

Apparent Molal Volumes of Interstitial Compounds Forming Components in Solution

R S CHAUHAN, R N PATHAK & RAM GOPAL*

Chemistry Department, Lucknow University, Lucknow 226 007

Received 20 June 1983; revised and accepted 9 September 1983

Dependence of φ_v (apparent molal volume) on C for urea and thiourea in methanol, methanol+hexane and methanol+heptane mixtures has been studied. The results indicate that the accommodation of the guest (in this case hexane or heptane) leads to a decrease in its apparent molal volume and the forces which lead to the formation of solid lattice of a host-guest system (urea or thiourea-hexane or heptane) appear to be already operative in solution.

One of the suggestions made to explain the abnormal negative slope of the apparent molal volume (φ_v) versus $\sqrt{C}$ curves of some electrolytes (the larger tetraalkylammonium and some common salts) in solvents of high dielectric constant^{1,2} is that the ions are accommodated inside the large vacant spaces left during packing of the solvent molecules; this possibility and electrostatic ion-solvent and ion-ion interactions somehow give a negative slope in the φ_v versus $\sqrt{C}$ curves in these cases. This suggestion although theoretically unsound, is interesting and calls for investigations in systems in which interstitial compounds^{3,4} are known to be formed and this prompted us to undertake the present investigation.

Methyl alcohol (AR, BDH) was purified by the standard procedure; *n*-hexane (Indian Drugs and Pharmaceuticals, Hyderabad) and *n*-heptane (Polypharm, Bombay) were purified by shaking them with one quarter of their respective volumes of sulphuric acid for several minutes; the process was repeated until the lower layer was colourless. The hydrocarbon layer was then washed twice with distilled water, dried over anhydrous calcium sulphate and distilled twice retaining the middle fraction for use: *n*-hexane, b.p. 68.3° (lit. 68.3°); *n*-heptane, b.p. 98.2° (lit. 98.4°). Urea and thiourea (M. Sarabhai Chemicals, Baroda) were recrystallized from conductivity water, dried and kept in a vacuum desiccator. All the solutions were prepared on molal basis. The experimental procedure for determining density and φ_v therefrom, was the same as given in earlier communications⁵⁻⁸.

The plots of φ_v versus C lead to the following general conclusions:

(i) The φ_v of urea (or thiourea) in methanol decreases with the increase in concentration (Fig. 1), indicating self-association among the solute molecules and confirming the results obtained by Hamilton and Stokes⁹.

(ii) The φ_v of hexane (or heptane) in methanol increases rapidly with the increase in its concentration (Fig. 1) indicating solute-solvent interaction.

(iii) The φ_v of urea (or thiourea) in methanol + hexane (or methanol + heptane) mixtures increases with increase in concentration; it also increases with the increase in the concentration of hexane or heptane (Fig. 2) in mixtures; on the other hand, φ_v of hexane (or

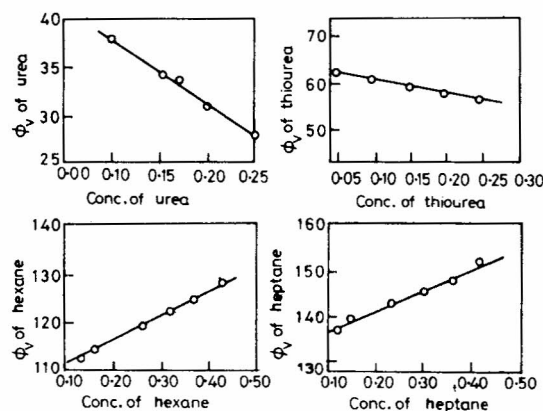


Fig. 1—Apparent molal volume (φ_v) versus concentration curves for urea (and thiourea) and hexane (or heptane) in methanol

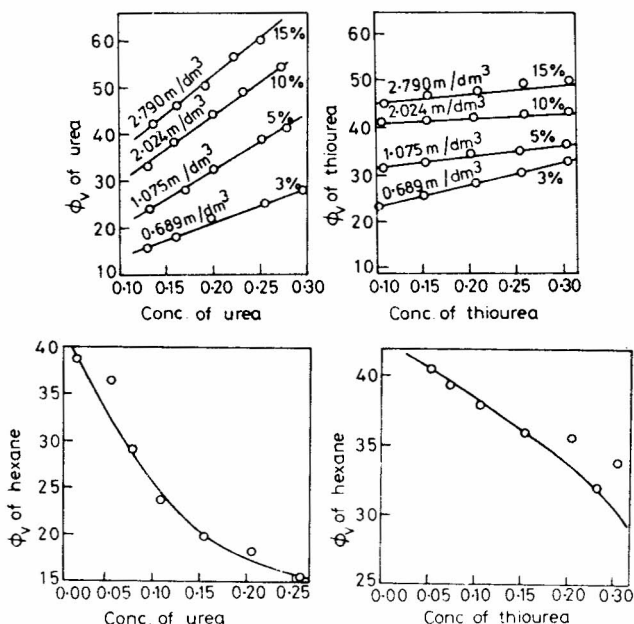


Fig. 2—Apparent molal volume (φ_v) versus concentration curves for urea (and thiourea) in methanol+hexane mixture and φ_v of hexane versus concentration of urea (or thiourea)

heptane) decreases with the increase in concentration of urea (or thiourea) (Fig. 2).

The above results point to the existence of different modes of molecular interactions in the presence and absence of the host and guest molecules. The following tentative picture of interaction may be suggested to explain these experimental results:

The decrease in ϕ_v of urea (or thiourea) in methanol, with increase in concentration is due to preferential dipole-dipole interaction among the solute molecules on account of its large dipole moment. On the other hand, due to the absence of dipole in hexane and heptane, there appears to be a net attractive interaction between methanol molecules and induced dipole moment in hexane (or heptane). This interaction would be maximum at infinite dilution and would decrease with increase in concentration of solute urea (or thiourea); hexane (or heptane). Now, when to a solution of urea (or thiourea) in methanol some hexane (or heptane) is added, there appears to be a preferential dipole-induced dipole attraction between hexane (or heptane) and urea (or thiourea). Dipole and induced-dipole interaction would be weaker between methyl alcohol and hexane (or heptane) in comparison to that between urea (or thiourea) and hexane (or heptane) because of large dipole moment of the urea. The preferential interaction between hexane (or heptane) and urea (or thiourea) breaks down the association of

urea (or thiourea) resulting in a net decrease in its ϕ_v with increase in concentration of hexane (or heptane). It seems that due to this interaction, apparently no break down of molecular association in these cases [hexane (or heptane), unlike urea (or thiourea), is not self-associated in methyl alcohol] occurs which could compensate for the loss in volume of hexane (or heptane) due to host-guest interaction [interstitial ion-pair formation between hexane or heptane (guest) and urea or thiourea (host)] and so ϕ_v of hexane (or heptane) decreases with increase in its concentration. This picture appears to explain the results obtained so far.

The authors' thanks are due to the UGC, New Delhi, for financial support.

References

- 1 Gopal R, Singh & Siddiqi M A, *J Indian chem Soc*, **47** (1970) 504.
- 2 Gopal R, Siddiqi M A & Singh K, *Z phys Chem (N F)*, **75** (1971) 7.
- 3 Eric J & Davis D, *J chem Educ*, **54** (1977) 537.
- 4 Ferguson Lloyd N, *The modern structural theory of organic chemistry* (Prentice-Hall Chemistry Series, USA) 1970, 162-163.
- 5 Gopal R, Agarwal D K & Kumar R, *Indian J Chem*, **14A** (1976) 803.
- 6 Gopal R & Pathak R N, *Indian J Chem*, **14A** (1976) 806.
- 7 Gopal R & Pathak R N, *Indian J Chem*, **16A** (1978) 150.
- 8 Gopal R & Pathak R N, *J Indian chem Soc*, **55** (1978) 128.
- 9 Hamilton D & Stokes R H, *J soln Chem*, **1** (1972) 213.