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The Volumes of Mixing of Liquids and Their Importance for the Modern Theory of Solutions

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The results of studies on volumes of mixing in liquid-liquid systems and in polymer solutions are surveyed and the causes of the volume change and its influence on the thermodynamic parameters of dissolution are examined.
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I. GENERAL IDEAS CONCERNING THE INFLUENCE ON THERMODYNAMIC PARAMETERS OF THE VOLUME CHANGE ON MIXING

The first studies on the volumes of mixing of liquids were carried out by Mendeleev[1,2] whose doctoral thesis was devoted to proving the fundamental postulates of his theory of solutions, particularly his ideas concerning the volume change on mixing the components. Subsequently many related data were obtained, which, however, did not receive due attention, since the volumes of mixing are small and it was believed possible to neglect them. All the theories of solutions (Hildebrand's theory of regular solutions, Guggenheim's theory of strictly regular solutions, etc.) were therefore based on the assumption that the volume is constant on dissolution. Theoretical internal energies of mixing (ΔU) were set equal to the enthalpy of mixing (ΔH). For example, the widely familiar Scatchard–Hildebrand equation was obtained on this basis[3]:

$$\Delta U=\Delta H=V(\delta_1-\delta_2)^2\varphi_1\varphi_2, \qquad (1)$$

where V is the volume of the solution, ϕ_1 and ϕ_2 are the volume fractions of the components of the solution, and δ_1 and δ_2 are the solubility parameters of the components equal to the square roots of the densities of their cohesion energies (DCE): $\delta=(\Delta E/V)^{1/2}$.

According to Eqns(1), dissolution can only be an endothermic process ($\Delta H>0$) and, when their values of δ are equal, the components should mix with a zero heat change. In reality neither the first nor the second postulate are valid. One of the causes of this is the volume change on mixing; the magnitude and sign of which have a significant influence on the thermodyanmic parameters. This can be readily shown using the equation of state[4]

$$\left(\frac{\partial U}{\partial V}\right)_T=-p+T\left(\frac{\partial p}{\partial T}\right)_V. \qquad (2)$$

On substituting Eqn.(2) in the expression

$$(\Delta H^m)_p=(\Delta U)_p+p(\Delta V^m)_p, \qquad (3)$$

we obtain

$$(\Delta H^m)_p=(\Delta U^m)_V+T\left(\frac{\partial p}{\partial T}\right)_V\cdot(\Delta V^m)_p. \qquad (4)$$

The derivative $(\partial U/\partial V)T\equiv p$ is the internal pressure in the liquid or a real gas, which depends on the extent of the intermolecular interaction. The pressure p_i amounts to ~3500 atm for not unduly polar organic liquids, 12000 atm for water, and ~40000 atm for mercury[5]. The derivative $(\partial p/\partial T)V\equiv\gamma$ is the temperature coefficient of pressure, related to the isothermal compressibility βT and the coefficient of thermal expansion αp by the expression

$$\gamma=\alpha_p/\beta_T. \qquad (5)$$

For liquids, γ varies from 10 to 14 atm K^{-1}. Consequently, even if the volume change on dissolution $(\Delta V^m)_p$ is indeed very small, the second term in Eqns.(4) is $(\Delta V^m)_p\times 3000$ (atm cm^3) (at room temperature) and makes a considerable contribution to $(\Delta H^m)_p$. $(\Delta U^m)_V$, which is calculated theoretically or determined experimentally at constant volume, can therefore differ significantly from the value of $(\Delta H^m)_p$ determined at constant pressure. For example, $(\Delta V^m)_p=0.65$ cm^3, $(\Delta H^m)_p=182$ cal, and $(\Delta U^m)_V=131$ cal for the benzene–cyclohexane system containing 0.5 mole of each component[6].

The entropies of mixing measured at constant volume and pressure also differ[4]. They are linked by the relation

$$T(\Delta S^m)_p=T(\Delta S^m)_V+T\left(\frac{\partial p}{\partial T}\right)_V(\Delta V^m)_p. \qquad (6)$$

Negative enthalpies or heats of mixing are frequently due to the negative sign of $(\Delta V^m)_p$, i.e. the decrease of volume on dissolution.

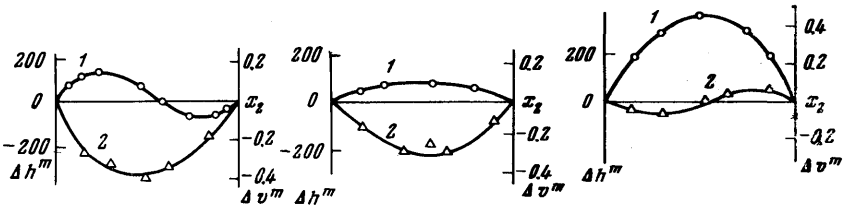


Figure 1. Dependence of the enthalpies Δh^m (curves *1*) and average volumes Δv^m (curves *2*) of mixing on the mole fraction of the second component x_2 for different systems: *a*) acetone–isopropyl alcohol; *b*) isopropyl alcohol–propionitrile; *c*) ethanol–acetonitrile[19].

The volume change observed on mixing liquids is the cause of the lower consolute temperature (LCT) of a special type, discovered by Rowlinson[7,8] for solutions of components with a similar chemical structure but differing in molecular size. Systems such as dodecane–ethane and n-hexadecane–n-hexane split into separate layers on heating to temperatures greatly exceeding the boiling point of the more volatile component. This type of LCT is characteristic of polymer solutions, since in this case the difference between the molecular sizes of the components is particularly marked[8]. The mechanism of layer formation in polymeric systems will be examined below.

Thus the volume change on dissolution or mixing plays an extremely great role. This is understandable, because negligible changes in distances between molecules can be the cause of enormous changes in the interaction energy, which is inversely proportional to the sixth power of the distance. In recent years there has therefore been a sharp growth of interest in measurements of the volume changes on mixing low-molecular-weigth liquids and on dissolution of polymers.

II. VOLUMES OF MIXING AND THE FREE VOLUME

The volume change on mixing substances is a consequence of the change in the free volume, since the intrinsic volume of the molecules hardly changes. The free volume is understood as the volume unoccupied by the intrinsic volume of the molecules of the given substance. We believe that it can be defined most correctly, as suggested by Hildebrand[9] and by Bondi[10], as the difference between the volume of one mole of the substance measured at a given temperature (V_T) and the intrinsic volume of the molecules contained in one mole (V_W):

$$V_E = V_T - V_w. \qquad (7)$$

The volume V_W is calculated as the sum of the volumes of the constituent atoms of the molecule and atomic groups taking into account the overlap of the shells of the atoms involved in the chemical bond. A scheme for such a calculation has been described[11] and the same communication contains tabulated volume increments, i.e. the volumes of different atomic groups. Hildebrand[9] calls the free volume calculated by Eqn.(7) the "empty volume" or the volume of vacancies V_E. Frenkel[12] proposed another method of calculating the free volume—as the difference between the volume of a body at a given temperature V_T and its volume V_0 at 0 K (on the assumption of maximum close packing):

$$V_f = V_T - V_0. \qquad (8)$$

The volume V_f calculated by Eqn.(8), which according to Hildebrand represents the "volume of expansion", differs from the values of V_E calculated by Eqn.(7).

According to modern ideas, the change in free volume on mixing liquids or on dissolution of solids can be due to three causes: (1) the difference in the cohesion energy between the molecules of the components; (2) the difference between the molecular sizes; (3) the differences between the molecular shapes. The latter two factors are referred to as geometrical. Attention to their role was first drawn by Mendeleev, who wrote that processes similar to the mixing of grains or spheres of different dimensions can occur on dissolution: "the smaller grains or spheres are accommodated in the gaps between the large spheres in a certain manner and the decrease in volume can then be readily demonstrated"[2].

The overall volume change observed on dissolution is represented by the sum of two components[13,14]:

$$\Delta V^m_{tot} = \Delta V^m_{inter} + \Delta V^m_{geom}$$

(ΔV^m_{inter} is the volume change due to the first cause).

III. THE VOLUME CHANGE ON MIXING LIQUIDS

The available data on the volumes of mixing for 800 liquid–liquid systems have been arranged systematically[15]. The Table compiled by the authors shows that only 20 systems are formed without a volume change (i.e. $\Delta v^m = 0$)†. These are systems whose components have both similar chemical structures and similar molecular sizes and shapes (the toluene–xylene, o-xylene–p-xylene, etc. systems). For the vast majority of two-component systems, $\Delta v^m \neq 0$. The volume changes can differ by three orders of magnitude (from 0.002 $cm^3\ mol^{-1}$ for the benzene–carbon tetrachloride system to 2.23 $cm^3\ mol^{-1}$ for a solution of triethylamine in methanol) and can have different signs.

It was assumed initially that the volume change on dissolution is caused only by the difference between the cohesion energies of the components. Thus, if the cohesion energy between unlike molecules $2\varepsilon_{12}$ is greater than between like molecules ($\varepsilon_{11} + \varepsilon_{22}$), unlike molecules should be attracted more strongly to one another, which should lead to a decrease of the volume (i.e. $\Delta v^m < 0$). Conversely, if the cohesion energy between like molecules is greater than

† Average thermodynamic parameters are normally employed when solutions are considered: the average molar enthalpy of mixing $\Delta h^m = \Delta H^m/(n_1 + n_2)$ and the average molar volume of mixing $\Delta v^m = \Delta V^m/(n_1 + n_2)$, where n_1 and n_2 are the numbers of moles of the components in the solution.

between unlike molecules, the molecules should be at greater distances in solution than in the pure substances, which should entail an expansion on dissolution ($\Delta v^m > 0$). At the same time, there may be a change in the internal energy of the system:

$$-\Delta u^m \simeq K[-\varepsilon_{11}-\varepsilon_{22}+2\varepsilon_{12}];$$
$$\text{if } |2\varepsilon_{12}| > |\varepsilon_{11}+\varepsilon_{22}|, \text{ then } \Delta u^m < 0;$$
$$\text{if } |2\varepsilon_{12}| < |\varepsilon_{11}+\varepsilon_{22}|, \text{ then } \Delta u^m > 0 .$$

Consequently, the signs of Δu^m and Δv^m should be identical.

Since $\Delta h^m = \Delta u^m + P\Delta v^m$, it was assumed that the signs of the heats and volumes of mixing should be identical, i.e. that contraction corresponds to exothermic mixing and expansion corresponds to endothermic mixing[2,16-18].

It has been shown[19] that this is not the case. There are data (Fig.1) demonstrating that the difference between the cohesion energies of the components is not the only cause of the volume change on dissolution; it is determined also by geometrical factors. The role of the latter was demonstrated in relation to a number of systems. Thus Marsh[20-22] used octamethylcyclotetrasiloxane as a model substance with large spherical molecules and benzene and carbon tetrachloride as substances with small molecules. Endothermic mixing and contraction, which in this case is a result solely of greater close packing, were observed for these systems.

The role of the geometrical factor in a "pure" form is manifested clearly in systems where the molecules have identical chemical structures but different dimensions, for example, in solutions of normal alkanes. The mixing of alkanes at room temperature is accompanied by the absorption of heat, which is greater the greater the difference between the molecular sizes of the mixed components[23,24]. On the basis of this experimental fact, Brønsted[25] formulated the principle of congruence, expressed by the equation

$$\Delta h^m = B(n_1-n_2)^2 x_1 x_2, \qquad (9)$$

where x_1 and x_2 are the mole fractions of the components in the solution, n_1 and n_2 are the numbers of carbon atoms in the molecules of n-alkanes, and B is a constant.

Table 1. The average energies (Δu^m, cal mol^{-1}), volumes (Δv^m, cm^3 mol^{-1}), and enthalpies (Δh^m, cal mol^{-1}) of mixing for mixtures of cyclic hydrocarbons[33].

System	Δu^m	Δv^m	Δh^m
Cycloheptane–cyclooctane	1.7	−0.03	−0.7
Cyclopentane–cyclohexane	3.1	0.042	6.2
Cyclohexane–cycloheptane	4.3	−0.034	1.7
Cyclopentane–cycloheptane	6.9	−0.102	−0.4
Cyclohexane–cyclooctane	12.0	−0.128	1.7
Cyclopentane–cyclooctane	13.2	−0.30	−10.1

If only cohesion energies were concerned, then expansion might be expected on mixing n-alkanes. In reality, the mixing of n-alkanes is accompanied by contraction, which is greater the greater the difference between the molecular sizes of the mixed components[26-30], as illustrated in Fig.2. Consequently, for mixtures of alkanes, $\Delta h^m > 0$ and $\Delta v^m < 0$. The ratio of these quantities is such that the internal energy of mixing, calculated from the equation $\Delta h^m = \Delta u^m + P\Delta v^m$, is always positive, i.e. the internal energy of the systems increases on mixing alkanes[24]. The positive value of Δu^m in such systems is due to the fact that the main type of interaction between the components is dispersion interaction, which is additive with respect to the length of chain molecules. The cohesion energy increses in the homologous series of n-alkanes, while the energy of contact between unlike molecules $2\varepsilon_{12}$ is smaller than for like molecules ($\varepsilon_{11} + \varepsilon_{22}$). The contraction in such systems is caused solely by geometrical factors; however, at room temperature, it is not large enough to alter the sign of the heat of solution, i.e. the Δu^m and Δh^m are positive.

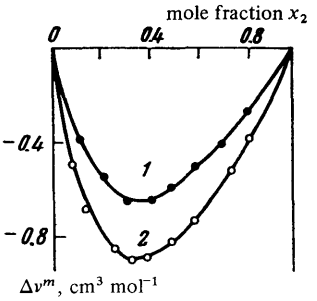


Figure 2. The average volumes of mixing Δv^m in different systems: 1) n-hexane–n-hexadecane; 2) n-pentane–n-hexadecane[26].

Positive internal energies of mixing and negative volumes of mixing are observed also on mixing cyclic hydrocarbons[33,34] (Table 1). Consequently, in this case the contraction is also due to geometrical causes. Thus, when two adjacent homologues are mixed, Δu^m is comparatively small, but increases with increase of the difference between the numbers of carbon atoms in the hydrocarbon molecule; under these conditions, there is as a rule an increase in the extent of contraction. The cyclopentane–cyclohexane system, whose formation involves expansion, constitutes an exception. However, the ratio of the absolute values of Δu^m and Δv^m is such that the signs of the Δh^m for these systems are different and it is very difficult to discover any kind of regularity.

The role of the geometrical factor is manifested also on mixing liquids between the molecules of which a dipole–dipole interaction takes place in addition to the dispersion interaction. This was demonstrated very clearly by Meares[35] in a study of the volumes and heats of mixing of two isomeric diesters: butylene diacetate (BDA) and diethyl succinate, the molecules of which are in essence dimers of ethyl acetate. The methylene group CH_2 and the oxygen atom have the same numbers of electrons in the outer orbital. The dispersion interaction in each contact between the molecules of these two diesters is therefore the same. They exhibit the same dipole–dipole interactions and their molecules have the same dimensions. The diesters therefore mix athermally and without a volume change. The heat of mixing of each with ethyl acetate is also zero, but there is a contraction due to the difference between the sizes of the mixed molecules.

All these findings show that, when systems having similar chemical structures but differing in molecular size are mixed, contraction is observed ($\Delta v^m < 0$), while $\Delta h^m \geqslant 0$. Thus the mixing of acetone with acetylacetone and acetonylacetone is accompaned by the absorption of heat and contraction[36] (Fig.3). In all these cases the contraction is due to purely geometrical factors.

When substances differing in chemical structure are mixed, the signs of the enthalpies and volumes of mixing are as a rule the same. Thus the mixing of alkanes with aliphatic ethers is accompanied by the absorption of heat and expansion, the values of which increase with increasing length of the hydrocarbon molecule or group[37]. The absorption of heat and expansion are also observed when carbon tetrachloride is mixed with chloroform and chlorobenzene and when n-hexane is mixed with acetone[23,38,39]. In all the systems enumerated, one of the components is more polar than the other and the energy expended on the rupture of bonds between the dipoles exceeds the energy gain due to the greater cohesion energy between unlike molecules. As a result, the internal energy of the system increases and the process is at the same time accompanied by expansion ($\Delta h^m > 0$ and $\Delta v^m > 0$).

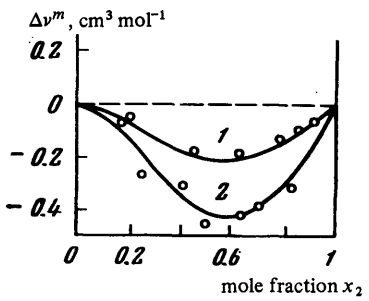


Figure 3. The average volumes of mixing Δv^m in different systems: 1) acetone–acetylacetone; 2) acetone–acetonylacetone[36].

More complex relations are observed for systems where there is a possibility of the formation of solvated complexes via hydrogen bonding or the interaction of π electrons. Systems in which hydrogen bonds can be formed can be divided into four groups in accordance with the classification of Belousov and Morachevskii[23], which is the same as the classification of Pimentel and McClellan[40].

1. Systems in which only one component tends to form hydrogen bonds (mixtures of alcohols, acids, and amines with straight-chain hydrocarbons and CCl_4). Endothermic heat changes are characteristic of such systems, because the decisive process in the formation of the solution is the rupture of hydrogen bonds between the molecules of the polar component. However, the volumes of mixing can have different signs. Thus the dissolution of straight-chain alcohols in straight-chain hydrocarbons is accompanied by expansion caused by the smaller cohesion energy between unlike molecules compared with like molecules. This is seen particularly clearly when an alcohol and a hydrocarbon having molecules of the same size are mixed. In this case the role of the geometrical factor is reduced to a minimum and the effect is determined solely by the difference between the cohesion energies, so that $\Delta h^m > 0$ and $\Delta v^m > 0$.[41,42]

If unlike molecules differ not only in chemical structure but also in shape, the geometrical factor again becomes decisive: contraction accompanies the mixing of alcohols and amines with carbon tetrachloride despite the fact that $\Delta h^m > 0$.[43–46]

2. Systems in which one of the components contains only proton-donating and the other only proton-accepting groups, i.e. hydrogen bonds can arise only between unlike molecules. These are solutions of ketones, aldehydes, and tertiary amines in chloroform and similar compounds. They are always formed exothermically ($\Delta h^m < 0$) and as a rule with contraction[15,23,47]. However, there are also exceptions. Thus the exothermic mixing of chloroform with methyl acetate is accompanied by expansion. In this case the geometrical factor again plays a dominant role: the chloroform molecule apparently cannot form a sufficiently close-packed structure with methyl acetate molecules ($\Delta V^m_{geom} > 0$, $\Delta V^m_{inter} < 0$, $\Delta V^m_{tot} > 0$).

3. Systems where one component contains simultaneously proton-donating and proton-accepting groups (acids, alcohols, water, and secondary amines) while the other contains only groups of one of these types (acetone, chloroform, etc.). In such systems the dissociation of the hydrogen bonds between like molecules can be partly or completely compensated by the formation of new hydrogen bonds between molecules of different kinds. The signs of the heat changes can therefore be different and can vary with the composition of the solution. The volume changes are also complex. For example, the mixing of straight-chain alcohols with acetone is accompanied by the absorption of heat due to the disruption of the alcohol structure, but this is accompanied by contraction and not expansion. Consequently $|\Delta V^m_{geom}| > |\Delta V^m_{inter}|$. When alcohols are mixed with chloroform, Δh^m changes sign as the solution composition is varied and over a large range of compositions exothermic mixing accompanied by expansion is observed[48].

4. Systems in which both components contain both proton-donating and proton-accepting groups. These are mixtures of alcohols with one another and mixtures of alcohols with acids and amines. When such substances are mixed, the size of the alkyl group plays the main role. The larger the group, the greater the dispersion interaction energy and properties characteristic of alkanes are manifested. Alcohols therefore mix with one another with absorption of heat, like n-alkanes. However, in contrast to mixtures of n-alkanes, expansion takes place in this instance, i.e. the interaction effect predominates over the geometrical factor ($\Delta V^m_{inter} > 0$ and $|\Delta V^m_{inter}| > |\Delta V^m_{geom}|$). The expansion is greater the greater the difference between the molecular sizes of the alcohols[49].

Aqueous solutions are of special interest. Water molecules are known to be capable of forming a three-dimensional network of hydrogen bonds, as a result of which water has a fairly distinct tetrahedral structure[50] with large cavities which can be penetrated by the molecules of other components. The dissolution of most substances in water is therefore accompanied by contraction[15]. This applies to aqueous solutions of alcohols, acetone, and even hydrocarbons. The mixing of water with methanol and ethanol is accompanied by the evolution of much heat and a marked contraction[51,52]. Evidently, in this case both $\Delta V^m_{inter} < 0$ and $\Delta V^m_{geom} < 0$. With increase in the size of the alkyl group, the exothermic effect and the degree of contraction diminish: 1-butanol is partially miscible with water and the mixing process is accompanied by the absorption of heat but there is again contraction, as in the mixing of water with alcohols having longer molecules[15]. The dominant role of the geometrical factor is manifested once more.

In all the previous examples the evolution of heat (decrease of enthalpy) was caused either by the greater interaction energy between unlike molecules or by the greater degree of contraction. A different situation arises when n-alkanes interact with water. They dissolve in water in very small

amounts and the process is accompanied by the evolution of heat and contraction, which is caused by the formation of very small crystalline clusters of water around hydrocarbon molecules[53,54] (so called hydrophobic bonds) and not by a strong interaction between unlike molecules.

In conclusion we shall consider solutions whose components are aromatic substances capable of strong donor–acceptor interactions involving the π electrons of the benzene ring. Aromatic compounds are self associated liquids and the energy expended on the disruption of these associated species on dissolution in straight-chain hydrocarbons is not compensated. The mixing of aromatic hydrocarbons with aliphatic and alicyclic hydrocarbons and with one another is usually accompanied by expansion and the absorption of heat[55–58]. This is observed even in a system such as benzene–toluene[58], which is frequently classified as ideal. However, $\Delta v^m = 0.35$ cm^3 mole^{-1} and $\Delta h^m = 15$ cal mol^{-1} for this system. A typical plot of the concentration dependence of Δh^m and Δv^m for mixutres of aromatic hydrocarbons is illustrated in Fig.4. However, the mixing with benzene of aromatic hydrocarbons which are elongated is accompanied by contraction. For example, there is a zero heat change in the mixing of benzene and bibenzyl and the process involves contraction[15,23]; the geometrical factor again plays the main role.

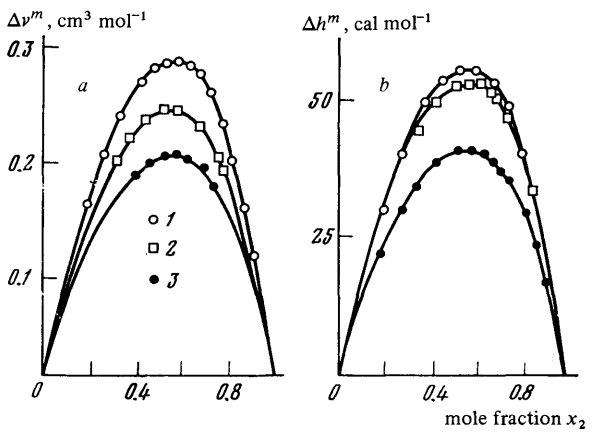


Figure 4. The average volumes Δv^m (*a*) and enthalpies Δh^m (*b*) of mixing for benzene–isomeric xylenes systems[55]: 1) *m*-xylene; 2) *o*-xylene; 3) *p*-xylene.

When benzene dissolves in carbon tetrachloride, the enthalpy and volume of mixing are positive and increase with temperature: $\partial \Delta h^m/\partial T > 0$ and $\partial \Delta v^m/\partial T > 0$ (Fig.5), which is attributed[59] to the formation of a compound at 239 K due to the interaction of the π electrons of the benzene ring and the vacant *d* levels of the chlorine atoms in the CCl_4 molecule, this compound dissociating on increase of temperature.

When aromatic hydrocarbons are mixed with substances whose molecules contain polar groups, complexes may be formed due to the interaction of the π electrons of the aromatic rings with the proton-donating groups. For this reason, these complexes are also not very stable at normal temperatures and the interaction between unlike molecules is weaker than between like molecules. The mixing of benzene with ethyl acetate is therefore accompanied by the absorption of heat and expansion, although these effects are much smaller than for solutions of ethyl acetate in n-alkanes[37]. The positive enthalpies of mixing are reduced still more in the benzene–ethyl benzoate system owing to the interaction between the aromatic rings of the components, the mixing process being accompanied by contraction.

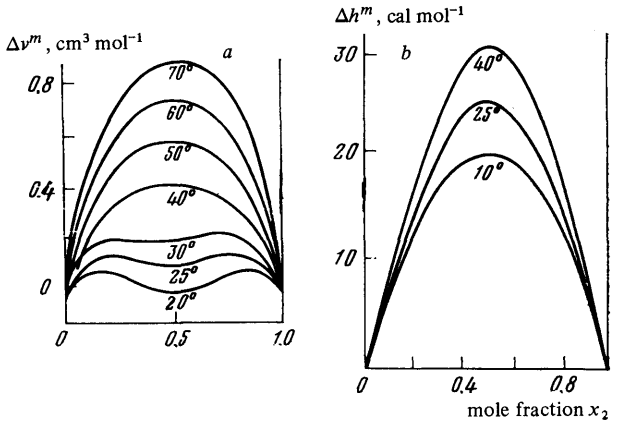


Figure 5. The ratios of the volumes of the solutions V^m to the sums of the volumes of the components V^0 (*a*)[59] and the average enthalpies of mixing Δh^m (*b*)[60] for the benzene–carbon tetrachloride system at different temperatures.

The presence of methyl substituents in the ring, which enhances the electron-donating capacity of the aromatic compound and gives rise to a dipole moment, is responsible for the possibility of additional interactions in solution. The mixing of ethyl benzoate with toluene is therefore less endothermic and involves a greater degree of contraction than the mixing with benzene[37].

The volumes and heats of mixing of aromatic hydrocarbons with aromatic amines have been measured in a series of studies[61–66]. For the majority of the compounds investigated, the signs of the excess volumes and heats are positive. According to the authors, this means that the energy expended on the dissociation of the hydrogen bonds N–H...N in the amines and the π–π bonds in the aromatic hydrocarbons themselves exceeds the energy of formation of new contacts of the N–π type.

If the bond dissociation energy in the pure components is compensated by the energy of formation of π-bonds between different aromatic compounds, then athermal mixing is observed. An example is provided by the benzene–pyridine system, which, however, is formed with contraction.

The molecules of aromatic compounds, which have electron-donating (proton-accepting) properties, are capable of forming hydrogen bonds with alcohols, but these are much weaker than the hydrogen bonds between the alcohol molecules. The mixing of benzene with alcohol therefore involves the absorption of heat and expansion[23,67].

All the facts enumerated above show that the volume changes in the mixing of the vast majority of liquids are non-additive and that geometrical factors play a major role in this process.

IV. THE VOLUMES OF MIXING IN THE DISSOLUTION OF POLYMERS

The first studies on the volumes of mixing of polymeric solutions, published in 1958,[68] showed that the dissolution of polyisobutylene (PIB) in n-heptane and of polystyrene (PS) in ethylbenzene is accompanied by contraction. Subsequently the volumes of mixing were measured also for other polymeric solutions[69–71]. Table 2 gives the signs of the volumes and enthalpies of mixing for certain polymeric solutions. In the first place there is a striking failure of solutions of high-molecular-weight hydrocarbons in lower alkanes to obey the Brønsted congruence rule [Eqn.(9)], according to which a very large endothermic effect should be observed for $n_1 \gg n_2$.[25] In reality the dissolution of polymers is frequently accompanied by the evolution of heat, which was first demonstrated by Delmas et al.[72]; at the same time, $\Delta u^m > 0$.[69] This shows undoubtedly that the negative values of Δh^m are caused by the negative values of Δv^m, which arise in this instance solely because of the difference between the molecular sizes of the mixed component.

Table 2. The consolute* temperature and the average enthalpies (Δh^m) and volumes (Δv^m) of mixing for polymer–solvent systems.

Polymer	Solvent	UCT, °C	LCT, °C	Δh^m	Δv^m
Polyisobutylene (PIB)	Isooctane	—	162^{92}	$<0^{72}$	$<0^{71}$
PIB	Benzene	23^{92}	160^{92}	$>0^{104}$	$>0^{71}$
Polystyrene (PS)	Ethylbenzene	—	295^{96}	$<0^{105}$	$<0^{71}$
PS	Cyclohexane	32^{95}	206.5^{95}	$<0^{104,106}$	$<0^{71}$
Poly(vinyl acetate) (PVA)	Ethyl acetate	—	204^{96}	$<0^{86}$	$<0^{71}$
PVA	Methanol	-3^{96}	209^{103}	$>0^{106}$	$<0^{71}$
Polyoxypropylenediol (POPD)	Hexane	44^{102}		$>0^{82}$	$=0^{82}$
POPD	Water	—	45^{82}	$<0^{82}$	$<0^{82}$

* UCT and LCT are respectively the upper and lower consolute temperatures.

The free volume of the polymer is always smaller than that of its low-molecular-weight analogue, since intermolecular bonds 3–4 Å long are replaced by chemical bonds on polymerisation. When a polymer is mixed with a low-molecular-weight liquid and a solution is formed, the polymer expands (the free volume of the solvent is supplied to it), while the solvent contracts. However, these effects are not balanced. If the second effect predominates, the dissolution involves contraction, while if the first effect predominates expansion takes place.

For identical structures of the polymer and solvent molecules, when the cohesion energies are identical for like and unlike molecules, the geometrical factor plays the main role and the process involves contraction[69–71,73,74], which is the cause of the exothermicity. If the units of the polymer molecules differ in their chemical structure from those of the solvent molecules, the difference between the cohesion energies begins to play a role. The weaker interaction between unlike molecules than between like molecules leads to positive changes in the internal energy, volume, and enthalpy. The same polymer therefore dissolves with contraction in some solvents and with expansion in others. This can be seen from the data presented in Fig.6, which were obtained by Bianchi and Guniberty[69].

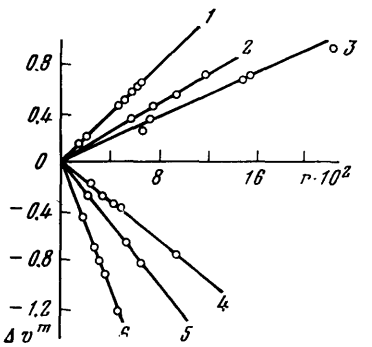


Figure 6. Variation of the volumes of polyisobutylene solutions[69]; solvent: 1) benzene; 2) toluene; 3) chlorobenzene; 4) cyclohexane; 5) methyl-cyclohexane; 6) n-heptane.

Natural rubber dissolves in benzene with expansion like low-molecular-weight hydrocarbons. Contraction is usually observed on dissolution of loosely packed polymers, for example PS[71,75–77], and also on dissolution of polyesters in water and carbon tetrachloride[68–83]. For example, polyoxyethylene and polyoxypropylene-diols dissolve in water with contraction[82], which may be due to the incorporation of their molecules into the water structure. The contraction observed when they dissolve in carbon tetrachloride is evidently associated with the formation of a more close-packed molecular arrangement in consequence of the difference between their dimensions[80,83].

Thus, like low-molecular-weight substances, polymers dissolve either with contraction or expansion.

V. THE INFLUENCE OF TEMPERATURE ON THE VOLUMES OF MIXING AND CONSOLUTE TEMPERATURES

The volume of mixing depends on temperature and Δv^m can become both more negative and more positive as the temperature increases. Thus the negative values of Δv^m for solutions of liquid alkanes increase with increasing temperature. This has been clearly shown by Davenport et al.[84] and is illustrated in Fig.7. A similar behaviour is observed in the n-hexane–n-hexadecane system. In these systems the main type of interaction is the dispersion interaction which is independent of temperature[85]. Consequently, Δu^m should not vary with temperature and an increase of the negative values of Δv^m alters the enthalpy of mixing. Thus at room temperature n-hexane mixes with n-hexadecane

with absorption of heat, the extent of which diminishes as the temperature rises[86,87]; Δh^m changes sign at 64 °C and at higher temperatures the dissolution becomes exothermic.

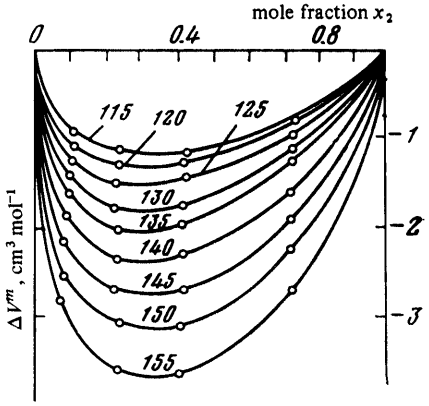


Figure 7. The average volumes of mixing of the methane–isopentane system (the numerals opposite the curves indicate the temperature in K)[84].

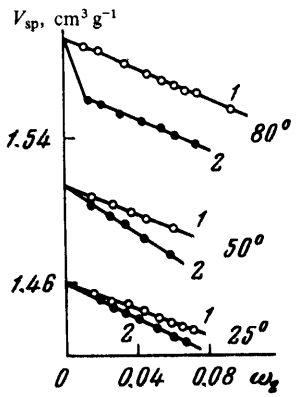


Figure 8. Dependence of the specific volumes of the polyisobutylene–isooctane system on the weight fraction of the polymer in solutions ω_2: 1) additive specific volumes of the solutions V^{sp}_{ad}; 2) experimental specific volumes of the solutions V^{sp}_{exp}.

The increase of the contraction at higher temperatures is caused by the difference between the coefficients of thermal volume expansion for the components, which depends on the difference between their free volumes. The free volume of the component having the higher molecular weight is smaller than that of the low-molecular-weight component, so that the thermal coefficient of the second component is greater than that of the first. However, in solution the low-molecular-weight component cannot expand on heating, as in the free state; with increase of temperature, it is therefore in a state close to that of a condensed gas, which leads to the association of its molecule and ultimately to the separation of the single-phase solution into two phases, i.e. to the appearance of a lower consolute temperature, which is in the temperature range above the boiling point of the more volatile component. The existence of the LCT of this type has been observed for solutions of hydrocarbons (n-hexane–n-hexadecane); this type of LCT is characteristic of solutions of all polymers, since the coefficient of volume expansion of the latter is smaller by an order of magnitude than that of low-molecular-weight liquids. For many polymeric solutions, the degree of contraction increases with increasing temperature (Fig.8) and the thermodynamic criteria of the LCT, in particular $\Delta h^m < 0$, are valid.

LCT of this type in the range 160–300 °C have been observed for many polymer–solvent systems[90–100].

For solutions of low-molecular-weight substances containing polar components, the degree of contraction diminishes with increase of temperature; this behaviour has been observed, in particular, for mixtures of alcohols with phenols, aniline, and formaldehyde[44]. This is usually attributed to the dissociation of the hydrogen bond between unlike molecules.

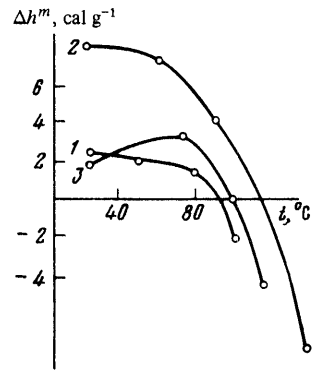


Figure 9. Temperature variation of the average enthalpies of mixing Δh^m in different systems: 1) polyisobutylene–benzene; 2) poly(vinyl acetate)–methanol; 3) polystyrene–cyclohexane (the weight fraction of the polymer in solution is $\omega_2 = 0.8$).

Prigogine and Defay[101] analysed the relation between the sign of the volume of mixing and the type of consolute temperature. They concluded that four cases can be observed for solutions of low-molecular-weight compounds:

1. UCT#: $\Delta h^m > 0$; $\Delta S^m > 0$; *a*) $\Delta v^m > 0$; *b*) $\Delta v^m < 0$.
2. LCT: $\Delta h^m < 0$; $\Delta S^m < 0$; *a*) $\Delta v^m > 0$; *b*) $\Delta v^m < 0$.

Systems of types 1*a* and 2*b* are encountered most frequently and there are also a certain number of systems of types 1*b*; examples of systems of types 2*a* are not known. The data presented in Table 2 show that, among polymer–solvent systems, exothermic systems with LCT involving contraction and systems with UCT, formed with absorption of heat and expansion, are typical; there are also systems with UCT, for which $\Delta h^m > 0$ and $\Delta v^m < 0$.

UCT = upper consolute temperature (Editor of Translation).

If the system has both a UCT and an LCT, then Δh^m must change sign as the temperature is varied (Fig.9).

VI. THEORIES OF SOLUTIONS AND VOLUMES OF MIXING

Despite the enormous amount of experimental data indicating the absence of additivity of the volume of the solution, most of the theories of solutions are based on the assumption that the volume remains unchanged on mixing. This is one of the causes of the discrepancies between theoretical results and experiment. The volume change exerts an influence in those cases where the remaining thermodynamic parameters of the dissolution process are measured at constant pressure (the commonest case). This question is discussed in the third edition of the book by Hildebrand et al.[109]. It is well known that the Scatchard–Hildebrand equation is valid only for the simplest systems of the type CCl_4–$SiCl_4$.[110] The equation does not hold even for mixtures of hydrocarbons, let alone more complex systems. It is therefore evidently necessary to take into account the volume change.

This was first done by Prigogine[111–113], who applied the principle of corresponding states to liquids with chain molecules. Prigogine's theory in its initial form was very complex and was not used for a long time, until Hijmans[114] and Patterson and coworkers[115] expressed it in a simpler form, which is described in a number of articles and books[85,116]. In Prigogine's theory a chain molecule is regarded as a sequence of r rigid quasi-spherical segments, whose behaviour differs from that of the free segments owing to the presence of chemical bonds between them. This leads to significant characteristic features of such systems, namely:

1. The surface of each segment is only partly free for intermolecular interactions, the remainder being blocked by neighbouring segments of the same molecule linked by valence forces to the given segment. The number of outer contacts between the molecules is therefore smaller than for free spherical segments.

2. The presence of chemical bonds between the segments limits their mobility, so that the number of degrees of freedom of each segment linked by valence forces (c) is smaller than the number of degrees of freedom of the free segment.

The theory deals only with external or configurational properties of liquids, i.e. properties which depend on the external degrees of freedom (translational and rotational movement) as well as hindered internal rotation in the molecule, which the authors[115] represent as a superposition of torsional vibrations on the transitions between different states of the rotational isomers. The idea of the outer contacts of the segments is expressed by the Lennard-Jones potential

$$\varphi(R)=4\varepsilon^*[(\sigma^*/R)^{12}-(\sigma^*/R)^6], \qquad (10)$$

where ε^* is the energy of the contact between the segments at 0 °C, σ^* the distance over which this contact is achieved (the diameter of the sphere of action), and R the distance between the molecules.

The normalising parameters are the so-called molecular units: for the internal energy–the quantity $u_0=Nq\varepsilon^*z$, which represents the energy of the contacts of all N molecules (z is the coordination number); for the volume—the quantity $v_0=Nr\sigma^{*3}$; for the entropy—the quantity $s_0=3NcR$ (R is the Boltzmann constant), etc. The above quantities can be expressed as follows:

Reduced free energy	$\tilde{U}=U/Nqz\varepsilon^*$;
Reduced volume	$\tilde{V}=V/Nr\sigma^{*3}$;
Reduced entropy	$\tilde{S}=S/3NcR$;
Reduced temperature	$\tilde{T}=T/T_0=3cRT/qz\varepsilon^*$.

The reduced temperature is defined as the ratio of the kinetic energy of the substance to its cohesion energy $z\varepsilon^*$. It depends on the parameter c/q, which Prigogine calls the structure factor, since this ratio is linked directly to the free volume, which is the most important characteristic of the structure of matter.

On passing to solutions, it is assumed that all the normalising parameters are additive. Thus

$$\langle v_0\rangle=x_1v_{01}+x_2v_{02} \qquad (11)$$

$$\langle u_0\rangle=x_1u_{01}+x_2u_{02} \qquad (12)$$

where x_1 and x_2 are the mole fractions of the components, v_{01}, v_{02}, u_{01}, and u_{02} are the corresponding reduced parameters, and $\langle v_0\rangle$ and $\langle u_0\rangle$ are the reduced parameters for the solution. With these assumptions, the reduced temperature of the solution $\langle\tilde{T}\rangle$ can be expressed by the equation

$$\langle\tilde{T}\rangle=\varphi_1\tilde{T}_1+\varphi_2\tilde{T}_2, \qquad (13)$$

where $\tilde{T}_1$ and $\tilde{T}_2$ are the reduced temperatures of the components and ϕ_1 and ϕ_2 are their volume fractions.

The volume of mixing is calculated from the equation

$$\Delta v^m=\langle v_0\rangle\{\tilde{V}-[\varphi_1\tilde{V}_1+\varphi_2\tilde{V}_2]\}, \qquad (14)$$

where $\tilde{V}$, $\tilde{V}_1$, and $\tilde{V}_2$ are the reduced volumes of the solution and the components respectively. Calculations by Eqn.(14) have shown that the mixing of substances consisting of molecules having similar chemical structures but differing in the dimensions of their chains should be accompanied by contraction.

For the homologous series of alkanes (from methane to polyethylene), polystyrene (from the dimer to infinite molecular weight), poly(ethylene oxides), polydimethylsiloxanes, and fluorinated alkanes, it has been shown[117–120] that the experimental data for the temperature variation of the volumes of mixing fit on a single curve. Consequently the principle of corresponding states can be applied also to polymeric liquids and even to polymeric glasses. It follows from the calculation carried out for solutions of certain polymers that they are formed with contraction[116].

Thus Prigogine's theory demonstrated the possibility, in principle, of calculating the volume of mixing as well as other thermodynamic functions. However, these calculations are difficult, owing to the difficulty of a quantitative choice of the parameters q, c, ε^*, and σ^*.

The theory of solutions developed by Flory and coworkers[121–124], which is based on all the postulates of Prigogine's theory but in which the reduced parameters have a clear physical significance and can be obtained from Tables, constituted a considerable step forward. The main reduced parameter in the so-called new Flory theory or the Flory–Prigogine theory is the intrinsic volume of the segment v^*, which is the sum of the volumes of all its constituent atoms, or the intrinsic volume of the molecules $V^*=rv^*$ (r is the number of segments in the molecule); it differs from the actual volume of the molecule by the free volume.

According to Hildebrand[9], the volume of one mole of a substance can be represented by the sum of the intrinsic volume of its molcules V_W and the free volume or the volume of the vacancies V_E (see above). If the overall volume occupied by N chain molecules is divided by the number of segments in this volume (Nr), then the local volume corresponding to a segment is obtained:

$$v=V/Nr. \qquad (15)$$

The reduced volume is

$$\tilde{v}=v/v^*=V/V^*=M/dV^*, \quad (16)$$

where V is the volume of one mole of the substance, M its molecular weight, and d the density.

Using the Tonks distribution function[125] for a two-dimensional system of N rigid species and having applied it to a one-dimensional system made up of a single chain of rigid segments, the authors[114,115] obtained the equation of state for a liquid with non-spherical chain molecules:

$$\frac{\tilde{p}\tilde{V}}{\tilde{T}}=\frac{\tilde{v}^{1/s}}{\tilde{v}^{1/s}-1}-\frac{1}{\tilde{v}\tilde{T}}; \quad (17)$$

at $p=0$ (this is close to the atmospheric pressure $p=1$) Eqn.(17) assumes a simpler form:

$$\tilde{T}=\frac{\tilde{v}^{1/s}-1}{\tilde{v}^{4/s}}. \quad (18)$$

Differentiation of Eqn.(18) with respect to temperature leads to an expression involving the derivative $\partial V/\partial T$, which is related to the volume by the coefficient of thermal expansion α; as a result, we obtain the equation

$$\tilde{v}^{1/s}-1=\frac{\alpha T}{3(1+\alpha T)}. \quad (19)$$

When α for the substance and the experimental temperature are known, Eqn.(19) makes it possible to calculate the reduced volume $\tilde{v}$. Next, the intrinsic volume of the segment is calculated by Eqn.(16) and the reduced temperature is calculated by Eqn.(18).

The talks formulated by the authors[114,115] reduces to the calculation of the thermodynamic properties of solutions from those of the components. Two parameters are then introduced to express the concentration of the solution: the fraction of the segments ϕ_i and the fraction of sites θ_i. The parameters ϕ_2 and θ_2 of the second component are calculated by the equations

$$\varphi_2=m_2v^*_{sp2}/(m_1v^*_{sp1}+m_2v^*_{sp2}), \quad (20)$$

$$\theta_2=1-\theta_1=(S_2/S_1)\varphi_2/[\varphi_1+(S_2/S_1)\varphi_2], \quad (21)$$

where m_2 and m_1 are the masses of components, $v^*{}_{sp}{}^1$ and $v^*{}_{sp}{}^2$ are the reduction parameters for the specific volume, and S_2/S_1 is the ratio of the sufrace areas of the molecules being mixed, which is calculated from model representations. For example, an alkane molecule is modelled by a cylinder with an average radius 2.49 Å and a length $l^*=1.19n+1.32$, where n is the number of carbon atoms. These dimensions are consistent with the crystallographic radii and the intrinsic volumes V^* of n-alkane molecules.

The reduced volume of the solution is calculated by the equation

$$\frac{\tilde{v}^{1/s}-1}{\tilde{v}^{4/s}}=\tilde{T}=(\varphi_1p^*_1T^*_1+\varphi_2p^*_2T^*_2)/(\varphi_1p^*_1+\varphi_2p^*_2-\varphi_1\theta_2X_{12}), \quad (22)$$

where X_{12} is the energy parameter of the interaction of the components and the additive volume of the solution is found from the equation

$$\tilde{v}_0=\varphi_1\tilde{v}_1+\varphi_2\tilde{v}_2. \quad (23)$$

The reduced volume of mixing is calculated as the difference between the reduced volume of the solution $\tilde{v}$ and the reduced additive value:

$$\Delta\tilde{v}^m=\tilde{v}-\tilde{v}_0. \quad (24)$$

Flory and coworkers[121–123] proposed equations, which make it possible to calculate the partial enthalpies and entropies of mixing ($\overline{\Delta H_1}$ and $\overline{\Delta S_1}$) and the difference between the chemical potentials of the components $\Delta\mu_1$, while Abe and Flory[124] showed that all these theoretical equations can be applied to mixtures of not only chain molecules but also spherical molecules (CCl_4, benzene, cyclohexane, neopentane, $TiCl_4$, $SnCl_4$, etc.).

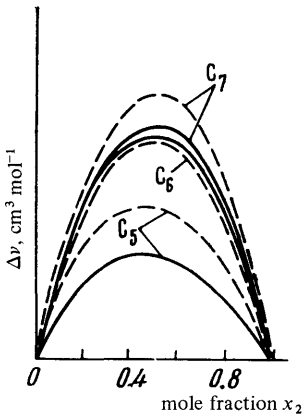


Figure 10. The volumes of mixing of benzene–alicyclic hydrocarbon systems[130]: continuous curves–experimental data; dashed curves–theoretical data.

The new Flory theory has been tested for a large number of mixtures of low-molecular-weight liquids and for solutions of polymers. It has been shown that, for mixtures of n-alkanes[121,122] and alkanes with cyclic hydrocarbons[124], mixtures of spherical molecules[124], mixtures of hydrocarbons with fluoro-derivatives, solution[3] of isooctane in CCl_4 and cyclohexane[126–129], and solutions of benzene and CCl_4 in toluene and xylene[55], the Flory theory always predicts the correct sign of the volume change and in most cases the calculated values of Δv^m are close to the experimental values (Fig.10). Fig.11 shows that the theory describes satisfactorily the experimental data also for solutions of polymers: in particular, the values of Δv^m for the natural rubber–benzene system[73], calculated by Eqn.(24), virtually agree with experiment; for solutions of poly-isobutylene in n-alkanes[74], the theory predicts the correct sign of the volume of mixing, but the values of Δv^m do not agree. An even greater discrepancy between the experimental and calculated Δv^m has been observed for solutions of polystyrene[76], although the theory predicts correctly the sign of Δv^m.

All the foregoing considerations show that the mixing of liquids and the dissolution of polymers are accompanied by a volume change which makes a significant contribution to all the thermodynamic potentials. Even a small contribution of the volume change can induce marked effects, for example, phase separation when the solution is heated.

The contraction effect on mixing liquids and on dissolving polymers leads to the occurrence of concentration fluctuations in solution, whose further growth leads to the formation of organised structures such as associated species or solvates. These organised structures, which are formed spontaneously, are classified as the so-called dissopative structures, considered in the modern thermodynamics of irreversible processes[130–131].

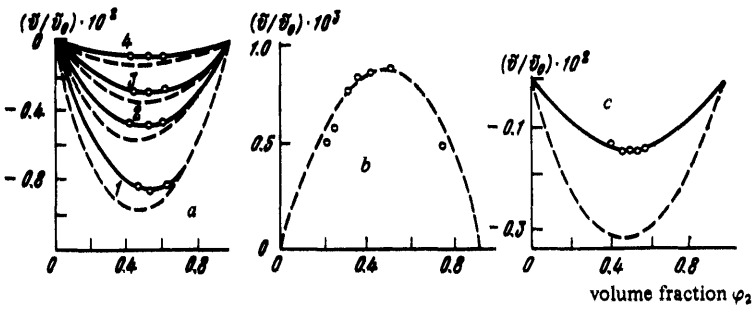


Figure 11. The relative volumes of mixing for different solutions: *a*) of polyisobutylene in n-alkanes[74] [1) in n-hexane; 2) in n-octane; 3) in n-decane; 4) in n-hexadecane]; *b*) of natural rubber in benzene[75]; c) of polystyrene in cyclohexane[76]. Continuous lines—experimental data; dashed lines—calculation based on the Flory theory.

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