0074
0.8715	1185.3	929.45	3.5764	6.9311	-0.0009	-0.0437	0.0169	0.0099	-0.0070
0.9358	1184.5	938.51	3.6287	6.8311	0.0008	-0.0255	-0.0015	-0.0061	-0.0046
1.0000	1183.6	947.56	3.6786	6.7385	0.0000	0.0000	0.0000	0.0000	0.0000
Methyl acrylate+1-hexanol									
0.0000	1306.9	815.10	3.1303	7.9189	0.0000	0.0000	0.0000	0.0000	0.0000
0.0770	1290.5	821.32	3.1368	7.9023	-0.0357	0.0743	0.2150	0.2406	0.0256
0.1542	1275.3	828.08	3.1497	7.8700	-0.0651	0.1331	0.3750	0.4214	0.0463
0.2299	1260.7	835.19	3.1646	7.8329	-0.0917	0.1854	0.5226	0.5876	0.0649
0.3057	1247.4	842.87	3.1863	7.7797	-0.1116	0.2216	0.6161	0.6944	0.0784
0.3834	1235.1	851.35	3.2154	7.7091	-0.1251	0.2428	0.6607	0.7476	0.0869
0.4612	1224.5	860.52	3.2534	7.6191	-0.1297	0.2446	0.6417	0.7306	0.0889
0.5340	1215.9	869.82	3.2963	7.5201	-0.1268	0.2316	0.5819	0.6675	0.0856
0.6068	1208.2	879.82	3.3442	7.4123	-0.1188	0.2097	0.5032	0.5821	0.0789
0.6720	1202.2	889.42	3.3920	7.3078	-0.1067	0.1822	0.4155	0.4853	0.0698
0.7370	1197.5	899.56	3.4457	7.1939	-0.0887	0.1450	0.2982	0.3551	0.0569
0.8046	1193.4	910.78	3.5051	7.0721	-0.0664	0.1029	0.1760	0.2176	0.0416
0.8722	1189.8	922.82	3.5664	6.9505	-0.0422	0.0612	0.0743	0.1000	0.0257
0.9361	1186.7	934.83	3.6238	6.8403	-0.0197	0.0264	0.0109	0.0225	0.0116
1.0000	1183.6	947.56	3.6786	6.7385	0.0000	0.0000	0.0000	0.0000	0.0000
Methyl acrylate+1-octanol									
0.0000	1352.4	821.91	3.2060	7.7318	0.0000	0.0000	0.0000	0.0000	0.0000
0.0770	1331.5	825.80	3.1892	7.7725	-0.0532	0.1171	0.4390	0.4783	0.0392
0.1554	1311.5	830.40	3.1803	7.7944	-0.0992	0.2169	0.7765	0.8495	0.0729
0.2304	1293.4	835.40	3.1787	7.7982	-0.1362	0.2953	1.0123	1.1121	0.0997
0.3053	1276.0	841.19	3.1834	7.7868	-0.1669	0.3582	1.1876	1.3092	0.1216
0.3830	1259.7	848.08	3.1994	7.7477	-0.1876	0.3964	1.2556	1.3912	0.1357
0.4603	1244.7	855.84	3.2244	7.6877	-0.1992	0.4132	1.2477	1.3904	0.1427
0.5321	1232.1	863.94	3.2569	7.6109	-0.2005	0.4076	1.1693	1.3116	0.1423
0.6038	1221.6	873.00	3.3023	7.5064	-0.1891	0.3744	0.9938	1.1263	0.1325

(*Contd.*)

Table 1—The values of u, ρ, π_i, V_f, π_i^E, V_f^E, G^E, H^E and S^E as a function of mole fraction (x_1) of methyl acrylate for methyl acrylate+1-alkanol binary mixtures at 298.15 K (*Contd.*)

x_1	u (m s^{-1})	ρ (kg m^{-3})	π_i (10^8 N m^{-2})	V_f (10^{-6} m^3 mol^{-1})	π_i^E (10^8 N m^{-2})	V_f^E (10^{-6} m^3 mol^{-1})	G^E (kJ mol^{-1})	H^E (kJ mol^{-1})	S^E (kJ mol^{-1} K^{-1})
Methyl acrylate+1-octanol									
0.6724	1212.9	882.70	3.3551	7.3882	-0.1687	0.3243	0.7792	0.8957	0.1165
0.7410	1205.4	893.54	3.4165	7.2555	-0.1397	0.2598	0.5396	0.6346	0.0950
0.8052	1199.4	904.90	3.4809	7.1213	-0.1057	0.1893	0.3126	0.3831	0.0706
0.8698	1193.7	917.57	3.5478	6.9870	-0.0693	0.1192	0.1304	0.1758	0.0454
0.9350	1188.3	931.86	3.6152	6.8566	-0.0327	0.0536	0.0182	0.0391	0.0209
1.0000	1183.6	947.56	3.6786	6.7385	0.0000	0.0000	0.0000	0.0000	0.0000
Methyl acrylate+1-decanol									
0.0000	1377.3	826.98	3.1098	7.9711	0.0000	0.0000	0.0000	0.0000	0.0000
0.0762	1352.1	829.62	3.0805	8.0467	-0.0726	0.1696	0.7460	0.8011	0.0551
0.1523	1330.6	832.76	3.0691	8.0768	-0.1273	0.2935	1.1682	1.2642	0.0961
0.2225	1310.1	836.23	3.0593	8.1025	-0.1770	0.4057	1.5497	1.6828	0.1332
0.3073	1286.5	841.27	3.0573	8.1079	-0.2273	0.5156	1.8704	2.0405	0.1701
0.3848	1267.0	846.87	3.0696	8.0753	-0.2590	0.5785	1.9822	2.1746	0.1924
0.4622	1248.9	853.55	3.0939	8.0119	-0.2788	0.6106	1.9741	2.1792	0.2051
0.5356	1233.0	861.08	3.1288	7.9225	-0.2856	0.6117	1.8705	2.0783	0.2079
0.6092	1219.8	869.82	3.1822	7.7895	-0.2741	0.5694	1.6068	1.8034	0.1966
0.6768	1209.4	879.08	3.2452	7.6385	-0.2496	0.5017	1.2870	1.4632	0.1762
0.7443	1200.6	889.68	3.3209	7.4644	-0.2123	0.4108	0.9236	1.0707	0.1471
0.8089	1193.9	901.40	3.4059	7.2781	-0.1640	0.3041	0.5568	0.6682	0.1114
0.8736	1189.2	914.80	3.5016	7.0791	-0.1051	0.1848	0.2052	0.2748	0.0696
0.9412	1185.6	931.06	3.6024	6.8809	-0.0427	0.0700	-0.0231	0.0043	0.0274
1.0000	1183.6	947.56	3.6786	6.7385	0.0000	0.0000	0.0000	0.0000	0.0000

$$Y^E = x_1(1-x_1)\sum_{i=0}^{n} A_i(1-2x_1)^i \quad \dots (10)$$

where Y^E is π_i^E or V_f^E or H^E or S^E or G^E. The values of coefficients, A_i in Eq. (10) were evaluated by using least-squares method with all points weighted equally. The values of coefficients, A_i of Eq. (10) for the excess functions and the corresponding standard deviations, σ are listed in Table 2. The variation of π_i^E, V_f^E, G^E, H^E and S^E with composition of the mixtures, along with smoothed values using Eq. (10) at 298.15 K are presented graphically in Figs 1–5, respectively.

Scaled particle theory

The equation of state of fluid in scaled particle theory is given by

$$\frac{p}{\rho_N k_B T} = \frac{1+\eta+\eta^2}{(1-\eta)^3} \quad \dots (11)$$

where ρ_N is number density N_A/V_o, where V_o is the ideal volume of the mixture, $\eta = V_H\rho_N$, V_H being hard core volume of the molecule and the other quantities have usual meanings[39].

The equation of state for mixture of hard convex molecules (not necessarily spherical) is given by[40] Eq. 12,

$$\frac{p}{\rho_N k_B T} = \frac{1}{(1-V\rho_N)} + \frac{AB\rho_N}{(1-V\rho_N)^2} + \frac{B^2C\rho_N^2}{3(1-V\rho_N)^3} \quad \dots (12)$$

where $A = \sum x_i R_i$,

$B = \sum x_i S_i$, $C = \sum x_i R_i^2$, $V = \sum x_i V_{Hi}$, and R_i, S_i and V_{Hi} are the mean radius of curvature, surface area and volume, respectively, of the molecule of species i, ρ_N is number density of mixture molecule. The values of R, S and V_H for various shapes are listed in Table S2 (Supplementary Data).

Table 2—Coefficients (A_i) of Eq. (10) for π_i^{E}, $V_{\mathrm{f}}^{\mathrm{E}}$, G^{E}, H^{E} and S^{E} and standard deviations (σ) for methyl acrylate+1-alkanol binary mixtures at 298.15 K

Excess property	A_0	A_1	A_2	A_3	A_4	σ
Methyl acrylate+1-butanol						
π_i^{E} (10^8 N m^{-2})	-0.1154	-0.1331	-0.0072	-0.0055	0.0315	0.0002
$V_{\mathrm{f}}^{\mathrm{E}}$ (10^{-6} m^3 mol^{-1})	-0.1742	0.3260	0.1049	0.0092	-0.0868	0.0006
G^{E} (kJ mol^{-1})	1.0660	1.1273	0.0572	0.0368	-0.2810	0.0019
H^{E} (kJ mol^{-1})	1.0814	1.2340	0.0776	0.0394	-0.3081	0.0021
S^{E} (kJ mol^{-1} K^{-1})	0.0156	0.1067	0.0196	0.0028	-0.0264	0.0002
Methyl acrylate+1-hexanol						
π_i^{E} (10^8 N m^{-2})	-0.5179	-0.0603	0.1198	-0.0385	0.0347	0.0006
$V_{\mathrm{f}}^{\mathrm{E}}$ (10^{-6} m^3 mol^{-1})	0.9617	0.3141	-0.2806	0.0153	-0.0435	0.0015
G^{E} (kJ mol^{-1})	2.4794	1.4536	-1.0351	0.1251	-0.3062	0.0068
H^{E} (kJ mol^{-1})	2.8317	1.5295	-1.1272	0.1418	-0.3263	0.0073
S^{E} (kJ mol^{-1} K^{-1})	0.3524	0.0761	-0.0928	0.0157	-0.0199	0.0005
Methyl acrylate+1-octanol						
π_i^{E} (10^8 N m^{-2})	-0.8046	-0.0142	0.2400	-0.1481	-0.0315	0.0005
$V_{\mathrm{f}}^{\mathrm{E}}$ (10^{-6} m^3 mol^{-1})	1.6509	0.2782	-0.6348	0.2303	0.1597	0.0012
G^{E} (kJ mol^{-1})	4.8509	2.7329	-2.9110	0.9735	1.0509	0.0056
H^{E} (kJ mol^{-1})	5.4244	2.7849	-3.1068	1.0692	1.0892	0.0060
S^{E} (kJ mol^{-1} K^{-1})	0.5735	0.0522	-0.1958	0.0937	0.0368	0.0004
Methyl acrylate+1-decanol						
π_i^{E} (10^8 N m^{-2})	-1.1362	0.1553	0.2261	-0.3374	0.1079	0.0016
$V_{\mathrm{f}}^{\mathrm{E}}$ (10^{-6} m^3 mol^{-1})	2.4624	0.0704	-0.8478	0.6446	0.0279	0.0037
G^{E} (kJ mol^{-1})	7.7523	3.3657	-3.9935	3.2007	0.6488	0.0233
H^{E} (kJ mol^{-1})	8.5840	3.3189	-4.2202	3.4354	0.6127	0.0246
S^{E} (kJ mol^{-1} K^{-1})	0.8317	-0.0467	-0.2264	0.2352	-0.0362	0.0012

The pressure derivative is related to ultrasonic speed through following relationship,

$$\gamma\left(\frac{dp}{d\rho}\right)_{\mathrm{T}} = u^2 \qquad \ldots (13)$$

where ρ is molecular density and γ is the ratio of specific heats. Relating Eq. (12) and (13) we get[25] Eq. (14).

$$\frac{Mu^2}{\Upsilon RT} = \frac{1}{\left(1-V\rho_{\mathrm{N}}\right)^2} + 2AB\frac{\rho_{\mathrm{N}}}{\left(1-V\rho_{\mathrm{N}}\right)^3} + B^2C\frac{\rho_{\mathrm{N}}^2}{\left(1-V\rho_{\mathrm{N}}\right)^4} \qquad \ldots (14)$$

Equation (14) is used to evaluate the ultrasonic speed in binary mixtures theoretically. For pure liquids, Eq. (14) is modified by introducing dimensionless shape parameters, $X=RS/V_H$ and $\eta= V_{\mathrm{H.}}\,\rho_{\mathrm{N}}$.

Table 3—Values of η for all the seven shapes for methyl acrylate and 1-alkanols calculated from Eq. (16)

Shape	Methyl acrylate	1-Butanol	1-Hexanol	1-Octanol	1-Decanol
Sphere	0.8863	0.8851	0.8965	0.9042	0.9095
Cube	0.8631	0.8616	0.8752	0.8843	0.8906
Tetrahedron	0.8360	0.8343	0.8502	0.8610	0.8685
Disc A	0.8682	0.8668	0.8798	0.8886	0.8948
Disc B	0.8178	0.8160	0.8334	0.8453	0.8535
Disc C	0.8505	0.8489	0.8636	0.8734	0.8803
Disc D	0.7483	0.7458	0.7688	0.7845	0.7955

$$\frac{Mu^2}{\gamma RT} = \frac{\left[1+(X-1)\eta\right]^2}{(1-\eta)^4} \quad \ldots (15)$$

Its solution is obtained as follows,

$$\eta = K - \sqrt{K^2 + L - 1} \quad \ldots (16)$$

where $K = 1+L(X\text{-}1)/2$ and $L = \sqrt{\gamma RT / Mu^2}$. The values of η are given in Table 3. The mean radius and surface area of a molecule can be written as

$$R = YV^{1/3} \text{ and } S = ZR^2 \quad \ldots (17)$$

where Y and Z are the parameters related to shape of the molecule. The values of X, Y and Z have been calculated for different shapes and are listed in Table S3 (Supplementary Data).

The deviations of calculated ultrasonic speed obtained using SPT from the experimental speeds for these systems at all mole fractions for various shape combinations of constituent molecules are calculated by using the equation[39]

$$du = \frac{\left(u_{\text{calc}} - u_{\text{expt}}\right)}{u_{\text{expt}}} \quad \ldots (18)$$

where u_{calc} is the theoretically calculated ultrasonic speed and u_{expt} is the experimental speed. The absolute values of deviations are summed up for all the mole fractions for a particular binary mixture giving Σdu. The theoretically calculated ultrasonic speeds for the binary mixture of methyl acrylate (as tetrahedron) with 1-alkanols (as sphere/cube/tetrahedron/disc A/disc B/disc C/disc D) at 298.15 K using scaled particle theory are given in Table 4. The theoretically calculated ultrasonic speeds for the binary mixture of methyl acrylate (as sphere/cube/disc A/disc B/disc C/disc D) with 1-alkanols (sphere/cube/tetrahedron/disc A/ disc B/disc C/disc D) at 298.15 K using scaled particle theory are given in Tables S4–S9 (Supplementary Data).

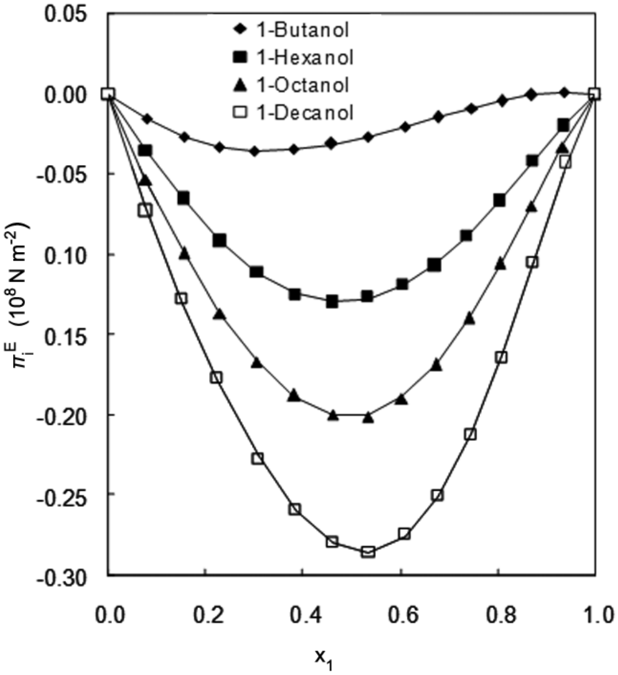

Fig. 1—Variation of excess internal pressure, π_i^E with mole fraction, x_1 of methyl acrylate for the methyl acrylate+1-alkanol binary mixtures at 298.15 K. The points show experimental values and curves show smoothed values using Eq. (10).

Results and Discussion

The results shown in Fig. 1 indicate that the π_i^E values are negative over entire mole fraction range and at all temperatures investigated for each binary system under study, except for methyl acrylate+1-butanol, which exhibit a sigmoid trend, with negative π_i^E value at lower methyl acrylate concentration and then become positive as the concentration of methyl acrylate increases in the mixture. The magnitude of π_i^E values follows the sequence: 1-butanol > 1-hexanol > 1-octanol > 1-decanol. As stated earlier, the molecules of 1-alkanols are associated through hydrogen bonding in pure state[31]. Mixing of methyl acrylate with 1-alkanols would induce mutual dissociation of the

Table 4—Ultrasonic speeds for methyl acrylate+1-alkanol binary mixtures assuming methyl acrylate acquiring tetrahedron shape and 1-alkanols acquiring seven different shapes computed using SPT along sum deviation (*Σdu*) at 298.15 K

x_1	u_{expt} (m s^{-1})	u_{calc} (m s^{-1})						
		Tetra+ sph	Tetra+ cube	Tetra+ tetra	Tetra+ disc A	Tetra+ disc B	Tetra+ disc C	Tetra+ disc D
Methyl acrylate+1-butanol								
0.0000	1242.6	1242.6	1242.6	1242.2	1243.0	1243.0	1243.0	1243.2
0.0777	1230.5	1246.8	1239.9	1236.9	1241.9	1238.7	1239.7	1241.4
0.1555	1220.1	1248.3	1236.7	1231.7	1239.9	1234.3	1236.1	1239.4
0.2273	1212.2	1247.9	1233.4	1227.0	1237.3	1230.2	1232.5	1237.4
0.2990	1205.9	1245.9	1229.8	1222.5	1234.2	1226.1	1228.7	1235.2
0.3791	1200.2	1242.2	1225.4	1217.5	1230.0	1221.5	1224.2	1232.4
0.4593	1195.7	1237.2	1220.7	1212.7	1225.3	1216.9	1219.5	1229.2
0.5344	1192.4	1231.6	1216.0	1208.3	1220.4	1212.4	1214.9	1225.6
0.6095	1189.9	1225.1	1211.2	1204.0	1215.1	1208.0	1210.1	1221.5
0.6789	1188.2	1218.5	1206.5	1200.1	1210.0	1203.7	1205.6	1216.9
0.7483	1186.9	1211.5	1201.7	1196.3	1204.5	1199.5	1200.9	1211.6
0.8099	1186.0	1204.9	1197.3	1193.0	1199.5	1195.6	1196.7	1206.2
0.8715	1185.3	1198.1	1192.8	1189.7	1194.4	1191.6	1192.4	1199.8
0.9358	1184.5	1190.7	1188.0	1186.4	1188.8	1187.5	1187.8	1192.2
1.0000	1183.6	1183.2	1183.2	1183.2	1183.2	1183.2	1183.2	1183.2
	*Σ*d*u*	0.3098	0.1850	**0.1243**	0.2205	0.1577	0.1767	0.2610
Methyl acrylate+1-hexanol								
0.0000	1306.9	1306.9	1306.9	1306.4	1307.3	1307.4	1307.3	1307.5
0.0770	1290.5	1306.9	1301.0	1298.5	1302.8	1300.4	1301.0	1303.0
0.1542	1275.3	1305.0	1294.5	1290.3	1297.5	1293.0	1294.2	1298.2
0.2299	1260.7	1301.2	1287.6	1282.0	1291.4	1285.5	1287.1	1293.1
0.3057	1247.4	1295.7	1280.1	1273.5	1284.4	1277.6	1279.4	1287.4
0.3834	1235.1	1288.5	1271.8	1264.6	1276.4	1269.1	1271.0	1281.0
0.4612	1224.5	1279.7	1262.9	1255.3	1267.6	1260.1	1262.0	1273.8
0.5340	1215.9	1270.2	1253.9	1246.4	1258.5	1251.3	1253.1	1266.3
0.6068	1208.2	1259.4	1244.4	1237.3	1248.7	1242.1	1243.6	1257.9
0.6720	1202.2	1248.8	1235.5	1228.9	1239.3	1233.5	1234.7	1249.3
0.7370	1197.5	1237.4	1226.0	1220.3	1229.4	1224.5	1225.4	1239.7
0.8046	1193.4	1224.6	1215.8	1211.1	1218.4	1214.6	1215.3	1228.2
0.8722	1189.8	1211.1	1205.0	1201.7	1206.8	1204.3	1204.7	1214.9
0.9361	1186.7	1197.5	1194.3	1192.5	1195.3	1194.0	1194.1	1200.3
1.0000	1183.6	1183.2	1183.2	1183.2	1183.2	1183.2	1183.2	1183.2
	*Σ*d*u*	0.4077	0.2829	**0.2257**	0.3188	0.2644	0.2773	0.3827
Methyl acrylate+1-octanol								
0.0000	1352.4	1352.4	1352.4	1351.9	1352.8	1352.9	1352.9	1353.0
0.0770	1331.5	1350.6	1345.2	1342.9	1346.9	1344.8	1345.3	1347.3
0.1554	1311.5	1346.9	1337.2	1333.3	1339.9	1336.0	1337.0	1341.0
0.2304	1293.4	1341.6	1328.7	1323.5	1332.3	1327.0	1328.3	1334.4
0.3053	1276.0	1334.7	1319.5	1313.3	1323.7	1317.4	1318.9	1327.1

(*Contd.*)

Table 4—Ultrasonic speeds for methyl acrylate+1-alkanol binary mixtures assuming methyl acrylate acquiring tetrahedron shape and 1-alkanols acquiring seven different shapes computed using SPT along sum deviation (Σdu) at 298.15 K (*Contd.*)

x_1	u_{expt} (m s^{-1})	u_{calc} (m s^{-1})						
		Tetra+ sph	Tetra+ cube	Tetra+ tetra	Tetra+ disc A	Tetra+ disc B	Tetra+ disc C	Tetra+ disc D
Methyl acrylate+1-octanol								
0.3830	1159.7	1325.6	1309.0	1302.1	1313.6	1306.7	1308.3	1318.6
0.4603	1244.7	1314.8	1297.6	1290.2	1302.4	1295.2	1296.9	1309.2
0.5321	1232.1	1303.0	1286.1	1278.6	1290.9	1283.8	1285.3	1299.3
0.6038	1221.6	1289.5	1273.6	1266.3	1278.2	1271.5	1272.9	1288.1
0.6742	1212.9	1274.7	1260.3	1253.5	1264.5	1258.6	1259.7	1275.7
0.7410	1205.4	1259.0	1246.7	1240.6	1250.3	1245.3	1246.1	1262.1
0.8052	1199.4	1242.5	1232.6	1227.6	1235.5	1231.6	1232.2	1247.0
0.8698	1193.7	1224.4	1217.4	1213.7	1219.5	1216.8	1217.1	1229.4
0.9350	1188.3	1204.5	1200.9	1198.9	1202.0	1200.6	1200.7	1208.4
1.0000	1183.6	1183.2	1183.2	1183.2	1183.2	1183.2	1183.2	1183.2
	Σdu	0.6081	0.4807	**0.4239**	0.5175	0.4653	0.4761	0.5903
Methyl acrylate+1-octanol								
0.0000	1377.3	1377.3	1377.3	1376.8	1377.7	1377.8	1377.8	1377.9
0.0762	1352.1	1375.3	1370.3	1368.1	1371.9	1369.8	1370.4	1372.1
0.1523	1330.6	1371.7	1362.5	1358.7	1365.1	1361.2	1362.3	1365.6
0.2225	1310.1	1366.9	1354.6	1349.5	1358.0	1352.7	1354.1	1359.1
0.3073	1286.5	1359.1	1343.9	1337.6	1348.1	1341.4	1343.2	1350.2
0.3848	1267.0	1349.9	1332.9	1325.7	1337.6	1330.1	1332.1	1341.1
0.4622	1248.9	1338.5	1320.7	1312.9	1325.6	1317.7	1319.7	1330.7
0.5356	1233.0	1325.6	1307.8	1299.7	1312.7	1304.8	1306.8	1319.5
0.6092	1219.8	1310.4	1293.3	1285.4	1298.2	1290.6	1292.4	1306.6
0.6768	1209.4	1294.3	1278.6	1271.1	1283.1	1276.2	1277.8	1293.0
0.7443	1200.6	1276.0	1262.4	1255.6	1266.3	1260.4	1261.7	1277.2
0.8089	1193.9	1256.2	1245.2	1239.6	1248.5	1243.7	1244.6	1259.4
0.8736	1189.2	1234.1	1226.3	1222.1	1228.6	1225.3	1225.8	1238.3
0.9412	1185.6	1208.2	1204.3	1202.1	1205.5	1203.9	1204.1	1211.6
1.0000	1183.6	1183.2	1183.2	1183.2	1183.2	1183.2	1183.2	1183.2
	Σdu	0.6766	0.5454	**0.4857**	0.5830	0.5258	0.5395	0.6456

hydrogen-bonded structures present in pure alkanols with subsequent formation of (new) H-bonds (C=O·······HO and O·······HO) between oxygen atoms of methyl acrylate and hydrogen atom of hydroxyl group of 1-alkanol molecules, leading to contraction in volume of the mixture. The observed positive π_i^E values for methyl acrylate+1-butanol mixtures (Fig. 1) in methyl acrylate rich region, can be considered due to formation of hydrogen bonding between methyl acrylate and 1-butanol molecules that leads to more closer packing of molecules resulting in a contraction in volume of the mixture, leading to an increase in the internal pressure of the mixture, hence, positive π_i^E values. The negative π_i^E values for methyl acrylate+1-hexanol/1-octanol/1-decanol mixtures indicate weak interactions between methyl acrylate and 1-hexanol/1-octanol/1-decanol molecules.

Figure 2 indicates that V_f^E values are positive for each binary system under study, except for methyl acrylate+1-butanol, which exhibit a sigmoid trend, with positive V_f^E value at lower methyl acrylate concentration and then become negative as the

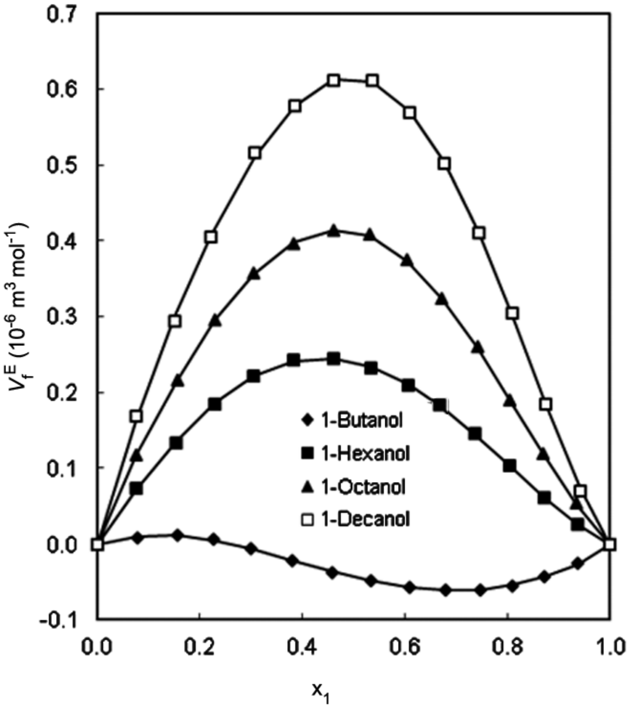

Fig. 2—Variation of excess free volume, V_f^E with mole fraction, x_1 of methyl acrylate for methyl acrylate+1-alkanol binary mixtures at 298.15 K. The points show experimental values and curves show smoothed values using Eq. (10).

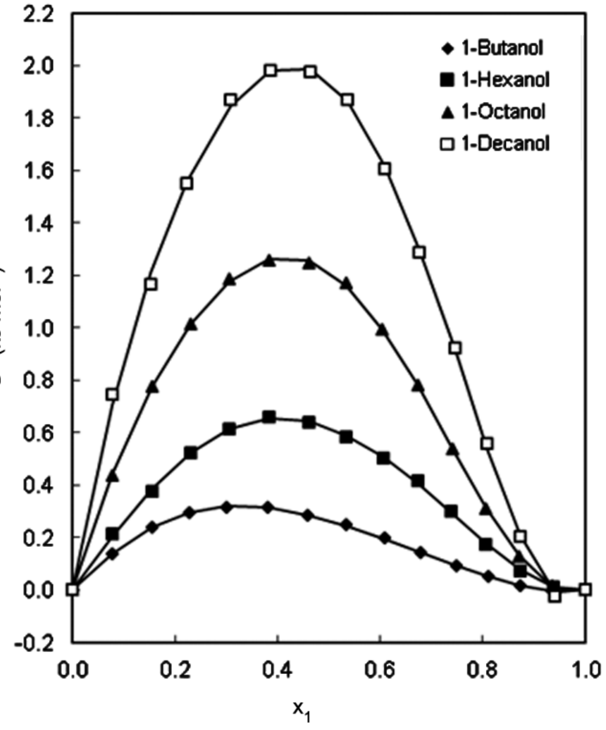

Fig. 3—Variation of excess free energy, G^E with mole fraction, x_1 of methyl acrylate for the methyl acrylate+1-alkanol binary mixtures at 298.15 K. The points show experimental values and curves show smoothed values using Eq. (10).

concentration of methyl acrylate increases in the mixture. The magnitude of V_f^E values follows the sequence: 1-butanol < 1-hexanol < 1-octanol < 1-decanol. The observed trends in V_f^E value indicate specific interactions in methyl acrylate+1-butanol, and weak interactions in methyl acrylate+1-hexanol/1-octanol/1-decanol mixtures. The observed negative V_f^E values for methyl acrylate+1-butanol mixtures (Fig. 2) in methyl acrylate rich region, can be considered due to formation of hydrogen bonding between methyl acrylate and 1-butanol molecules that leads to more closer packing of molecules resulting in a contraction in volume of the mixture, and hence, decreasing the free volume of the mixture leading to negative V_f^E values. But opposite to our expectation, the positive trends are observed in V_f^E values for methyl acrylate+1-hexanol/1-octanol/1-decanol mixtures (Fig. 2) over whole composition range. It has been repotred[31] that hydrogen bonding in 1-alkanols decrease considerably with increase in alkyl chain length in alkanol molecules. This leads to the formation of loosely packed hydrogen bonded aggregates between unlike molecules in methyl acrylate+1-hexanol/1-octanol/1-decanol mixtures as compared to those in methyl acrylate+1-butanol mixtures, which results in an expansion in volume, i.e., increase in the free volume of the mixture leading to positive V_f^E values. The trends observed in π_i^E and V_f^E values indicate that the order of interactions between methyl acrylate and 1-alkanol molecules in these binary mixtures follows the order: 1-butanol > 1-hexanol > 1-octanol > 1-decanol, which is in agreement with the results reported in our earlier work[26,27]. Another factor that would contribute to positive V_f^E values is the steric hindrance due to increase in size of alkyl group in 1-alkanols. As the number of methyl group in the alkyl chain increases from 1-butanol to 1-decanol, the closer approach of methyl acrylate and 1-alkanol molecules becomes increasingly difficult, resulting in decreased interaction between unlike molecules, resulting in positive V_f^E values.

The values of G^E and H^E (Figs 3 and 4) values are positive for all the four binary mixtures over the entire

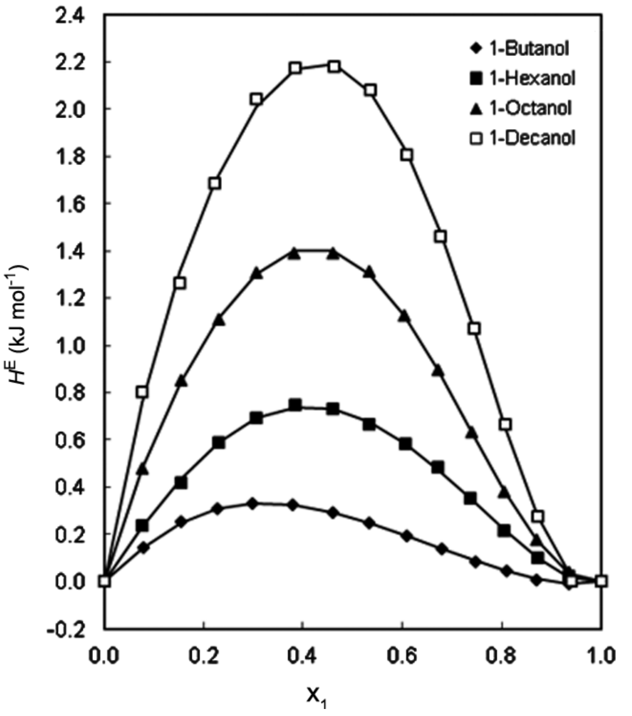

Fig. 4—Variation of excess enthalpy, H^E with mole fraction, x_1 of of methyl acrylate the methyl acrylate+1-alkanol binary mixtures at 298.15 K. The points show experimental values and curves show smoothed values using Eq. (10).

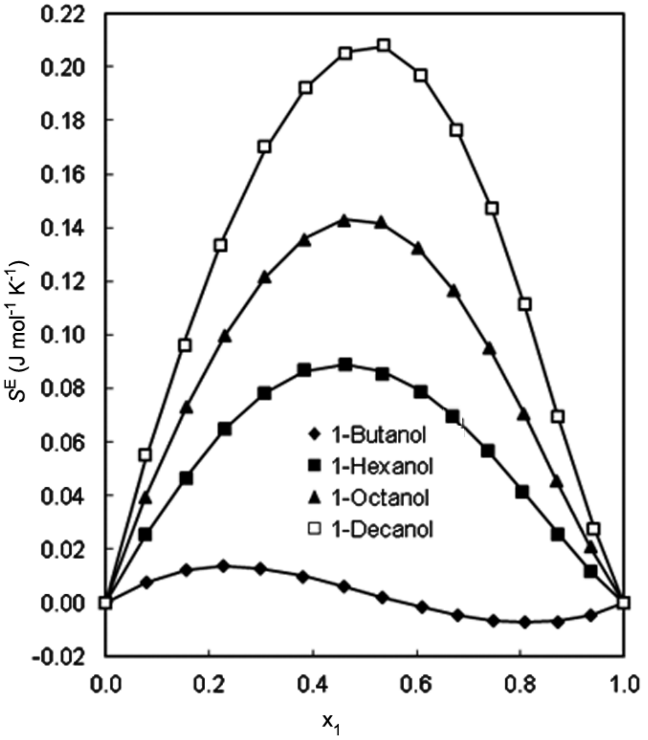

Fig. 5—Variation of excess entropy, S^E with mole fraction, x_1 of of methyl acrylate the methyl acrylate+1-alkanol binary mixtures at 298.15 K. The points show experimental values and curves show smoothed values using Eq. (10).

mole fraction range, except for small negative values for methyl acrylate+1-butanol mixture at higher methyl acrylate mole fractions (x_1 > 0.9). The magnitude of G^E and H^E values for these mixtures follow the sequence: 1-butanol < 1-hexanol < 1-octanol < 1-decanol, which in turn indicate the order of interactions in these mixtures. The S^E values are positive for methyl acrylate+1-hexanol/1-octanol/1-decanol mixtures over the entire mole fraction range (Fig. 5); and for methyl acrylate+1-butanol mixture exhibits a sigmoid trend, with positive S^E value at lower methyl acrylate concentration and then become negative as the concentration of methyl acrylate increases in the mixture (Fig. 5). The negative S^E values for methyl acrylate+1-butanol mixture at higher methyl acrylate concentration further support the conclusion drawn from are in agreement that π_i^E and V_f^E values; that formation of hydrogen bonding between methyl acrylate and 1-butanol molecules that leads to more ordered packing of molecules, resulting in a decrease in entropy of the mixture, resulting in negative S^E values. The S^E values for these mixtures follow the order: 1-butanol < 1-hexanol < 1-octanol < 1-decanol, which indicate that the order of interactions in these mixtures follows the sequence: 1-butanol > 1-hexanol > 1-octanol > 1-decanol.

In the systems under investigation, no complex formation has been reported so scaled particle theory can be applied to these systems. A close perusal of Table 4 and Tables S4-S9 reveals that the deviations between experimental and theoretically calculated values of u are lowest for each system studied, when methyl acrylate is assigned tetrahedron shape in solution. This suggests that methyl acrylate molecules may acquire tetrahedron shape in the mixtures. For tetrahedron shape of methyl acrylate, the minimum deviations are observed when 1-alkanols (1-butanol, 1-hexanol, 1-octanol, 1-decanol) are also assigned tetrahedron shapes (Table 4). Thus, for all the four binary systems studied, tetrahedron+tetrahedron the combinations of shape for methyl acrylate+1-alkanol molecules exhibits minimum deviations in u calculated from scaled particle theory.

It is also observed from Table 7 that the magnitude of the deviations (Σdu) in these methyl acrylate+1-alkanol mixtures follows the order: 1-butanol < 1-hexanol < 1-octanol < 1-decanol. This is in accordance with the order of free volumes for these mixtures. With increasing alkyl chain length of 1-alknaols, steric hindrance increases, making it difficult for tetrahedron methyl acrylate molecules to closely approach the tetrahedron alkanol molecules. Also, it becomes more difficult for alkanol molecules to maintain their tetrahedron shape due to increase in alkyl chain length. Thus, the tendency of alkanols to retain tetrahedron shape becomes difficult on moving from 1-butanol to 1-decanol, which results in the increased sum deviations in the order: 1-butanol < 1-hexanol < 1-octanol < 1-decanol.

Conclusions

The regular solution theory has been used to estimate various excess thermodynamic parameters and theoretical ultrasonic speeds, respectively, of methyl acrylate+1-alkanaol (C_4–C_{10}) binary mixtures by using the density and ultrasonic speed data. The variations of excess thermodynamic parameters with compositions indicate the presence of weak interactions between methyl acrylate and 1-hexanol/ 1-octanol/1-decanol molecules, and these interactions follow the order: follows the order: 1-butanol > 1-hexanol > 1-octanol > 1-decanol. The scaled particle theory has been used to predict the ultrasonic speeds for these mixtures theoretically by assigning various possible shapes to component molecules. The comparison results with experimental values indicate that the scaled particle theory predicts the ultrasonic speeds reasonably well.

Supplementary Data

Supplementary data associated with this article, viz., Tables S1–S9, are available in the electronic form at http://www.niscair.res.in/jinfo/ijca/IJCA_55A(01)23-33_SupplData.pdf.

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