(4) Desnoyers, J. E., de Visser, C., Perron, G., Picker, P., *J. Solution Chem.*, **5**, 605 (1976).
(5) Desnoyers, J. E., Jolicoeur, C., *Mod. Aspects Electrochem.*, **5**, 1 (1969).
(6) de Visser, C., Heuvelsland, W. J. M., Somsen, G., *J. Solution Chem.*, **4**, 311 (1975).
(7) de Visser, C., Perron, G., Desnoyers, J. E., *J. Am. Chem. Soc.*, submitted.
(8) de Visser, C., Somsen, G., *J. Phys. Chem.*, **78**, 1719 (1974).
(9) de Visser, C., Somsen, G., *Z. Phys. Chem.* (*Frankfurt am Main*), **92**, 159 (1974).
(10) de Visser, C., Somsen, G., *J. Chem. Soc., Faraday Trans. 1*, **69**, 1440 (1973).
(11) Fortier, J.-L., Leduc, P.-A., Desnoyers, J. E., *J. Solution Chem.*, **3**, 323 (1974).
(12) Fortier, J.-L., Simard, M. A., Unpublished results.
(13) Grolier, J.-P. E., Benson, G. C., Picker, P., *J. Chem. Eng. Data*, **20**, 243 (1975).
(14) Haly, A. R., Snaith, J. W., *Biopolymers*, **10**, 1681 (1971).
(15) Heuvelsland, W. J. M., Somsen, G., in preparation.
(16) Hoeve, C. A. J., Kakivaya, S. R., *J. Phys. Chem.*, **80**, 745 (1976).
(17) Kell, G. S., *J. Chem. Eng. Data*, **12**, 66 (1967).
(18) Kiyohara, O., Perron, G., Desnoyers, J. E., *Can. J. Chem.*, **53**, 3263 (1975).
(19) Millero, F., "Water and Aqueous Solutions: Structure, Thermodynamics and Transport Processes", Horne, R. A., Ed., Wiley-Interscience, New York, N.Y., 1972, Chapter 13.
(20) Millero, F. J., Ward, G. K., Lepple, F. K., Hoff, E. V., *J. Phys. Chem.*, **78**, 1636 (1974).
(21) Perron, G., Desrosiers, N., Desnoyers, J. E., *Can. J. Chem.*, **54**, 2163 (1976).
(22) Perron, G., de Visser, C., Desnoyers, J. E., *Can. J. Chem.*, submitted.
(23) Petersen, R. C., *J. Phys. Chem.*, **64**, 184 (1960).
(24) Picker, P., *Cancer Res. Devel.*, **7**, 11 (1974).
(25) Picker, P., Leduc, P.-A., Philip, P. R., Desnoyers, J. E., *J. Chem. Thermodyn.*, **3**, 631 (1971).
(26) Picker, P., Tremblay, E., Jolicoeur, C., *J. Solution Chem.*, **3**, 377 (1974).
(27) Prosen, E. J., Kilday, M. V., *J. Res. Natl. Bur. Stand., Sect. A*, **77**, 581 (1973).
(28) Redlich, O., Meyer, D. M., *Chem. Rev.*, **64**, 221 (1964).
(29) Rohdewald, P., Möldner, M., *J. Phys. Chem.*, **77**, 373 (1973).
(30) Saphon, S., Bittrich, H.-J., *Z. Phys. Chem.* (*Leipzig*), **252**, 113 (1973).
(31) Stimson, H. F., *Am. J. Phys.*, **23**, 614 (1955).
(32) Vaslow, F., *J. Phys. Chem.*, **70**, 2286 (1966).

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Heats of Mixing for the Ternary System Ethanol–1-Propanol–Cyclohexane at 25 °C

Isamu Nagata* and Kenji Kazuma
Department of Chemical Engineering, Kanazawa University, Kanazawa, 920, Japan

Heats of mixing are measured at 25 °C for the title ternary system and its two constituent binaries of alcohols and cyclohexane using a isothermal semicontinuous dilution calorimeter. Experimental data are satisfactorily correlated by associated solution models.

This paper presents the first issue of a series of measurements of heats of mixing for ternary liquid mixtures. Isothermal semicontinuous titration calorimeters have recently been described (*2, 4, 5, 8–10, 15*) that are especially suitable for measurements of enthalpies of mixing of liquid mixtures. Heats of mixing for the ethanol–1-propanol–cyclohexane and the binary ethanol–cyclohexane and 1-propanol–cyclohexane systems at 25 °C are presented using the Van Ness-type calorimeter.

Several methods are available in predicting heats of mixing for multicomponent mixtures from binary data. However, such predictions are mainly of empirical nature because solution theories, at the present time, do not allow quantitative predictions for strongly nonideal liquid mixtures. The method of Nagata (*3*) appears to be useful for a ternary system composed of two alcohols and saturated hydrocarbon. The application of this method to the ethanol–1-propanol–cyclohexane system is discussed.

Experimental Section

Materials. All materials used in this study were the reagent grade of Nakarai Chemicals, Ltd. Benzene was recrystallized three times. Cyclohexane was passed through a 1.2 m, 10 mm i.d. glass column packed with silica. The alcohols were fractionally distilled over drying materials: ethanol (calcium oxide), 1-propanol (anhydrous copper sulfate). Refractive indices were measured with a Shimadzu Pulfrich refractometer at 25 °C: benzene, 1.4879; cyclohexane, 1.4237; ethanol, 1.3594; 1-propanol, 1.3838.

Apparatus. The calorimeter was the same as that designed by Tanaka et al. (*9*) with the following features. (1) The wall inside the mixing vessel is kept free of any dampness from the bath water by using a mixing vessel of fixed dimensions. (2) Use of a flange-type lid to seal the mixing vessel makes the calorimeter simple because the calorimeter does not require a precise bore tube and it is easy to wash the calorimeter after each experimental run. Figure 1 shows a schematic diagram of the calorimeter. A 140-ml silvered Dewar flask has a strip window to make it possible to see the inside of the flask. Flask A is sealed by the Teflon plug B. One of the components to be mixed is weighed into the flask, all air being vent through the air vent R. The second component is stored in the feed bulb C of 70 ml capacity. A glass connecting line leads from the top of the feed bulb to a stainless steel hypodermic tube, which passes through the plug, and its open end is inserted in the small mercury-filled cup K. The feed component in the feed bulb C is stored over mercury, which is introduced into the bottom of the feed bulb through a glass tube leading to the mercury reservoir D. The cooling system attached to the Teflon plug B consists of the cooling module (Netsu Denshi Co., Type CP-1.4-17-10) M, the stainless steel heat sink N, and the copper cooling plate O, which is connected to the copper cooling rod P, which passes through the Teflon plug B into the mixing vessel. Silicone grease is introduced among those components to minimize thermal resistances. A stabilized dc supply powers the cooling module. The stirrer consists of the small Teflon-coated magnet H and the paddles G mounted on a stainless steel rod, which is supported by the stainless steel frame I.

The thermistor (Shibaura Denshi Co., Type NSLB, resistance at 25 °C is about 35 kΩ) S is mounted in a thin-walled brass tube

Table I. Smoothing Equations and Standard Deviations for the Benzene (1)–Cyclohexane (2) System at 25 °C

	Data source	H^E_{calcd} (J mol^{-1})	Standard deviation σ^a (J mol^{-1})
1	Murakami and Benson (*2*)	$x_1x_2[3203.40 - 157.93(x_2 - x_1) + 111.78(x_2 - x_1)^2 - 46.29(x_2 - x_1)^3]$	1.04
2	Stokes et al. (*8*)	$x_1x_2[3518.1 - 1041.1x_2 + 955.6x_2^2 - 313.4x_2^3]$	0.92
3	Tanaka et al. (*9*)	$x_1x_2[3200.51 - 180.95(x_2 - x_1) + 117.97(x_2 - x_1)^2 - 59.61(x_2 - x_1)^3]$	0.53
4	Touhara et al. (*10*)	$x_1x_2[3185.20 - 140.37(x_2 - x_1) + 156.98(x_2 - x_1)^2 - 74.85(x_2 - x_1)^3]$	1.38
	This work	$x_1x_2[3200.34 - 162.91(x_2 - x_1) + 102.42(x_2 - x_1)^2 - 58.04(x_2 - x_1)^3]$	0.74

[a] $\sigma = \{\sum_n(H^E_{exptl} - H^E_{calcd})^2/n\}^{1/2}$, where n = number of experimental points.

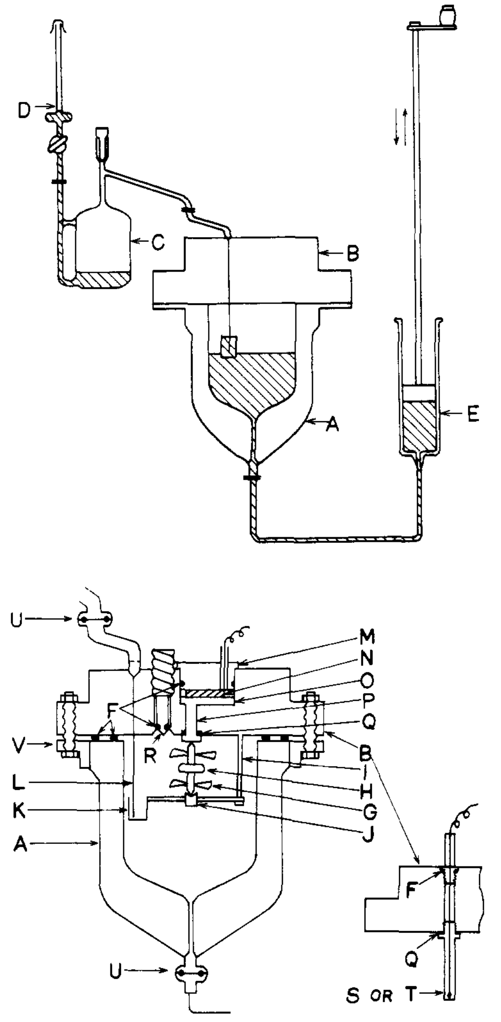

Figure 1. Schematic diagram of calorimeter: A, Dewar flask; B, Teflon plug; C, feed bulb for second component; D, mercury reservoir; E, piston burette; F, Viton O-ring; G, stirrer paddle; H, Teflon-coated magnet; I, stainless stell stirrer frame; J, stainless steel stirrer support; K, stainless steel mercury cup; L, feed tube (hypodermic syringe); M, stainless steel heat sink; N, cooling module; O, copper cooling plate; P, copper cooling rod; Q, Teflon washer; R, air vent, sealed with Bakelite screw and Teflon needle; S, thermistor (35 KΩ); T, heater (52 Ω manganin wire heater) in brass tube; U, glass or Teflon joint; V, brass collar.

which passes through the plug B. It is connected to a Wheatstone bridge circuit which includes a dc amplifier (Ohkura Electric Co., Model AM1001B) and a recorder (Yokogawa Electric Co., Model LER 12A). The heater (resistance is about 52 Ω) T, which is a manganin wire heater wound on a glass capillary, is mounted in a thin-walled brass tube.

The temperature of the solution within the mixing vessel is maintained by the cooling module within ±0.001 °C for an extended period of time after the calorimeter is immersed in a thermostated water bath. A more detailed description of the isothermal dilution calorimeter and operating procedures is given elsewhere (*16*).

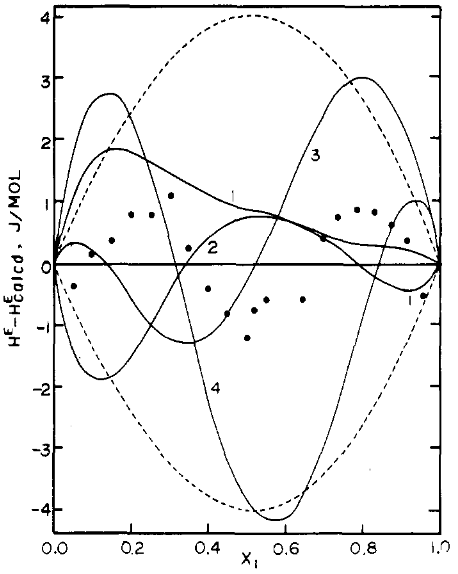

Figure 2. Comparison of heats of mixing for benzene(1)–cyclohexane(2) system at 25 °C: ●, deviations of our experimental points; 1, data of Murakami and Benson (*2*); 2, data of Stokes et al. (*8*); 3, data of Tanaka et al. (*9*); 4, data of Touhara et al. (*10*); dashed curves represent ±0.5% deviation.

Results

The heats of mixing of the benzene-cyclohexane system at 25 °C were measured to test the performance of the calorimeter. Figure 2 shows a comparison of data collected for the benzene-cyclohexane, illustrating the deviations of H^E of previous investigations from the curve by which the present data were correlated. The experimental data points were fitted by the Redlich-Kister equation having four constants. All the smoothing equations and the standard deviations given by the respective authors are summarized in Table I. The points in Figure 2 represent the deviations of our experimental results from the smoothed values obtained by the Redlich-Kister equation. The solid curves indicate the deviations of the smoothed results of the other authors from our smoothed data. All sets of experimental data remain almost within a ±0.5% range. Our results for the ethanol-cyclohexane system agree closely with those of Stokes and Burfitt (*7*) as shown in Figure 3. Figure 4 illustrates that there is a systematic deviation between two sets of data for the 1-propanol-cyclohexane system. Our results are slightly higher than the data of Vesely and Pick (*14*). Since two sets of data for the ethanol-1-propanol system reported in the literature (*4*, *5*) agree closely with each other, we did not attempt any additional run for this system. Table II lists the experimental results for the three binary systems. Ternary mixtures were formed by addition of 1-propanol to a binary mixture of ethanol and cyclohexane. Three runs constituting 93 data points were observed for the ternary system. They are given in Table III.

Data Reduction

Binary Systems. Nonathermal associated solution models based on the Flory-Huggins theory consist of the sum of

Table II. Heats of Mixing at 25 °C for Binary Systems, J mol^{-1}

Benzene (1)-cyclohexane (2)		Ethanol (1)-cyclohexane (2)		1-Propanol (1)-cyclohexane (2)	
x_1	H^E	x_1	H^E	x_1	H^E
0.0493	144.7	0.0352	274.5	0.0194	227.9
0.0997	278.9	0.1027	426.0	0.0655	373.4
0.1499	397.5	0.1896	537.5	0.1522	516.2
0.2001	501.3	0.2879	607.1	0.2496	597.9
0.2506	590.0	0.3381	627.1	0.3396	622.9
0.3018	664.5	0.3883	638.3	0.4173	614.1
0.3517	720.6	0.4355	642.2	0.4818	598.5
0.4007	761.2	0.4823	638.4	0.5365	558.6
0.4507	787.7	0.5267	629.0	0.5858	523.5
0.5017	799.0	0.5684	614.5	0.6034	509.0
0.5179	799.8	0.6865	538.3	0.6344	482.3
0.5496	795.8	0.7066	520.0	0.6780	441.4
0.5550	794.2	0.7324	494.3	0.7290	387.5
0.5970	778.4	0.7599	464.6	0.7743	334.3
0.6002	776.1	0.7898	426.7	0.8226	272.7
0.6435	746.6	0.8196	384.5	0.8688	209.0
0.6439	746.8	0.8611	316.4	0.9194	133.5
0.6907	701.2	0.9015	239.7	0.9620	64.6
0.7373	641.2	0.9407	154.6		
0.7829	567.8	0.9779	60.3		
0.8280	480.4				
0.8724	379.4				
0.9158	265.6				
0.9581	139.2				

Table III. Heats of Mixing at 25 °C for the Ethanol(1)-1-Propanol(2)-Cyclohexane(3) System, J mol^{-1}

$x_1 = 0.2493$ $x_3 = 0.7507$			$x_1 = 0.4970$ $x_3 = 0.5030$			$x_1 = 0.7434$ $x_3 = 0.2566$		
x_1	x_2	H^E	x_1	x_2	H^E	x_1	x_2	H^E
0.2358	0.0544	608.2	0.4656	0.0630	622.3	0.6915	0.0698	453.7
0.2216	0.1111	623.8	0.4505	0.0934	613.5	0.6592	0.1132	435.6
0.2079	0.1660	629.0	0.4185	0.1579	591.2	0.6218	0.1635	413.9
0.1951	0.2174	626.9	0.3853	0.2247	563.6	0.5847	0.2135	391.7
0.1838	0.2626	619.5	0.3623	0.2710	541.6	0.5495	0.2609	370.2
0.1717	0.3112	606.0	0.3382	0.3194	516.9	0.5154	0.3066	349.0
0.1592	0.3616	586.9	0.3198	0.3602	494.6	0.4805	0.3536	327.0
0.1378	0.4473	543.1	0.2951	0.4061	467.8	0.4445	0.4021	303.7
0.1282	0.4856	519.3	0.2811	0.4343	450.5	0.4197	0.4354	287.6
0.1203	0.5176	497.7	0.2660	0.4647	431.1	0.3944	0.4694	270.9
0.1129	0.5470	476.5	0.2469	0.5032	405.5	0.3762	0.4940	258.7
0.1112	0.5539	471.3	0.2454	0.5061	403.8	0.3481	0.5318	239.8
0.1148	0.5595	481.6	0.2328	0.5316	385.7	0.3236	0.5647	223.4
0.1068	0.5717	457.1	0.2161	0.5651	360.0	0.2894	0.6107	200.2
0.0997	0.6003	434.0	0.2007	0.5961	339.4	0.2649	0.6437	183.5
0.0935	0.6249	413.4	0.1859	0.6260	317.0	0.2458	0.6693	170.5
0.0885	0.6452	395.8	0.1727	0.6525	296.8	0.2273	0.6943	157.5
0.0839	0.6633	379.5	0.1620	0.6740	280.3	0.2137	0.7126	148.5
0.0795	0.6809	363.3	0.1523	0.6935	265.1	0.2096	0.7181	145.7
0.0754	0.6977	347.4	0.1455	0.7073	253.7	0.2040	0.7256	141.9
0.0727	0.7083	337.4	0.1434	0.7114	250.7	0.1904	0.7439	132.5
0.0697	0.7204	325.6	0.1378	0.7228	241.8	0.1722	0.7684	120.0
0.0661	0.7349	311.2	0.1343	0.7298	235.5	0.1564	0.7896	109.1
0.0647	0.7406	305.1	0.1256	0.7472	221.2	0.1443	0.8059	100.8
0.0625	0.7493	296.6	0.1180	0.7626	208.4	0.1342	0.8195	93.8
0.0602	0.7584	287.2	0.1119	0.7749	198.2	0.1262	0.8302	88.3
0.0578	0.7682	277.1	0.1067	0.7853	189.4	0.1227	0.8350	85.7
0.0583	0.7663	278.4	0.1029	0.7930	183.1			
0.0528	0.7883	255.1	0.0992	0.8004	176.8			
0.0471	0.8112	230.0	0.0952	0.8084	170.1			
0.0426	0.8292	209.9	0.0911	0.8166	163.1			
0.0388	0.8443	192.7						
0.0355	0.8576	177.4						
0.0328	0.8685	164.6						

chemical and physical interaction contributions. The models are the Mecke-Kempter and the Kretschmer-Wiebe equations which differ from each other in the definition of the association constant to describe a chemical contribution term.

The nonathermal Mecke-Kempter equation for heats of mixing described by Treszczanowicz et al. (*11-13*) may be summarized by the following

$$H^E = -h_a x_a[\ln(1 + K\phi_a)/K\phi_a - \ln(1 + K)/K] + \beta(x_a v_a + x_h v_h)\phi_a\phi_h \qquad (1)$$

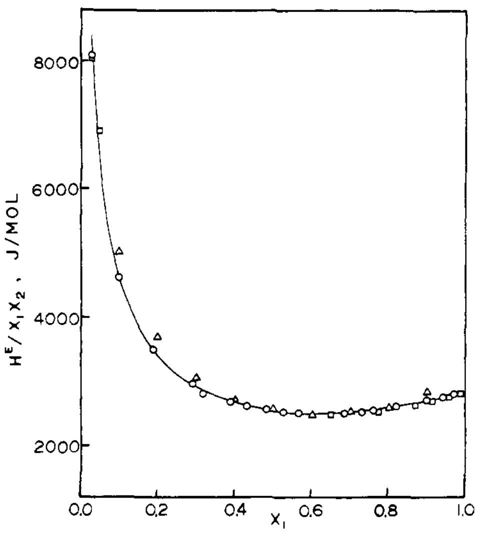

Figure 3. Heats of mixing for the ethanol (1)–cyclohexane(2) system at 25 °C: ○, this work; □, Stokes and Burfitt (*7*); △ Vesely and Pick (*14*).

Table IV. Association Constants of Alcohols at 50 °C

Compound	*K* M[a]	 *K*[b]
Methanol	450	450
Ethanol	190	190
1-Propanol	110	90
1-Butanol	95	80
1-Pentanol	88	72
1-Hexanol	85	66
1-Octanol	72	58
1-Decanol	66	54

[a] M = Mecke-Kempter equation. [b] K = Kretschmer-Wiebe equation.

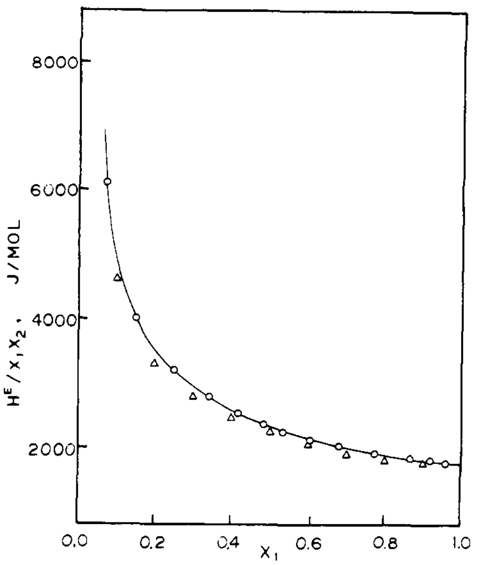

Figure 4. Heats of mixing for the 1-propanol(1)–cyclohexane(2) system at 25 °C: ○, this work; △, Vesely and Pick (*14*).

The van't Hoff equation characterizes a relation between the chemical equilibrium constant K and the enthalpy of a hydrogen bond formation h_a.

$$\frac{\mathrm{d}\ln K}{\mathrm{d}(1/T)} = -\frac{h_a}{R} \tag{2}$$

The value of -6 kcal mol^{-1} for h_a was assumed to be temperature independent. Table IV presents the values of the chemical equilibrium constants for pure alcohols. Calculated results for 21 binary alcohol-saturated hydrocarbon systems are listed in Table V together with the results obtained by the Kretschmer–Wiebe equation which were cited from a previous paper (*3*). Heats of mixing for alcohol–alcohol systems are represented

Table V. Calculated Results for Binary Alcohol-Saturated Hydrocarbon Mixtures with Mecke–Kempter Equation

System	Temp, °C	No. of data points	β (cal cm^{-3})	Abs arith mean dev (cal mol^{-1}) M[a]	 K[b]	Data source
Ethanol–cyclohexane	25	20	4.894	0.80	3.73	This work
Ethanol–1-hexane	25	14	3.080	1.27	3.39	1
	35	9	3.287	2.36	3.76	
	45	8	3.680	4.82	6.68	
Ethanol–1-heptane	20	13	3.184	1.46	5.21	5
	25	12	3.202	1.87	5.00	
	30	18	3.240	1.16	4.88	
Ethanol–1-octane	20	12	3.145	3.86	7.58	5
	25	12	3.205	2.39	6.01	
	30	15	3.268	2.22	5.66	
1-Propanol–cyclohexane	25	18	2.872	3.18	1.05	This work
	25	9	2.688	2.52	1.74	14
1-Propanol–1-hexane	25	8	2.025	1.90	3.03	1
	35	8	2.211	2.32	0.59	
	45	9	2.507	2.19	4.98	
1-Propanol–1-heptane	20	12	1.834	3.10	4.28	5
	25	13	1.873	2.72	3.63	
	30	13	1.886	2.51	2.79	
1-Propanol–1-octane	20	12	1.971	2.78	5.04	5
	25	13	1.936	3.23	4.83	
	30	14	1.898	3.80	5.18	
1-Propanol–1-tetradecane	20	14	2.104	11.87	14.79	5
	25	14	2.099	10.99	12.22	
	30	15	2.051	9.55	10.17	
1-Butanol–1-hexane	25	8	1.475	3.23	1.96	1
	35	9	1.693	3.22	2.61	
	45	8	1.985	2.57	5.28	

Table V Continued

System	Temp, °C	No. of data points	β (cal cm^{-3})	Abs arith mean dev (cal mol^{-1}) M[a]	K[b]	Data source
1-Pentanol–1-heptane	20	13	1.404	4.06	3.90	5
	25	14	1.490	4.34	3.74	
	30	14	1.484	3.68	3.11	
1-Pentanol–1-octane	20	12	1.663	3.85	5.34	5
	25	13	1.583	4.15	3.81	
	30	14	1.501	4.66	3.60	
1-Pentanol–1-tetradecane	20	14	2.107	4.95	6.44	5
	25	13	1.985	5.78	5.01	
	30	13	1.847	6.23	5.92	
1-Hexanol–1-hexane	25	9	1.299	3.31	3.85	1
	35	9	1.373	2.26	2.58	
	45	8	1.512	2.51	2.99	
1-Octanol–1-hexane	25	8	1.068	2.19	3.17	1
	35	7	1.148	1.87	3.67	
	45	8	1.321	2.18	5.91	
1-Octane–1-heptane	20	12	0.997	2.86	3.95	5
	25	11	1.082	1.90	3.51	
	30	13	1.138	2.39	3.89	
1-Octane–1-octane	20	14	1.103	2.89	4.04	5
	25	14	1.107	2.49	3.43	
	30	13	1.085	2.52	4.79	
1-Octanol–1-tetradecane	20	13	1.327	4.61	6.71	5
	25	14	1.352	3.90	6.08	
	30	14	1.344	3.19	5.99	
1-Decanol–1-heptane	20	13	1.119	1.97	3.81	5
	25	14	1.038	1.71	3.55	
	30	14	0.940	2.44	4.65	
1-Decanol–1-octane	20	13	0.964	1.34	3.00	5
	25	14	0.912	1.50	3.00	
	30	14	0.850	2.30	4.37	
1-Decanol–1-tetradecane	20	14	1.165	2.98	5.49	5
	25	14	1.143	2.86	5.55	
	30	14	1.093	3.30	6.02	

[a] M = Mecke–Kemper equation. [b] K = Kretschmer–Wiebe equation.

Table VI. Predicted Results for Ternary Alcohol–Alcohol-Saturated Hydrocarbon Systems at 25 °C

System	No. of data points	Percentage deviation Δ,[a] % This work I[b]	II[c]	III[d]	IV[e]	Nagata I	II	III	IV	Data source
Ethanol–1-propanol–cyclohexane	30	2.71	2.84	3.76	3.42	2.33	2.98	2.13	1.80	This work
Ethanol–1-propanol–1-heptane	32	1.30	1.58	1.66	1.42	4.89	5.44	5.38	4.08	6
Ethanol–1-pentanol–1-heptane	35	3.54	3.47	3.38	4.11	3.65	4.30	4.93	4.98	6
Ethanol–1-octanol–1-heptane	30	3.13	2.89	2.66	3.05	5.31	6.43	4.86	3.00	6
Ethanol–1-decanol–1-heptane	30	3.89	3.48	2.48	3.17	4.82	5.84	4.26	2.45	6
1-Propanol–1-pentanol–1-heptane	30	5.43	5.45	5.15	5.54	1.83	1.84	2.19	1.81	6
1-Propanol–1-octanol–1-heptane	35	5.24	5.27	5.02	5.40	3.50	3.66	3.26	3.08	6
1-Propanol–1-decanol–1-heptane	30	6.79	6.73	6.10	6.39	4.87	4.99	4.49	4.53	6
Ethanol–1-propanol–1-octane	30	3.64	3.25	3.65	2.58	8.50	8.83	9.18	7.85	6
Ethanol–1-pentanol–1-octane	30	3.16	3.07	3.46	3.77	5.78	6.40	6.86	5.94	6
Ethanol–1-octanol–1-octane	30	4.03	3.43	3.25	2.47	7.16	8.30	6.69	4.03	6
Ethanol–1-decanol–1-octane	30	4.48	3.98	3.20	3.00	6.46	7.50	5.86	3.22	6
1-Propanol–1-pentanol–1-octane	37	2.36	2.37	2.22	2.43	2.99	3.00	3.34	2.95	6
1-Propanol–1-octanol–1-octane	30	4.25	4.18	3.62	4.05	4.16	4.35	4.22	3.60	6
1-Propanol–1-decanol–1-octane	30	6.35	6.25	5.67	6.09	4.87	5.04	4.65	4.38	6
1-Propanol–1-pentanol–1-tetradecane	30	7.86	7.82	7.67	8.04	11.37	11.40	11.60	11.28	6
1-Propanol–1-octanol–1-tetradecane	35	6.47	6.27	5.66	6.31	9.11	9.33	9.28	8.46	6
1-Propanol–1-decanol–1-tetradecane	30	7.22	7.02	6.34	7.12	9.86	10.09	10.10	9.16	6
Total average		4.55	4.41	4.16	4.36	5.08	6.10	5.74	4.81	

[a] $\Delta = (100/n)\sum_n\{|H^E_{\text{exptl}} - H^E_{\text{calcd}}|/H^E_{\text{exptl}}\}$, where n = no. of experimental points. [b] I, $\bar{K} = K_a\bar{x}_a^2 + 2K_a^{1/2}K_b^{1/2}\bar{x}_a\bar{x}_b + K_b\bar{x}_b^2$. [c] II, $\bar{K} = K_a\bar{x}_a + K_b\bar{x}_b$. [d] III, $\bar{K} = K_a\bar{x}_a^2 + 2\bar{x}_a\bar{x}_b/(\bar{x}_a/K_a + \bar{x}_b/K_b) + K_b\bar{x}_b^2$. [e] IV, $\bar{K} = 1/(\bar{x}_aK_a + \bar{x}_bK_b)$, where $\bar{x}_a = x_a/(x_a + x_b)$ and $\bar{x}_b = x_b/(x_a + x_b)$.

by the Scatchard–Hildebrand equation (β = 0.286 cal cm^{-3} for ethanol–1-propanol at 25 °C). A survey of Table V suggests that in most cases the Mecke–Kempter equation gives better results than the Kretschmer–Wiebe equation does. The same thing was confirmed by Treszczanowicz et al. (*12, 13*), although they used the values of K and h_a different from those given in this work.

Ternary Systems. Following an empirical approach proposed by Nagata (*4*) to predict heats of mixing for ternary alcohol–

alcohol-saturated hydrocarbon systems using the Kretschmer–Wiebe equation, we may derive an alternative equation based on the Mecke–Kempter equation.

$$H^E = -h_a x_{ab}[\ln(1 + \bar{K}\bar{\phi}_{ab})/\bar{K}\bar{\phi}_{ab} - \ln(1 + \bar{K})/\bar{K}] + (\beta_{ab}\phi_a\phi_b + \beta_{ah}\phi_a\phi_h + \beta_{bh}\phi_b\phi_h)(x_a v_a + x_b v_b + x_h v_h) \quad (3)$$

where $\bar{\phi}_{ab} = 1 - \phi_h$, $x_{ab} = 1 - x_h$, and $\bar{K}$ is estimated by four methods.

$$\text{I} \quad \bar{K} = K_a \bar{x}_a^2 + 2\sqrt{K_a K_b}\bar{x}_a \bar{x}_b + K_b \bar{x}_b^2 \quad (4)$$

$$\text{II} \quad \bar{K} = K_a \bar{x}_a + K_b \bar{x}_b \quad (5)$$

$$\text{III} \quad \bar{K} = K_a \bar{x}_a^2 + 2\bar{x}_a \bar{x}_b/(\bar{x}_a/K_a + \bar{x}_b/K_b) + K_b \bar{x}_b^2 \quad (6)$$

$$\text{IV} \quad \bar{K} = 1/(\bar{x}_a/K_a + \bar{x}_b/K_b) \quad (7)$$

where $\bar{x}_a = x_a/(x_a + x_b)$ and $\bar{x}_b = x_b/(x_a + x_b)$. Ternary heats of mixing of Ramalho and Ruel (*6*) for 17 systems were correlated by using the parameters obtained from their constituent binary data. Available data to be predicted for ethanol–1-propanol–cyclohexane were limited to 30 points which were selected at random over the composition range. Table VI includes the percentage relative deviations of predicted values from experimental data, indicating that an empirically modified version of the Mecke–Kempter equation gives slightly better results than does that of the Kretschmer–Wiebe equation. The predicted results based on the Mecke–Kempter equation are essentially not concerned with $\bar{K}$ values estimated by various methods.

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Glossary

h_a	enthalpy of formation of a hydrogen bond, −6.0 kcal mol^{-1}
H^E	heat of mixing, cal mol^{-1}
$\underline{K}$	chemical equilibrium constant of pure alcohol
$\bar{K}$	chemical equilibrium constant of pseudo-single alcohol
R	gas constant
T	temperature, K
v	liquid molar volume of pure component, ml mol^{-1}
x	liquid mole fraction
$\bar{x}_a$	$x_a/(x_a + x_b)$

Greek Letters

β	physical interaction parameter, cal cm^{-3}
ϕ	volume fraction
$\bar{\phi}$	volume fraction of pseudo-single alcohol

Subscripts

a,b	alcohols
ab	pseudo-single alcohol
h	hydrocarbon

Literature Cited

(1) Brown, I., Fock, W., Smith, F., *Aust. J. Chem.*, **17,** 1106 (1964).
(2) Murakami, S., Benson, G. C., *J. Chem. Thermodyn.*, **1,** 559 (1969).
(3) Nagata, I., *J. Chem. Eng. Data*, **20,** 110 (1975).
(4) Pflug, H. D., Pope, A. F., Benson, G. C., *J. Chem. Eng. Data*, **13,** 408 (1968).
(5) Ramalho, R. S., Ruel, M., *Can. J. Chem. Eng.*, **46,** 456 (1968).
(6) Ramalho, R. S., Ruel, M., *Can. J. Chem. Eng.*, **46,** 467 (1968).
(7) Stokes, R. H., Burfitt, C., *J. Chem. Thermodyn.*, **5,** 623 (1973).
(8) Stokes, R. H., Marsh, K. N., Tomlin, R. P., *J. Chem. Thermodyn.*, **1,** 211 (1969).
(9) Tanaka, R., Murakami, S., Fujishiro, R., *Bull. Chem. Soc. Jpn.*, **45,** 2107 (1972).
(10) Touhara, H., Ikeda, M., Nakanishi, K., Watanabe, N., *J. Chem. Thermodyn.*, **7,** 887 (1975).
(11) Treszczanowicz, A., *Bull. Acad. Poln. Sci., Ser. Sci. Chim.*, **21,** 189 (1973).
(12) Treszczanowicz, A., Treszczanowicz, T., Rogalski, M., Paper presented at the 3d International Conference on Chemical Thermodynamics, Baden, 1973, p 18.
(13) Treszczanowicz, A., Treszczanowicz, T., ref 12, p 11.
(14) Vesely, F., Pick, J., *Collect. Czech. Chem. Commun.*, **32,** 4134 (1967).
(15) Winterhalter, D. R., Van Ness, H. C., *J. Chem. Eng. Data*, **11,** 189 (1966).
(16) Winterhalter, D. R., Ph.D. Thesis, Rensselaer Polytechnic Institute, 1965.

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