$$\frac{(\tau_o/\rho_o)^{1/2}}{\mu_o/\rho_o}\, r_o$$

t^+ = dimensionless temperature for nonreacting system,

$$\frac{1}{\beta}\left(1-\frac{T}{T_o}\right) \ ; \ (t^+)' = \frac{1}{\beta'}\left(1-\frac{T}{T_o}\right)$$

u^+ = dimensionless velocity,

$$\frac{u}{(\tau_o/\rho_o)^{1/2}}$$

y^+ = dimensionless distance,

$$\frac{(\tau_o/\rho_o)^{1/2}}{\mu_o/\rho_o}\, y$$

Subscripts and Superscripts

b = subscript denoting bulk mean conditions
o = subscript denoting wall conditions
$-$ = molal basis
= value in reacting system

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Thermodynamics of Solvent Selectivity in Extractive Distillation of Hydrocarbons

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The selectivity of a polar solvent is expressed in terms of an approximate theory of solutions. The theoretical results are insufficiently precise for the accurate prediction of activity coefficients, but the analysis shows that in the absence of chemical effects selectivity depends primarily on the difference in molar volumes of the hydrocarbons to be separated and on the polar energy density of the solvent. The effectiveness of a solvent is related to its polarity (which should be large) and to its molecular size (which should be small). In cases where chemical effects are important or where the molar volumes of the hydrocarbons to be separated are only slightly different, selectivity also depends on the relative ability of the hydrocarbons in acting as electron donors and on the ability of the solvent to act as an electron acceptor in forming acid-base complexes. The theoretical conclusions, which are based on modern thermodynamics and on the theory of intermolecular forces, are in agreement with experimental observations. The results obtained in this work provide theoretical criteria for the selection of an optimum solvent for a given separation and give semiquantitative explanations of solution phenomena related to extractive distillation.

Separation of hydrocarbon mixtures by extractive distillation has been practiced industrially for many years, even though there has been only limited understanding of the fundamental phase equilibria which form the thermodynamic basis of this operation. In general it is known that the addition of polar solvents to hydrocarbon mixtures results, for example, in increased volatilities of paraffins relative to naphthenes, olefins, and diolefins, and in increased volatilities of naphthenes relative to aromatics; therefore the addition of a polar solvent enables facile separation by distillation of certain mixtures which otherwise can only be separated with difficulty. However almost all thermodynamic work in this area has been confined to obtaining vapor-liquid equilibria for isolated systems, and very little has been written on the fundamental molecular physics which could explain how selectivity works. This paper discusses selectivity from the viewpoint of modern thermodynamics and intermolecular forces and aims to provide a molecular basis for explaining why some solvents are more selective than others. The theory of solutions is at present insufficiently advanced to provide an exact quantitative treatment with which to predict the desired activity coefficients. However recent theoretical work in solution thermodynamics and results of physicochemical studies in intermolecular forces can be utilized to give a semiquantitative picture of solution behavior, to provide useful criteria in selection of an optimum solvent for a given separation, and to supply a theoretical framework for the correlation of experimental data.

The ability of a solvent to increase the volatility of one type of hydrocarbon relative to another is called its *selectivity*. The volatility of component i relative to that of component j is related to the selectivity by

$$\alpha_{ij} = S_{ij}\frac{P_i^\circ}{P_j^\circ} = \frac{\gamma_i P_i^\circ}{\gamma_j P_j^\circ} \quad (1)$$

An essential requirement for a good extractive solvent is that for a given separation S be significantly different from unity. In addition to good selectivity a suitable extracting solvent must also possess other qualities; it must be stable, noncorrosive, inexpensive, etc. These qualities have been amply discussed elsewhere (*24*). This work considers only the selectivity of extracting agents and, on the basis of an approximate theory of solutions and with the help of chemical considerations, provides some semiquantitative insight into those properties of hydrocarbons and solvents which account for selectivity.

SOLUTION MODELS

The thermodynamic properties of solutions are best described in terms of a model whose properties correspond as closely as possible to those of the actual solution, and for maximum utility such a model should depend only on the properties of the pure components which comprise the solution. No model has as yet been proposed which completely fulfills this aim in a quantitative manner; for precise information on the thermodynamic properties of solutions experimental data on the solution itself are still required. However for an approximate description of solution behavior and for a semiquantitative estimate of solubility effects it is both possible and instructive to make use of solution models.

Such models are based on either one of two different viewpoints; the first of these, known as the "physical approach," considers all deviations from ideal behavior to be the result of physical, intermolecular (van der Waals) forces which may act so as to repel or attract molecules without however breaking or forming chemical bonds. The other viewpoint, known as the "chemical approach," seeks to explain all deviations from ideality by postulating the existence of new species which are formed as a result of the solution process. The true state of affairs is undoubtedly a hybrid of these two extreme viewpoints. Unfortunately it is very difficult to construct a theory of solutions which simultaneously takes physical and chemical effects into account. One can however profitably examine the problem of solvent selectivity first using one, and then the other approach, while fully realizing each time the limitations imposed by an extreme, narrow viewpoint.

AN APPROXIMATE PHYSICAL MODEL FOR POLAR-NONPOLAR SOLUTIONS

A relatively simple solution model is that proposed by Scatchard and Hildebrand for nonpolar solutions (14, 19). In extractive distillation of course a polar solvent is present in the solution; to be useful in this work therefore it is necessary to extend the Scatchard-Hildebrand model to include effects due to polar-nonpolar interactions. Some ideas for such an extension were first proposed by van Arkel (*23*) but were never carried through in a quantitative manner.

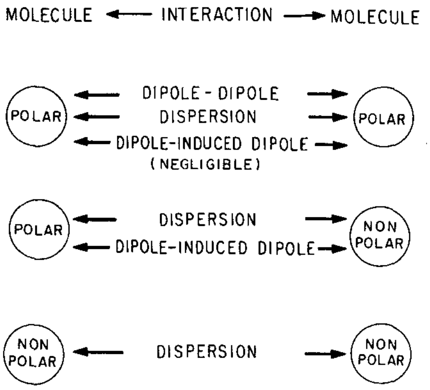

Fig. 1. Physical interactions in a solution containing one polar and one nonpolar component.

The excess Gibbs free energy change of mixing at constant pressure is related to the energy, excess entropy and volume change of mixing by

$$\Delta G^E{}_p = \Delta E^M{}_p + p\Delta V^M{}_p - T\Delta S^E{}_p \quad (2)$$

When one follows Scott (*21*), the changes in energy and in excess entropy at constant pressure can be related to those at constant volume by expanding in the volume change ΔV^M:

$$\Delta E^M{}_p = \Delta E^M{}_v + \left[T\left(\frac{\partial p}{\partial T}\right)_v - p\right]\Delta V^M + \ldots\ldots (3)$$

$$\Delta S_p{}^E = \Delta S_v{}^E + \left(\frac{\partial p}{\partial T}\right)_v \Delta V^M + \ldots\ldots \quad (4)$$

Neglecting higher terms and substituting Equations (3) and (4) into Equation (2) one gets

$$\Delta G^E{}_p = \Delta E^M{}_v - T\Delta S^E{}_v \quad (5)$$

The energy of mixing can be divided into two parts: one corresponding to changes in the potential energy which results from the fact that a molecule upon solution experiences a change in nearest neighbors, and a second corresponding to changes in the rotational and vibrational energy which results from the fact that a molecule's ability to rotate and vibrate in solution is generally different from that prevailing in the pure material. Thus

$$\Delta E^M{}_v = \Delta E\ (\text{pot}) + \Delta E\ (\text{rot, vib}) \quad (6)$$

For the purposes of this work it is very useful to make two reasonable, simplifying assumptions:

1. The excess entropy is directly related to the excess energy resulting from changes in molecular rotation and vibration; that is

$$T\Delta S^E{}_v = \Delta E\ (\text{rot, vib}) \quad (7)$$

2. The potential energy of a mixture is a quadratic function in the volume fraction; thus

$$-E\ (\text{pot}) = \frac{\sum_i^n \sum_j^n x_i x_j V_i V_j c_{ij}}{\sum_i^n x_i V_i} \quad (8)$$

For a binary mixture Equations (5), (6), (7), and (8) yield

$$\Delta G^E{}_p = (x_1V_1 + x_2V_2)\,\phi_1\phi_2 A_{12} \quad (9)$$

where $A_{12} = c_{11} + c_{22} - 2c_{12}$ = exchange energy per unit volume.

The attractive feature of this approximate model is that it avoids the very difficult calculation of the contributions due to changes in the rotational and vibrational energy; the nature of the equations is such that these contributions cancel when calculating the excess free energy. While it would be difficult to justify Equation (7) on the basis of an exact theoretical treatment, there is a good physical basis for Equation (8) and there is much empirical evidence (12, 18) to support the fact that because of a cancellation effect the excess free energy of many polar-nonpolar solutions is given to a good approximation by an equation of the form shown in Equation (9).

To utilize Equation (9) it is necessary to compute the various c terms; these are directly related to the intermolecular forces. Consider a solution of one polar and one nonpolar component and let 1 refer to the former and 2 to the latter. The intermolecular forces contributing to c_{11} are London dispersion forces and polar forces, while only dispersion forces contribute to c_{22}. However the interaction between the two components, reflected by c_{12}, consists of a dispersion term and a term due to the dipole induced in the nonpolar component by the polar one. Thus

$$c_{11} = \left(\frac{\Delta E^n{}_{\text{vap}} + \Delta E^p{}_{\text{vap}}}{V}\right)_1 = \delta_1{}^{n^2} + \delta_1{}^{p^2} \quad (10)$$

$$c_{22} = \left(\frac{\Delta E_{\text{vap}}}{V} \right)_2 = \delta_2^{\,2} \qquad (11)$$

$$c_{12} = \left(\frac{\Delta E^n{}_{\text{vap}_1} \cdot \Delta E_{\text{vap}_2}}{V_1 V_2} \right)^{1/2} + \frac{\Delta E^i{}_{12}}{(V_1 V_2)^{1/2}}$$

$$= \delta^n{}_1\, \delta_2 + \xi_{12} \quad (12)$$

and

$$A_{12} = \delta_1{}^{n^2} + \delta_1{}^{p^2} + \delta^2{}_2 - 2[\delta^n{}_1\, \delta_2 + \xi_{12}] \qquad (13)$$

In the special case where component 1 is also nonpolar

$$\delta^p{}_1 = \xi_{12} = 0 \qquad (14)$$

and Equation (13) degenerates to the familiar form

$$A_{12} = (\delta_1 - \delta_2)^2 \qquad (15)$$

A schematic diagram illustrating the various intermolecular forces is shown in Figure 1. The inductive energy between two polar molecules is always small compared with the polar energy and is here included in the term $\delta^p{}_1$.

For quantitative application it is of course necessary to make some statements about the calculation of $\delta^n{}_1$, $\delta^p{}_1$, and ξ_{12}. These are discussed below. Before going into these details however one should understand that the formalism represented by Equations (9) and (13) leads directly to the calculation of the selectivity. Suppose one is concerned with the separation of two hydrocarbons designated by subscripts 2 and 3; polar solvent 1 is to be used as the extractive agent. The selectivity will of course be a maximum when the polar solvent is present in excess; it is therefore most useful in comparing the selectivities of various polar solvents to evaluate S when the solution is infinitely dilute with respect to components 2 and 3. At infinite dilution the selectivity S_{23} is given by

$$S_{23} = \exp \left[\frac{V_2 A_{12} - V_3 A_{13}}{RT} \right] \qquad (16)$$

CONTRIBUTION OF POLAR FORCES TO THE ENERGY OF VAPORIZATION

To evaluate $\delta^n{}_1$ and $\delta^p{}_1$ it is necessary to split the energy of vaporization into a nonpolar and a polar part. Two formulas for making this calculation based on an idealized model have been given by Böttcher (*6*), but for the purposes of this work it is more suitable to use the homomorph method described by Bondi and Simkin (*4*). In accordance with this method the nonpolar part of the energy of vaporization of a polar molecule is equal to the energy of vaporization of the polar molecule's nonpolar analogue at the same reduced temperature. (For example the analogue of acetonitrile is ethane.) While this method is not exact, it is at least entirely reasonable (3) and when applied consistently can lead to useful results in keeping with the semiquantitative aims of solution model theory. Table 1 gives a few polar and nonpolar solubility parameters for some common polar solvents.

THE INDUCTION ENERGY

When a polar molecule approaches a polarizable molecule, a dipole is induced in the latter which always results in an attractive energy. In addition to this inductive effect there may also be present energy associated with specific (chemical) forces which, in some cases, may lead to complex formation. The term ξ_{12} in Equation (13) therefore contains all energies acting between molecules 1 and 2 except those due to London dispersion forces. One might expect that the key to solvent selectivity lies in the term ΔE^i, since it is clear that if the polar solvent can induce a large energy of attraction in one hydrocarbon and not in the other, it will be selective. However, as shown below, some simple considerations from molecular physics suggest that this expectation is most unlikely.

TABLE 1. POLAR AND NONPOLAR SOLUBILITY PARAMETERS

Polar solvent	Temp., °C.	Solubility parameter, (cal./cc.)$^{1/2}$ δ^p	δ^n
Methyl ethyl ketone	25	5.11	7.65
Acetone	45	6.01	7.28
Acetonitrile	45	8.10	7.59
Phenol	25	6.51	9.84
Furfural	25	7.01	9.45

In the absence of chemical effects it is possible in principle to compute the inductive energy between a polar molecule and a nonpolar but polarizable molecule by electrostatic theory (*6*). Consider a point dipole of moment μ at the center of a spherical molecule of radius a. If such a dipole is placed into a dielectric medium having a dielectric constant ϵ, the energy required to separate the dipole from the dielectric is given by

$$\Delta E^i = \left(\frac{\epsilon - 1}{2\epsilon + 1} \right) \frac{\mu^2}{a^3} \qquad (17)$$

If the point dipole is not situated at the center but rather at a point s units away from the center, then the right-hand side of Equation (17) must be multiplied by a correction factor;

$$F = 1 + \frac{6(2\epsilon + 1)}{3\epsilon + 2} \left(\frac{s}{a} \right)^2 + \frac{18(2\epsilon + 1)}{4\epsilon + 3} \left(\frac{s}{a} \right)^4 + \ldots\ldots \qquad (18)$$

The correction factor, which is never less than unity, accounts for the fact that the induction energy for an exposed dipole is always greater than that for a buried dipole.

Equations (17) and (18) are insufficiently detailed for use in the calculation of activity coefficients. However the important point brought out by these equations is that the inductive energy (in the absence of chemical forces) cannot account for solvent selectivity in the case of hydrocarbons. This conclusion is based on the fact that the only property of the nonpolar species which enters Equations (17) and (18) is the dielectric constant; hence if the inductive energy between a polar solvent and a hydrocarbon is to vary significantly from one hydrocarbon to another, there must be an appreciable variation of dielectric constants in hydrocarbons. In fact however the dielectric constants of all hydrocarbons are very close to one another, being in the neighborhood of 2. The inductive energy for a polar solvent-hydrocarbon solution therefore depends strongly on the polarity (μ) and size (a^3) of the polar component but very little on the nature of the hydrocarbon. Typical values for ΔE^i as computed from Equations (17) and (18) are in the region 1 to 2 kcal./mole.

CONTRIBUTIONS TO THE SELECTIVITY: THE EFFECT OF MOLECULAR SIZE

Equation (16) relates the selectivity to the various energy terms leading to the desired nonideality of solution which is the basis of extractive distillation. When Equation (13) is substituted in Equation (16) and some rearrangements are made, the selectivity can be expressed in a very useful manner:

$$RT \ln S_{23} = [\delta_1{}^{p^2}(V_2 - V_3)] + [V_2(\delta_1{}^n - \delta_2)^2 - V_3(\delta_1{}^n - \delta_3)^2] + [2V_3\xi_{13} - 2V_2\xi_{12}] \qquad (19)$$

The three bracketed terms in Equation (19) show, respectively, the separate contributions to the selectivity of the polar effect, the dispersion effect, and the inductive effect of the solvent. It is convenient to rewrite Equation (19) as

$$RT \ln S_{23} = P + D + I \qquad (20)$$

where

$$P = \delta_1{}^{p^2}(V_2 - V_3) \qquad (21)$$

$$D = V_2(\delta_1{}^n - \delta_2)^2 - V_3(\delta_1{}^n - \delta_3)^2 \quad (22)$$

$$I = 2V_3\xi_{13} - 2V_2\xi_{12} \qquad (23)$$

Equations (20) through (23) are not sufficiently precise for accurate prediction of vapor liquid equilibrium data, but they do lead to some interesting and useful conclusions concerning the selective action of an extractive solvent.

As indicated earlier, the inductive energy does not differ significantly for different hydrocarbons. It can therefore be concluded that in the absence of chemical effects the inductive term does not make a major contribution to the selectivity.

The polar effect is proportional to the difference in molar volume between the two hydrocarbons to be separated. Therefore one might expect that whenever V_2 and V_3 are significantly different, the polar contribution is the dominant one. When typical experimental values are substituted into Equations (20) to (23), it is found that the polar term is considerably larger than the sum of D and I and frequently very much larger. Of course in the special case where components 2 and 3 are identical in size, the polar term vanishes. This situation, which is fortunately very rare, is considered later on.

The result indicating that the polar contribution depends on the difference in molar volume follows from the assumption in the solution model that the potential energy of a mixture is a function of the volume fraction rather than of the mole fraction. On a molecular level this means that the larger hydrocarbon molecule has a higher probability of interacting with the polar solvent than the smaller hydrocarbon. Hence the effect of the polar contribution is to cause larger positive deviations from Raoult's law for the larger hydrocarbon.

The approximate solution model predicts that whenever hydrocarbons of significantly different molar volume are to be separated, the polar effect causes the hydrocarbon with the larger molecule to have the higher activity coefficient. This conclusion is in agreement with the well-known result that when one separates a mixture of paraffins, naphthenes, and aromatics having the same number of carbons, the volatilities are in the same order as the molar volumes: paraffins highest, naphthenes next, and aromatics last. To illustrate the effect of molecular size Table 2 shows experimentally observed selectivities at infinite dilution for a number of representative systems. Table 2 also shows the induction energy between the polar solvent and each hydrocarbon; these induction energies were computed from the experimental data. The results indicate that, as suggested by Equation (21), the larger hydrocarbon always has the larger activity coefficient and that, as predicted by electrostatic theory, there is no correlation between selectivity and inductive energy.

However it must be remembered that the conclusions above are based on the assumption that there are no chemical effects between polar solvent and hydrocarbon. Equation (21) says that in the absence of chemical effects the larger hydrocarbon has the higher activity coefficient, and the data in Table 2 support this statement; however if the larger hydrocarbon can form a complex with the polar solvent (as discussed later) whereas the smaller one does not, then the conclusion based on Equation (21) may no longer be valid. For example in excess phenol at 25°C. the activity coefficient of ethyl benzene (V = 123 cc./g. mole) is 5.3, whereas that of cyclohexane (V = 109 cc./g. mole) is 11.8 (*17*). Since the aromatic complexes with the polar solvent whereas the naphthene does not, the volatility of the aromatic is reduced sufficiently to lower its activity coefficient relative to that of cyclohexane even though the aromatic has the larger volume. In those cases where the smaller hydrocarbon complexes and the larger one does not, the conclusion based on Equation (21) is of course still valid.

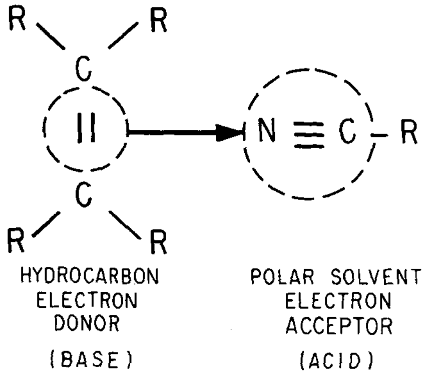

Fig. 2. Schematic diagram of chemical interaction (complexing). Arrow shows donation of electrons.

Equation (21) not only shows the effect of molecular size but also predicts that when one separates hydrocarbons of different molar volumes, the selectivity is sensitive to the polar solubility parameter. This means that the effectiveness of a solvent depends on its polarity, which should be large, and on its molar volume, which should be small. For example Equation (21) correctly predicts that for the separation of say cyclohexane from benzene, acetone is a better solvent than methyl ethyl ketone and that acetonitrile is a better solvent than phenol (Table 1).

Finally Equation (21) gives the interesting result that when one separates hydrocarbons of nearly the same molar volume, the polar solubility parameter of the solvent must be large if selectivity on the basis of molecular size is to be realized. As a limit consider the case where the molar volumes of the two hydrocarbons are equal. In that case the polar contribution vanishes, and Equation (22) can be rearranged to give

TABLE 2. EFFECTS OF MOLECULAR SIZE ON SELECTIVITY*

Polar solvent and temp.	Hydrocarbon components	Molar volume, (ml./g. mole)	Selectivity S_{23} and data ref.		Induction energy, (cal./g. mole)
Methyl ethyl ketone 25°C.	*n*-Heptane	147	2.84	(*17*)	1,150
	Toluene	107			1,230
	n-Heptane	147	3.92	(*17*)	1,150
	Benzene	89			1,220
	n-Decane	196	1.39	(*17*)	1,070
	n-Heptane	147			1,150
Acetone 45°C.	*n*-Hexane	136	4.27	(*9, 20*)	1,400
	Benzene	92			1,450
Phenol 25°C.	*n*-Heptane	147	1.72	(*17*)	2,010
	Cyclohexane	109			1,560
	Cyclohexane	109	4.06	(*17*)	1,560
	Benzene	89			1,570
	n-Heptane	147	5.1	(*17*)	2,010
	Toluene	107			1,650
Furfural 25°C.	Ethyl cyclohexane	143	1.99	(*17*)	1,890
	Cyclohexane	109			1,800
	Cyclohexane	109	4.35	(*17*)	1,760
	Benzene	89			1,800
	n-Heptane	147	12.5	(*17*)	2,140
	Benzene	89			1,800
	n-Heptane	147	2.5	(*17*)	2,140
	n-Butane	101			1,850

* The data in this table consider only those cases where the larger hydrocarbon does not form a complex with the polar solvent. See text.

$$D = 2V\left[\delta_1{}^n - \frac{1}{2}(\delta_2+\delta_3)\right]\left[\delta_3-\delta_2\right] \tag{24}$$

In this case the dispersion term is proportional to the difference in solubility parameter between the two hydrocarbons to be separated; for two hydrocarbons of the same size (and of about the same vapor pressure) such differences are always small and thus the dispersion term cannot account for significant selectivity. For components of identical size therefore solvent polarity is not useful and selectivity on the basis of a physical effect (such as dispersion forces in D) is not promising. For such cases selectivity must be based on chemical forces which will selectively increase the induction energy between the solvent and one of the hydrocarbons; these are discussed below. Fortunately however separation of components of identical size are very rare. For example consider the industrially important separation of the C_4 hydrocarbons. While the C_4 hydrocarbons are all of similar size, there is still a small but significant difference in their molar volumes (as shown in Table 3) due primarily to the fact that the C=C double bond length is somewhat shorter than the C—C single bond length. Therefore even in this separation some selectivity can still be achieved on the basis of size difference provided that the solvent's polar solubility parameter is large. However it is apparent from the analysis above that in those cases where size differences become exceedingly small, improved selectivity can only be obtained by selectively altering the induction energy with a chemical effect.

CHEMICAL EFFECTS IN SOLUTION: EQUILIBRIA OF COMPLEX FORMATION

The chemical viewpoint of solutions considers that nonideality in solution arises because of association and solvation; in accordance with this concept the true species in solution are loosely bonded aggregates consisting of two (or more) molecules of the same species (association) or of different species (solvation).

The inductive energy as calculated by electrostatic theory does not include any specific forces leading to complex formation. However it has been known for some time that unsaturated hydrocarbons, such as benzene, ethylene, or their derivatives, may form complexes with various substances, such as iodine, sulfur dioxide, nitro compounds, cyanides, etc. Such complexes are believed to be the result of acid-base interactions following the Lewis definitions (*16*) that a base is an electron donor and that an acid is an electron accepter. Since the π electron in unsaturated hydrocarbons is strongly polarizable, it follows that aromatics, olefins, and some acetylenes have basic properties whereas paraffins do not. Hence it is to be expected that solvent selectivity is, in many cases, related to the ability of a solvent to form complexes of different degrees of stability with the hydrocarbons which are to be separated. The hydrocarbon forming the most stable complex will of course have the lowest volatility. A schematic diagram of complex formation is given in Figure 2.

There are various methods of obtaining information on the stability of complexes; some of these have been reviewed by Andrews (2). A relatively simple and direct method is to obtain spectroscopic data in either the visible or the ultraviolet range; these spectral data yield an equilibrium constant for the complex (2, 5). In many cases the appearance of a new color is a qualitative indication of complex formation; a classic example is given by the fact that whereas iodine forms violet solutions in the physical solvents heptane and carbon tetrachloride, it forms brown solutions with the basic chemical solvents toluene, xylene, and mesytilene.

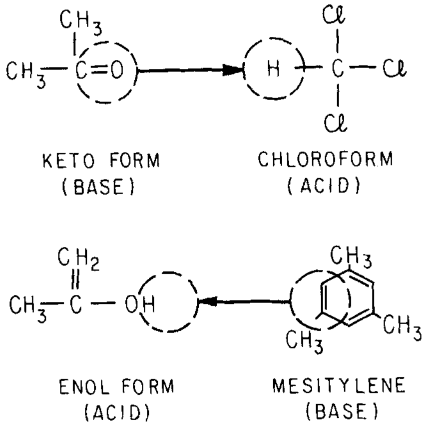

Fig. 3. Amphoteric properties of acetone for forming complexes. Arrows show donation of electrons.

COMPLEX STABILITY

A theoretical analysis of complex formation (2) suggests that the stability of a complex depends primarily on the ionization potential of the hydrocarbon (which is an inverse measure of basicity) and on the electron affinity of the electron acceptor (which is a measure of acidity). A stable complex will be formed between a base having a low ionization potential and an acid having a large electron affinity. Ionization potentials of hydrocarbons have been tabulated by Field and Franklin (*10*) and by Watanabe (*22*), but owing to experimental difficulties electron affinities have been measured for only a very small number of species. However in comparing the ability of various polar solvents to form complexes one may obtain an approximate guide in the sigma scales for acidity proposed by Hammett (*13*). This empirical scale is a measure of the extent to which different radicals can attract electrons. The scale shows for example that cyanide, nitro, and aldehyde groups are strongly electron attracting, and therefore solvents containing such groups should be capable of forming relatively stable charge-transfer complexes with certain hydrocarbons. However other considerations, as illustrated below, show that the sigma scale is not always a reliable criterion of acidity.

The above discussion leads to the conclusion that whenever two hydrocarbons of very nearly the same size are to be separated by extractive distillation solvent, selectivity can be enhanced by choosing a solvent which will form a more stable complex with one hydrocarbon than with the other. The difference in stability depends on the difference in ionization potentials of the hydrocarbons and on the ability of the polar solvent to accept electrons. For example consider the separation of the C_4 hydrocarbons. The ionization potentials of these substances are given in Table 3, which also shows the relative volatility when furfural (an aldehyde) is used as the polar solvent. The fact that isobutane is more volatile than normal butane cannot be ascribed to a difference in complex stability but must be due to the polar and dispersion effects discussed above, as well as to a slight favorable difference in vapor pressures. The decrease in volatility with increasing unsaturation however is undoubtedly due, at least in part, to the difference in the stability of the complexes formed with furfural.

The discussion above is necessarily quite simplified, since other factors, notably steric and tautomeric effects, also contribute to the stability of complexes. For example the sigma scale of Hammett predicts that keto groups are basic rather than acidic, and indeed it is well known that acetone forms complexes with such acids as hydrogen chloride and chloroform. One might therefore expect that acetone would be a poor agent for forming complexes with olefins and aromatics. In fact however the equilibrium constant for complex formation with mesitylene is three times larger for acetone than it is for nitroethane (*1*). This surprising result is due to the fact that acetone exhibits tautomerism, since it can exist in either the keto or the enol form; the former of these is basic, but the latter is highly acidic. Thus acetone exhibits amphoteric effects in its ability to form complexes as illustrated schematically in Figure 3. Similar conclusions may be reached with the concept of complex resonance (*7*). This example shows the danger of trying to set up any simple rules of general validity for the prediction of acidity.

In a typical case of course chemical and physical effects both contribute to the selectivity. It appears however that the physical effect operating on size difference is usually the most important one. For example Gerster and co-workers (*11*) find that in the separation of *n*-pentane from *n*-pentene-1 very good selectivity is obtained with acetonitrile. This is not surprising, since acetonitrile has a very high polar solubility parameter and nitriles have acidic properties which would lead to complexing with the pentene. On the other hand fairly good selectivity was also found with ethylene diamine. Since this solvent is basic, complexing is not to be expected, and in fact ultraviolet examination showed no evidence for complex formation between this solvent and an olefin (*1*). However ethylene diamine has a very high polar solubility parameter; for this solvent therefore selectivity must be due primarily to the small but not insignificant difference in size between *n*-pentane and pentane 1.

CONCLUSIONS

The analysis of solution behavior as based on an approximate model of solutions predicts that selectivity depends primarily on the difference in size between the hydrocarbons to be separated, on the polar energy of vaporization of the solvent (which should be large), and on the molar volume of the solvent (which should be small). These predictions are supported by experimental evidence. On the other hand the chemical viewpoint of solution properties shows that selectivity also may depend on the ability of a solvent to form complexes of different stability with the various hydrocarbons in the solution; this stability is determined by the electron-donating properties of the hydrocarbon and by the electron-accepting properties of the solvent. In a typical application all of these factors must be considered in selecting an optimum solvent for a given separation.

The thermodynamic and physicochemical analysis presented here is not sufficiently exact for the precise quantitative prediction of phase-equilibrium relationships. For this purpose it is still necessary to have access to experimental data. However, as illustrated in this paper, simple solution models coupled with appropriate concepts from the theory of intermolecular forces may be used successfully for semiquantitative estimates, for guidance in interpretation of experimental data, and for qualitative explanations and predictions of solution phenomena. A more quantitative treatment of this subject will be published soon.

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NOTATION

A = exchange energy per unit volume
a = radius of polar molecule
c = proportionality factor, energy per unit volume
D = dispersion contribution to the selectivity, Equation (22)
ΔE = change in internal energy
F = correction factor
ΔG = change in Gibbs free energy
I = induction contribution to the selectivity, Equation (23)
P = polar contribution to the selectivity, Equation (21)
P° = vapor pressure
p = total pressure
R = gas constant
ΔS = change in entropy
S = selectivity
s = position of point dipole, measured from center of molecule
T = absolute temperature
V = molar volume
x = mole fraction

Greek Letters

α = relative volatility
ϵ = dielectric constant
δ = solubility parameter
μ = dipole moment
γ = activity coefficient
ϕ = volume fraction
ξ = induction energy per unit volume

Table 3. Molar Volumes, Ionization Potentials, and Relative Volatilities of C_4 Hydrocarbons

Hydrocarbon	Molar volume at 25°C., (ml./g. mole)	Ionization potential, e.v. (±0.1)	Rel. vol. at 65 lb./sq. in. abs. and 130°F. in furfural (*8*)
Isobutane	105	10.8	2.60
n-Butane	101	10.8	2.02
1-Butene	95	9.72	1.72
Isobutylene	94	9.35	1.67
2-Butene (trans)	91	9.21	1.19
2-Butene (cis)	91	9.20	1.07
1, 3-Butadiene	88	9.07	1.0

Superscripts

E = excess
i = induction
M = mixing
n = nonpolar
p = polar

Subscripts

i,j = components
P = constant pressure
V = constant volume
vap = vaporization
1 = polar component
2,3 = nonpolar component

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