THERMODYNAMIC INTERACTIONS IN BINARY MIXTURES OF 2-METHOXYETHANOL WITH ALKYL AND ARYL ESTERS AT 298.15, 303.15 AND 308.15 K

Tejraj M. AMINABHAVI and Shrinivas K. RAIKAR

Department of Chemistry,
Karnatak University, Dharwad 580 003, India

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Dedicated to Professor Petr Munk, University of Texas, Austin, U.S.A. on the occasion of his 60th birthday.

Densities, viscosities, refractive indices, and sound velocities of 2-methoxyethanol + ester mixtures have been measured at 298.15, 303.15 and 308.15 K. These data have been used to calculate excess volume, excess isentropic compressibility, excess refraction, excess viscosity and excess Gibbs energy of activation of flow. These quantities have been fitted to quadratic equations to estimate the parameters and standard errors. The results have been interpreted in terms of the intermolecular interactions between the mixing components.

2-Methoxyethanol, commonly called as methyl cellosolve (designated as CS) is a widely used industrial solvent in view of its solvating properties and quasi-aprotic character[1]. It is an ether alcohol showing physico-chemical characteristics that are intermediate between protic and dipolar aprotic solvents. In view of this, it has attracted much attention as a solvent medium in electrochemical research[2-4]. Some studies on excess thermodynamic properties of binary mixtures containing 2-methoxyethanol have also been reported[5-7]. However, experimental data on thermodynamic, acoustic, optical and hydrodynamic properties of binary mixtures of 2-methoxyethanol with alkyl or aryl esters are not available. Such data are required in the understanding of interactions in mixtures in addition to engineering design areas such as distillation, separation and liquid–liquid extraction in petrochemical industries.

In view of this, in this paper, we present experimental data on densities ρ, viscosities η, refractive indices n_D and sound velocities u, of the binary mixtures of 2-methoxyethanol with methyl acetate, ethyl acetate, n-butyl acetate, methyl benzoate and ethyl benzoate at 298.15, 303.15 and 308.15 K over the whole composition of the mixture. From these properties, excess volume V^E, excess isentropic compressibility β^E, excess refraction R^E, excess viscosity η^E and excess Gibbs energy of activation of flow ΔG^{*E}

have been calculated. These properties are used to study the intermolecular interactions in binary mixtures.

EXPERIMENTAL

2-Methoxyethanol (Thomas Baker, Bombay), methyl acetate (Sisco Chemicals, Bombay), ethyl acetate (Glaxo Laboratories, Bombay), n-butyl acetate (S.D. fine, AR), methyl benzoate (Naarden, Holland) and ethyl benzoate (C.D.H, New Delhi have been double distilled and purified by the recommended procedures before use[8,9]. The purity of these solvents was ascertained by the constancy of their boiling temperatures during final distillation and also by comparing their densities and refractive indices at 298.15 K which agreed favorably with the literature (see Table I). Further purity of the solvents was ascertained by gas chromatography. All the solvents were pure up to 99+ mole %.

Mixtures were prepared by mixing the appropriate volumes of liquids in specially designed ground glass stoppered ampules and weighed in a single-pan Mettler balance (Switzerland) to an accuracy of ±0.05 mg. Preferential evaporation losses of the solvents from the mixtures were kept to minimum as evidenced by a repeated measurement of the physical properties over an interval of 2 – 3 days during which time no changes in the physical properties were observed. The possible error in the mole fractions is estimated to be around 0.0001.

Densities ρ, of pure liquids and their binary mixtures in the composition range 0.1 – 0.9 at an increment of 0.1 molar fraction were measured by using a pycnometer having a bulb volume of about 10 cm^3 and a capillary with an internal diameter of 1 mm. For each measurement, sufficient time was allowed to attain thermal equilibrium in a INSREF (Model 016 AP) precision thermostat, the bath temperature of which was monitored to ±0.01 K with a calibrated thermometer. The fluctuations in bath temperature did not exceed ±0.1 K and evaporation losses remained insignificant during the time of actual measurement. The reported densities at 298.15, 303.15 and 308.15 K are considered significant to four figures. An average of triplicate measurements was taken into account and these were reproducible within ±0.5%.

TABLE I
Comparison of literature data (refs[8,9]) for pure solvents at 298.15 K

Solvent	ρ, g cm^{-3}		η, mPa s		n_D	
	Lit.	Obs.	Lit.	Obs.	Lit.	Obs.
2-Methoxyethanol	0.9602	0.9599	1.600	1.722	1.4002	1.3997
Methyl acetate	0.9279	0.9257	0.364	0.388	1.3589	1.3580
Ethyl acetate	0.8946	0.8941	0.426	0.433	1.3698	1.3702
n-Butyl acetate	0.8764	0.8758	0.688	0.673	1.3918	1.3909
Methyl benzoate	1.0790[a]	1.0788[a]	1.673[a]	1.656[a]	1.5146	1.5149
Ethyl benzoate	1.0372[a]	1.0374[a]	1.751[a]	1.741[a]	1.5035	1.5031

[a] Compared at 303.15 K.

Viscosities were measured with Cannon Fenske viscometers (sizes 75 and 100) ASTM D 445, supplied by Industrial Research Glassware Ltd, NJ, U.S.A. An electronic stop watch with a precision of ±0.01 s was used for flow time measurements. Triplicate measurements of flow times were reproducible within ±0.02%. The kinematic viscosity, ν given by $\nu = \eta/\rho = A\,t - B/t$, where η is absolute viscosity, ρ is density, A and B are the viscometric constants and t is the efflux time. The term B/t is the kinetic energy correction and may usually be neglected if properly sized viscometer is used. In this case, the viscosity data can be readily obtained from the measurement of the efflux times. The coefficients A for several viscometers were provided by the manufacturer and checked at room temperature by measurement of the viscosity of pure water. Absolute viscosities η, in mPa s were then calculated by using the relation, $\eta = \nu\rho$. The estimated error in viscosity measurement is around ±0.2% or even less in some cases. Viscosities of pure components are of acceptable accuracy as evidenced by a comparison of the data given in Table I.

Refractive indices for the sodium-D line were measured with a thermostatted Abbe refractometer (Bellingham and Stanley Ltd., London) with an error of less than 0.0001 units. However, these data were approximated to the fourth places (see Table II). A thermostatically controlled bath, constant to ±0.01 K was used in these measurements. Calibration checks of the refractometer were done routinely with the help of a test glass piece of known refractive index provided with the instrument.

Ultrasonic velocities were measured by using a variable path single crystal interferometer (Mittal Enterprises, New Delhi, Model M-84). A crystal controlled high frequency generator was used to excite the transducer at a frequency of 1 MHz. The frequency was measured with an accuracy of 1 in 10^6 by using a digital frequency meter. The current variations across the transducer were observed on a micro ammeter. The interferometer cell was filled with the test liquid and was connected to the output terminal of the high frequency generator through a shielded cable. Water was then circulated around the measuring cell from a thermostat maintained at the desired temperature. The other experimental details are given earlier[10,11]. The isentropic compressibilities were calculated as: $\beta = 1/u^2\rho$. The average uncertainty in β is around ±0.01 per cent.

RESULTS AND DISCUSSION

The experimental results of density, viscosity, refractive index and ultrasonic velocity of binary mixtures at 298.15, 303.15 and 308.15 K measured for the entire composition of the mixtures are listed in Table II. Excess volume and excess viscosity are then calculated from the observed densities and viscosities by using the following equations

$$V^{\mathrm{E}} = V_{\mathrm{m}} - (x_1 V_1 + x_2 V_2) \qquad (1)$$

$$\eta^{\mathrm{E}} = \eta_{\mathrm{m}} - (x_1 \eta_1 + x_2 \eta_2)\,, \qquad (2)$$

where V, x, and η are the molar volume, molar fraction and dynamic viscosity. The subscripts 1, 2 and m, respectively, represent the properties of pure components and of the mixtures. The molar volume V_{m}, is computed from the measured density, ρ_{m} as

$$V_{\mathrm{m}} = (x_1 M_1 + x_2 M_2)/\rho_{\mathrm{m}}\,. \qquad (3)$$

TABLE II

Densities ρ, viscosities η, refractive indices n_D and sound velocities u of binary mixtures of 2-methoxyethanol with various co-solvents; x_1 is molar fraction of co-solvent in the mixture

x_1	ρ, g cm^{-3}	η, mPa s	n_D	u, m s^{-1}
	A. 2-Methoxyethanol (1) + methyl acetate (2)			
		298.15 K		
0.0000	0.9257	0.388	1.3580	1161
0.0993	0.9293	0.429	1.3625	1179
0.2004	0.9328	0.484	1.3671	1197
0.2993	0.9364	0.549	1.3715	1214
0.4009	0.9400	0.636	1.3754	1232
0.4996	0.9434	0.729	1.3796	1252
0.6014	0.9469	0.862	1.3838	1273
0.7013	0.9503	1.012	1.3880	1293
0.8006	0.9537	1.218	1.3920	1314
0.9001	0.9571	1.453	1.3961	1337
1.0000	0.9599	1.722	1.3997	1357
		303.15 K		
0.0000	0.9189	0.370	1.3554	1142
0.0993	0.9227	0.407	1.3602	1158
0.2004	0.9266	0.457	1.3650	1175
0.2993	0.9303	0.517	1.3697	1194
0.4009	0.9340	0.596	1.3734	1214
0.4996	0.9377	0.679	1.3777	1233
0.6014	0.9416	0.797	1.3821	1255
0.7013	0.9452	0.929	1.3862	1276
0.8006	0.9487	1.112	1.3903	1299
0.9001	0.9524	1.317	1.3943	1322
1.0000	0.9554	1.548	1.3971	1343
		308.15 K		
0.0000	0.9122	0.352	1.3528	1122
0.0993	0.9162	0.387	1.3575	1139
0.2004	0.9202	0.432	1.3627	1156
0.2993	0.9242	0.486	1.3680	1174
0.4009	0.9282	0.556	1.3719	1193
0.4996	0.9321	0.632	1.3758	1214
0.6014	0.9362	0.738	1.3799	1236
0.7013	0.9400	0.858	1.3839	1258
0.8006	0.9438	1.025	1.3880	1280
0.9001	0.9476	1.200	1.3920	1304
1.0000	0.9507	1.390	1.3949	1326

TABLE II
(*Continued*)

x_1	ρ, g cm^{-3}	η, mPa s	n_D	u, m s^{-1}
	B. 2-Methoxyethanol (1) + ethyl acetate (2)			
		298.15 K		
0.0000	0.8941	0.433	1.3702	1145
0.0974	0.8996	0.470	1.3717	1158
0.1945	0.9052	0.514	1.3736	1173
0.2964	0.9112	0.572	1.3766	1189
0.3997	0.9175	0.644	1.3795	1207
0.4973	0.9237	0.736	1.3826	1226
0.5922	0.9300	0.838	1.3861	1246
0.6956	0.9372	0.992	1.3891	1270
0.8008	0.9448	1.190	1.3926	1297
0.9012	0.9523	1.421	1.3960	1326
1.0000	0.9599	1.722	1.3997	1357
		303.15 K		
0.0000	0.8875	0.410	1.3671	1119
0.0974	0.8935	0.444	1.3692	1136
0.1945	0.8992	0.484	1.3707	1152
0.2964	0.9055	0.536	1.3741	1168
0.3997	0.9117	0.601	1.3772	1188
0.4973	0.9182	0.683	1.3808	1208
0.5922	0.9247	0.775	1.3842	1229
0.6956	0.9319	0.912	1.3872	1254
0.8008	0.9397	1.086	1.3907	1282
0.9012	0.9475	1.286	1.3940	1311
1.0000	0.9554	1.548	1.3971	1343
		308.15 K		
0.0000	0.8814	0.390	1.3643	1096
0.0974	0.8874	0.420	1.3668	1116
0.1945	0.8931	0.456	1.3690	1133
0.2964	0.8995	0.514	1.3717	1151
0.3997	0.9060	0.564	1.3759	1172
0.4973	0.9126	0.636	1.3788	1191
0.5922	0.9192	0.719	1.3822	1212
0.6956	0.9268	0.840	1.3853	1237
0.8008	0.9347	0.994	1.3887	1263
0.9012	0.9426	1.173	1.3922	1293
1.0000	0.9507	1.390	1.3949	1326

TABLE II
(*Continued*)

x_1	ρ, g cm^{-3}	η, mPa s	n_D	u, m s^{-1}
	C. 2-Methoxyethanol (1) + butyl acetate (2)			
		298.15 K		
0.0000	0.8758	0.673	1.3909	1195
0.0967	0.8806	0.703	1.3910	1201
0.1995	0.8861	0.736	1.3915	1209
0.2988	0.8920	0.787	1.3921	1218
0.3986	0.8986	0.841	1.3929	1228
0.4983	0.9059	0.922	1.3937	1241
0.6028	0.9145	1.010	1.3946	1258
0.6970	0.9233	1.130	1.3952	1274
0.7987	0.9340	1.285	1.3963	1295
0.9012	0.9464	1.480	1.3979	1322
1.0000	0.9599	1.722	1.3997	1357
		303.15 K		
0.0000	0.8704	0.630	1.3883	1178
0.0967	0.8753	0.656	1.3885	1184
0.1995	0.8809	0.686	1.3891	1192
0.2988	0.8868	0.731	1.3897	1201
0.3986	0.8933	0.780	1.3903	1211
0.4983	0.9008	0.849	1.3914	1223
0.6028	0.9094	0.928	1.3923	1240
0.6970	0.9183	1.034	1.3933	1258
0.7987	0.9292	1.170	1.3944	1281
0.9012	0.9416	1.340	1.3961	1309
1.0000	0.9554	1.548	1.3971	1343
		308.15 K		
0.0000	0.8652	0.592	1.3859	1158
0.0967	0.8700	0.615	1.3862	1163
0.1995	0.8756	0.641	1.3870	1171
0.2988	0.8815	0.680	1.3872	1180
0.3986	0.8881	0.723	1.3882	1190
0.4983	0.8956	0.785	1.3889	1204
0.6028	0.9043	0.855	1.3901	1220
0.6970	0.9133	0.948	1.3913	1238
0.7987	0.9242	1.066	1.3924	1261
0.9012	0.9368	1.217	1.3942	1288
1.0000	0.9507	1.390	1.3949	1326

TABLE II
(*Continued*)

x_1	ρ, g cm^{-3}	η, mPa s	n_D	u, m s^{-1}
	D. 2-Methoxyethanol (1) + methyl benzoate (2)			
		298.15 K		
0.0000	1.0836	1.825	1.5149	1406
0.0991	1.0754	1.735	1.5050	1403
0.2001	1.0662	1.689	1.4970	1400
0.3023	1.0564	1.686	1.4878	1394
0.3992	1.0462	1.675	1.4788	1391
0.4989	1.0349	1.646	1.4689	1386
0.5981	1.0229	1.675	1.4581	1381
0.6990	1.0094	1.668	1.4460	1375
0.7991	0.9947	1.699	1.4321	1369
0.8983	0.9785	1.693	1.4173	1363
1.0000	0.9599	1.722	1.3997	1357
		303.15 K		
0.0000	1.0788	1.656	1.5127	1389
0.0991	1.0705	1.571	1.5026	1385
0.2001	1.0612	1.523	1.4945	1382
0.3023	1.0513	1.524	1.4856	1377
0.3992	1.0413	1.511	1.4769	1374
0.4989	1.0299	1.478	1.4669	1369
0.5981	1.0180	1.508	1.4559	1364
0.6990	1.0045	1.500	1.4439	1360
0.7991	0.9899	1.525	1.4298	1354
0.8983	0.9739	1.522	1.4162	1350
1.0000	0.9554	1.548	1.3971	1343
		308.15 K		
0.0000	1.0740	1.510	1.5096	1369
0.0991	1.0656	1.427	1.5003	1366
0.2001	1.0563	1.385	1.4926	1362
0.3023	1.0463	1.378	1.4834	1359
0.3992	1.0362	1.366	1.4745	1355
0.4989	1.0250	1.340	1.4652	1351
0.5981	1.0131	1.362	1.4538	1346
0.6990	0.9997	1.356	1.4421	1342
0.7991	0.9851	1.375	1.4278	1336
0.8983	0.9691	1.372	1.4145	1332
1.0000	0.9507	1.390	1.3949	1326

TABLE II
(*Continued*)

x_1	ρ, g cm^{-3}	η, mPa s	n_D	u, m s^{-1}
	E. 2-Methoxyethanol (1) + ethyl benzoate (2)			
		298.15 K		
0.0000	1.0421	1.932	1.5031	1374
0.1045	1.0364	1.883	1.4959	1370
0.1990	1.0310	1.824	1.4896	1368
0.2979	1.0251	1.803	1.4825	1363
0.4016	1.0184	1.757	1.4742	1362
0.5007	1.0113	1.774	1.4651	1360
0.6025	1.0033	1.752	1.4552	1360
0.6973	0.9951	1.773	1.4450	1358
0.7982	0.9851	1.761	1.4322	1358
0.8977	0.9739	1.783	1.4174	1358
1.0000	0.9599	1.722	1.3997	1357
		303.15 K		
0.0000	1.0374	1.741	1.5007	1355
0.1045	1.0316	1.703	1.4937	1352
0.1990	1.0262	1.650	1.4873	1350
0.2979	1.0202	1.631	1.4802	1348
0.4016	1.0134	1.587	1.4719	1347
0.5007	1.0064	1.598	1.4632	1346
0.6025	0.9984	1.581	1.4535	1345
0.6973	0.9902	1.592	1.4428	1345
0.7982	0.9803	1.581	1.4302	1344
0.8977	0.9693	1.602	1.4156	1344
1.0000	0.9554	1.548	1.3971	1343
		308.15 K		
0.0000	1.0327	1.578	1.4984	1337
0.1045	1.0268	1.550	1.4914	1334
0.1990	1.0213	1.501	1.4848	1332
0.2979	1.0154	1.480	1.4781	1329
0.4016	1.0086	1.441	1.4699	1328
0.5007	1.0015	1.448	1.4610	1328
0.6025	0.9935	1.431	1.4516	1327
0.6973	0.9853	1.439	1.4408	1327
0.7982	0.9756	1.431	1.4280	1327
0.8977	0.9645	1.444	1.4134	1326
1.0000	0.9507	1.390	1.3949	1326

Excess Gibbs energy of activation of flow can be calculated from Eq. (*4*) based on the Eyring viscosity equation[12] as

$$\Delta G^{*E} = RT\,[\ln(\eta_m V_m) - \{x_1 \ln(\eta_1 V_1) + x_2 \ln(\eta_2 V_2)\}]\,. \qquad (4)$$

The excess isentropic compressibility β^E, for the mixtures is calculated based on volume fraction ϕ_i, instead of molar fraction.

Thus,

$$\beta^E = \beta_m - \beta_1\phi_1 - \beta_2\phi_2\,, \qquad (5)$$

where ϕ_i is defined as

$$\phi_i = x_i V_i / \sum_{i=1}^{2} (x_i V_i)\,. \qquad (6)$$

Excess molar refractions R^E, is similarly calculated as

$$R^E = R_m - R_1\phi_1 - R_2\phi_2\,. \qquad (7)$$

Here, the molar refractivity R_i, may be calculated from the conventional mixing rules of Lorentz–Lorenz and Eykman[13,14].

All the excess properties are correlated by a Redlich–Kister equation[15]

$$Y^E = C_1C_2 \sum_{i=0}^{3} a_i (C_2 - C_1)^i\,, \qquad (8)$$

where Y^E stands for V^E, η^E, ΔG^{*E}, β^E and R^E. The symbol C_i in Eq. (*8*) stands for either x_i or ϕ_i. The coefficients a_i, were determined from fitting Eq. (*8*) to the experimental data and the optimum values of a_i together with the average absolute deviations σ, of the calculated densities, dynamic viscosities, refractive indices and ultrasonic velocities are reported in Table III. The variations of excess properties with mole fractions at 298.15 K are shown in Figs 1 –3 and the values calculated from Eq. (8) are illustrated by the smooth curves.

The dependence of excess volume of the binary mixtures on mole fraction x_1 of 2-methoxyethanol at 298.15 K is shown in Fig. 1. It is observed that for mixtures of 2-methoxyethanol with methyl acetate or ethyl acetate, the values of V^E are negative over the whole range of mixture composition suggesting dipole–induced dipole specific interactions. 2-Methoxyethanol possesses a dipole moment μ = 2.04, while methyl and ethyl acetates possess μ = 1.72 and 1.82, respectively and hence, specific interactions are attributed to charge-induced dipole interactions. However, in case of 2-methoxyethanol + n-butyl acetate, methyl benzoate or ethyl benzoate, the positive V^E observed over the whole range of mixture composition suggest nonspecific dispersion type interactions. The increase in V^E for these mixtures may be the result of pronounced molar volume differences between the mixing components. For none of the mixtures studied

TABLE III
Correlation parameters and standard errors

Quantity	T, K	a_0	a_1	a_2	a_3	σ
		A. 2-Methoxyethanol + methyl acetate				
V^E, cm^3 mol^{-1}	298.15	−0.220	0.046	0.272	−0.319	0.003
	303.15	−0.249	0.101	0.189	−0.335	0.005
	308.15	−0.303	0.100	0.338	−0.496	0.006
β^E, TPa^{-1}	298.15	−32.77	−0.49	7.72	−57.89	0.520
	303.15	−29.98	11.48	17.49	−18.89	0.290
	308.15	−29.41	21.38	−4.38	−43.69	0.570
$R^E_{(L-L)}$, cm^3 mol^{-1}	298.15	0.149	0.084	−0.097	0.156	0.007
	303.15	0.282	0.092	−0.331	0.478	0.010
	308.15	0.374	0.393	−0.827	0.089	0.009
$R^E_{(Eyk)}$, cm^3 mol^{-1}	298.15	0.315	0.191	−0.237	0.376	0.017
	303.15	0.624	0.205	−0.784	1.128	0.024
	308.15	0.839	0.902	−1.934	0.228	0.021
η^E, mPa s	298.15	−1.297	0.467	0.034	−0.269	0.004
	303.15	−1.114	0.396	0.040	−0.276	0.004
	308.15	−0.955	0.297	0.133	−0.305	0.004
ΔG^{*E}, kJ mol^{-1}	298.15	−1.084	−0.096	−0.593	0.420	0.011
	303.15	−1.044	−0.065	−0.705	0.374	0.011
	308.15	−0.995	−0.177	−0.734	0.692	0.013
		B. 2-Methoxyethanol + ethyl acetate				
V^E, cm^3 mol^{-1}	298.15	−0.196	−0.034	−0.055	−0.346	0.005
	303.15	−0.249	−0.095	−0.317	−0.599	0.007
	308.15	−0.234	−0.056	−0.372	−0.448	0.006
β^E, TPa^{-1}	298.15	−22.61	3.04	4.15	−22.95	0.200
	303.15	−49.15	4.94	−58.98	−57.55	0.440
	308.15	−77.29	−29.55	−46.59	−59.66	1.090
$R^E_{(L-L)}$, cm^3 mol^{-1}	298.15	−0.134	−0.324	−0.003	−0.758	0.012
	303.15	0.015	−0.427	−0.042	−0.725	0.020
	308.15	0.149	−0.208	−0.258	−0.349	0.019
$R^E_{(Eyk)}$, cm^3 mol^{-1}	298.15	−0.284	−0.755	0.000	−1.746	0.028
	303.15	0.065	−0.993	−0.083	−1.660	0.046
	308.15	0.377	−0.488	−0.588	−0.793	0.045
η^E, mPa s	298.15	−1.363	0.524	−0.150	0.075	0.003
	303.15	−1.181	0.433	−0.117	0.080	0.003
	308.15	−1.007	0.408	−0.046	−0.108	0.004
ΔG^{*E}, kJ mol^{-1}	298.15	−1.511	−0.049	0.092	0.205	0.008
	303.15	−1.477	−0.080	0.146	0.216	0.009
	308.15	−1.378	0.155	−0.501	0.252	0.020

TABLE III
(*Continued*)

Quantity	T, K	a_0	a_1	a_2	a_3	σ
			C. 2-Methoxyethanol + n-butyl acetate			
V^E, cm^3 mol^{-1}	298.15	0.598	−0.144	0.218	−0.136	0.003
	303.15	0.623	−0.102	−0.018	−0.302	0.006
	308.15	0.654	−0.052	0.007	−0.283	0.006
β^E, TPa^{-1}	298.15	13.38	8.38	−2.91	3.22	0.690
	303.15	18.30	20.98	−12.47	13.14	0.330
	308.15	21.86	23.38	−27.81	57.28	0.550
$R^E_{(L-L)}$, cm^3 mol^{-1}	298.15	−0.923	0.152	−0.486	−0.401	0.005
	303.15	−0.831	−0.043	−0.383	−0.018	0.006
	308.15	−0.809	−0.161	−0.144	0.187	0.009
$R^E_{(Eyk)}$, cm^3 mol^{-1}	298.15	−2.016	0.357	−1.140	0.934	0.011
	303.15	−1.799	−0.104	−0.892	−0.032	0.014
	308.15	−1.744	−0.382	−0.334	0.448	0.022
η^E, mPa s	298.15	−1.118	0.430	−0.116	0.007	0.004
	303.15	−0.969	0.371	−0.083	−0.027	0.003
	308.15	−0.834	0.298	−0.031	−0.045	0.003
ΔG^{*E}, kJ mol^{-1}	298.15	−1.234	0.089	−0.055	0.191	0.010
	303.15	−1.193	0.110	−0.151	0.188	0.009
	308.15	−1.144	0.052	−0.121	0.359	0.008
			D. 2-Methoxyethanol + methyl benzoate			
V^E, cm^3 mol^{-1}	298.15	0.368	0.069	0.000	−0.266	0.005
	303.15	0.470	0.136	−0.091	−0.363	0.006
	308.15	0.524	0.232	−0.172	−0.272	0.004
β^E, TPa^{-1}	298.15	−7.70	0.71	−5.87	−6.95	0.410
	303.15	−4.33	−1.25	16.91	−15.61	0.310
	308.15	−6.04	−3.41	18.20	−5.71	0.220
$R^E_{(L-L)}$, cm^3 mol^{-1}	298.15	−1.099	−0.213	−0.861	−1.535	0.019
	303.15	−1.041	0.053	−2.234	−0.953	0.022
	308.15	−0.869	0.099	−1.959	−0.167	0.028
$R^E_{(Eyk)}$, cm^3 mol^{-1}	298.15	−3.418	−0.627	−2.138	−3.831	0.046
	303.15	−3.279	0.013	−5.430	−2.483	0.054
	308.15	−2.855	0.123	−4.714	−0.563	0.069
η^E, mPa s	298.15	−0.433	−0.174	−0.248	−0.285	0.014
	303.15	−0.412	−0.152	−0.231	−0.278	0.014
	308.15	−0.378	−0.173	−0.204	−0.241	0.010
ΔG^{*E}, kJ mol^{-1}	298.15	−0.366	−0.284	−0.383	−0.685	0.018
	303.15	−0.404	−0.276	−0.423	−0.711	0.022
	308.15	−0.416	−0.341	−0.404	−0.686	0.017

TABLE III
(*Continued*)

Quantity	T, K	a_0	a_1	a_2	a_3	σ
			E. 2-Methoxyethanol + ethyl benzoate			
V^E, cm^3 mol^{-1}	298.15	0.717	0.314	0.441	−0.207	0.005
	303.15	0.831	0.328	0.527	−0.177	0.003
	308.15	0.896	0.321	0.638	−0.226	0.005
β^E, TPa^{-1}	298.15	18.86	23.60	−8.41	9.16	0.510
	303.15	12.55	13.17	13.90	16.39	0.358
	308.15	13.36	23.36	−13.08	17.98	0.418
$R^E_{(L-L)}$, cm^3 mol^{-1}	298.15	−1.785	−0.052	0.146	−0.641	0.010
	303.15	−1.663	−0.009	−0.196	−0.360	0.007
	308.15	−1.596	0.108	−0.358	−0.510	0.013
$R^E_{(Eyk)}$, cm^3 mol^{-1}	298.15	−4.995	−0.273	0.305	−1.622	0.025
	303.15	−4.695	−0.124	−0.673	−1.106	0.022
	308.15	−4.535	0.114	−0.904	−1.325	0.033
η^E, mPa s	298.15	−0.278	−0.300	0.375	−0.193	0.015
	303.15	−0.237	−0.229	0.353	−0.133	0.013
	308.15	−0.192	−0.206	0.377	−0.106	0.011
ΔG^{*E}, kJ mol^{-1}	298.15	0.114	−0.484	−0.260	1.072	0.018
	303.15	0.140	−0.427	−0.206	1.133	0.018
	308.15	0.192	−0.433	−0.194	1.325	0.016

here, the V^E plots show sharp maxima or minima. This may be indicative of the absence of stable molecular complexes in solution.

The effect of temperature on V^E shows a systenfatic effect in all cases (data not displayed graphically to avoid over crowding). In case of 2-methoxyethanol + methyl acetate mixture, the negative V^E results increase at equimolar composition from −0.051 cm^3 mol^{-1} at 298.15 K to −0.068 cm^3 mol^{-1} at 308.15 K. A similar effect is also observed in case of 2-methoxyethanol + ethyl acetate mixture. However, in case of 2-methoxyethanol + n-butyl acetate, the positive V^E results vary from 0.149 cm^3 mol^{-1} at 298.15 to 0.164 cm^3 mol^{-1} at 308.15 K. The same effect is also observed with mixtures of 2-methoxyethanol with methyl or ethyl benzoate. The positive V^E data for 2-methoxyethanol + methyl benzoate system are intermediate to those of n-butyl acetate and ethyl benzoate containing mixtures. For 2-methoxyethanol + ethyl benzoate mixture, equimolar V^E at 298.15 is 0.181 cm^3 mol^{-1}, but at 308.15 K it is 0.230 cm^3 mol^{-1}.

The dependence of excess isentropic compressibility on volume fraction of 2-methoxyethanol at 298.15 K is also included in Fig. 1. These results confirm the conclusions drawn for the excess molar volumes. It is found that β^E results are positive for mixtures of 2-methoxyethanol + ethyl benzoate or + butyl acetate; however, for other mixtures, β^E values are negative over the whole composition of the mixture. Since no sharp minima or maxima are observed with all the mixtures for the dependence of V^E or β^E suggesting that no stable molecular complexes are formed in solution. However, the temperature dependence of β^E results are not included in Fig. 1. It may be noted that with a rise in temperature, β^E results vary differently for different mixtures. For instance, with 2-methoxyethanol + methyl acetate or + n-butyl acetate, β^E tend to increase with a rise in temperature. A decreasing tendency was shown in case of 2-methoxyethanol + ethyl acetate. However, with mixtures of 2-methoxyethanol with methyl or ethyl benzoate, β^E values do not show any systematic dependence.

The results of excess molar refractions as calculated from the Lorentz–Lorenz, $R^E_{(L-L)}$ and Eykman, $R^E_{(Eyk)}$ relations are shown in Fig. 2. While the general trend in their behavior remains more or less identical for both $R^E_{(L-L)}$ and $R^E_{(Eyk)}$ over the whole of the mixture composition, larger negative and positive R^E values are exhibited for the Eykman relation than Lorentz–Lorenz rule. It may be further noted that the positive excess molar refraction are observed for mixtures of 2-methoxyethanol + methyl acetate or + ethyl acetate, and negative values for the remaining mixtures. This trend is

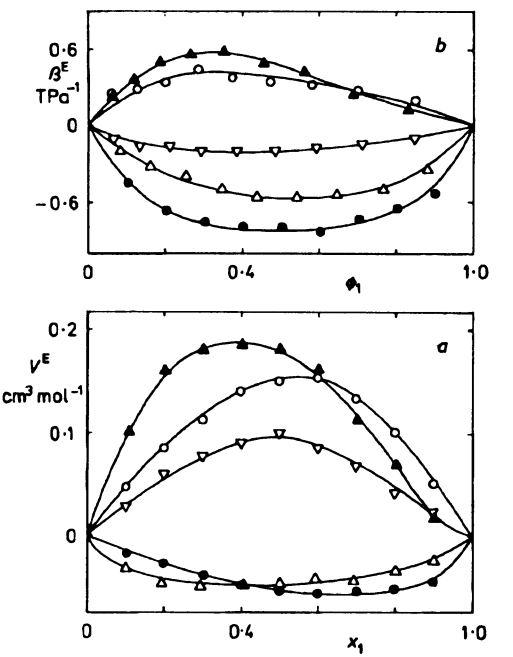

FIG. 1
Excess molar volumes (*a*) and excess isentropic compressibility (*b*) at 298.15 K. ● 2-methoxyethanol + methyl acetate; Δ 2-methoxyethanol + ethyl acetate; ○ 2-methoxyethanol + n-butyl acetate; ▽ 2-methoxyethanol + methyl benzoate; ▲ 2-methoxyethanol + ethyl benzoate; —— Redlich–Kister correlation

reverse to that for the property of excess molar volume shown in Fig. 1. The effect of temperature on R^E shows an increase with a rise in temperature suggesting increased molecular interactions at higher temperatures due to increased orbital mixing between the components.

From the results of viscosity, excess molar viscosity and excess molar Gibbs energy of activation have been calculated and their dependencies are displayed in Fig. 3. Such quantities have also been studied in the literature[16 - 18]. It is observed that both η^E and ΔG^{*E} values are negative for those mixtures for which dispersion interactions are operative. According to earlier published reports[19,20], positive values of ΔG^{*E} are observed in mixtures where specific interactions (hydrogen-bonding, dipole–dipole, etc.) among the mixing molecules are prevalent, whereas negative ΔG^{*E} values denote a characteristic behavior of liquid systems where dispersion forces are dominant[21]. This is indeed the case as evidenced by the negative values of η^E and ΔG^{*E} values for mixtures of 2-methoxyethanol with methyl acetate, ethyl acetate, n-butyl acetate or methyl benzoate. However, in case of 2-methoxyethanol + ethyl benzoate, we find that both η^E and ΔG^{*E} values show sign inversions at higher compositions of 2-methoxyethanol in the mixture. The effect of temperature on η^E is very systematic i.e., η^E values increase

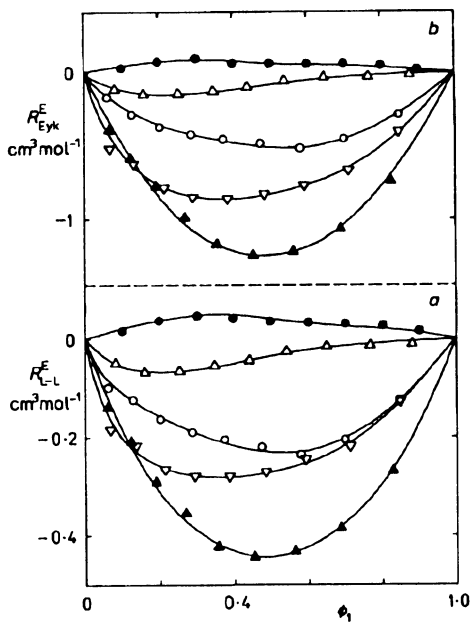

FIG. 2
Excess molar refractions from Lorentz–Lorenz (*a*) and Eykman (*b*) relations at 298.15 K. The symbols as in Fig. 1

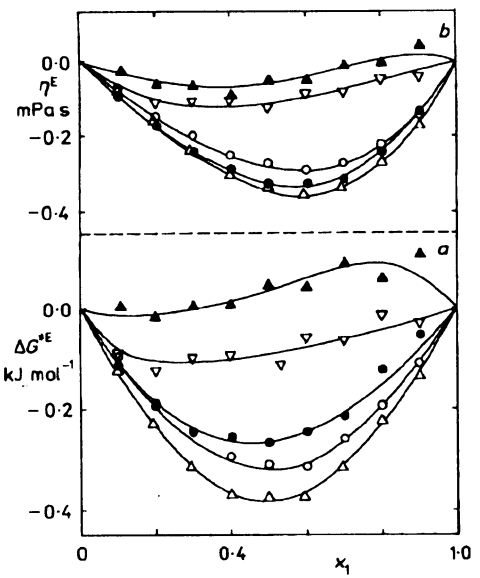

FIG. 3
Excess molar Gibbs energy of activation of flow (*a*) and excess viscosity (*b*) at 298.5 K. The same symbols as in Fig. 1

with a rise in temperature for all the mixtures. Similarly, ΔG^{*E} values also increase with temperature except for 2-methoxyethanol + methyl benzoate mixture; the latter shows a decrease in ΔG^{*E} with a rise in temperature.

It can be concluded, from the above results, that specific interactions are operative between 2-methoxyethanol and lower esters (methyl and ethyl acetate) whereas, higher esters show rather dispersive-type interactions in mixtures.

SYMBOLS

ρ	density, g cm^{-3}
η	absolute viscosity, mPa s
n_D	refractive index for sodium D-line
u	sound velocity, m s^{-1}
ν	kinematic viscosity
V^E	excess molar volume, cm^3 mol^{-1}
η^E	excess molar viscosity, mPa s
x	molar fraction
ϕ	volume fraction
V	molar volume of the liquid, cm^3 mol^{-1}
M	molecular weight
ΔG^{*E}	excess molar Gibbs energy of activation of flow, kJ mol^{-1}
R	gas constant
T	temperature in absolute
σ	standard deviation
R^E	excess molar refraction, cm^3 mol^{-1}
β^E	excess isentropic compressibility, TPa^{-1}
a	coefficients of Eq. (*8*)

Subscripts

1, 2	components of the mixture
i	i-th component of the mixture
m	mixture properties
E	excess

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