CONCENTRATION AND TEMPERATURE DEPENDENCE OF HEATS OF MIXING OF 1-BUTANOL, 2-BUTANOL, AND 2-METHYL-2-PROPANOL WITH CYCLOHEXANE*

František VESELÝ, Vladimír DOHNAL, Miriam VALENTOVÁ, and Jiří PICK

Department of Physical Chemistry,
Prague Institute of Chemical Technology, 16628 Prague 6

The concentration dependences of excess enthalpies were measured in an isothermal calorimeter within the range of $25-50°C$ at six temperatures for the binary systems 1-butanol-cyclohexane and 2-butanol-cyclohexane and at five temperatures for the system 2-methyl-2-propanol-cyclohexane. A conspicuous temperature and concentration dependence of the maximum value of enthalpy of mixing was found for the latter system. Heats of mixing of all three systems were correlated by the SSF equation. The results of correlation are comparable with the experimental error (0.5%) in the entire range of mole fractions of alcohols.

Heat of mixing is nowadays one of the most accurate and most often measured excess properties because it yields valuable indirect information on the structure of solutions and intermolecular interactions. For these reasons, rather a big interest has recently been devoted to the systems whose one component is an alcohol. Numerous modifications of the original Dolezalek theory[1] of associated solution have brought success in the interpretation of heats of mixing of alcohols with different nonpolar solvents[2-12].

But not always we meet with sufficient number of suitable experimental data both for a wider concentration and temperature range. Therefore in this work we have set ourselves the aim to measure the needed data for the title systems* and to find the most suitable correlation relation for the concentration dependence of excess enthalpy. Simultaneously we take up one of previous papers[14] where the associating components were 1-propanol and 2-propanol.

EXPERIMENTAL

Cyclohexane and *1-butanol* were purified by the methods desribed previously[15]. Their boiling points, refractive indices and densities are identical with the values given there.

2-Butanol, A. R. (Reanal), was twice distilled on a column (approximately 60 theoretical plates) filled with stainless steel helices, and the remainder of water was removed by molecular sieves Nalsit A4. Its physical constants were as follows: NBP 99·4°C (ref.[16] 99·41°C), n_D^{25} 1·3952 (ref.[16] 1·39525), d_4^{25} 0·80258 (ref.[16] 0·80251).

2-Methyl-2-propanol, A.R. (Reanal), was first purified by azeotropic distillation with benzene[17] on the same column as 2-butanol, and then freed from undesirable impurity 2-methyl-1-propene by a multiple crystallization. The final product was dried-up by molecular sieves Nalsit A4. The water content was lower than 0·02 mass %. Melting point of the alcohol was 25·58°C (ref.[18] 25·50°C), NBP 82·27°C (ref.[16] 82·32°C), n_D^{27} 1·3840 (ref.[16] 1·38401), d_4^{27} 0·77846 (ref.[16] 0·77838).

Heats of mixing were measured in an isothermal calorimeter of our own design. The calorimeter along with the automatic control systems and technique of measurement have been described formerly[19,20] in detail.

RESULTS AND DISCUSSION

The heats of mixing for all three systems were measured in the entire range of mole fractions of alcohol (x_B) at temperatures of 25, 30, 35, 40, 45, and 50°C. With respect to the melting point of 2-methyl-2-propanol, the temperature of 25°C was omitted for this system. Unlike Polák and coworkers[21] we did not succeed in keeping 2-methyl-2-propanol in supercooled liquid state. Glass beads in mixing vessel which otherwise aid well in thorough mixing the liquids proved to be reliable centres of crystallization.

All the measured values of excess enthalpies H^E (J mol^{-1}) are given in Table I. For the values of H^E within 500 − 1 300 J mol^{-1} the experimental error was 0·5 to 0·3%. In concentration ends after multiple diluting, the inaccuracy reached 1 − 2%.

Heats of mixing of 1-butanol with cyclohexane were measured at 25, 35, and 45°C by Smirnova and Kurtynina[22] and in the same laboratory also by Belousov and co-workers[23]. For the temperature of 45°C, their measurements are in excellent agreement with our data in the whole range of mole fraction of alcohol, and the maximum difference 1% is fully within the framework of the experimental error of both the calorimeters. At the temperatures 25 and 35°C, the agreement is already less satisfactory, and it is impossible to give unique reasons for it. At the temperature of 35°C and $x_B < 0·5$, our data are systematically as much as 4% higher, at the temperature of 25°C, on the contrary, lower (2 − 3%). With regard to a smaller number of measurements of the authors cited (11 − 13 points for each temperature) and a simpler type of their calorimeter, we believe that our H^E values are more probable. An evidence for it is given by too surprising agreement (within tenth %) with the data by French and Stokes[13] for 45°C and $x_B < 0·2$. French and Stokes measured under the same conditions excess enthalpies for the remaining two systems[13]. The comparison of our and their values is very satisfactory, and the differences do not exceed 1%.

TABLE I

Dependence of heat of mixing H^E (J mol^{-1}) in systems cyclohexane(A)-C$_4$-alkanol(B) on mole fraction at different temperatures

x_B	H^E	δ^a	x_B	H^E	δ^a
		1-Butanol			
		25°C			
0·0370	294·8	0·2	0·4554	614·4	1·5
0·0830	406·0	−1·0	0·4567	612·9	0·7
0·1091	451·6	−0·7	0·4926	595·8	1·7
0·1402	500·0	2·0	0·5213	575·6	−0·5
0·1822	549·9	1·5	0·5840	525·0	−2·5
0·2336	592·1	−1·2	0·5876	521·9	−2·5
0·2628	612·4	1·2	0·6189	492·7	−3·0
0·2863	618·8	−3·2	0·6538	453·9	−6·9
0·3215	630·0	−2·0	0·6932	418·8	0·7
0·3503	632·6	−2·5	0·7367	366·6	−0·5
0·3784	633·5	−0·5	0·7834	308·7	0·0
0·4133	628·1	0·5	0·8386	236·6	1·2
0·4162	633·3	6·4	0·8976	154·4	2·0
		30°C			
0·0550	382·1	−0·8	0·4156	685·4	4·0
0·1061	491·9	1·8	0·4535	668·7	2·3
0·1393	546·0	2·5	0·4866	649·3	1·0
0·1683	582·3	−0·2	0·5327	617·6	1·8
0·2057	620·0	−3·5	0·5650	586·1	0·0
0·2315	644·0	−1·8	0·5962	553·4	−6·3
0·2664	667·3	−1·3	0·6264	524·1	−4·5
0·3050	685·0	0·8	0·6610	487·9	−2·3
0·3122	682·0	−4·3	0·7246	413·5	1·3
0·3358	690·2	0·0	0·7914	322·3	0·2
0·3689	692·0	−2·0	0·8505	239·0	3·0
0·4094	684·5	1·3	0·9347	108·6	2·8
0·4150	685·0	3·3			
		35°C			
0·0726	470·5	−0·8	0·5163	685·6	3·6
0·1170	563·5	1·3	0·5322	666·0	−2·8
0·1386	599·5	1·5	0·5618	640·3	−1·5
0·1700	643·7	0·8	0·5641	637·4	−2·3
0·1981	673·9	−2·0	0·6066	595·6	0·3
0·2374	711·6	−0·3	0·6318	560·7	−5·9

TABLE I
(Continued)

x_B	H^E	δ^a	x_B	H^E	δ^a
			35°C		
0·2674	728·8	—2·6	0·6668	521·7	—2·0
0·3112	746·1	—2·3	0·7140	461·8	0·5
0·3577	750·1	—2·8	0·7592	397·5	0·8
0·3838	751·8	1·8	0·8018	330·3	—2·0
0·4188	743·8	3·8	0·8516	255·5	2·0
0·4502	729·6	3·6	0·9183	143·5	1·0
0·4845	709·0	3·6			
			40°C		
0·0601	484·4	0·0	0·5165	742·5	2·9
0·1058	592·8	—1·6	0·5350	721·1	—1·8
0·1294	640·6	2·3	0·5613	691·8	—5·2
0·1666	597·3	1·0	0·5995	651·3	—3·6
0·2097	747·4	—0·5	0·6283	618·5	—1·3
0·2629	788·4	—2·3	0·6610	578·3	1·3
0·3092	805·9	—4·7	0·6980	523·1	—2·1
0·3358	816·7	1·3	0·7418	457·2	—1·8
0·3726	815·1	0·5	0·7934	377·4	1·3
0·4134	809·0	4·9	0·8815	224·2	1·3
0·4438	792·7	2·3	0·9242	145·2	0·8
0·4728	774·7	1·6			
			45°C		
0·0555	517·8	—21·	0·4397	857·8	0·3
0·1035	655·3	5·6	0·4629	845·9	2·1
0·1396	719·2	1·3	0·5162	804·2	2·4
0·1720	767·7	0·5	0·5605	756·8	—0·3
0·2141	807·8	—9·2	0·5803	730·8	—3·7
0·2211	822·2	—1·6	0·6172	689·4	—0·8
0·2460	842·2	—2·6	0·6670	618·5	—0·5
0·2649	861·0	3·4	0·6918	582·1	—0·5
0·2742	864·6	1·6	0·7320	515·1	—1·9
0·3002	873·7	—0·5	0·7755	440·0	—2·0
0·3349	878·0	—3·7	0·8235	356·1	—0·8
0·3571	883·9	1·6	0·8788	250·0	—0·5
0·3678	882·0	0·5	0·9358	132·8	—1·9
0·4163	874·9	6·3			

TABLE I
(*Continued*)

x_B	H^E	δ^a	x_B	H^E	δ^a
			50°C		
0·0616	584·9	−2·4	0·4598	930·1	9·4
0·1050	712·4	3·2	0·4832	903·5	0·8
0·1271	759·5	2·7	0·5210	865·2	−2·4
0·1672	829·7	1·9	0·5478	837·8	−0·5
0·2095	883·9	−0·8	0·5802	801·8	4·8
0·2361	909·5	−2·7	0·5982	767·8	−7·2
0·2638	930·4	−3·5	0·6338	723·1	−1·1
0·3077	948·7	−6·7	0·6686	664·8	−5·1
0·3618	955·0	−6·2	0·7041	612·2	1·6
0·3681	957·0	−3·2	0·7372	546·5	−5·4
0·4137	950·3	3·0	0·7969	435·9	−2·7
0·4174	948·3	2·7	0·8800	264·3	−3·5
0·4198	945·3	0·8			
			2-Butanol		
			25°C		
0·0591	462·3	−3·0	0·5321	908·0	5·7
0·1111	607·5	8·4	0·5584	877·1	0·0
0·1569	703·7	4·0	0·5890	846·6	−0·2
0·2025	781·1	−3·0	0·6154	815·8	0·7
0·2390	832·3	−6·9	0·6610	755·1	4·0
0·2798	880·7	−7·2	0·6742	730·1	−0·5
0·3087	903·7	−10·1	0·7208	651·4	−0·5
0·3597	943·3	0·0	0·7568	579·6	−4·7
0·3870	954·1	3·2	0·7940	501·9	−6·9
0·4163	958·3	5·5	0·8595	357·9	−4·7
0·4626	950·8	7 4	0·9377	162·6	−5·9
0·5037	928·4	5·5			
			30°C		
0·0610	515·3	−3·3	0·5024	997·2	7·6
0·1100	661·6	7·3	0·5352	967·7	3·0
0·1582	767·9	5·0	0·5638	937·5	0·2
0·2167	866·7	−2·5	0·5937	903·8	0·5
0·2663	930·2	−7·0	0·6097	880·9	−2·0

TABLE I
(Continued)

x_B	H^E	δ^a	x_B	H^E	δ^a

30°C

x_B	H^E	δ^a	x_B	H^E	δ^a
0·2923	955·3	−9·6	0·6580	816·8	4·5
0·3218	980·3	8·8	0·6875	760·3	−2·8
0·3636	1 009·4	−2·0	0·7223	693·7	−5·8
0·3901	1 020·1	−1·8	0·7937	547·9	−2·0
0·4185	1 025·5	5·8	0·8566	391·2	−8·3
0·4370	1 022·3	5·0	0·9302	199·2	−4·5
0·4730	1 012·8	7·0			

35°C

x_B	H^E	δ^a	x_B	H^E	δ^a
0·0571	545·6	−3·8	0·4218	1 091·6	3·6
0·0962	683·9	6·1	0·4551	1 089·0	7·7
0·1492	808·7	1·0	0·4978	1 067·7	7·2
0·1718	858·7	4·1	0·5306	1 040·5	4·6
0·2080	922·5	2·0	0·5643	1 007·0	4·1
0·2365	963·1	−1·5	0·6151	939·6	0·5
0·2698	1 002·1	−5·6	0·6618	867·5	−1·0
0·2961	1 026·2	−8·7	0·7003	793·2	−3·6
0·3224	1 048·3	−8·4	0·7324	730·7	−1·5
0·3642	1 072·5	−6·9	0·7945	587·4	−4·6
0·3898	1 086·7	0·2	0·8567	426·5	−6·1
0·4183	1 092·3	4·1	0·9203	245·6	−5·6

40°C

x_B	H^E	δ^a	x_B	H^E	δ^a
0·0605	605·9	−3·4	0·4650	1 148·2	4·9
0·1063	766·0	5·7	0·4986	1 129·4	4·7
0·1561	885·0	3·1	0·5295	1 103·7	3·4
0·1808	935·1	2·3	0·5592	1 073·4	3·1
0·2084	982·4	−1·0	0·5880	1 036·8	1·6
0·2345	1 021·7	−3·4	0·6137	1 000·7	1·6
0·2660	1 062·6	−5·2	0·6575	931·8	3·9
0·2861	1 085·7	−5·1	0·6612	913·6	−7·6
0·3197	1 112·6	−8·1	0·7125	828·0	−6·8
0·3402	1 132·3	−2·1	0·7535	729·7	−0·5
0·3691	1 146·2	−1·6	0·7928	619·2	5·3
0·3918	1 153·7	0·3	0·8508	477·5	0·3
0·4172	1 157·5	2·9	0·9203	263·6	3·9

x_B	H^E	δ^a	x_B	H^E	δ^a
		45°C			
0·0612	654·5	−1·0	0·4883	1 201·8	3·2
0·1105	832·4	−0·8	0·5018	1 194·9	5·6
0·1542	951·3	6·3	0·5362	1 167·0	−7·7
0·1982	1 033·0	−1·8	0·5620	1 133·8	2·9
0·2168	1 065·8	−1·6	0·5800	1 107·8	−0·3
0·2347	1 102·4	6·9	0·6213	1 046·7	−0·5
0·2691	1 140·4	−1·6	0·6579	983·0	−0·5
0·3018	1 170·3	−5·8	0·6614	969·8	−7·1
0·3320	1 190·9	−8·7	0·7058	895·0	8·2
0·3758	1 215·0	−4·8	0·7203	850·3	−4·2
0·4003	1 222·4	−1·6	0·7542	772·3	−1·9
0·4204	1 227·3	3·4	0·7953	659·9	−7·7
0·4302	1 221·0	−1·6	0·8533	502·0	1·3
0·4604	1 217·0	3·4	0·9300	252·1	0·0
		50°C			
0·0606	695·5	0·5	0·5267	1 239·8	4·0
0·1106	892·2	5·1	0·5424	1 226·2	6·4
0·1543	1 022·6	7·8	0·5764	1 177·9	−0·3
0·2074	1 123·9	1·1	0·5802	1 167·7	−5·4
0·2342	1 166·8	0·5	0·6153	1 116·6	−3·5
0·2694	1 212·5	−0·8	0·6402	1 074·1	−3·2
0·2970	1 240·3	−2·4	0·6608	1 041·4	3·2
0·3283	1 261·4	−6·4	0·7104	939·1	7·0
0·3553	1 279·1	−3·8	0·7577	809·0	−6·4
0·3847	1 293·0	1·1	0·7971	706·7	−0·3
0·4209	1 294·6	1·3	0·8711	475·2	−1·6
0·4586	1 285·5	0·3	0·9388	236·9	−1·1
0·4943	1 267·4	4·6			
		2-Methyl-2-propanol			
		30°C			
0·0704	495·6	6·5	0·5084	864·0	−3·8
0·1003	562·8	−5·8	0·5500	858·6	−1·8
0·1340	627·4	−2·5	0·5977	835·9	−4·8
0·1667	670·8	−4·0	0·6245	820·6	−3·5
0·2068	721·8	2·8	0·6505	802·2	−1·3
0·2418	752·7	1·3	0·6740	781·2	−0·3

TABLE I
(Continued)

x_B	H^E	δ^a	x_B	H^E	δ^a

2-Methyl-2-propanol
30°C

0·2757	780·8	1·8	0·7075	751·3	8·1
0·3402	826·2	4·0	0·7574	675·3	2·8
0·3682	839·5	2·5	0·8012	593·0	1·8
0·4130	856·6	1·5	0·8501	483·6	0·8
0·4497	863·9	−0·5	0·9025	339·8	−1·5
0·4807	866·5	−1·5	0·9498	184·5	−4·5

35°C

0·0594	512·8	9·2	0·5017	905·7	−3·6
0·1090	643·2	−7·9	0·5210	901·5	−4·4
0·1355	690·7	−7·7	0·5647	884·3	−6·4
0·1632	733·6	−3·1	0·5948	870·7	−3·6
0·2113	792·7	4·6	0·5964	875·1	1·8
0·2596	831·4	3·1	0·6317	844·6	−2·3
0·3114	867·9	5·4	0·6503	824·4	−5·6
0·3308	873·7	0·5	0·6994	774·5	0·3
0·3622	892·5	4·6	0·7222	746·6	3·8
0·4095	905·9	2·0	0·7673	672·2	3·3
0·4113	909·0	4·9	0·8105	586·2	3·3
0·4540	909·8	−1·3	0·8676	447·3	2·8

40°C

0·0586	554·3	−8·6	0·5185	948·8	0·3
0·1110	708·8	−9·4	0·5389	936·5	−3·9
0·1639	801·6	−5·2	0·5401	938·1	−1·8
0·1970	842·6	−1·3	0·5710	919·8	−3·6
0·2194	859·2	−5·5	0·5982	899·7	−5·2
0·2600	903·1	7·3	0·6471	861·8	1·3
0·2968	924·3	6·0	0·6515	858·1	2·3
0·3288	942·2	8·3	0·6966	790·4	−9·4
0·3711	949·3	0·0	0·7519	715·0	2·9
0·4086	957·9	0·5	0·7944	629·3	0·5
0·4092	962·7	5·2	0·8370	535·4	4·7
0·4476	958·3	−1·8	0·8592	478·6	5·2
0·4869	953·9	−2·6	0·9289	266·6	−2·9

TABLE I

(Continued)

x_B	H^E	δ^a	x_B	H^E	δ^a
		45°C			
0·0616	619·7	11·1	0·4094	1 024·7	−1·3
0·1095	774·9	−6·1	0·4095	1 028·2	2·4
0·1415	836·1	−11·1	0·4537	1 021·6	−2·4
0·1612	872·3	−5·6	0·5529	983·9	−2·4
0·2296	951·3	0·3	0·5930	944·2	−12·2
0·2570	978·2	6·9	0·6272	917·0	−6·3
0·3091	1 010·0	9·5	0·6536	886·1	−6·6
0·3560	1 018·3	1·1	0·7073	820·1	3·4
0·3589	1 018·2	0·3	0·7368	764·8	−1·6
0·3802	1 026·1	3·4	0·7772	690·3	3·4
0·4051	1 031·1	5·6	0·8338	564·3	10·3
0·4092	1 026·1	0·4	0·8905	398·8	−5·2
		50°C			
0·0803	737·5	4·3	0·5337	1 061·2	−0·3
0·1246	872·1	−4·0	0·5584	1 043·0	−0·3
0·1660	953·1	−3·6	0·5617	1 041·0	0·3
0·2123	1 015·4	0·0	0·6009	1 002·5	−1·1
0·2630	1 058·7	0·5	0·6538	937·6	−1·1
0·2921	1 078·7	3·2	0·6877	884·3	−3·2
0·3302	1 090·7	−1·1	0·7096	844·5	−5·9
0·3562	1 099·0	0·0	0·7331	805·6	−1·1
0·3604	1 100·0	0·3	0·7767	715·0	0·3
0·3923	1 105·1	1·3	0·8088	638·3	0·6
0·4103	1 104·5	0·8	0·8581	508·1	4·3
0·4525	1 101·6	3·5	0·9005	379·5	7·5
0·5076	1 077·1	0·0			

a Deviation between experimental and calculated H^E.

In 1966 Sosnkowska–Kehiaian and coworkers[24] published heats of mixing in the system 2-methyl-2-propanol–cyclohexane for 30 and 50°C. They used a non-iso-thermal calorimeter of their own design with a relatively large vapour space. They estimated the experimental error to be lower than 2·5%. For the temperature of 50°C and $x_B < 0.4$, the agreement of their and our measurements is more than good. in the region $x_B > 0.4$, our data are about 2% lower. The H^E values reported by them for 30°C are, on the contrary, at all the concentrations, as much as 4% higher.

Heats of mixing for the same system were measured at 45°C by Kopp and Quitzsch[25]. They do not report the experimental H^E values but only constants of the Redlich–Kister expansion. So a direct comparison loses adequacy, and we can only state that their correlated data are for $x_B < 0.2$ unrealistically low, even though in the region $x_B < 0.3, 0.7 >$ the difference is satisfactory (2%).

In this connection we wish to draw one's attention to the fact that the disagreement of our and literature data may be caused by a strong hygroscopicity of 2-methyl-2-propanol, which unfortunately is mentioned, in connection with the preparation of measurements, by no authors.

We found out that the water content in badly closed flask with liquid alcohol increased in 8 hours to 1 mass %. And whereas the heat of mixing of anhydrous alcohol for $x_B = 0.4103$ was 1 028.1 J mol^{-1}, for that "sample" was measured 1 044.7 J mol^{-1} (both at 45°C).

Therefore we always measured only with immediately distilled and dried 2-methyl-2-propanol and carried out only 2—3 ensuing dilutions.

It can be seen from Table I that the maximum values of H^E increase at all the temperatures in the range 1-butanol, 2-methyl-2-propanol, 2-butanol. Whereas the position of maximum does not differ too much for primary and secondary butanols ($x_B = 0.37$ and 0.42, respectively), and does not change with temperature, for 2-methyl-2-propanol $x_B = 0.49$ at 30°C, and is conspicuously shifted to lower values of x_B with increasing temperature ($x_B = 0.39$ at 50°C).

It is also worth paying attention to the fact that at lower temperatures for $x_B > 0.6$, the heat of mixing of 2-methyl-2-propanol is highest, and only at 50°C corresponds to the order of maximum values of H^E.

The temperature dependence of excess enthalpies is relatively large for all three systems. For instance, H^E (25°C) = 957 J mol^{-1} and H^E (50°C) = 1 293 J mol^{-1} for 2-butanol and $x_B = 0.4$. If excess molar heat capacity c_P^E does not practically change in this system in the region of H^E maximum (13.3 J K^{-1} mol^{-1} at 30°C and 13.5 J K^{-1} mol^{-1} at 45°C), then c_P^E for the same concentration for 1-butanol is equal to 11.8 J K^{-1} mol^{-1} (30°C) and 13.3 J K^{-1} mol^{-1} (45°C).

Non-linearity of the temperature dependence of H^E for 2-methyl-2-propanol manifests itself most conspicuously in the region $x_B\langle 0.2, 0.5\rangle$. On the contrary, H^E changes only little with temperature already for $x_B > 0.7$ in the same system ($c_P^E \approx 4$ J K^{-1} mol^{-1}).

The quantitative judgement and interpretation of heats of mixing of all three alcohols with cyclohexane on the basis of some models of continuous association[2,3] will be a subject of a following paper in this Journal.

With regard to the above-mentioned importance of heats of mixing in theories of solutions, it is suitable that the corresponding data should be compiled as smoothed concentration and temperature dependences which would represent the experimental values with the accuracy comparable to the experimental error.

This requirement is especially difficult to meet in case of solutions of alcohols with nonpolar solvents where the shape of curves of mixing is expressively asymmetric. Even if today a number of correlation relations are known, not even great number of their adjustable parameters ensure a good-quality representation of experimental data.

On the basis of our previous works[26,27], the most suitable relation for C_4-alkanols with cyclohexane has proved to be that one known in the literature as the SSF equation[28]:

$$H^E/RT = x_B(1 - x_B) \sum_{j=1}^{p/2} A_{2j-1}/[x_B + (1 - x_B) A_{2j}]^2 . \qquad (1)$$

TABLE II

Systems cyclohexane(A)–C_4-alkanol(B). Values of constants in Eq. (1).

t, °C	A_1	A_2	A_3	A_4	A_5	A_6	$\bar{\delta}^a$	σ^b
				1-Butanol				
25	0·6063	0·6352	0·0121	0·0446			1·7	2·65
30	0·6414	0·6275	0·0126	0·0426			2·0	2·85
35	0·6803	0·6256	0·0149	0·0453			2·0	2·66
40	0·7292	0·6343	0·0179	0·0485			·· 2·1	2·71
45	0·7853	0·6511	0·0227	0·0539			2·1	3·25
50	0·8376	0·6452	0·0234	0·0526			3·3	4·40
				2-Butanol				
25	1·1140	0·7562	0·0129	0·0358			4·5	5·67
30	1·1857	0·7732	0·0176	0·0441			4·5	5·80
35	1·2658	0·7990	0·0249	0·0561			4·4	5·40
40	1·3253	0·8070	0·0289	0·0593			3·5	5·36
45	1·3867	0·8222	0·0372	0·0698			3·7	4·89
50	1·4591	0·8502	0·0496	0·0835			3·2	4·27
				2-Methyl-2-propanol				
30	1·5490	1·3360	0·0782	0·1414	0·0002	−0·0391	1·8	3·10
35	1·5190	1·3647	0·1106	0·1928	0·0050	0·0192	1·8	2·52
40	1·4563	1·3597	0·1388	0·2557	0·0179	0·0539	2·3	3·41
45	1·4161	1·4191	0·2034	0·3152	0·0241	0·0602	2·4	3·33
50	1·4474	1·1536	0·1183	0·1454			1·9	3·06

[a] Mean absolute deviation (J mol^{-1}), [b] standard deviation (J mol^{-1}).

The quantities A_{2j-1} and A_{2j} are the adjustable constants, p their number, $T(K)$ the temperature, R $(J\ K^{-1}\ mol^{-1})$ the gas constant and x_B the mole fraction of alcohol.

The constants in Eq. (1) were determined for all the systems and individual temperatures by nonlinear optimization on using the Newton–Raphson algorithm. Their number was established on the basis of statistical criterion of significance of difference of two variances (F-test)[26]. The values of constants together with mean absolute deviations (δ) and standard deviations (σ) are summarized in Table II. In the third and sixth columns of Table I, the differences (δ) are given between H^E values measured and calculated from Eq. (1).

On the basis of results obtained and on comparing with other correlation relations (e.g. the Redlich–Kister expansion as modified by McFall and coworkers[29] requires for the same σ as much as double number of constants than the SSF equation) the heats of mixing calculated from Eq. (1) can be considered, even in the region of low concentrations of C_4-alkanols, as comparable to the direct experimental data.

REFERENCES

1. Dolezalek F.: Z. Phys. Chem. *64*, 727 (1908).
2. Renon H., Prausnitz J. M.: Chem. Eng. Sci. *22*, 299, 891 (1967).
3. Liebermann E., Wilhelm E.: Monatsh. Chem. *106*, 389 (1975).
4. Nagata I.: J. Chem. Eng. Data *20*, 110 (1975).
5. Nagata I.: Z. Phys. Chem. (Leipzig) *259*, 1151 (1978).
6. Nagata I.: Z. Phys. Chem. (Wiesbaden) *107*, 39 (1977).
7. Nagata I.: Z. Phys. Chem. (Leipzig) *259*, 1109 (1978).
8. Nagata I., Kawamura Y.: Thermochim. Acta *34*, 43 (1979).
9. Ashraf F. A., Vera J. H.: Fluid Phase Equil. *4*, 211 (1980).
10. Nguyen T. H., Ratcliff G. A.: J. Chem. Eng. Data *20*, 256 (1975).
11. Abrams D. S., Prausnitz J. M.: AIChE J. *21*, 116 (1975).
12. Hanks R. W., Tan R. L., Christensen J. J.: Thermochim. Acta *27*, 9 (1978).
13. French H. T., Stokes R. H.: J. Phys. Chem. *85*, 3347 (1981).
14. Veselý F., Uchytil P., Zábranský M., Pick J.: This Journal *44*, 2869 (1979).
15. Veselý F., Pick J.: This Journal *34*, 1854 (1969).
16. Brown I., Fock W., Smith F.: J. Chem. Thermodyn. *1*, 273 (1969).
17. Timmermans J.: *Physico-Chemical Constants of Pure Organic Compounds*, Elsevier, Amsterdam 1950.
18. Geiseler G., Suehnel K., Quitzsch K.: Z. Phys. Chem. (Leipzig) *254*, 261 (1973).
19. Veselý F., Hynek V., Svoboda V., Holub R.: This Journal *39*, 355 (1974).
20. Majer V., Svoboda V., Hynek V., Pick J.: This Journal *43*, 1313 (1978).
21. Polák J., Murakami S., Lam V. T., Pflug H. D., Benson G. C.: Can. J. Chem. *48*, 2457 (1970).
22. Smirnova N. A., Kurtynina L. M.: Zh. Fiz. Khim. *43*, 1883 (1969).
23. Belousov V. P., Kurtynina L. M., Kozulyaev A. A.: Vest. Leningrad. Univ., Fiz., Khim. *10*, 163 (1971).

24. Sosnkowska-Kehiaian K., Récko W., Wóycicki W.: Bull. Acad. Pol. Sci., Ser. Sci. Chim. *14*, 475 (1966).
25. Kopp R., Quitzsch K.: Z. Phys. Chem. (Leipzig) *255*, 538 (1974).
26. Prchal M., Dohnal V., Veselý F.: This Journal *47*, 3171 (1982).
27. Prchal M., Dohnal V., Veselý F.: This Journal *48*, 1104 (1983).
28. Rogalski M., Malanowski S.: Fluid Phase Equil. *1*, 137 (1977).
29. McFall T. A., Post M. E., Christensen J. J., Izatt R. M.: J. Chem. Thermodyn. *13*, 441 (1981).

Translated by J. Linek.