Physical and Chemical Forces in Solvent Selectivity for Hydrocarbons

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An analysis is given of the role of physical and chemical forces in determining the selectivity of a solvent for different hydrocarbons. The physical contribution to selectivity depends on the polar energy density of the solvent and on the difference in size of the hydrocarbons to be separated; this effect is well-demonstrated by solvent selectivity data for paraffins where no chemical forces are important. The chemical contribution depends on the ability of the solvent to form acid-base complexes with the hydrocarbon. Chemical forces leading to complex formation can be detected by measurements on the heat of mixing, the volume change of mixing, and on the ultraviolet absorption of solvent-hydrocarbon mixtures; some illustrations of such measurements are presented. Finally an equation is proposed for correlating selectivity data in extractive distillation, and its applicability is demonstrated with activity coefficient data for saturated and unsaturated hydrocarbons in various polar solvents.

A common problem in the separation of hydrocarbons occurs when two or more components in the liquid mixture have nearly the same volatility. In that case separation by ordinary distillation is difficult or perhaps even impossible, and it is necessary to add a new component which will appreciably change the relative volatility of the hydrocarbons. This additional component, known as the *entrainer* or *extracting solvent,* must be able to differentiate between the two hydrocarbons which are to be separated, which is another way of saying that if the solvent is to be effective it must have a high selectivity. Previously (*13*) it was shown that the thermodynamics of solvent selectivity depends on the intermolecular forces which act amongst polar and nonpolar molecules and that these forces can be conveniently subdivided into physical and chemical forces. This paper reports some further studies in analysis and detection of intermolecular forces which give rise to selectivity and illustrates how some of the ideas developed here may be used in the correlation and interpretation of experimental phase equilibrium data.

PHYSICAL FORCES

When a polar solvent is mixed with a nonpolar hydrocarbon, the important physical forces are those between the dipoles of the polar component, the induced dipole forces which act between the polar and nonpolar species, and the dispersion forces which act between all the species. On the basis of a simplified model it was shown (*13*) that when the polar solvent is present in excess, the selectivity (and hence the relative volatility) can be expressed in terms of a polar, a dispersion, and an induction contribution. It was further shown that in the absence of chemical forces the polar term was the dominant one whenever there was a significant difference in the sizes of the two hydrocarbons to be separated; the model predicts that in the absence of chemical forces the larger hydrocarbon will have the larger activity coefficient and that the logarithm of the selectivity is proportional to the square of the polar solubility parameter of the extracting solvent. Hence it is possible to separate two hydrocarbons merely on the basis of size difference, as shown schematically in Figure 1. A polar molecule moves about, colliding with nonpolar hydrocarbons. In each collision the polar molecule kicks the hydrocarbon in the sense that it causes the hydrocarbon to have a positive deviation from Raoult's law. If hydrocarbons 1 and 2 are present in equal molar concentrations, it is clear that the larger hydrocarbon 1 will be kicked more frequently than the smaller hydrocarbon 2. As a result hydrocarbon 1 will exhibit a larger positive deviation from Raoult's law than hydrocarbon 2, merely because hydrocarbon 1 exhibits a larger cross section for interaction with the polar component. This is equivalent to saying that the larger hydrocarbon will have the larger activity coefficient.

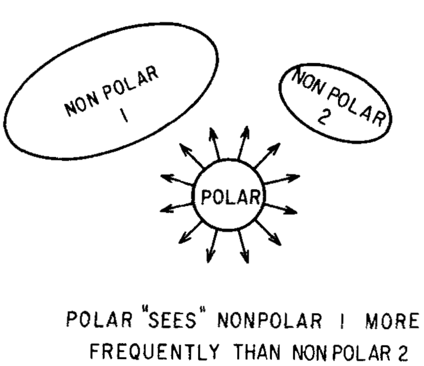

Fig. 1. Effect of molecular size on selectivity.

The effect of molecular size on selectivity is well-illustrated by activity coefficient data for paraffins in polar

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solvents; in saturated hydrocarbons chemical forces are not important, and therefore the qualitative conclusions of the simplified model apply without modification. Figure 2 shows that for normal paraffins in three polar solvents the logarithm of the activity coefficient is approximately a linear function of the paraffin size. Since the selectivity of component 1 relative to component 2 is the ratio of activity coefficient of 1 to that of 2, the nearly linear data in Figure 2 point out that for saturated hydrocarbons the logarithm of the selectivity is closely proportional to the size difference of the hydrocarbons which are to be separated.

CHEMICAL FORCES

Saturated hydrocarbons are relatively inert materials, and hence their interaction with polar solvents involves no chemical forces. However olefins, acetylenes, and aromatics have highly polarizable pi electrons which can cause loose bonding, or complex formation, with electrophilic groups such as cyano, nitro, or hydroxyl radicals. Such loose aggregates are often called *acid-base* complexes;* their importance in extractive processes is due to the fact that if a hydrocarbon forms a complex, its volatility is decreased, and the more stable the complex the lower will be the volatility.

Complex formation can be detected in many ways, and three of these are considered here. First the formation of a complex can be detected by examining the heat of mixing between the polar species and the hydrocarbon. This heat of mixing consists of two parts: one generated by the physical forces which are always present, and another generated by the chemical forces which are present only in the event that complex formation occurs. The physical forces always give rise to an endothermic (positive) heat of mixing, whereas the chemical complexing forces always give rise to an exothermic (negative) heat of mixing. *The actually measured heat of mixing is the sum of these two contributions* and hence may be positive or negative depending on which contribution is larger. However for similar hydrocarbons the heat of mixing will be larger (algebraically) for the more saturated hydrocarbon. For example consider the difference between the heat of mixing of acetone with cyclohexane and that of acetone with benzene. Data for the former system were obtained with a calorimeter described elsewhere (*2*), and data for the latter system have been reported previously (*4, 11*); the new results are shown in Figure 3. For the noncomplexing cyclohexane the heat of mixing is one order of magnitude larger than that for the complexing benzene. The small heat of mixing for the acetone-benzene system does not mean that this system is nearly ideal but rather that in the vicinity of room temperature the chemical and physical contributions to the enthalpy of solution tend nearly to cancel each other. Since the heat of complex formation is exothermic, complex stability falls with rising temperature; less complex is formed as the temperature increases, and therefore the chemical contribution to the heat of mixing must decrease. As a result the heat of mixing for the acetone-benzene system should rise with temperature as is observed (*4, 11*).

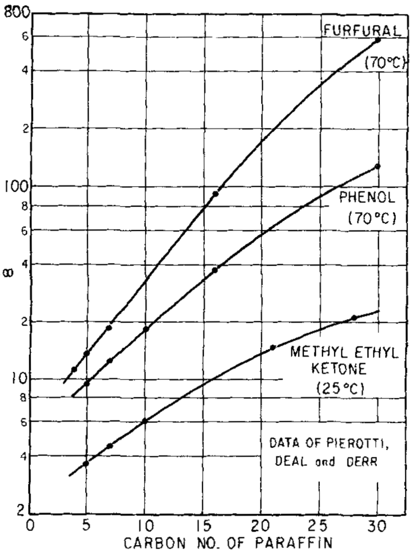

Fig. 2. Size effect in solvent selectivity: activity coefficients of normal paraffins in polar solvents at infinite dilution.

TABLE 1. EQUILIBRIUM CONSTANTS FOR COMPLEX FORMATION WITH NITROETHANE AT 25°C.

Hydrocarbon	Ionization potential, e.v.	Equilibrium constant, liter/g.-mole
Benzene	9.2	0.020
Toluene	8.9	0.022
Mesitylene	8.3	0.093

The effect of unsaturation on complex formation and hence on the heat of mixing is shown best by comparing data for a set of hydrocarbons having a fixed number of carbon atoms but varying in their degree of unsaturation. Accordingly heat of mixing data were obtained for a series of C_6 hydrocarbons with nitroethane. Figure 4, which shows the results, indicates that as complex stability rises with unsaturation, the heat of mixing tends to fall toward the exothermic side; the heat of mixing is a maximum for saturated hexane and a minimum for unsaturated benzene. Original data for Figure 4 are available elsewhere (*1*).

Complex formation can also be detected from volumetric data. When a complex is formed between two (or more) molecules, the volume occupied by the complex is always less than that occupied by the molecules which form it, and therefore complex formation produces a shrinkage. However when two liquids are mixed, effects other than complex formation also affect the volume change on mixing; therefore, as in the heat of mixing, there are both physical and chemical contributions to the excess volume. The various physical contributions have been considered by Meares (*8, 9, 10*) and by Scatchard (*15*). There are two physical contributions which are important in mixtures of hydrocarbons and polar liquids. One of these, which is usually dominant, is due to the difference in cohesive energy densities and makes a positive contribution to the excess volume; the other, which is of lesser importance, is proportional to the difference in microscopic compressibilities and almost always makes a negative contribution to the excess volume. Both of these physical effects are such that the excess volume is proportional to the product of the volume fractions. Chemical effects however are proportional to the product of the mole fractions, and therefore in a system where the molar volumes of the two liquids are quite different, complexing can frequently be detected by an S-shaped excess volume curve which is positive for part of the composition variable and negative for another part, or else by a curve which is everywhere positive but shows two maxima and a minimum. There are many examples of the former type of curve, one being that for the acetone-chloroform system (*6*). The latter type

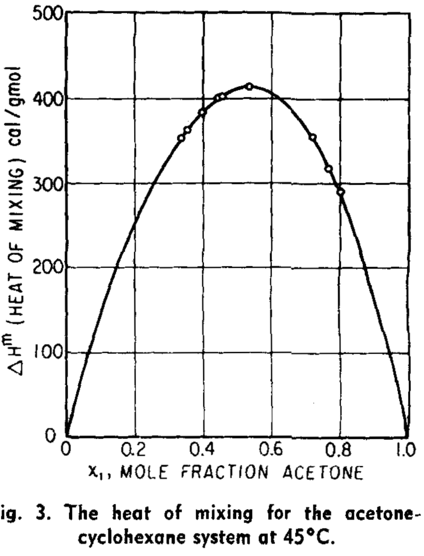

Fig. 3. The heat of mixing for the acetone-cyclohexane system at 45°C.

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* The word base here refers to the electronic definition of bases of G. N. Lewis and does not refer to the ability of a substance to attract a hydrogen ion.

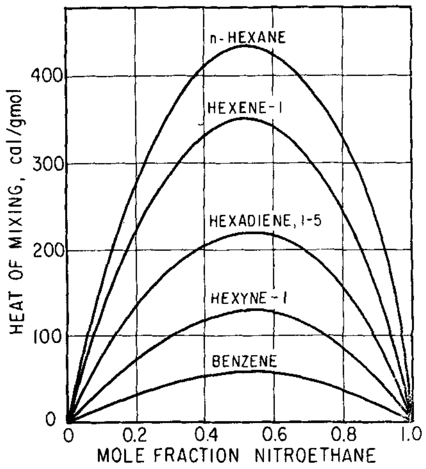

Fig. 4. Effect of unsaturation of the hydrocarbon on the heats of mixing for nitroethane-hydrocarbon systems at 45°C.

of curve is much less frequent, but an example of it is given by the carbon tetrachloride-benzene system at low temperatures (*16*).

While it is difficult to give a useful quantitative relationship between complex formation and volume change on mixing, the qualitative criteria are the same as those for the heat of mixing, since in both cases complex formation causes the measured quantity to be more negative. This effect is illustrated in Figure 5, where the effect of hydrocarbon unsaturation is strikingly shown by the excess volumes of several hydrocarbons with nitroethane. In those cases where complexing occurs the excess volume is negative except for hexene-1 where it is positive for a small concentration range. Only for cyclohexane is the excess volume positive throughout.

The complexing effect of different polar solvents on benzene is shown in Figure 6, where, qualitatively, the better the solvent the more negative the excess volume. Di-isobutyl ketone appears to complex only slightly with benzene, probably because of the steric interference of the bulky isobutyl groups which prevent complexing between the carbonyl group and the pi electrons of benzene. (The excess volume of benzene with sterically more favorable acetone is negative for all concentrations.) The results in Figure 6 clearly suggest that $\beta\beta'$ dipropionitrile is likely to be a more highly selective solvent for aromatics than di-isobutyl ketone or acetophenone.

Original data for Figures 5 and 6 are available elsewhere (*1*).

The most direct method for determining the presence of a complex is that with ultraviolet spectroscopy. If a complex is formed, the electronic distribution about the nuclei is sufficiently disturbed to produce an ultraviolet absorption spectrum for the complex which is different from the sum of those of the two complexing components. A simple test therefore is to compare the absorption of a polar-nonpolar mixture, with that of the polar and that of the nonpolar taken separately. This can be conveniently done with a double-cell technique, where the polar electron acceptor is designated as an acid and the nonpolar electron donor as a base. If the absorption in one cell is different from that in the other, a complex must have been formed, and the intensity of the difference is a measure of the complex stability. For precise quantitative work the necessary optical arrangement and the experimental procedure is a little more complicated; however it is possible to use optical measurements to compute equilibrium constants for complex formation as has been described by Ketelaar (*7*), Benesi and Hildebrand (*3*), and many others. In the past such measurements have been made primarily with inorganic electron acceptors, but there is good reason to believe that this method is also applicable to common organic polar materials which may be useful extracting solvents. Accordingly optical measurements were made for three mixtures of hydrocarbons with nitroethane. The details of this work are presented elsewhere (*2*), but some of the results are shown in Table 1. The ability of a hydrocarbon to transfer an electron is indicated (inversely) by its ionization potential, and, as expected, the results in Table 1 show that complex stability increases with rising hydrocarbon basicity.

EFFECT OF TEMPERATURE

In the absence of chemical forces the model previously presented shows that the selectivity falls with rising temperature. If chemical forces are present, increasing temperature decreases complex stability, and hence a rise in temperature will also lower the selectivity owing to chemical effects. It would appear then that extractive processes are most efficient at lower temperatures. However in extractive distillation selectivity must clearly improve when the solvent concentration is increased; unfortunately however an increase in concentration of the high boiling polar solvent will, at constant pressure, increase the operating temperature. As a result increasing solvent concentration at a fixed distillation pressure has both an advantage and a disadvantage, and therefore a plot of selectivity vs. ratio of solvent to hydrocarbon may go through a maximum. An example of this effect is shown by the data of Qozati and Van Winkle (*14*) for the system ethylcyclohexane-ethylbenzene-hexylene glycol.

TABLE 2. COLLISION VOLUMES FOR SOME HYDROCARBONS

Component	Collision volume, cc./g.-mole
n-Butane	69.2
Isobutane	69.6
n-Pentane	72.1
n-Hexane	75.0
n-Heptane	77.9
Cyclohexane	70.5
Benzene	68.0
Butene-1	64.6
cis Butene-2	63.4
Pentene-1	67.9

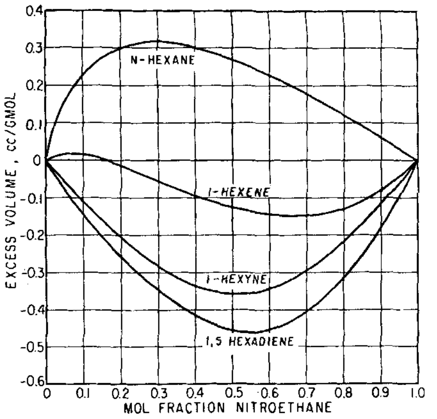

Fig. 5. Volume change on mixing nitroethane with hydrocarbons at 25°C.

CORRELATION AND INTERPRETATION OF DATA

Analysis of the role of physical forces in extractive distillation has led to the conclusion that it is possible to separate hydrocarbons on the basis of size difference. In that case the most effective solvent is one having a large polar energy of vaporization and a small molecular size. Analysis of the role of chemical forces in extractive distillation leads to the conclusion that it is possible to separate hydrocarbons on the basis of a difference in tendency toward complex formation. In that case the most effective solvent is one having a large electron affinity (acidity). In typical extractive distillation separations both physical and chemical effects are important, but if experimental data are to be interpreted and correlated, a clear separation between the two effects must be made.

The simplified solution model for selectivity due to physical forces predicted that the polar effect is given by the product of an intensity term (the square of the polar solubility parameter) and a capacity term (difference in molar volumes of the hydrocarbons).

The capacity term follows from the assumption that the molecular cross section for interaction is proportional to the molar volume, but this is necessarily a crude assumption since the molar volume is determined not only by the molecular size but also by geometrical packing characteristics. Therefore for quantitative work it is more useful to set the cross section for interaction proportional to some collision volume which is determined primarily by microscopic dimensions. A precise definition of collision volume is quite arbitrary, but for correlation purposes a useful definition is given by

$$\Psi = [V_w^{1/3} + V_f^{1/3}]^3 - k\beta P_I V \quad (1)$$

The physicochemical details in support of this definition are given elsewhere (2); for present purposes it is important only to recognize that Ψ is a volumetric term which for any hydrocarbon can be calculated quite easily with only the pure-component properties of that hydrocarbon. Some collision volumes are given in Table 2.

A correlating equation for the selectivity in the presence of excess solvent can now be written in the form

$$\ln S_{12} = \frac{(\delta_3^P)^2 (\Psi_1 - \Psi_2)}{RT} + \Phi (K_{13} K_{23}) \quad (2)$$

The first term gives the physical (size effect) contribution to the selectivity, whereas the second term gives the chemical contribution in an unspecified function which depends only on the stabilities of the complexes formed by the hydrocarbons with the polar solvent. The exact form of the function Φ is not indicated, but four cases can be distinguished:

If $K_{13} = 0$ and $K_{23} = 0$ then $\Phi = 0$
If $K_{13} = K_{23}$ then $\Phi = 0$
If $K_{23} > K_{13}$ then $\Phi > 0$
If $K_{23} < K_{13}$ then $\Phi < 0$

Figure 7 shows how Equation (2) may be used to correlate previously published solvent selectivity data (5, 12). The continuous line is a plot of Equation (2) with $\Phi = 0$; that is the continuous line gives the selectivity in those cases where there are no chemical effects. This calculated line correctly predicts the experimentally observed selectivities for several systems containing only saturated hydrocarbons as indicated by the filled-in black points.

Since the function Φ is not specified, data for systems where chemical effects are important can be correlated by Equation (2) in only a semiempirical way. In the cases considered here $K_{23} > 0$, whereas $K_{13} = 0$; that is in all these cases the chemical and physical effects act in unison to raise the relative volatility of component 1, and therefore the experimental points lie above the calculated base line for physical effects. Although such cases are not shown in Figure 7, it is quite possible to have the chemical and physical effects act in opposite directions; for example in the separation of hexadiene (molar volume 116 cc./g.-mole) from butane (molar volume 100 cc./g.-mole) the physical (size) effect will raise whereas the chemical (complexing) effect will lower the volatility of hexadiene relative to that of butane.

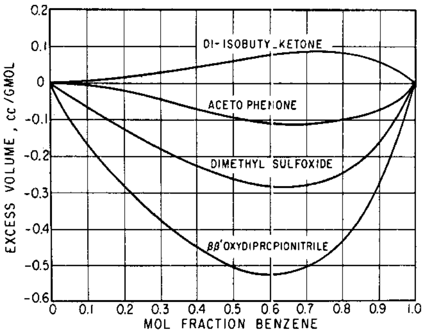

Fig. 6. Volume change on mixing benzene with polar solvents at 25°C.

The dotted lines on Figure 7 may be considered as lines of constant chemical activity; for any particular polar solvent the dotted line will be higher for molecules of higher unsaturation as is shown by comparing the line for systems containing benzene and furfural with that for systems containing pentene and furfural.

Analysis of the role of intermolecular forces in extractive separations cannot yet eliminate the need for experimental data. However such analysis can help in a preliminary screening of promising solvents and can contribute to minimizing experimental effort by providing a guide for the interpretation and correlation of phase equilibrium data.

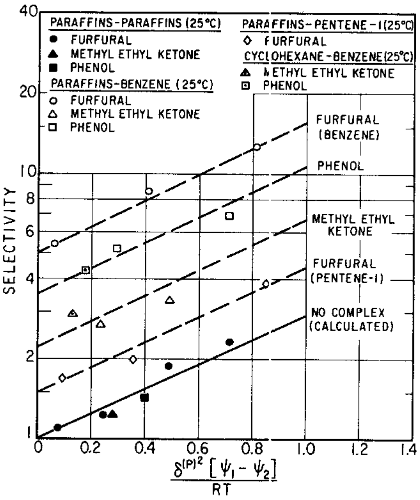

Fig. 7. Effect of complex formation on solvent selectivity.

ACKNOWLEDGMENT

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NOTATION

k = Meares' constant
K = equilibrium constant for complex formation
P_I = internal pressure
R = gas constant
S_{12} = selectivity = $\gamma_1^\infty / \gamma_2^\infty$
T = absolute temperature
V = molar volume
V_f = free volume
V_w = van der Waals volume

Greek Letters

β = isothermal compressibility
Ψ = collision volume
γ^∞ = activity coefficient at infinite dilution
Φ = function
δ_3^P = polar solubility parameter of solvent

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