Heats of Mixing and Excess Thermodynamic Properties at 25°C. of Binary Systems of Methanol, Ethyl Alcohol, 1-Propanol, and 2-Propanol with Ethyl Acetate

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A satisfactory design method for extractive and azeotropic distillation columns should include enthalpy balances on each plate to allow calculation of the quantity of both liquid and vapor leaving and entering the plate. Colburn (*3*) brought out clearly in the case of *n*-butane–isobutene separation using furfural as the extracting agent, the importance of taking into account the heat effects produced on mixing the components and showed that approximately 30% error occurs in the net heat evolved. Neglect of this large quantity in design obviously results in considerable uncertainty in operation of the tower. However, a search into the literature reveals that there are few data on heat of mixing and that this subject has not been investigated to a degree comparable to that of vapor-liquid equilibria. In many cases the reported data form a small fraction of what is actually required for design purposes.

Excess thermodynamic properties, which are expressed relative to ideal behavior of a system, can be easily and accurately determined from vapor-liquid equilibrium measurements. These properties reveal the extent of departure of a system from ideal behavior and, more important, the degree of association or dissociation of a component in a particular mixture.

The present investigation was conducted to determine experimentally the heat of mixing of the binary systems of methanol, ethyl alcohol, 1-propanol, and 2-propanol with ethyl acetate in a new type of calorimeter which was initially tested with methanol-benzene mixtures and found to give good results. Also, it was proposed to calculate the excess thermodynamic properties of the four binary systems of alcohols with ethyl acetate from the smoothed vapor-liquid equilibrium data.

MATERIALS

Benzene of the following properties was used without further purification.

Boiling point, °C.	80.1
Density$^{25/4}$, grams per cc.	0.87374
Refractive/Ind, = n_D^{25}	1.49806

The methods of purification and the physical properties of methanol, ethyl alcohol, 1-propanol, 2-propanol, and ethyl acetate have been described (*6*).

APPARATUS

A good review of various calorimeters was given by Weissberger (*11*). In 1952 Scatchard, Ticknor, Goates, and McCartney (*8*) described a very simple calorimeter which consists essentially of a circular tube provided with two wells: one for the thermistor, and the other for the heater. The two liquids, for which the heat of mixing is to be determined, are separated by a quantity of mercury in the tube. The whole assembly is then placed in a large Dewar flask and rotated through an angle of 270° either manually or mechanically. Mercury in the calorimeter serves as an effective stirring medium. This type of calorimeter has the disadvantage of a constant exchange of heat between the calorimeter and the ambient air in the large Dewar flask for which it is necessary to apply a correction. This correction varied as much as 8 to 20% of the total heat of mixing in the experiments of Scatchard and others. In 1953, Tsao and Smith (*10*) described another calorimeter, some features of which were modified and used in this work.

A semisectional view of the calorimeter in full size and a line diagram of the various connections are shown in Figures 1 and 2. *A* is a special Dewar flask made of borosilicate glass and was ground at the top to fit a ground-glass stopper, *B*. The capacity of the calorimeter is about 140 ml. It was heavily silvered both inside and outside and is almost flat, instead of hemispherical, at the inner bottom to avoid the formation of dead pockets when liquids

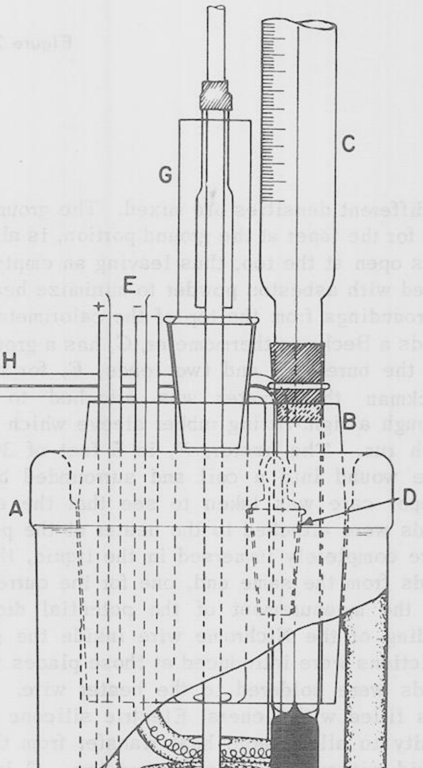

Figure 1. Semisectional view of calorimeter

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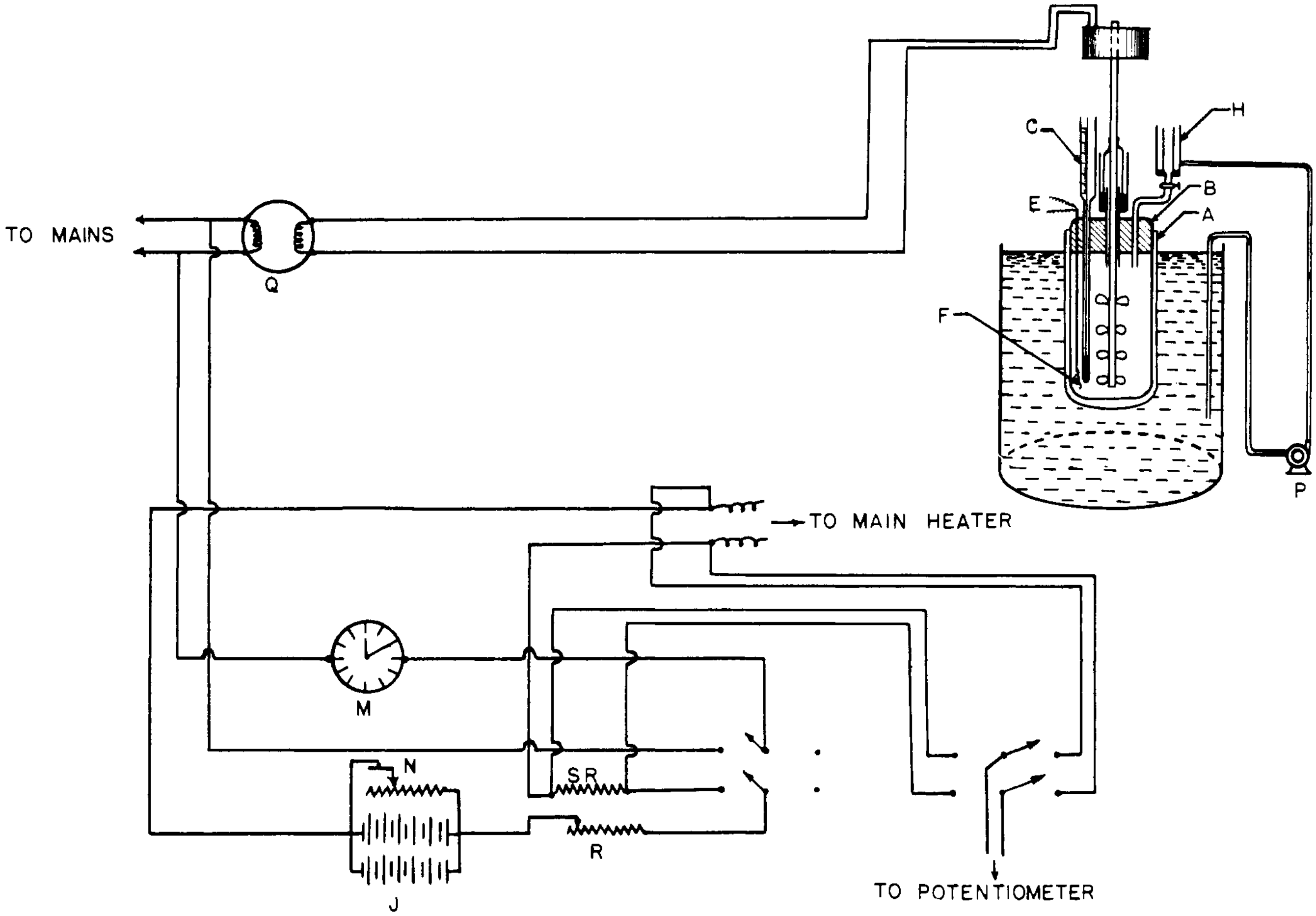

Figure 2. Line diagram of various connections to calorimeter

of different densities are mixed. The ground-glass stopper, but for the taper at the ground portion, is almost cylindrical. It is open at the top, thus leaving an empty space which is filled with asbestos powder to minimize heat transfer to the surroundings from the top of the calorimeter. This stopper holds a Beckman thermometer, *C*, has a ground-glass joint, *D* for the buret, *H*, and two leads, *E*, for the heater. The Beckman thermometer was attached to the calorimeter through a tight-fitting rubber sleeve which was changed for each run. The heater, *F*, is 5 feet of 30-gage Nichrome wire wound into a coil and surrounded by a glass tube. Proper care was taken to see that the electrical copper leads were attached to the heater at the points where they were completely immersed in the liquid, thus avoiding two leads from the same end, one for the current and the other for the measurement of the potential drop. To prevent sliding of the Nichrome wire inside the glass tube, constrictions were introduced at those places where the copper leads were soldered to the heater wire. The glass coil was filled with General Electric silicone oil of light viscosity to allow rapid heat transfer from the heater to the liquid without appreciable time lag. *G* is a glass stirrer with three paddles of the same size, spaced at approximately 0.5-inch intervals, and another at the entrance of the stirrer shaft into the calorimeter. The bottom paddle was adjusted to about 0.25 inch from the bottom of the Dewar flask. To prevent vapor loss through the stirrer shaft, the standard type of mercury seal was provided. The stirrer was rotated by a small motor, and the speed was controlled by means of a powerstat.

H is a jacketed 50.0-ml. borosilicate glass buret certified by the National Bureau of Standards. Water from a constant temperature water bath maintained at 25° ± 0.01°C. was circulated by a midget rotary pump.

The calorimeter was mounted on a rectangular framework of ⅝-inch steel rods and the Dewar flask rested in a brass cup contoured to the shape of the bottom of the Dewar. The calorimeter was clamped at the top to the framework to prevent any vibrations during stirring.

The current to the heating coil was supplied by two 6-volt batteries, *J*, arranged in series, including a rheostat in the circuit. The potential drop across the heating coil was measured with a standard potentiometric circuit using a Leeds & Northrup Type K-1 potentiometer. The current passing through the heater was measured by noting the potential drop across a standard manganin resistor of 0.01 ohm. These two voltage drops were measured with the same potentiometer by making connections through a double-throw switch. This allowed readings to be taken quickly.

The working current to the potentiometer was supplied through a rheostat in the circuit by two 3-volt dry battery cells.

The time was measured by an electric stopwatch, *M*, which was synchronized with the heater circuit.

N, a dummy resistor, was used to discharge the batteries for an hour or so before a run, so that they would come to a constant voltage.

TECHNIQUE OF MEASUREMENT

The calorimeter was checked by measuring the heats of mixing of methanol-benzene mixtures. Data on this system were reported by Wolf, Pahlke, and Wehage (*14*) at 20°C.; Williams, Rosenberg, and Rothenberg (*12*) at 20°C.; Scatchard, Ticknor, Goates, and McCartney (*8*) at 20°C.; and Tsao and Smith (*10*) at 25°C.

About 70.0 ml. of one of the components were introduced from a calibrated buret into the special Dewar flask and the second component was placed in the jacketed buret. The whole assembly was placed in a constant temperature bath and water from this bath was circulated through the jacket of the buret. The liquid in the buret was allowed to attain the temperature of the bath for 1 to 1.5 hours. During this period, the contents of the buret were frequently stirred by means of a long copper rod, the end of which was bent into a loop of such diameter as to pass freely into the buret. At the end of this period, the temperature was recorded by a thermometer accurate within 0.1°C. The contents of the Dewar flask were next brought to this temperature by the supply of current to the heater. When both the components were at the same temperature, a known amount of the component in the buret was admitted into the Dewar flask and the drop or rise in temperature was carefully noted by means of the Beckman thermometer, which could be read with a magnifying lens to 0.005°C. It was, however, not necessary to know the final temperature using the technique employed in this investigation. Next the heater circuit was turned on and the stop watch was started at the same time. The rate of heating was so set in the beginning that there was 0.10° C. rise for every minute. The power input to the heater was calculated after noting the current passing through the heater by measuring the voltage drop across the standard resistor, the voltage drop across the heater itself, and the total time required to bring the contents to the initial temperature. During the course of a run, about four to five readings were taken after each successive addition of the component from the buret. The speed of the stirrer was observed to be fairly constant at 250 to 300 r.p.m., a speed at which thorough mixing was produced without an appreciable effect on temperature. The heating current was fairly constant as evidenced by the constancy in the voltage drop across the standard resistor. The variation in the resistances of the heater wire was negligible over a temperature range of 2° to 3°C.

The maximum error resulting from vaporization and condensation effects and in the measurement of experimental heat of mixing data was estimated as follows:

Vaporization-Condensation Effects

Vapor space volume in calorimeter = 60 ml.

Assumptions

1. Activity coefficients from 40°C. data can be used at 25°C. for computation of vaporization loss
2. Equilibrium between vapor and liquid

Calculation

1. Calculate moles of component 1 in air space above liquid at start
2. Calculate moles of component 2 in vapor space above liquid after component 2 was added and equilibrium reached
3. Calculate heat effect caused by vaporization of the quantity of component 2
4. Calculate heat effect caused by condensation of the displaced quantity of component 1
5. Compute the net heat effect and the per cent error. For methanol-ethyl acetate it was found to be 0.8% (Run III)

Evaluation of Measurement Errors

Voltage measurement	0.2%
Resistance measurement	0.2%
Time measurement	Negligible
Temperature measurement liquid from buret	0.25%
Energy input, stirer	0.20%
Mass measurement	0.50%
Heat transfer to surroundings	Negligible
Total % measurement	1.35%
Total of vaporization and measurement errors about	2.35% maximum

CALCULATIONS

Heat of Mixing. The heat of mixing was calculated using the following equation:

$$\delta H^M_X = \frac{(V)\,(V_s)\,(t)}{(R_s)\,(4.1840)\,(n)} \tag{1}$$

where

ΔH^M_X = integral heat of mixing, calories per mole
V = potential drop across heater, volts
V_S = potential drop across standard resistor, volts
R_S = resistance of standard resistor, ohms
n = total number of moles of mixture
t = time, seconds

Excess Thermodynamic Properties. The following method was adopted after a number of other unsuccessful attempts to calculate the excess thermodynamic properties from vapor-liquid equilibrium data. The experimental and calculated values for heat of mixing agree with each other within limits of experimental accuracy of the heat of mixing measurements.

A preliminary smoothing of the activity coefficient values was made using one of the solutions of Gibbs-Duhem equation. The variation of the activity coefficient with composition was such that the van Laar equations could be employed to represent the experimental data, despite the fact that van Laar made restrictive assumptions in deriving the equations. As pointed out by Wohl (*13*) and Carlson and Colburn (*2*), the constants as rearranged by the latter workers are regarded as mere empirical constants without attaching any physical significance to them. Values of *A* and *B* reported earlier (*6*) were used to calculate the activity coefficients at even values of composition. This was repeated for each isothermal run.

Since excess free energy can be expressed by Equations 2 and 5,

$$\Delta G^E_X = 2.303\,RT\,(X_1 \log \gamma_1 + X_2 \log \gamma_2) \tag{2}$$

$$\left(\frac{\partial \Delta G^E_X}{\partial T}\right)_X = -\,\Delta S^E_X \tag{3}$$

$$\Delta G^E_X = \Delta H^E_X + T\left(\frac{\partial \Delta G^E_X}{\partial T}\right)_X \tag{4}$$

$$\Delta G^E_X = \Delta H^E_X - T\Delta S^E_X \tag{5}$$

$$\Delta G^E_X = \Delta H^M_X + T\left(\frac{\partial \Delta G^E_X}{\partial T}\right)_X \tag{6}$$

$$\Delta H^E_X = \Delta H^M_X \tag{7}$$

when the same reference state is chosen for both cases. The reference state chosen is that of the pure component at the same temperature.

It was assumed in these calculations that a linear variation of excess free energy with temperature is valid over the range 25° to 60°C. In other words, it was assumed that the excess entropy of mixing is independent of temperature.

Correlation of Heat of Mixing Data. Scatchard and others (*8*) proposed an empirical equation based on an analogy of excess free energy in which the heat of mixing was expressed as a power series in $(x_1 - x_2)$ as follows:

$$\Delta H^M_X = x_1 x_2\,[A_0 + A_1\,(x_1 - x_2) + A_2\,(x_1 - x_2)^2 + \cdots] \tag{8}$$

where x_1, x_2 are the mole fractions of components 1 and 2, respectively, and *A*'s are constants which are functions of temperature and the system properties.

Table I. Experimental Heat of Mixing at 25°C.

Benzene, X_1[a]	Methanol, ΔH_X^M (kj/Mole)
0.9664	0.0574
0.9098	0.1530
0.8360	0.2641
0.7528	0.3768
0.5760	0.5811
0.4678	0.6734
0.3446	0.7345
0.2145	0.7139
0.1015	0.5899
0.0334	0.3446

[a] Mole fraction of methanol.

Table II. Experimental Data on Heat of Mixing at 25°C.

Methanol–Ethyl Acetate		Ethyl Alcohol–Ethyl Acetate	
X_1[a]	ΔH_X^M (kj/mole)	X_1[a]	ΔH_X^M (kj/mole)
0.9796	0.0659	0.9637	0.2246
0.9438	0.1599	0.9091	0.4880
0.8990	0.2869	0.8487	0.7473
0.8371	0.4443	0.7846	0.9660
0.7805	0.5771	0.7282	1.1149
0.7401	0.6604	0.6690	1.2506
0.6530	0.8894	0.5965	1.3590
0.5698	0.9771	0.5355	1.4048
0.4941	1.0424	0.4792	1.4252
0.4075	1.0539	0.4045	1.4176
0.3211	0.9952	0.3245	1.3297
0.2246	0.8538	0.2429	1.1784
0.1680	0.7420	0.1774	0.9563
0.1025	0.5005	0.0763	0.4965
0.0678	0.3702		

1-Propanol–Ethyl Acetate		2-Propanol–Ethyl Acetate	
X_1[a]	ΔH_X^M (kj/mole)	X_1[a]	ΔH_X^M (kj/mole)
0.9592	0.2698	0.9484	0.3611
0.9062	0.5447	0.8803	0.7529
0.8387	0.8351	0.8030	1.0823
0.7576	1.1191	0.7097	1.3884
0.6714	1.3562	0.6117	1.6227
0.5914	1.5714	0.5580	1.6727
0.5857	1.5817	0.4820	1.7062
0.5732	1.5143	0.4239	1.7048
0.5070	1.6414	0.3682	1.6680
0.5059	1.6090	0.2920	1.5347
0.4241	1.6420	0.2297	1.3437
0.4026	1.5753	0.1432	0.9760
0.3265	1.5045	0.0667	0.5046
0.2898	1.4139		
0.2364	1.2691		
0.1825	1.1098		
0.1615	0.9698		
0.0842	0.6269		
0.0730	0.4997		

[a] Mole fraction of alcohol.

This expansion into power series is valid for excess thermodynamic properties such as free energy, heat of mixing, excess entropy of mixing, and excess volume of mixing. It cannot be applied, however, to the free energy change in mixing or entropy of mixing, as these later functions are not finite as the concentration of one of the components approaches zero.

Tsao and Smith (*10*) and Klinkenberg (*5*) indicated that the constants in the heat of mixing equations do not have simple physical significance and cannot be considered more than empirical constants. The number of constants to be used depends upon the dissymmetry of the system and also on the accuracy of the experimental data. Thacker and Rowlinson (*9*) found that in most of the polar systems they studied, a two-constant equation represented the data fairly well. In extreme cases of dissymmetry and where the data were sufficiently accurate, Tsao and Smith employed a six-constant equation to describe the heat of mixing data of the methanol-toluene system.

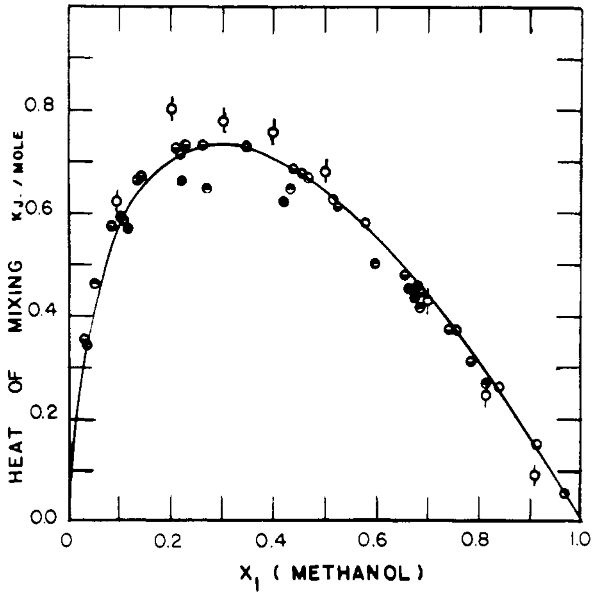

Figure 3. Heat of mixing for the system methanol-benzene

ϕ Wolf and others (*14*)
● Scatchard and others (*8*)
◓ Williams and others (*12*)
◕ Tsao and Smith (*10*)
○ Present work

The constants (*A*'s) in the equations were evaluated using the method of least squares.

RESULTS AND DISCUSSION

Methanol-Benzene System. The experimental heat of mixing data at 25°C. are given in Table I and are compared graphically with those of previous workers (*8, 10, 12, 14*) in Figure 3. There is good agreement between the results of the present work and those of Tsao and Smith (*10*). The data of the other workers, except those of Williams and others (*12*), were taken at different temperatures and thus a valid comparison is not possible. Despite the fact that Tsao and Smith employed a titration technique to maintain constant temperature, thus minimizing the exchange of heat between the calorimeter and the surroundings, there is good agreement. This indicates acceptable accuracy for the method used in this investigation. As in their case, the maximum error in all the measurements was estimated to be of the order of 2 to 3%. An attempt was made to fit the data into the form of Equation 8, but inclusion of even five constants did not show good agreement.

Alcohol-Ethyl Acetate Systems. The experimental heat of mixing data are listed in Table II and the excess thermodynamic properties calculated from vapor-liquid equilibrium data reported in (*6*) by means of Equations 2 through 6 and are shown in Table III. Figures 4 to 7 (left) include solid curves (for the systems designated) calculated by means of Equation 8 and the experimental points determined by the heat of mixing experiments. Figures 4 to 7 (right) include as solid curves the excess thermodynamic properties calculated by means of Equations 2 through 6 and also the experimental heat of mixing data.

The constants used in Equation 8 for the various systems are given in Table IV.

Methanol-Ethyl Acetate System. Data on this system were not reported in the literature. The agreement between the experimental data and the values calculated by means of vapor-liquid equilibria is not good, but the deviation is little more than the limits of experimental accuracy of the measurements.

Table III. Excess Thermodynamic Properties at 25°C.

	Mole Fraction Alcohol										
	0.05	0.10	0.20	0.30	0.40	0.50	0.60	0.70	0.80	0.90	0.95
	Excess Free Energy, Cal./Mole										
Methanol-ethyl acetate	37.01	69.13	121.31	159.82	181.8	188.50	180.08	156.84	118.93	66.56	34.866
Ethyl alcohol-ethyl acetate	33.89	63.68	112.70	147.25	167.51	173.71	165.99	144.47	109.54	62.05	32.33
1-Propanol-ethyl acetate	...	53.44	94.44	123.21	139.38	144.95	138.32	120.30	90.10	50.94	...
2-Propanol-ethyl acetate	28.39	53.95	97.07	124.76	141.92	147.17	140.65	122.50	92.89	52.0	27.38
	$T\Delta S^E_X$, Cal./Mole										
Methanol-ethyl acetate	25.04	38.66	61.71	72.74	73.18	65.50	52.61	37.41	21.75	8.03	...
Ethyl alcohol-ethyl acetate	44.11	78.70	133.85	167.98	182.88	181.24	165.0	136.36	95.66	64.84	26.38
1-Propanol-ethyl acetate	...	103.80	178.35	225.81	248.82	249.50	230.28	193.35	115.96	75.9	...
2-Propanol-ethyl acetate	57.83	110.6	205.24	245.26	272.76	276.64	258.3	219.4	162.21	88.46	45.97
	Excess Enthalpy of Mixing, Cal./Mole										
Methanol-ethyl acetate	62.05	107.79	184.02	232.56	254.98	254.0	232.69	194.25	140.68	74.59	34.58
Ethyl alcohol-ethyl acetate	78.00	142.38	246.55	315.23	350.39	354.95	330.99	280.95	205.20	126.89	58.71
1-Propanol-ethyl acetate	...	157.24	272.79	349.02	388.8	394.45	368.60	313.65	206.60	126.84	...
2-Propanol-ethyl acetate	86.22	164.65	302.31	370.02	414.68	423.81	398.95	341.9	255.10	140.46	73.35

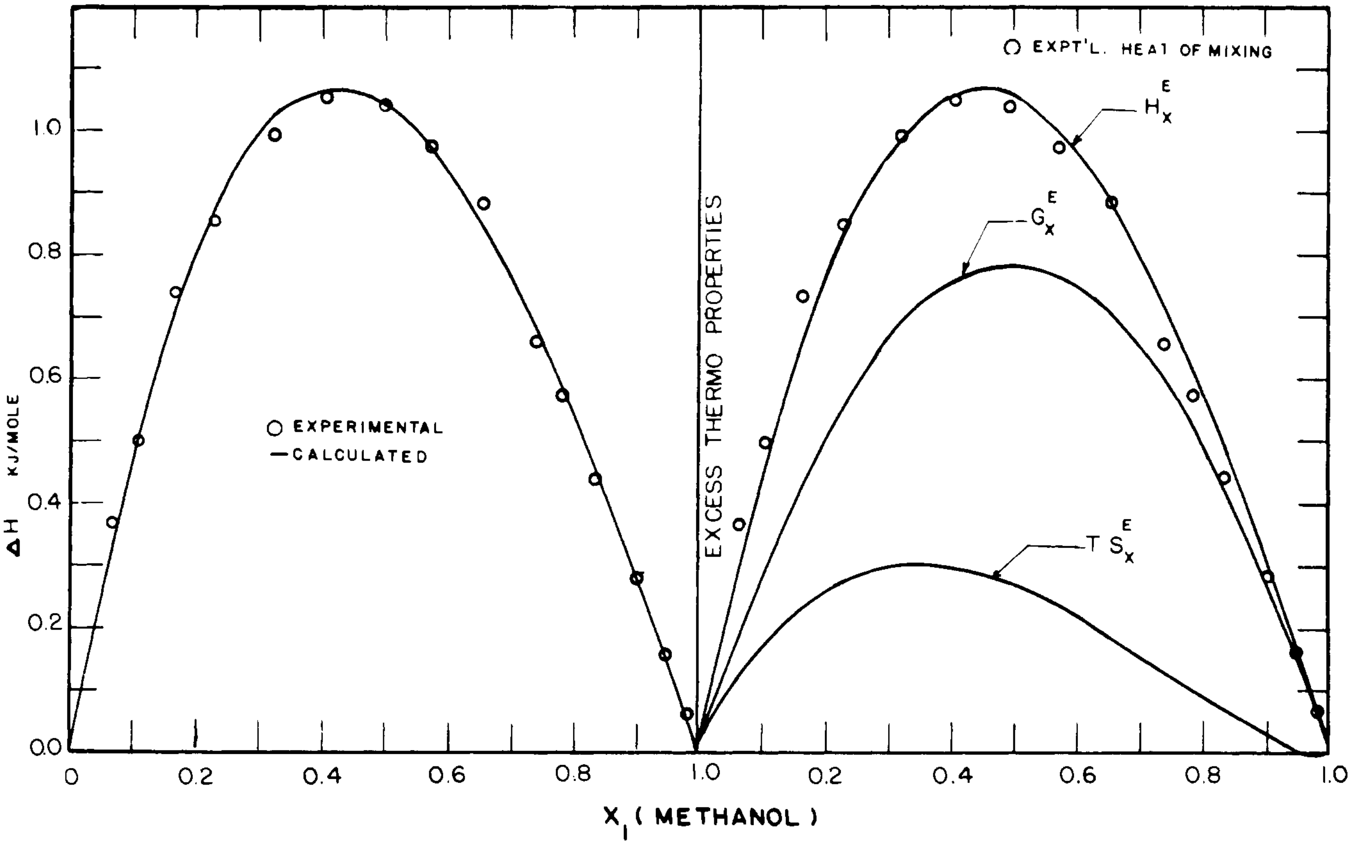

Figure 4. Heat of mixing and excess thermodynamic properties for methanol-ethyl acetate system at 25° C.

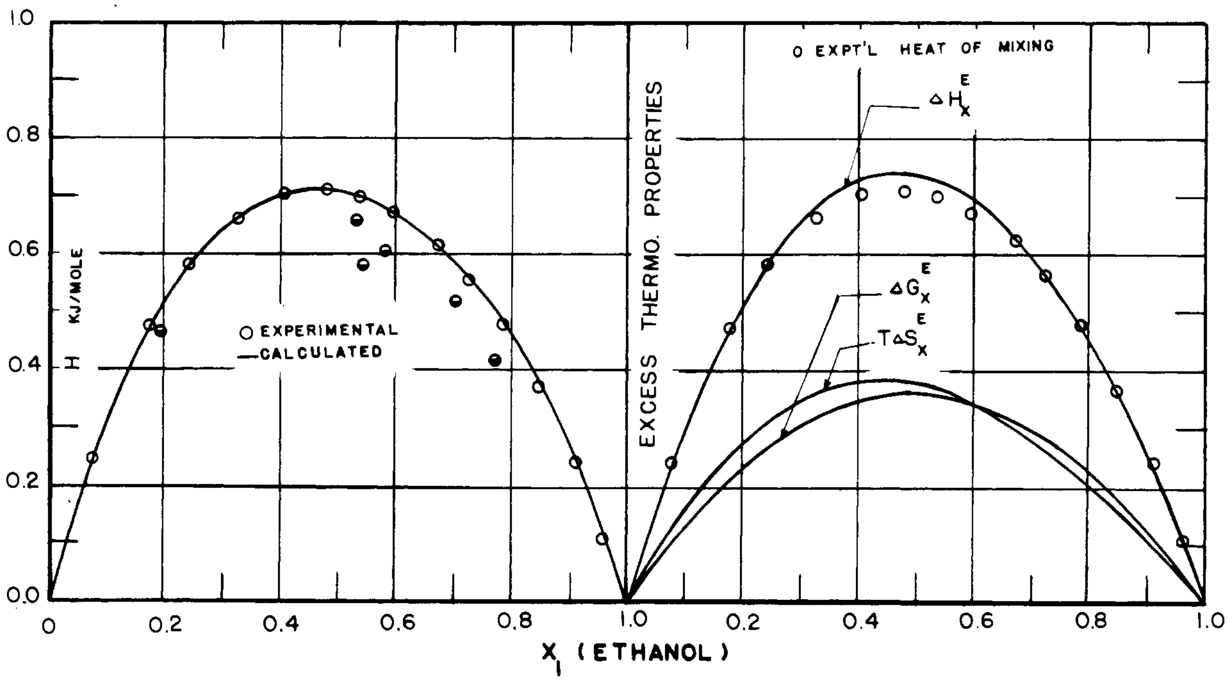

Figure 5. Heat of mixing and excess thermodynamic properties for ethyl alcohol-ethyl acetate system at 25° C.

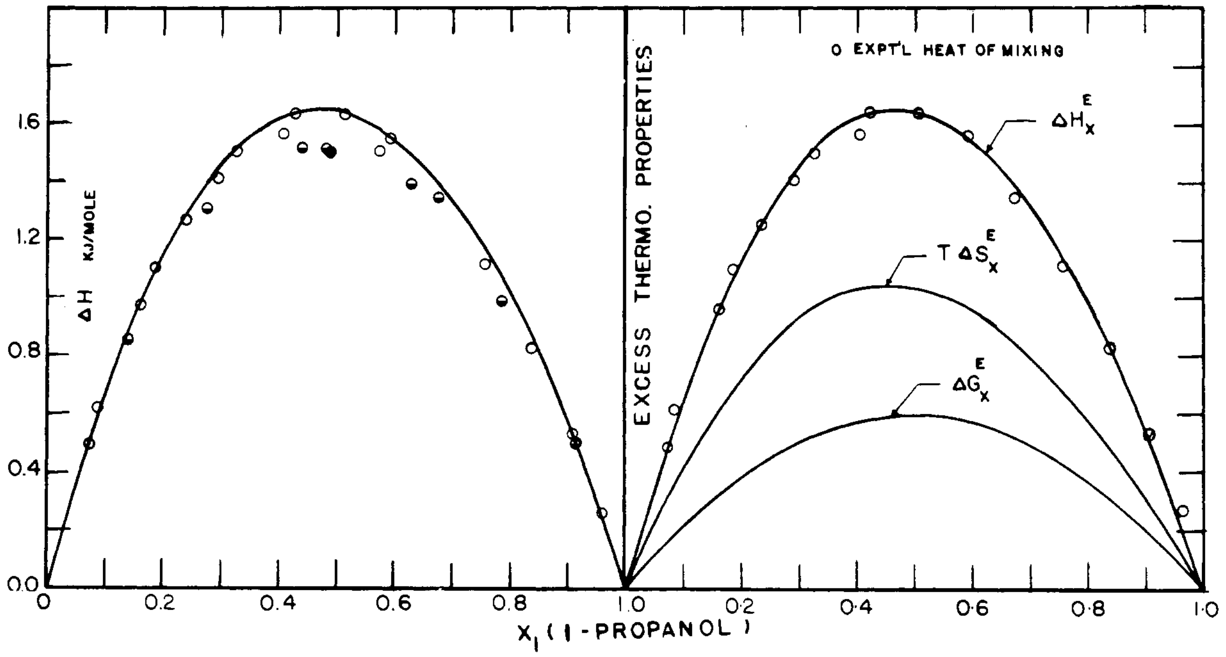

Figure 6. Heat of mixing and excess thermodynamic properties for 1-propanol-ethyl acetate system at 25° C.

The calculated excess entropy of mixing shows positive values over the range of methanol concentrations.

Ethyl Alcohol-Ethyl Acetate System. Heat of mixing data at 25°C. for this system were reported in the International Critical Tables (*4*). The calculated values derived from vapor-liquid equilibria deviated from those reported to an extent not accounted for through the limits of accuracy of heats of mixing measurements. Therefore, the heat of mixing data were determined for this system. The agreement between the I.C.T. values and the present work is poor. Since the values obtained from vapor-liquid equilibria agree closely with the experimental data of this work, it is believed that the results of this work are more accurate.

The excess entropy of mixing is positive throughout the entire concentration range. This probably indicates that the alcohol complexes are always broken rather than formed. This may be attributed to the increased chain length of the electron-repelling alkyl group. This is in accordance with the findings of Beech and Glasstone (*1*).

1-Propanol-Ethyl Acetate System. Heat of mixing data at 25°C. were reported in the International Critical Tables, but were redetermined in this investigation for the same reasons. The agreement between the two sets of data is poor in the region of 40 to 60% of alcohol and the deviations are beyond those falling within the limits of experimental error.

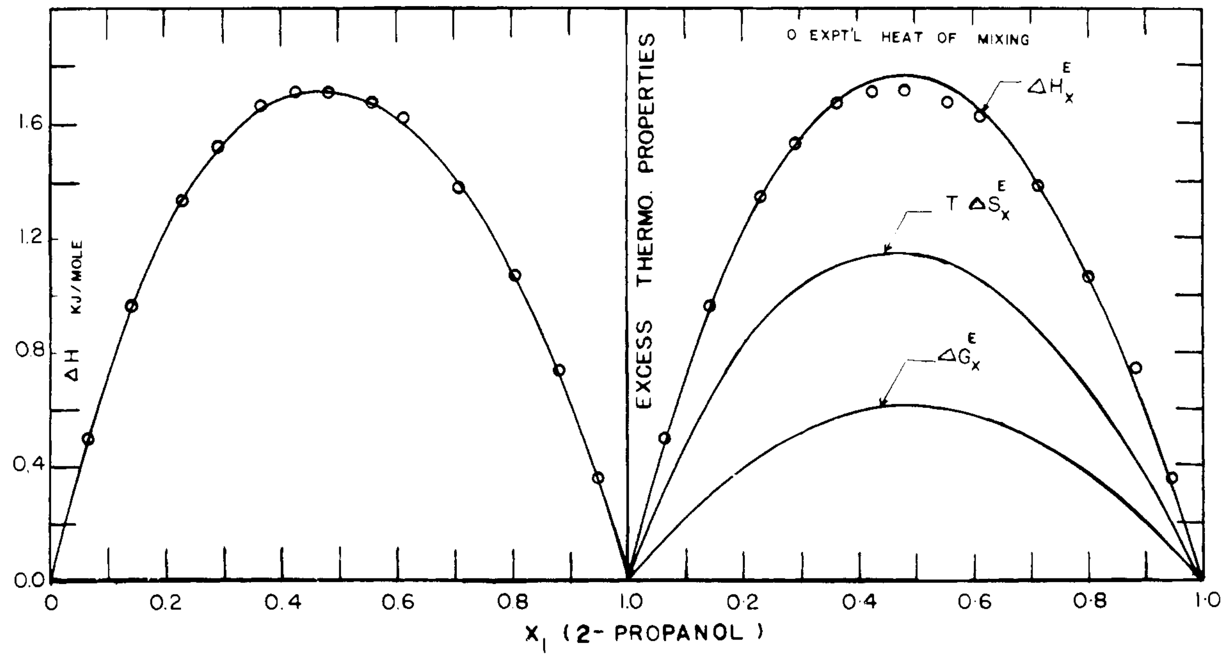

Figure 7. Heat of mixing and excess thermodynamic properties for 2-propanol–ethyl acetate system at 25° C.

Table IV. Binary Constants in Heat of Mixing Equation, Temperature 25° C.

	A_0	A_1	A_2
(1) Methanol–ethyl acetate (2)	4.1781	−1.4369	0.2366
(1) Ethyl alcohol–ethyl acetate (2)	5.6859	−0.5920	1.2607
(1) 1-Propanol–ethyl acetate (2)	6.5834	−0.7907	0.4311
(1) 2-Propanol–ethyl acetate (2)	6.8546	−0.5787	1.2003

The same conclusions as those drawn in the case of the ethyl alcohol-ethyl acetate system, can be drawn from excess entropy of mixing data on this system.

2-Propanol-Ethyl Acetate System. Data on heat of mixing at 25°C. for this system are not reported in the literature and were determined in this investigation. The agreement between the experimental data and those calculated from vapor-liquid equilibria is close throughout the entire range of composition. Beech and Glasstone (*1*), from the observation of solid hydrate formation of *tert*-butanol, concluded that branching of the chain favors the complex formation, but the calculated excess entropy of mixing data show no such tendencies in this system. On the other hand, decomposition of complexes is shown to a greater extent than is shown in the 1-propanol-ethyl acetate mixtures. Because thermal effects on mixing are so great, indicating depolymerizations of complexes, the influence of branching is barely perceptible.

A critical comparison of the excess thermodynamic properties for alcohol-ethyl acetate binary systems shows that excess free energy values decrease while the excess entropy of mixing and heat of mixing increase with increase in chain length of the alkyl group. It is reasonable to suppose that further increase in chain length of the alcohol component will eventually lead to a pseudo-ideal system—i.e., one in which $\Delta G_X^E = 0$—due to the cancellation of entropy and enthalpy of mixing terms in Equation 5. They are not, however, ideal systems in the strict sense as defined by Rushbrooke (*7*).

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NOMENCLATURE

A, B = van Laar constants
A_0, A_1 = constants in heat of mixing equation
ΔG_X^E = excess free energy, calories per gram mole
ΔH_X^E = excess enthalphy of mixing, calories per gram mole
ΔH_X^M = heat of mixing, calories per gram mole
R = gas constant
ΔS_X^E = excess entropy of mixing, entropy units per gram mole
T = absolute temperature
t = time seconds
V = potential drop across heater, volts
V_S = potential drop across standard resistor
X's = mole fraction in liquid
γ = activity coefficient

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