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Excess partial molar enthalpies and free energies in methanol–isobutanol mixtures at 20°C. The effect of size difference

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Abstract

The excess partial molar enthalpies, $H_m^E(i)$, and free energies, $G_m^E(i)$, (where i is methanol or isobutanol) were determined at 20.00°C in methanol–isobutanol mixtures. The Bhatia–March approach (J. Phys. F, 5 (1975) 1100), taking into account the size difference between the components within the framework of the conformational solution theory, was applied to explain the composition dependence of $H_m^E(i)$ and $G_m^E(i)$. It was reasonably successful : however, it did not seem to work for the other isomeric butanol and methanol mixtures.

INTRODUCTION

Molten Na–Cs mixtures, unlike the Na–K analogue, have peculiar thermodynamic features. In the Na-rich region, the small-angle X-ray scattering intensity is very high [1], and the liquidus curve has a rather flat portion [2]. These features were successfully explained by taking into account the size difference between Na and Cs atoms within the framework of the classical conformational treatment [3]. With only two adjustable parameters, the observed [4, 5] composition dependence of not only the chemical potential (a first-order derivative of the Gibbs free energy) but also the concentration fluctuation (a second-order derivative) could be reproduced rather closely. One of these two adjustable parameters is the size ratio of the constituents, which was fixed at a reasonable value. Hence this model was initially formulated on one adjustable parameter.

In the present paper, we examine whether, or to what extent, the same

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approach could explain the thermodynamic properties of the methanol–isobutanol system, which has a similar value for the size ratio. We compare the observed and the theoretical partial molar free energies and enthalpies, and their composition dependence. The excess integral molar free energies and enthalpies have been reported for mixtures of methanol and isomeric butanols (including isobutanol) at 25°C by Polak et al. [6]. In their determination of the excess integral free energies, the vapour phase compositions were determined using a dynamic circulation still. Therefore, the excess partial molar free energies can be calculated. However, the values of the partial molar free energies of methanol and those of isobutanol in the isobutanol-rich region are not self-consistent with the Gibbs–Duhem relation. Thus we decided to determine the excess partial molar free energies by a static method [7] and also the partial molar enthalpies directly [8].

EXPERIMENTAL

Methanol from Aldrich (99.9 + %, A.C.S. HPLC grade) and isobutanol from Aldrich (99.5%, HPLC grade) were used without further purification. Analytical gas chromatography indicated that both are as pure as claimed. However, an impurity in isobutanol affected the vapour pressure measurement. In the appendix, we show how the vapour pressure of the isobutanol was corrected for such an impurity.

The total vapour pressures were measured by a static method described elsewhere [7]. We chose 20.00°C for the temperature of this study because the full scale of the pressure gauge used was 100 Torr. The method of various corrections and that of data analysis due to Boissonnas (a differential method) are described in detail in ref. 7. The excess partial molar enthalpies of isobutanol (IB), $H_m^E(\mathrm{IB})$, were measured by the burette method and those of methanol (M), $H_m^E(\mathrm{M})$, by the ampoule method, both described earlier [8]. The ampoule method gave more accurate values, ±20 J mol^{-1}, while the accuracy by the burette method was about ±80 J mol^{-1}.

DATA ANALYSIS

Here we define the various quantities used in the subsequent discussion. The excess partial molar enthalpy of the ith component is defined as

$$H_m^E(i) = (\partial H^E/\partial n_i)_{p,T,n_j} \tag{1}$$

where n_i is the amount of the ith component. The excess (integral) molar enthalpy H_m^E is written as

$$H_m^E = H^E \Big/ \sum n_i \tag{2}$$

$$H_m^E = \sum x_i H_m^E(i) \tag{3}$$

where x_i is the mole fraction of the ith component. It must be stressed that the physical meanings of $H_m^E(i)$ and H_m^E are quite different, although their notation is similar. The same expressions apply for Gibbs free energy and entropy by changing H to G and S, respectively.

The chemical potential of the ith component in the liquid mixtures μ_i is written

$$\mu_I = \mu_i(\text{pure}) + RT \ln x_i + G_m^E(i) \tag{4}$$

or, with the activity coefficient τ_i, $G_m^E(i)$ is written

$$G_m^E(i) = RT \ln \tau_i \tag{5}$$

If the partial vapour pressure of the ith component p_i is known, then $G_m^E(i)$ is calculated as

$$G_m^E(i) = RT \ln[p_i/(x_i p_i^\ominus)] + c_i \tag{6}$$

where $p_i^\ominus$ is the vapour pressure of the ith component in its pure state at the same temperature. The second term c_i is the correction due to non-ideality of the gas phase mixture, and is written as

$$c_i = (B_{ii} - V_i^\ominus)(p - p_i) + p(1 - p_i/p)\delta \tag{7}$$

where B_{ii} is the second virial coefficient, p is the total vapour pressure, and δ is defined for a binary system as

$$\delta = 2B_{12} - B_{11} - B_{22} \tag{8}$$

For a grossly non-ideal system, the absolute value of the first term on the right-side of eqn. (6) is large and the second term c_i is negligible. In the present case, however, c_i is not insignificant.

As pointed out earlier [8], the method of measuring $H_m^E(i)$ (i being M or IB) is literally operating the differentiation of eqn. (1). Thus, a small amount of the ith component was added to a mixture and the change in enthalpy was measured directly. The important point is to make sure that the amount added Δn_i is small enough to guarantee the relation, $\Delta H^E/\Delta n_i \approx (\partial H^E/\partial n_i)$. This was checked by changing the amount Δn_I: the resulting ΔH^E was proportional to this [8].

The vapour pressure data are listed in Table 1; z_M is the mole fraction of

TABLE 1

Measured vapour pressures

No.	z_M	Bath temp./K	Total press. in Torr (1 Torr = 1.333224 mbar)	
			Measured	Impurity corr.
I-1	1.0000	293.179	96.411	96.411
I-2	0.9609	293.178	93.125	93.135
I-3	0.9205	293.178	89.807	89.807
I-4	0.8779	293.178	86.372	86.372
I-5	0.8311	293.178	82.659	82.659
I-6	0.7846	293.177	78.955	78.955
I-7	0.7286	293.177	75.263	75.263
I-8	0.6933	293.176	71.468	71.468
I-9	0.6506	293.177	68.280	68.280
I-10	0.6103	293.178	64.533	64.533
I-11	0.5736	293.177	61.398	61.398
II-32	0.5486	293.232	59.405	59.400
II-31	0.5315	293.232	57.859	57.854
II-30	0.5140	293.231	56.308	56.302
II-29	0.4961	293.231	54.668	54.661
II-28	0.4773	293.231	52.954	52.947
II-27	0.4579	293.231	51.173	51.165
II-26	0.4379	293.232	49.284	49.275
II-25	0.4171	293.232	47.384	47.374
II-24	0.3958	293.232	45.403	45.392
II-23	0.2734	293.230	43.296	43.284
II-22	0.3507	293.232	41.167	41.154
II-21	0.3278	293.232	39.009	38.994
II-20	0.3053	293.232	36.876	36.860
II-19	0.2835	293.233	34.810	34.792
II-18	0.2624	293.233	32.820	32.800
II-17	0.2464	293.233	30.937	30.915
II-16	0.2242	293.233	29.183	29.159
II-15	0.2098	293.232	27.807	27.780
II-14	0.1962	293.233	26.519	26.489
II-13	0.1835	293.232	25.312	25.279
II-12	0.1700	293.231	24.034	23.998
II-11	0.1569	293.231	22.794	22.754
II-10	0.1435	293.231	21.531	21.487
II-9	0.1302	293.231	20.271	20.222
II-8	0.1166	293.232	19.001	18.947
II-7	0.1025	293.231	17.676	17.617
II-6	0.08761	293.232	16.278	16.212
II-5	0.07199	293.231	14.811	14.739
II-4	0.05520	293.230	13.244	13.164
II-3	0.03855	293.233	11.707	11.618
II-2	0.01994	293.233	9.988	9.890
II-1	0.00000	293.233	8.176	8.068

TABLE 2

Total vapour pressures corrected for 20.00°C and the calculated partial pressures in Torr (1 Torr = 1.333224 mbar)

x_M	p(Total)	Boissonnas		Integration	
		p_M	p_{IB}	p_M	p_{IB}
1.0000	96.261	96.261	0	96.261	0
0.9609	92.995	92.579	0.416	92.582	0.413
0.9201	89.671	88.871	0.800	88.885	0.786
0.8769	86.242	85.067	1.174	85.085	1.157
0.8296	82.534	80.977	1.557	80.994	1.540
0.7828	78.840	76.917	1.923	76.932	1.908
0.7365	75.153	72.878	2.275	72.890	2.263
0.6910	71.367	68.738	2.630	68.749	2.618
0.6481	68.180	65.265	2.915	65.272	2.908
0.6074	64.435	61.184	3.251	61.192	3.243
0.5707	61.308	57.781	3.527	57.788	3.520
0.5441	59.135	55.419	3.716	55.425	3.710
0.5267	57.596	53.747	3.849	53.753	3.844
0.5090	56.054	52.072	3.982	52.077	3.976
0.4909	54.420	50.298	4.122	50.303	4.117
0.4719	52.713	48.445	4.268	48.451	4.263
0.4524	50.939	46.520	4.419	46.525	4.414
0.4322	49.054	44.475	4.580	44.480	4.574
0.4113	47.161	42.422	4.740	42.427	4.734
0.3898	45.188	40.282	4.906	40.287	4.901
0.3674	43.094	38.011	5.083	38.017	5.077
0.3447	40.968	35.707	5.261	35.712	5.256
0.3218	38.818	33.376	5.442	33.381	5.436
0.2993	36.693	31.073	5.619	31.079	5.614
0.2776	34.632	28.840	5.792	28.845	5.786
0.2567	32.648	26.691	5.957	26.696	5.952
0.2370	30.772	24.658	6.114	24.663	6.109
0.2189	29.023	22.763	6.260	22.769	6.254
0.2045	27.652	21.277	6.375	21.283	6.369
0.1911	26.365	19.883	6.482	19.889	6.476
0.1786	25.162	18.579	6.582	18.585	6.577
0.1654	23.887	17.199	6.689	17.205	6.683
0.1525	22.649	15.856	6.792	15.862	6.786
0.1394	21.387	14.489	6.898	14.495	6.892
0.1263	20.127	13.125	7.003	13.131	6.997
0.1130	18.857	11.748	7.109	11.754	7.103
0.09928	17.533	10.314	7.220	10.320	7.213
0.08477	16.133	8.796	7.337	8.803	7.331
0.06960	14.668	7.208	7.454	7.214	7.454
0.05331	13.100	5.508	7.592	5.514	7.586
0.03721	11.558	3.836	7.722	3.841	7.717
0.01923	9.838	1.970	7.868	1.969	7.868
0.00000	8.022	0.000	8.022	0.000	8.022

M in the entire volume of the apparatus, which is very close to x_M, because more than 99% of the total amount in the apparatus is in the liquid phase. First, corrections were made for an impurity in the isobutanol, as shown in the appendix. Using these data and assuming $x_M = z_m$, the partial pressures were calculated by the Boissonnas and integration [9] methods, described briefly below. Knowing the partial pressures, we corrected for the amounts in the gase phase in the apparatus and adsorbed on the walls of the apparatus, to improve the values of x_M. The procedure was repeated until the successive values of x_M converged within 1×10^{-7}. Two iterations were sufficient. Next we corrected for the temperature deviation from 20.00°C for each data point using the Gibbs–Konovalov relation [10]. Using these corrected values of p, we repeated the same procedure and arrived at the final results listed in Table 2.

The full analysis of 2-butoxyethanol–H_2O mixtures using the Boissonnas method was described in detail elsewhere [7]. Briefly, the Duhem–Margules relation is converted to

$$\Delta p_{IB} = \Delta p / [1 - (x_{IB}/x_M)(p_M/p_{IB})] \tag{9}$$

Thus, the successive changes in the total pressures Δp are converted to those of the partial pressures of IB, Δp_{IB}. Another possible method [9] is that the entire data set (x_{IB}, p_{IB}) is improved as a whole by integration of the Duhem–Margules relation

$$\ln p_{IB} = \ln p_{IB}^{\ominus} - \int_0^{x_M} (x_M/x_{IB})\, d \ln p_M \tag{10}$$

Three iterations were sufficient starting from Raoult's partial pressures for IB, for the two sets of (x_{IB}, p_{IB}) data to converge to less than ±0.0001 Torr, much better than the experimental sensitivity, ±0.002 Torr.

RESULTS AND DISCUSSION

The results of vapour pressure measurements and those of subsequent data analyses are summarized in Table 1, 2 and 3. Table 1 lists the measured values. The last column contains the vapour pressures corrected for an impurity in isobutanol (see the appendix for details.) Table 2 is the result of the iteration mentioned above, yielding the mole fraction in the liquid phase x_M and the total vapour pressures p(Total) corrected for the temperature variation by the Gibbs–Konovalov method [7, 10]. The partial pressures were calculated by the Boissonnas method [7, 11] and the integration method [9], as mentioned above. From the values of the partial pressures, the excess partial molar free energies $G_m^E(i)$ (where i is M or IB) can be calculated using eqn. (6). The uncertainties of the resulting values of $G_m^E(M)$ and $G_m^E(IB)$ were estimated using the difference in the values of

TABLE 3

Excess partial free energies in J mol^{-1} at 20.00°C

x_M	$G^E_m(M)$ [a]	$G^E_m(M)$ [b]	$G^E_m(IB)$ [a]	$G^E_m(IB)$ [b]	G^E_m
1.0000	0	0			0
0.9609	2.17 ± 0.05	2.98	680 ± 10	650	28.2
0.9201	8.6 ± 0.2	10.2	520 ± 20	490	48.5
0.8769	19.1 ± 0.3	21.6	404 ± 18	377	65.3
0.8296	34.0 ± 0.3	37.5	305 ± 13	279	78.7
0.7826	50.5 ± 0.2	54.8	230 ± 10	206	87.6
0.7365	67.5 ± 0.2	72.8	172 ± 7	149	92.9
0.6910	80.3 ± 0.2	86.5	138 ± 5	117	95.8
0.6481	110.0 ± 0.2	117.0	76 ± 3	55	95.1
0.6074	110.7 ± 0.2	118.7	74 ± 3	55	93.6
0.5707	123.1 ± 0.1	131.8	56 ± 2	37	91.3
0.5441	137.9 ± 0.1	147.2	37 ± 2	19	88.8
0.5267	142.2 ± 0.1	151.9	32 ± 2	15	86.9
0.5090	148.3 ± 0.1	158.4	25 ± 2	8	84.8
0.4909	152.4 ± 0.1	162.9	21 ± 2	5	82.4
0.4719	156.9 ± 0.1	167.7	17 ± 2	1	79.8
0.4524	160.9 ± 0.1	172.3	13 ± 1	−2	77.0
0.4322	162.6 ± 0.2	174.4	12 ± 1	−3	74.0
0.4113	168.5 ± 0.2	180.8	7 ± 1	−6	70.7
0.3898	172.9 ± 0.2	185.6	4 ± 1	−8	67.2
0.3674	175.6 ± 0.2	188.9	3 ± 1	−9	63.4
0.3447	179.0 ± 0.2	192.8	1 ± 1	−11	59.5
0.3218	182.3 ± 0.2	196.7	−1 ± 1	−12	55.4
0.2993	184.1 ± 0.2	199.0	−2 ± 1	−12	51.4
0.2776	186.1 ± 0.2	201.5	−3 ± 1	−12	47.5
0.2567	188.7 ± 0.2	204.5	−4 ± 1	−12	43.6
0.2370	189.6 ± 0.3	205.9	−4 ± 1	−12	39.9
0.2189	188.4 ± 0.3	205.1	−3 ± 1	−11	36.6
0.2045	189.3 ± 0.3	206.5	−4 ± 1	−10	33.9
0.1911	189.5 ± 0.4	206.9	−4 ± 1	−10	31.4
0.1786	189.3Å0.4	207.0	−4 ± 1	−10	29.1
0.1654	188.9Å0.4	207.0	−4 ± 1	−9	26.7
0.1525	188.8 ± 0.5	207.2	−4 ± 1	−9	24.3
0.1394	187.9 ± 0.5	206.6	−3 ± 1	−8	21.9
0.1263	187.8 ± 0.5	206.8	−3 ± 1	−8	19.6
0.1130	187.9 ± 0.6	207.2	−3 ± 1	−7	17.2
0.09928	186.8 ± 0.7	206.2	−3 ± 1	−6	14.7
0.08477	184.0 ± 0.8	204.0	−3 ± 1	−6	12.1
0.06960	179 ± 1	199	−2 ± 1	−5	9.6
0.05331	174 ± 1	195	−1.9 ± 0.9	−3.6	7.0
0.03721	169 ± 1	190	−1.4 ± 0.7	−2.6	4.6
0.01923	151 ± 1	173	−0.1 ± 0.1	−0.6	2.7
0.00000			0	0	0.0

[a] Without the gas phase virial correction.

[b] With the gas phase virial correction, see eqn. (6).

partial pressures obtained by the two methods. The second and the fourth columns of Table 3 contain the values of $G_\mathrm{m}^\mathrm{E}(i)$ (where i is M or IB) before the virial corrections with estimated uncertainties. In the third and fifth columns, values with virial corrections are listed. The estimated uncertainties remain the same. The values given in ref. 6 were used for the virial coefficients.

The measured values of $H_\mathrm{m}^\mathrm{E}(\mathrm{M})$ and $H_\mathrm{m}^\mathrm{E}(\mathrm{IB})$ are listed in Table 4. Figure 1 shows the plots of $H_\mathrm{m}^\mathrm{E}(\mathrm{M})$, $H_\mathrm{m}^\mathrm{E}(\mathrm{IB})$, $G_\mathrm{m}^\mathrm{E}(\mathrm{M})$ and $G_\mathrm{m}^\mathrm{E}(\mathrm{IB})$ determined at 20.00°C. The excess partial molar free energies at 25.00°C, $G_\mathrm{m}^\mathrm{E}(\mathrm{M})$ and $G_\mathrm{m}^\mathrm{E}(\mathrm{IB})$, were calculated by eqn. (6) using the partial pressure data of Polak et al. [6], and are plotted in Fig. 1. Their first three data points at low methanol concentrations are not self-consistent in terms of the Gibbs–Duhem relation, i.e. the values of $G_\mathrm{m}^\mathrm{E}(\mathrm{M})$ and $G_\mathrm{m}^\mathrm{E}(\mathrm{IB})$ both change with slopes of the same sign. Nevertheless, the general trend appears to be similar. From the values on the smooth curves in Fig. 1, the excess (integral) molar enthalpies H_m^E were calculated; they are listed in Table 5 and plotted in Fig. 2. In Fig. 3, the values of G_m^E listed in Table 3 are plotted. The data of Polak et al. [6] at 25.00°C are also plotted for comparison. In the figures, H_m^E

TABLE 4

Measured excess partial molar enthalpies $H_\mathrm{m}^\mathrm{E}(\mathrm{M})$ and $H_\mathrm{m}^\mathrm{E}(\mathrm{IB})$ in J mol^{-1} at 20.00°C

x_M	$H_\mathrm{m}^\mathrm{E}(\mathrm{M})$	x_M	$H_\mathrm{m}^\mathrm{E}(\mathrm{M})$	x_M	$H_\mathrm{m}^\mathrm{E}(\mathrm{M})$
Ampoule method					
0.03929	479	0.2922	350	0.7520	92
0.06270	458	0.4101	364	0.7560	91
0.1082	438	0.5050	217	0.7597	91
0.2593	365	0.5146	206	1.0000	−1
0.2766	352	0.5238	214	1.0000	1
				1.0000	0
Burette method					
0.0000	5	0.5603	156	0.9680	799
0.0000	8	0.5651	144	0.9735	838
0.0000	20	0.5698	158	0.9792	886
0.0000	−55	0.7681	334	0.9851	891
0.1874	65	0.7737	377	0.9910	883
0.1920	52	0.7851	397	0.9970	946
0.1964	62	0.7909	412	0.9478	817
0.3767	76	0.7967	384	0.9541	801
0.3807	69	0.9303	705	0.9350	701
0.3848	82	0.9355	717	0.9408	707
0.3890	34	0.9407	765	0.9467	826
0.5465	128	0.9461	751	0.9527	814
0.5509	160	0.9516	798	0.9588	766
0.5556	126	0.9557	789	0.9710	792

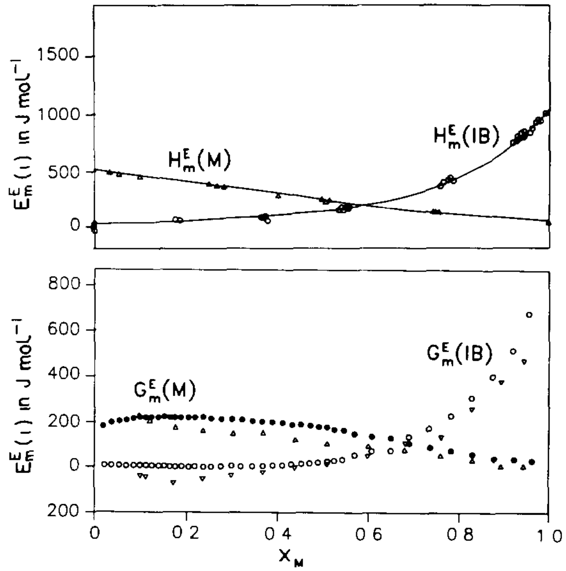

Fig. 1. $H^E_m(i)$ and $G^E_m(i)$ (where i is M or IB) plotted against the mole fraction of methanol x_M at 20.00°C: ●, G^E_m(M), and ○, G^E_m(IB) at 20.00°C (this work); △, G^E_m(M), and ▽, G^E_m(IB), at 25.00°C [6].

and G^E_m for the methanol-*sec*-butanol and the methanol-*tert*-butanol systems [6] are also plotted for discussion below.

Next, we examine whether or to what extent the treatment by Bhatia and March [3] can explain the general trend in their composition dependence of $H^E_m(i)$ and $G^E_m(i)$, where i is M or IB. From the expression for the excess molar free energy G^E_m [3], it follows that

$$H^E_m = Wx_M(1 - x_M)/(1 - \beta x_M) \tag{11a}$$

$$H^E_m(\mathrm{M}) = W(1 - x_M)^2/(1 - \beta x_M)^2 \tag{11b}$$

$$H^E_m(\mathrm{IB}) = W(1 - \beta)x_M^2/(1 - \beta x_M)^2 \tag{11c}$$

$$G^E_m = H^E_m - RT[-x_M \ln r - \ln(1 - \beta x_M)] \tag{12a}$$

$$G^E_m(\mathrm{M}) = H^E_m(\mathrm{M}) - RT[\ln r + \ln(1 - \beta x_M) - \beta(1 - x_M)/(1 - \beta x_M)] \tag{12b}$$

$$G^E_m(\mathrm{IB}) = H^E_m(\mathrm{IB}) - RT[\ln(1 - \beta x_M) + \beta x_M/(1 - \beta x_M)] \tag{12c}$$

$$\beta = (r - 1)/r$$

where r is the volume ratio (volume of IB)/(volume of M) and W is related to the exchange energy, the difference in interaction energies between the average of M–M and IB–IB pairs and the IB–M pair.

The excess molar volumes of the methanol–isobutanol mixtures are non-zero, but rather small, <0.1 ml/mol⁻¹ [6]. Therefore, for the volume ratio r, we use that of the molar volumes in their pure states for the entire composition range. Thus, $r = 92.89/40.73 = 2.28$ is fixed. Considering the

TABLE 5

Excess (integral) molar enthalpies H_m^E in J mol^{-1} at 20.00°C

x_M	H_m^E	x_M	H_m^E	x_M	H_m^E
0	0	0.35	142	0.7	149
0.05	28	0.4	151	0.75	140
0.1	53	0.45	158	0.8	129
0.15	75	0.5	162	0.85	111
0.2	95	0.55	164	0.9	88
0.25	113	0.6	164	0.95	52
0.3	128	0.65	157	1.0	0

crudeness of the treatment, this may be sufficient. The question now is with only one remaining adjustable parameter W, whether or to what extent eqns. (11) and (12) can predict a general trend in composition dependence of $H_m^E(i)$ and $G_m^E(i)$, (where i is M or IB). Equations (11) can be fitted fairly well to the observed $H_m^E(i)$ values with $W/RT = 0.21$, but eqns. (12) give much smaller values for $G_m^E(i)$ with this value of W/RT. Equations (12), however, are fitted well to the experimental values of $G_m^E(i)$ with $W/RT = 0.34$, while eqns. (11) give much higher values of $H_m^E(i)$ than those observed. A value for W/RT of 0.31 appears to be a good compromise for both $H_m^E(i)$ and $G_m^E(i)$, as shown in Fig. 4. While the values of $H_m^E(i)$ are

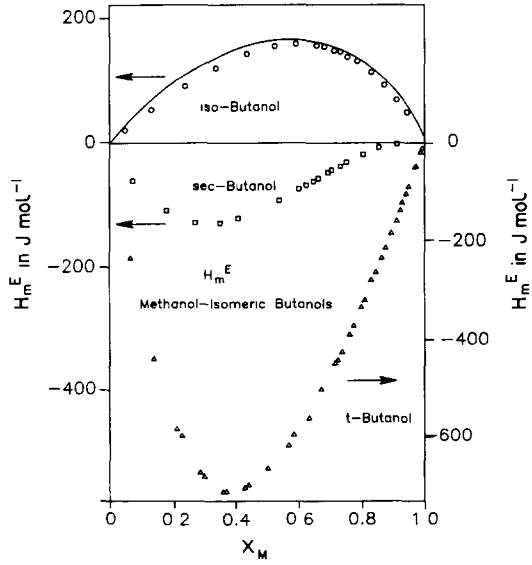

Fig. 2. H_m^E for the methanol–isobutanol mixtures plotted against the mole fraction of methanol x_M. ——, at 20.00°C (this work); and ○, methanol–isobutanol [6]; □, methanol–*sec*-butanol [6]; △, for methanol–*tert*-butanol [6], all at 25.00°C.

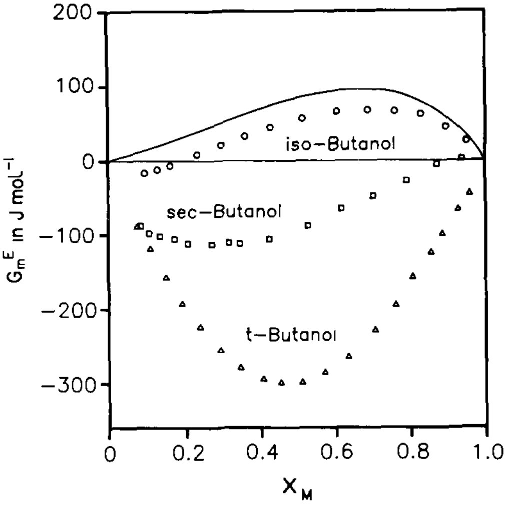

Fig. 3. G^E_M for methanol–isobutanol mixtures plotted against the mole fraction of methanol x_M: ——, at 20.00°C (this work); and O, methanol–isobutanol [6]; □, methanol–*sec*-butanol [6]; △, methanol–*tert*-butanol [6], all at 25.00°C.

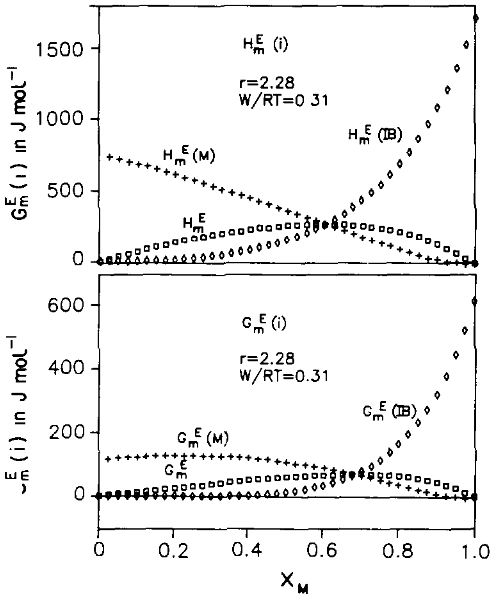

Fig. 4. Calculated values of $H^E_m(i)$ and $G^E_m(i)$ by eqns. (11) and (12), with $r = 2.28$ and $W/RT = 0.31$: +, i is M; ◇, i is IB; □, for the integral molar quantities, H^E_m or G^E_m.

somewhat higher and those of $G_m^E(i)$ are lower than those observed, the general trend is remarkably similar to that observed. The curves of $H_m^E(M)$ and $H_m^E(IB)$ cross each other at about $x_M = 0.6$, i.e. the maximum of H_m^E occurs at $x_M = 0.6$, and those of $G_m^E(M)$ and $G_m^E(IB)$ cross at about $x_M = 0.7$, exactly as observed. Moreover, the composition dependence of $G_m^E(i)$ in the range $x_M < 0.4$ is almost the exact replica of what is observed. These results seem to suggest that the size difference of the components is the predominant effect on the thermodynamic properties of methanol–isobutanol mixtures.

If this is the case, then mixtures of methanol with the other isomeric butanols must be considered. The size ratios are quite similar to that of the methanol–isobutanol case (2.28); 2.26 for *n*-butanol, 2.27 for *sec*-butanol, and 2.33 for *tert*-butanol. The excess (integral) molar enthalpies and free energies are available for the mixtures of methanol and isomeric butanols at 25°C [6]. For *sec*-butanol for *tert*-butanol mixtures with methanol, H_m^E and G_m^E are plotted in Figs. 2 and 3. The question then is whether eqns. (11a) and (12a) can be fitted to these plots. The resulting G_m^E and H_m^E plots with a few trial values of W/RT with fixed $r = 2.28$, are shown in Fig. 5. The minima in H_m^E and G_m^E are quite different from those observed. Indeed,

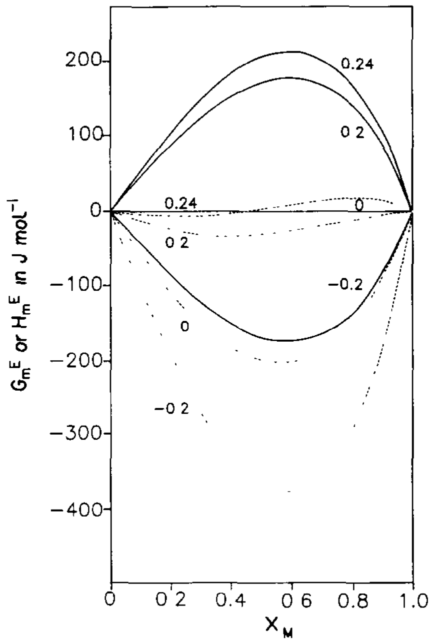

Fig. 5. Calculated values of H_m^E and G_m^E, with $r = 2.28$: ——, H_m^E; – – –, G_m^E. The numbers indicate the values of W/RT. The numerals to the left-hand-side of the graph are for G_m^E, and those to the right for H_m^E.

numerical calculations indicate that eqns. (11) give the extremum (the maximum if $W/RT > 0$ and the minimum if $W/RT < 0$) at a value of x_M from 0.59 to 0.63, for the value of r from 2 to 3 respectively. Therefore, the observed minima at about $x_M = 0.3$ for *sec*-butanol and at about $x_M = 0.4$ for *tert*-butanol can not be predicted within the framework of the present treatment. This poses an interesting question as to why the isobutanol–methanol system appears to be explained by eqns. (11) and (12).

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APPENDIX: CORRECTION FOR A VOLATILE IMPURITY

When the vapour pressure of a pure substance is determined, volatile impurities including air are removed by several freeze–pump–thaw operations. Their remaining minute amounts are then removed and monitored by measuring the vapour pressure over the liquid sample, followed by removing the vapour phase including these impurities. This procedure is repeated until the two successive values of the vapour

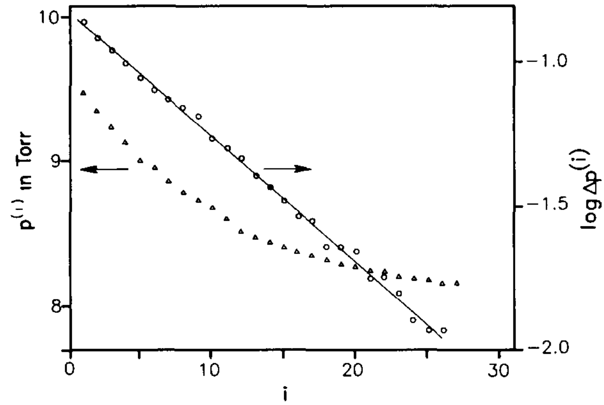

Fig. A1. The measured total pressures in Torr (1 Torr = 1.333224 mbar) of the isobutanol specimen $P^{(i)}$ plotted against the number of repetitive measurements *i*. $\Delta p^{(i)} = p^{(i)} - p^{(i+1)}$, see the text in the appendix.

pressure become the same within the experimental sensitivity, which was 0.002 Torr for the pressure gauge used; this normally takes several cycles. The vapour pressure of pure methanol at 20.00°C was determined in this way.

For isobutanol, however, the situation was different. The sample, 99.5 + %, shaken with molecular sieve 3A pellets, was vacuum-transferred into the cell. It was subjected to freeze–pump–thaw operations more than a dozen times. Then the vapour pressure over the liquid was measured repeatedly, removing the vapour phase each time. After 27 repetitions, the vapour pressure still decreased by 0.012 Torr. Thus we suspected the presence of an impurity that is slightly less volatile than isobutanol, although the amount of such an impurity should be less than 0.5 mol%. The total vapour pressures are plotted in Fig. A1 for each *i*th measurement. The *i*th total pressure measured $p^{(i)}$ consists of the vapour pressure of pure isobutanol $p^{\ominus}$ and the partial pressure of the impurity $p^{(i)}_{\text{imp}}$, with the mole fraction of impurity $x^{(i)}_{\text{imp}}$ and Henry's constant k

$$\begin{aligned} p^{(i)} &= p^{\ominus} + p^{(i)}_{\text{imp}} \\ p^{(i)}_{\text{imp}} &= k x^{(i)}_{\text{imp}} \end{aligned} \tag{A1}$$

After the *i*th measurement, the gas phase of volume V at temperature T is evacuated; thus the mole fraction of the impurity at the $(i+1)$th measurement will be

$$\begin{aligned} x^{(i+1)}_{\text{imp}} &= [N x^{(i)}_{\text{imp}} - (p^{(i)}_{\text{imp}} V)/RT)]/N \\ &= x^{(i)}_{\text{imp}}[1 - (kV)/(NRT)] \\ &= \alpha\, x^{(i)}_{\text{imp}} \end{aligned} \tag{A2}$$

where N is the total amount in the liquid phase in the apparatus. Hence

$$p_{\mathrm{imp}}^{(i)} = \alpha\, p_{\mathrm{imp}}^{(i-1)} = \ldots = \alpha^{(i-1)} p_{\mathrm{imp}}^{(1)} \tag{A3}$$

The difference in the successive total pressures $\Delta p^{(i)}$ is written

$$\begin{aligned}\Delta p^{(i)} &= p^{(i)} - p^{(i+1)}\\ &= p_{\mathrm{imp}}^{(1)} \alpha^{i} [(1-\alpha)/\alpha]\end{aligned} \tag{A4}$$

or

$$\log \Delta p^{(i)} = i \log\ \alpha + \log[p_{\mathrm{imp}}^{(1)}(1-\alpha)/\alpha]$$

Plots of $\log \Delta p^{(i)}$ against i are shown in Fig. A1, confirmining eqn. (A4). From the slope and the intercept, $\alpha = 0.905$ and $p_{\mathrm{imp}}^{(1)} = 1.405 \pm 0.15$ Torr, or $p_{\mathrm{imp}}^{(27)} = 0.108 \pm 0.015$ Torr. With the appropriate values of N and V, the value of k becomes about 1000 Torr. Because the value of k is very small, in comparison with 1.6×10^6 Torr for N_2 in isobutanol and 4×10^5 Torr for CH_4 in n-butanol, the impurity in question must be much less volatile. It could very well be an isomeric butanol that could not be completely removed. The mole fraction of the impurity at the first vapour pressure measurement amounts to $p_{\mathrm{imp}}^{(1)}/K \approx 0.0014$ (0.14 mol%), a reasonably self-consistent value.

The specimen after the 27th measurement was used for subsequent vapour pressure measurements by successively adding methanol. For this series, series II, the vapour pressure due to this impurity, proportional to the mole fraction of isobutanol in the mixture, was subtracted from the measured total pressure, see the last column of Table 1.