Relation of Binary Heats of Mixing and Distribution of Ketone between Phases in some Ketone-Water-Solvent Ternaries

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A MIXTURE OF WATER and a nonelectrolyte can often be separated by extracting the nonelectrolyte with a water-insoluble solvent. The efficiency with which the solvent performs the extraction is measured most simply by the ratios of mole fraction of the nonelectrolyte to be removed (the solute) in the solvent-rich phase to the mole fraction in the water-rich phase for the various equilibrium mixtures. The ability to predict these ratios would be of value in screening potential solvents for a separation process. Binary solution effects which appeared as likely indexes of separation efficiency were the heats of mixing of water-solute and solvent-solute mixtures. Heats of mixing were measured at 25° C. for the following eight binaries: acetone-water, acetone–*n*-heptane, acetone-monochlorobenzene, acetone–1,1,2-trichloroethane and 2-butanone (methyl ethyl ketone)–water, 2-butanone–*n*-heptane, 2-butanone–monochlorobenzene, and 2-butanone–1,1,2-trichloroethane. These systems constitute the miscible binaries for the six ternaries: acetone-water–*n*-heptane, acetone-water-monochlorobenzene, acetone-water–1,1,2-trichloroethane, 2-butanone–water–*n*-heptane, 2-butanone–water-monochlorobenzene, and 2-butanone–water–1,1,2-trichloroethane. Liquid-liquid equilibrium data, all at 25° C., were available in the literature (*6, 7, 11, 12*) for these systems. The measured heats of mixing were correlated qualitatively with the published equilibrium distribution data and the trends in separation efficiency interpreted on the basis of the opportunities for hydrogen bond formation. Solvents showing greater saturation with respect to hydrogen bonding with the solute were more efficient as separating agents when compared on the mole basis.

EXPERIMENTAL

The heats of mixing were measured in a Dewar flask which was immersed in a constant temperature bath (Figure 1). The technique was relatively simple. A measured amount of pure component was admitted into the mixing chamber of the Dewar. The jacketed buret was filled with the second component and allowed to come to temperature equilibrium with the bath water being circulated through the jacket (5 to 10 minutes). A slight air pressure was then applied to the buret and the desired amount of second component forced rapidly into the mixing chamber. The Dewar flask contents were stirred continuously at about 200 r.p.m. The temperature rise or fall was measured by the five-junction thermopile immersed in the mixture. The reference junction of the thermopile was maintained in the constant temperature bath.

The heat capacity of the calorimeter plus its contents was determined by dissipating a measured amount of electrical energy in the heating coil and noting the subsequent rise in temperature of the calorimeter. A plot of logarithm of temperature difference between calorimeter and bath *vs.* time was constructed to facilitate calculation of net heat effects. A somewhat idealized plot for a mixing experiment in which the heat effect was exothermic is shown in Figure 2. The straight-line relation between ln $(T - T_s)$ and time during periods when neither reactants nor electrical energy were being added to the calorimeter can be predicted, providing that the rate of heat transfer to the surroundings was directly proportional to the temperature driving force $(T - T_s)$. Apparently, this proportionality held true for this apparatus, because excellent straight-line plots were obtained over the quiescent periods.

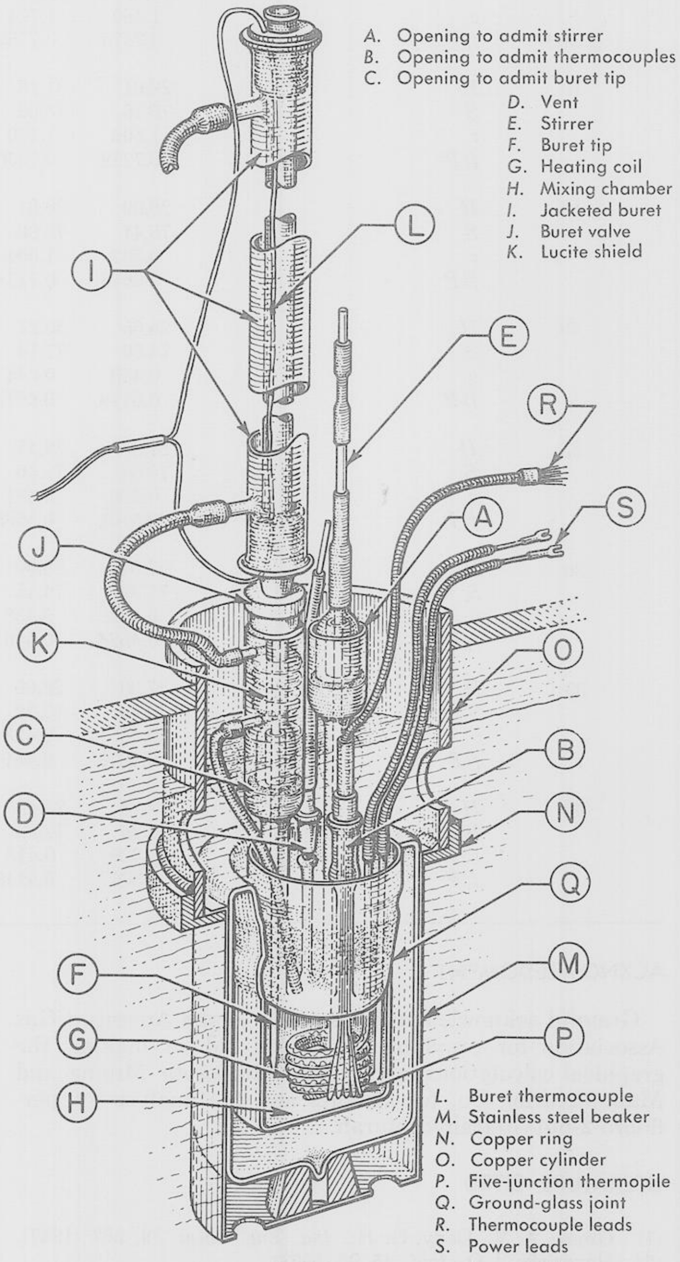
CALCULATION OF NET HEAT EFFECTS

Equation 1 was derived for calculating the heat of mixing from time-temperature plots such as that shown in Figure 2.

$$\Delta H_x^M = \frac{1}{N_T}\left[- C_p(T_1 - T_0) + C_{pB}(T_{B0} - T_0) - K'(\overline{T}_{01} - T_s)\,\Delta\tau_{01} + \Delta H^{v\prime}\right] \quad (1)$$

C_p, the heat capacity of the calorimeter and its contents, was calculated from the temperature rise noted during the heating period $(\Delta\tau_{23})$, the rate of addition of electrical energy, and a parameter derived from the rating period.

$$C_p = \frac{\Delta\overline{H}^e}{\left(\dfrac{T_3 - T_2}{\tau_3 - \tau_2}\right) - \left(\dfrac{dT/d\tau}{T - T_S}\right)_R (\overline{T}_{23} - T_S)} \quad (2)$$



A. Opening to admit stirrer
B. Opening to admit thermocouples
C. Opening to admit buret tip
D. Vent
E. Stirrer
F. Buret tip
G. Heating coil
H. Mixing chamber
I. Jacketed buret
J. Buret valve
K. Lucite shield
L. Buret thermocouple
M. Stainless steel beaker
N. Copper ring
O. Copper cylinder
P. Five-junction thermopile
Q. Ground-glass joint
R. Thermocouple leads
S. Power leads

Figure 1. Dewar flask for measuring heats of mixing

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The rating period parameter is $\left(\frac{dT/d\tau}{T - T_S}\right)_R$, the slope of the $\ln(T - T_S)$ *vs.* time plot during this period. K', an effective heat transfer coefficient, is given by Equation 3:

$$K' = -C_p \left(\frac{dT/d\tau}{T - T_S}\right)_R \tag{3}$$

Equation 3 is an energy balance over a differential interval of the rating period.

RELIABILITY OF MEASUREMENT

The frequently measured (*5, 10, 14*) heat of mixing for the methanol-benzene system was redetermined as a check on the accuracy of the experimental technique. The numerical results are presented in Table I and shown graphically along with the data of Tsao and Smith (*14*) and Murti (*5*) in Figure 3. As indicated in Table I, certain runs were made with a mixture of the two pure components initially in the mixing chamber of the Dewar. This procedure kept the temperature drop per run to .2° C. or less. Since measurements were made with reactants initally at 26° C., the temperature range of the measurements can be set at 25° ± 1° C. Tsao and Smith made isothermal measurements at 25° C. by heating and adding the second component simultaneously. The agreement of this work with that of Tsao and Smith is good. The curve drawn in Figure 3 is a mean curve for the data of this work. Near the top of the curve the greatest deviation is 1%. Tsao and Smith recorded a slightly greater negative heat of mixing.

A small correction was made to the measured heat of mixing for the change in enthalpy of the vapor space during the mixing of the two liquids ($\Delta H^{v'}$). Among the assumptions made in deriving the simple formula used are (1) the mixing process is isothermal, (2) the binary pairs obey Raoult's Law, and (3) equilibrium between liquid and vapor was rapidly attained after mixing. The corrections made were usually less than 1%. Because of the uncertainty experienced in estimating the errors caused by vaporization effects, an attempt was made to place reasonable limits upon them by using the following equation for the limit:

$$|\Delta H^{v'}_{\text{max.}}| = \frac{V}{RT}(\lambda_1 P_1^0 + \lambda_2 P_2^0) \tag{4}$$

The calculated limiting errors from vaporization are tabulated along with the experimental data in Table I.

Table I. Heats of Mixing at 25° C. for Methanol-Benzene

Mole Fraction Methanol		ΔH_x^M,	Max. % Uncertainty Caused by
Initial	Final	kjoules/mole	Vaporization
0	0.10	0.598	7.8
0.10	0.20	0.7125	2.5
0.60	0.40	0.706	3.6
0.60	0.40	0.701	3.6
0.80	0.60	0.546	3.3
0.80	0.60	0.537	3.4
1.00	0.80	0.299	3.0
1.00	0.80	0.295	3.0

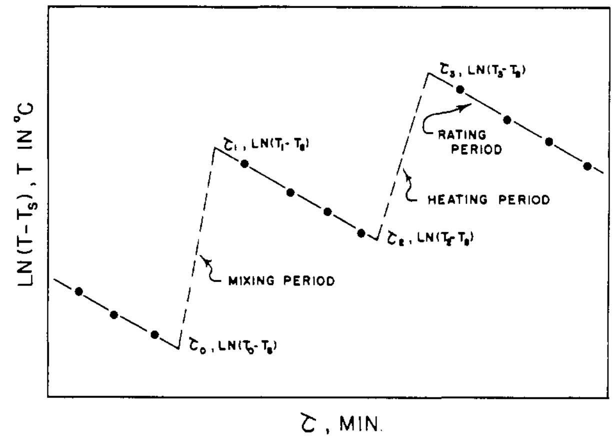

Figure 2. Idealized semilog time-temperature difference plot for an exothermic heat of mixing run

Table II. Properties of Materials

Material	Source	Refractive Index, n_D^{25} Measured	Lit. (2)
Acetone			
Sample *A*	Baker analyzed reagent	1.3560	1.35609
Sample *B*	Baker analyzed reagent	1.35605	1.35609
2-Butanone	Eastman organic chemicals	1.3761	1.37612
n-Heptane	Phillips Petroleum pure grade (99 mole % min.)	1.38515	1.38517
Monochlorobenzene	Eastman organic chemicals	1.5217	1.52138
1, 1, 2-Trichloroethane	Eastman organic chemicals (technical grade)	1.4672	1.46868
Methanol	Baker analyzed reagent	1.3267	1.32669
Benzene	Baker analyzed reagent	1.4975	1.49790

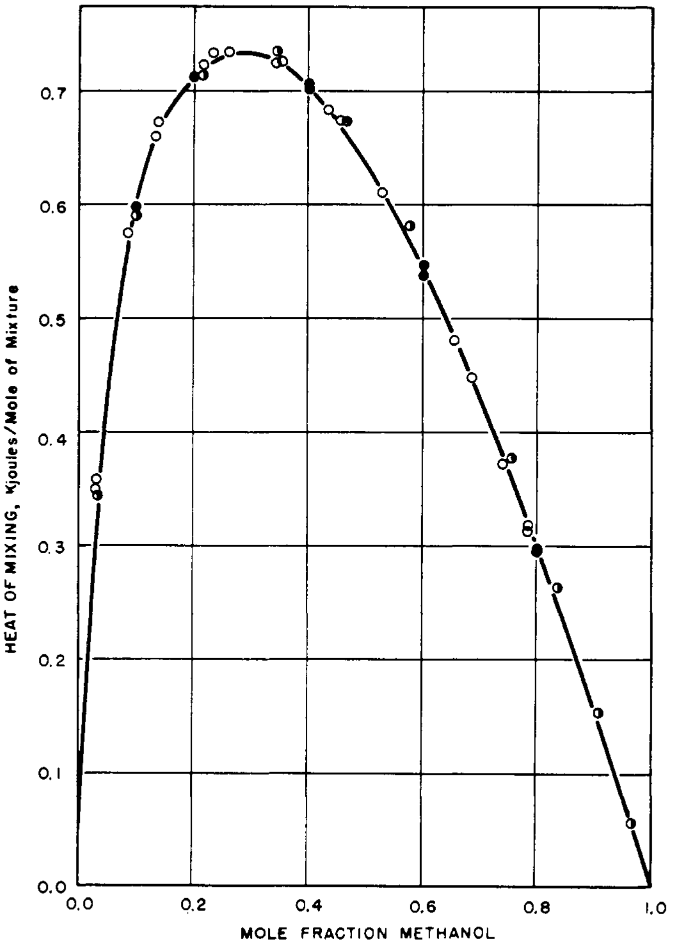

Figure 3. Methanol-benzene heat of mixing at 25° C.

● This work ◑ Murti (5) ○ Tsao and Smith (*14*)

MATERIALS

The sources of supply and measured refractive indexes of the materials used are listed in Table II. No further purification was carried out except for the 1, 1, 2-trichloroethane which was twice distilled in a packed column. The water used was once distilled.

EXPERIMENTAL RESULTS

Heat of mixing for the eight ketone binaries investigated are given in Table III. The ketone concentration of calorimeter contents before and after mixing is indicated as for the methanol-benzene data. The data are shown graphically in Figures 4 and 5. An empirical equation was fitted to the data points of all but the ketone-water systems. The equation, first presented by Scatchard (*10*), has the form:

$$\Delta H_x^M = x_1x_2[A_0 - A_1(x_1 - x_2) + A_2(x_1 - x_2)^2 + \dots + A_n(x_1 - x_2)^n + \dots] \qquad (5)$$

The constants for this equation are listed in Table IV.

The heat of mixing measurements were taken with the reactants initially at 25° C. and consequently can be regarded only as measurements in the vicinity of 25° C. because of the temperature rise or fall on mixing. All temperatures recorded after mixing had taken place were within the range 21° to 31° C.

Heat of mixing data were previously presented for the acetone-water system by Sandoninni (*9*) at 15° C. and by Kister and Waldman (*4*) at 25° C. and by Wolff (*15*) for the acetone-*n*-heptane system at 20° C. The results are not shown graphically but a table of differences between published values and the data of this work has been prepared (Table V). Agreement with the data of Sandoninni is poor; however, the measurements were taken at temperatures differing by 10° C. and this may account for the discrepancy. Disagreement with the data of Kister and Waldman is greater than estimated experimental error (about 1%). They do not describe their apparatus or technique fully, and no explanation can be advanced for the poor agreement. Agreement with the data of Wolff is excellent.

Table III. Experimental Heats of Mixing

Mole Fraction Ketone		ΔH_x^M, Kjoules per Mole	Max. % Uncertainty Caused by Vaporization
Initial	Final		
	Acetone-*n*-Heptane		
0	0.125	0.896	3.0
0.125	0.250	1.382	4.2
0.250	0.500	1.702	2.8
0.750	0.500	1.707	2.7
0.875	0.750	1.356	2.9
1.000	0.875	0.844	2.0
	Acetone-Monochlorobenzene		
0	0.5	−0.018	88
0	0.5	−0.017	96
1.0	0.5	−0.036	48
1.0	0.5	−0.034	50
	Acetone-1,1,2-Trichloroethane		
0	0.240	−0.821	2.3
0	0.240	−0.791	2.4
0	0.240	−0.804	2.4
0	0.500	−1.072	1.8
0	0.500	−1.071	1.8
1.0	0.501	−1.094	1.8
1.0	0.500	−1.077	1.8
1.0	0.750	−0.7725	2.2
1.0	0.750	−0.802	2.1
1.0	0.749	−0.811	2.2
	Acetone-Water		
0	0.050	−0.384	1.2
0	0.125	−0.626	1.0
1.0	0.129	−0.637	1.0
1.0	0.251	−0.596	1.3
1.0	0.251	−0.618	1.2
1.0	0.375	−0.418	2.0
1.0	0.499	−0.174	1.0
1.0	0.498	−0.176	1.0
1.0	0.624	0.067	14
1.0	0.750	0.237	4.4
1.0	0.721	0.202	4.9
1.0	0.874	0.271	4.0
1.0	0.874	0.274	4.2
1.0	0.950	0.157	8.0
	2-Butanone-*n*-Heptane		
0	0.125	0.712	1.1
0	0.251	1.105	1.5
0	0.500	1.341	1.1
1.0	0.500	1.325	1.0
1.0	0.750	0.991	1.3
1.0	0.875	0.609	0.9
	2-Butanone-Monochlorobenzene		
0	0.250	−0.209	4.0
0	0.2505	−0.207	4.0
0	0.500	−0.315	2.6
0	0.500	−0.306	2.6
1.0	0.500	−0.3195	2.5
1.0	0.500	−0.311	2.6
1.0	0.750	−0.253	3.1
1.0	0.749	−0.251	3.1
	2-Butanone-1,1,2-Trichloroethane		
0	0.2767	−0.901	1.1
0	0.2765	−0.913	1.1
0	0.535	−1.145	0.9
0	0.534	−1.148	0.9
1.0	0.534	−1.163	0.9
1.0	0.535	−1.170	0.9
1.0	0.775	−0.800	1.2
1.0	0.776	−0.804	1.2
	2-Butanone-Water		
0	0.0250	−0.219	1.0
0	0.0503	−0.340	0.7
0	0.0700	−0.375	0.7
0	0.0700	−0.379	0.7
1.0	0.700	0.504	1.1
1.0	0.700	0.492	1.1
1.0	0.799	0.544	1.1
1.0	0.898	0.410	1.7

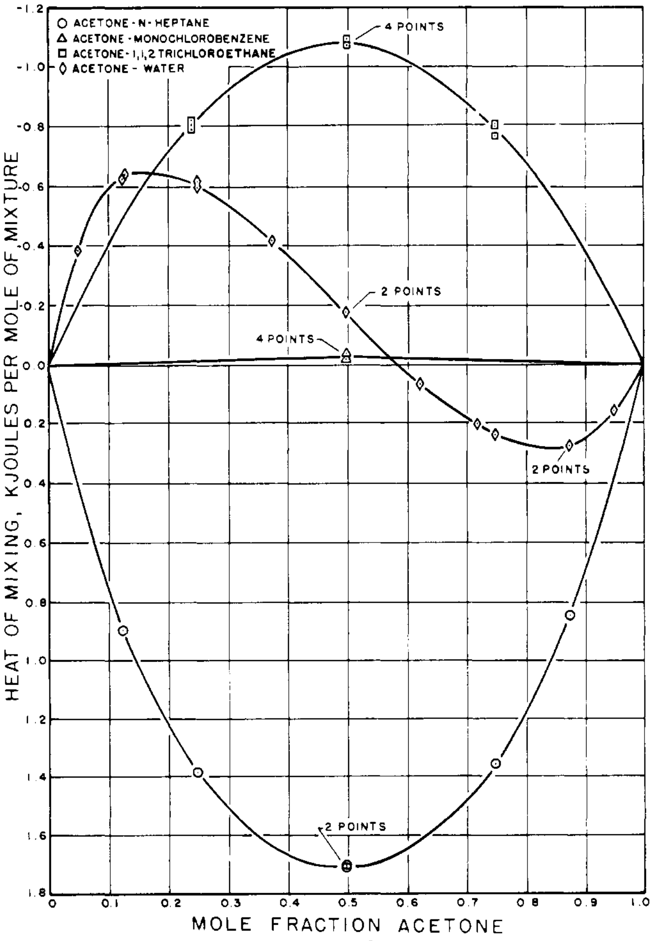

Figure 4. Heats of mixing for acetone systems

Liquid-liquid equilibrium data for the six ternaries are presented in the form of distribution curves in Figures 6 and 7. The data were taken from various literature sources as indicated. The form of the distribution curve is that of Treybal, Weber, and Daley (*13*). The ratio of mole fraction

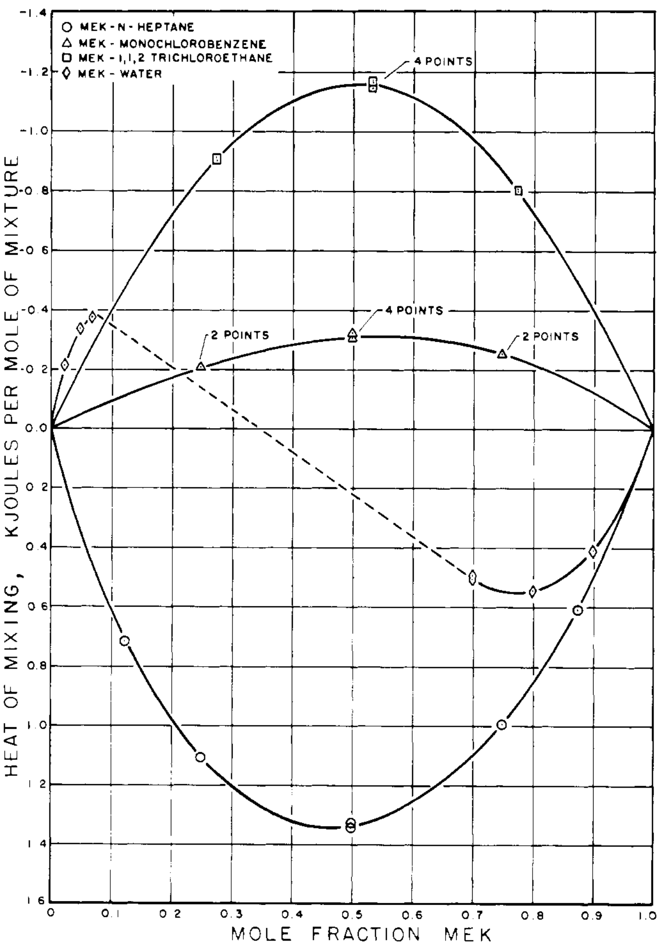

Figure 5. Heats of mixing for 2-butanone (MEK) systems

ketone in solvent-rich layer to mole fraction ketone in water-rich layer is the distribution coefficient, designated *B*. On the mole basis, the ketone is always found in greater concentration in the solvent phase for the ternaries studied.

DISCUSSION

The interpretation of the solution behavior of nonelectrolytes is greatly aided by the rules of solution interaction presented by Ewell, Harrison, and Berg (*3*). They attribute deviations from ideal solution behavior to the sum of the effect of hydrogen bond formation and the effect of differences in internal pressure (energy of vaporization per unit volume) of the solution components. Hydrogen bond formation is a chemical effect; the effect of differences in internal pressure is physical. They minimize the importance of physical effects when hydrogen bonding can occur. They further classify various compounds according to hydrogen-bonding ability and predict the probable nonidealities displayed by solutions of compounds of the various classes.

Table IV. Constants for Equation 5

Systems	A_0	A_1	A_2
Acetone–*n*-heptane	6.816	−0.246	1.998
2-Butanone–*n*-heptane	5.332	−0.667	1.186
Acetone-chlorobenzene	−0.104	0	0
2-Butanone–chlorobenzene	−1.251	−0.233	0.106
Acetone–1, 1, 2-trichloroethane	−4.316	0.1735	−0.0265
2-Butanone–1, 1, 2-trichloroethane	−4.644	−0.108	0.325

Table V. Differences between Published and Experimental Heat of Mixing

	Published Value Minus Experimental Value		
	Acetone-Water		Acetone–*n*-heptane,
x Acetone	Sandoninni (*9*)	Kister, Waldman (*4*)	Wolff (*15*)
0.125	−0.107	+0.035	−0.021
0.250	−0.160	+0.024	−0.022
0.500	−0.165	+0.070	−0.005
0.750	. . .	+0.024	. . .
0.875	. . .	+0.021	. . .

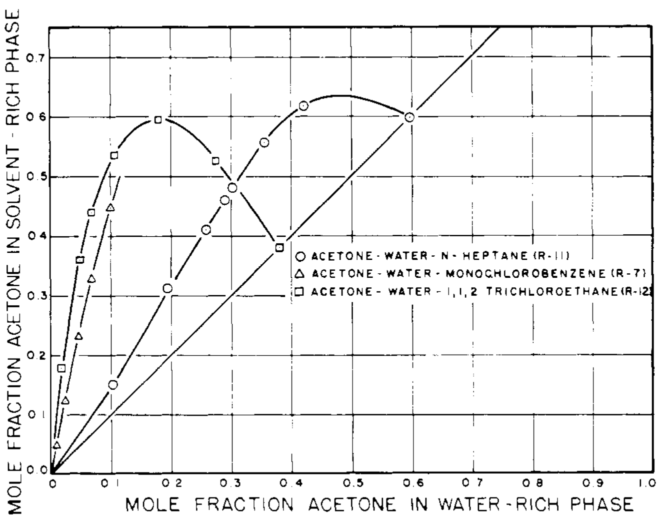

Figure 6. Molal distribution curves for acetone-water-solvent systems at 25° C.

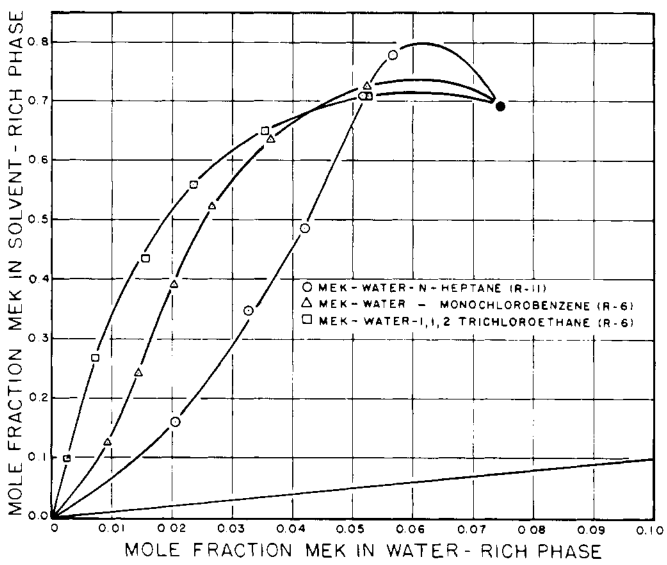

Figure 7. Molal distribution curves for 2-butanone–water-solvent systems at 25° C.

In connection with these rules, two numerical quantities are of value in further interpretation of solution behavior. They are, first, lim $\Delta\bar{H}_1^M$, defined as:

$$\lim_{N_1\to O}\left(\frac{\partial \Delta H^M}{\partial N_1}\right)_{N_2}$$

It is equal to the slope of the ΔH_x^M curve at the origin (*1*). The second quantity is the limiting value of the distribution coefficient, designated lim *B*. It is the slope at the origin of the distribution curve as plotted by Treybal, Weber, and Daley (*13*). It is proposed that values of lim $\Delta\bar{H}_1^M$ reflect directly on the amount of hydrogen bonding occurring at high dilution because solute molecules are free to react with solvent molecules without interference from other solute molecules. Values of lim *B* are direct measures of extraction efficiency for the systems studied. Values of lim $\Delta\bar{H}_1^M$ for the

Table VI. Limiting Values of $\Delta \overline{H}_l^M$

System	$\lim_{N_1 \to 0} \Delta \overline{H}_1^M$, Kjoules/Mole
Acetone	
-*n*-Heptane	9.1
-Chlorobenzene	−0.1
-1, 1, 2-Trichloroethane	−4.5
-Water	−10.0
2-Butanone	
-*n*-Heptane	7.2
-chlorobenzene	−0.9
-1, 1, 2-Trichloroethane	−4.2
-Water	−10.5

Table VII. Limiting Values of Distribution Coefficient

System	$\lim_{x_1 \to 0} B$
Acetone-water	
-*n*-Heptane	1.57
-Chlorobenzene	5.6
-1, 1, 2-Trichloroethane	9.3
2-Butanone-water	
-*n*-Heptane	4.85
-Chlorobenzene	9.75
-1, 1, 2-Trichloroethane	39.0

eight binaries are given in Table VI. Limiting values of distribution coefficient are given in Table VII.

It is interesting to compare the experimental results to the behavior predicted by the theory of Ewell, Harrison, and Berg. The ketones belong to Class III of liquids in their scheme. A hydrogen bond can form at the oxygen molecule, providing that an active hydrogen is available. *n*-Heptane is inert toward hydrogen bond formation. According to Table III, 9.1 kjoules are absorbed per mole of acetone upon mixing in *n*-heptane at limitingly small acetone concentrations. This is apparently a physical effect, because hydrogen bonds are neither broken nor formed on solution. The ketone-*n*-heptane systems can be thought of as reference systems for comparison of hydrogen bonding activity in that no opportunities exist for formation of bonds between the ketones and *n*-heptane.

Chlorobenzene has active hydrogens by virtue of its unsaturated C—H bonds, and hydrogen bonding between ketone and chlorobenzene is anticipated. The increase in heat evolution over that noted for ketone-*n*-heptane systems confirms this. The increases in lim $\Delta \overline{H}_1^M$ are −9.1 and −8.1 kjoules per mole for acetone-chlorobenzene and 2-butanone-chlorobenzene, respectively. Pauling (*8*) places the hydrogen bond energy at about 21 kjoules per mole. This suggests that, on the average, only about one half of the ketone molecules partipate in hydrogen bonding at limitingly small concentration of ketone. The 1,1,2-trichloroethane molecule has several hydrogens available for bonding. The increases in lim $\Delta \overline{H}_1^M$ are −13.6 and −11.4 for acetone-1,1,2-trichloroethane and 2-butanone-1,1,2-trichloroethane, respectively which indicates a greater saturation with respect to hydrogen bonding.

The limiting values of $\Delta \overline{H}_1^M$ for the ketone-water binaries indicate a net formation of hydrogen bonds at low ketone concentrations. The situation with respect to hydrogen bonding is reversed as ketone concentration increases, and the heat of mixing curve becomes endothermic at a water concentration less than 0.4 *M*. Evidently, the formation of hydrogen bonds between ketone and water at low ketone concentration is countered by the breakdown of the water structure with a subsequent net decrease in hydrogen bonding and finally, endothermic behavior as ketone concentration approaches unity.

Selectivity of the solvents for ketone increases in the order *n*-heptane < chlorobenzene < 1,1,2-trichloroethane. This is in harmony with the observed apparent increase in hydrogen bonding among the systems as expressed by the inequality ketone-*n*-heptane < ketone-chlorobenzene < ketone-1,1,2-trichloroethane. All three of the solvents, however, are more selective for the ketone than the water, but the ketone-water systems display the greatest limiting values of $\Delta \overline{H}_1^M$. This paradox is best explained by attributing it to the three-dimensional hydrogen-bonded structure of water (*3*) which is diffcultly entered by the ketone molecule. Thus, the ketone molecule is taken up preferentially into the more loosely bound solvent structure.

NOMENCLATURE

A_0, A_1, A_2 = empirical constants of Equation 5
B = distribution coefficient
C_p = heat capacity of calorimeter and contents, kjoules/° C.
C_{pB} = heat capacity of component added from buret, kjoules/° C.
ΔH_x^M = heat of mixing, kjoules/mole of mixture
$\Delta \overline{H}_1^M$ = partial molal heat of mixing, component 1, kjoules/mole
$\Delta H^{v\prime}$ = change in enthalpy of vapor space during mixing period, kjoules
$\Delta \overline{H}^e$ = rate of electrical energy input during heating period, kjoules/min.
K' = effective heat transfer coefficient, kjoules/min. ° C.
N_T = total moles of mixture
P_1^0, P_2^0 = vapor pressure, component 1 and 2, respectively, atm.
R = gas constant, cc. atm./mole ° F.
T = temperature, ° C.
T_{B0} = temperature of buret contents at start of heating period, ° C.
T_S = temperature of surroundings, ° C.
V = volume, cc.
x_1, x_2 = mole fraction component 1 and 2, respectively
λ_1, λ_2 = latent heat of vaporization, components 1 and 2, respectively, kjoules/mole
τ = time, min.

Subscripts in Equations 1, 2, and 3

0 = start of mixing period
1 = end of mixing period
2 = start of heating period
3 = end of heating period, start of rating period
R = rating period

LITERATURE CITED

(1) Dodge, B. F., "Chemical Engineering Thermodynamics," p. 388, McGraw-Hill, New York, 1944.
(2) Dreisbach, R. R., "Physical Properties of Chemical Substances," Dow Chemical Co., Midland, Mich., 1952.
(3) Ewell, R. H., Harrison, J. M., Berg, Lloyd, *Ind. Eng. Chem.* **36**, 871 (1944).
(4) Kister, A. T., Waldman, D. C., *J. Phys. Chem.* **62**, 245-6 (1958).
(5) Murti, P. S., Van Winkle, Matthew, IND. ENG. CHEM., CHEM. ENG. DATA SER. **3**, 65-71 (1958).
(6) Newman, M., Hayworth, C. B., Treybal, R. E., *Ind. Eng. Chem.* **41**, 2039 (1949).
(7) Othmer, D. F., White, R. E., Truger, E., *Ibid.*, **33**, 1240 (1941).
(8) Pauling, Linus, "The Nature of the Chemical Bond," p. 284, Cornell University Press, Ithaca, N. Y., 1939.
(9) Sandoninni, *Atti reale accad. naz. Lincei* **1**, 448 (1925), excerpted from "International Critical Tables," **V**, 155 (1928).
(10) Scatchard, George, Ticknor, L. B., others, *J. Am. Chem. Soc.* **74**, 3721 (1952).
(11) Treybal, R. E., Vrondak, O. J., *Ind. Eng. Chem.* **41**, 1761 (1949).
(12) Treybal, R. E., Weber, L. D., Daley, J. F., *Ibid.*, **38**, 817 (1946).
(13) *Ibid.*, p. 819.
(14) Tsao, C. C., Smith, J. M., *Chem. Eng. Progr. Symposium Ser.* **7**, 107-17 (1953).
(15) Wolff, Hans, *Z. Elektrochem.* **57**, 419 (1953).

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