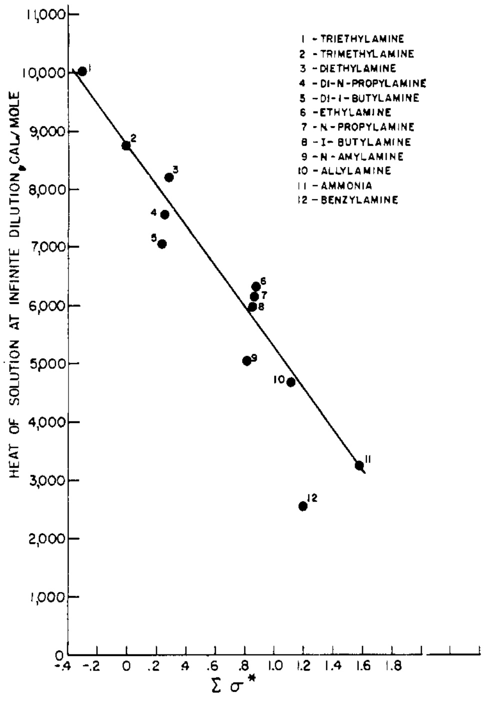

Figure 7. The heat of solutions of amines in water is a function of the total inductive effect

Subscripts

a = water
b = amine

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Selective Solvents for Separation of *n*-Pentane from 1-Pentene by Extractive Distillation

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EXTRACTIVE distillation is widely used on a commercial scale as a method for separating butanes from butylenes. Extractive solvents in commercial use include furfural-water (*3*), acetone-water (*6*), and acetonitrile-water (*4*). These same solvents are also suitable for effecting a separation between butylenes and butadiene, and between methyl butenes and isoprene. The present investigation was undertaken to find solvents which would be superior to those now in commercial use for paraffin-olefin-diolefin separations. Specifically, it was desired to find solvents or solvent mixtures which would produce either an improved selectivity, capacity, or both.

Unfortunately, the theory of nonideal liquid mixtures is not sufficiently well-developed to allow a sound prediction to be made of the performance of any proposed extractive solvent (*2, 10*). An experimental approach is thus necessary to determine the optimum type of structure which extractive solvent molecules should have. Study of a large number of different solvents is required to determine which types of functional groups on the solvent molecule are the most effective, and which of the many possible spacings and arrangements of these groups are the optimum.

Very few literature data exist on the vapor-liquid equilibrium behavior of paraffin-olefin-solvent mixtures. Hess, Naragon, and Coghlan did report such information for a large number of different solvents (*8*), but their data are difficult to use as in most cases their measurements were made at a single pressure (60 p.s.i.g.) and for a single concentration; thus it is not possible to compare different solvents at the same temperature. Other solvent evaluation studies have been reported (*5, 11*), but these are for the separation of aromatics from napthenes and paraffins by extractive distillation. These studies were of no assistance in the present program.

SCOPE OF THIS INVESTIGATION

Emphasis on evaluation of a large number of different solvents made it necessary to limit the number of tests with any given solvent. It was decided to limit the range of experimental composition to an essentially 100% solvent concentration, to vary the temperatures between 0° and 45° C., and to limit to a single pair the hydrocarbons to be separated, *n*-pentane-1-pentene. These C_5 hydrocarbons were chosen in preference to C_4 hydrocarbons to permit the use of low pressure, all-glass apparatus; the difference in the performance of C_4 and C_5 hydrocarbons in the presence of a solvent is not large and may be estimated (*1*). A diolefin was not studied in this work because solvents

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suitable for paraffin-olefin separations are also usually suitable for olefin-diolefin separations.

The effect of composition and temperature upon the relative volatility of any two components in a multicomponent mixture is as follows (*7*):

$$\alpha_{12} = \frac{\gamma_1 P_1 z_2}{\gamma_2 P_2 z_1} \qquad (1)$$

Equation 1 may be readily applied to a ternary mixture consisting of the two components to be separated (components 1 and 2) and the extractive solvent (component 3). In this instance the term γ_1 is the activity coefficient of component 1 as it exists in the ternary mixture; γ_1 is a strong function of composition, and a lesser function of temperature. The term γ_2 has similar significance. The terms P_1 and P_2 are the pure component vapor pressures and are strong functions of temperature. The ratio z_2/z_1 takes into account gas law deviations and the effect of total pressure upon vapor pressure, and is readily evaluated at moderate or low pressures (*9*).

Activity coefficient values may be computed from experimental vapor-liquid equilibrium measurements by the following equation which applies for binary or multicomponent mixtures:

$$\gamma_1 = (z_1 \pi y_1)/(P_1 x_1) \qquad (2)$$

In Equation 2, π is the total pressure, and y_1 and x_1 are the experimental equilibrium vapor and liquid compositions for component 1. A similar equation may be written for components 2 and 3.

Various empirical but thermodynamically consistent equation forms are available for expressing activity coefficients as a function of composition at constant temperature. The three-suffix Margules equations of Wohl (*7, 12*) show that γ_1/γ_2 varies with composition in a ternary mixture as follows:

$$\log \gamma_1/\gamma_2 = A_{21}(x_2 - x_1) + x_2(A_{12} - A_{21})(x_2 - 2x_1)$$
$$+ x_3 [A_{13} - A_{32} + 2x_1(A_{31} - A_{13}) - x_3(A_{23} - A_{32}) - C(x_2 - x_1)] \qquad (3)$$

Equation 3 substituted into Equation 1 would thus predict the relative volatility of component 1 to component 2 in the presence of a selective solvent (component 3) provided the six *A* constants and one *C* constant in Equation 3 were known.

Finding the relative volatility produced by each extractive solvent at any one temperature would require a minimum of seven experimental determinations. To permit the examination of a fairly large number of solvents in a reasonable time, the scope of the present work was limited to the measurement of α_{12} under conditions where components 1 and 2 were at essentially 100% concentration.

Table I. Experimental Vapor-Liquid Equilibrium Results for n-Pentane and 1-Pentene Solvent Binary Systems

			Activity Coeff. at Zero C_5 Concn. in Liquid		
No.	Solvent	Temp., ° C.	*n*-Pentane, γ_1^0	1-Pentene, γ_2^0	γ_1^0/γ_2^0
1	Tetrahydrofuran $CH_2CH_2OCH_2CH_2$ (cyclic)	0	1.97	1.40	1.41
		25	1.72	1.22	1.41
		35	1.63	1.10	1.42
		45	1.56	1.10	1.42
2	Diethyl ketone $C_2H_5COC_2H_5$	0	2.94	1.97	1.49
		25	2.56	1.79	1.43
		35	2.42	1.74	1.39
		45	2.33	1.67	1.39
3	Diethyl carbonate $C_2H_5OCOOC_2H_5$	0	3.49	2.20	1.59
		25	2.90	1.91	1.52
		35	2.73	1.81	1.51
		45	2.57	1.73	1.49
4	Methyl ethyl ketone $CH_3COC_2H_5$	0	4.15	2.40	1.73
		25	3.42	2.11	1.62
		35	3.18	2.02	1.58
		45	2.99	1.92	1.56
5	Pentanedione $CH_3COCH_2COCH_3$	0	5.47	3.15	1.74
		25	4.74	2.75	1.72
		35	4.51	2.66	1.70
		45	4.30	2.54	1.69
6	Cyclopentanone $CH_2CH_2COCH_2CH_2$ (cyclic)	0	5.71	3.28	1.74
		25	4.79	2.91	1.65
		35	4.56	2.81	1.63
		45	4.22	2.69	1.57
7	Acetone CH_3COCH_3	0	6.79	3.69	1.84
		25	5.28	3.16	1.67
		35	4.81	2.94	1.64
		45	4.41	2.80	1.58
8	Butyronitrile, C_3H_7CN	0	6.44	3.60	1.79
		25	5.35	3.30	1.62
		35	4.94	3.08	1.60
		45	4.58	2.97	1.54
9	Acetylpiperidine $C_3H_6(NCOCH_3)C_2H_4$ (cyclic)	0	7.13	4.17	1.71
		25	5.88	3.47	1.69
		35	5.53	3.33	1.66
		45	5.15	3.13	1.65
10	Acetophenone, $C_6H_5COCH_3$	25	6.24	3.77	1.65
11	Pyridine, C_6H_5N	25	6.19	3.88	1.60
12	Diethyl oxalate $C_2H_5OCOCOOC_2H_5$	0	8.42	4.61	1.83
		25	6.67	3.82	1.75
		35	6.07	3.59	1.69
		45	5.56	3.40	1.64
13	Propionitrile C_2H_5CN	0	10.53	5.27	2.00
		25	8.28	4.48	1.85
		35	7.61	4.25	1.79
		45	7.00	4.00	1.75
14	Dimethylacetamide $(CH_3)_2NCOCH_3$	0	11.87	5.95	1.99
		25	9.16	4.95	1.85
		35	8.32	4.66	1.78
		45	7.62	4.23	1.80

This limitation was somewhat restictive, but without it the task would be too long.

Equation 3 shows that when $x_1 = x_2 = 0$ and $x_3 = 1$, $\log \gamma_1/\gamma_2 = A_{13} - A_{23}$. Thus experimental evaluation of only the binary constants A_{13} and A_{23} is required.

CHOICE OF VAPOR-LIQUID METHOD

After the decision was made to obtain vapor-liquid equilibrium data for pentane-solvent and pentene-solvent binary mixtures at various temperatures, for various solvents, and at very small C_5 concentrations in the liquid phase, it was necessary to choose the type of vapor-liquid apparatus. Most vapor-liquid measurements involve establishment of equilibrium conditions, measurement of the pressure and temperature, and sampling and analysis of the vapor and the liquid. Instead of different analytical schemes for the many systems to be tested, a modification of the method of Baumgarten and Gerster (*1*) was employed. Weighed amounts of the two components were first added to the equilibrium vessel; boiling was begun, and equilibrium was established; measurements of the pressure and temperature were taken. When the liquid consists of a C_5-solvent binary mixture having a nearly 100% solvent concentration, the activity coefficient of the solvent is close to unity. Thus Equation 2 may be used to compute the solvent concentration in the vapor. If the holdup of the vapor space is known accurately, the moles of C_5 and solvent in the vapor may also be computed; by substracting these values from the moles of C_5 and solvent originally charged to the system, the composition and amount of the liquid phase may also be computed. Information is then available to compute values of the C_5 activity coefficient from Equation 2 without analysis of the vapor and liquid in the equilibrium chamber.

DETAILS OF ARRARATUS AND PROCEDURE

The equilibrium apparatus was essentially a closed vessel containing the C_5 hydrocarbon-solvent mixture; air and other noncondensable gases were previously removed. Values of equilibrium pressure were measured for a system of given total amount and composition at each of several constant temperatures.

The equilibrium cell, a 200-cc. round-bottomed flask, was held in a thermostatically-controlled bath and was fitted with thermometer well and magnetic stirrer. Connected to the cell through various openings were a mercury manometer, a chamber for introducing the C_5 component, and an acetone–dry ice, cold-finger–type of condenser (Figure 1). Most tests were carried out using 70 to 100 grams of solvent, and 1 to 2 grams of C_5. The temperatures were 0°, 25°, 35°, and 45° C.; the corresponding total pressures varied from 6.5 to 628 mm. of mercury; most total pressures ranged from 30 to 200 mm. of mercury.

Because the amount of C_5 introduced into the cell had to

Table I. (Continued)

No.	Solvent	Temp., ° C.	Activity Coeff. at Zero C_5 Concn. in Liquid		γ_1^0/γ_2^0
			n-Pentane, γ_1^0	1-Pentene, γ_2^0	
15	*n*-Methylpyrrolidone $CH_2CH_2(NCH_3)COCH_2$ (cyclic)	0	14.10	6.53	2.16
		25	10.74	5.48	1.96
		35	9.87	5.18	1.90
		45	9.00	4.90	1.83
16	Acetonylacetone $CH_3COCH_2CH_2COCH_3$	0	13.77	6.67	2.06
		25	10.50	5.63	1.87
		35	9.56	5.30	1.80
		45	8.72	5.02	1.74
17	Tetrahydrofurfuryl alcohol, $C_4H_7O—CH_2OH$ (cyclic)	25	11.15	6.89	1.62
18	Dimethylsulfolane $(CH_3)_2C_4H_8SO_2$	25	12.60	6.46	1.95
19	Dimethylcyanamide $(CH_3)_2CN_2$	0	17.72	8.13	2.18
		25	13.46	6.87	1.96
		35	12.10	6.38	1.90
		45	11.00	6.03	1.83
20	Methyl Carbitol $CH_3OCH_2CH_2OCH_2CH_2OH$	25	13.70	7.98	1.72
21	Dimethylformamide $(CH_3)_2N\text{-}CO\text{-}H$	0	18.75	8.63	2.17
		25	14.06	7.18	1.96
		35	12.77	6.67	1.92
		45	11.33	6.30	1.80
22	Methyl Cellosolve $CH_3\text{-}O\text{-}CH_2CH_2OH$	25	14.5	8.6	1.69
23	Furfural CHCHO(CCHO)CH (cyclic)	0	22.43	11.33	1.98
		25	16.55	8.85	1.87
		35	14.68	8.12	1.81
		45	13.10	7.49	1.75
24	Acetonitrile CH_3CN	0	27.29	12.00	2.27
		25	20.40	9.45	2.16
		35	17.28	8.68	1.99
		45	15.42	7.97	1.94
25	Ethylene chlorhydrin $ClCH_2CH_2OH$	25	24.0	13.4	1.79
26	γ-Butyrolactone $CH_2CH_2OCOCH_2$ (cyclic)	0	37.30	15.39	2.42
		25	26.99	12.44	2.17
		35	23.91	11.59	2.07
		45	21.14	10.75	1.97
27	Methanol, CH_3OH	25	27.0	17.7	1.53
28	β-Chloropropionitrile $ClCH_2CH_2CN$	25	28.5	13.1	2.18
29	Pyrrolidone $CH_2CH_2NHCOCH_2$ (cyclic)	25	33.49	16.80	1.99
		35	30.12	15.52	1.94
		45	26.94	14.51	1.86
30	Propylene carbonate $C_3H_6CO_3$ (cyclic)	25	33.8	16.1	2.10
31	Nitromethane CH_3NO_2	25	53.5	21.5	2.49
32	Ethylenediamine $NH_2CH_2CH_2NH_2$	25	61.0	28.9	2.11
33	Ethylene carbonate $CH_2OCOOCH_2$ (cyclic)	36.8	63.80	33.25	1.92
		45.1	53.35	29.30	1.82

be known accurately, it was first sealed into a small glass ampoule, weighed, and then inserted into the hydrocarbon chamber with its capillary tip projecting through a special hollow stopcock used later for breaking off the glass capillary tip. The system was now evacuated, and the valve was closed between the equilibrium flask and the stopcock used for breaking the ampoule. A carefully weighed amount of solvent was next added to the equilibrium flask which was evacuated until an absolute pressure of less than 1 mm. of mercury was achieved. The vapor pressure of the pure solvent was then determined experimentally at 0°, 25°, 35°, and 45° C. Next the C_5 hydrocarbon was allowed to enter the equilibrium chamber, and the equilibrium pressure and temperature were measured.

The *n*-pentane and 1-pentene were obtained from the Phillips Petroleum Co. as 99% pure. The solvents were the purest grade obtainable.

The experimental activity coefficients were corrected to zero C_5 hydrocarbon concentration by the use of two-suffix Margules equations (*12*). The corrected values are designated as γ_1^0 and γ_2^0. Results for all of the solvents tested are given in Table I.

DISCUSSION OF RESULTS

Magnitude of *n*-Pentane Activity Coefficients. It is of interest to examine the magnitude of the *n*-pentane activity coefficients to determine if they can be correlated with the chemical structure of the solvent. For the simpler types of solvents—those consisting of a single functional group attached to methyl or methylene groups—two generalizations are possible.

The first of these is that values of γ_1^0 decrease as the number of methylene groups in the solvent increases. For example, values of γ_1^0 at 25° C. for the solvents acetonitrile, propionitrile, and butyronitrile were 20.4, 8.28, and 5.35, respectively. The same trend may be noted for the various ketones tested. When the solvents are acetone, methyl ethyl ketone, and diethyl ketone, the γ_1^0 values at 25° C. are 5.28, 3.42, and 2.56. Apparently the effectiveness of the polar group in promoting nonideality is "diluted" as the number of methylene groups increases.

A second generalization of interest is that the magnitude of γ_1^0 depends, for a given number of methylene or methyl groups in the solvent molecule, upon the nature of the functional or polar group. For example, γ_1^0 in the presence of acetone is 5.28, while γ_1^0 at the same temperature in the presence of propionitrile is 8.28. Also at 25° C., γ_1^0 with nitromethane is 53.5, whereas γ_1^0 with methanol is 27.0. And, considering simple difunctional solvent molecules, γ_1^0 at 25° C. is 24.0 for ethylene chlorhydrin and γ_1^0 at 25° C. for ethylenediamine is 61.0.

These two generalizations have been expressed quantitatively for paraffins in ketones and for paraffins in a few specific solvents by Pierotti and others (*10*).

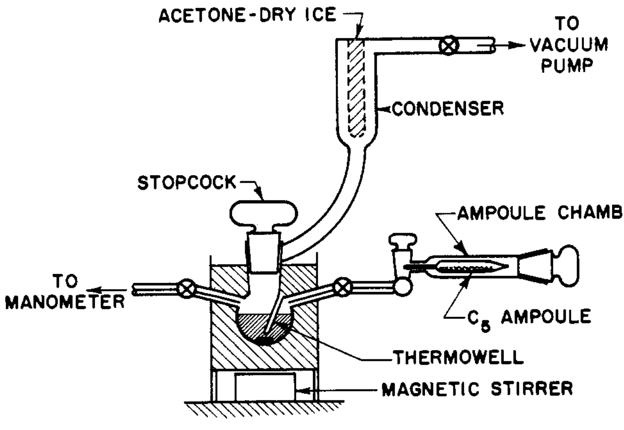

Figure 1. Experimental apparatus

The effect of closing a straight-chain solvent into a five-membered ring may be shown by comparing the results for diethyl ketone and cyclopentanone. At 25° C., the value of γ_1^0 for the former is 2.56, and 4.79 for the latter.

It is difficult to suggest general trends for the difunctional solvents because the relative location of the polar groups is an important factor affecting the magnitude of the γ_1^0 values obtained. For example, solvent 5 in Table I contains a single CH_2 group between the two CO groups whereas acetonylacetone (number 16) has two CH_2 groups between the two CO groups; with this exception, the two solvents are structurally similar. Yet γ_1^0 for the former is 4.74 whereas γ_1^0 for the latter is 10.50 at 25° C. Five of the solvents (3, 12, 26, 30, and 33) tested contained both ketone groups and ether linkages; the arrangement of these simple groups also has a very large effect upon the magnitude of the γ_1^0 values obtained.

Five of the solvents tested contained the $=N—CO—$ group. Decreasing the number of methylene groups, as in proceeding from solvent 9 to solvent 14, produces the expected result of raising the γ_1^0 values. When a methyl group is replaced with hydrogen, the values of γ_1^0 are raised even further; this is illustrated in proceeding from solvent 14 to solvent 21, and in proceeding from solvent 15 to 29. Solvents 14 and 29 differ only by two hydrogen atoms, yet the difference in results produced by the difference in the arrangement of the atoms in the molecule is large.

Magnitude of 1-Pentene Activity Coefficients. Inspection of the activity coefficient results for the 1-pentene shows that for any solvent and at any temperature the value of γ_2^0 is smaller in magnitude than the corresponding value for γ_1^0. The presence of the double bond in the 1-pentene molecule permits greater interaction to exist between olefin and solvent molecules than between paraffin and solvent molecules, and the volatility of the olefin is reduced accordingly. The relationship between γ_1^0 and γ_2^0 for all of the solvents tested at 25° C. is shown in Figure 2. This plot demonstrates that except for seven of the 32 solvents tested, a very definite relationship exists between the values of γ_1^0 and γ_2^0: as values of γ_1^0 increase, values of γ_2^0 also increase, although not in the same direct proportion. The empirical straight line drawn through all but seven of the points on the log-log plot is described by the following equation:

$$\gamma_1^0 = 1.34\ (\gamma_2^0)^{1.19} \tag{4}$$

or

$$\gamma_2^0 = 0.78\ (\gamma_1^0)^{0.84} \tag{5}$$

The close relationship between the γ_1^0 and γ_2^0 values for 25 of the 32 solvents tested at 25° C. is quite remarkable when the variation in the nature of these solvents is considered. The seven solvents which deviated from the general pattern, numbers 17, 20, 22, 25, 27, 29, and 32, are substances which have the ability to form strong hydrogen bonds: tetrahydrofurfuryl alcohol, methyl carbitol, methyl Cellosolve, ethylene chlorhydrin, methanol, pyrrolidone, and ethylenediamine; of all of the solvents tested, only these seven contained either and —OH group or an —NH group as part of the molecule.

Results Expresses as Ratio of γ_1^0/γ_2^0. In order to interpret the results in terms of selectivity produced by the various solvents for a paraffin-olefin separation by extractive distillation, it is necessary to consider values of the ratio of the C_5 activity coefficients. Figures 3 and 4 present values of γ_1^0/γ_2^0 plotted as a function of log γ_1^0. Figure 3, top shows the results obtained at 25° C., while Figure 3, bottom compares the 25° C. results with those obtained at 0° and 45° C.

As Figure 3, top is merely an alternate representation of Figure 2, an equation to represent the results of Figure 3, top may be derived from Equation 5. Dividing the identity

$\gamma_1^0 = \gamma_1^0$ by Equation 5, the following relationship is obtained:

$$\gamma_1^0/\gamma_2^0 = 1.28\ (\gamma_1^0)^{0.16} \qquad (6)$$

Actually, Figure 3, top is a more sensitive method for plotting the experimental results, and the constants in Equations 4 to 6 were obtained from it. Because of this increased sensitivity, the points on Figure 3, top deviate more from the correlation line, and the lowering of selectivity produced by the solvents which form hydrogen bonds becomes more apparent.

The main conclusion to be drawn from study of Figure 3, top is that for nonhydrogen-bonding solvents, the selectivity increases with an increase in the degree of nonideality of either of the hydrocarbon-solvent binary systems. However, as the degree of nonideality (or magnitude of the activity coefficient values) increases, the capacity of the solvent for dissolving the hydrocarbons decreases at a given level of temperature and pressure. According to Equation 6, the value of γ_1^0/γ_2^0 increases only by 12% every time the value of γ_1^0 is doubled.

The effect of temperature upon selectivity is shown in Figure 3, bottom, where the experimental values of γ_1^0/γ_2^0 for 0° and 45° C. are shown as a function of log γ_1^0. The correlation line for 25° C. is shown on Figure 3. Two conclusions are apparent from Figure 3, bottom: that at a given value of γ_1^0 selectivity is increased by a decrease in temperature, and that the rate of selectivity increase for a given temperature change is greatest at the higher values of γ_1^0. The result for 0° C. is given by the relation

$$\gamma_1^0/\gamma_2^0 = 1.32\ (\gamma_1^0)^{0.17} \qquad (7)$$

and the result for 45° C. is given by

$$\gamma_1^0/\gamma_2^0 = 1.26\ (\gamma_1^0)^{0.15} \qquad (8)$$

Effect of Temperature Upon Selectivity and Capacity. More careful study as to the effect of temperature upon the activity coefficient results can be made if the C_5 activity coefficients are considered individually. Figure 4 shows values of log γ_1^0 or log γ_2^0 as a function of reciprocal absolute temperature. This type of plotting is desirable as the slopes of the lines obtained are related to the values of L_1, the

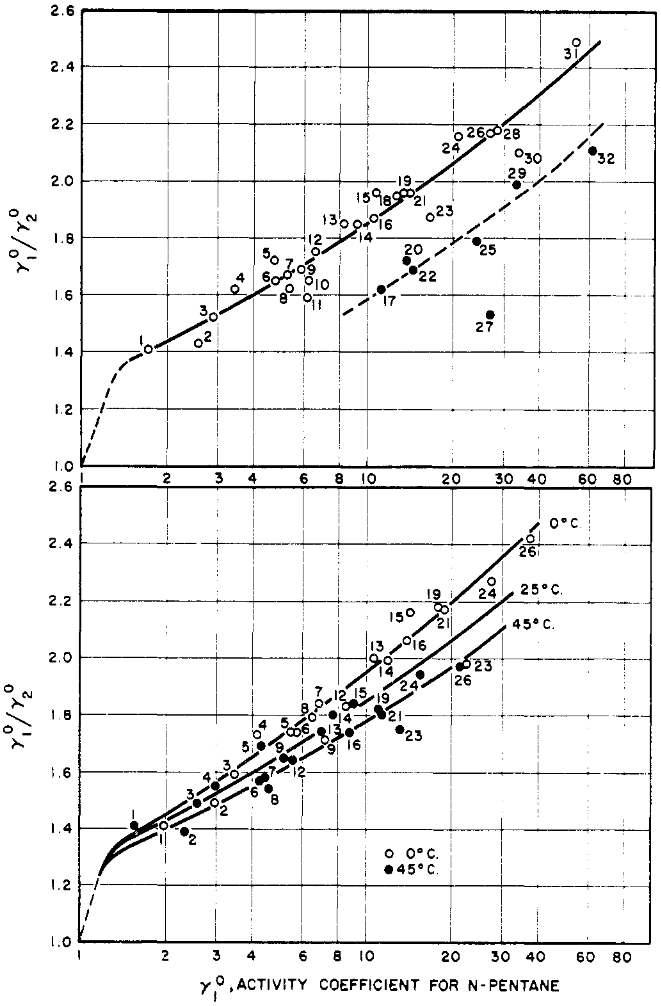

Figure 3. Top: ratio of activity coefficients for *n*-pentane and 1-pentene as a function of *n*-pentane activity coefficients; values are for 25° C. Bottom: nonhydrogen-bonding solvents are shown; correlation line for 25° C. is repeated. Numbers list solvents that are mixed with either C_5 hydrocarbon in Table I

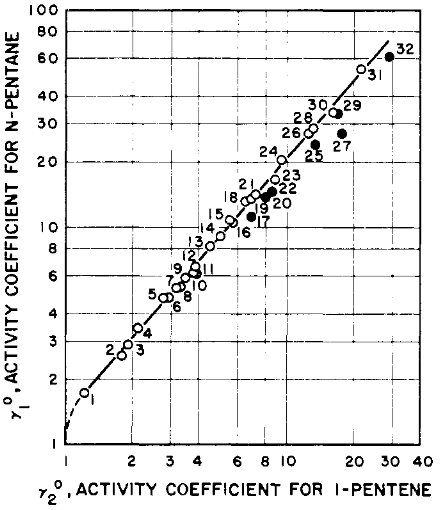

Figure 2. Values of activity coefficient for *n*-pentane as a function of corresponding activity coefficient values for 1-pentene at 25° C.

Numbers list solvents in Table I that are mixed with either C_5 hydrocarbon; solid points designate hydrogen-bonding solvents

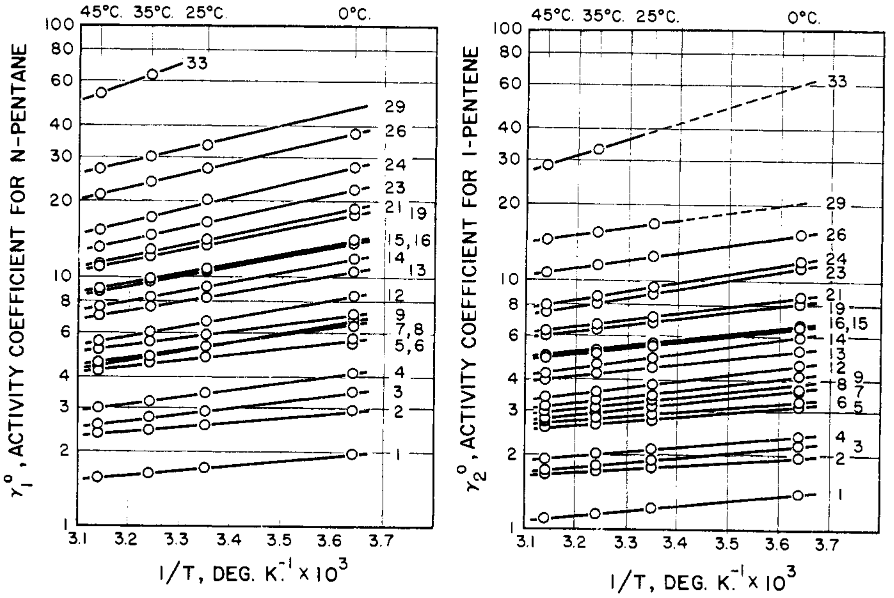

Figure 4. Left: effect of temperature upon activity coefficient calues at infinite dilution in various solvents for *n*-pentane; right, for 1-pentene

Numbers list solvents in Table I

Table II. Heats Absorbed on Solution of Liquid *n*-Pentane and 1-Pentene in Various Solvents over Range 0° to 45° C.

	Partial Heats of Soln. for 0% C_5 Compn., B.t.u./Lb. Mole C_5 Dissolved, When C_5 Component is	
Solvent	*n*-Pentane	1-Pentene
Tetrahydrofurane	1620	1730
Diethylketone	1540	1170
Diethylcarbonate	2180	1720
Methylethylketone	2370	1600
Pentanedione	1980	1540
Cyclopentanone	1980	1420
Acetone	2950	1980
Butyronitrile	2440	1910
Acetylpiperidine	2320	2050
Diethyloxalate	2970	2190
Propionitrile	2920	1980
Dimethylacetamide	3170	2360
n-Methylpyrrolidone	3210	1910
Acetonylacetone	3270	2030
Dimethylcyanamide	3410	2150
Dimethylformamide	3560	2260
Furfural	3810	2950
Acetonitrile	4090	2940
γ-Butyrolactone	4090	2570

partial heats of solutions, by the thermodynamic relation

$$\frac{d \log \gamma_1^0}{d(1/T)} = \frac{L_1}{2.303R} \qquad (9)$$

where R is 1.987 B.t.u. per pound-mole in ° R. Figure 4 shows that straight lines were obtained in every case, indicating that the partial heats of solution did not vary over the temperature range studied, 0° to 45° C.

Heats of solution values, given in Table II, indicate the general trend that as the degree of nonideality of the hydrocarbon-solvent binary pair increases, so does the magnitude of the heats of solution (Figure 5). Although results for any given solvent may deviate considerably from the proposed correlation line, Figure 5 should be helpful for estimating purposes.

Results for Mixed Solvents. Table III presents results for a few mixed solvents. The mixed solvents were treated as a single pseudo-component in the calculations, and the results are given for *n*-pentane mixed solvent and 1-pentene mixed solvent, pseudo-binary systems. A large number of furfural-additive mixtures were studied previously by Baumgarten and Gerster (*1*) for use as solvents in extractive distillation applications, and their method of treatment applies in this case also.

The first three items of Table III show the effect of adding 5% of a second solvent component to methyl Cellosolve. The results indicate that this small amount of added component is not sufficient to effect any appreciable difference in the γ_1^0/γ_2^0 ratio. Item 4 shows that when the additive concentration is increased to 20%, a moderate change in γ_1^0/γ_2^0 can be effected.

A large increase in the individual γ-values (Table III, item 1) confirms an earlier conclusion that hydrogen-bonding solvents cause abnormally large C_5 activity coefficient values without producing correspondingly large γ_1^0/γ_2^0 ratios. The same result is shown for Item 5.

Results for mixtures (Table III, items 7 and 10) make selectivity data also available for the individual components of the solvent mixtures. Figure 6 shows that the selectivity produced by the mixed solvent lies intermediate between the selectivity produced by each component of the solvent mixture. Thus these very few data do not indicate any selectivity advantage for a mixed solvent compared with another pure solvent if in both instances the values of γ_1^0 are the same.

A few cases were studied where certain high-boiling solvent components were added to simple solvents to form a mixed solvent. The high boiling substances were chosen for evaluation as their ability to promote extremely high selectivities had already been demonstrated in liquid-liquid extraction applications; however, to make them suitable for

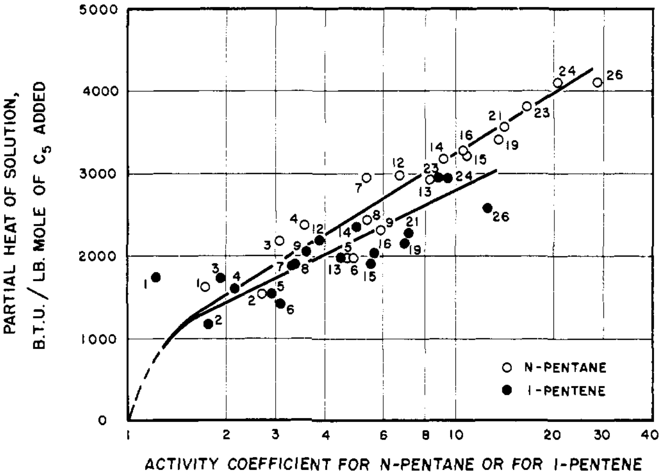

Figure 5. Partial heats of solution for *n*-pentane or 1-pentene in various solvents at 0 to 45° C.

Numbers refer to solvents in Table I

Table III. Experimental Vapor-Liquid Equilibrium Results for *n*-Pentane and 1-Pentene Mixed Solvent Pseudo-Binary Systems

			Activity Coeff. at Zero C_5 Concn. in Liquid		
No.	Mixed Solvent	Temp., ° C.	*n*-Pentane γ_1^0	1-Pentene γ_2^0	γ_1^0/γ_2^0
	Methyl Cellosolve				
1	Water, 5 vol. %	25	24.7	14.6	1.69
2	Tetramethylene cyclic sulfone, 5 vol. %	25	15.6	9.2	1.70
3	Nitromethane, 5 vol. %	25	15.3	9.0	1.70
4	Tetramethylene cyclic sulfone, 20 vol. %	25	18.3	10.1	1.81
	Pyridine				
	Water, 10 vol. %	25	20.0	11.8	1.70
6	β-β′-Oxydipropionitrile, 10 vol. %	25	7.8	4.7	1.66
7	γ-Butyrolactone, 32.1 vol. %	25	10.4	5.8	1.79
	Benzene				
8	Tetramethylene cyclic sulfone, 50 vol. %	25	10.2	5.9	1.73
9	β-β′-Oxydipropionitrile, 50 vol. %	25	10.3	5.9	1.75
	Ethyl Methyl Ketone				
10	γ-Butyrolactone, 50 mole %	0	11.07	5.51	2.01
		25	8.46	4.72	1.79

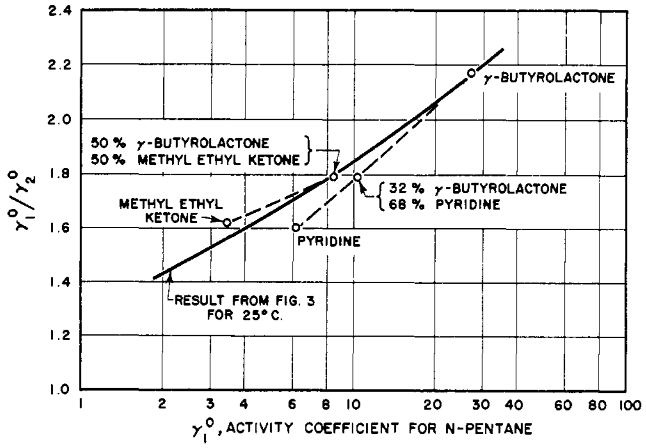

Figure 6. Comparison of activity coefficient ratios in pure solvents with those in solvent mixture; all data at 25° C.

use as extractive distillation solvents it was necessary to dilute them with lower-boiling substances. With such mixtures (Table III, items 4, 6, 8, and 9) the effective components of the solvent mixture lost much of their selective power due to dilution effects.

CHOICE OF OPTIMUM EXTRACTIVE SOLVENT

A number of conclusions may be drawn from the present study which should be helpful in choosing an optimum extractive distillation solvent for a paraffin-olefin or even an olefin-diolefin separation.

The first of these is that solvents which form strong hydrogen bonds—those containing —OH or = NH groups—are likely to produce a lower selectivity than those which do not. A second conclusion indicates that for nonhydrogen bonding solvents, all types of solvents—those containing either one or several functional groups, those having five- or six-membered rings and those which do not—appear to produce about the same selectivity if they produce the same degree of nonideality with paraffin or olefin. No particular functional group appears to be appreciably more effective than any other, nor does any particular spacing or arrangement of this group or groups appear to be the optimum. Thus no solvent or group of solvents can be recommended as particularly outstanding.

A third important conclusion is that the degree to which the selectivity is lowered with increasing temperature is greatest for the solvents which produce the highest nonideality.

With these conclusions in mind, an optimum extractive solvent can now be chosen. First assume a solvent circulation rate; as an example, assume a solvent dosage of 9 moles of solvent per mole of non-solvent reflux. The solvent concentration on the liquid of the top trays of the column will then not exceed 90 mole %. To obtain as high a selectivity as possible at the chosen capacity, the value of γ_1^0 should be chosen as high as possible. The limiting factor here is miscibility; mixtures of solvent and *n*-pentane should be just completely miscible at 90% solvent concentration. (Immiscibility always occurs first on the top trays of an extractive column.) Miscibility limits can be estimated as $x_1 = 1/\gamma_1$ for high solvent concentrations; in the present example, γ_1 would be about $1/(1 - 0.90)$ or 10, and γ_1^0 by the two-suffix Margules equation would be about 17. Figure 3, bottom, shows that if the tower temperature is 45° C., and a solvent is chosen which has a value of $\gamma_1^0 = 17$ at this temperature, γ_1^0/γ_2^0 will be 1.95; the corresponding selectivity is then the highest that can be expected at the chosen solvent circulation rate. Other solvent circulation rates are then chosen, and the corresponding solvents and selectivities are determined as before. An economic balance for each case will then show the point where lowered costs due to improved selectivity are just counterbalanced by increased costs due to higher solvent circulation rate.

It is possible, of course, for the selectivity to be greater than that predicted by Figure 3, bottom. If any type of chemical bonding is present between the solvent and one of the feed components, as is the case between cuprous ammonium acetate and 1,3-butadiene, the selectivity may be quite different.

It should be emphasized that not all of the solvents tested in this study were completely stable even at the comparatively low temperatures employed. They were nevertheless studied because of interest in their structure.

A final word of caution: This study was limited completely to solvent concentrations in the liquid of 100%, and although the two-suffix Margules equations (*12*) should be adequate for predicting activity coefficient behavior at 90 or even 80 mole % solvent concentration from data taken at 100% solvent concentration, fairly important deviations between predicted and experimental selectivity behavior may become evident at lower solvent concentrations.

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NOMENCLATURE

A_{12} = limit log $\gamma_1(x_1 \rightarrow 0, x_2 \rightarrow 1)$
A_{23} = limit log $\gamma_2(x_2 \rightarrow 0, x_3 \rightarrow 1)$
C = ternary constant in three-suffix Margules equation
L = partial molar heat absorbed on solution of liquid in liquid
P = vapor pressure of pure component
R = gas-law constant
T = absolute temperature
x = mole fraction of component in liquid
y = mole fraction of component in vapor
z = correction for nonideality of gases and volume of liquid
α_{12} = relative volatility, or $(y_1/x_1)/(y_2/x_2)$
γ = activity coefficient of component
γ^0 = activity coefficient of component at infinite dilution of component in liquid phase
π = total pressure of system

Subscripts

1 = component 1, *n*-pentane
2 = component 2, 1-pentene
3 = component 3, solvent or mixed solvent

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